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I am submitting herewith a dissertation written by Stephen Dennis Wilson entitled “Static and dynamic magnetism in the electron-doped high-temperature superconductor $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ and in the f -electron, non-Fermi liquid alloy $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$.” I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment for the requirements of the degree of Doctor of Philosophy, with a major in Physics.

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**Static and dynamic magnetism in the electron-doped high-temperature
superconductor $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ and in the *f*-electron, non-Fermi
liquid alloy $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$**

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Dedication

This dissertation is dedicated to both my fiancée Melissa and to my parents. Their encouragement and support has been a cherished part of my life that has been integral in my graduate career.

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Abstract

Here we present detailed studies of the spin dynamics within the electron-doped high temperature superconductor $\text{Pr}_{.88}\text{LaCe}_{.12}\text{CuO}_{4-\delta}$ (PLCCO) and within the non-Fermi liquid metal $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ (ScUPd). Comprehensive neutron scattering experiments were carried out mapping the evolution of magnetism within these systems as they are tuned across their respective phase diagrams. The novel features of the magnetic spectra within these systems are correlated with known anomalies in their quasiparticle behaviors driven through either the appearance of a superconducting phase in PLCCO or the emergence of a non-Fermi liquid phase in ScUPd.

For the high- T_c cuprate $\text{Pr}_{.88}\text{LaCe}_{.12}\text{CuO}_{4-\delta}$, a detailed study of the evolution of the low energy spin excitations in this system is presented. In the unannealed, nonsuperconducting parent compound of PLCCO, the magnon excitations are well modeled as spin wave excitations arising from the long-range antiferromagnetic (AF) order in the system. As the system is doped into the superconducting phase towards optimal superconductivity, long-range AF order in the system is suppressed and low energy spin excitations behave drastically different than those observed in the NSC parent system. Instead of following the simple Bose statistics expected for spin wave magnon modes, the low energy excitations in superconducting concentrations show a form of hyperscaling in which the dynamic susceptibility is observed to scale as a function of ω/T . This likely reflects the influence of quantum critical excitations coupling to the spin degrees of freedom that arise from the quantum critical point in the phase diagram of PLCCO (where AF order is suppressed to 0K near optimal doping).

High energy spin excitations in an under-doped concentration of PLCCO ($T_c=21\text{K}$) are also reported. Our experiments show that in contrast to the seemingly universal pattern of dispersion reported the spin excitations of hole-doped cuprates, the high energy excitations in this n -type system instead resemble those observed in the parent compounds of the high- T_c cuprates. Rather than the “hourglass”-type dispersion observed in hole-doped cuprates, the dispersion in this n -type system remains a broadened commensurate spot at low energies that disperses outward into a ring-like excitation at higher energy transfers. The actual dispersion for this underdoped concentration at higher energies is anomalously sharper than that reported for the parent systems, Pr_2CuO_4 and La_2CuO_4 .

Another facet of the spin excitations in PLCCO given particular focus is the newly discovered resonance mode in nearly optimally doped concentrations of PLCCO ($T_c=24\text{K}$). We find that the resonance mode in this system follows the universal relation $E_R=5.8k_B T_c$ for the resonance energies observed in all classes of cuprates. The resonance, when taken with the known commensurate response and high energy dispersion in the electron-doped cuprates, is therefore shown to stand as the long unifying feature in magnetic spectra of the cuprates, regardless of doped carrier-type.

Field-induced changes in the magnetic spectrum of this optimally doped concentration of PLCCO ($T_c=24\text{K}$) are also discussed. Particular focus is given to the suppression of the resonance mode and field-induced spin density wave order in this system. The suppression of the resonance mode is seen to track the condensation energy

in relative magnitude as a function of applied magnetic field, thereby suggesting that the mode itself is fundamentally connected to the mechanism of high- T_c superconductivity.

For our studies of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$, systematic neutron measurements mapped out magnetic excitations over a broad doping range. Concentrations near $x=0.30$, where the non-Fermi liquid (NFL) phase first appears, exhibit a seemingly local and nearly temperature-independent response in the spin excitation spectra. This parallels earlier results reported for another NFL system, UCu_4Pd , whose spin dynamics acquire a local temperature insensitive character near the NFL phase boundary. We find that this spin behavior is characteristic of the proximity of a spin-glass quantum critical point in the phase diagram of these systems and possibly intrinsic to the appearance of NFL dynamics in these classes of materials.

Preface

Portions of this dissertation are derived from recently published work. Below, I have listed the full publication information for each work which has been published along with its corresponding chapter in this dissertation.

<i>Chapter</i>	<i>Reference</i>
Chapter 3:	Stephen D. Wilson, Shiliang Li, Pengcheng Dai, Wei Bao, Jae-Ho Chung, Hye-Jung Kang, Seung-Hun Lee, Seiki Komiyama, Yoichi Ando, and Qimiao Si, "Evolution of the low energy spin dynamics in electron-doped high-temperature superconductor $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ ". <i>Phys. Rev. B</i> 74 , 144514 (2006).
Chapter 4:	Stephen D. Wilson, Shiliang Li, Hyungje Woo, Pengcheng Dai, H. A. Mook, C. D. Frost, Seiki Komiyama, and Yoichi Ando, "High Energy Spin Excitations in the Electron-Doped Superconductor $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ with $T_c=21\text{K}$ ". <i>Phys. Rev. Lett.</i> 96 , 157001 (2006).
Chapter 5:	Stephen D. Wilson, Pengcheng Dai, Shiliang Li, Songxue Chi, Hye-Jung Kang, and J. W. Lynn, "Resonance in electron-doped high- T_c superconductor $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ ". <i>Nature</i> 442 , 59 (2006).
Chapter 8:	Stephen D. Wilson, Pengcheng Dai, Seung-Hun Lee, Jae-Ho Chung, D. Adroja, J. W. Lynn, and M. B. Maple, "Quantum Critical Scaling and origin of Non-Fermi- Liquid behavior in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$." <i>Phys. Rev. Lett.</i> 94 , 056402 (2005).

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Chapter 1: Introduction to superconductivity and neutron scattering

1.1 Introduction to superconductivity

The discovery of superconductivity in 1911 in mercury by H. Onnes presented a wholly unexpected and profoundly challenging problem for solid state physics [1]. A sudden drop in the electrical resistance of the material to levels below measurement sensitivity at a sharply defined temperature signified the discovery of this new phase of matter. This achievement is intrinsically linked to the technical breakthrough made by the same group a few years earlier in the liquefaction of He. As most elemental superconductors exhibit their superconducting phase transition below or around 4K, this advance in cryogenics necessarily preceded the discovery of the simplest superconductors found in nature. The definition of superconductivity, however, in 1933 was broadened beyond the limited scope of a state of zero electrical resistance by Meissner and Ochsenfeld's discovery of the spontaneous expulsion of magnetic flux from the superconducting system upon entering the superconducting phase [2]. Their discovery that, below some threshold field value, a superconductor will expel all magnetic flux within it upon entering the superconducting state defined a unique thermodynamic state distinct from a system merely with infinite conductivity. This provided an experimental advance integral to the eventual theoretical understanding of the superconducting groundstate.

It was not until 1957—when the fully quantum theory of Bardeen, Cooper, and Schrieffer (BCS theory) was published—that the phenomenon of superconductivity could be microscopically understood [3]. Within this breakthrough approach, electrons are bound together in pairs as they travel through the solid. One-electron fluctuations (from scattering or other sources) about the paired current carrying momentum, $\mathbf{q}$, only serve to increase the free energy of the system. Only those statistically improbable fluctuations in which a majority of the paired electrons participate will alter the common $\mathbf{q}$ shared by all paired electrons and lower the free energy. This effectively renders an almost infinitely lived metastable electronic groundstate with infinite conductivity.

Although the BCS approach demonstrated that any net-attractive interaction between electrons will result in electron-pairing, the effective pairing between electrons in the BCS pairing mechanism is mediated through a time-retarded interaction with lattice vibrations (phonons) in the system. When the energy difference between the two one-electron states is smaller than the pairing phonon frequency, then two time-reversed electrons are bound together into Cooper pairs via the virtual exchange of phonons. Once these bound Cooper pairs form long range phase coherence, then the superconducting phase appears. The electron-pairing in this phonon-mediated BCS mechanism was formulated for spin-singlet formation ($S=0$) with no net angular momentum ($L=0$) for the

paired state, ie. $|\uparrow\rangle \otimes |\downarrow\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$. The $L=0$ or “s-wave” pairing in this

phonon-based mechanism exhibits an electronic wavefunction isotropic in space and a uniform (or nodeless) superconducting gap, Δ_{Sc} . The $S_{total}=1, 0$ pairing integral to the superconducting phase allows electrons to shed their Fermi statistics, founded in the Pauli exclusion principle, and to condense as bosons into a superconducting condensate. This

condensate of Cooper pair bosons is an intriguing example of a purely quantum phenomenon manifesting itself on a macroscopic scale.

Experimental confirmation of this phonon-based mechanism of superconductivity was apparent in a number of forms. Perhaps most fundamental is the strong electron-phonon coupling observed in these conventional superconductors, both through a strong isotope effect on T_c and through the observation of drastic changes in particular phonon lineshapes upon cooling into the SC phase. The detailed description of coherence factors in the Hamiltonian of the superconducting groundstate and their subsequent observation in ultrasound experiments present a further triumph for the BCS formalism. In addition to this, the ability of BCS theory to calculate the universal ratio of $2\Delta_{SC}/k_B T_c$ observed within conventional superconductors to within experimental uncertainties represents a further testament to its merit.

Although phonon-based BCS theory effectively models the electronic behavior in the large class of conventional superconductors—including materials such as elemental superconductors (e.g. Pb), binary systems (e.g. Cu_3Sn), and intermetallics (e.g. NbTi)—there subsequently appeared a number of classes of systems whose superconducting properties differed from those predicted by strictly phonon-base BCS theory. The discovery of superconductivity in organic systems in 1979 [4] led to work speculating the existence of so-called “polaron” superconductivity [5] whose higher energy scale could in principle be tuned to generate organic systems with higher T_c ’s. Anomalous superconductivity was also discovered in a number of heavy fermion systems where magnetism is thought integral to superconductivity, such as CeIrIn_5 [6] and also in fullerene systems such as K_3C_{60} [7]. In this latter class of systems, however, phonons are still responsible for the condensation of the SC phase. In fact, superconductivity was even discovered to occur in perovskite oxide structures, systems previously thought unfavorable to SC, as early as 1964 with the synthesis of SrTiO_3 [8]. This latter discovery stands as the precursor to the unveiling in 1986 of a new class of superconductors with the highest transition temperatures ever recorded and exhibiting the greatest potential for applications of SC technology: the high- T_c cuprates.

1.2 Introduction to high- T_c cuprates

The discovery of superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ by Bednorz and Muller in 1986 [9] signified a radical departure from the established notion of superconductivity and its limitations. One of the most significant features of superconductivity in this system was the relatively high (a record at the time) superconducting transition temperature at $T_c \sim 30\text{K}$. This, coupled with the fact that the undoped parent compound of this system is actually an antiferromagnetically ordered insulator, led to the speculation that this system and other high- T_c cuprates discovered soon thereafter may constitute a new class of superconductivity altogether. In the years immediately following the initial discovery of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, the physics community unearthed a large number of superconducting cuprate variants with even higher transition temperatures such as the bilayer cuprate $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [10] ($T_c = 90\text{K}$). Transition temperatures eventually reached as high as 163K in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ under externally applied pressure.

In addition to the discovery of the abnormally high transition temperatures in these materials, other properties seemed to suggest a deviation from the well-established BCS theory [11]. Although these new cuprate superconductors behaved as Type-II superconductors, they exhibited unusually small superconducting coherence lengths ($\xi \sim 10 \rightarrow 50 \text{ \AA}$) and lacked the significant isotope effect expected in the BCS view of the superconducting pairing mechanism. Even more compelling is the lack of an appreciable change in the phonon spectrum as these systems enter the superconducting state (although recent measurements now observe weak modifications [12, 13, 14, 15, 16]). These observations suggest an alternate electron pairing mechanism in the high- T_c cuprates deviating from the pure electron-phonon interaction envisioned in BCS theory.

Another important facet in the properties of the high- T_c cuprates is that the superconducting pairing symmetry is in fact d-wave ($S=0, L=2$). It has been shown clearly that the Cooper-pairing spatial configuration is $d_{x^2-y^2}$ through a variety of probes including ARPES and phase sensitive tunneling measurements [17]. This pairing symmetry, which deviates from the majority of conventional superconductors, has provided important theoretical constraints in describing the mechanism of high- T_c .

The high- T_c cuprate alloys are all comprised fundamentally of two-dimensional copper oxygen planes into which charge carriers (holes or electrons) were doped. The simplest cuprate structure, the monolayer cuprate is depicted in Figure 1.1. In this T-structure each copper site is surrounded by an octahedron of oxygen sites, and the regions between the CuO_2 planes are referred to as “charge reservoir” regions. These are the sites in the crystal structure where the ionic charge donors are substituted and doping results. The undoped parent compounds of the cuprates are all Mott insulators exhibiting long-range antiferromagnetic (AF) order. This Mott insulating state denotes that these systems have partially filled conduction bands (an odd number of electrons per unit cell) yet remain insulating despite the simple band theory prediction that they are metals. The insulating state instead arises due to the large on-site Coulomb repulsion experienced by the conduction electrons, and this subsequently results in the splitting of the conduction band into upper and lower Hubbard bands with an energy gap of several eV between them.

Upon doping charge carriers into the planar CuO_2 layers, these cuprate systems evolve from AF ordered insulators into paramagnetic metals [18]. The qualitative phase diagram for the single-layer cuprates is shown in Fig. 1.2. Undoped, the parent compounds are antiferromagnetically ordered with the magnetic unit cell doubling the chemical unit cell in the copper oxygen planes and commensurate with the chemical unit cell along the c -axis (Fig. 1.2). After doping holes into the system, the long-range AF order is rapidly suppressed, and a low temperature spin-glass phase appears. Hole-doping eventually results in the creation of a superconducting phase whose transition temperature, T_c , increases with continued doping until a maximal value is reached (referred to as optimum-doping). Doping beyond this optimal value results in a subsequent decrease in the superconducting transition temperature, which continues until the phase is destroyed entirely. This generates a generic superconducting dome feature in the phase diagram of the cuprates. Doping electrons into the copper oxygen planes renders a qualitatively similar phase diagram except with the persistence of the AF phase

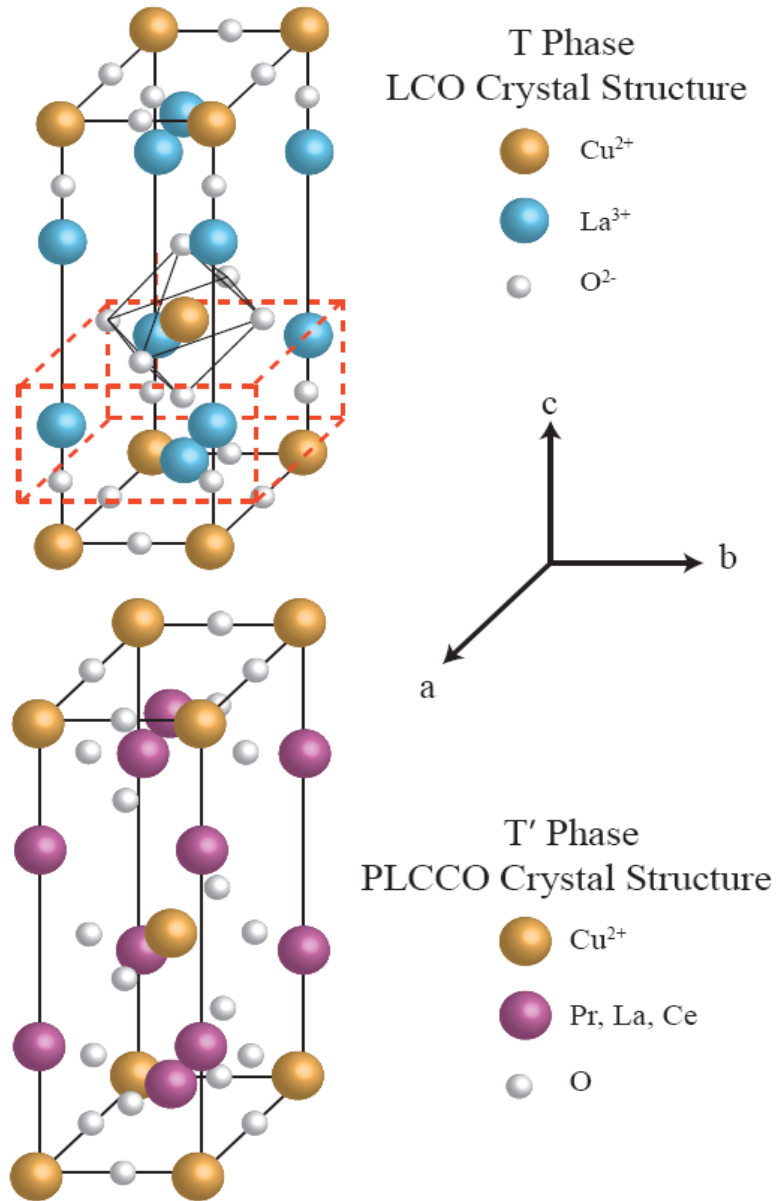


Fig. 1.1 T-phase and T'-phase crystal structures of monolayer high- T_c cuprates, La_2CuO_4 and $\text{Pr}_{1-x}\text{LaCe}_x\text{CuO}_{4-\delta}$. The two dimensional copper oxygen planes are separated by charge reservoir regions into which charge carriers are doped via alloying. The dashed red box encloses one charge reservoir region in the lower half of the unit cell (another would be the symmetrically equivalent region on the other side of the center Cu site). Each copper site is surrounded by an octahedron of oxygen sites in this T-phase structure while the apical sites on each octahedron are absent in the T' structure.

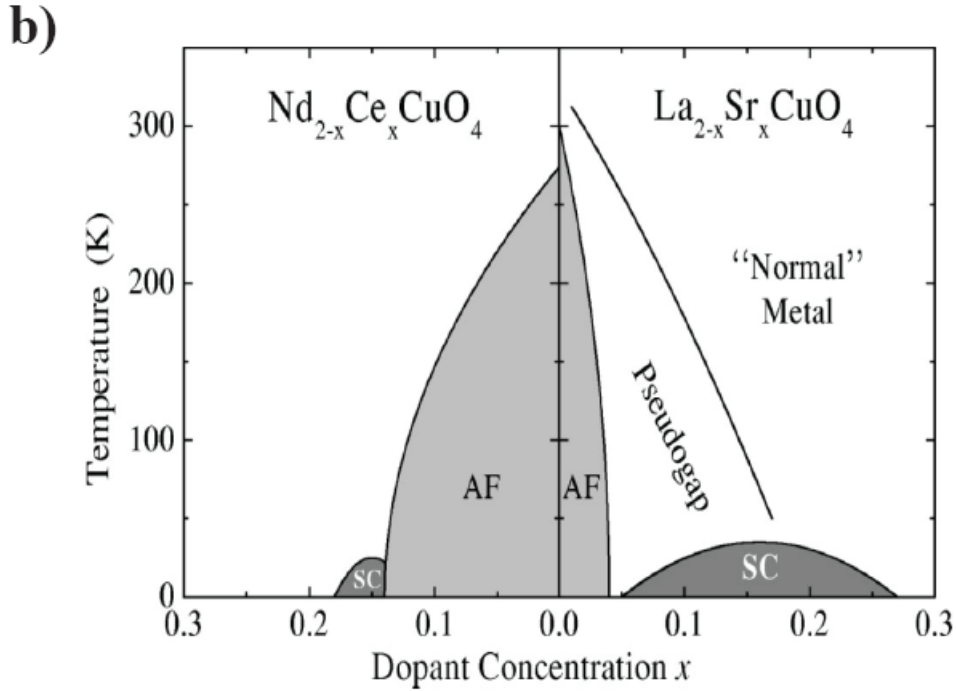
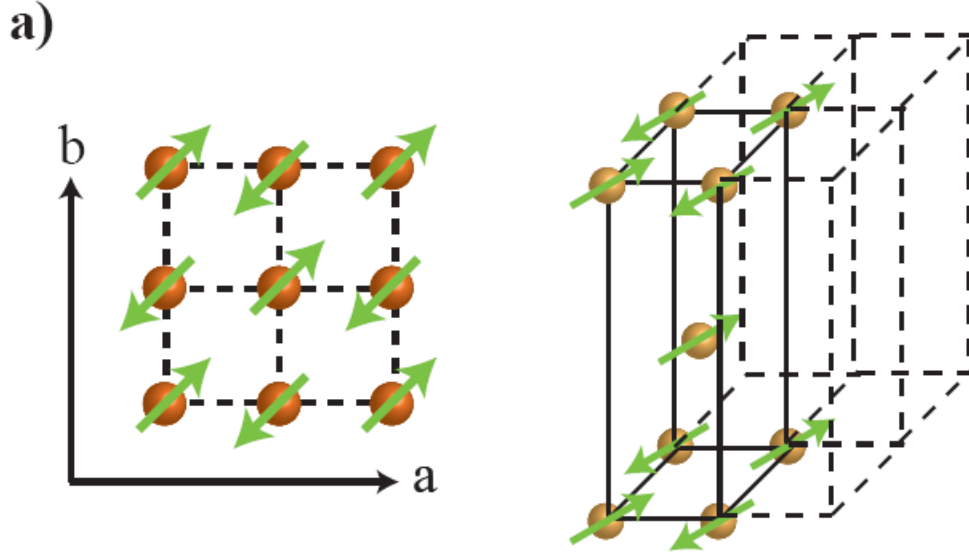


Fig. 1.2 Magnetic spin structure and phase diagram of the monolayer high- T_c cuprates. (a) The magnet unit cell doubles the chemical unit cell in the ab -plane as shown here. The specific spin orientation is depicted for La_2CuO_4 , with spins diagonal to the bond direction. (b) Qualitative phase diagram for the monolayer cuprates reproduced from Damascelli et al. [21]. The superconducting dome appears for both hole and electron doping, although in the electron-doped case, AF order persists to much higher doping levels. The pseudogap phase in the hole-doped cuprate $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is also depicted.

over larger doping levels; however, this phase diagram neglects the necessity for an oxygen reduction process in *n*-type cuprates, which will be discussed in Chapter 3.1.

In addition to the phases discussed above, the hole-doped high- T_c cuprates also exhibit the so-called pseudo-gap phase in the underdoped portions of their phase diagrams. Although the order parameter associated with this phase remains unclear, indications of its existence have been mapped out with a variety of probes such as NMR [19], electron transport [20], tunneling, angle-resolved photoemission [21], and neutron measurements [22]. This phase marks a clear boundary in which non-Fermi liquid behavior is observed in the normal state electronic properties of these systems, and the region is occasionally referred to as a “strange metal”. The pseudo-gap phase in the hole-doped cuprates and its implications as a precursor phase for high- T_c [23] are extremely interesting research avenues; however, the presence of an equivalent pseudogap phase in the *n*-type cuprates is currently a topic of considerable debate.

Of particular importance is debate over the nature and role of magnetism in these high- T_c cuprate systems. Although long-range antiferromagnetic order is rapidly suppressed with hole-doping, strong AF spin fluctuations have been shown to persist in all superconducting concentrations [24]. This, when coupled with the universal AF order in the parent compounds of the cuprates, suggests that magnetism may play a key role within the underlying superconducting mechanism. The anomalously high-energy scale of magnetism in the parent compounds also lends itself to this. This appears through the nearly two-dimensional AF order within the CuO_2 plaquettes of the parent systems with nearest neighbor exchange coupling values on the order of $J_{ab} \sim 100$ meV and $J_{ab} \gg J_c$ [25, 26, 27]. Although three-dimensional Neel breaks down around 200-300K due to the smaller energy scale of the out-of-plane exchange coupling, quasi two-dimensional AF spin fluctuations persist until much higher temperatures [28]. Of primary interest is the precise nature in which this long-range AF order evolves as these cuprate systems are tuned across their phase diagrams. For this reason, studying the modifications observed in both the static and dynamic magnetism in cuprate systems as they evolve from Mott insulators into paramagnetic metals with a superconducting phase transition can provide detailed knowledge of the interaction between magnetism and the underlying superconducting mechanism.

In an attempt to generate this comprehensive picture of the magnetism within the high- T_c cuprates, a colossal experimental effort has been undertaken over the past two decades by researchers all over the world. Perhaps the most influential probe in studying the detailed magnetic properties of the cuprates, and by far the most aptly suited, has been neutron scattering. Before proceeding to review the major magnetic features uncovered by neutron scattering in the cuprates over the past 20 years, I will first discuss some of the basic principles of neutron scattering and attempt to highlight the underlying power of the technique in studying magnetic properties of solid state materials.

1.3 Introduction to neutron scattering

Neutrons as a probe hold several unique advantages in studying solid state systems. The neutron itself is a charge 0 Fermion with a spin of $S = \frac{1}{2}$ and a resulting magnetic dipole moment. The charge neutrality of the neutron renders it a fundamentally

weakly interacting probe with the ability to penetrate and survey the bulk of a sample. Additionally, the intrinsic wavelength of the neutron provides an ideal matching to the crystal lattice spacings found within most condensed matter systems. The available energies and energy resolution of neutrons as a scattering probe are also uniquely suited to resolving fluctuating order and excitations within solid state systems. This ability to resolve both long and short timescale order and to average over the entirety of a given system highlights the powerful nature of neutrons as a diffraction probe.

The general scattering principles involved are simply to measure the number of neutrons scattered into a given solid angle at a known energy ($\hbar\omega$) and momentum transfer (κ). The laws of conservation of momentum and energy are expressed via the relations: $\kappa = k_f - k_i$ and $\hbar\omega = E_f - E_i$, where $k = \frac{2\pi}{\lambda}$ and i, f refer to the initial and

final states of the scattered neutron. Neutrons scattered into a known solid angle Ω and over a spread of known energies are counted over some time interval at a given value of (κ , $\hbar\omega$) and are directly proportional to the scattering cross section, σ , multiplied by the flux of incident neutrons on the target. Expressions for the cross section and its differential forms contain the essential physics measured and will be discussed in the following paragraphs. Unless otherwise stated, the cross sections discussed are those for unpolarized neutrons.

The short ranged atomic potential experienced by the neutron can effectively be approximated by a Fermi pseudopotential of the form $V(r) = (2\pi\hbar^2/m)b\delta(r)$, where b is the scattering length for a given nucleus. This scattering length is determined experimentally and relies on a variety of factors, including the particular nuclide and the spin state of the nucleus-neutron system. Scattering lengths and the resulting neutron cross sections for various atomic nuclei actually vary quite dramatically and seemingly erratically as elements are traversed by the relative Z (proton number) and N (neutron number) values. As an example, the coherent scattering cross section, σ_{coh} , of a light element such as Be is 7.63 barns and is comparable to much heavier Pb with $\sigma_{\text{coh}} = 11.115$ barns. This fact can be exploited to probe systems with lighter elements, such as hydrogen, that have a near negligible cross section for other photon-based scattering probes (such as X-ray scattering). The scattering cross section for each element can be separated into two components—the coherent cross section, σ_{coh} , and the incoherent cross section, σ_{inc} . Since for a system of a given isotope, each atomic site will reflect a variety of nuclear spin states (I), the resulting cross section felt by the neutron for each site will vary depending on the nuclear spin state I . The cross section observed can then be effectively approximated as resulting from an average over the scattering lengths of abundance of nuclear isotopes present and their allowable spin values. This value is referred to as the coherent cross section $\sigma_{\text{coh}} = 4\pi\langle b \rangle^2$ and can resolve interference effects, which will be discussed shortly. This also results in terms for isotopic incoherent scattering and nuclear-spin incoherent scattering. The variance from the mean scattering length values is used to determine the incoherent cross section $\sigma_{\text{inc}} = 4\pi[\langle b^2 \rangle - \langle b \rangle^2]$ and does not generate interference effects in diffraction.

For a neutron scattering from a single atom scattering site, the wavelength of the neutron (on the order of Å) greatly exceeds the range of the nuclear forces (on the order

of a fm) resulting in spherically symmetric isotropic scattering (s-wave). Now looking instead at a Bravais lattice of scattering sites, the partial cross section for nuclear scattering derived using the Born approximation is [29]:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E} \right)_{coh} = \frac{\sigma_{coh} k_f N}{4\pi k 2\pi \hbar} e^{U^2} \sum_l e^{i\kappa \cdot l} \int_{-\infty}^{\infty} e^{\langle UV \rangle} e^{-i\omega t} dt \quad (1-1)$$

where e^{U^2} is the Debye Waller factor. The $\langle UV \rangle$ term depends on the displacement of sites from their equilibrium positions taken in the harmonic approximation, where $U = -i\kappa \cdot u_0(0)$ and $V = -i\kappa \cdot u_l(t)$, and $u(t)$ are the time dependent terms of atomic displacement. Expanding the $e^{\langle UV \rangle}$ term, the first order term yields the nuclear elastic scattering. Doing this for a Bravais lattice of scattering sites, the resulting nuclear elastic partial cross section is:

$$\left(\frac{d\sigma}{d\Omega} \right)_{coh} = \frac{(2\pi)^3 \sigma_{coh} N}{4\pi v_0} e^{-U^2} \sum_{\tau} \delta(\kappa - \tau) \quad (1-2)$$

The delta function reflects the Bragg condition for scattering in which elastic reflections occur only for momentum transfers equal to a reciprocal lattice vector τ of the system. For a non-Bravais lattice, the cross section becomes:

$$\left(\frac{d\sigma}{d\Omega} \right)_{coh} = \frac{(2\pi)^3 N}{4\pi v_0} \sum_{\tau} \delta(\kappa - \tau) |F(\kappa)|^2 \quad (1-3)$$

where $|F(\kappa)|^2 = \sum_d \bar{b}_d e^{i\kappa \cdot d} e^{-U^2}$ is the nuclear structure factor summed over all sites, d , in the unit cell. The delta-function and structure factor terms reflect the presence of cooperative effects in the coherent scattering cross section, whereas for incoherent nuclear elastic scattering, the cross section is simply:

$$\left(\frac{d\sigma}{d\Omega} \right)_{inc} = \frac{N}{4\pi} \sum_d \sigma_{inc} e^{-U^2} \quad (1-4)$$

and depends only on scattering sites correlated with themselves [29]. Higher order terms in the expansion of $e^{\langle UV \rangle}$ give the cross section for nuclear inelastic lattice processes governed by phonon excitations. Specifically, the second order term gives the cross section for coherent one phonon scattering and is extremely useful in mapping out the phonon dispersion relations in crystal systems. The resulting cross section for coherent one phonon creation is:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{coh+1} = \frac{k_f (2\pi)^3}{k_i 2v_0} \sum_s \sum_{\tau} \frac{1}{\omega_s} \left| \sum_d \frac{\bar{b}_d}{\sqrt{M_d}} e^{U^2} e^{i\kappa \cdot d} (\kappa \cdot e_{ds}) \right|^2 \langle n_s + 1 \rangle \delta(\omega - \omega_s) \delta(\kappa - q - \tau) \quad (1-5)$$

and will be discussed in more detail in Chapter 6.7.

In addition to probing nuclear scattering sources, the intrinsic spin of the neutron and its resulting magnetic dipole moment can also probe the local magnetism from unpaired electrons within condensed matter systems. Although the dipole-dipole interaction between the neutron and unpaired electrons is effectively weaker than the stronger nuclear scattering forces, the resulting cross section of magnetic scattering is on the same order of magnitude as nuclear scattering due to the long range of the magnetic

interaction. For an electron with a magnetic moment, μ_e , and momentum, p , the magnetic field felt by the neutron is $B = \frac{\mu_o}{4\pi} \left[\nabla \times \left(\frac{\mu_e \times \hat{R}}{R^2} \right) - \frac{2\mu B}{\hbar} \frac{p \times \hat{R}}{R^2} \right]$. The generalized partial scattering cross section of the neutron is then given by [29]:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{k_f}{k} \left(\frac{m}{2\pi \hbar^2} \right)^2 \left| \langle \alpha' \beta' | V_m | \alpha \beta \rangle \right| \delta(E_\alpha - E_{\alpha'} + \hbar \omega) \quad (1-6)$$

where $V_m = -\mu_n \cdot B$ is the potential experienced by the neutron within the scattering system, and α, β and α', β' refer the initial and final states of the electron (α) and neutron (β) systems, respectively. The delta function term in energy simply equates the change in the electron system's energy to the energy lost or gained by the scattered neutron, $\hbar \omega$. For a system of localized electrons, the magnetic cross section in a Bravais crystal becomes [30]:

$$\frac{\partial^2 \sigma}{\partial \omega \partial E} = \frac{\gamma r_0}{2\pi \hbar} \frac{k_f}{k} N \frac{g}{2} F(\kappa)^2 \sum_{\alpha, \beta} (\partial_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta) \sum_l e^{i\kappa \cdot l} \int_{-\infty}^{\infty} \langle e^{-i\kappa \cdot u_0(0)} e^{-i\kappa \cdot u_0(t)} \rangle \langle S_0^\alpha(0) S_l^\beta(t) \rangle e^{-i\omega t} dt \quad (1-7)$$

where α, β are summed over x, y, z components; S is the time-dependent spin operator for an electron at site l ; γr_0 is 1.913 times the classical electron radius; and $F(\kappa)$ is the electrons' magnetic form factor. The form factor is simply the Fourier transform of the unpaired electron density and can be calculated from numerical approximation or measured. The most enlightening component of the above formula is that the neutron's cross section in scattering from a system of localized spins is directly proportional to the Fourier transform of the electron spin-spin correlation function, $\langle S_0^\alpha(0) S_l^\beta(t) \rangle$, in both space and time. This function provides information regarding the correlation between the α^{th} spin component of an electron on a given site with β^{th} component of those on all other sites (including itself) after some time interval t . Through this relation, it becomes clear that, through mapping out the magnetic cross section in (κ, ω) space, both static and fluctuating order in a spin system can be studied and a great deal of information ascertained.

As an example, the correlation function can be broken up into both inelastic and elastic scattering components, probing both fluctuating and static order, respectively. Looking first at the elastic magnetic scattering in a non-Bravais lattice, the differential coherent cross section becomes [30]:

$$\left(\frac{\delta \sigma}{\delta \Omega} \right)_{coh} = (\gamma r_0)^2 N \frac{(2\pi)^3}{v_0} \sum_\tau \partial(\kappa - \tau) \left| \sum_d e^{i\tau \cdot d} e^{U^2} \frac{g}{2} \langle S_d \rangle F_d(\tau) [\hat{\tau} \times (\hat{\mu}_d \times \hat{\tau})] \right|^2 \quad (1-8)$$

In this expression, the directional dependence of the magnetic scattering becomes clear. The magnitude of the scattering intensity depends, not only on the ordered moment of unpaired electrons, but also on the relative orientation of the ordered moment direction and the measured wave vector. This is a generic feature of magnetic scattering in which the cross section is only sensitive to the moments oriented perpendicular to the scattering wave vector. The vector relation between the cross section and the ordered moment

direction is often exploited to determine the precise magnetic ordering direction in a given spin system.

The scattering cross section can also be expressed in terms of the scattering function $S(\kappa, \omega)$, where $\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right) = \frac{k_f}{k_i} S(\kappa, \omega)$. After measuring the scattering function $S(\kappa, \omega)$, the imaginary component of the dynamic susceptibility, $\chi''(\kappa, \omega)$, can be calculated via the fluctuation-dissipation theorem, where $S(\kappa, \omega) = \frac{1}{\pi} \langle n(\omega) + 1 \rangle \chi''(\kappa, \omega)$.

The term $\langle n(\omega) + 1 \rangle = \left(1 - e^{\frac{-\hbar\omega}{k_B T}} \right)^{-1}$ and the resulting cross section can then be expressed as [30]:

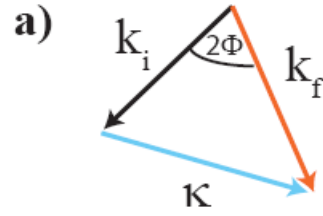
$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right) = \frac{k_f}{k_i} F(\kappa)^2 \frac{\gamma r_0}{\mu_B} \frac{2}{\pi g^2} \langle n(\omega) + 1 \rangle \chi''(\kappa, \omega) \quad (1-9)$$

The newly determined values for $\chi''(\kappa, \omega)$ can then be compared with theoretical predictions of the resulting susceptibility.

1.4 Experimental procedures

In order to probe the scattering cross section of materials, experiments must be carried out at a variety of neutron spectrometers whose primary attributes are largely determined by the neutron source at which they are located. Although there are a large variety of spectrometer types, the types of neutron spectrometers discussed here will comprise those used in the research I will discuss in the following chapters.

The triple-axis spectrometer is located at continuous neutron sources, such as research reactors. It is fundamentally comprised of three stages or axes, which in turn are used to position a detector to measure a specified point in reciprocal space. The first axis consists of the monochromator crystal, which chooses the neutron wavelength (k_i) incident on the sample. This is effectively achieved through the simple Bragg condition of a given reflection from the monochromator crystal itself. The second axis consists of the sample being studied, which is then positioned so that the needed κ (wave vector transfer) in reciprocal space is probed. Finally, the third axis consists of the analyzer crystal which, through the Bragg condition of the specified reflection, chooses the final wavelength of the neutrons scattered to the detector. All three axes are coupled in the progression from monochromator to sample to analyzer, such as is shown in Figure 1.3. This method of choosing a given point in reciprocal space and measuring the resulting scattering function comprises an extremely powerful and commonly used technique in neutron scattering. By measuring the appropriate background and nuclear scattering terms, one can extract a measurement of the dynamic susceptibility for a system and then proceed to chart its (κ, ω) dependence. With the advent of spallation neutron sources, one can now also obtain entire maps of (κ, ω) space at once; however, the strength of the



“Scattering Triangle”

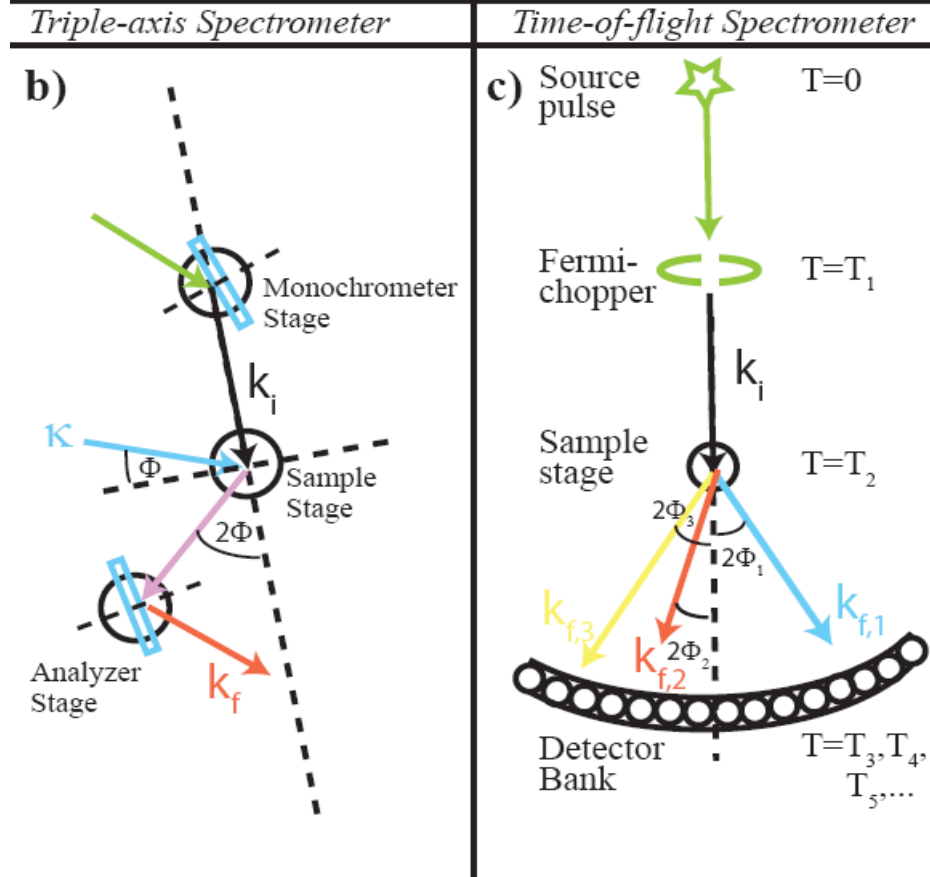


Fig. 1.3 Schematic of scattering processes for triple-axis and time-of-flight spectrometers. (a) Simple picture of the fundamental scattering triangle law in which momentum is conserved. (b) Schematic of the fundamental components of a triple axis spectrometer. Reflections from the monochrometer and analyzer stages are utilized to define the incident and final energies for the experiment, while the sample stage orients the correct Q-space position into the analyzer stage. (c) Schematic for the time ordered processes in a time-of-flight spectrometer. The rotating Fermi-chopper selects a monochromatic beam incident on the sample based on the known distance and pulse time of the source. Once the incident energy is selected, the known distances of the sample stage and detector bank allow the final scattered energies to be determined. Position-sensitive detectors and the known positioning of the detector channels allow for Q-space resolution, which is coupled to the time-channels of the detectors (which resolve the final scattered energies).

triple-axis technique is its ability to perform studies in a focused range in (κ, ω) space or often times about a single point.

The kinematics of a neutron reflecting off of the monochromator with a certain energy $\left(\frac{\hbar^2 k_i^2}{2m_n}\right)$, scattering from the sample at a desired wave vector transfer (κ) , and then

reflecting off of the analyzer with the desired final neutron energy $\left(\frac{\hbar^2 k_f^2}{2m_n}\right)$ places

constraints on which points are accessible in (κ, ω) space, since in scattering, the k_i and k_f wave vectors must be adjoined by the resulting κ wave vector probed. This in effect forms a “scattering triangle” that can only be closed within a certain range of energies and wave vector transfers (Fig. 1.3). Therefore, navigating (κ, ω) space often requires choosing various incident energies, final energies, or scattering zones (symmetrically equivalent positions in reciprocal space) in order to reach and study the desired position. For a reactor source, the incident energy range is limited by the moderator of the neutron source. Due to this, there exist primarily three types of moderators: thermal, cold, and hot. The moderator consists of a material with a strong scattering cross section that statistically moderates the neutrons traveling through it to its energy range (temperature) through multiple collisions. Thermal moderators typically create a peak neutron flux around 30 meV with ($\sim 300\text{K}$) with a flux profile often dependent on the specifics of the reactor. Cold neutron moderators utilize liquid hydrogen to create a peak neutron flux $\sim 4\text{meV}$. Hot neutron moderators are used to obtain higher incident energies $E_i > 60\text{ meV}$. There are also a variety of factors chosen due to the necessary resolution of an experiment. Although they will not be discussed in detail here, neutron collimation and the use of smaller incident energies allow for superior resolution.

The use of Bragg scattering conditions in order to monochromate the incident and final neutron energies has the complicating influence of allowing higher harmonics into the scattered beam. Since the Bragg condition is governed by $n\lambda = 2d\sin(\Phi)$, for a given scattering value of Φ there will exist $n=1,2,3,\dots$ wavelengths present if the scattering crystal has allowed higher order reflections at the appropriate d -spacings. For instance, in a pyrolytic graphite (PG) crystal an incident wavelength λ can be chosen at a given angle through using the $(0, 0, 2)$ reflection along the c -axis. Since the $(0, 0, 4)$ is also an allowed reflection, then along this same scattering angle will also appear scattered neutrons of wavelength $\lambda/2$. This process results in possible incident energies of nk_i or n^2E_i that must be filtered out in order to isolate a single desired scattering process. This filtering can be accomplished in a number of ways, and one common method is the use of PG filters that have a very unique transmission profile. Using these filters allows certain magic energies to be chosen for transmission (i.e. $E_i \sim 13.5, 14.7, 30.5, 35\text{ meV}$), while their higher harmonics are absorbed.

For long wavelength neutrons, another type of filtering can be utilized in which there exists a so-called “Bragg cutoff” for transmission above a given energy. This works through the basic Bragg scattering condition that $2k_i > \kappa$. For $k_i < \kappa/2$, there will exist no Bragg scattering for those energies and a cutoff in transmission will be established once the Bragg condition is satisfied (i.e. $k_i > \kappa/2$). For example, consider an

polycrystalline material with a low incoherent cross section and small lattice spacing, such as Be powder with hexagonal symmetry and $a=2.29 \text{ \AA}$. The first allowed reflection is (1, 0, 0) with $\kappa \sim 2.74 \text{ \AA}^{-1}$, which means that neutrons with k_i below $\kappa/2$ sit below the cutoff. This creates a step function-like filter with transmission below $\sim 4 \text{ meV}$, and eliminates higher order reflections from the monochromator. These are the two primary methods of eliminating this contamination utilized in my experiments, although other methods such as using monochromating crystals with lower symmetry (e.g. Si) are also viable, depending on the experimental requirements.

Time-of-flight spectrometers are designed based on the principal of maximizing the advantage gained when using a time-resolved neutron spallation source (Fig. 1.3). Since the spallation source consists of pulsing high-energy protons on a target at a specified time and thus generating a broad spectrum of resulting neutrons at given time intervals, the time-of-flight instrument must utilize this aspect. This is often achieved through the creation of a large array of detectors in the forward scattering direction of the beam. A given initial energy of neutrons is chosen to be incident on the sample by the use of a timed neutron gate called a “chopper”. The chopper effectively only allows neutrons traveling a certain speed from the spallation source to strike the sample. From the time that the monochromatic neutron beam is incident on the sample (which is known due to the chosen E_i) neutrons scattered at a variety of wave vector transfers, and final energies are measured simultaneously through the detector bank arrays and their time channels. From the simple kinematics of the scattering collisions and resulting energy transfers to the scattered neutrons, a map of (κ, ω) space is generated. This technique is particularly powerful for an overall picture or an initial survey of the various features of a system’s scattering cross section. However, since the incident time-integrated neutron flux is comparatively low and the compensation for this is to measure large areas of reciprocal space at once, this technique is not ideal for a focused study of a particular feature as a function of an environmental variable (e.g.. temperature, magnetic field, etc.) which is often of great interest. It should be noted that time-of-flight spectrometers can also be built at reactor sources with the use of additional chopper gates to actually create a time resolved source from the continuous flux of the reactor. The large flight paths of the scattered neutrons and the advance of position-sensitive detector arrays also enable high-resolution measurements at high incident energies not possible on triple-axis spectrometers.

In conducting an experiment, the position in (κ, ω) space is chosen relative to a starting reference point. This reference point is defined by the initial alignment of the sample to be studied. A given scattering plane is chosen and a known Bragg reflection within that plane must be defined at a given angle in order to calibrate the spectrometer to the specific orientation of sample to be studied. This is most efficiently performed on a triple-axis spectrometer using neutrons to find the sample’s alignment. It can also in principle be done on a time-of-flight instrument, although this becomes difficult when aligning and coaligning more than one sample. X-rays are also often used, although at the disadvantage that only the surface alignment is probed and not the bulk. Once the alignment is completed, often shielding is placed around areas close to the sample holder or area in order to reduce background scattering. Gadolinium, boron, and cadmium are efficient neutron absorbers and provide significant background reduction (although

radiological concerns due to prompt gamma radiation prohibit their use at some sources). After the shielding is applied, the aligned sample and the necessary sample environment are loaded into the spectrometer and the experiment commences.

Experimentally, the neutrons measured at a given solid angle in (κ, ω) space originate from a number of different processes. In order to isolate the relevant neutron counts for a given process, the neutrons scattered from other “background” processes must be identified and removed. Many of these background neutron counts come from the fast neutron background intrinsic to the spectrometer setup and source environment. These can be isolated in a variety of ways, the easiest of which can be achieved by simply shielding the sample or removing it entirely and repeating the measurement.

Another source of background is often incoherent scattering from components of the spectrometer which can scatter elastically into the detector (although shielding attempts to minimize this). Background also is generated by the sample in the form of elastic and inelastic processes which are not of interest. One example is multiphonon scattering which is present as a continuum of scattering at various energies rather than more easily recognizable one-phonon scattering. Background scattering also arises from components of the sample holder that typically consist of Al due to its high neutron transparency and from elastic and inelastic processes from the various components of the spectrometer (such a phonon scattering in the monochromator). Since in the work presented here, we are concerned only with magnetic scattering, it is useful to review simply cursory experimental tests we use to determine if a signal is magnetic and arises from the sample.

In isolating magnetic scattering, the most common initial approach is to test the dependence of the scattering on changes to the sample environment. Scattering not associated with the sample will not have any dependence on the sample environment parameters, and this readily allows for the removal of a large amount of spurious scattering. Magnetic scattering will eventually disappear above a given temperature depending on the specifics of the system and the origin of the spin signal. A useful test then is to compare neutron spectra collected at high temperatures with that collected at low temperatures (e.g. below the ordering temperature of some magnetic phase). Low temperature spectra also have the added advantage of minimizing contributions from phonon scattering (both one-phonon and multiphonon) through minimizing the Bose population factor. Thus, in many cases the magnetic signal at low- T is maximized while the contamination from phonon background processes is minimized. This of course does not apply to magnetic excitations that also follow Bose statistics such as spin waves.

Another quick test probing the magnetic origin of a given scattering signal is to check its κ -dependence. By measuring the neutron cross section at several symmetrically equivalent positions in κ -space, a number of things can be inferred. Since the scattering functions for phonon processes are proportional to κ^2 projected and the phonon polarization vector’s projection along κ , the cross section observed in higher order zones in reciprocal space will get larger. For magnetic scattering however, the cross section is instead proportional to the magnetic form factor for the ion, which as stated early is simply the Fourier transform of the electron spin density (for spin only signal). The form factor instead decreases at larger Q , and hence the magnetic signal will instead taper off as it is measured in progressively higher order scattering zones. Despite these quick tests,

at times magnetic scattering can be hard to discern due to background processes which mask the signal.

The most powerful and conclusive way to resolve a magnetic signal is to utilize polarized neutron scattering techniques. These polarized experiments are, however, often severely limited due to the reduced incident neutron flux resulting from the creation of a polarized neutron beam and the multiple cross sections that must be measured. When possible, polarized neutron measurements are an extremely effective tool for resolving a large number of scattering processes separately, and further details of the technique will be discussed in Chapter 3.

Comment on notation:

For the remainder of this dissertation, I refer to the neutron wave vector transfer as, $\mathbf{Q}$, where $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$. I will also refer to positions in reciprocal space using reciprocal lattice unit (r.l.u.) notation where $\mathbf{Q}$ [r. l. u.] = (H, K, L) corresponds to $\mathbf{Q}$ [$\text{\AA}^{-1}$] = $(H 2\pi/a, K 2\pi/b, L 2\pi/c)$. In some instances the notation $\mathbf{Q}_{\text{plane}} = (H, K)$ will be used. This is used to denote quasi-two dimensional features that are rod-like along the L -direction, and in this case only H and K values within the CuO_2 plane are meaningful. For excitations measured at a finite energy, the stated energy value, $\hbar\omega$ or E , is the energy transferred to the system by the scattered neutron or the neutron energy lost during the inelastic process. Neutron intensity values in many plots are labeled as (counts/ [unit time]) for convenience and to give a relative sense of scale; however, the actual measure controlling each counting span is the monitor counts measured by the spectrometer's monitor detector (a low efficiency fission chamber). This ensures that the same incident flux of neutrons interacts with the sample per counting division. Another beneficial property is achieved through the monitor's normalization of the neutron's resolution volume due to the monitor's variable efficiency at different incident energies (only when a fixed final neutron energy is analyzed).

Chapter 2: Neutron scattering and hole-doped high- T_c

This chapter is meant to simply provide a quick and general overview of the important experimental results derived from studying magnetism in hole-doped high- T_c systems via neutron scattering. References to more detailed phenomenon in hole-doped systems will be made in later sections when our results on n -type PLCCO are compared and contrasted to magnetic features thought to exist universally within the classes of p -type compounds.

2.1 Parent Compounds

The undoped parent systems of the high- T_c cuprates are universally AF ordered insulators. Spin ordering and magnetic excitations in these systems are governed by the unusually large superexchange coupling within the copper-oxygen layers. As mentioned earlier, the magnetic exchange between copper sites within the copper-oxygen plane is on the order of $J_{ab} \sim 100$ meV and is much greater than the out-of-plane exchange $J_{ab} \gg J_c$. This results in a quasi-two dimensional antiferromagnetic lattice of spins whose true Néel ordering temperature is determined by the much weaker out-of-plane exchange. Two-dimensional spin correlations within the CuO_2 planes survive far above this Néel ordering temperature due to the much larger in-plane superexchange coupling. When looking at the spin behavior of these systems at finite energy scales, the system is well modeled as a two-dimensional quantum Heisenberg antiferromagnet on a square lattice. The Hamiltonian for the spin system is: $H = J_{nn} \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j + J_{nnn} \sum_{i,k} \mathbf{S}_i \cdot \mathbf{S}_k$. For monolayer

La_2CuO_4 , the dispersive spin excitations observed were quantitatively described using this Heisenberg model [31] along with linear spin-wave calculations with nearest and next-nearest neighbor exchange couplings of $J_{nn}=104$ meV and $J_{nnn}=-18$ meV, respectively.

The situation is slightly different in the bilayer cuprate systems (systems with 2 CuO_2 planes within the unit cell). The spin Hamiltonian for these bilayer systems contains an additional term reflecting the coupling between nearest neighbor spins in neighboring bilayers. For nearest neighbor terms it can be represented as $H = J_{\parallel} \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j + J_{\perp} \sum_{i,j'} \mathbf{S}_i \cdot \mathbf{S}_{j'}$, where $\langle i,j \rangle$ pairs are within the CuO_2 planes and $\langle i,j' \rangle$

represent nearest sites coupled between different layers. This bilayer coupling term results in a splitting of the spin-wave excitations into both acoustic (odd) and optical (even) modes in the magnon spectrum under the linear spin wave approximation. As a result, spin excitations in the odd channel, which measures spins in opposing bilayers rotating in the same direction, acquire a $\sin^2$ modulation along L whose periodicity is dependent on the c -axis lattice constant and the distance between the bilayers. Similarly, excitations in the even channel, where spins in opposing bilayers rotate in opposite directions, acquire a $\cos^2$ modulation in their spectrum. The optical mode has a gap in the spectrum of YBCO(6.15) at $\hbar\omega = 74$ meV, and the spin wave spectrum is again well modeled using the Heisenberg formalism with a $J_{nn} \sim 125$ meV for spins within in the

plane and a $J_{\text{perp}} \sim 10$ meV for spins between the bilayers [32]. The respective excitation branches for YBCO(6.15) are qualitatively illustrated in Figure 2.1.

The parent compounds for the electron-doped cuprates, Pr_2CuO_4 and Nd_2CuO_4 , show a qualitatively similar behavior in their high-energy spin wave dispersion to that of La_2CuO_4 . These undoped *n*-type parents give a comparable $J_{\text{nn}} \sim 120$ meV [33], although a notable difference in the zero-field, static, spin structure is evident between these systems and the parent systems of hole-doped cuprates. For hole-doped parent systems, as shown in Figure 2.1, the spin directions of Cu^{2+} moments are parallel between neighboring CuO_2 planes [18]. This is referred to as a collinear configuration. For electron-doped parent systems, however, the zero field spin structure is instead noncollinear [34]. This simply means that spin directions in neighboring CuO_2 planes are now instead orthogonal to each other in one of several allowable phases (Fig. 2.1). As a consequence, the allowed AF Bragg reflections from these two structures differ slightly. Most importantly, the AF zone center $(0.5, 0.5, 0)$ in collinear spin structures is a disallowed reflection in the noncollinear spin state for static order. Along this ordering wave vector, in Pr_2CuO_4 inelastic spin wave excitations are gapped due to the inter-plane magnetic anisotropy with a higher energy gap appearing due to the in-plane anisotropy [35]. Aside from these low energy gaps resulting from perturbation terms due to anisotropy effects, the spin behavior of these parent systems are remarkably well modeled by the quantum 2D-Heisenberg Hamiltonian on a square lattice stated above.

2.2 Low energy incommensurability in *p*-type

One of the key questions in understanding the role of magnetism in high- T_c superconductivity is: How do both static and fluctuating magnetic order evolve as the system is tuned from an AF insulator into a paramagnetic superconductor? Over the past twenty years, there has been an extensive experimental effort in probing how magnetism evolves in several classes of hole-doped systems. Of particular importance is how the long-ranged AF Néel order in the parent compound evolves upon hole-doping. It is helpful to focus first on the well-established results for the hole-doped system, LSCO, whose phase diagram is reproduced in Fig. 2.2. AF order in this system is quickly suppressed and completely destroyed at hole-doping concentrations of $\sim 2\%$ (where $x \sim 0.02$). Until this doping is reached, static AF Bragg reflections are observed at the commensurate $\mathbf{Q} = (0.5, 0.5, 0)$ ordering wave vector in reciprocal space (Fig. 1.5).

The suppression of long-range, three dimensional AF order above 2% doping drives the system into a spin-glass phase at low temperatures. The magnetic response of this phase renders a drastically different behavior in terms of static order observed. Rather than a magnetic reflection centered at $\mathbf{Q} = (0.5, 0.5, 0)$, two incommensurate peaks appear displaced a distance δ from the AF ordering wave vector and rotated by 45 degrees (Fig. 2.2). This incommensurate ordering is indicative of a spin density wave modulation along the diagonal between the bond directions in the CuO_2 planes that is seemingly one-dimensional [36]. For low doping levels within the AF phase, but near the phase's suppression, this diagonal spin density wave modulation develops below the Néel temperature and precipitates from the destruction of the 3D AF matrix through

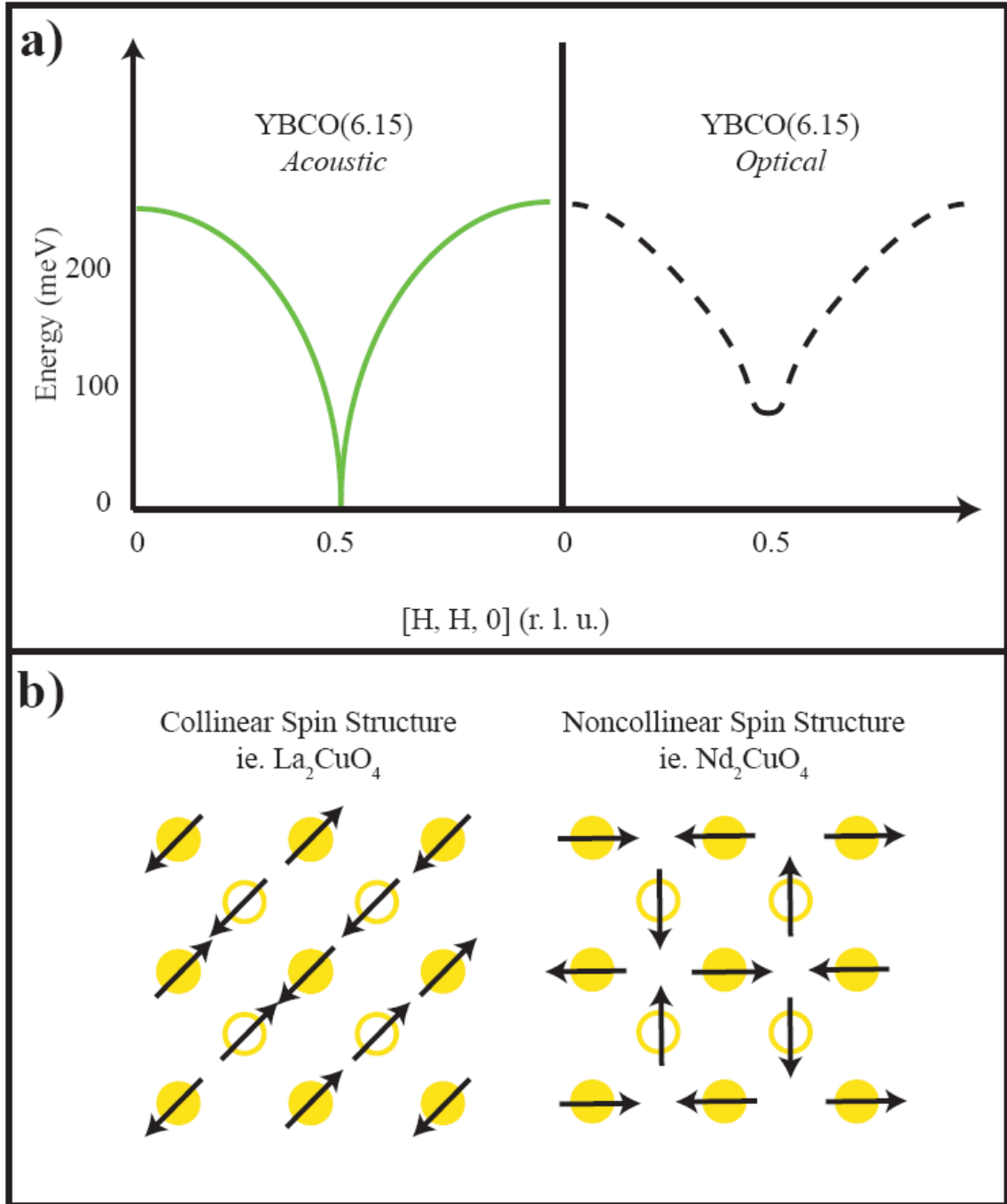


Fig. 2.1 Spin wave dispersion of parent compound YBCO(6.15) and collinear/noncollinear spin structures. a) Qualitative picture of the spin wave dispersion reported in YBCO(6.15) Ref. 32. The left panel denotes the gapless acoustic mode and the right panel shows the optical gap in this system at ~ 75 meV. b) Examples of spin structures observed within the parent compounds of both hole and electron-doped cuprates. Neighboring planes have parallel spins in the collinear spin structure, whereas they are rotated by 90 degrees from one another in the noncollinear-type orientation.

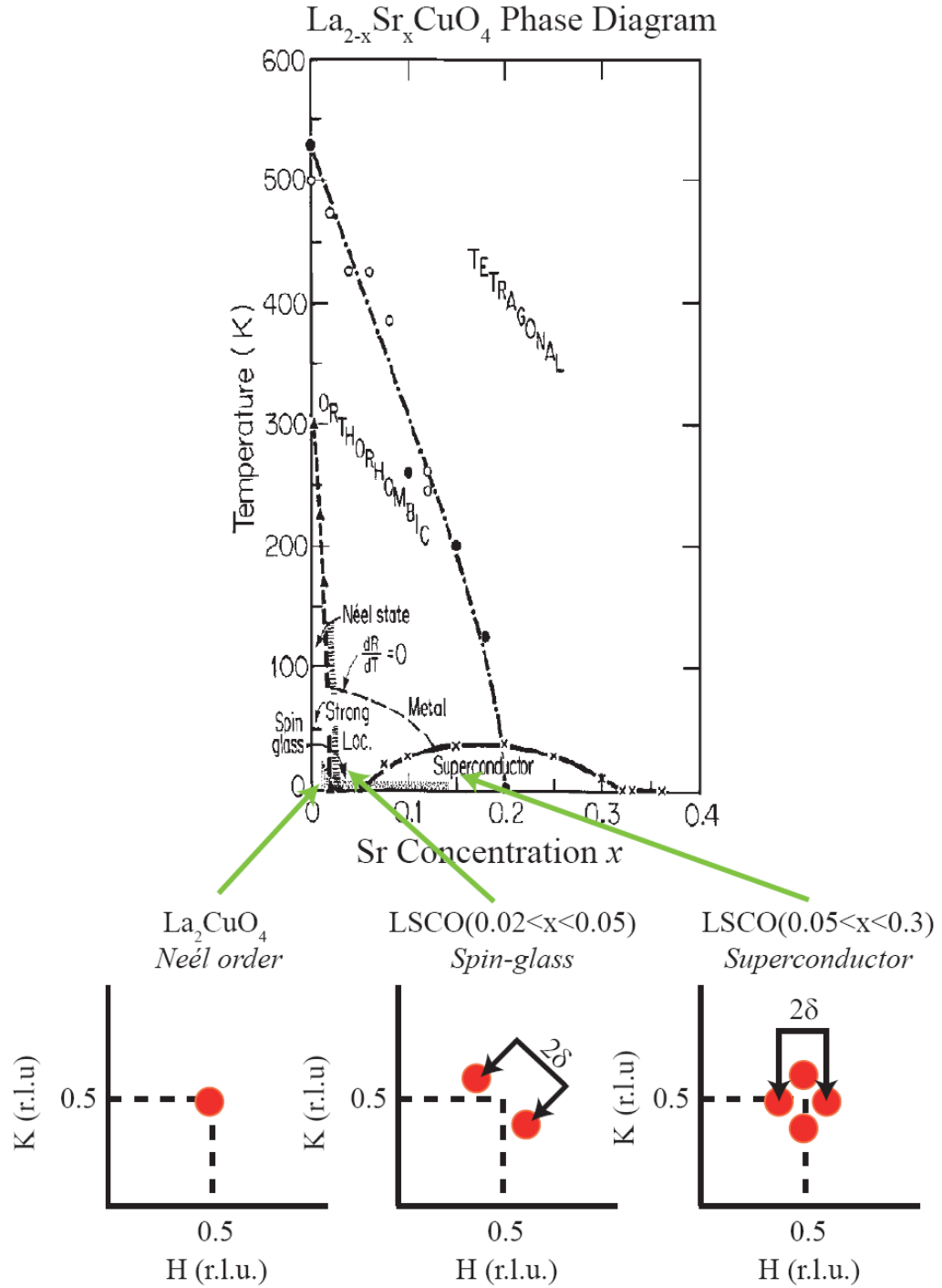


Fig. 2.2 Phase diagram and Q-space visualization of static magnetic order in LSCO. At zero doping, La_2CuO_4 exhibits long range 3D AF order with a magnetic superlattice reflection at $(0.5, 0.5, 0)$. Upon doping $\sim 2\%$ holes into the system this AF order rotates into the diagonal spin density wave modulation phase with two incommensurate peaks separated from $(0.5, 0.5, 0)$ by δ . Superconducting concentrations beginning at $\sim 5\%$ hole doping show a further evolution in which a quartet of incommensurate spin density wave reflections appear.

microscopic electronic phase separation (where regions of 2% hole doping and 0% doping are formed) [37].

Upon further hole-doping, a low-temperature superconducting phase appears at ~5% hole-doping. There occurs a simultaneous shift in the structure of the magnetic order in LSCO with the appearance of the superconducting phase. The incommensurate peaks observed in the spin-glass phase split and rotate by 45 degrees such that the spin density modulation is now along the bond directions in the CuO_2 real-space plane. These peaks are quasi-two-dimensional with long coherence lengths within the CuO_2 plane and exhibit short coherence lengths along the c -axis [38]. This incommensurate spin density wave modulation coexists with the superconducting phase, and the incommensurability (displacement δ away from $\mathbf{Q}=(0.5, 0.5, 0)$) increases roughly linearly with the T_c of the system [39]. Of particular importance is that the appearance of this quartet of incommensurate spin density wave peaks parallels the magnetism observed within “stripe-ordered” $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.125$). In this system, once the doping level reaches $x \sim 1/8$, superconductivity is drastically suppressed and a static stripe phase appears. A stripe phase is a charge ordering phase in which the doped holes are separated into one dimensional rivers of charge separated by AF ordered regions [40]. Although it is known that a static stripe phase directly competes with superconductivity, it is thought that, on shorter time scales, the fluctuating stripe order may in fact contribute to electron pair formation [41].

Upon reaching ~14% doping in LSCO (near optimal doping), the spin density wave order disappears due to the opening of a low energy spin gap. Low energy spin fluctuations above this gap, however, are also split along the same incommensurate wave vectors. In fact, for all superconducting concentrations of LSCO, the low energy spin fluctuations are split along the respective incommensurate ordering wave vectors. This marks drastically different behavior than would be expected from spin wave excitations originating from a dilute three-dimensional antiferromagnet. The incommensurate nature of the low energy spin excitations in LSCO has since been discovered to be a generic feature to all hole-doped high- T_c systems. The hole-doped monolayer system $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ also shows an incommensurate low energy response that was most dramatically demonstrated in the stripe-ordered ($x = 1/8$) concentration [42]. Bilayer systems $\text{YBa}_2\text{Cu}_3\text{O}_{7+\delta}$ [43] and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ [44] also both exhibit an incommensurate quartet of peaks above a low energy spin gap, thereby proving this behavior is not unique to monolayer systems. In order to fully understand the behavior of the incommensurate magnetism in these hole-doped systems, the detailed dispersion of these low energy fluctuations must be fully mapped out. Doing so allows insight into the exchange interactions and magnetic coupling at energy scales relevant to the formation of the superconducting phase.

2.3 Saddle-point dispersion in p -type

The low energy incommensurate spin excitations in the hole-doped cuprates have a ubiquitous pattern of dispersion that has been a recent area of focus. For low energies (potentially above a spin-gap), a quartet of incommensurate magnon peaks disperse inward toward the commensurate position with increasing energy. This dispersion

inward continues until all four peaks reach the commensurate position (sometimes referred to as a “resonance” point) at $Q_{\text{plane}}=(0.5, 0.5)$. Upon continued increases in energy, the four peaks disperse outward from the commensurate position either into a ring-like continuum or into four peaks rotated by 45 degrees from their original orientation. (This is still an issue of debate.) Following this, the incommensurate excitations continue dispersing outward until there are no longer any discernable one-magnon excitations. This results in what is either referred to as saddle-point type dispersion or “hour-glass” dispersion (Fig. 2.3). In the following, I will discuss the various hole-doped cuprate systems where this phenomenon has been observed.

The full hour glass dispersion pattern was first reported in two different hole-doped cuprate systems simultaneously. The discoveries came in both bilayer, underdoped YBCO(6.6) [45] and in monolayer, stripe-ordered, $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.125$) [42], which provided a surprising parallel in spin excitations between a 70K superconductor and a stripe-ordered system in which superconductivity had been suppressed below 3K. Despite the drastically differing T_c 's, an identical pattern of dispersion was observed between the two systems with a rotation of the incommensurate peak structure by 45 degrees above the commensurate dispersion point. Later experiments on YBCO(6.5) claimed that the high-energy dispersion is instead a ring-like excitation similar to that observed in the spin wave excitations of the parent systems instead of the rotated 4 peak structure [46]. The precise structure of the high-energy dispersion, however, is highly sensitive to doping and may account for the discrepancy between the two results for YBCO. It is also important to note that this dispersion is observed in the acoustic (odd) channel of YBCO, although recent experiments have now made similar measurements of the dispersion in the even channels for several YBCO concentrations in which the commensurate resonance point seems to be absent [47].

Later experiments on LSCO reported an identical saddle-point dispersive structure to the spin excitations in this monolayer system [48], and recent experiments have also uncovered this dispersive behavior in another hole-doped bilayer compound, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ [44], thus further cementing this feature as something universal to all classes of hole-doped cuprates. The drastically different dispersive behavior at low energies (inward dispersing quartet of peaks) and high energies (outward dispersing quartet of peaks or continuum) has been suggested to be indicative of two different energy scales dominating these two respective regimes. One possible interpretation put forth is that this behavior originates from spin excitations generated by a dynamically ordered stripe phase. In this view, at low energies spin excitations are dominated by spin wave excitations originating from correlations between different stripe ladders. At higher energies though, the neutron begins to probe spin excitations within one stripe ladder, thereby generating a crossover in the dispersion at the commensurate position in the hourglass. However, another interpretation is that this hour-glass dispersion can simply be understood phenomenologically in terms of the Fermi-surface topology and the resulting Fermi-surface nesting that occurs for portions of the Fermi surface connected by Q_{AF} . Whereas the origin of this behavior in the p -type cuprates remains an issue of debate, the presence of this universal dispersion in a large number of cuprate classes often overshadows the discussion of another universal feature in the magnetism of these systems: the magnetic resonance mode.

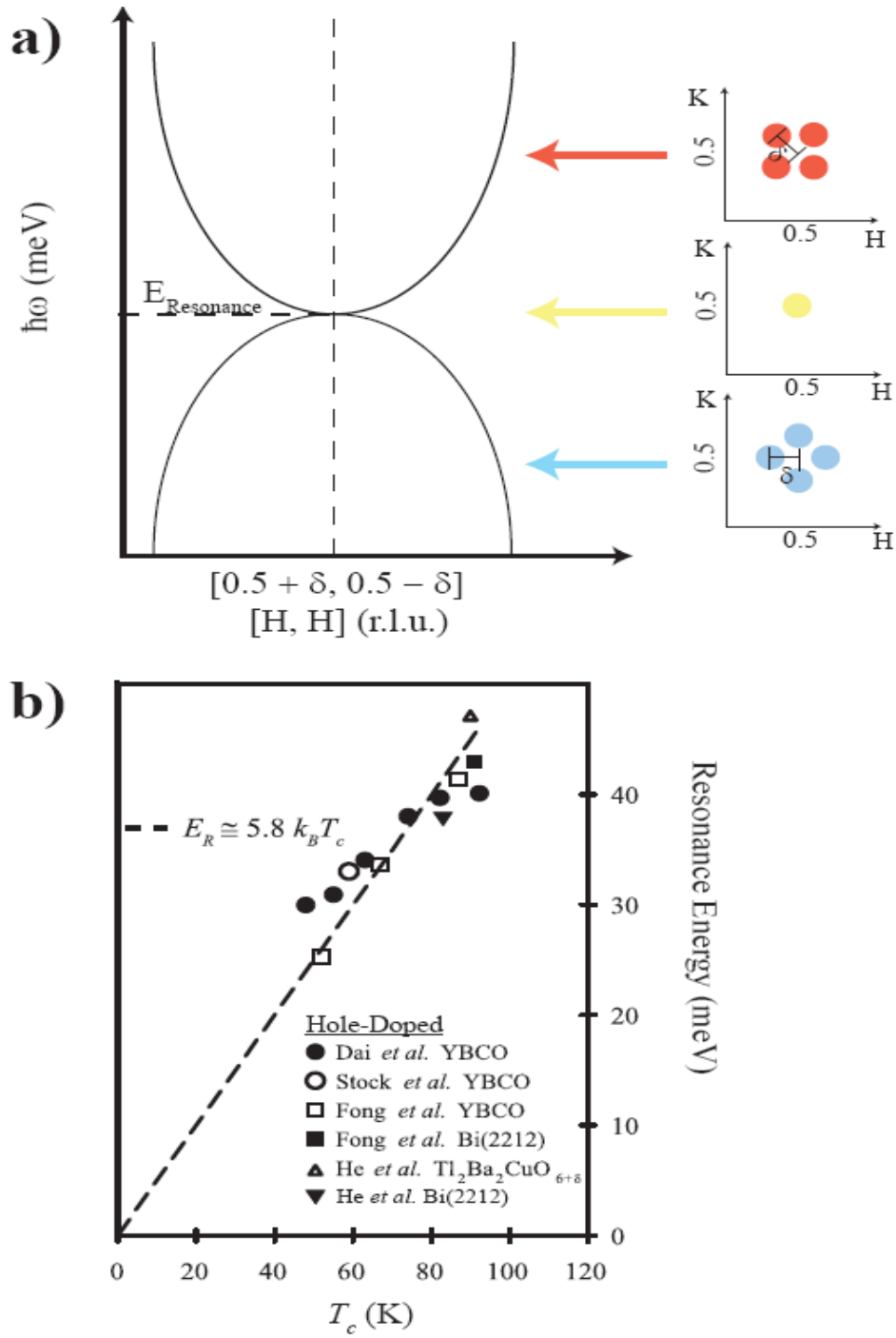


Fig. 2.3 Universal hourglass-type dispersion and universal scaling of the resonance energy in hole-doped cuprates. a) Qualitative depiction of the saddle point dispersion discussed in the text with $\mathbf{Q}$ -space visualization of the structure of spin fluctuations in each energy regime: low energy incommensurate, resonance, and high-energy incommensurate/continuum energy regimes. b) Universal scaling plot of resonance energy versus T_c for several classes of hole-doped cuprates.

2.4 Resonance mode

The resonance mode in the high- T_c cuprates is a collective spin excitation centered at the in-plane AF ordering wave vector $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$. It is fundamentally connected to the superconducting phase and appears only below T_c in optimally doped cuprates. The mode itself has a long lifetime and is sharp in energy (typically resolution limited) and reflects fluctuating spin correlations with a minimum range of $\sim 50\text{-}80$ Å (~ 12 unit cells). First discovered in hole-doped YBCO [49], the resonance mode has since been discovered in a number of other hole-doped cuprate classes. These include both the monolayer cuprate $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [50] and the bilayer compound $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ [51], thereby demonstrating the resonance as a feature independent of any one system's intrinsic properties.

Systematic studies later revealed that the characteristic frequency at which the resonance mode occurs is linearly proportional to the superconducting T_c of the system. This is depicted through the universal relation of $E_R \approx 5.8k_B T_c$ observed between all hole-doped variants (Fig. 2.3). One notable exception to this relation is the absence of the resonance mode in any concentration of LSCO. The failure to find the resonance in this system might be due to disorder effects known to exist in this system such as the canting of spins out of the CuO_2 planes due to distortion on the oxygen octahedral sites. This may render a broadening of the resonance mode in both energy and momentum space, making experimental detection difficult.

Whereas for optimally doped cuprates the resonance completely vanishes above T_c , underdoped systems in the YBCO compound have shown that the mode retains a substantial portion of its spectral weight above T_c . The detailed temperature dependence retains a clear enhancement of the mode upon entering the superconducting phase; however, the presence of the mode above T_c has led to speculation of magnetic signal resulting from preformed pairs in the system. Systematic doping dependence studies have also shown that the onset of this intensity above T_c may be coupled to the pseudogap phase in YBCO as well [52].

Several theories have attempted to model the resonance and its significance in the high- T_c cuprates. If superconductivity is in fact driven by pairing mediated by spin fluctuations, one would expect to observe drastic changes in the spin spectrum of the system as it enters the superconducting phase. This has led to theoretical attempts to envision the resonance excitation in such a pairing role, and recent experimental and theoretical work has shown that the mode indeed possesses enough energy to account for the condensation into the superconducting phase [47, 53]. Another view is that the resonance is simply the consequence of the formation of superconductivity in a system with d -wave pairing and that the mode itself is a spin exciton formed by the opening of a d -wave gap [54]. There are also a number of other models attempting to describe the origin of the resonance mode (such as $\text{SO}(5)$ theory [55]); however, at this moment the investigation is still experimentally driven and considerable debate concerning its underlying origin remains.

Chapter 3: Evolution of low energy spin excitations in PLCCO

Portions of the data and discussion in the following sections with the exception of sections 3.2 and 3.9 have been published recently and can be found in Ref. 56.

3.1 Introduction to phase diagram of PLCCO

Electron-doped cuprates differ from their hole-doped counterparts in the regard that, as-grown, these systems are nonsuperconducting. They require a post-growth annealing treatment in an oxygen poor environment in order to realize a superconducting phase [57]. The annealing process itself is performed at a fixed temperature, under a known oxygen partial pressure, and for a specified length of time. This process is most easily monitored by the removal of small amounts of oxygen from the sample that can be readily measured in a Thermometric-Gravitational-Analyzer or TGA. In addition to this oxygen removal, for $\text{Pr}_{1-x}\text{LaCe}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ the annealing also generates an ordered impurity phase embedded within the matrix of the host lattice [58]. The impurity itself is a cubic $(\text{RE}, \text{Ce})_2\text{O}_3$ with $a_{\text{impurity}}=2\sqrt{2}a$ within the ab -plane and with a $\sim 10\%$ lattice mismatch with the host matrix along the c -axis. Recent experiments have shown that, due to the growth process, the electron-doped system PLCCO is in fact copper deficient once formed [59]. This copper deficiency is highly detrimental to high- T_c superconductivity, which occurs primarily within the CuO_2 layers and thus renders these systems nonsuperconducting due to randomly distributed defects in the copper oxygen planes. Once annealed however, the impurity phase stabilizes within the host matrix, and Cu sites within the newly formed impurity lattice diffuse to the defects in neighboring CuO_2 planes in the PLCCO lattice. This process can effectively “heal” the copper oxygen planes and facilitate the eventual formation of the superconducting phase.

The exact relation between the as-grown Cu deficiency and the oxygen removed during the annealing process has not been precisely understood yet to date. Most likely both processes modify the effective electron carrier concentration in different fashions requiring a detailed understanding of these systems’ phase diagrams. In order to fully explore the phase diagram of an electron-doped cuprate such as PLCCO (whose crystal structure shown in Fig. 1.1), there now appears two possible tuning parameters that are coupled. The first is the Ce concentration x , which in principle dopes electrons into the CuO_2 plane, and the second is the precise annealing condition used to treat the sample following its growth. This means that the phase diagram of the electron-doped copper oxides is three-dimensional as a function of both Ce and oxygen concentration (as shown in Fig. 3.1 for PLCCO). There are therefore two distinct ways to traverse the phase diagram of the n -type cuprates: samples can be prepared at a fixed annealing condition but grown with variable Ce doping levels [60], or alternatively, samples can be grown with a fixed Ce concentration but with variable annealing treatment [61,62].

Although previous efforts in mapping out the phase diagram of PLCCO have focused on using the former method of a fixed annealing treatment, we choose to traverse the phase diagram of PLCCO using the latter method with a fixed Ce concentration and varied oxygen removal. This allows the advantage of comparing the behavior of samples with different electronic properties without the added complication of differing degrees

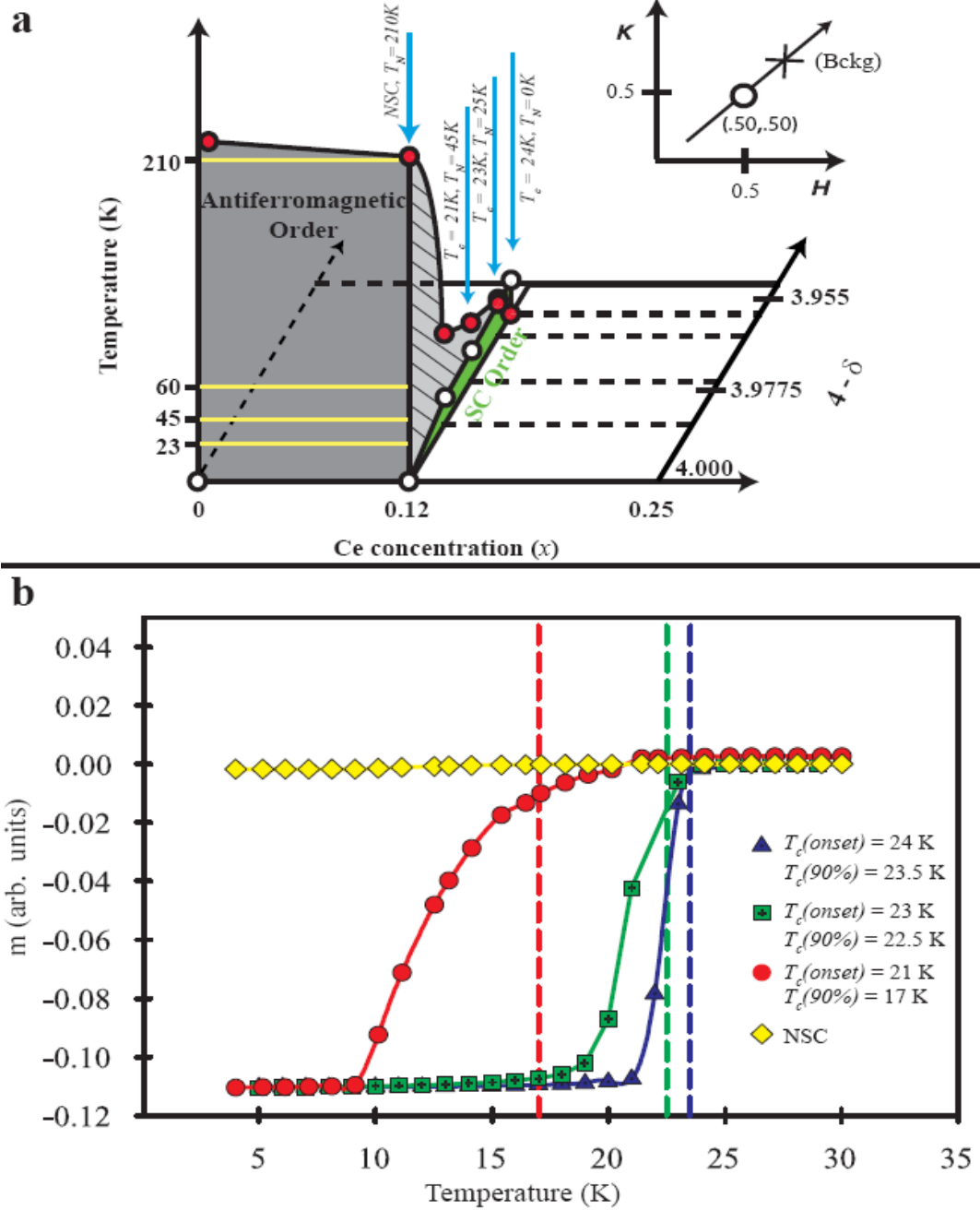


Fig. 3.1 Phase diagram of $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ (PLCCO) and magnetic bulk susceptibility measurements for PLCCO samples studied. a) Phase diagram of PLCCO from Kang et al. [62] with the $T_c = 23\text{ K}$ sample added. The blue arrows denote the sample compositions and locations on the phase diagram that were probed in the neutron experiments. The inset shows the direction of Q-scans with the circle denoting $(0.5, 0.5, 0)$ and the cross indicating where the offset background was measured. b) Bulk susceptibility measurements showing the superconducting phase transitions for the samples studied. Both the onset temperature of superconductivity and the point of 90% of the normal state response (shown as dashed lines) are reported. Susceptibilities have been normalized to one another for plotting purposes.

of chemical inhomogeneity between samples (stemming from the alloying process). The resulting phase diagram for a fixed Ce concentration of 12% is shown in Figure 3.1. It is clear that, although the substitution of 12% Ce only results in a slight suppression of the AF order in as-grown samples, the annealing process induces a rapid suppression of the long-range AF order and the eventual appearance of a superconducting phase transition. With continued oxygen removal, the superconducting phase is enhanced to an optimum T_c where the static AF order is completely suppressed. For samples that exhibit a superconducting phase, an additional quasi-two-dimensional spin density wave (SDW) order appears at the disallowed three-dimensional AF ordering wave vector $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$ in the CuO_2 plane [61,62]. Due to the magnetic structure factor of the noncollinear spin system in the parent compounds Pr_2CuO_4 and as-grown $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ [62], the $\mathbf{Q}=(0.5, 0.5, 0)$ position is a disallowed reflection for 3D AF order. This signifies that AF magnetic order that emerges at this $\mathbf{Q}=(0.5, 0.5, 0)$ wave vector in superconducting concentrations is instead quasi-two-dimensional with minimal correlations between neighboring CuO_2 planes. For this reason we catalogue it as a separate phase on the phase diagram, and we will refer to it as spin density wave (SDW) order: a commensurate analog to the quasi-two-dimensional incommensurate SDW order observed in the monolayer hole-doped cuprate LSCO. The SDW order has an onset T_{SDW} of approximately the AF ordering temperature (T_N) for underdoped superconducting PLCCO samples. Both the 3D AF order and the quasi-2D SDW order are completely suppressed near optimal doping ($T_c \sim 24$ K) as shown in Fig. 3.1. This allows for the advantage of studying how spin dynamics evolve as PLCCO is tuned from an AF semiconductor into a mixed phase superconductor (AF+SDW+SC) and finally into a phase pure superconductor.

3.2 Nature of static order in PLCCO

Before proceeding, it is worth first reviewing the precise nature of the magnetic phases in the phase diagram of PLCCO. This section is a self-contained description of a spin-polarized neutron experiment studying the properties of the quasi-two-dimensional AF order that arises in SC PLCCO concentrations.

From the earlier work of Kang et al. [62], the spin structure of the three-dimensional AF order in NSC PLCCO and coexisting with SC in underdoped PLCCO samples is noncollinear with the spin structure shown in Fig. 3.2. In SC samples, as mentioned earlier, there appears a second magnetic phase at the $(0.5, 0.5, 0)$ position that is disallowed for the noncollinear AF Néel order. This phase has been shown to be quasi-two-dimensional with little correlation along the c -axis and long correlation lengths within the ab -plane. One difficulty in studying this magnetic signal at $(0.5, 0.5, 0)$ is that it coincides with the nuclear scattering from the embedded impurity phase, $(\text{Pr}_{1-x}\text{LaCe}_x)\text{O}_3$, whose superlattice reflections also appear at $\mathbf{Q}=(0.5, 0.5, 0)$. This effectively masks a great deal of the magnetic signal due to the greatly increased nuclear scattering background at this position.

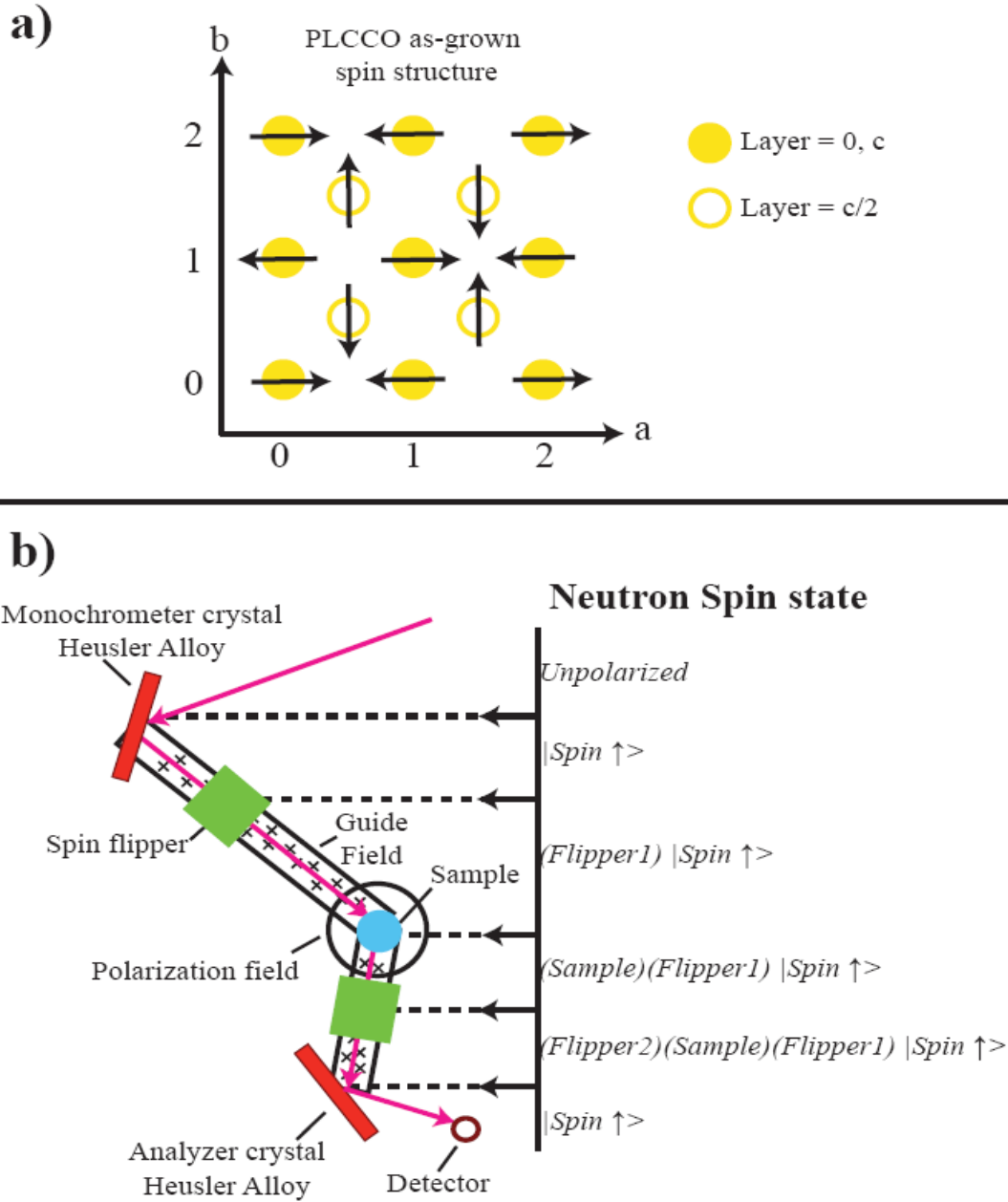


Fig. 3.2 Noncollinear spin structure of as-grown PLCCO and schematic of polarized neutron triple-axis experimental setup. a) Precise spin structure for 3D AF order in PLCCO as determined from Ref. 62. Neighboring CuO_2 planes are denoted by open and solid circles for clarity. b) Example of a polarized beam setup for a triple-axis spectrometer. The spin states of the neutron are denoted on the right along with the order of operators based on the flight and scattered state of the neutron. The components, labeled here, are described in the text along with their influence on the neutron spin state.

In an attempt to test the precise spin structure of this quasi-two dimensional AF phase, we performed spin-polarized neutron scattering experiments on a $T_c = 21\text{K}$ PLCCO sample that possesses coexisting magnetic order with SC below $T_{SDW} \sim 40\text{K}$. Polarized neutron experiments have the unique advantage of intrinsically separating the magnetic and nuclear scattering processes involved at a given position in reciprocal space. Before covering the results of our experiments, it is helpful first to review some of the fundamental principles of polarized neutron scattering.

The setup for a typical polarized neutron experiment on a triple axis spectrometer is shown in Fig. 3.2. The incident beam is polarized by the spin dependent reflectivity of a Heusler alloy monochromating crystal (eg. Cu_2MnAl). We will denote the spin state reflected as $\uparrow$ and the spin polarization direction as the z -direction. Following the monochromator, the spin state and polarization of the neutron is preserved via a weak guide field along the flight path of the neutron. The neutron then passes through a spin flipping device (typically a RF Mezei coil). This component utilizes a field orthogonal to the neutron polarization direction in order to induce a precession of the neutron moment about the applied field axis. With an appropriately tuned field strength and length of interaction, neutrons of a given energy can be made to effectively “flip” their spin state from $\uparrow$ to $\downarrow$ upon exiting the coil. This allows variable control of the spin state of the neutron incident upon the sample since the monochromator is only capable of reflecting $\uparrow$ neutrons. Once the neutron is incident upon the sample, the diffracted beam, depending on the origin of the scattering process and the neutron polarization, will either preserve or flip the neutron spin. A set of magnetic coils at the sample position are simultaneously used to precisely tune the neutron polarization direction relative to the scattering wave vector $\mathbf{Q}$ (the importance of this will be discussed shortly). The diffracted neutrons then pass through another Mezei coil gate which can be tuned to either preserve or flip the scattered spin state of the neutron prior to reaching the polarizing analyzer. Finally, the Heusler analyzing crystal reflects only neutrons of the spin state $\uparrow$ to the detector, which are then counted.

Simply put, this spectrometer configuration allows for precise control over the incident spin state of the neutron on the sample, control over the angle between the neutron polarization and the scattering wave vector, and over resolving the polarization of the neutrons diffracted from the sample. Using the notation of Moon et al. [63], I will refer to the reflected beam polarization as (+). If this is flipped, it then becomes (-). For the measured cross section, there are four possibilities controlled by the neutron spin states that are denoted as (++), (--), (+-), or (-+). The first sign refers to the incident polarization of the neutron on the sample, and the second refers to the sign of the polarization immediately after being scattered by the sample. These different scattering cross sections along with the known angle between the polarization vector of the neutron and the scattering angle allow for precise separation of various scattering processes.

As mentioned earlier, scattered neutrons as a probe are only sensitive to the components of the magnetic moments perpendicular to scattering wave vector. This can be exploited in polarized neutron experiments. From Ref. 63, the generalized spin dependent cross section for neutrons scattering from a system in the Born approximation is:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)^{s's} = \sum_q P_q \sum_{q'} \frac{k'}{k} \left| \langle q' | \sum_i e^{i\mathbf{Q} \cdot \mathbf{r}_i} U_i^{ss'} | q \rangle \right|^2 \partial(\Delta \hbar \omega_{neutron} + \Delta E_{system}) \quad (3-1)$$

where $U_i^{ss'} = \langle s' | b_i - p_i S_{\perp i} \cdot \boldsymbol{\sigma} + B_i I_i \cdot \boldsymbol{\sigma} | s \rangle$

In this notation, k and k' are initial and final wave vectors of the scattered neutron, s and s' are the initial and final spin states of the neutron, and q and q' are the states of the scattering system. P_q is simply the probability that the system is in state q and i indexes sites in the unit cell. Now looking at the atomic scattering amplitude term $U_i^{ss'}$: the coherent nuclear scattering length is denoted as b_i , $\boldsymbol{\sigma}$ is the neutron spin operator, p_i is the magnetic scattering prefactor $\gamma r_0(g/2)(S)F(Q)$, I_i is nuclear-spin operator, and B_i is the nuclear-spin dependent prefactor. $S_{\perp} = \hat{S} - (\hat{S} \cdot \hat{Q})\hat{Q}$, as discussed earlier in Chapter 1, is the projection of the moment perpendicular to the scattering vector.

Now the various components of the atomic scattering amplitudes can be broken into the $(++)$, $(--)$, $(+-)$, and $(-+)$ experimental configurations through using the Pauli spin operator properties. This yields the relations [63]:

$$U^{++} = b - pS_{\perp z} + BI_z \quad (3-2)$$

$$U^{--} = b + pS_{\perp z} - BI_z \quad (3-3)$$

$$U^{+-} = -p(S_{\perp x} + iS_{\perp y}) + B(I_x + iI_y) \quad (3-4)$$

$$U^{-+} = -p(S_{\perp x} - iS_{\perp y}) + B(I_x - iI_y) \quad (3-5)$$

Again, the coordinate system is defined by the direction of the neutron's polarization, which is always along z . From inspection, a few relatively simple relations become obvious. First and foremost, it is clear that only the components of the magnetic moment perpendicular to the neutron polarization vector contribute to the spin flip scattering by the sample. That is, in the spin flip cross sections U^{+-} and U^{-+} only transverse spin operators appear. Thus for instance, in a ferromagnet with the magnetic moment direction oriented along the neutron polarization wave vector, there will appear no components of magnetic scattering signal in either spin flip channel. Another useful relation appears when the neutron polarization wave vector is oriented along the scattering wave vector ($z \parallel Q$). In this case, the magnetic scattering signal (ignoring polarized nuclei) is entirely contained within the spin-flip cross sections since $S_{\perp z} = 0$. In addition, it is useful to note that the nuclear coherent scattering is always contained within the non-spin-flip cross sections U^{++} and U^{--} .

Now it is helpful to turn to the case of a magnetic Bragg reflection. Neglecting nuclear polarization terms, for a neutron polarization that is along Q the cross sections are simply [63]:

$$\frac{d\sigma^{++}}{d\Omega} = \sum_{i,j} e^{i\mathbf{Q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} b_i b_j^* = \frac{d\sigma^{--}}{d\Omega} \quad (3-6)$$

$$\frac{d\sigma^{\pm\mp}}{d\Omega} = \sum_{i,j} e^{i\mathbf{Q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} p_i p_j^* (S_{\perp i} \cdot S_{\perp j} \mp i\hat{z} \cdot (S_{\perp i} \times S_{\perp j}^*)) \quad (3-7)$$

This demonstrates again that the scattering is divided into two magnetic components (spin-flip scattering) and nuclear components (non-spin-flip scattering).

For moments oriented in an arbitrary direction and for the neutron polarization instead aligned perpendicular to $\mathbf{Q}$ (which we will define as the x -direction), the non-spin-flip scattering acquires additional magnetic terms; however, the spin-flip scattering is easily shown to be comprised of the spin components both perpendicular to the neutron polarization and perpendicular to $\mathbf{Q}$ (ie. along the y -axis):

$$\frac{d\sigma^{\pm\mp}}{d\Omega} = \sum_{i,j} e^{i\mathbf{Q}\cdot(\mathbf{r}_i - \mathbf{r}_j)} p_i p_j^* (S_{\perp iy} S_{\perp jy}^*) \quad (3-8)$$

These relations can now be used to test the nature of the quasi-two-dimensional AF order coexisting with SC in underdoped PLCCO. For our experiment, we used the polarized spectrometer BT-2 at the NIST Center for Neutron Research. The spectrometer setup was identical to that used in Fig 3.2. A final energy of 14.7 meV was used with neutron collimators of 60'-40'-40'-100' (guide-sample-analyzer-detector). The same $T_c=21\text{K}$ PLCCO sample studied in Ref. 62 was aligned in the $[H, K, 0]$ zone and mounted in a cryostat. Due to the limiting flux of the polarizing neutron beam, we chose to study the magnetic order through collecting only the $(++)$ and $(+-)$ cross sections under two different neutron polarization orientations across the sample position.

Initially, we studied the case where the neutron polarization direction was directed parallel to the scattering wave vector ($z \parallel \mathbf{Q}$). I will refer to this as the “horizontal field” case. Flipping ratios for the Mezei coils were 19:1 (19 out of 20 neutrons were flipped successfully) for this horizontal field configuration giving a 95% flipping efficiency. Elastic scans were performed through the AF zone center $\mathbf{Q}=(0.5, 0.5, 0)$ both above and below the onset temperature of the quasi-two-dimensional AF order. These scans show a clear peak centered at $(0.5, 0.5, 0)$ at $T = 2\text{K}$ which disappears by $T = 50\text{K}$ (as shown in Fig. 3.3). Identical elastic scans were then repeated with the guide field adjusted such that the neutron polarization was instead oriented along an axis perpendicular to $\mathbf{Q}$ and out of the scattering plane ($z \parallel c$ -axis). Scans taken in this configuration are referred to as “vertical” field scans. Flipping ratios for the Mezei coils were 26:1 for this vertical field configuration giving a 96% flipping efficiency.

Looking at these scans now in more detail, I refer first to Fig. 3.3a, which shows both horizontal and vertical field scans over-plotted at $T=2\text{K}$ in the $(+-)$ channel. Open black squares denote the horizontal field scans at low- T while the equivalent horizontal field data are plotted as open red squares. The clear peak in this spin-flip channel immediately denotes the magnet nature of the signal. Furthermore the scans taken at both horizontal and vertical field are identical. This allows significant insight into the nature of the magnetic order at this wave vector. Whereas the horizontal field scans in the $(+-)$ channel probe all components of the magnetic moments perpendicular to $\mathbf{Q}$, the vertical field scans now instead provide a measure of the magnetic moments both perpendicular to $\mathbf{Q}$ and orthogonal to the c -axis (since $z \parallel c$). The fact that both configurations produce identical intensities is an indication that the moments are oriented precisely within the scattering plane with no component along the c -axis.

Equivalent scans at $T = 50\text{K}$ in Fig. 3.3b show no peak in the spin-flip channel, verifying that the magnetic signal disappears at high temperatures. In addition, this also gives a gauge as to the extent that nuclear scattering bleeds through into the spin-flip channel due to imperfect flipping and polarization ratios. The absence of a resolvable peak verifies that this effect is negligible relative to the magnetic signal we see in

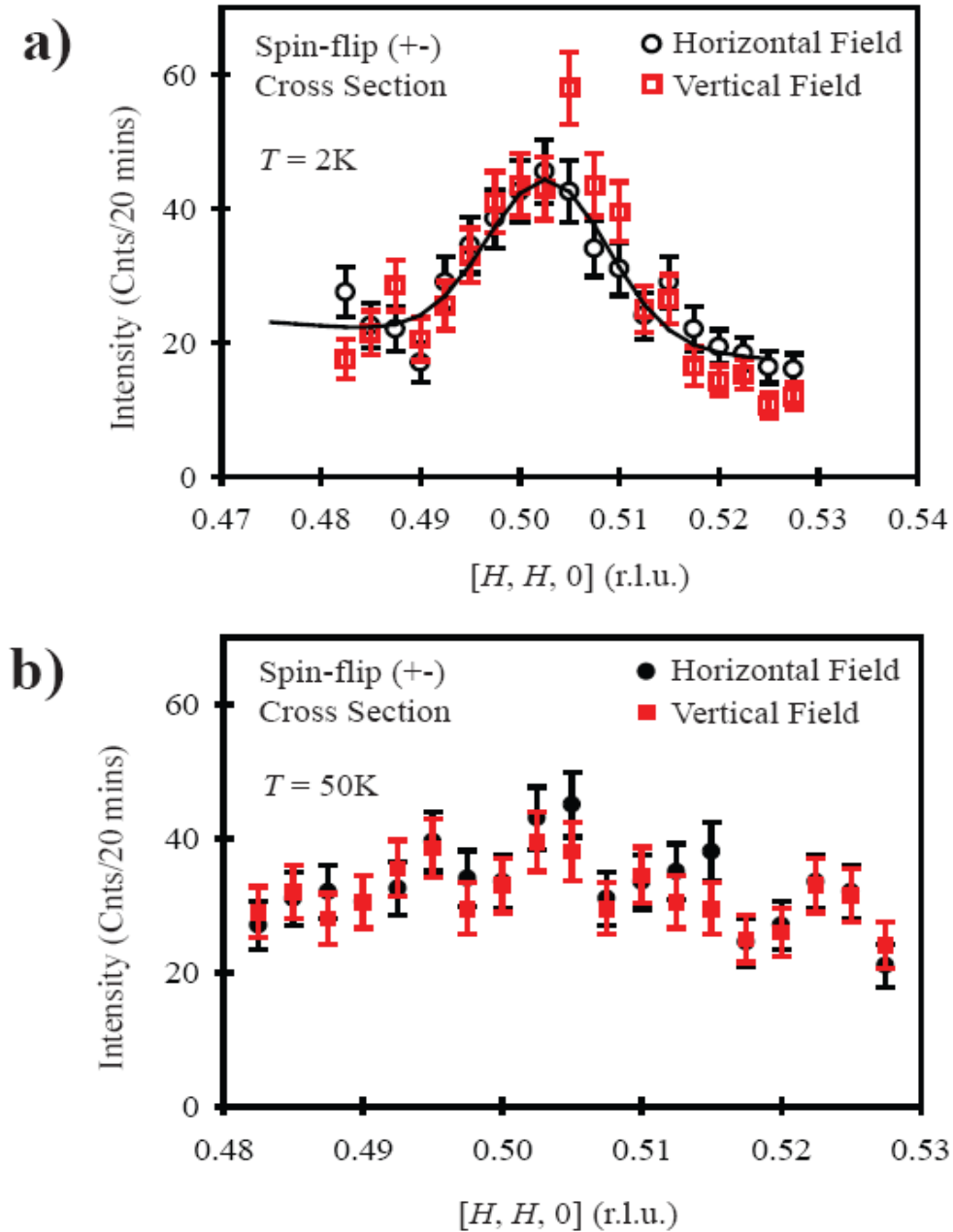


Fig. 3.3 BT-2 measurement of spin-flip scattering cross sections for $\mathbf{Q}=(0.5, 0.5, 0)$ at 2K and 50K for PLCCO ($T_c=21\text{K}$). a) Horizontal (circle symbols) and vertical (square symbols) field scans at $T=2\text{K}$. The identical magnetic peaks at low-T suggest AF order correlated precisely within the CuO_2 plane. b) Horizontal (circle symbols) and vertical (square symbols) field scans at $T=50\text{K}$. The absence of a magnetic peak also verifies the minimal contamination of the polarized beam through the absence of any residual nuclear scattering peak.

Fig. 3.3a. A quick check of the nuclear scattering signal can be performed through examining the $(++)$ cross section in both 2K and 30K as shown in Fig. 3.4. These plots show no appreciable change in the nuclear scattering as the system is warmed above the ordering magnetic ordering temperature (from 2K to 50K).

In principle, the precise direction of the moments in the CuO_2 plane can be resolved through measuring high order reflections and performing a full polarization analysis. Our initial attempt to do this resulted in some inconsistencies due to the spectrometer's inability to precisely align the neutron polarization field along the scattering $\mathbf{Q}$ for higher order reflections. An additional complication also arose due to the presence of three-dimensional magnetic order at the most accessible higher order reflection $\mathbf{Q}=(0.5, 1.5, 0)$. This three dimensional order registers as magnetic signal in spin-flip channels and prevents the unambiguous isolation of the quasi-two-dimensional magnetic signal. The most definitive conclusion then is simply that the quasi-two-dimensional order consists of Cu-moments lying within the ab -plane with no detectable degree of spin-canting such as that observed in LSCO.

3.3 Introduction and motivation

As spin fluctuations may play a crucial role in the mechanism of high- T_c superconductivity [47, 64], it is imperative to have a comprehensive picture of how the spin dynamics of the undoped AF parent compounds evolve as they are tuned toward optimally-doped superconductivity. Whereas a comprehensive picture of this carrier-induced modification to the spin dynamics has emerged for different classes of hole-doped high- T_c materials [65], experiments exploring spin fluctuations in electron-doped copper oxides are just beginning [66]. As a consequence, studies of electron-doped materials provide a unique litmus for testing the electron-hole symmetry in spin dynamical properties. If spin fluctuations are fundamental to the mechanism of high- T_c superconductivity, they should have universal features for all copper-oxide systems.

As reviewed earlier in Chapter 2.3 and 2.4, for the case of hole-doped high- T_c superconductors, such as $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (YBCO), the most prominent features in their spin excitation spectrum are a sharp magnetic excitation termed “resonance,” observed by inelastic neutron scattering and a quartet of incommensurate spin excitations that follow an hour-glass type dispersion. The discovery of the resonance mode in n -type PLCCO as a unifying feature in the spin excitation spectrum of hole and electron-doped cuprates will be discussed in the later in Chapter 4. However, the concept of the resonance as a unifying feature in the spin excitation spectrum of both hole- and electron-doped cuprates contrasts the prevalent asymmetry known between the commensurate low energy spin fluctuations centered at $\mathbf{Q}_{\text{plane}}=(1/2, 1/2)$ in the electron-doped cuprate systems [66,67,68] and the observed incommensurate spin excitations at $\mathbf{Q}=(0.5\pm\delta, 0.5\pm\delta)$ in several classes of hole-doped materials [69]. Although the doping dependence of the resonance excitation has been observed to follow $E_{\text{Resonance}} \approx 5.8k_B T_c$ regardless of carrier type [67] and the doping evolution of the incommensurate spin fluctuations in hole-doped materials is also controlled by T_c [39,43], the doping dependence of the low energy commensurate spin fluctuations in electron-doped materials remains unexplored.

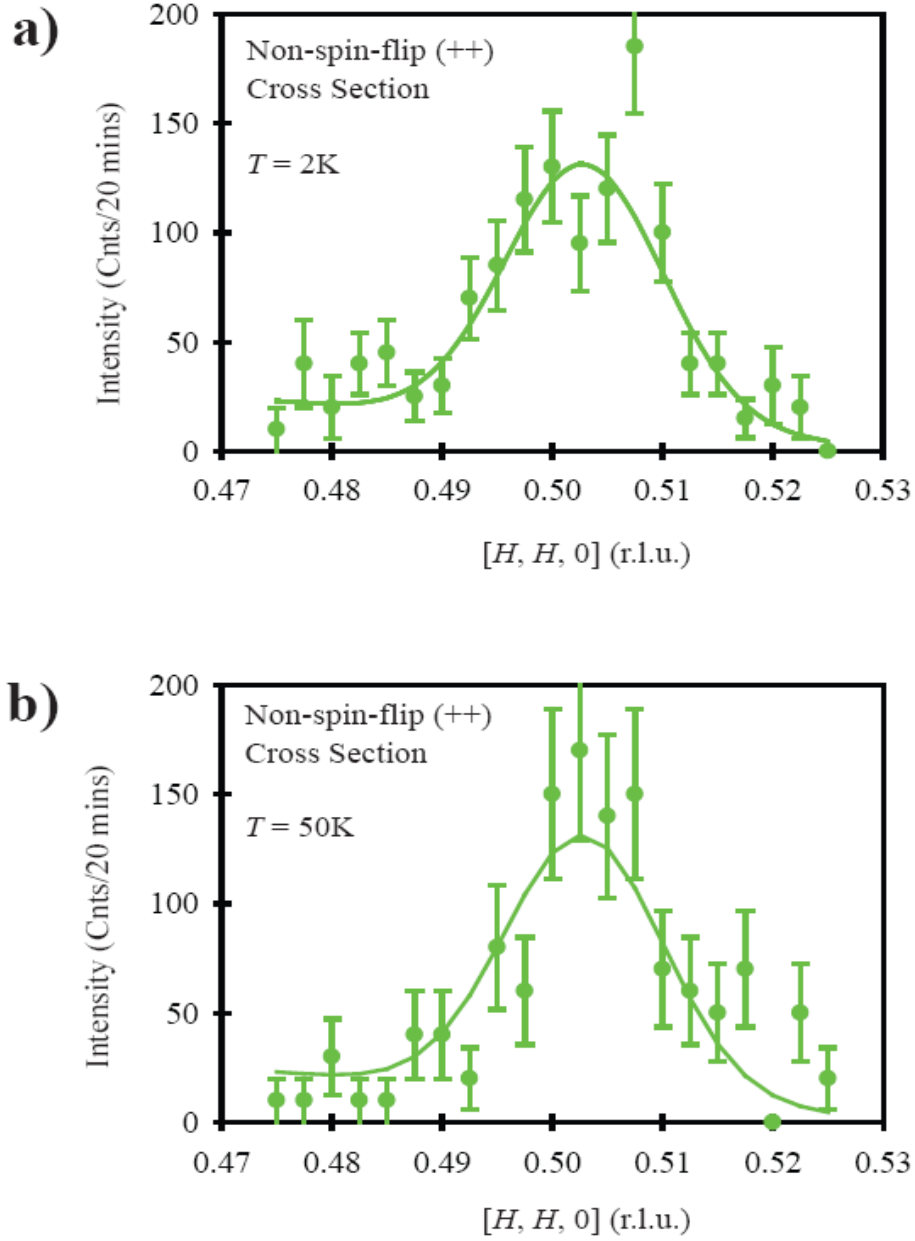


Fig. 3.4 BT-2 measurement of non-spin-flip scattering cross sections for $\mathbf{Q}=(0.5, 0.5, 0)$ at 2K and 50K for PLCCO ($T_c=21\text{K}$). a) 2K nuclear scattering peak from the impurity phase with this underdoped PLCCO sample. b) 50K nuclear peak arising from the impurity phase in $T_c=21\text{K}$ PLCCO. Within the error of the statistics collected, there doesn't appear any change in this nuclear reflection upon warming from 2K to 50K.

In order to perform the first comprehensive exploration of the doping dependence of low energy magnetic excitations in an *n*-type cuprate, we chose to investigate the evolution of low frequency spin fluctuations in the electron-doped cuprate $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$. When compared with the prototypical electron-doped copper oxide $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ (NCCO), studying spin fluctuations in PLCCO offers several distinct advantages: First, crystalline electric field (CEF) levels of Pr^{3+} in the tetragonal unit cell of PLCCO have a nonmagnetic, singlet ground state that avoids complications arising from the magnetic ground state of Nd^{3+} in NCCO [34,70]. Second, PLCCO can be tuned from an as-grown nonsuperconducting (NSC) antiferromagnet into an optimally doped superconductor, without static AF order, through an annealing process [60,61,62] (as discussed in section 3.1); whereas static AF order coexists with superconductivity in NCCO even at optimal doping [66,71,72]. Finally, the cubic $(\text{Pr},\text{La},\text{Ce})_2\text{O}_3$ impurity phase arising from the annealing process (discussed in section 3.1) in PLCCO has a nonmagnetic ground state as compared to the magnetic ground state of the $(\text{Nd},\text{Ce})_2\text{O}_3$ impurity phase in NCCO [73]. This removes any potentially spurious signal arising from the ordering of the rare earth moments within the impurity phase. The magnetic signal arising from the ordered impurity contribution (in the case of NCCO) arises at the AF ordering wave vector $(0.5, 0.5, 0)$ due to the impurity phase's doubling of the chemical unit cell in the CuO_2 plane. This can lead to a signal mistakenly attributed to as arising from the Cu^{2+} spin system; however, the nonmagnetic groundstate of Pr^{3+} in PLCCO and its accompanying impurity phase removes this complication since the Pr rare earth moments remain paramagnetic and do not order down the lowest temperatures probed in our experiments. In the following sections, I will present a comprehensive study of the low energy spin dynamics in PLCCO from $0.5 \text{ meV} \leq \hbar\omega \leq 5 \text{ meV}$ in a variety of samples as PLCCO is tuned from an as-grown NSC antiferromagnet into a nearly optimally doped superconductor ($T_c=24 \text{ K}$) through the aforementioned oxygen removal process.

3.4 Experimental details

For the systematic experiments discussed in the following section, our PLCCO samples were grown in an infrared mirror image furnace using the traveling solvent floating zone technique. This yielded high-quality single crystals with a mosaic of $<0.5^\circ$. The mosaic was determined by the full-width-half maximum of the fit structural Bragg peaks (typically the $(1, 1, 0)$ or $(2, 0, 0)$ positions). Following their growth, samples were annealed in either a high vacuum environment ($P < 10^{-6} \text{ mbar}$) or in an argon gas environment at variable temperatures. The resulting magnetic susceptibility and superconducting phase transition were measured in a SQUID magnetometer and are shown for each sample in Fig. 3.1 for samples studied in sections 3.5 to 3.8. The superconducting transition temperature is indicated by both the onset of the diamagnetic signal, T_c (onset), and through the dashed lines showing the 90% position of normal-state bulk susceptibility, T_c (90%). For the remainder of this chapter, I will reference these samples by their respective onset temperature of superconductivity, T_c (onset). Additionally, the as-grown sample, with a mass of $\sim 3.0 \text{ g}$, is nonsuperconducting and is labeled as NSC. The masses of the other PLCCO samples are $\sim 1.8 \text{ g}$, $\sim 4.8 \text{ g}$, and $\sim 3.0 \text{ g}$.

for the $T_c=21$ K, $T_c=23$ K, and $T_c=24$ K samples, respectively. An argon annealing atmosphere was used in treating the $T_c=21$ K sample at 940 °C for 24 hours, and it is the identical sample studied first in Ref. 61. The other two samples reported on here were annealed for four days under a high vacuum environment at 765 °C and 775 °C for the $T_c=23$ K, and $T_c=24$ K samples, respectively.

As a reminder, we will again refer to positions in reciprocal space at wave vector $Q=(q_x, q_y, q_z)$ in $\text{\AA}^{-1}$ using (H, K, L) (r.l.u.) notation, where $(H, K, L)=(q_x a/2\pi, q_y b/2\pi, q_z c/2\pi)$ for the tetragonal PLCCO unit cell (space group: $I4/mmm$ $a=b=3.98$ $\text{\AA}$, $c=12.27$ $\text{\AA}$). In sections 3.5-3.8, the neutron experiments were performed at the NIST Center for Neutron Research on the SPINS and BT-9 triple-axis spectrometers. Data was collected on the cold-neutron spectrometer SPINS with a fixed final energy of $E_f=5.0$ meV and collimations of open-80'-sample-80'-open-detector for NSC, $T_c=21$ K, and $T_c=23$ K samples, whereas an $E_f=3.7$ meV with identical collimations was used for SPINS experiments on the $T_c=24$ K samples. For data collected from BT-9, an $E_f=14.7$ meV was used with collimations of 40'-60'-sample-80' -open-detector. Unless otherwise stated, PLCCO samples were aligned within the $[H,K,0]$ scattering plane for experiments on SPINS, and within the $[H,H,L]$ scattering zone for BT-9. Alignment in the $[H,K,0]$ scattering zone allows for an effective integration along the c -axis of the quasi-two-dimensional, inelastic scattering from the Cu spins in uncorrelated CuO_2 planes (through relaxed out-of-plane resolution), whereas alignment in the $[H,H,L]$ scattering zone allows an accurate determination of the onset of the three-dimensional AF phase in the system. Masses for the samples used in these neutron experiments correspond to the masses stated above in the bulk magnetization measurements with the exception of experiments probing the $T_c=24$ K system. For experiments on this optimally-doped PLCCO system, a set of three $T_c=24$ K samples were co-aligned with a total mass of ~ 9 g [67]. All samples were mounted and loaded into a liquid-He cooled cryostat, and the experiments were performed in the range from $T = 2$ K to 220 K.

In section 3.9, two sets of PLCCO samples are studied. For the optimally-doped PLCCO $T_c=24$ K data, the identical samples, spectrometer, and experimental setup used in section 3.8 were utilized. However, for the $T_c=21$ K samples, two underdoped PLCCO crystals were grown and annealed under vacuum $P<10^{-6}$ mbar for 4 days at $T=765$ °C. These samples were then coaligned with a total mass of ~ 5 g within the $[H, K, 0]$ zone on the PANDA cold triple-axis spectrometer at the FRM-II neutron source. The spectrometer configuration used was open-open-sample-open-open, and the sample was loaded into a closed-cycle refrigerator (displex) for the experiment.

Typical longitudinal scans taken through reciprocal space are illustrated in the upper inset of Fig. 3.1. These scans travel along $[H, H]$ in the $[H, K, 0]$ plane and are centered at the $Q=(0.5, 0.5, 0)$ wave vector. In order to measure the nonmagnetic background at the $(0.5, 0.5, 0)$ position in energy scans, equivalent energy scans were collected offset from the correlated $(0.5, 0.5, 0)$ peak (as illustrated by the cross in Fig. 3.1a's inset). This allows a background measurement that includes both spectrometer generated and sample intrinsic backgrounds.

3.5 As-grown PLCCO

We first chose to study the behavior of as-grown PLCCO, prior to any annealing treatment. For this untreated system, long-range AF order persists up to a $T_N = 210$ K as shown in Fig. 3.5a. This plot is simply the integrated fit area above background (using a Gaussian lineshape) of the magnetic peaks arising at $Q=(0.5, 1.5, 0)$ plotted as a function of temperature. The rapid intensity increase below about 80 K arises from the induced Pr^{3+} moment through Cu^{2+} - Pr^{3+} interaction [74]. Scans through the allowed three-dimensional AF ordering wave vector $Q=(0.5, 1.5, 0)$ show the appearance of a resolution-limited AF Bragg reflection centered at $Q=(0.5, 1.5, 0)$, which diminishes above T_N (Fig. 3.5b). Due to the noncollinear structure of the zero field spin arrangement in PLCCO, the in-plane AF Bragg reflection at $Q=(0.5, 0.5, 0)$ is disallowed, resulting in a gapped excitation spectrum at this wave vector [62,75]. Constant- E scans along the $[H, H, 0]$ direction show this low energy gap in Figs. 3.6b-d. In Fig. 3.6, Q -scans at $T = 2$ K through the $Q = (0.5, 0.5, 0)$ position at finite energy transfer of $\hbar\omega = 0.5$ meV show no magnetic scattering, whereas for $\hbar\omega \geq 1.5$ meV clear resolution-limited spin-wave peaks are observed centered at $Q=(0.5, 0.5, 0)$. These resolution-limited spin-wave peaks are well fit by Gaussians and give minimum in-plane correlation lengths of $\xi_{\min} = 248 \pm 40$ Å at $\hbar\omega = 1.5$ meV, and $\xi_{\min} = 187 \pm 21$ Å at $\hbar\omega = 4.0$ meV. The correlation lengths are derived from FWHM of the inverse Fourier transform of the Gaussian peaks in reciprocal

space (i.e. $F(h) = ae^{-\frac{1}{2}\left(\frac{h}{w}\right)^2} \rightarrow F(x) = ae^{-\frac{1}{2}(xw)^2}$). Since the effect of the spectrometer's finite resolution is simply to convolute the width of the resolution with the width of the spin signal, a minimum correlation length can be reported without removing this resolution width. Now plotting in Fig. 3.6a the constant- Q scans at the $Q=(0.5, 0.5, 0)$ position, this low energy gap becomes clearer. Background points taken at $Q=(0.53, 0.53, 0)$ are over-plotted with raw data taken at the peak $Q=(0.5, 0.5, 0)$ position, showing the presence of the low energy gap to be $E_{\text{gap}} \approx 1.25$ meV. This gap energy along with the enhancement in the observed magnetic scattering for $\hbar\omega > 5$ meV is consistent with previous studies of the parent compound Pr_2CuO_2 in which the opening of an in-plane anisotropy gap was observed in addition to the lower interplane gap [34,75].

The temperature dependence of the low energy spin waves in this NSC sample is shown in Figs. 3.7a-c. For energies above the gap, the spin-wave excitations increase in intensity with increasing temperature (for $T < T_N$) following the Bose population factor $[n(\omega)+1] = 1/(1-\exp(-\hbar\omega/k_B T))$. Removing the nonmagnetic background contributions to the scattering, we obtain $S(Q, \omega)$ and determine the imaginary part of the dynamic susceptibility, $\chi''(Q, \omega)$, using $S(Q, \omega) \propto [n(\omega)+1] \chi''(Q, \omega)$. Now plotting $\chi''(Q, \omega)$ in Figs. 3.7d-f, the T -independence of the dynamic susceptibility for $E > E_{\text{gap}}$ becomes clear. The peaks in $\chi''(Q, \omega)$ at these energies remain T -independent consistent with the excitations simply following the Bose statistics expected for spin-wave excitations. The presence of Bose-populated spin wave excitations in this NSC sample is similar to those observed in parent compounds La_2CuO_4 and Pr_2CuO_4 [32,35]. Above T_N , however, the low energy spin gap closes and spin fluctuations appear in the $\hbar\omega = 0.5$ meV channel. This is most likely due to the emergence of classical critical fluctuations arising from the

NSC PLCCO

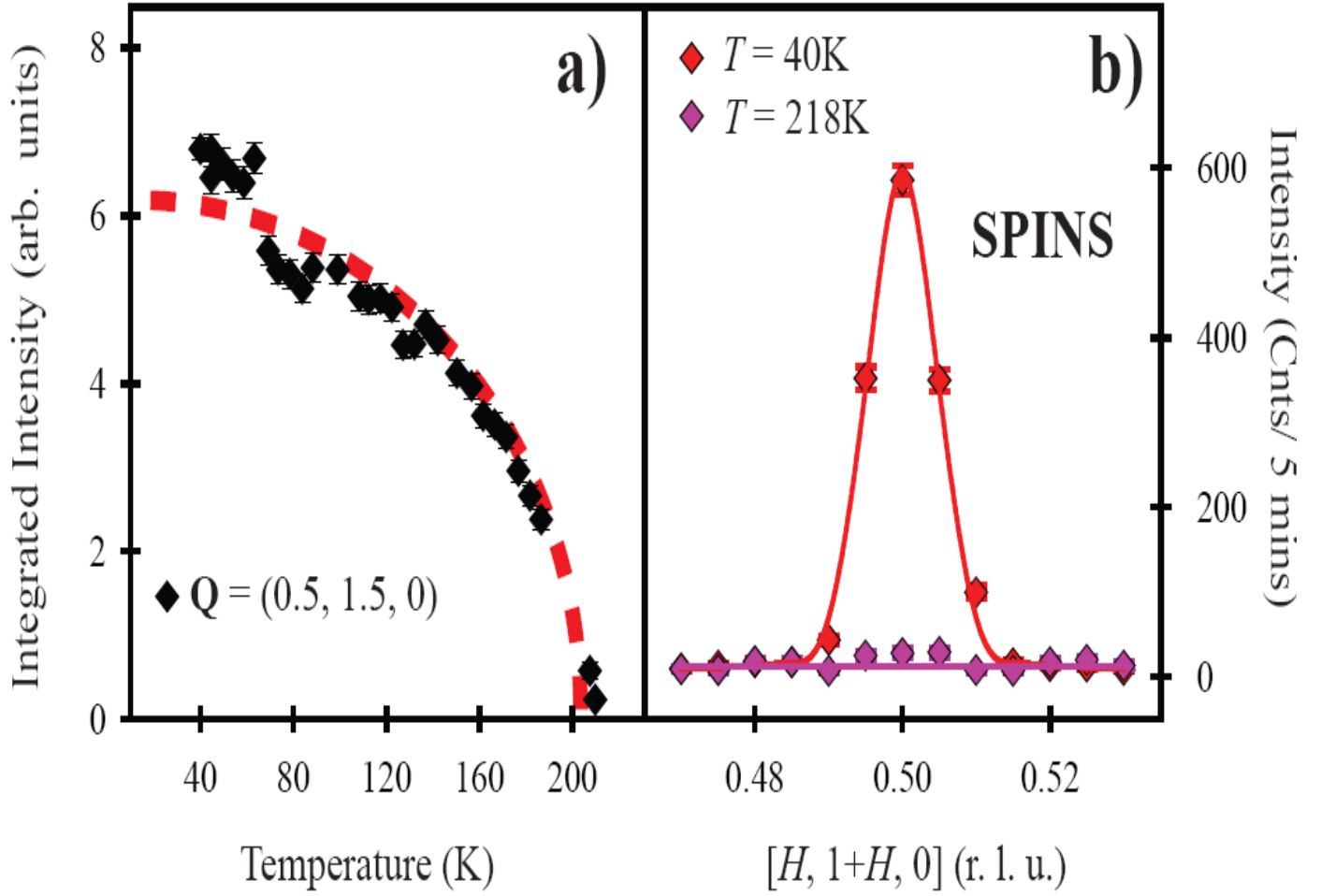


Fig. 3.5 AF Order parameter for as-grown non-superconducting $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$. a) Integrated intensity of the $(0.5, 1.5, 0)$ AF Bragg reflection as a function of temperature. The dashed line is simply a guide to the eye. The sharp increase below $\sim 80\text{K}$ is due to the polarization of paramagnetic Pr^{3+} by AF-ordered Cu^{2+} moments through the pseudo-dipolar interaction below this temperature. b) Representative Q-scans taken at $E = 0$ through $Q = (0.5, 1.5, 0)$ along the $[H, H, 0]$ direction. The sharp resolution limited peak present at $T = 40\text{K}$ (red diamonds) signifies the presence of 3D AF-order, which disappears by $T = 218\text{K}$ (purple diamonds).

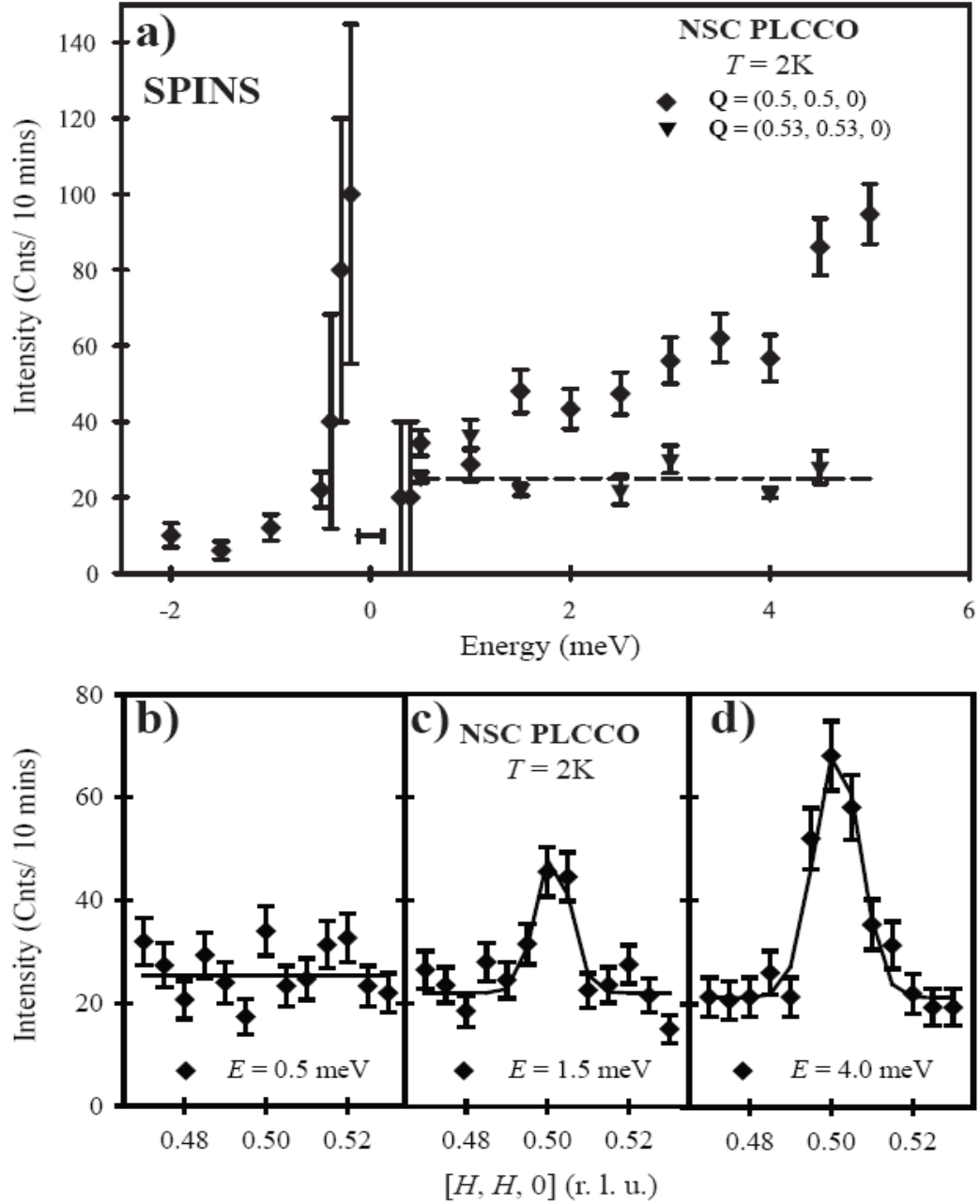


Fig. 3.6 Low energy spin excitations in NSC PLCCO. a) Constant-Q scans taken at $T=2\text{ K}$. The peak signal was collected at $Q=(0.5, 0.5, 0)$ (black diamonds) and the nonmagnetic background was measured at $Q=(0.53, 0.53, 0)$ (black triangles). The dashed line is a linear fit to the energy dependence of the nonmagnetic background. The instrumental energy resolution of $\text{FWHM}=0.259\text{ meV}$ is determined from vanadium scans and is shown as a solid bar under the elastic incoherent peak. b-d) Constant-E scans along the $[H, H, 0]$ direction at $\hbar\omega = 0.5, 1.5$, and 4.0 meV and collected at $T = 2\text{ K}$. Peaks are fitted by Gaussians centered at $Q=(0.5, 0.5, 0)$ and are resolution-limited.

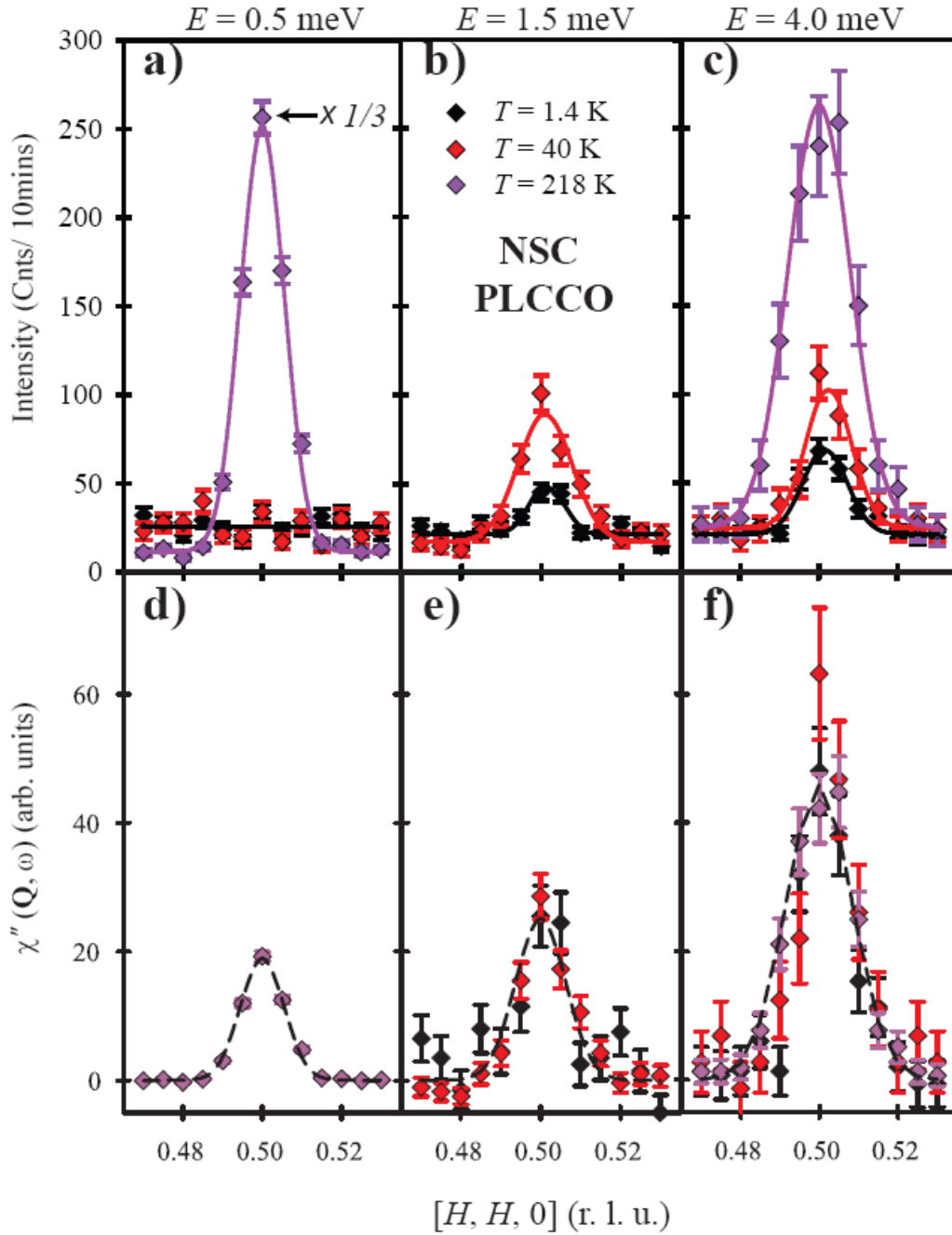


Fig. 3.7 Temperature dependence of the inelastic neutron scattering intensity and the dynamic susceptibility in NSC PLCCO. a-c) Raw scattering intensities for Q-scans along the $[H, H, 0]$ direction for various temperatures at $\hbar\omega = 0.5, 1.5$, and 4.0 meV. Peaks in scattering are fitted by Gaussians on a linear background. A clear gap in scattering at $\hbar\omega = 0.5$ meV persists above 40 K until the three-dimensional order breaks down above T_N . d-f) Measured dynamic susceptibility at various temperatures for $\hbar\omega = 0.5, 1.5$, and 4.0 meV. Dashed lines are Gaussian fits to $T = 218$ K $\chi''(Q, 0.5$ meV) in panel (d), $T = 2$ K $\chi''(Q, 1.5$ meV) in panel (e), and $T = 2$ K $\chi''(Q, 4.0$ meV) in panel (f).

suppression of AF order at $T = 210$ K, or due to a crossover from three-dimensional to two-dimensional spin fluctuations as the weak out-of-plane Cu exchange coupling breaks down above T_N . The overall picture of spin dynamics in this NSC sample is well described by spin waves arising from the long-range AF order in this system, which now provides a baseline for studying how these spin excitations evolve as the system is tuned into superconductivity.

3.6 PLCCO $T_c=21$ K: Underdoped

Now I will discuss similar experiments performed on an underdoped, superconducting PLCCO sample that is annealed to a $T_c = 21$ K with a coexisting $T_N \approx 40$ K [61]. This is also the identical sample on which the results from the neutron spin-polarized data in section 3.2 were reported. Looking first at the low energy fluctuations in this system about the AF ordering wave vector, the results are plotted in Fig. 3.8. Raw scattering intensities from energy scans at $Q=(0.5, 0.5, 0)$ from $-2.0 \leq \hbar\omega \leq 5.0$ meV are shown in Fig. 3.8a for temperatures above and below both T_c and T_N as solid circles, whereas the nonmagnetic background collected at $Q=(0.53, 0.53, 0)$ is overplotted as solid triangles. The validity of $(0.53, 0.53, 0)$ as a background position is confirmed through looking at Figs. 3.8c-e, which show no remnants of the correlated peak at $(0.5, 0.5, 0)$ at this offset position. One immediate difference appearing between the energy spectra of this underdoped superconductor and the NSC sample is the appearance of a peak in the low- T dynamic susceptibility along with the absence of a low energy spin-gap. Figures 3.8c-e show this gapless peak through Q -scans at $\hbar\omega = 0.5, 1.5$, and 4 meV, where the $T=2$ K response displays a clear enhancement at $\hbar\omega = 1.5$ meV. Solid lines show that Gaussian fits centered at $(0.5, 0.5, 0)$ on linear backgrounds can again well describe the observed peaks in Figs. 3.8 c-e. The $T=2$ K excitations exhibit widths much broader than the resolution-limited spin-wave peaks of the NSC system (Figs. 3.6c and 3.6d). Calculating the Fourier transforms of these Gaussian peaks yields the minimum in-plane dynamic correlation lengths of $\xi_{\min}=123 \pm 21$ Å at $\hbar\omega = 0.5$ meV, $\xi_{\min}=165 \pm 20$ Å at $\hbar\omega = 1.5$ meV, and $\xi_{\min}=121 \pm 27$ Å at $\hbar\omega = 4.0$ meV. Using the resolution-limited widths of the NSC PLCCO from the previous section as reference, the true in-plane dynamic spin correlation lengths, ξ , are calculated to be $\xi=220 \pm 21$ Å at $\hbar\omega = 1.5$ meV and $\xi=160 \pm 47$ Å at $\hbar\omega = 4.0$ meV for the $T_c=21$ K PLCCO. The substantially broader Q -widths in Figs. 3.8c-e than those of the resolution-limited spin waves in the NSC PLCCO suggest that these excitations cannot arise from the classical spin-wave scattering from the three-dimensional static Néel ordered phase in the sample [66, 68].

Upon warming, the low- T peak in the dynamic susceptibility vanishes and excitations at $\hbar\omega \leq 3.5$ meV populate upward until the system is warmed above T_N . Above T_N , however, there is a crossover in the magnetic response, and the spectral weight for $\hbar\omega \leq 3.5$ meV begins to decrease with increasing temperature. This crossover is also shown in Fig. 3.8b in which the intensity of the $\hbar\omega = 0.5$ meV excitations and the static $\hbar\omega = 0$ meV SDW moment are both plotted as a function of temperature. With increasing temperature from 2 K, the $\hbar\omega = 0.5$ meV fluctuations increase in intensity

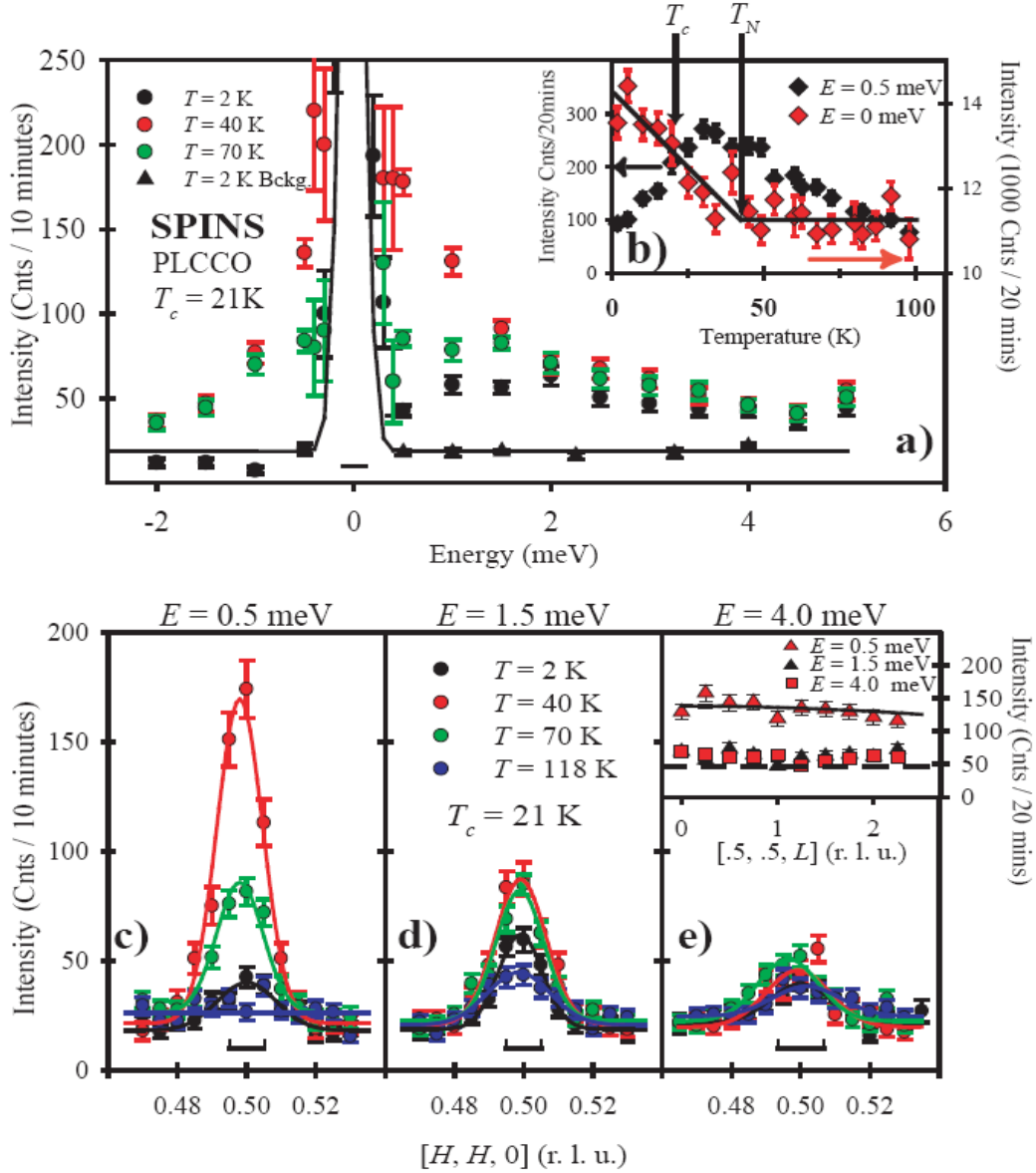


Fig. 3.8 Temperature dependence of low energy spin excitations measured on the $T_c=21$ K sample. a) Representative constant- Q scans at 2 K, 40 K, and 70 K collected at $Q=(0.5, 0.5, 0)$ (circles), where the solid black line shows the background scattering collected at $Q=(0.53, 0.53, 0)$ (triangles). At $T = 2$ K, a clear enhancement can be seen around $\hbar\omega=2$ meV. The solid bracket underneath the incoherent elastic line is the measured energy resolution by a vanadium standard. b) The temperature dependence of the $\hbar\omega = 0$ meV and $\hbar\omega = 0.5$ meV scattering at $Q=(0.5,0.5,0)$. The arrows mark the onset of T_N and T_c . c-e) Q -scans of the $T_c=21$ K PLCCO along $[H, H, 0]$ for $\hbar\omega = 0.5, 1.5$, and 4 meV and $T = 2$ K, 40 K, 70 K and 118 K. Center brackets are instrumental resolutions measured by resolution-limited spin-wave peaks from the long-range AF ordered as-grown NSC sample. The inset in panel (e) shows Q -scans along the c -axis, where solid line is the Cu^{2+} form factor squared and the dashed line marks the background.

until the breakdown of the static SDW order near T_N . On further warming, these $\hbar\omega = 0.5$ meV fluctuations begin to damp until disappearing for temperatures above 118 K (Figs. 3.8b and 3.8c). These excitations are also found to be quasi-two-dimensional within the CuO_2 layers through experiments which orient the crystal in the $[H, H, L]$ scattering plane. This is demonstrated through $[0.5, 0.5, L]$ scans in the inset of Fig. 3.8e, where the L -dependence of the spin excitations at $\hbar\omega = 0.5, 1.5, 4$ meV is rod-like and simply decays following the Cu^{2+} magnetic form factor (solid line). The isotropic form factor for Cu^{2+} was used and was calculated using the analytic approximation from Ref. 76. This weak correlation perpendicular to the CuO_2 planes indicates that spin excitations are uncorrelated along the c -axis and reflect the highly anisotropic exchange coupling between Cu sites within the CuO_2 plane ($J > 100$ meV) and the much weaker out-of-plane exchange [68].

For $\hbar\omega > 3.5$ meV, the magnetic scattering intensity at $\mathbf{Q}=(0.5,0.5,0)$ is T -independent from $T = 2$ K to 120 K as shown in Figs. 3.8a and 3.8e. In contrast, the spin scattering at $\hbar\omega \leq 3.5$ meV is strongly coupled to the appearance of the AF phase. Hence, this regime of T -independent $S(\mathbf{Q}, \omega)$ provides additional evidence of a crossover in the behavior of the spin dynamics that is now instead reflected in the energy scale of the observed spin fluctuation spectrum. A changeover in the response of the system can also be tested by plotting $\chi''(\mathbf{Q}, \omega)$ at various energies for temperatures both above and below T_N , as shown in Fig. 3.9. The top panels in Figs. 3.9a-c show the measured dynamic susceptibility below T_N . From these, the population of the lowest energy excitations at $\hbar\omega = 0.5$ meV can be seen to simply follow Bose statistics with $\chi''(\mathbf{Q}, \omega)$ remaining constant. At $\hbar\omega = 1.5$ meV, there exists a slight decrease in the susceptibility upon warming to 40 K, most likely due to the vanishing peak in the susceptibility (which is present at 2 K, see Fig. 3.8). The susceptibility at $\hbar\omega = 4.0$ meV, however, recovers this behavior of following the Bose population factor with no T -dependence in $\chi''(\mathbf{Q}, \omega)$ up to $T = 40$ K. For temperatures above T_N , the dynamic susceptibility decreases sharply with increasing T for all energies studied as shown in Figs. 3.9d-f. This is simply reflective of the decrease in magnetic scattering with increasing T (for $T > T_N$) at $\hbar\omega = 0.5$ and 1.5 meV. The decrease in $\chi''(\mathbf{Q}, \omega)$ at $\hbar\omega = 4.0$ meV, instead, arises from the observed T -independent $S(\mathbf{Q}, \omega)$ for temperatures up to 120 K. This is in sharp contrast to the $\hbar\omega = 4.0$ meV spin-wave excitations in as-grown PLCCO, where the intensity of $S(\mathbf{Q}, \omega)$ is entirely controlled by the Bose statistics (Figs. 3.7c and 3.7f). An interesting question then arises: How do these regimes of energy and temperature ($\hbar\omega, T$) that couple to either the AF phase or the paramagnetic phase (giving rise to this T -independent response in $S(\mathbf{Q}, \omega)$) evolve with increased doping? I will address this question in the following sections through both the experimental observation (the next two sections) and data analysis (section 3.11).

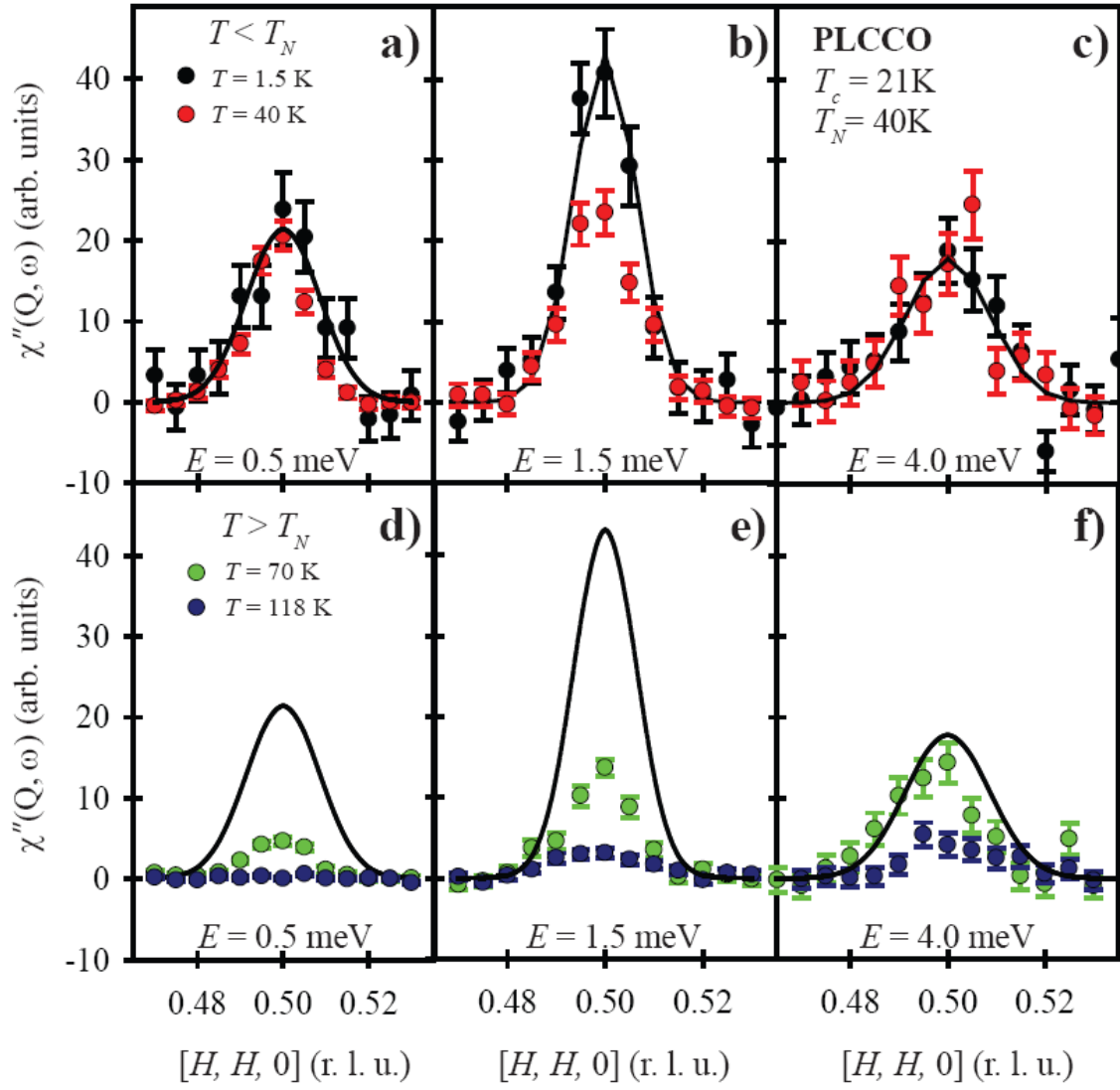


Fig. 3.9 Temperature dependence of $\chi''(\mathbf{Q}, \omega)$ at the $\mathbf{Q}=(0.5, 0.5, 0)$ position for $\hbar\omega = 0.5, 1.5$, and 4.0 meV. a-c) $\chi''(\mathbf{Q}, \omega)$ for $T \leq T_N$ ($T = 2$ K and 40 K). d-f) $\chi''(\mathbf{Q}, \omega)$ for $T \geq T_N$ ($T = 70$ K and 118 K). In all panels, solid lines are Gaussian fits to the $T = 2$ K dynamic susceptibility at the corresponding energy.

3.7 PLCCO $T_c=23$ K: Slightly underdoped

We now describe results on a PLCCO sample with $T_c = 23$ K (Fig. 3.1b). Experiments probing the static magnetic ordering of this system show an AF Bragg reflection at the $Q = (0.5, 0.5, 1)$ position with a $T_N \approx 25$ K (Fig. 3.10a). Q-scans through this AF ordering wave vector along the $[0.5, 0.5, L]$ direction reveal that this weak reflection disappears for $T > 25$ K (Fig. 3.10b), and the order parameter in Fig. 3.10a was mapped out by counting the peak intensity of the $(0.5, 0.5, 1)$ reflection as the sample temperature was swept. Full $\mathbf{Q}$ -scans confirmed that there were no background or width changes in the peak structure for the lowest and highest T 's measured, thus validating the use of the peak intensity to determine T_N . In Fig. 3.11a, the measured scattering at $Q = (0.5, 0.5, 0)$ for $-1.5 \leq \hbar\omega \leq 5.0$ meV is plotted as crossed-boxes, and nonmagnetic background collected at $Q = (0.56, 0.56, 0)$ is plotted as solid triangles. Examining these low- E fluctuations, substantial differences appear between the spectra of this $T_c=23$ K sample and those of the $T_c=21$ K system. The excitations at the $Q=(0.5, 0.5, 0)$ position remain gapless; however, they lack a clearly defined peak in the low- T susceptibility at $T=2$ K. A comparison of the $T=2$ K magnetic excitations at $\hbar\omega=0.5, 1.5$, and 4.0 meV is shown between the $T_c=23$ K and $T_c=21$ K PLCCO samples in Figs. 3.11 c-e. The dashed lines show Gaussian fits to the scattering observed in the $T_c=21$ K sample whose enhancement at $\hbar\omega=1.5$ meV contrasts the continual decrease of scattering intensity with increasing energy transfer seen in the $T_c=23$ K PLCCO (crossed-box symbols). Additionally, these plots show that the excitations observed in the $T_c=23$ K system have broadened in Q at all energies relative those observed in the $T_c=21$ K sample. The Fourier transforms of the Gaussian fits in Figs. 3.11c-e give minimum in-plane dynamic spin correlation lengths of $\xi_{\min}=86 \pm 10$ Å at $\hbar\omega=0.5$ meV, $\xi_{\min}=87 \pm 12$ Å at $\hbar\omega=1.5$ meV, and $\xi_{\min}=67 \pm 11$ Å at $\hbar\omega=4.0$ meV. Correcting for the instrumental resolution yields $\xi=93 \pm 14$ Å at $\hbar\omega=1.5$ meV and $\xi=72 \pm 13$ Å at $\hbar\omega=4.0$ meV for the $T_c=23$ K PLCCO system.

The temperature dependence of the magnetic excitations in Fig. 3.11 a shows a similar type of crossover in the spin dynamics to those observed in the under-doped $T_c=21$ K system. The regimes of these two types of spin dynamics are again determined by the energy and temperature scale of the AF order in the system, now with a $T_N \approx 25$ K. For $T < T_N$, there exists a slight enhancement upon warming of the spin fluctuations at $\hbar\omega < 2.5$ meV, whereas for $T > T_N$ and $\hbar\omega \geq 2.5$ meV the observed scattering intensity remains T -independent over a broad temperature range ($T=2$ K $\rightarrow$ 60 K). The relative intensity of the magnetic scattering at $T=100$ K is difficult to determine due to uncertainties in the nonmagnetic background contributions, whereas there was no observed change in background scattering between $T=2$ K and 60 K. The enhancement coupled to the AF order is significantly damped and no longer strictly follows the Bose population factor. Instead, only a weak increase in the population of the $\hbar\omega=0.5$ meV fluctuations is observed (as shown in Fig. 3.11b) as the system is warmed toward T_N . The coupling of these low energy fluctuations to T_N as a function of T is also significantly broadened (Fig. 3.11b), in contrast to that of the $T_c=21$ K PLCCO (Fig. 3.8b). On the other hand, the temperature and energy region in which the magnetic

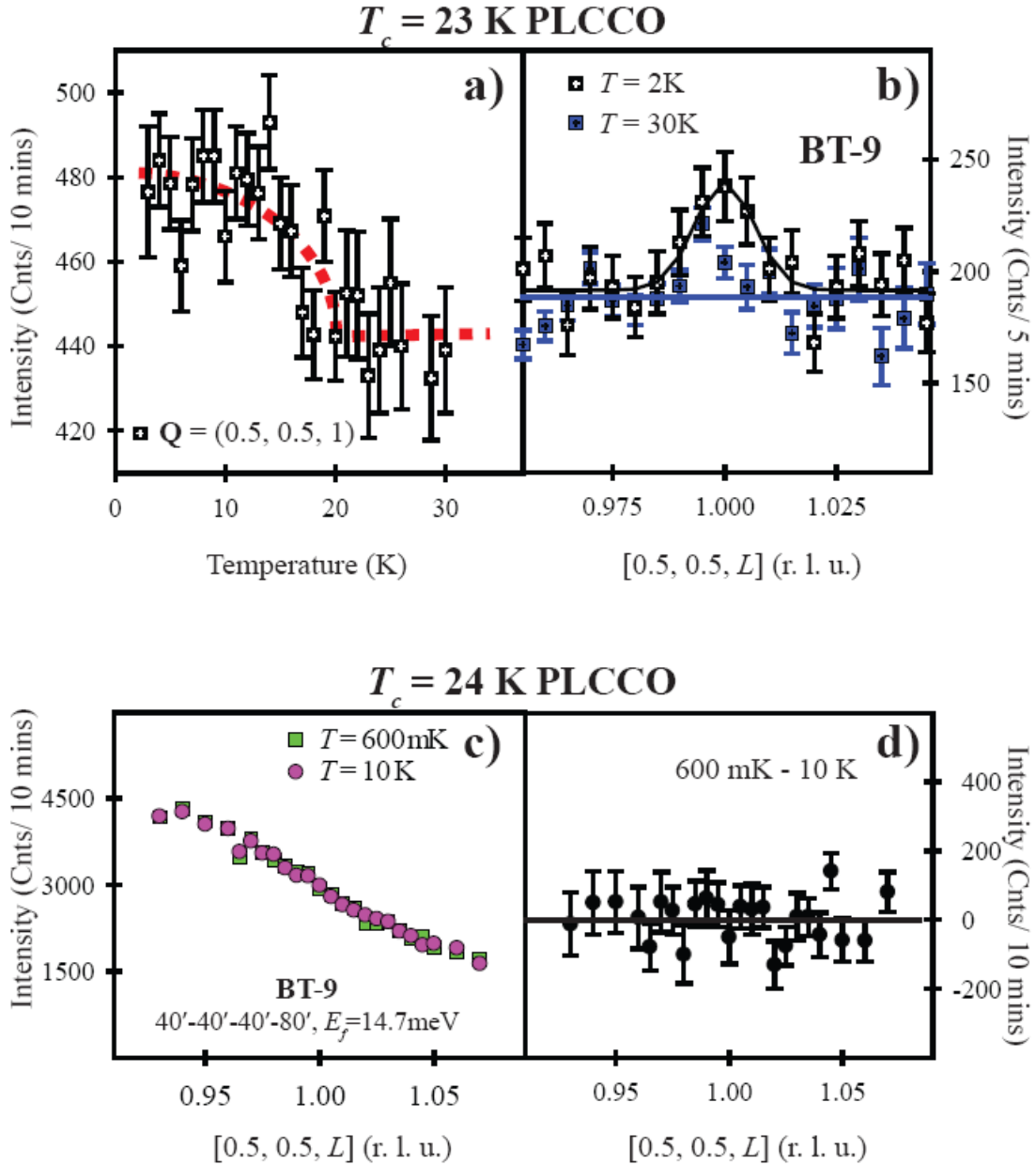


Fig. 3.10 Order parameters for three-dimensional AF order in both $T_c=23\text{K}$ and $T_c=24\text{K}$ PLCCO systems. a) Peak intensity collected at the AF Bragg position $(0.5, 0.5, 0)$ as a function of temperature for a $T_c=23\text{K}$ PLCCO sample. The dashed line is a guide to the eye. b) Full Q-scans through the $(0.5, 0.5, 1)$ AF Bragg reflection both below T_N (2K) and above T_N (30K) verifying that the AF ordering temperature for this $T_c=23\text{K}$ sample is $T_N \sim 25\text{K}$. c) Full Q-scans through $(0.5, 0.5, 1)$ both at 600mK (squares) and at 10K (circles) for the $T_c=24\text{K}$ PLCCO system. d) Subtraction of data from panel (c) in which the 600mK – 10K Q-scan data shows no observable peak or change as a function of temperature. This is a clear indication that the AF order in the $T_c=24\text{K}$ sample is absent.

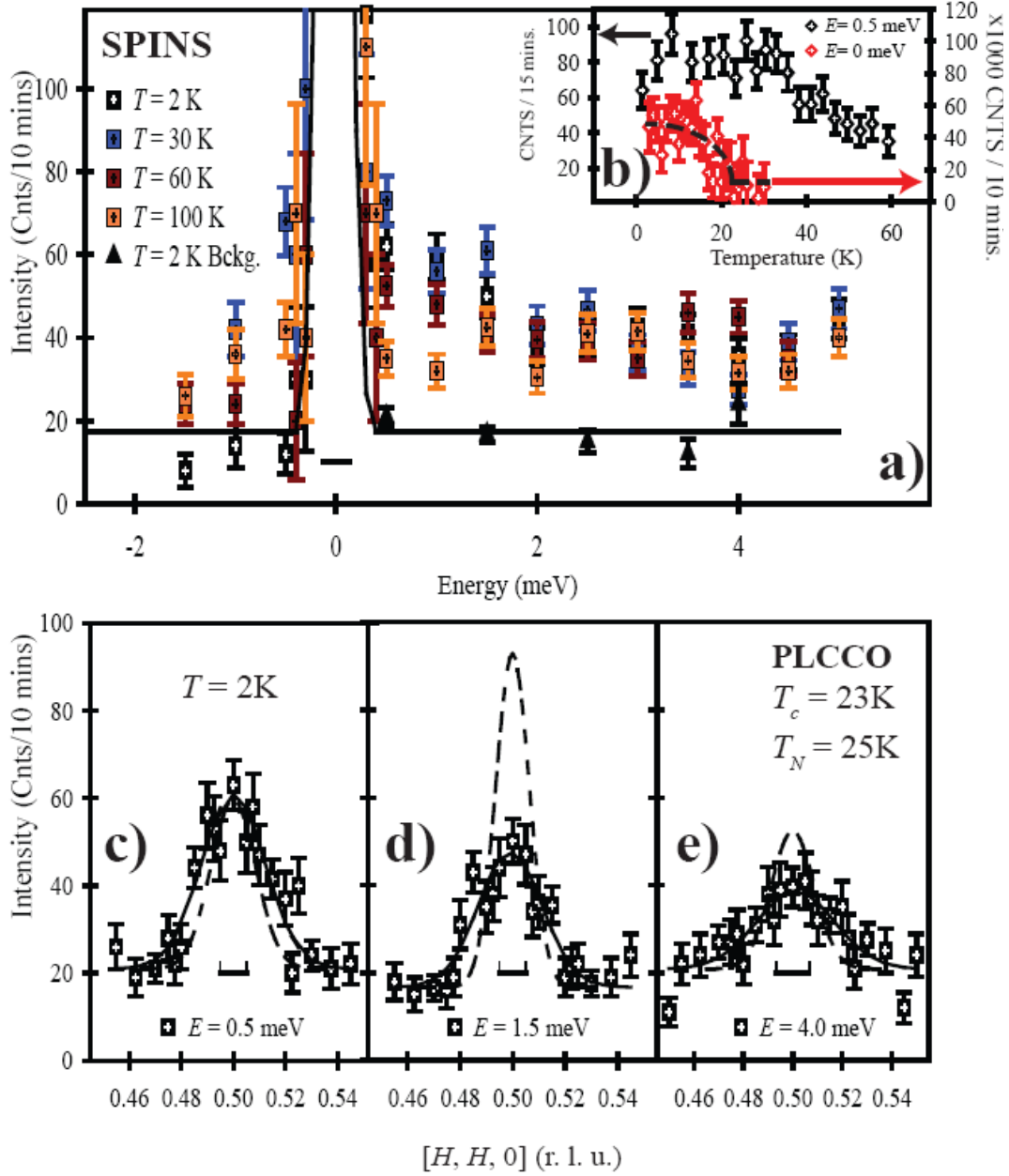


Fig. 3.11 Temperature dependence of the low energy spin fluctuations in the $T_c=23$ K PLCCO. a) Constant- Q scans at $Q=(0.5, 0.5, 0)$ at 2 K, 30 K, 60 K and 100 K. The solid black line shows the background scattering at $Q=(0.56, 0.56, 0)$ and the horizontal bar beneath the incoherent elastic peak is the instrumental resolution. b) Temperature dependence of the inelastic ($\hbar\omega = 0.5$ meV) scattering at $Q=(0.5, 0.5, 0)$ and elastic ($\hbar\omega = 0$ meV) scattering at $Q=(0.5, 0.5, 1)$ Bragg position also shown in Fig. 3.10a demonstrating a magnetic order at $T_N \approx 25$ K. c-e) Q -scans of the $T_c=23$ K PLCCO along the $[H, H, 0]$ direction for $\hbar\omega = 0.5, 1.5$, and 4 meV, respectively, at $T = 2$ K. The dashed lines show identical scans from the $T_c=21$ K sample with its (1,1,0) Bragg intensity normalized to that of the $T_c=23$ K sample. Center brackets are instrumental resolutions and solid lines are Gaussian fits on flat backgrounds.

scattering intensity is temperature independent increases, reflecting the much weaker AF phase in this sample along with the reduced energy scale of T_N .

3.8 PLCCO $T_c=24$ K: Optimally doped

Now turning to the optimally doped $T_c=24$ K sample, previous experiments have shown that there exists no static AF order co-existing with superconductivity in this sample down to 600 mK [62,67]. Elastic Q-scans along L through the AF ordering wave vector $(0.5, 0.5, 1)$ are shown in Figs. 3.10c-d. Subtraction of spectra taken at 600mK and 10K shows no change or correlated peak (Fig. 3.10d) demonstrating conclusively that AF order has been completely destroyed in this optimally-doped PLCCO system. The low energy excitations for this system are plotted in Fig. 3.12. Figures 3.12a-c show the raw scattering intensities observed for $\hbar\omega = 0.5, 1.5$, and 3.5 meV at various temperatures. Spin excitations in these energies are fitted by Gaussians on linear backgrounds and give minimum in-plane dynamic spin correlation lengths of $\xi_{\min}=96 \pm 15$ Å at $\hbar\omega=0.5$ meV, $\xi_{\min}=80 \pm 10$ Å at $\hbar\omega=1.5$ meV, and $\xi_{\min}=94 \pm 24$ Å at $\hbar\omega=3.5$ meV at $T=2$ K [67]. These widths are within error to those observed in the $T_c=23$ K sample when neglecting the slight change in instrumental resolution on changing E_f from 5.0 meV to 3.7 meV. This is reasonable since the measured Q-widths are appreciably larger than the instrument resolution in both geometries [67].

Upon warming from $T=2$ K to $T=30$ K, there is no change in the measured magnetic scattering intensity at all energies down to $\hbar\omega=0.5$ meV. Further increase in temperature to $T=55$ K renders a slight reduction in scattering at $\hbar\omega=0.5$ meV and 1.5 meV channels, with no change measured in the 3.5 meV excitations. At $T=95$ K, the peak at $\hbar\omega=0.5$ meV has completely vanished. There also exists a strong suppression of the $\hbar\omega=1.5$ meV fluctuations at $T=80$ K. In contrast, there are no changes in the $\hbar\omega=3.5$ meV fluctuations up to 80 K. Figures 3.12d-e show the measured $\chi''(Q, \omega)$ for the same energies reflecting a continued decrease in the susceptibility with increasing temperature. The dashed lines in this figure show Gaussian fits centered at $(0.5, 0.5, 0)$ for the $T=2$ K susceptibility in each respective E -channel to highlight the dramatic decrease in $\chi''(Q, \omega)$ at different energies (Figs. 3.12d-f). At the highest measured temperature ($T=95$ K), the system becomes gapped at $\hbar\omega=0.5$ meV similar to the two other underdoped PLCCO systems. This high-temperature gap in the spin excitations will be discussed further in the next section of this chapter. The absence of any regime in which the dynamic susceptibility remains constant, reflective of bosonic excitations similar to those observed in the $T_c=21$ K samples, demonstrates a drastic deviation from the two-distinct regimes of magnetic response observed in the $T_c=21$ K PLCCO. Therefore, low energy spin excitations in PLCCO evolve from coupling to the onset of the AF phase in underdoped materials to essentially temperature independent from 2 K to 30 K for the optimally doped sample. This is shown again in Fig. 3.13a through energy scans collected at a fixed Q . Circle symbols show the magnetic signal collected at $Q=(0.5, 0.5, 0)$, and the yellow triangles denote the background intensities measured at $Q=(0.56, 0.56, 0)$. There was no temperature dependence in the background up to 40K, and these constant- E scans show again that there is no change in the magnetic signal upon warming from 2K to 30K at all energies probed. The slight depression in the 55K intensities at the lowest energies

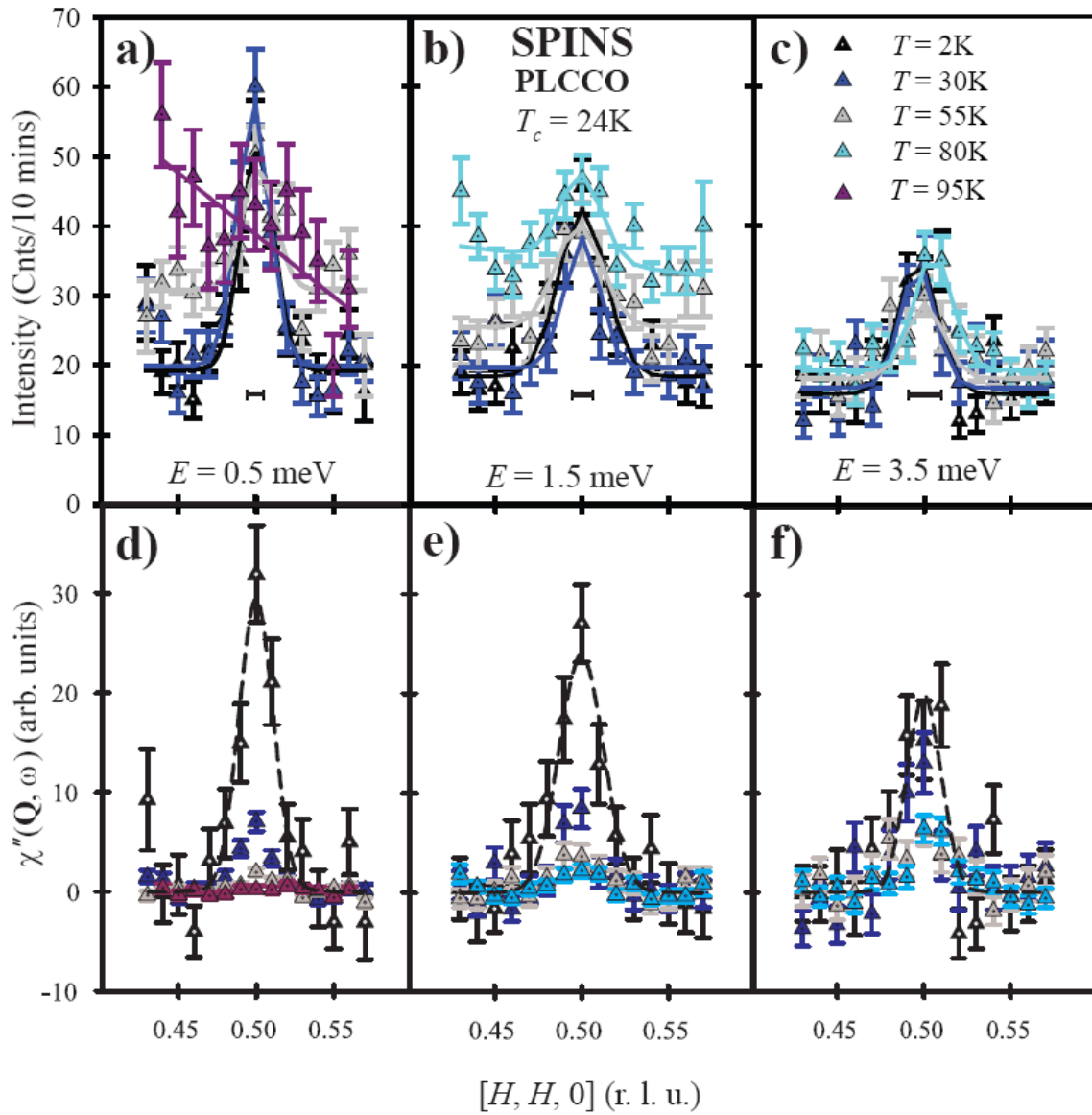


Fig. 3.12 Temperature dependence of the low energy spin fluctuations and dynamic susceptibility in the $T_c = 24$ K sample. a-c) Constant-E scans at $T = 2, 30, 55, 80$, and 95 K through the $Q = (0.5, 0.5, 0)$ position along the $[H, H, 0]$ direction. Solid lines are Gaussian fits on linear backgrounds. Solid brackets show the resolution of the spectrometer. The increased background scattering with increasing temperature at $\hbar\omega = 0.5$ and 1.5 meV may arise from single/multi-phonon scattering and/or air scattering. d-f) $\chi''(Q, \omega)$ at $T = 2, 30, 55, 80$, and 95 K. Dashed lines are Gaussian fits to the $T = 2$ K dynamic susceptibility.

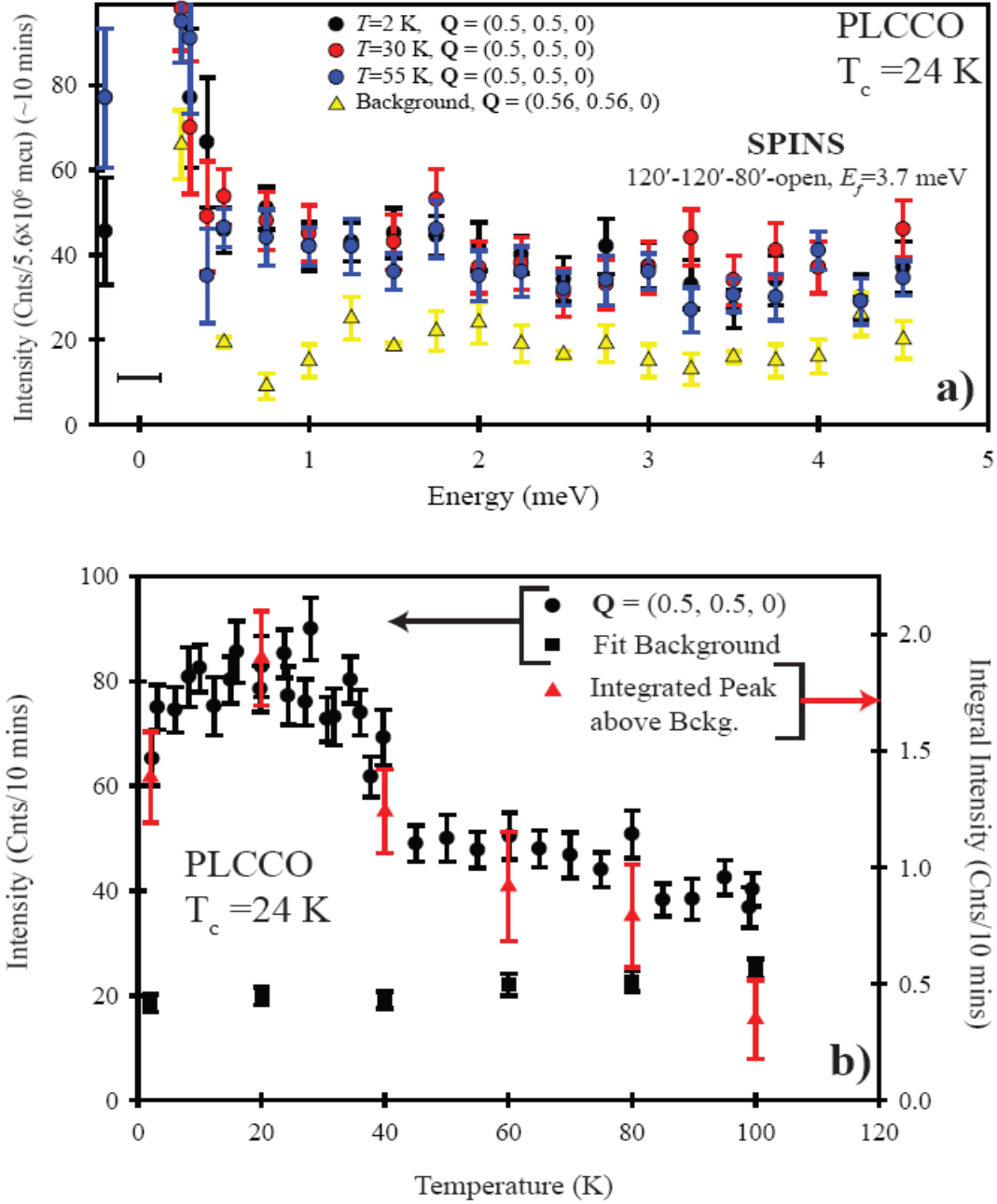


Fig. 3.13 Low energy constant- Q scans and the detailed T -dependence of the $\hbar\omega = 0.5$ meV spin fluctuations for the $T_c=24$ K PLCCO system. a) E -scans taken at signal $Q=(0.5, 0.5, 0)$ (circles) and background $Q=(0.56, 0.56, 0)$ (triangles) positions. FWHM of the energy resolution is shown by the horizontal bar beneath the incoherent elastic line. b) T -dependence of the magnetic signal at $\hbar\omega = 0.5$ meV spin fluctuations (circles) and the nonmagnetic background (squares). Integrated intensities of the $(0.5, 0.5, 0)$ peak at this finite energy transfer are plotted as red triangles for select temperature (referencing the left axis). A broad peak centered at ~ 20 K appears in the T -dependence of the $\hbar\omega = 0.5$ meV fluctuations.

shown in Fig. 3.12 is not evident in Fig. 3.13a due to the increase in the background levels. The details of the temperature dependence of the low energy magnetic spectrum of this system will be revisited in Chapter 5 with renewed focus placed on the coupling of spin excitations to superconducting phase in this concentration.

3.9 PLCCO Low Energy Excitations: High- T Spin Gap

The temperature dependence of the $\hbar\omega = 0.5$ meV excitations presents an unusual aspect to the excitation spectrum of the low energy spin dynamics in PLCCO. At high temperatures (typically on the order of ~ 100 K) the lowest energy spin fluctuations are completely damped out, whereas spin fluctuations at higher energies ($\hbar\omega \geq 4$ meV) remain unaffected. Figures 3.9c-e and Figures 3.12d-f demonstrate this behavior, and the opening of a high-temperature spin-gap becomes clear. In this section, I will present two studies of this phenomenon in two samples of PLCCO: one underdoped $T_c=21$ K sample and the other the same optimally doped $T_c=24$ K sample discussed in the previous section.

First in expanding upon the results from the optimally-doped $T_c=24$ K sample, the exact same samples and experimental conditions as those in the previous section (section 3.8) were used to map out the detailed T -dependence of the lowest energy spin excitations. The detailed temperature dependence of the $\hbar\omega = 0.5$ meV excitations is shown in Fig. 3.13b. The magnetic signal was collected at the peak position $\mathbf{Q}=(0.5, 0.5, 0)$ and the temperature of the sample varied. At select temperatures, full $\mathbf{Q}$ -scans were taken along $[H, H, 0]$ and were fit by Gaussians on a flat background. The nonmagnetic background levels were determined from these fits and are plotted in Fig. 3.13b as solid black squares. Looking now at the temperature dependence of this 0.5 meV channel, the magnetic signal shows a broad peak centered around ~ 20 K that begins a steady decrease above ~ 35 K. This decrease continues until the 0.5 meV channel completely vanishes at ~ 100 K. The peak structure of the temperature dependence of the 0.5 meV channel and the steady decrease above 35K is confirmed by integral intensities collected through $\mathbf{Q}$ -scans at select temperatures. The integral peak areas (fitted as Gaussians on flat backgrounds) are over-plotted as red triangles in Fig. 3.13b. Several representative $\mathbf{Q}$ -scans are shown in Fig. 3.14a, demonstrating again the relative decrease of magnetic scattering in the 0.5 meV channel with increasing T . Unfortunately, due to time constraints, an accurate background could not be collected for 100K E -scans in order to more clearly demonstrate this effect in the $T_c=24$ K sample. Future experiments conducted from 100K to 200K should be able to focus and more accurately map out the evolution of this low energy spin-gap and the spin excitations above it.

A similar phenomenon was observed in the $T_c=21$ K PLCCO concentration as first shown in Fig. 3.8a-c. In order to expand upon this result, experiments were conducted on two coaligned $T_c=21$ K samples at the PANDA spectrometer (for further details on the experiment setup and the samples themselves, please refer to Chapter 4.2). The increased sample mass from coaligning these two samples and the stronger magnetic signal intrinsic to this underdoped concentration proved to be more ideally suited in probing the detailed temperature dependence of the low energy excitations in PLCCO. The low energy excitations collected at both 2K and 120K in this now underdoped system are shown for $\hbar\omega = 0.5$ meV in Fig. 3.14b, thus verifying the presence of the same high- T

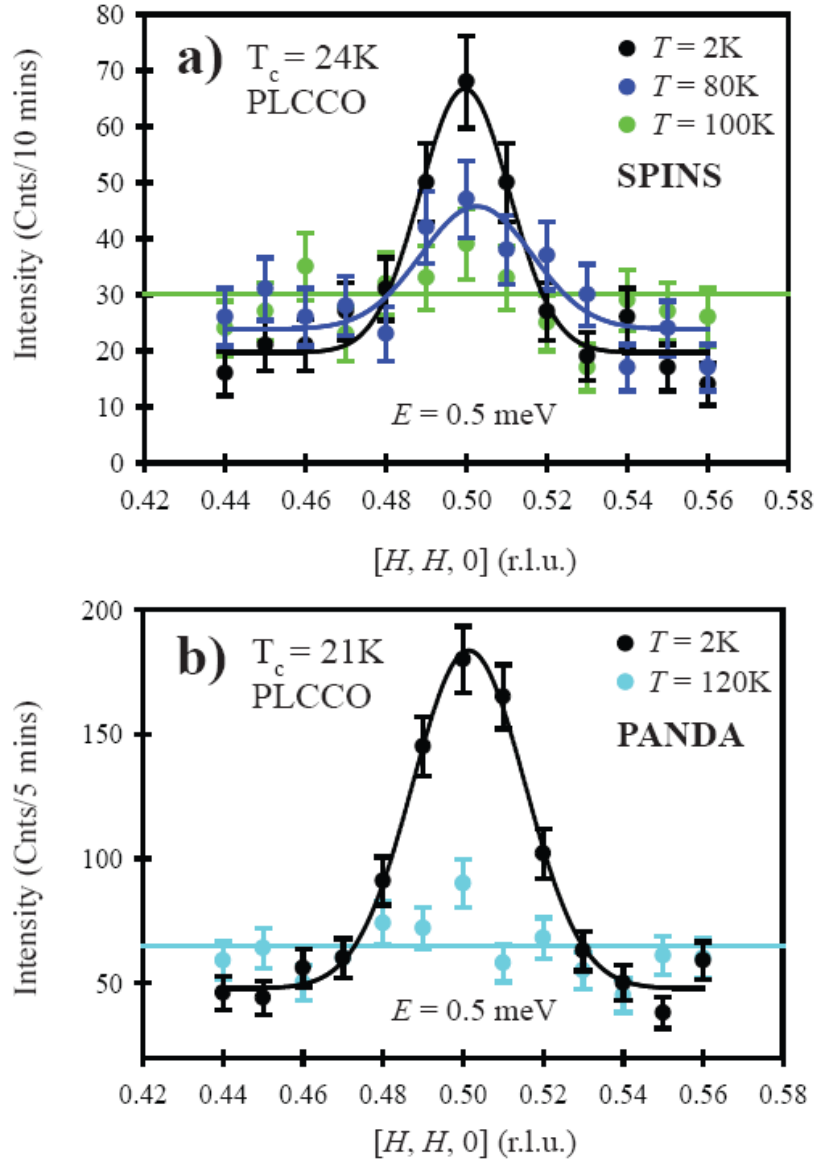


Fig. 3.14 **Q**-scans showing the high- T spin gap in PLCCO $T_c=24\text{K}$ and $T_c=21\text{K}$. a) **Q**-scans along $[H, H, 0]$ at $\hbar\omega = 0.5 \text{ meV}$ and a variety of temperatures in the $T_c=24\text{K}$ PLCCO system. At 100K the correlated peak at $(0.5, 0.5, 0)$ has completely vanished, while higher energy spin excitations remain. b) $\hbar\omega = 0.5 \text{ meV}$ $[H, H, 0]$ scans for the underdoped PLCCO $T_c=21\text{K}$ sample. The complete suppression of the 0.5 meV spin excitations at 120K and the creation of a low energy gap is verified in these two coaligned samples.

spin gap phenomenon in these two samples. The strong spin fluctuations present and centered about the AF ordering wave vector $(0.5, 0.5, 0)$ at $T=2\text{K}$ are completely absent once the system is warmed to 120K.

Now looking at the effect of warming in this sample at a variety of energy transfers in Fig. 3.15, the detailed evolution of the magnetic fluctuations from 2K to 120K for energies $\hbar\omega = 0.5 \rightarrow 7.0$ meV becomes clear. At 120K, the 0.5 meV spin fluctuations have completely disappeared, whereas the absolute intensity of the 5 meV spin excitations remain unaffected. This is in fact quite surprising since 120K is a large energy scale relative to 5.0 meV (roughly twice as large). It is highly suggestive of a spin gap, which opens around ~ 1 meV, and above this spin gap the scattering function $S(Q, \omega)$ remains roughly constant. Spin excitations greater than 0.5 meV uniformly show ~ 32 Cnts/5 mins signal above background in all Q-scans plotted in Fig. 3.15. A 120K E -scan taken at $(0.5, 0.5, 0)$ with the nonmagnetic background subtracted further shows this gap in Fig. 3.16.

The presence of this high-temperature spin gap in both underdoped PLCCO with coexisting AF order and in optimally-doped PLCCO, which is a phase pure superconductor, suggests that this gap feature is something intrinsic to all PLCCO concentrations. One possible origin could be the reemergence of residual dynamic AF correlations, which become the dominant energy scale once both SC and three-dimensional AF order are washed out at high temperatures. A similar low energy spin gap is certainly present in the AF ordered as-grown PLCCO system, as shown in Fig. 3.7. Although it is known that this gap in the as-grown samples closes by 210K, the precise evolution has not been mapped out. As for the superconducting systems, there is unfortunately insufficient data to determine the systematic details of how this gap evolves both as a function of temperature and doping. Fully exploring this facet of the spin excitations in PLCCO therefore stands as an open question for future experiments to map out.

3.11 Scaling in the spin dynamics of PLCCO

The identification of the continuous suppression of T_N as the optimal superconductivity phase is approached in PLCCO as a function of the annealing process [61] suggests the possibility of a magnetic QCP, regardless of the precise nature of the magnetic structure (homogeneous or inhomogeneous). To fully establish the existence of such a QCP requires the study of magnetic dynamics, which we have shown in the previous sections using inelastic neutron scattering. We focus on two signatures of a QCP. First, a QCP is accompanied [77, 78, 79, 80, 81, 82, 83, 84] by a quantum critical region at finite temperatures and finite energies—bounded below by a scale that gradually goes to zero as the QCP is reached—where the dynamics manifest the excitations of the QCP. Second, in this quantum critical regime, the dynamics are scale-invariant, a particular form of which is an ω/T scaling [79,81]. Such an ω/T scaling has been systematically studied in heavy Fermion metals [85, 86, 87] in which the existence of a magnetic QCP is not in doubt [88]. In the following, we will determine how our data can be described by the standard QCP theory.

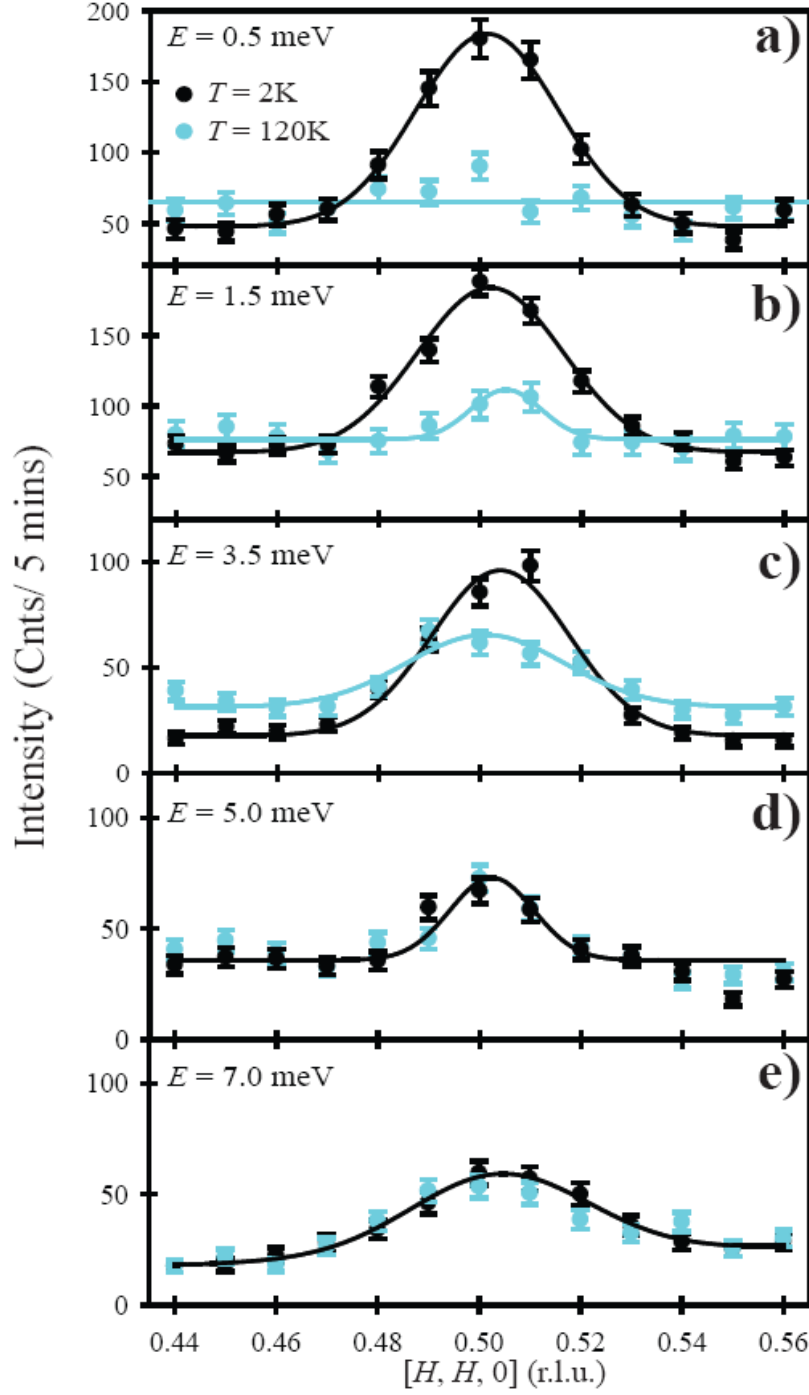


Fig. 3.15 Detailed evolution of the high- T spin gap in PLCCO $T_c=21$ K. a-e) $\mathbf{Q}$ -scans along $[H, H, 0]$ at 2K (black symbols) and 120K (teal symbols) for $\hbar\omega = 0.5, 1.5, 3.5, 5.0$, and 7.0 meV, respectively. Fits are Gaussian lineshapes on linear backgrounds. The subtle evolution of the low-energy gap in the magnetic excitations at 120K becomes clear through examining the evolution of the scattering intensities with increasing energy. Above 4.0 meV there is no measurable change in the magnetic scattering intensities upon warming from 2K to 120K.

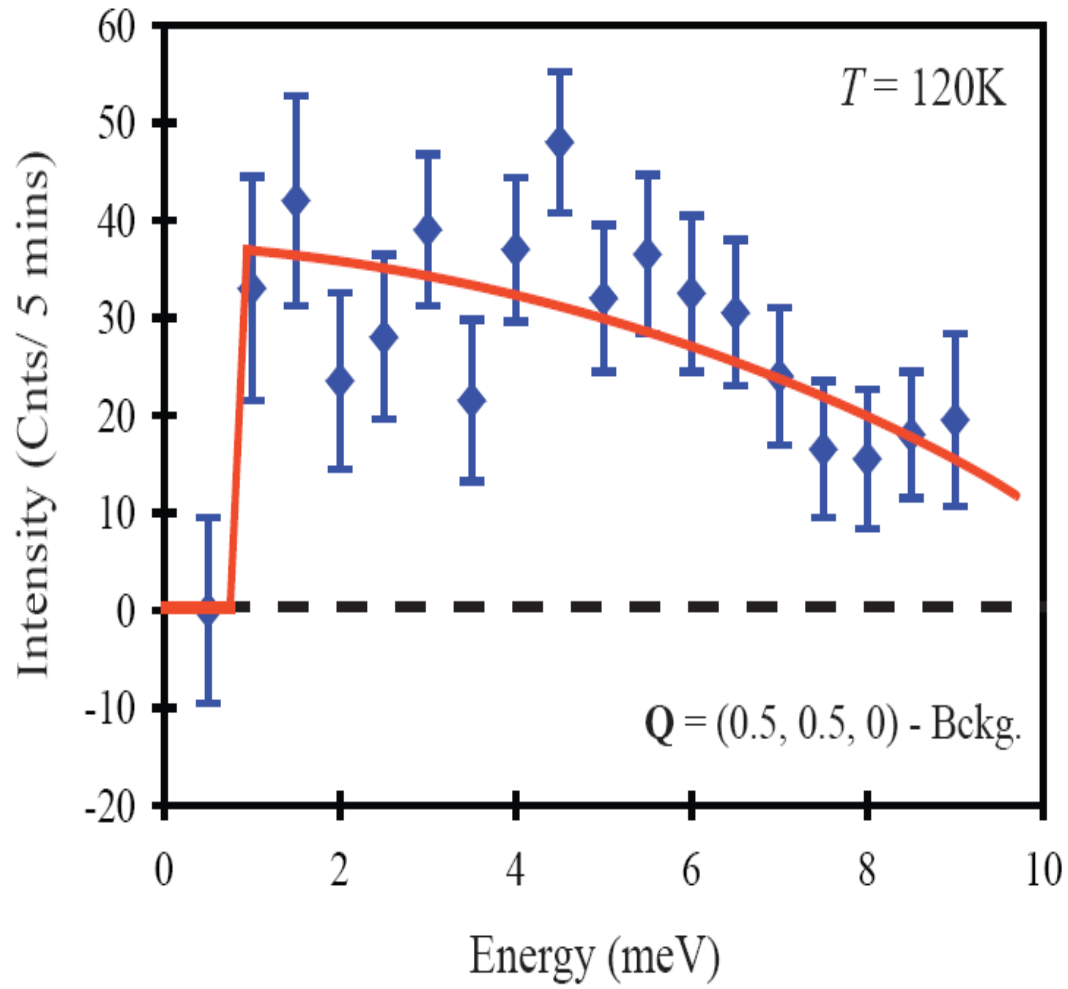


Fig. 3.16 $T=120\text{K}$ E -scan for PLCCO $T_c=21\text{K}$ with nonmagnetic background removed. Energy scan collected at $Q=(0.5, 0.5, 0)$ at 120K with the nonmagnetic background subtracted. The background was measured at $Q=(0.56, 0.56, 0)$ and through full Q -scans at select energies. The solid red line is a guide to the eye.

To perform a scaling analysis for the $T_c=21$ K PLCCO, we note that the ω/T scaling can be written as $\chi''(\mathbf{Q}, \omega)T^\alpha = F(\mathbf{Q}, \omega/T)$, where the scaling exponent α and the scaling function $F(\mathbf{Q}, \omega/T)$ are determined through the best-observed collapse of the data onto one universal curve [89]. The quantum critical scaling is different from the critical scattering from classical AF second order phase transition, as the former is controlled by T itself, whereas the characteristic energy scale ω_c in the latter case is determined by reduced temperature $t=|T-T_N|/T_N$ ($|t| \ll 1$) [90]. The Heisenberg antiferromagnet with $T_N=40$ K, ω_c should fall within the quasi-elastic part of the energy spectra and thus not contribute to the observed magnetic scattering in Fig. 3.8. By plotting all data above the 30 K energy scale ($\hbar\omega \geq 3$ meV) as a function of ω/T and minimizing χ^2 (Ref. 86), we find $\alpha = 1$ independent of the functional form of $F(\mathbf{Q}, \omega/T)$ (Fig. 3.17a). Using this value for the exponent leads to a scaling plot of $\chi''(\mathbf{Q}, \omega)T$ as a function of ω/T (Fig. 3.17b). Such a plot also identifies the scaling regime, which is bounded at low energy (2 meV) and temperatures (Fig. 3.17c). The data within the scaling regime in Fig. 3.17c clearly show a collapse onto a universal curve as plotted in Fig. 3.17d. We fit the latter using $F(y) \propto y/(1+(y/C)^2)$ and find $C = 0.44 \pm 0.02$. This collapse of the data over more than two decades of ω/T strongly suggests the presence of universal dynamics. If these universal dynamics indeed reflect a nearby QCP, the scaling behavior must break down at low energies and temperatures, with the cut-off scale determined by the distance to the QCP. Indeed, for small ω the ω/T scaling is observed only at temperatures above about 30 K (Fig. 3.17b). The fact that this temperature scale is of the order of T_N suggests that the cut-off to scaling is connected with the development of the AF order. Likewise, at the lowest measured temperature, $T = 2$ K, the ω/T scaling is seen only at $\hbar\omega$ above about 2 meV (Fig. 3.17b), which, within the error bars, is equal to the low- ω cut-off temperature multiplied by the universal constant C .

Now turning to how this scaling regime evolves in samples tuned closer to optimal doping, the same type of scaling analysis can be performed for the low-energy magnetic spectra of the $T_c=23$ K PLCCO. Since our neutron diffraction measurements at $\mathbf{Q}=(0.5, 0.5, 1)$ show a $T_N \approx 25$ K (Fig. 3.10a), this sample should be much closer to the magnetic QCP than the $T_c=21$ K ($T_N=40$ K) PLCCO. Figure 3.18a shows the summary of the $\chi''(\mathbf{Q}, \omega)T$ of the $T_c=23$ K PLCCO over-plotted on the universal scaling fit to the $T_c=21$ K sample (dashed line). A scale factor, A , was used to normalize the $\chi''(\mathbf{Q}, \omega)$ at $\mathbf{Q}=(0.5, 0.5, 0)$ for the $T_c=23$ K PLCCO to that of the $T_c=21$ K PLCCO, which reflects the fact that the Q -width in the former is much broader (Figs. 3.11c-e). Besides the overall scale factor, we find that all data with $\hbar\omega \geq 1$ meV and/or $T \geq 25$ K fall on the universal curve, consistent with the $T_c=23$ K PLCCO being closer to the QCP point. The ω/T scaling regime is seemingly correlated with the gradual suppression of the AF order as optimal superconductivity is approached, indicating the presence of a magnetic quantum critical point in electron-doped superconductors. However, the dynamic in-plane spin correlation length as stated earlier is observed to decrease with increasing T_c and decreasing T_N , suggesting that this QCP in PLCCO cannot arise from criticality towards a three-dimensional long-range AF order at 0 K [79]. Instead, the data are similar to what happens in the Li-doped La_2CuO_4 [89] and in certain spin-glass QCP

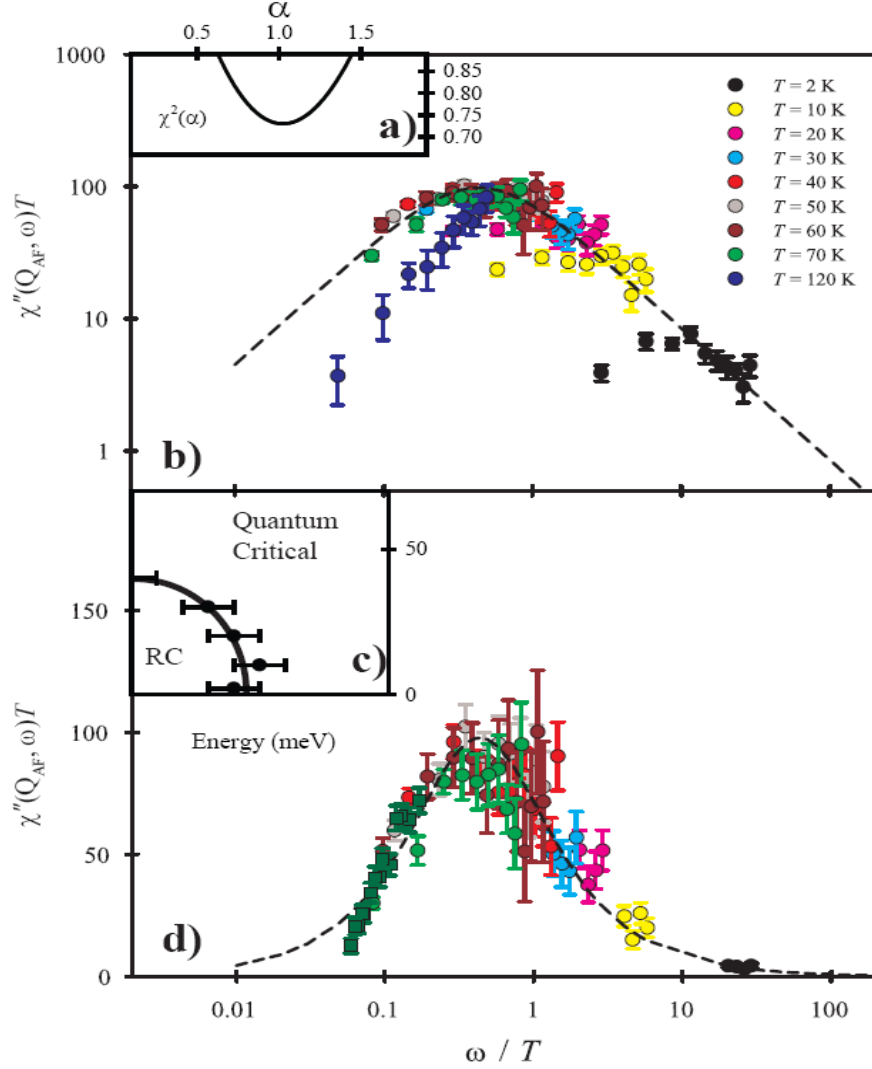


Fig. 3.17 ω/T scaling in the dynamic susceptibility of PLCCO with $T_c=21$ K and $T_N=40$ K. a) The results from a minimization of $\chi^2(\alpha)$ for all $\chi''(\mathbf{Q}, \omega)$ data with $80 \text{ K} \geq T \geq 30 \text{ K}$ and for data with $T < 30 \text{ K}$ and $\hbar\omega > 2 \text{ meV}$. The bin size of 0.5 along the $\log(\omega/T)$ scale is the only assumption made in obtaining $\alpha = 1$. b) The log plot of $\chi''(\mathbf{Q}, \omega)T$ as a function of ω/T shows three distinct regions: 1) data with $80 \text{ K} \geq T \geq 30 \text{ K}$ and with $T < 30 \text{ K}$ and $\hbar\omega > 2 \text{ meV}$ are within the quantum critical scaling regime and collapse onto a universal curve, 2) the data at 118 K show a clear high temperature departure from this quantum critical scaling behavior, 3) the data with $T < 30 \text{ K}$ and $\hbar\omega < 2 \text{ meV}$ show a low temperature departure from the scaling regime. The breakdown of scaling at 120 K could be due to uncertainties in determining the backgrounds. c) Summary of the ω/T scaling regime. d) $\chi''(\mathbf{Q}, \omega/T)T$ as a function of ω/T now plotted with only the data in the quantum critical scaling regime shown in panel (c). This provides a clearer picture of the universal collapse for data within the valid scaling regime.

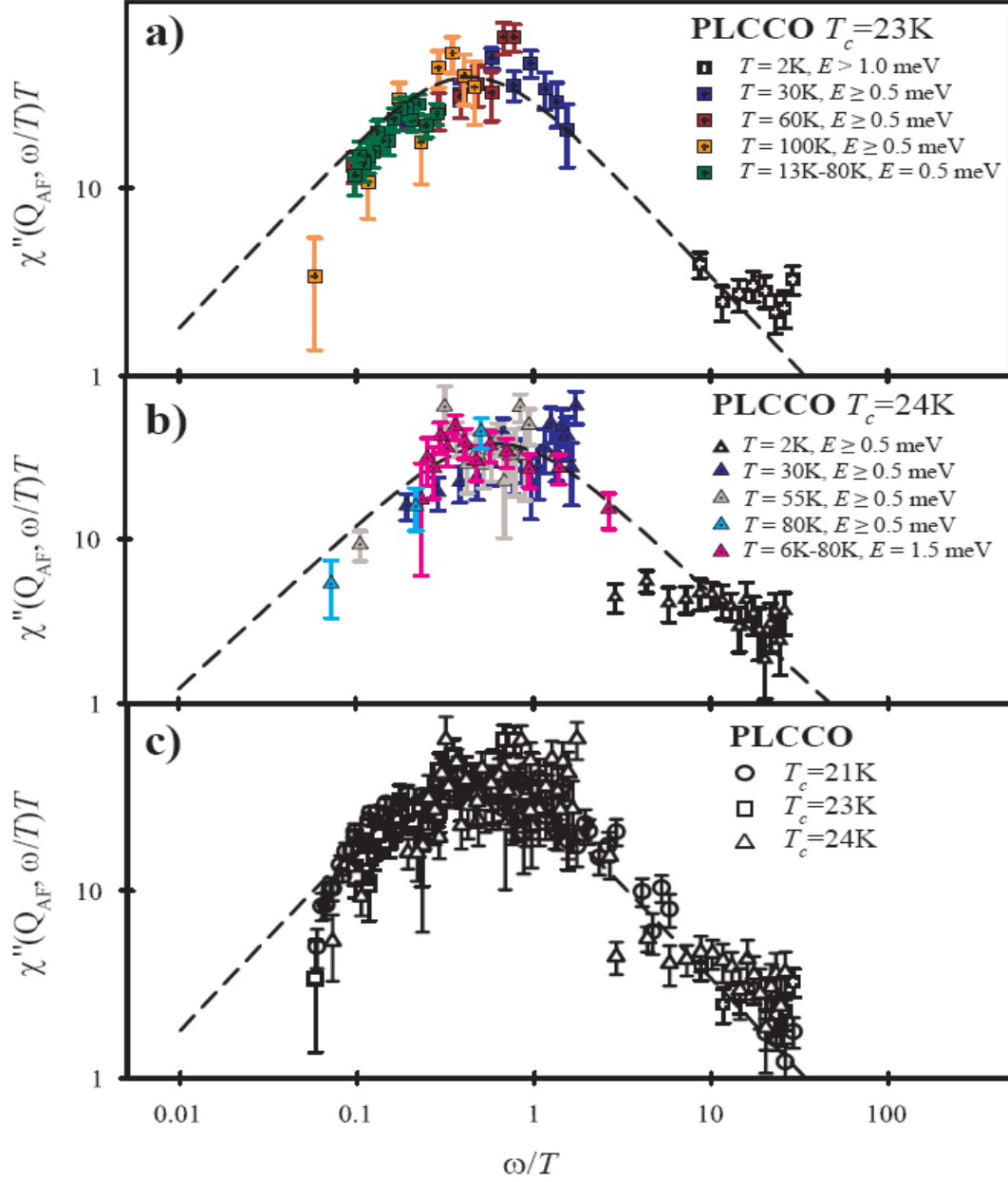


Fig. 3.18 ω/T scaling in the dynamic susceptibility of PLCCO with $T_c=23\text{ K}$, $T_N=25\text{ K}$ and $T_c=24\text{ K}$ (with no coexisting AF order). a) A log plot of $\chi''T$ as a function of ω/T for the $T_c=23\text{ K}$ sample over-plotted on the universal curve from Fig. 3.17b. By normalizing the $(1, 1, 0)$ Bragg intensities of both samples, we find $A=4.5$, which indicates that magnetic scattering at $\mathbf{Q}=(0.5, 0.5, 0)$ is considerably weaker in the $T_c=23\text{ K}$ PLCCO system. This scaling plot reflects the modified scaling regimes in this $T_c=23\text{ K}$ sample as discussed in the text. b) $\chi''T$ plotted as a function of ω/T for the $T_c=24\text{ K}$ sample again over-plotted on the universal curve from Fig. 3.17b. c) Scaling relation now plotted for all three superconducting samples, $T_c=21\text{ K}$, $T_c=23\text{ K}$, and $T_c=24\text{ K}$, and their respective scaling regimes showing a universal collapse onto the curve from Fig. 3.17b.

heavy Fermion systems [85,87]. Although there is at present no comprehensive theory for the expected properties of a metallic spin-glass QCP, the reduced magnetic transition temperature and the continuous nature of the transition (Fig. 3.1c) imply that the scaling behavior in the $T_c=23$ K PLCCO should persist down to lower energies and temperatures than that of the $T_c=21$ K sample.

Continuing this analysis on the magnetic fluctuations observed in the $T_c=24$ K sample, an identical scaling plot is shown in Fig. 3.18b. A constant scale factor was again used to normalize the scaling fit from the $T_c=21$ K sample to overlay with the data from the $T_c=24$ K sample. As the system is tuned closer to the QCP, there should now be larger ranges of energies and temperatures ($\hbar\omega$, T) in which the scaling remains valid. Indeed, now all energies and temperatures (for which a suitable nonmagnetic background was measured) are shown to collapse on the same universal curve determined for the $T_c=21$ K sample (dashed line in Fig. 3.18b). This encompasses the entire range of energy and temperature probed from $0.5 \geq \hbar\omega \geq 4.0$ meV and $2 \geq T \geq 80$ K with the exception of a notable divergence at the $\hbar\omega = 0.5$ meV spin fluctuations measured at $T = 2$ K in Fig. 3.178b. This divergence from the scaling fit for spin dynamics with $\hbar\omega \leq 1.25$ meV may result from the system being tuned slightly beyond the QCP. In this case, the low energy/temperature spin dynamics crossover into the quantum disordered regime and no longer obey the scaling relation of quantum critical excitations. Since the system does not exhibit AF order to at least 600 mK, we cannot determine how close the sample is to the $T_N=0$ K QCP. Nevertheless, the overall trend for the three superconducting PLCCO investigated is that of increasing regimes of validity for the dynamic ω/T scaling as the system is tuned closer to the QCP itself. Finally, the valid scaling regimes for all three SC PLCCO samples are over-plotted in Fig. 3.18c, showing a universal collapse onto a common function, with the exception of the lowest energy excitations at $T=2$ K for the $T_c=24$ K sample as discussed earlier. The universal collapse signifying ω/T scaling and the systematic evolution of scaling regime as AF order is suppressed with annealing strongly suggest the presence of a magnetic QCP in the electron-doped PLCCO. Recent transport and optical measurements on electron-doped $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO) have identified singular behaviors that appear compatible with the influence of a QCP [91, 92]. Our results suggest that such a QCP may have a magnetic origin, possibly due to the presence of a spin-glass QCP. We note that previous work has shown the presence of a spin-glass QCP in the hole-doped cuprates [93], thus suggesting that this magnetic QCP might be a common feature in high- T_c superconductors regardless of doped-carrier type.

3.12 Discussion and conclusions

In the preceding sections, I have presented the results of systematic measurements of the doping evolution of the low energy spin fluctuations in the electron-doped cuprate, PLCCO, as the system is tuned from an as-grown NSC antiferromagnet into a phase-pure optimally doped superconductor. The as-grown, semiconducting PLCCO system exhibits gapped low energy spin fluctuations consistent with those observed in the parent compound Pr_2CuO_4 . Tuning the system into an optimally doped superconductor changes these low energy spin excitations dramatically. Instead of a gapped spin wave spectrum, the superconducting PLCCO samples exhibit gapless low energy spin dynamics that

exhibit two differing regimes of response in $(\hbar\omega, T)$: the first of these coupling to the onset of the AF order in the system and the second appearing as spin dynamics whose scattering is weakly temperature dependent over large temperature ranges. The regime that couples to the AF order in these samples is seen to evolve from $T < 40$ K and $\hbar\omega < 2.5$ meV in the $T_c=21$ K sample to $T < 25$ K and $\hbar\omega < 1.5$ meV in the $T_c=23$ K PLCCO.

At optimal doping ($T_c=24$ K), where the static AF phase is suppressed to below 600 mK, the observed magnetic scattering for $T \leq 30$ K or $\hbar\omega \geq 1.5$ meV is T -independent, suggestive of the possible influence of quantum critical fluctuations in the system. Subsequent scaling analysis of the data revealed a collapse of appropriate regions of $(\hbar\omega, T)$ onto a universal curve for all three superconducting PLCCO systems studied, thereby providing microscopic evidence for a QCP in the electron doped PLCCO. Additionally, the first system discussed, $T_c=21$ K PLCCO, displays a peak in the low- T susceptibility centered at $\Gamma_0 \approx 2.0$ meV, which vanishes upon warming, whereas systems tuned closer to optimal doping ($T_c=23$ K and $T_c=24$ K) display only continuously decreasing magnetic response with increasing energy transfer. A high-temperature spin-gap present in both under- and optimally-doped PLCCO samples was investigated. This phenomenon appears around ~ 100 K and merits further study in relation to a potential pseudogap energy scale in PLCCO. Our experiments described in this chapter have provided a systematic investigation into the evolution of the low energy spin dynamics in an electron-doped copper oxide, PLCCO, thereby providing valuable constraints on microscopic theories seeking to model the spin excitations as the materials evolve from a long-range ordered antiferromagnet into an optimally doped superconductor.

Chapter 4: High-energy spin excitations and dispersion in PLCCO

Portions of the data and discussion in the following sections with the exception of sections 4.3 and 4.5 have been published recently and can be found in Ref. 68.

4.1 Introduction and motivation

As mentioned in Chapter 1, high- T_c superconductivity in copper oxides manifests itself when sufficient holes or electrons are doped into the CuO_2 planes of their insulating antiferromagnetic parent compounds. It has long been a goal of the high- T_c community to understand the precise nature through which magnetism evolves in these cuprate systems as they are driven from AF insulators into paramagnetic metals with a superconducting phase transition. As part of this investigation, the importance of short time-scale magnetic order in the form of spin fluctuations has been focused upon as potentially playing a role in the underlying mechanism of high- T_c electron-pairing [53]. For the undoped parent compounds, where AF order gives a diffraction peak at wave vector $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$, spin waves at energies below 60 meV found by neutron scattering show commensurate excitations around $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ because of the large AF nearest neighbor exchange coupling ($J_{nn} > 100$ meV, Figs. 4.1a, 4.1c) [25, 26, 27]. This failure to resolve the counter-propagating spin wave modes (resulting in a commensurate peak in $\mathbf{Q}$ -scans) is simply due to the finite resolution of the spectrometer and the close separation of the counter-propagating modes (due to the enormous J). The effective dispersion for an AF ordered parent compound of the monolayer cuprates is depicted schematically in Fig. 4.1a. Upon hole-doping to induce a metallic normal state and superconductivity at low- T , the low-energy spin fluctuations of monolayer cuprates $\text{La}_{2-x}(\text{Sr},\text{Br})_x\text{CuO}_4$ (LSCO) form a quartet of incommensurate peaks at wave vectors away from $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ [42, 94, 95, 96] that may arise from the presence of static or dynamic spin stripes [97]. For hole-doped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (YBCO) with $x \geq 0.45$, the magnetic excitation spectra have a commensurate resonance at $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ and incommensurate spin fluctuations similar to that of LSCO below this resonance mode [43, 45, 49, 98, 99, 100, 101]. For energies above the resonance, however, the excitations are spin-wave-like (i.e. ring-like) for $x \leq 0.5$ [100, 102] and become a square continuum at $x=0.6$ [45]. In the extremely underdoped regime ($x=0.353$, $T_c=18$ K), Stock et al. [102] showed that spin fluctuations remain commensurate at $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ and have a damped spin resonance around 2 meV along with a glassy central mode at the elastic position.

Although the evolution of spin excitations in hole-doped superconductors has become increasingly clear, it is crucial to now determine the evolution of spin excitations in electron-doped materials, as particle-hole symmetry is an important ingredient of any theory purporting to explain the mechanism of high- T_c superconductivity. Unfortunately, due to the difficulty of growing large high-quality single crystals required for inelastic neutron scattering experiments (shown in Fig. 4.2), there exist only a few studies exploring only the low-energy ($\hbar\omega \leq 10$ meV) spin dynamics in electron-doped materials

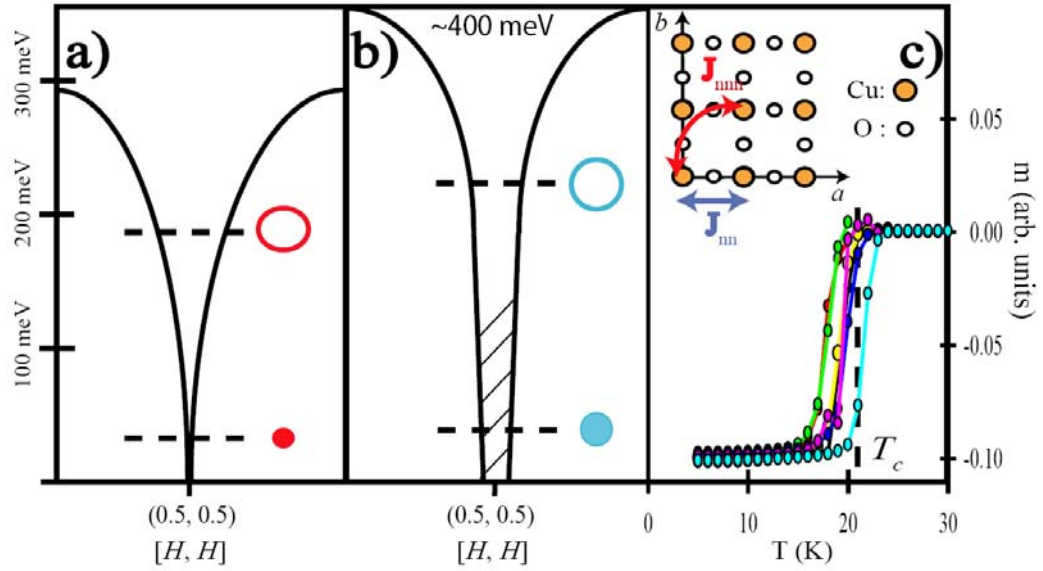


Fig. 4.1 Schematic of the dispersions of the spin excitations in the monolayer parent/superconducting compounds of the *n*-type copper oxides and susceptibility measurements for PLCCO crystals. a) Magnetic dispersion observed in insulating Pr_2CuO_4 and b) superconducting PLCCO. c) Magnetic susceptibility measurements of T_c 's in arbitrary units for the seven samples. The inset shows the magnetic unit cell in the CuO_2 plane with exchange couplings J_{nn} and J_{nnn} .

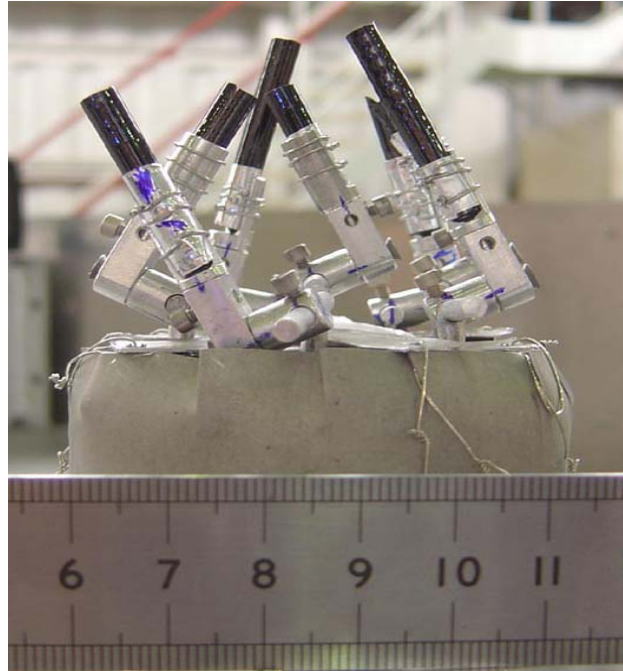


Fig. 4.2 Picture of 7 coaligned crystals used for time-of-flight neutron experiment on the MAPS spectrometer

such as $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ (NCCO) [103, 104] and $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ [56] (as presented in Chapter 3), and consequently the overall magnetic response of electron-doped materials remains largely unknown. In order to address this lack of a complete picture of the magnetic dispersion in the n -type cuprates, we chose to study the complete spectrum of spin excitations in underdoped PLCCO ($T_c = 21$ K, $T_N = 55$ K). This sample was chosen for two reasons: First, this material is between the as-grown AF insulator and optimally-doped PLCCO and therefore exhibits a larger magnetic signal than that of the optimally doped PLCCO [56, 61, 62, 60]. Second, as discussed in Chapter 3.3, Pr^{3+} possesses a nonmagnetic singlet ground state in PLCCO, different from the Nd^{3+} magnetic ground state in NCCO and therefore removes uncertainty in the origin of any magnetic signal observed.

In the following sections, I will present the results from experiments mapping out the detailed dispersion of the magnetic excitations in the underdoped PLCCO $T_c=21$ K system. Inelastic neutron scattering measurements that probe the low-temperature ($T=7$ K) dynamic spin response of this electron-doped system for energies from 0.5 meV to 330 meV will be presented. The $\mathbf{Q}$ - and $\hbar\omega$ -dependence of the generalized magnetic susceptibility $\chi''(\mathbf{Q}, \omega)$ are determined for this n -type system for the first time over such a broad energy scale.

4.2 Experimental details

For the following experiments, we grew seven high-quality (mosaicity $<1^\circ$) PLCCO single crystals shown in Fig. 4.2 (with a total mass of 20.5 grams) using the traveling solvent method in a mirror image furnace. To obtain superconductivity, we annealed the as-grown nonsuperconducting samples in a vacuum ($P < 10^{-6}$ mbar) at $T = 765 \pm 1^\circ\text{C}$ for four days. Although both ends of the same cylindrical shaped crystal were found to have identical T_c 's, there are small (± 1 K) differences in T_c 's for separately annealed samples. Figure 4.1c shows magnetic susceptibility measurements on all seven crystals used in our neutron experiments. They have an average $T_c = 21 \pm 1$ K. For the experiments in the following sections, I will again define the wave vector $\mathbf{Q}$ at (q_x, q_y, q_z) as $(H, K, L) = (q_x a/2\pi, q_y a/2\pi, q_z c/2\pi)$ reciprocal lattice units (r.l.u) in the tetragonal unit cell of PLCCO (space group $I4/mmm$, $a=3.98$, and $c=12.27$ Å).

In section 4.3, two of the seven crystals grown and annealed with identical T_c 's = 21K were coaligned in the $[H, K, 0]$ zone (samples #12 and #13) for experiments on the cold-triple-axis PANDA spectrometer at the FRM-II neutron facility. These crystals were then mounted in a closed cycle refrigerator with a total coaligned mass of ~ 5.5 g. Experiments were then performed on the PANDA spectrometer with a fixed neutron $k_f = 1.5$ Å $^{-1}$ and a spectrometer configuration of open-open-sample-open-open. A cooled Be-filter was placed after the sample and before the analyzer in order to remove higher order harmonics in the neutron beam. Data was collected within the sample temperature range of $T = 2$ K to $T = 120$ K, and the low energy magnetic dispersion could be determined from $\hbar\omega = 0.5$ meV to $\hbar\omega = 9$ meV.

For experiments in section 4.4, all seven PLCCO crystals were co-aligned to within 1° in the $[H, H, L]$ zone using HB-1/HB-1A triple axis spectrometers at the High-Flux-Isotope reactor, Oak Ridge National Laboratory (Fig. 4.2). Our inelastic neutron

scattering experiments were then performed on the MAPS time-of-flight spectrometer with the incident beam parallel to the c -axis (L -direction) of PLCCO at the ISIS facility. The samples were mounted in a closed cycle refrigerator and cooled to $T \sim 7\text{K}$. Four different incident beam energies of $E_i = 40, 115, 200,$ and 400 meV were used, and the scattering was normalized to absolute units using a vanadium standard. For time-of-flight measurements, this vanadium standard facilitates this absolute normalization through using the ratio of the measured scattering of the sample and the known scattering strength of a similarly shaped mass of vanadium.

In performing the vanadium normalization, both monochromatic vanadium scans (at identical experimental conditions to the sample runs) and a full-white beam vanadium scan are taken in order to achieve a proper calibration. The white-beam normalization corrects for varying efficiencies of the individual detectors, while the monochromatic vanadium runs allow for the corresponding detector counts to be normalized to a known cross section. Since vanadium has a well characterized and strong incoherent elastic scattering signal, the elastic incoherent scatter from the vanadium standard can be utilized simultaneously to calibrate all the relevant detectors for a given E_i and chopper speed setting.

The scattering function $S(Q, \omega) = \left(\frac{\sigma_{inc}}{4\pi} \right)^{van} \frac{N^{van}}{N^{sample}} \frac{H_{sample}(\omega)}{H_{van}}$ then is used to

determine the absolute units for the sample scattering in $[mbarns\ s.r.^{-1}\ meV^{-1}\ f.u.^{-1}]$. The

value of $\left(\frac{\sigma_{inc}}{4\pi} \right)^{van} = 404 \frac{mbarns}{s.r.}$ and the ratio $H(\omega)$ values are recorded numbers

determined by the spectrometer computer (using the monochromatic vanadium and corresponding sample run files). The values for N are simply the number of scattering sites in either the sample or the vanadium standard. The conversion of magnetic scattering into units of μ_B^2/eV will be discussed later in section 4.5.

4.3 Low-energy magnetic dispersion

In order to determine the dispersion of the lowest energy excitations (something not easily done on the MAPS spectrometer) in underdoped PLCCO $T_c=21\text{K}$, we studied the static order and magnetic excitations about the $\mathbf{Q}=(0.5, 0.5, 0)$ wave vector on the PANDA cold-triple axis spectrometer using a set of $\mathbf{Q}$ two coaligned PLCCO($T_c=21\text{K}$) crystals. The existence of the quasi-two dimensional SDW order in these underdoped PLCCO samples was verified through scans through the $\mathbf{Q}=(0.5, 0.5, 0)$ position at a variety of temperatures. Fig. 4.3 shows temperature scans at the peak position $\mathbf{Q}=(0.5, 0.5, 0)$ for these two crystals. The onset of SDW order is $T_{SDW} \sim 55\text{K}$ consistent with results reported earlier in section 3.6 and in Ref. 62. The slight difference of about $\sim 10\text{ K}$ in T_{SDW} between this and earlier results can easily be explained by the now much sharper T_c in these newly grown samples (Fig. 4.3c) and the more precise knowledge of their location within PLCCO's phase diagram. The broader T_c of the $T_c=21\text{K}$ sample studied in section 3.6 (plotted in Fig. 3.1) adds a large amount of uncertainty in correlating the superconducting T_c of this sample with the onset of SDW order. The now sharper T_c 's of these samples are a consequence of the improved vacuum annealing technique employed

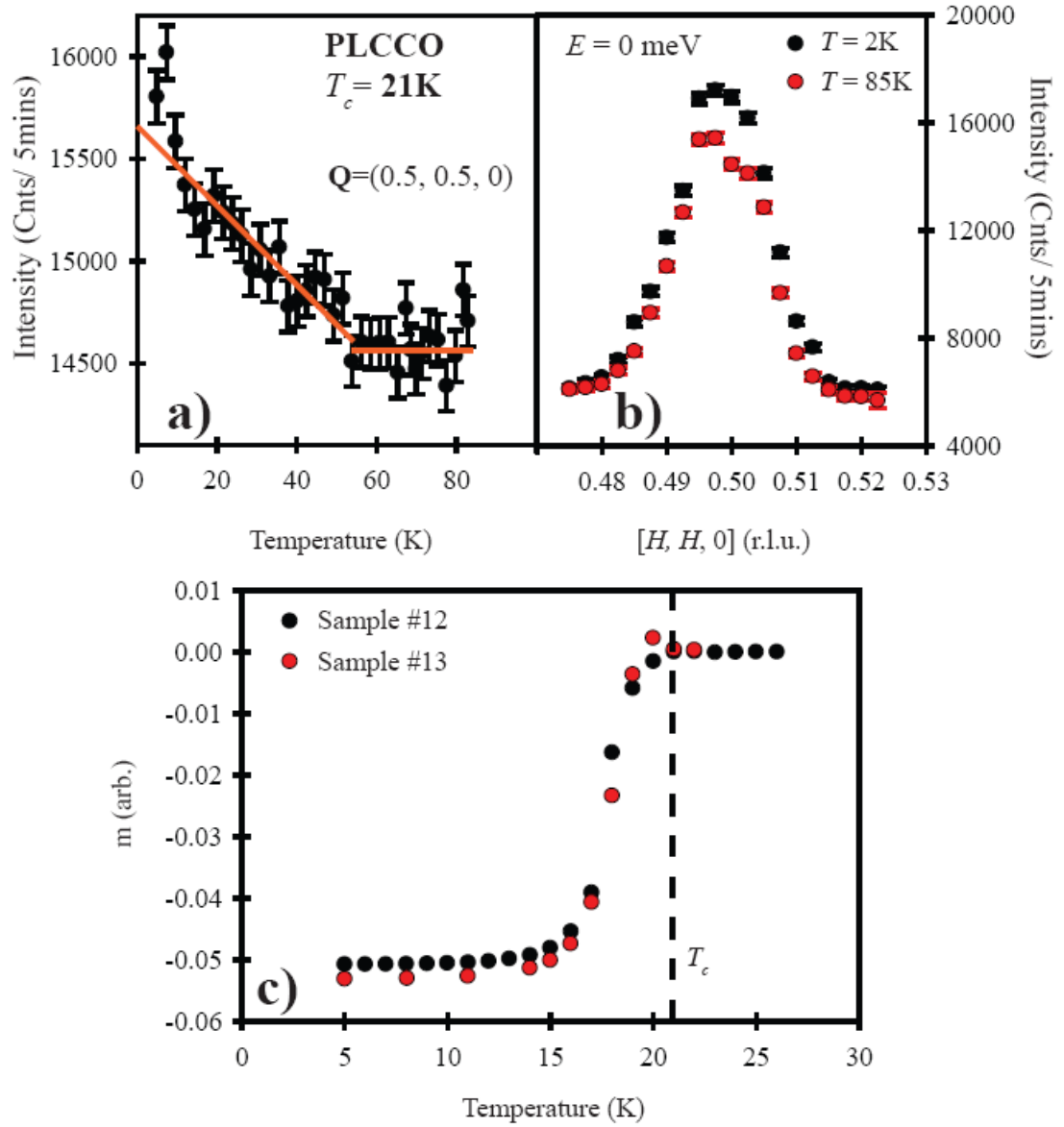


Fig. 4.3 Static SDW order in PLCCO $T_c=21\text{K}$ samples collected on the PANDA spectrometer and bulk susceptibility plots for samples #12 and #13. a) Peak intensity counts collected at $Q=(0.5, 0.5, 0)$ as a function of temperature. Solid line is a guide to the eye showing the onset of quasi-two-dimensional AF order at $T_{SDW} \sim 55\text{K}$. b) Elastic Q -scans through $Q=(0.5, 0.5, 0)$ along $[H, H, 0]$ both above ($T = 85\text{K}$) and below T_{SDW} ($T = 2\text{K}$). c) Susceptibility measurements of PLCCO $T_c=21\text{K}$ samples #12 and #13 that were coaligned and used in the PANDA measurements.

in treating these new $T_c=21\text{K}$ crystals (described in section 4.2) rather than the older argon annealing technique described in section 3.2.

The resulting distribution and dispersion for the 2K magnetic excitations in this underdoped PLCCO system are plotted in Fig. 4.4a for $\hbar\omega = 0.2$ to 7 meV. $\mathbf{Q}$ -scans plotted along $[H, H, 0]$ for various energies show that the spin excitations centered at $(0.5, 0.5, 0)$ remain commensurate with increasing energy transfer and broaden in $\mathbf{Q}$. The vertical dashed lines in Fig. 4.4a show the approximate calculated resolution of the spectrometer projected along the $[H, H, 0]$ axis. Even though at lower energies the small final energy used ($k_f = 1.5 \text{ \AA}^{-1}$) in this experiment allows for an excellent resolution of the low energy excitations, by 7 meV, however, the spectrometer resolution constitutes a significant majority of the measured excitation width, and the continued dispersion is difficult to evaluate.

Now focusing instead on the detailed structure of the spin excitations in these $T_c=21\text{K}$ samples, low- T E -scans taken at the peak position $(0.5, 0.5, 0)$ with the nonmagnetic background subtracted are plotted in Fig. 4.4b. An identical peak in the low- T spin susceptibility is observed as that reported in Chapter 3.6. The increase in intensity at 0.5 meV at the lowest energy measured in the susceptibility most likely arises from contamination of the elastic scattering due to the poorer resolution of this PANDA experiment (with no collimation) relative to the earlier SPINS experiments (see Chapter 3.4 for experimental setup for SPINS results). The solid line in Fig. 4.4b is a fit using a

damped Lorentzian function $F(x) = \frac{Ax}{1 + \left(\frac{x - x_0}{b}\right)^2}$, where $A = 120.1$, $x_0 = 0.624$, and $b =$

1.24257. This low energy peak is remarkably similar to recent work by Stock et al. [105] in which a low energy soft mode ($\hbar\omega \sim 2$ meV) was observed along with a central mode ($\hbar\omega = 0$ meV) in the underdoped YBCO(6.35) system. Within this system's long timescale, glassy spin fluctuations are centered about the elastic position (comprising the central mode at $\hbar\omega = 0$ meV) and are driven by the damped soft mode around 2 meV. This parallel between the low energy soft mode in YBCO and PLCCO, however, breaks down when comparing the central mode of YBCO(6.35) and the static SDW peak in $T_c=21\text{K}$ PLCCO. As shown via the polarized experiments on this underdoped PLCCO system in Chapter 3.2, the elastic scattering in PLCCO is truly static AF order within the CuO_2 plane, whereas within YBCO(6.35) the spins remain glassy and paramagnetic without any true long-range order [105].

4.4 High-energy magnetic dispersion

In order to probe the dispersion of high-energy spin excitations and their precise structure as they disperse toward the AF zone boundary, the high resolution afforded by time-of-flight neutron spectrometry with position-sensitive detectors is required. For our time-of-flight measurements, we utilized the high-resolution MAPS spectrometer with 4-fold symmetric low angle detector banks. This allows for the folding of data from equivalent positions in symmetrically distributed detector banks. Thus, for samples with the appropriate symmetry and alignment, the signal can be folded and the statistics

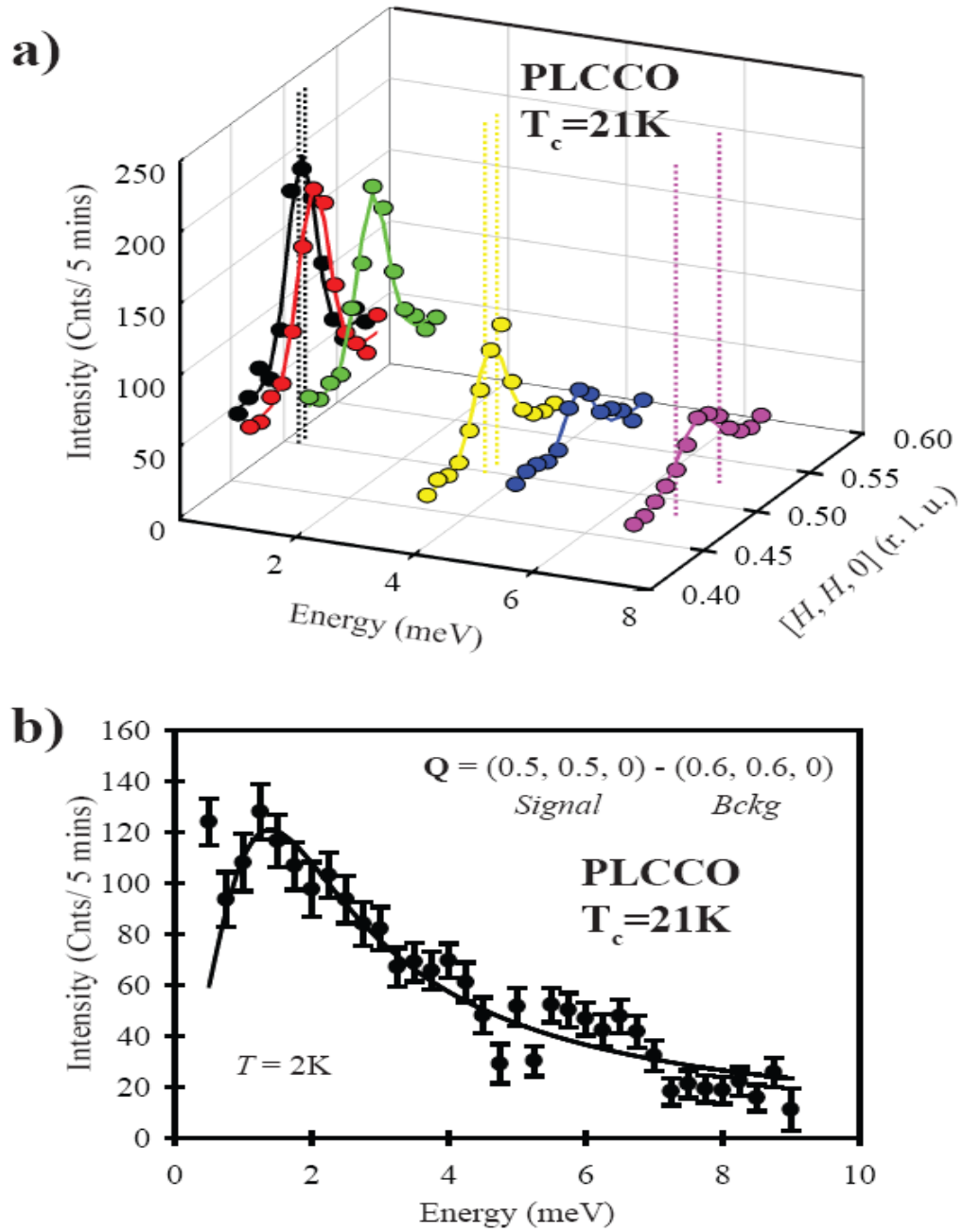


Fig. 4.4 Low energy dispersion and peak in the susceptibility of PLCCO $T_c=21\text{K}$ on PANDA spectrometer. a) $T = 2\text{K}$ plot of $[H, H, 0]$ scans at various energy transfers. Vertical dashed lines represent the FWHM of the calculated spectrometer resolution. b) E -scan at $T=2\text{K}$ at $Q=(0.5, 0.5, 0)$ with the nonmagnetic background subtracted ($Q=(0.6, 0.6, 0)$) showing a peak in the susceptibility near $\sim 1.5\text{meV}$. The solid line is a damped Lorentzian fit, as described in the text.

improved up to four times. Despite this signal enhancement through detector folding, large sample masses are still required due to the weak Cu^{2+} spin signal and the low time integrated neutron flux at neutron spallation sources. In order to compensate for this, we coaligned seven crystals in the $[H, H, L]$ zone (including the two crystals from Sect. 4.3) with a total mass of $\sim 20.5\text{g}$, as described in section 4.2.

Since in time-of-flight neutron experiments the $\mathbf{Q}$ -vector of the scattering process is coupled to the energy transfer of the signal measured, care must be taken in analyzing the resulting coupled $(\mathbf{Q}, \omega)$ intensity spectrum. Fortunately, due to the quasi-two-dimensional nature of the spin excitations of this PLCCO cuprate system [56] (and other monolayer cuprates), much of this problem is avoided through aligning the sample such that the c -axis is parallel to the incident neutron beam. In this configuration, maps of scattering along the $[H, H, L]$ and $[-H, H, L]$ axes can be collected for a variety of energy transfers simultaneously (using only a single incident neutron energy, E_i). Even though the L -value of the scattering is strongly coupled to the changes in energy transfer for these various maps of scattering, the near negligible (aside from form factor) dependence of the magnetic scattering along L makes this an effective means of mapping the excitations. For this reason, positions in reciprocal space will be referred to by the corresponding $[H, H]$ and $[-H, H]$ values along with the respective energy, $\hbar\omega$. A variety of incident energies are still utilized in the following experiments due to resolution and k_f/k_i effects. Since time-of-flight scattering is in many ways similar to triple-axis scattering with a fixed neutron E_i , at higher energy transfers the effective energy resolution actually improves. At low energy transfers, there is a broad resolution-generated tail whose large intensity often acts as a lower bound for the window of energies that can be analyzed for a particular neutron E_i value. This can be tuned at the expense of neutron-flux by accessing higher harmonics of the spectrometer's chopper frequency, which in turn improve the experiment's energy resolution.

An upper bound on the available energy window for a given E_i is of course simply the value of E_i itself due to the k_f/k_i factor in the neutron cross section. In reality, however, due to increased background from chopper effects and other spectrometer factors, a useful gauge is typically $\sim 75\%$ of E_i as a useful upper bound for resolvable signal. By playing with these two factors and varying the incident neutron energy, a mapping of the spin excitations in $\mathbf{Q}$ -space can be achieved over a broad range of $\hbar\omega$.

All of the final data presented in the following discussion has been folded using the MSLICE program. Cuts/slices were chosen so that the folding axis did not fold the signal close to a detector edge due to spurious scattering signal arising to electronic noise in the detectors at those positions. In any case, where the energy window dictated that one folding direction might integrate in some of this spurious signal, then the folding procedure for that direction was foregone. The validity of the folding process (which is highly dependent on the sample alignment) was verified by comparison of the known commensurate excitations at 5 meV in each detector bank before and after folding. Four clear magnetic peaks appeared centered in each detector bank (at $(0.5, 0.5)$, $(-0.5, -0.5)$, $(0.5, -0.5)$, and $(-0.5, 0.5)$) prior to folding. After folding, a single sharp peak remained, and the final cuts through the resulting single 5 meV (at $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$) excitation confirmed that the width of the resulting single magnetic peak was unaffected. This verifies that the sample alignment and folding procedure do not introduce any spurious

structure to the higher energy excitations where the folding is necessary in order to resolve the magnetic signal.

Turning now to the data collected for the PLCCO $T_c=21\text{K}$ system, Figure 4.5 summarizes images of neutron scattering intensity $S(\mathbf{Q}, \omega)$ centered about $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$ at $T=7\text{ K}$ in units of $[mbarns\ sr^{-1}\ meV^{-1}\ f.u.^{-1}]$ without any background subtraction. At the lowest energy ($\hbar\omega = 4 \pm 1\text{ meV}$) probed (Fig. 4.5a), the scattering consists of a strong peak centered at $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$ with some phonon contamination evident at larger wave vectors. A constant-energy cut through the image reveals a commensurate peak on a flat background (Fig. 4.5f). The peak is significantly broader than the instrumental resolution (horizontal bar) and gives a correlation length of $\sim 70\text{ \AA}$. Upon increasing energy, the peak at $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$ broadens in width (Fig. 4.5b) and weakens in intensity (Fig. 4.5g). With a further increase in energy to $\hbar\omega = 145 \pm 15\text{ meV}$, the scattering becomes a spin-wave-like ring (Figs. 4.5c and 4.5h). One-dimensional cuts through Fig. 4.5d at $\hbar\omega = 200 \pm 15\text{ meV}$ along four different directions (Figs. 4.6a-d) confirm that the scattering is indeed isotropic and symmetric around $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$ like spin waves. With increasing energy, the ring continues to disperse outward until magnetic scattering is no longer discernible at $\hbar\omega = 315 \pm 15\text{ meV}$ (Fig. 4.5j).

Figure 4.7a summarizes the dispersion of spin excitations determined from the cuts in Figs. 4.5f-j. The dashed boxes show the positions of crystalline electric field (CEF) excitations arising from the Pr^{3+} rare earth ions in the tetragonal structure of PLCCO [70]. Compared to intensities of Pr^{3+} CEF levels, Cu^{2+} spin fluctuations in PLCCO are extremely weak and cannot be separated from the strong Pr^{3+} scattering at certain CEF energy positions. For reference, figure 4.7b shows an energy cut along $\mathbf{Q}=(0.5, 0.5, L)$ for the $E_i=115\text{ meV}$ data in which it is clear that CEF intensities at $\hbar\omega \approx 20$ and 85 meV are significant relative even to the incoherent elastic scattering.

To estimate the strength of the magnetic exchange coupling, we consider a two-dimensional AF Heisenberg Hamiltonian with the nearest (J_{nn}) and the next nearest (J_{nnn}) neighbor coupling (Fig. 4.1c). Since the zone boundary spin fluctuations sensitive to J_{nnn} were unobservable (Fig. 4.5j), we set $J_{nnn} = 0$ and determined that $J_{nn}=162 \pm 13\text{ meV}$ renders the best fit to the data for $\hbar\omega \geq 100\text{ meV}$. The corresponding calculated one-magnon cross sections are plotted as the solid lines in Figs. 4.5h-4.5j, and the resulting dispersion relation is shown as the solid line in Fig. 4.7a. At high energies ($\hbar\omega \geq 100\text{ meV}$), the calculated spin wave dispersion coincides fairly well with the data, but the value of J_{nn} is considerably larger than the hole- (La_2CuO_4 , $J_{nn}=104$, $J_{nnn}=-18\text{ meV}$) [31] and electron- (Pr_2CuO_4 , $J_{nn}=121\text{ meV}$) [27] doped parent compounds (Fig. 4.7a). Assuming as-grown insulating PLCCO has a similar AF exchange coupling as Pr_2CuO_4 [27, 56], our data suggest that the high-energy spin fluctuations in electron-doped PLCCO disperse faster than the spin waves of the insulating compound. Therefore, they are unlikely to arise from the weak static AF order in the material discussed in section 4.3.

Although high-energy spin excitations in PLCCO are spin-wave-like, the observed scattering for $\hbar\omega \leq 80\text{ meV}$ is substantially broader than that predicted by the linear spin-wave theory (Fig. 4.5a). A cut at $\hbar\omega = 8 \pm 1\text{ meV}$ through the $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$ point along the $[-1, 1]$ direction confirms this point (Fig. 4.7c). In this panel, the dashed blue line is a best fit line to the data of a Gaussian on a linear background,

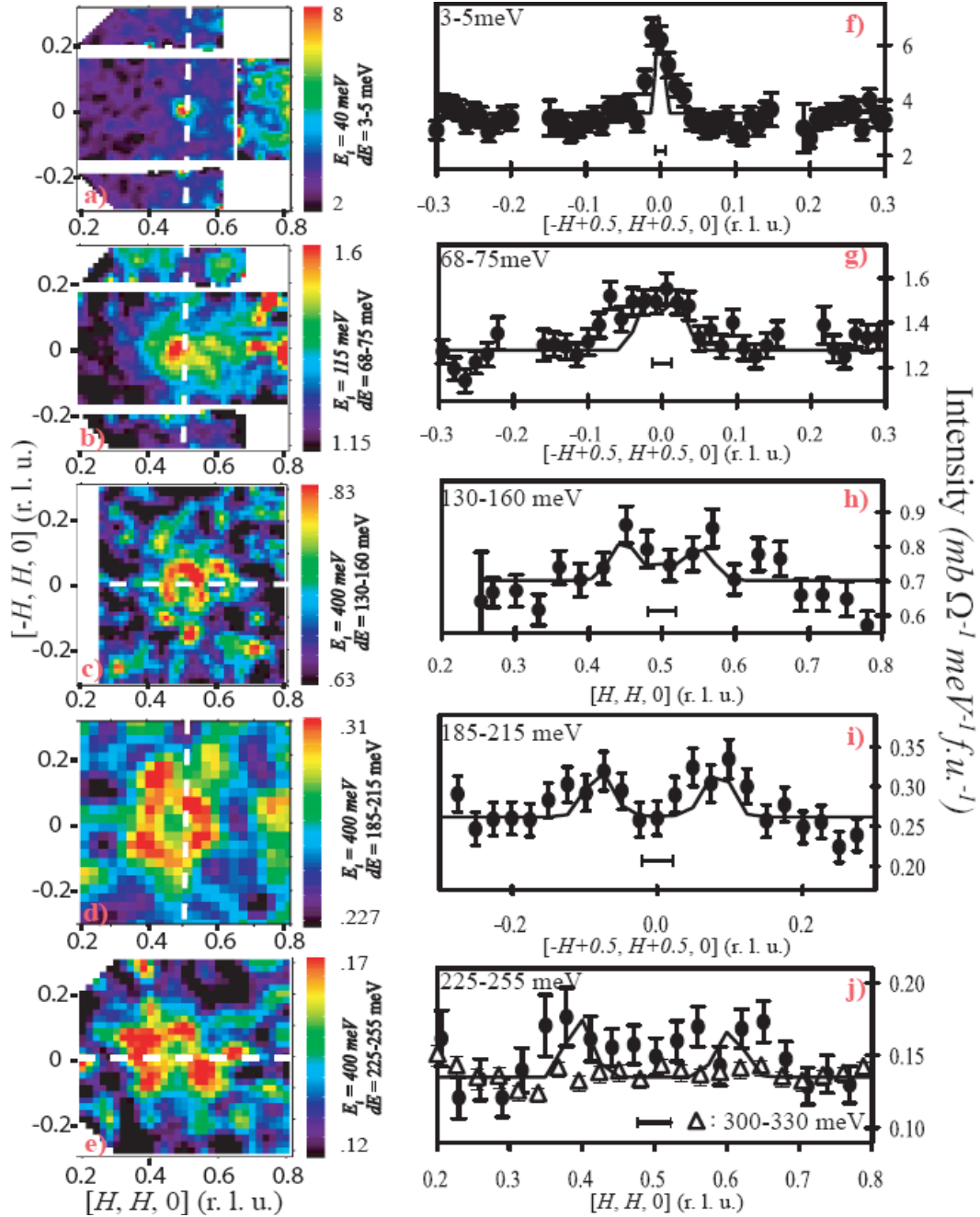


Fig. 4.5 Maps of $S(\mathbf{Q}, \omega)$ in the (H, K) plane at a) $\hbar\omega = 4 \pm 1$, b) 71.5 ± 3.5 , c) 150 ± 10 , d) 200 ± 15 , and e) 240 ± 15 meV. The incident beam energy $E_i = 40, 115, 200$, and 400 meV data have counting times of 18, 60, 44, and 76 hours, respectively, with a source proton current of $170 \mu\text{A}$. f-j) Narrow $\mathbf{Q}$ -cuts passing through $(0.5, 0.5)$ along the dashed line directions shown in a-e). Upper open triangles in j) show a thicker cut at $\hbar\omega = 315 \pm 15$ meV along the $[1, 1]$ direction (integrated from -0.2 to 0.2 along the $[-1, 1]$ direction). Solid lines are the calculated one-magnon cross sections from the linear spin wave fit to the data with $J_{\text{nn}} = 162$ meV

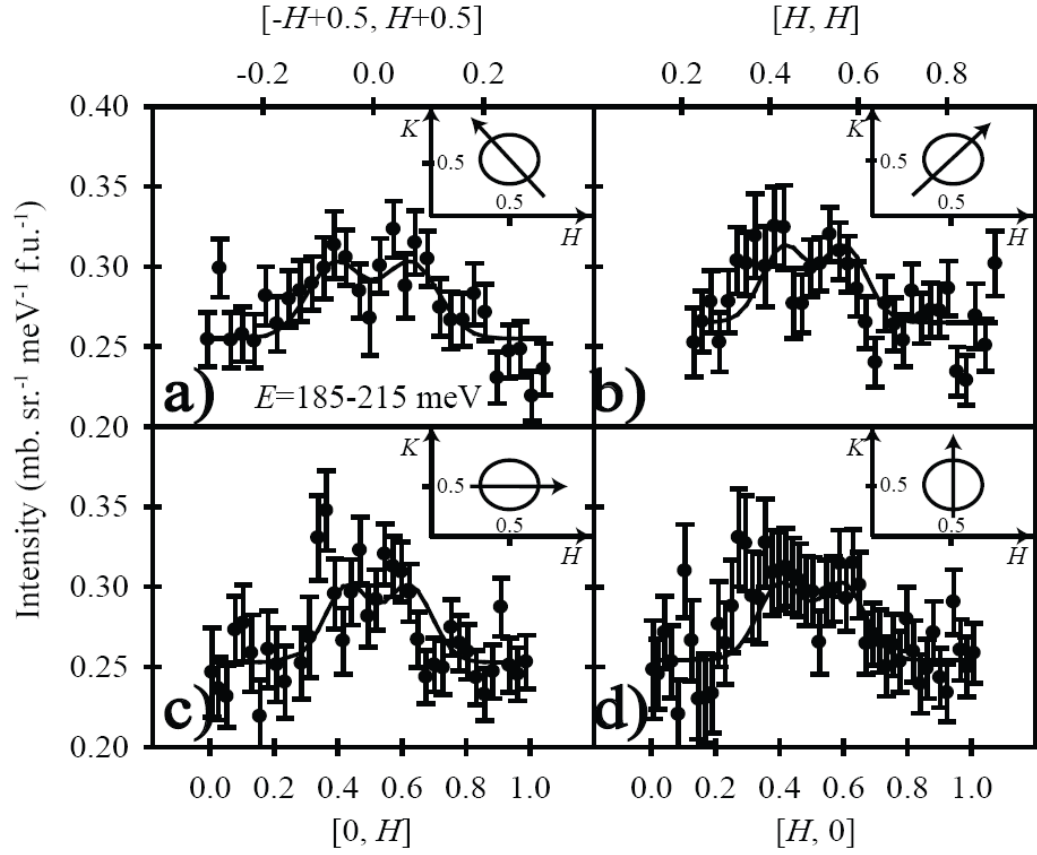


Fig. 4.6 $\hbar\omega = 200\text{ meV}$ cuts through magnetic excitation ring at $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ for PLCCO $T_c = 21\text{K}$ at $T = 7\text{K}$. a) Cut along the $[-H, H]$ direction at $\hbar\omega = 200\text{ meV}$ b) Cut along the $[H, H]$ direction at $\hbar\omega = 200\text{ meV}$ c) Cut along the $[0, H]$ direction at $\hbar\omega = 200\text{ meV}$ d) Cut along the $[H, 0]$ direction at $\hbar\omega = 200\text{ meV}$. Insets in each panel show a schematic of the cut direction through the ring-like excitation centered at $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$.

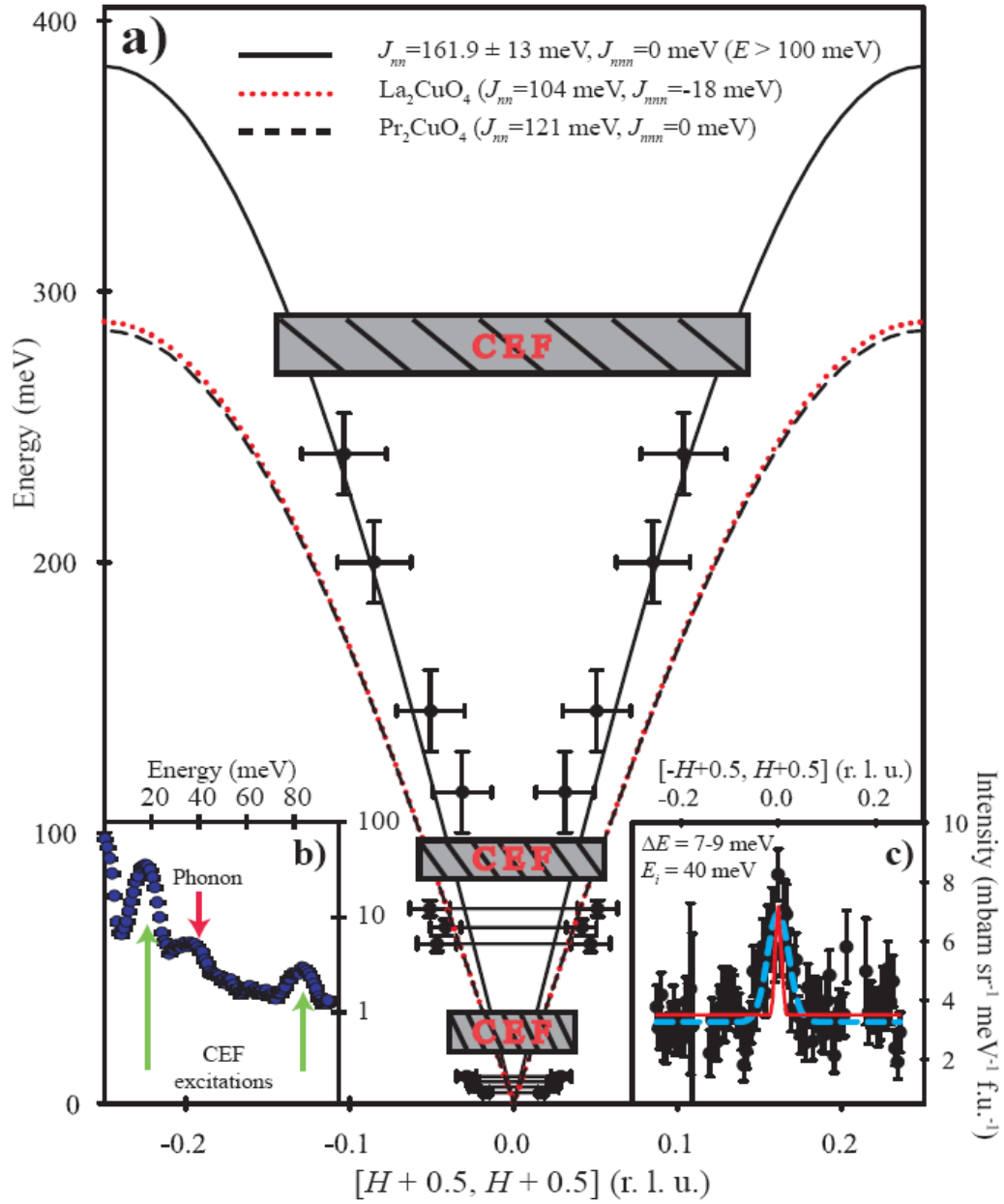


Fig. 4.7 The high-energy dispersion of spin excitations in PLCCO $T_c=21\text{K}$. a) Points connected by solid lines denote only one continuous peak centered around $(0.5, 0.5)$ and represent the FWHM of a Gaussian fit with the instrument resolution deconvoluted. Solid boxes show energy levels of Pr^{3+} CEF scattering. Solid, dotted, dashed, dash-dotted lines show dispersions from linear spin-wave fits with various exchange couplings. b) Log vs. linear energy-cut averaged from $H=0.45$ to 0.55 along the $[H, H]$ direction and from $H=-0.05$ to 0.05 along the $[-H, H]$ direction. CEF and phonon contamination energies are marked by arrows. c) Q-cut along the $[-H, H]$ direction with $\hbar\omega=8\pm 1\text{ meV}$ with a Gaussian fit in a blue dashed line and the calculated one-magnon cross section in solid red with $J_{nn} = 121\text{ meV}$.

whereas the sharper solid red line is the calculated instrument resolution for this particular cut. This demonstrates a broadened response at low energies relative to the resolution-limited spin waves and contrary to the expected response of excitations emanating from long-range AF order. For energies below 20 meV, the dispersion of spin fluctuations has a nearest neighbor coupling of $J_{nn} = 29 \pm 2.5$ meV (dash-dotted line in Fig. 4.7a). Therefore, the dispersion of PLCCO can be separated into two regimes. For energies ($4 \leq \hbar\omega \leq 80$ meV), the excitations are broad and weakly dispersive. For $\hbar\omega \geq 100$ meV, the fluctuations are spin-wave-like with J_{nn} larger than that of the insulating parent compound.

In addition to determining the dispersion of spin excitations in PLCCO, the absolute spin susceptibility $\chi''(\mathbf{Q}, \omega)$ measurements in Fig. 4.6 also allow us to calculate the energy dependence of the local susceptibility $\chi''_{loc}(\omega)$, defined as

$$\chi''_{loc}(\omega) = \frac{\int \chi''(\mathbf{Q}, \omega) d^3\mathbf{Q}}{\int d^3\mathbf{Q}} \quad [26, 43].$$

Figure 4.8a shows how $\chi''_{loc}(\omega)$ varies as a function of $\hbar\omega$ for electron-doped superconducting PLCCO. Similar to hole-doped materials [26, 42, 45, 46, 96, 102, 106], electron-doping suppresses the spectral weight of spin fluctuations in PLCCO at high ($\hbar\omega \geq 50$ meV) energies. For energies below 50 meV, $\chi''_{loc}(\omega)$ increases with decreasing energy and does not saturate at $\hbar\omega = 4 \pm 1$ meV, the lowest energy probed on MAPS. Assuming that the $\chi''_{loc}(\omega)$ in crystals of MAPS experiments ($T_c = 21 \pm 1$ K) is similar to that of the previously studied $T_c = 21$ K PLCCO samples in sections 3.6 and verified in these samples in section 4.3, we can normalize the low-energy magnetic response of the $T_c = 21$ K sample obtained on SPINS spectrometer at NIST to that of the MAPS data. The outcome, shown as inset of Fig. 4.8, reveals a new energy scale of 2-3 meV for superconducting PLCCO. This new energy scale appears as this clearly defined peak at 2 meV and sharply contrasts the nearly energy independent response of $\chi''_{loc}(\omega)$ expected for traditional spin waves arising from an AF ordered phase (shown as a dashed line in Fig. 4.8 for AF ordered La_2CuO_4).

4.5 Determining $\chi''_{loc}(\omega)$ and linear spin-wave calculations

Before proceeding to the discussion of the results from the MAPS data presented in section 4.4, it is worthwhile to review a few details involved in the analysis of the MAPS data. First, I will review how I determined absolute values of the local susceptibility from the MSLICE program in the appropriate units of μ_B^2/eV , and, second, I will review the linear spin wave calculations used in determining the cross section and dispersion for the data plotted in Fig. 4.7.

In determining $\chi''_{loc}(\omega)$ for our PLCCO measurements, appropriate energy slices were first determined within the MSLICE program such that the magnetic scattering about $\mathbf{Q} = (0.5, 0.5, 0)$ was well centered in the middle of the detector banks when possible. This data, when properly ‘‘HOMER’ed’’, should give the scattering intensity $S(\mathbf{Q}, \omega)$ in units of $[\text{mbarn s.r.}^{-1} \text{eV}^{-1} \text{f.u.}^{-1}]$. In order to integrate the entire distribution of the magnetic signal at a given energy, a one-dimensional cut must be taken across the

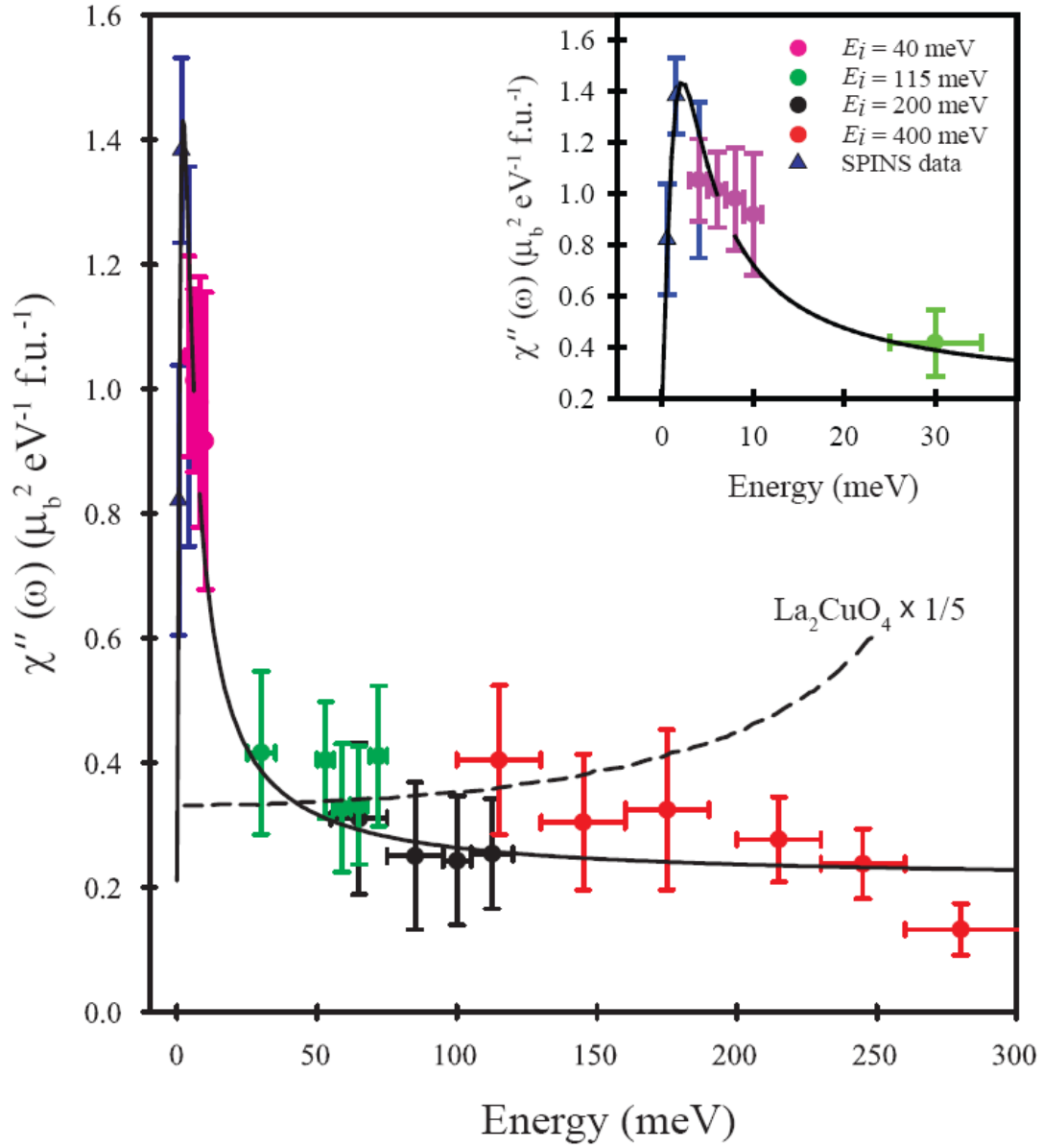


Fig. 4.8 Energy dependence of local susceptibility $\chi''(\omega)$ in PLCCO determined from integration over wave vector of the observed magnetic scattering around $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$. The dashed line shows $\chi''(\omega)$ times 0.2 for La_2CuO_4 [32, 106]. Since $\mathbf{Q}$ -cuts were made along the $[-H, H]$ direction, the background scattering can be approximated by a constant. The blue triangles indicate normalized cold neutron triple-axis data on a $T_c=21$ K PLCCO at energies below 3 meV obtained on the SPINS spectrometer at NIST center for neutron research [56]. The inset shows an expanded view of $\chi''(\omega)$ vs. $\hbar\omega$ at low energies. The solid line is a damped Lorentzian on a constant background.

chosen energy slice that encompasses the entire signal in question (the entire magnetic Brillouin zone should be accounted for). This can be achieved by defining the width of the cut (which I will call W) to be significantly larger than the width of the distributed magnetic signal. The resulting one-dimensional cut across the energy slice now represents an intensity profile of the magnetic scattering averaged over the width, W , of the cut. Care should be taken to ensure that the binned steps of the cut across the slice are sufficiently small when compared to the chosen width to avoid artifacts intrinsic to the data binning (at least ~ 10 times smaller). An approximate line shape that suitably models the cut across the energy slice above some chosen background must then be chosen (this usually is a single-peaked function since the averaged intensity typically peaks near the zone center). The integral of this fit function then gives the one-dimensional integral of the average value (over width W) of the magnetic scattering across the first Brillouin zone. A reasonable background profile can usually be achieved by choosing cuts orthogonal to $\mathbf{Q}$ so that nonlinear background terms arising from multiphonon processes can be minimized. Avoiding energies where single-phonon processes dominate is also necessary unless a detailed model of phonon relations/dispersions for the system is available.

The resulting one-dimensional integral can then be multiplied by the chosen W over which it was averaged in order to obtain a two-dimensional integral of the intensity. In the case of the quasi-two dimensional spin scattering of the monolayer cuprates and for k_i/c , the intensity of spin fluctuations orthogonal to the slice-plane (along the c -axis) can be assumed to be uniform along L . In calculating the three dimensional integral of $\int \chi''(\mathbf{Q}, \omega) d^3\mathbf{Q}$, the L -dimension of the first Brillouin zone can simply be multiplied into the two-dimensional result. This factor, however, will simply cancel out when normalized by the volume of the first Brillouin zone in calculating $\chi''_{loc}(\omega)$. The resulting integral is then divided by the volume of the first Brillouin zone, which then renders the

integral of $S(\omega) = \frac{\int S(\mathbf{Q}, \omega) d^3\mathbf{Q}}{\int d^3\mathbf{Q}}$ for a given energy in units of [mbarn eV⁻¹ f.u.⁻¹].

Using the relation: $S(\mathbf{Q}, \omega) = \frac{2}{\pi} \left(\frac{\gamma r_0}{\mu_B g} \right)^2 \frac{1}{1 - e^{\frac{-\hbar\omega}{k_B T}}} \chi''(\mathbf{Q}, \omega)$, the scattering function

can be converted to terms of the dynamic susceptibility. For high-energy transfers and relatively low temperatures, the Bose factor falls out as a trivial factor of one. This conversion renders the local susceptibility in units of [μ_B^2 eV⁻¹ f.u.⁻¹]. The total fluctuating moment can then be determined through the integral of $\chi''_{loc}(\omega)$ over all energies (and given in units of [μ_B^2 f.u.⁻¹]). Another factor not discussed thus far is the removal of the electronic form factor for the Cu²⁺ from the scattering cross section. The form factor should be removed from the SPE files prior to the integration described above. For a quick first order calculation in many cases at low- $\mathbf{Q}$, this is a negligible $\sim 3\%$ overall effect and does not effect the determined structure or dispersion of the spin excitations.

The fundamental concept of spin waves and the linear spin wave approximation is made most clear for the example of a ferromagnetic lattice of localized spins with

Hamiltonian $H = -\sum_{r,r'} J(r-r') S_r \cdot S_{r'}$. For an isolated site in this spin system with a given spin angular momentum S , there are $-S, -S+1, \dots, S-1, S$ available values for its respective spin components. If we assume that the axis of mean spin direction is z , then ideally all sites possess spin $S_z = S$. If this is perturbed by fluctuations (for instance temperature) then the value S_z for a given site will deviate from this maximal value (referred to as a spin deviation). This deviation and all others on different sites in the spin system from the maximal value for S_z can be represented by a continuous displacement in the form a traveling periodic wave (a spin wave) [29]. The wave amplitude squared at any one site gives the probability of a discrete spin deviation at that site. The quantized energy unit, n , of spin waves is the resulting number of spin deviations, which in the case of the ferromagnet is $n=S-S_z$ for a particular lattice site. Looking now at the spin angular momentum operators, the raising and lowering angular momentum operators are given by [29]:

$$S^+ |n\rangle = (2Sn)^{1/2} \left(1 - \frac{n-1}{2S}\right)^{1/2} |n-1\rangle \quad (4-1)$$

$$S^- |n\rangle = (2S(n+1))^{1/2} \left(1 - \frac{n}{2S}\right)^{1/2} |n+1\rangle \quad (4-2)$$

As a reminder, these operators are expressed as acting on states of a given spin deviation n , where $n = S-S_z$. Creation and annihilation operators for the spin deviation quantum are the usual $a|n\rangle = (n)^{1/2}|n-1\rangle$ and $a^+|n\rangle = (n+1)^{1/2}|n+1\rangle$. The linear spin wave approximation then is to simply assume that $S^- = (2S)^{1/2}a^+$ and $S^+ = (2S)^{1/2}a$, which has a simplifying advantage when constructing the Hamiltonian for the system. This assumption only works well for small spin deviations or for values of S_z close to S .

Linear spin wave calculations for excitations arising from the creation of magnons from an AF ordered phase are described in detail in both Lovesey [30] and Squires [29] textbooks, and I will try and review some of the key points here. It first is helpful to first re-index the chemical unit cell from tetragonal symmetry to orthorhombic symmetry as shown in Fig. 4.9a. This enlarges the unit cell by $\sqrt{2}$ on each side within the CuO_2 plane. The AF magnetic structure discussed for the collinear case similar to that of La_2CuO_4 , except with the moment directions aligned along the Cu-O bond directions, was assumed. The AF magnetic structure can then be envisioned as two interpenetrating magnetic sublattices as shown in Fig. 4.9b that are separated by a distance $\rho = (a_{\text{orth}}/2, a_{\text{orth}}/2)$ in real space. The cross section for one-magnon creation for this structure is then [30]:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = (\gamma r_0)^2 \frac{k_f}{k_i} \left[\frac{1}{2} F(Q) \right]^2 \frac{1}{4} (1 + \hat{k}_z)^2 e^{U^2} \frac{(2\pi)^3}{N v_0} \sum_{\alpha=0,1} \sum_{q,\tau} (n(\omega) + 1) \partial(\hbar\omega_{q,\alpha} - \hbar\omega_{\text{neutron}}) \partial(Q - q - \tau) \times$$

$$(u_q^2 + v_q^2 + 2u_q v_q \cos \rho \cdot \tau) \quad (4-3)$$

where $\mathbf{Q}$ is the momentum transfer of the neutron, q is the wave vector of the system, and τ is the reciprocal lattice vector of the resulting sublattice. The $(1 + \hat{k}_z)$ term is sometimes referred to as the orientation factor and $\hat{k}_z$ is the unit vector projection of momentum transfer along z (defined as the magnetization direction).

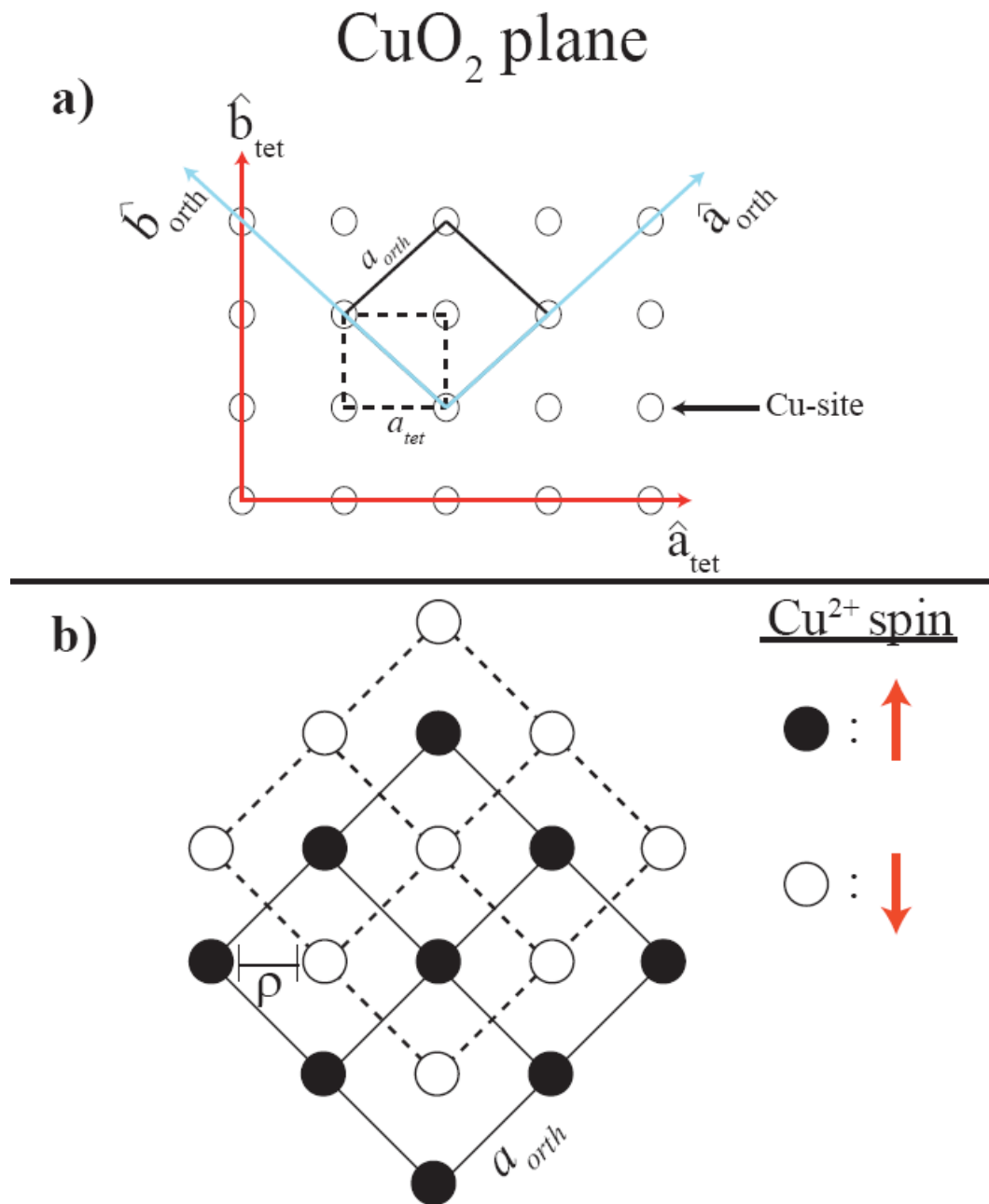


Fig. 4.9 Tetragonal and orthorhombic chemical and magnetic units cells for PLCCO. a) The relation between the tetragonal unit cell and the rotation into the orthorhombic unit cell is illustrated. The lattice parameter a_{tet} is lengthened by the $\sqrt{2}$ in converting to a_{orth} . b) AF order viewed as interpenetrating ferromagnetic sublattices as described in the text.

For the AF case where the moments on each sublattice are equal in magnitude, we assume that there is no external magnetic field present and that there exists no internal uniaxial anisotropy field. These assumptions result in the (nearest neighbor coupling only) dispersion relation $\hbar\omega_q = 2rJS(1 - \gamma_q^2)^{1/2}$ and the terms [30]:

$$u_q^2 = \frac{SN}{\varepsilon_q}(1 + \varepsilon_q) \quad (4-4)$$

$$v_q^2 = \frac{SN}{\varepsilon_q}(1 - \varepsilon_q) \quad (4-5)$$

$$u_q v_q = \frac{-\gamma_q}{\varepsilon_q} SN \quad (4-6)$$

In formulas (4-4) through (4-6), ε_q is simply $\varepsilon_q = (1 - \gamma_q^2)^{1/2}$, and the γ_q parameter is the traditional definition of $\gamma_q = \frac{1}{r} \sum_b e^{iq \cdot b}$.

The sum in the definition of γ_q is carried out over nearest neighbors, where b is the real space distance to the nearest neighbor and r is the number of nearest neighbor sites. For the orthorhombic unit cell $\gamma_q = \cos(\pi q_h) \cos(\pi q_k)$. Care should be taken to realize that q_h and q_k are defined to be within the magnetic Brillouin zone, and they should not be interchanged with the traditional use of $[H, K, L]$ without first accounting for this (i.e. $H = q_h + \tau_h$). Returning to the expression for the spin wave cross section we now get:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = (\gamma r_0)^2 \frac{k_f}{k_i} \left[\frac{1}{2} F(Q) \right]^2 \frac{1}{4} (1 + \hat{k}_z^2) e^{U^2} \frac{(2\pi)^3}{Nv_0} \sum_{\alpha=0,1} \sum_{q,\tau} (n(\omega) + 1) \partial(\hbar\omega_{q,\alpha} - \hbar\omega_{neutron}) \partial(Q - q - \tau) \times \left(2SN \frac{\sqrt{1 + \gamma_q}}{\sqrt{1 - \gamma_q}} \right) \quad (4-7)$$

This expression can now be convolved with the calculated resolution of the spectrometer in order to fit the spin wave dispersion and used to calculate the expected scattering from spin wave excitations in the system. In addition, the anisotropic form factor for Cu^{2+} described in Ref. 107 was utilized in accounting for the electronic form factor for our model of spin wave excitations in PLCCO. For the results presented in section 4.5, the convolution of the spectrometer resolution response with the above cross section was performed using the TOBYFIT program (provided by Toby Perring) and is plotted as solid lines fit to the data in panels Fig. 4.5f-j.

4.6 Discussion and Conclusions

We are now in a position to compare the spin excitations of electron-doped PLCCO with that of the hole-doped LSCO [42, 48] and YBCO [45, 100, 101, 106]. For hole-doped materials such as LSCO [42, 94, 95, 96] and YBCO with $x \geq 0.45$ [43, 45, 100, 101], the low-energy spin fluctuations are incommensurate and display an inward dispersion toward a resonance point with increasing energy. This is not observed in

electron-doped materials as shown in section 4.4. Instead, spin fluctuations in PLCCO have a broad commensurate peak centered at $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$ at low-energies ($\hbar\omega \leq 50$ meV), which disperses outward into a continuous spin-wave, ring-like scattering at high energies ($\hbar\omega \geq 100$ meV), similar to lightly doped YBCO with $x=0.353$ [105]. At present, it is not clear how theoretical models based on spin stripes [97] can reconcile the differences in spin excitations between the hole- and electron-doped materials.

For hole-doped LSCO with $T_c=38.5$ K, the mean-squared fluctuating moment $\langle m^2 \rangle = \int \chi''(\omega) d\omega$ integrated up to 40 meV is $\langle m^2 \rangle = 0.062 \pm 0.005 \mu_B^2 \text{ f.u.}^{-1}$ [96].

For comparison, $\langle m^2 \rangle$, calculated from $\chi''(\omega)$ up to 40 meV, is only $0.024 \pm 0.003 \mu_B^2 \text{ f.u.}^{-1}$ in PLCCO and is about three times smaller than that of LSCO. The total fluctuating moment integrated from 0 to 300 meV (Fig. 4.7) gives $\langle m^2 \rangle = 0.089 \pm 0.009 \mu_B^2 \text{ f.u.}^{-1}$, a value an order of magnitude larger than the static moment squared reported by Kang et al. for this system ($0.0016 \mu_B^2 \text{ f.u.}^{-1}$) [61]. Since the total moment sum rule for the spin-1/2 Heisenberg model requires one-magnon fluctuating moment squared to be smaller than the ordered static moment squared [108], the observed high-energy spin-wave-like excitations are unlikely to arise from the small ordered moment.

In the standard Hubbard model and its strong-coupling limit, the t-J model with only the nearest-neighbor hopping t , there should be complete particle-hole symmetry and therefore, the electron- and hole-doped copper oxides should behave identically. The observed large difference between incommensurate and commensurate spin fluctuations in hole- and electron-doped materials has mostly been attributed to their differences in the strength of second nearest-neighbor (t') and third (t'') nearest-neighbor hopping. This also explains their differences in Fermi surface topology within the t-J model [109, 110, 111], although it may also be due to their proximity to two different quantum critical points [112]. In the most recent calculation using the slave-boson mean-field theory and random phase approximation [110], incommensurate spin fluctuations at $\mathbf{Q}=(0.3\pi, 0.7\pi)$ have been predicted for optimally doped NCCO. However, this is not observed in our PLCCO (Figs. 4.5a-4.5e). Similarly, the energy dependence of the $\chi''(\mathbf{Q}, \omega)$ at $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$ has been predicted to exhibit a peak between $0.1\omega/J$ [109, 110] and $0.4 \omega/J$ [111]. Although qualitatively similar to the predictions, $\chi''(\omega)$ in Fig. 4.8 has a peak at a much smaller energy of $0.02 \omega/J$. Comparison of future calculations in absolute units with our data should determine whether itinerant magnetism models can account quantitatively for the observed dynamic susceptibility in superconducting PLCCO.

Chapter 5: Resonance mode in PLCCO $T_c=24K$

Portions of the data and discussion in the following sections with the exception of section 5.5 have been published recently and can be found in Ref. 67.

5.1 Introduction and motivation

Whereas in conventional superconductivity the microscopic mechanism driving pair formation is known to be the electron-phonon interaction, the fundamental pairing mechanism of high- T_c superconductivity remains an issue of considerable debate. One widely considered possibility is that magnetic excitations may play an analogous role to that of phonons in conventional superconductors. The belief in a fundamental relation between magnetism and superconductivity in the high- T_c cuprates stems partly from the fact that the high- T_c superconducting phase itself arises from the universal antiferromagnetic order in the parent compounds of these systems once charge carriers, either holes or electrons, are doped into them. In fact, a sharp magnetic excitation known as the resonance mode that directly couples to superconductivity has been observed universally in all classes of the hole-doped high- T_c cuprates. The resonance is a sharp magnetic excitation centered at the wavevector $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ in the two-dimensional reciprocal space of the CuO_2 planes, which corresponds to the antiferromagnetic (AF) Bragg position of the undoped parent compounds (Fig. 5.1a). It was first discovered in the hole-doped bilayer high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (YBCO) where each unit cell has two Cu-O planes [49]. Its intensity grows below T_c and its energy ($\hbar\omega$) scales approximately with $k_B T_c$ (Fig. 5.1e) [43, 45, 102, 113, 114]. For optimally hole-doped cuprates, the resonance appears only below T_c further cementing its fundamental and ubiquitous connection with the superconducting phase in the cuprates.

At energies below the resonance in p -type systems, spin fluctuations peak at incommensurate wavevectors [45] and disperse inward toward the resonance [115, 116]. Such behavior is remarkably similar to that of the hole-doped $\text{La}_{2-x}(\text{Ba},\text{Sr})_x\text{CuO}_4$ [42, 48]. Although the resonance has also been observed in the hole-doped bilayer $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi(2212)) [51, 117] and in the single layer $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [50], the wavevector and energy dependence of the mode has been determined only for YBCO [43, 45, 49, 102, 113, 114] because of the small available single crystal volumes in the Bi(2212) and $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$. Therefore, it has not been possible to directly and systematically compare the neutron results with those of the photoemission, which are obtained mostly for Bi(2212) [21, 118]. The resonance is intimately related to superconductivity [106], and its interaction with charged quasi-particles observed by photoemission [21, 118], optical conductivity [119], and tunneling [120] suggests that it plays a similar role as phonons in conventional superconductors; however, the relevance of the resonance to high- T_c superconductivity has been in doubt because so far it has been found only in hole-doped materials [121].

If the resonance mode stands as a truly universal feature fundamental to all of high- T_c , then it should appear in both p - and n -type cuprates as both most likely share a

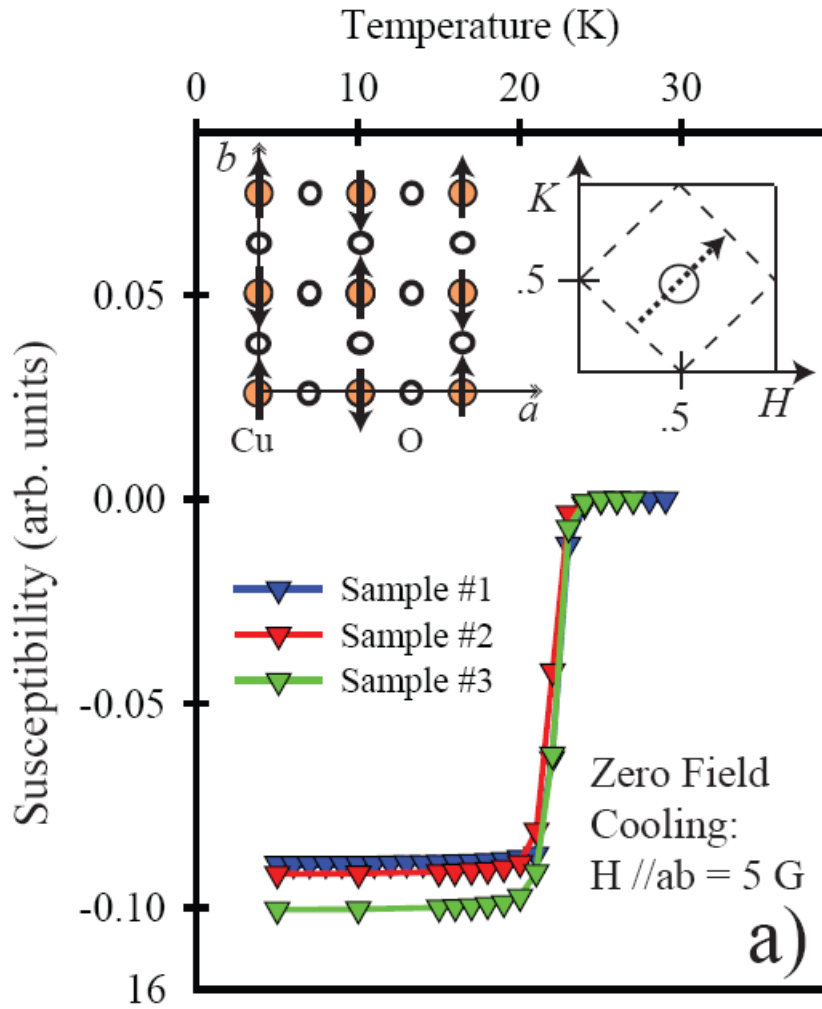


Fig. 5.1 Bulk susceptibility measurements for the three coaligned $T_c=24\text{K}$ samples. a) Bulk susceptibility measurements of three $T_c=24\text{K}$ samples in a Quantum-Design SQUID magnetometer. A 5 Gauss field was applied parallel to the ab -plane for the measurement. The top-left inset shows a single CuO_2 sheet along with its respective magnetic order. The top-right inset shows scans in $\mathbf{Q}$ -space across the magnetic Brillouin zone.

common origin for the superconducting phase intrinsic to their CuO_2 planes. Whereas our previous experiments presented in Chapter 4 have demonstrated that the incommensurate features in the spin excitation spectrum of the hole-doped cuprates are not present in the spin spectrum of the n -type cuprates, the presence of the resonance mode in an electron-doped system has not yet been investigated. Searching for the potential presence of the resonance mode in an electron-doped system can address several important questions. The first of these is: Is there a fundamental link between the incommensurate spin excitations, the hour-glass type dispersion, and the resonance mode in the magnetic spectrum of the cuprates? Discovery of the resonance mode in a system with a known commensurate low-energy response would seem to preclude any fundamental connection between the hour-glass dispersion and the resonance mode itself. The second question is: Since there does not seem to exist any electron-hole symmetry in the low energy response of the cuprates (incommensurate SDW excitations in hole-doped vs. commensurate spin wave-like excitations in electron-doped), does there exist any universal feature in the magnetic spectra of the cuprates that is universally present regardless of doped carrier-type? In order to address these questions, we performed a series of experiments on the optimally electron-doped cuprate $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ ($T_c=24\text{K}$) and analyzed the detailed temperature dependence of spin excitations about the wave vector $\mathbf{Q}=(0.5, 0.5, 0)$ in the energy range $0.5 \leq \hbar\omega \leq 20 \text{ meV}$.

5.2 Experimental details

For our experiments, we grew three large single crystals of $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ (PLCCO) using the traveling solvent floating zone technique ($\sim 3 \text{ g}$ each) and annealed the samples to obtain optimal superconductivity with $T_c = 24 \text{ K}$. Samples were annealed under vacuum ($P < 10^{-6} \text{ mbar}$) at 775°C for 100 hours as described in section 3.4. The resulting T_c 's following the annealing process are identical and are plotted in Fig. 5.1a. These three crystals were then coaligned in the $[H, K, 0]$ for our experiments with a total mosaic $< 1^\circ$. Previous experiments by Kang et al. [61, 62], have shown that for this optimally doped PLCCO system there exists no coexisting AF or quasi-two-dimensional SDW magnetic order. In order to verify that these crystals possess no static AF order, scans were performed through the AF ordering wave vector $\mathbf{Q}=(0.5, 0.5, 1)$ with the sample cooled to below $T = 600\text{mK}$, and no signature of AF order was observed (see Fig. 3.10 and description in section 3.8 for details). This now presents the unique window for studying the detailed spin excitation spectra in a phase-pure electron-doped superconductor (without coexisting AF order)—something not possible in the other prototypical electron-doped cuprate, $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [104].

Once these crystals were properly characterized, experiments were performed at several neutron sources in order to accurately characterize the spin spectrum from $\hbar\omega=0.5 \text{ meV} \rightarrow 16 \text{ meV}$. Cold neutron experiments mapping the spin excitations for $0.5 \leq \hbar\omega \leq 4 \text{ meV}$ were performed on the SPINS cold-triple-axis spectrometer at the NIST Center for Neutron Research. The SPINS spectrometer was setup with a fixed $E_f=3.7 \text{ meV}$ and with collimation: 120'-120'-80'-open. A cooled Be-filter was also placed after the sample to eliminate higher order contamination from the neutron beam. For thermal neutron experiments, both the HB-1 triple-axis spectrometer at the High Flux Isotope Reactor at

Oak Ridge National Lab and the BT-9 triple-axis spectrometer at the NIST Center for Neutron Research were used. In experiments on HB-1, a fixed final energy of $E_f=13.5$ meV was used with collimations: 48'-40'-60'-240'. For the experiments on BT-9 fixed final energies of $E_f=14.7$ meV and 28.0 meV were used with collimations of 40'-40'-40'-80'. All inelastic experiments on BT-9 and HB-1 utilized a PG-filter on the E_f side of the spectrometer in order to filter out $\lambda/2$ contamination, and for all the experiments, the samples were mounted and cooled in a liquid He-cooled cryostat.

5.3 Low energy excitations in PLCCO $T_c=24$ K revisited

We first probe the low-energy magnetic excitations of PLCCO using the SPINS cold neutron triple-axis spectrometer. The low energy excitations of this system were first described in section 3.8 and are revisited here with emphasis given to spin fluctuations coupled to the onset of superconductivity in this PLCCO system. For the purpose of convenience, the low energy excitations for this $T_c=24$ K system (originally plotted in Fig. 3.10) are replotted in Fig. 5.2 and the T -dependence is expanded upon. The magnetic excitations are commensurate and centered around $\mathbf{Q} = (0.5, 0.5, 0)$ at all temperatures (Figs. 5.2a-c) similar to that of NCCO [66]. They can be well described by Gaussians on linear backgrounds and are not resolution limited. For $\hbar\omega = 0.5$ meV, Gaussian fits on linear backgrounds give an amplitude $A = 31.3 \pm 4.2$ counts/10 mins, width $W = 0.011 \pm 0.0016$ r.l.u., background $Bckg = 19.2 \pm 1.2$ counts/10 mins at 2 K; $A = 38.3 \pm 4.9$ counts/10 mins, $W = 0.0104 \pm 0.0014$ r.l.u., $Bckg = 19.9 \pm 1.2$ counts/10 mins at 30K. For $\hbar\omega = 3.5$ meV, $A = 19.9 \pm 5.2$ counts/10 mins, $W = 0.098 \pm 0.0027$ r.l.u., $Bckg = 16.1 \pm 1.3$ counts/10 mins at 2 K; $A = 16.6 \pm 4.9$ counts/10 mins, $W = 0.0094 \pm 0.0029$ r.l.u., $Bckg = 16.9 \pm 1.2$ counts/10 mins at 30K. At $\hbar\omega = 0.5$ meV, the integrated intensities (defined as the sum of raw scanned intensities above the linear fitted background) are 96 ± 15 counts/10 mins at 2 K and 105 ± 14 counts/10 mins at 30 K. At $\hbar\omega = 3.5$ meV, they are 61 ± 12 counts/10 mins at 2 K and 61 ± 12 counts/10 mins at 30 K. Fourier transforms of the Gaussian peaks in Figs. 5.2a-c give the dynamic spin correlation lengths of $\xi \approx 96 \pm 15$, 80 ± 10 , and 94 ± 24 Å for $\hbar\omega = 0.5$, 1.5, and 3.5 meV, respectively. With increasing temperature, the scattering above background is virtually unchanged from 2 K to 30 K but decreases slightly at 55 K due to increased background (Figs. 5.2a-c). The temperature dependence of the scattering at $\hbar\omega = 1.5$ meV shows no observable anomaly across T_c (Fig. 5.2d), thus suggesting that the magnetic excitations are gapless and different from that of NCCO [66]. The energy scans at $\mathbf{Q} = (0.5, 0.5, 0)$ confirm that the magnetic scattering between 0.5 meV and 4.5 meV is virtually temperature independent between 2 K and 30 K (Fig. 5.2e), and therefore does not follow the population factor $1/(1 - e^{-\hbar\omega/k_B T})$ expected for simple bosonic excitations.

This survey of the T -dependence of the low-energy magnetic excitations shows that there is no observable coupling to the superconducting phase within the energy window $0.5 \leq \hbar\omega \leq 4.0$ meV. Instead, the low- E spin excitations are seemingly T -independent over a surprisingly large temperature range relative to the energy of the excitation. For instance, the T -independent response at $\hbar\omega=0.5$ meV from 2K to 30K shows magnetic excitations unaffected by a temperature energy scale five times larger

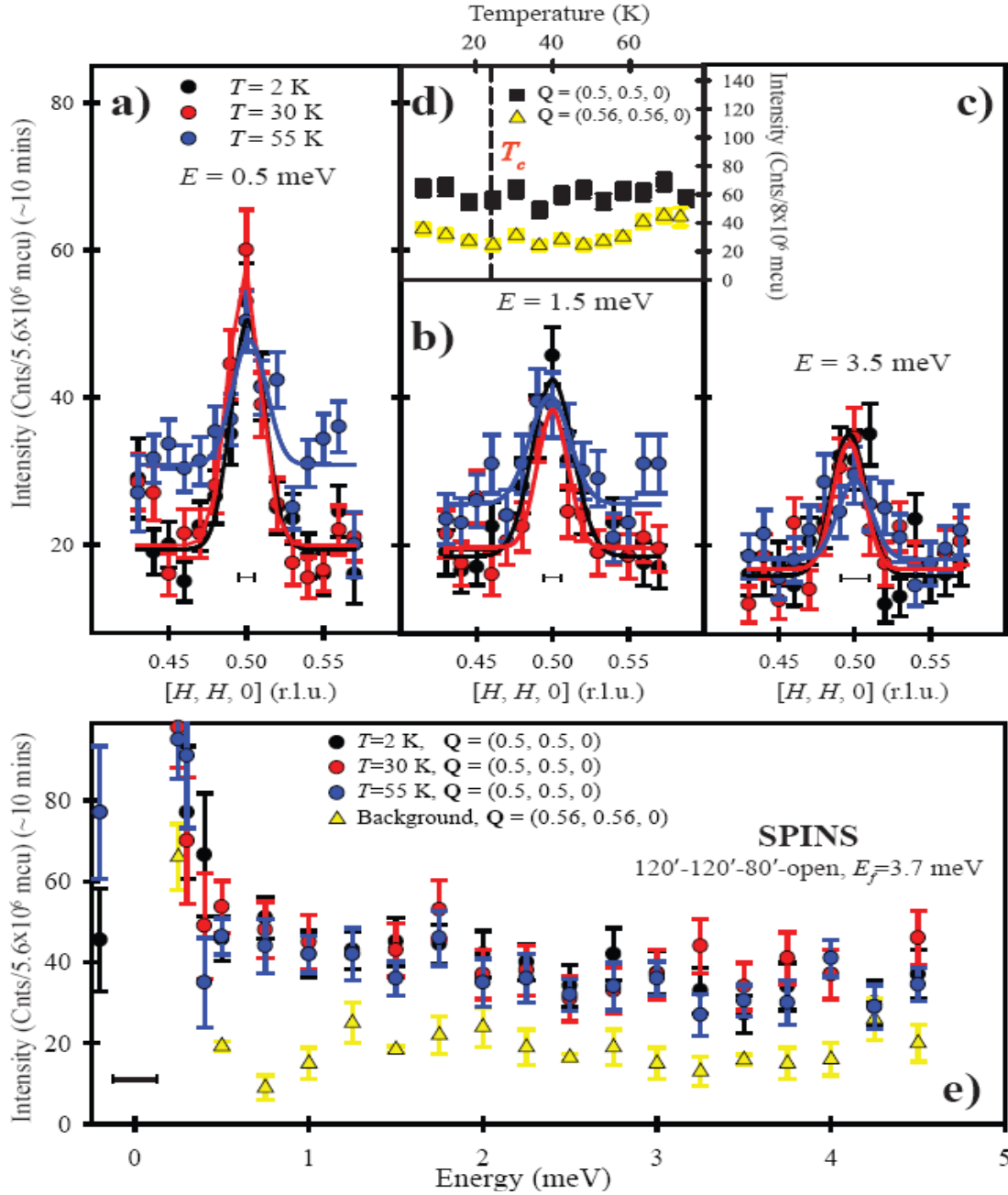


Fig. 5.2 The wavevector, energy, and temperature dependence of the magnetic scattering around $Q = (0.5, 0.5, 0)$ for $0.5 \leq \hbar\omega \leq 4.5$ meV. a-c), Q -scans along the $[H, H, 0]$ direction for $\hbar\omega = 0.5, 1.5$, and 3.5 meV at $T = 2, 30$, and 55 K. Center brackets are instrumental resolutions. d) Temperature dependent scattering at $Q = (0.5, 0.5, 0)$ and $(0.56, 0.56, 0)$ for $\hbar\omega = 1.5$ meV. The background is independent of temperature below ~ 50 K and the magnetic signal becomes much weaker at 80 K. e) Constant- Q scans at the ridge of magnetic scattering at 2 K, 30 K, and 55 K, compared with the temperature-independent background scattering for $2 \leq T \leq 30$ K.

than the scale of the excitation itself. This most likely arises from the proximity of a QCP in the phase diagram as discussed in section 3.11 and will not be discussed further in this chapter.

5.4 Resonance mode at $E_R = 11$ meV

To study the magnetic excitations for energies above 4.5 meV, we used the HB-1 and BT-9 thermal neutron triple-axis spectrometers. Figures 5.3a-c show $\mathbf{Q}$ -scans through (0.5, 0.5, 0) for $\hbar\omega = 3.5, 8.0$, and 10 meV at $T = 2, 30$, and 80 K. In contrast to the temperature independent low-energy ($\hbar\omega \leq 4.5$ meV) magnetic excitations below T_c (Fig. 5.2), the integrated intensity above background around (0.5, 0.5, 0) at $\hbar\omega = 8$ and 10 meV shows a significant enhancement on cooling from 30 K to 2 K, but hardly changes on warming from 30 K to 80 K (Fig. 5.3a-c). For $\hbar\omega = 10$ meV, Gaussian fits on sloped linear backgrounds give reasonable fits to the data with amplitudes $A = 122 \pm 4$ counts/10 mins, width $W = 0.023 \pm 0.001$ r.l.u., background $Bckg = 218 \pm 9$ counts/10 mins at 2 K; $A = 84 \pm 9$ counts/10 mins, $W = 0.024 \pm 0.004$ r.l.u., $Bckg = 212 \pm 7$ counts/10 mins at 30 K; and $A = 87 \pm 9$ counts/10 mins, $W = 0.023 \pm 0.004$ r.l.u., $Bckg = 200 \pm 7$ counts/10 mins at 80 K. The $\mathbf{Q}$ -width of the peak at $\hbar\omega = 10$ meV is temperature independent and resolution-limited, giving a minimum $\xi \approx 45 \pm 5$ Å (Fig. 5.3c). Similar scans using better collimations on BT-9 (Fig. 5.4e) are again resolution-limited, giving $\xi \approx 51 \pm 7$ Å. These scans were fit by Gaussian line shapes with $A = 25.4 \pm 3.4$ counts/10 mins, $W = 0.022 \pm 0.004$ r.l.u., $Bckg = 80 \pm 3$ counts/10 mins at 2 K and $A = 15.2 \pm 2.7$ counts/10 mins, $W = 0.023 \pm 0.005$ r.l.u., $Bckg = 78 \pm 2$ counts/10 mins at 30 K.

The enhancement observed upon cooling into the superconducting phase at $\hbar\omega = 10$ meV and 8 meV is suggestive of magnetic fluctuations coupled to the superconducting phase in these energy channels. To investigate this further, constant $\mathbf{Q}$ -scans centered at the $\mathbf{Q} = (0.5, 0.5, 0)$ position were performed at a variety of temperatures. Figure 5.3d shows the results of these energy scans at the peak center [$\mathbf{Q} = (1/2, 1/2, 0)$] and overlaid with the background [$\mathbf{Q} = (0.5875, 0.5875, 0)$] positions for temperatures $T = 2, 30$, and 80 K. The weak, dispersion-less peak at $\hbar\omega = 6$ meV and the sharp increase in background scattering with increasing energy transfer are due to the Pr^{3+} crystalline electric-field (CEF) excitations (centered around $\hbar\omega \sim 18$ meV) in the tetragonal unit cell of PLCCO [70]. The intensity of these CEF features is temperature independent between 2 K and 30 K within the statistics of our measurements and thus can be regarded as background scattering. Therefore, this CEF scattering intensity simply renders a shift in the background scattering on which the sharply localized magnetic excitations at $\mathbf{Q} = (0.5, 0.5, 0)$ rest (see section 5.5). The temperature difference spectrum (2 K - 30 K) shows a clear intensity gain around ~ 11 meV at $\mathbf{Q} = (0.5, 0.5, 0)$ (Fig. 5.3e). This appears to indicate the presence of a collective mode at a localized energy ($\hbar\omega = 11$ meV) appearing upon entering the superconducting phase and reminiscent of the known properties of the resonance mode in hole-doped cuprates. Unfortunately, due to kinematic constraints of the scattering geometry chosen for this HB-1 experiment and due to increased background levels at small scattering angles, energies above 13 meV could not be measured. Initial attempts were made to measure the scattering signal in the

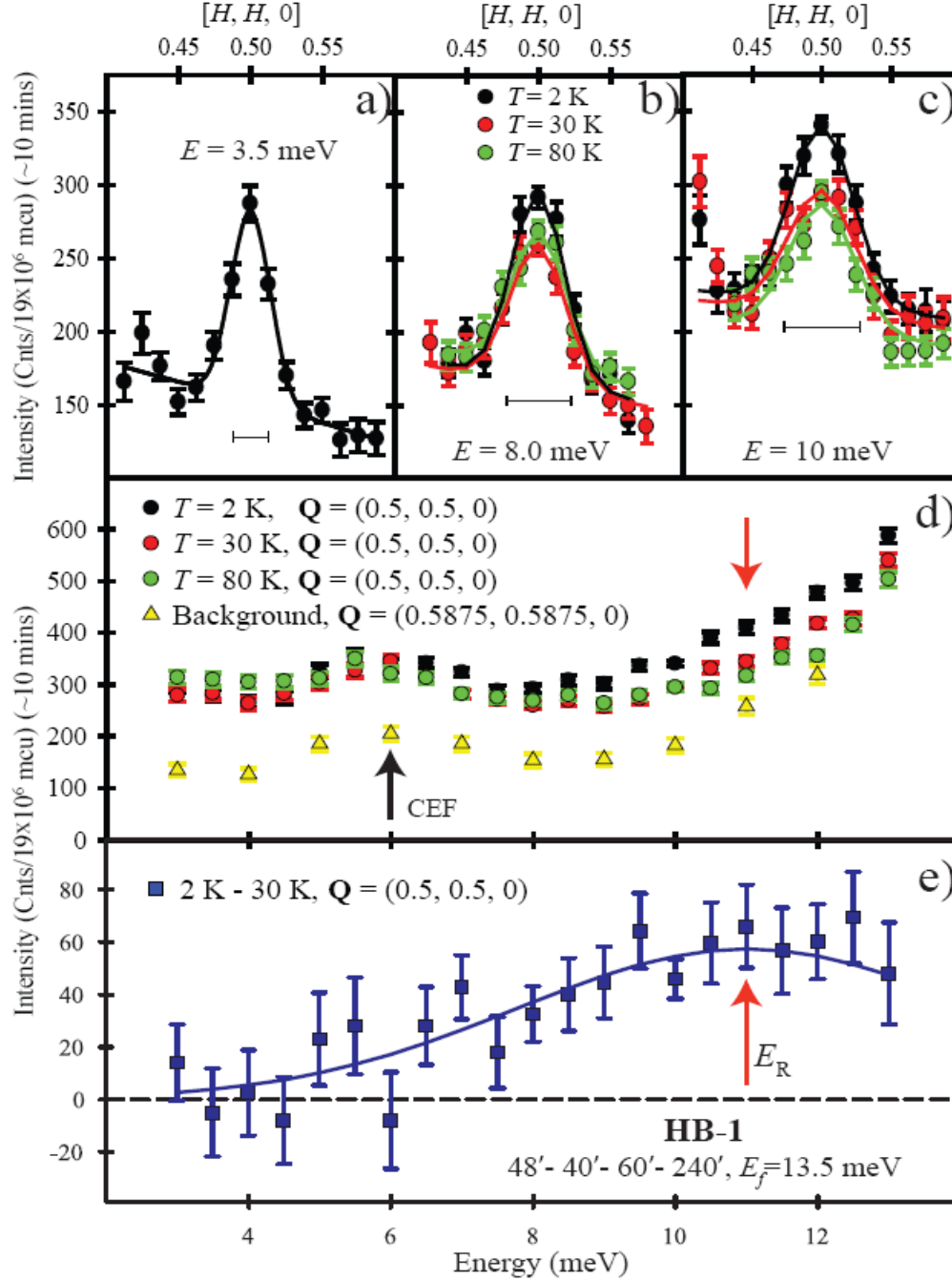


Fig. 5.3 HB-1 wavevector and energy dependence of the scattering around $\mathbf{Q} = (0.5, 0.5, 0)$ below and above T_c . a-c) $\mathbf{Q}$ -scans along the $[H, H, 0]$ direction for $\hbar\omega = 3.5, 8$, and 10 meV at $T = 2, 30$, and 80 K. The gradual rise in the background scattering with increasing energy (and decreasing scattering angle) is due to the tail of the strong Pr^{3+} crystalline electric field (CEF) excitation at 18 meV and the low-angle background scattering. d) Energy scans at $\mathbf{Q} = (1/2, 1/2, 0)$ where the magnetic scattering peaks and background scattering at $\mathbf{Q} = (0.587, 0.587, 0)$. e) Temperature difference spectrum between 2 K and 30 K suggests a resonance-like enhancement at ~ 11 meV.

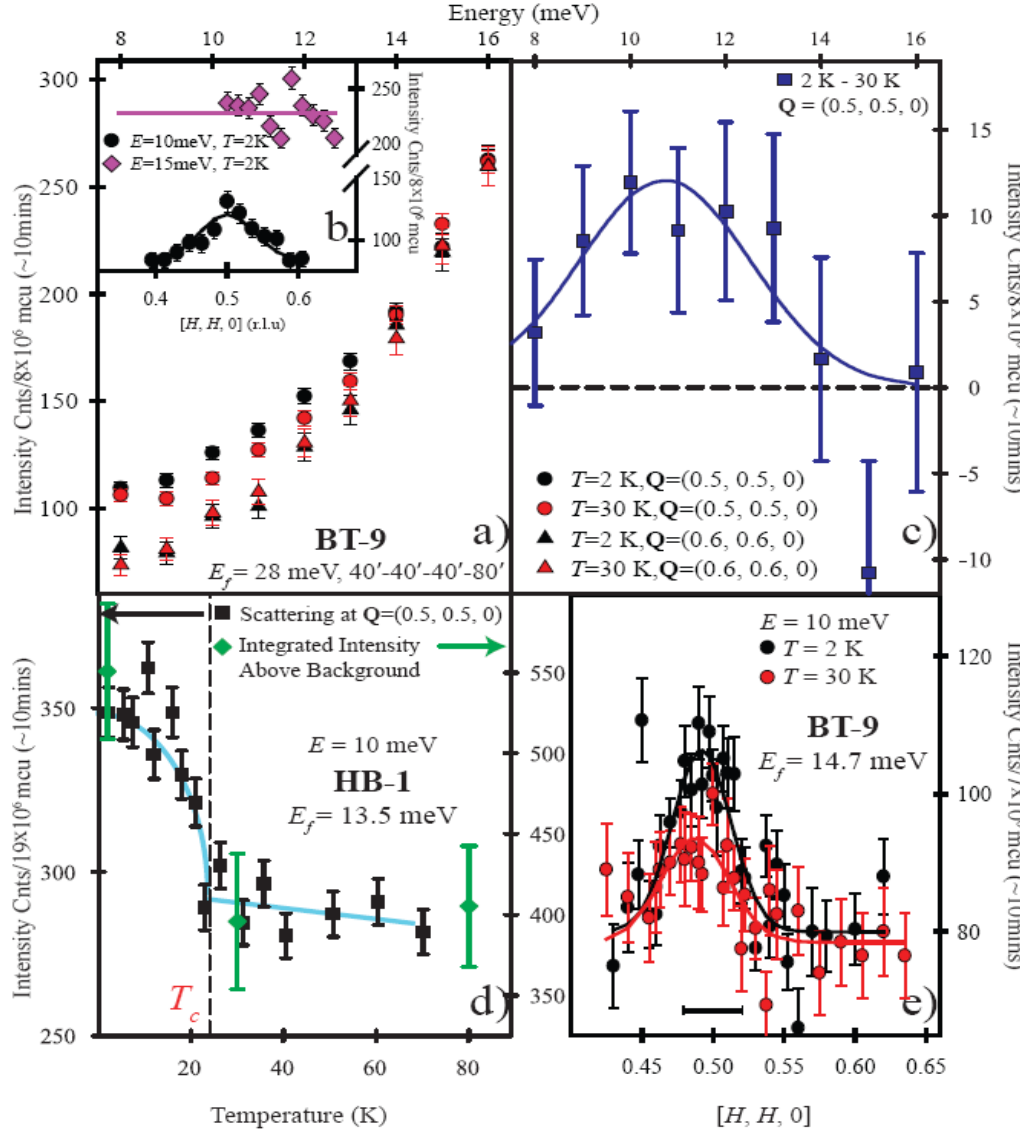


Fig. 5.4 BT-9 wavevector, energy, and HB-1 temperature dependence of the scattering around $Q = (0.5, 0.5, 0)$. a) Energy scans along the ridge of magnetic scattering at $(0.5, 0.5, 0)$ were counted for ~2 hours/point to obtain the statistics shown. The background scattering at $(0.6, 0.6, 0)$ was counted ~30 minutes/point and showed no observable difference between 2 K and 30 K. b) Wavevector scans along the $[H, H, 0]$ direction around $(0.5, 0.5, 0)$ at $\hbar\omega = 10$ and 15 meV. c) Temperature difference (2 K - 30 K) spectrum at $Q = (0.5, 0.5, 0)$ shows the resolution-limited resonance at $\hbar\omega = 11$ meV. The calculated energy resolution of the spectrometer is ~3.7 meV in FWHM at $\hbar\omega = 10$ meV. d) Black squares show temperature dependence of the neutron intensity (~1 hour/point) at $(0.5, 0.5, 0)$ and 10 meV obtained on HB-1. Green diamonds are integrated intensity of the localized signal centered around $Q = (1/2, 1/2, 0)$ above backgrounds in Fig. 5.3c. The line is a guide to the eye. e) Q -scans at $\hbar\omega = 10$ meV obtained on BT-9 with $E_f = 14.7$ meV and collimations $40'-40'-40'-80'$.

neighboring zone at $\mathbf{Q}=(0.5, 1.5, 0)$ that would afford a larger energy window and reduced scattering angle constraints; however, the magnetic signal in this higher- $\mathbf{Q}$ magnetic zone was substantially reduced and (given the already weak nature of the magnetic signal) precluded further measurement. Our solution was to simply increase the final energy of the measured neutrons in order to access slightly higher energy transfers while remaining in the first scattering zone. This choice allowed us to retain the stronger scattering signal in the lowest magnetic scattering zone centered at $\mathbf{Q} = (0.5, 0.5, 0)$ at the expense of worsened energy/momentum resolution.

Now changing to a higher fixed final energy of $E_f=28$ meV in order to access a broader range of energies, E -scans on the BT-9 spectrometer were performed both below and above the superconducting transition temperature. Figure 5.4a shows the energy dependence of the scattering at $\mathbf{Q} = (0.5, 0.5, 0)$ and background $(0.6, 0.6, 0)$ positions from these BT-9 scans. The scattering at $(0.5, 0.5, 0)$ around ~ 11 meV is systematically higher below T_c while the background intensity at $(0.6, 0.6, 0)$ is temperature independent between 2 K and 30 K. Through plotting the temperature difference spectrum below and above T_c (2 K - 30 K), Fig. 5.4c shows a clear resolution-limited resonance peak centered at $\hbar\omega \approx 11$ meV, consistent with Fig. 5.3e. A constant energy scan at $\hbar\omega = 10$ meV confirms that the peak is centered at $(0.5, 0.5, 0)$ (Fig. 5.4b) while a similar scan at $\hbar\omega = 15$ meV shows only background scattering (Fig. 5.4b). Only half of the $\mathbf{Q}$ -scan at $\hbar\omega=15$ meV could be completed due to the kinematic constraints of the neutron scattering triangle, but the partial scan shows no indication of a peak structure centered at the scan center, $\mathbf{Q}=(0.5, 0.5, 0)$. Finally and most importantly, in Fig. 5.4d we plot the temperature dependence of the scattering at $\mathbf{Q}=(0.5, 0.5, 0)$ and the integrated intensity of $\mathbf{Q}$ -scans through $(0.5, 0.5, 0)$ above the background for the energy channel $\hbar\omega = 10$ meV (collected on the HB-1 spectrometer). Since from Fig. 5.3c the background and the width of the 10 meV magnetic peak do not change appreciably upon cooling from 80K to 2K, measuring the peak value of the 10meV spin scattering presents a verifiable means of discerning the detailed temperature dependence of the scattering intensity in this channel. Turning again to Fig. 5.4d, the peak intensity at $\hbar\omega = 10$ meV and the integrated intensity above background both increase dramatically below the onset of T_c and are remarkably similar to that of the optimally doped YBCO [49, 113] and Bi(2212) [50]. This kink in the spectral weight upon cooling into the superconducting phase of a collective magnetic mode localized in energy (in our case at $\hbar\omega=11$ meV) is the hallmark of the resonance excitation in the hole-doped cuprates. Taken together, the data in Figs. 5.3 and 5.4 represent the observation of a resonance mode paralleling those observed in hole-doped cuprates and present the resonance as a unifying feature in the spin spectrum between n - and p -type cuprates.

5.5 Crystal electric field levels and their influence on background scattering

One of the unique features of the electron-doped high- T_c superconductors is that they all contain rare-earth lanthanides Nd, Pr, Ce, or Sm. For Pr ions in the tetragonal $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ crystal structure, the crystalline electric field (CEF) potential decomposes from the $J = 4$ ground-state multiplet into a nonmagnetic singlet ground state (Γ_4), a split broadened excited state around 18 meV, and various other excited states at

higher energies [70, 122]. Since these CEF excitations are in general a single ion effect, one does not expect the CEF levels in our superconducting $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_4$ (PLCCO) to be much different from that in $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ [70, 122]. We have confirmed the presence of the 18 meV CEF level (Fig. 5.5c), and our measurements have also revealed a weak CEF level at $\hbar\omega = 6$ meV previously not reported. The fact that this 6 meV excitation lies close to the known CEF excitation at 18 meV requires that care be taken when analyzing the data in the 12 meV region between these two levels. Since excitations between CEF levels is theoretically possible depending on the detailed level scheme, the possibility of an intramultiplet excitation from the 6 meV level to the 18 meV level with an excitation energy of 12 meV should be considered when analyzing the data for the resonance mode in PLCCO (with an energy centered at $E_R = 11$ meV). In the following, I will provide detailed arguments of why the resonance excitation at $E_R = 11$ meV does not arise from any CEF excitation and how the CEF level scheme can be regarded merely as a background for our experiments.

In the small momentum limit, the neutron scattering cross section for N noninteracting ions is [122, 123]:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \propto N f^2(\mathbf{Q}) \frac{k_f}{k_i} \sum_{n,m} \rho_m |\langle n | J_z | m \rangle|^2 \delta\left(\frac{E_n - E_m}{\hbar} - \omega\right) \quad (5-1)$$

where $|\langle n | J_z | m \rangle|^2$ is the transition probability between n and m states, $f(\mathbf{Q})$ is the magnetic form factor, and k_i and k_f are incident and outgoing neutron wavevectors, respectively; $\rho_m = Z^{-1} \exp(-E_m / k_B T)$, where E_m is the m -th energy level and $Z = \sum_m (e^{-E_m / k_B T})$ is the sum over all the states; $e^{-E_m / k_B T}$ describes the occupation of the m -th level at a temperature T . Using this cross section formula, several general cases can be examined where the calculated scattering from CEF excitations in this PLCCO system can be compared to the known properties of the previously reported resonance mode at 11 meV.

For our calculations we will assume two possible CEF models both plotted in Fig. 5.5a. In both CEF models the energy levels at $\hbar\omega = 0, 6, 16, 18, 19$ meV correspond to $m = 1, 2, 3, 4, 5$, respectively. Since the complete CEF level scheme for PLCCO is unknown, we used the experimentally measured CEF intensity at 6 meV (Fig. 5.3) and 18 meV (Fig. 5.5c) and assumed the transition probabilities $|\langle 1 | J_z | 1 \rangle|^2 = 0$, $|\langle 1 | J_z | 2 \rangle|^2 = 2$, $|\langle 1 | J_z | 3 \rangle|^2 = 17.64$, $|\langle 1 | J_z | 4 \rangle|^2 = 32.53$, and $|\langle 1 | J_z | 5 \rangle|^2 = 43.2$. This constitutes the assumed transitions for CEF model 1, and, ignoring higher energy levels, the black and red solid lines show the expected temperature dependence of this CEF scheme at 2 K and 30 K respectively. Now for CEF model 2, an additional transition probability was added with $|\langle 2 | J_z | 4 \rangle|^2 = 50$, and a localized mode should appear at 12 meV when temperature changes from 2 K to 30 K (blue dashed line).

Using the results from these rough CEF calculations, there are two primary arguments concerning why the observed localized mode at $\mathbf{Q} = (0.5, 0.5, 0)$ and $\hbar\omega = 11$

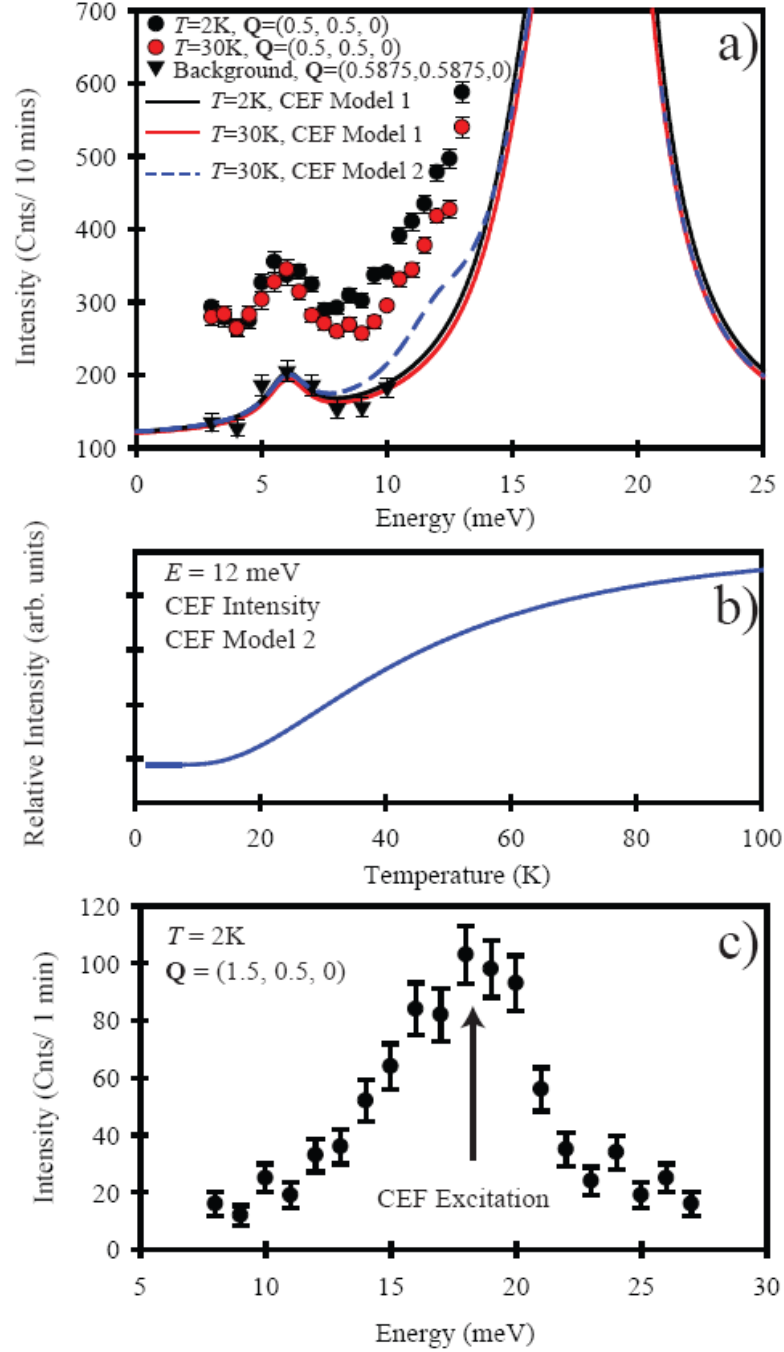


Fig. 5.5 CEF level schemes and excitations in PLCCO ($T_c=24\text{K}$). a) Signal $Q=(0.5, 0.5, 0)$ and background $Q=(0.5875, 0.5875, 0)$ intensities overlaid with CEF model calculations. CEF transition probabilities in both models were normalized to the observed scattering from CEF excitations at $\hbar\omega = 6$ and 18 meV . b) Calculated T -dependence of the 12 meV channel utilizing the CEF model 2 transition parameters described in the text. The increase in intensity at 12 meV with increasing T contrasts the observed behavior of the resonance mode (which appears only at low- T). c) Raw data collected on HB-1 showing the 18 meV CEF excitation.

meV cannot be due to the temperature dependence of the CEF levels in PLCCO. The first of these is, that in order to make a localized mode in energy around 11 meV, one must thermally populate the 6 meV CEF level and assume a huge transition probability from 6 meV to 18 meV (shown as CEF model 2 in Fig 5.5a). Although this is theoretically possible, the 12 meV localized mode should only appear when the temperature is increased from 2 K to 30 K in order to populate the 6 meV CEF level (Fig. 5.5b). Instead experimentally, we observed the 11 meV resonance mode when the temperature is cooled from 30 K to 2 K. Therefore, the 11 meV localized mode in Fig. 5.4c that we observe cannot be due to a transition from the 6 meV CEF level to the 18 meV CEF level.

The second major argument stems from the intrinsic properties of CEF excitations. Since the CEF levels are a single ion excitations, they are in general dispersion-less (or weakly $\mathbf{Q}$ -dependent) to a good approximation. Therefore, the temperature dependence of a CEF level cannot peak only at $\mathbf{Q} = (0.5, 0.5, 0)$. Indeed, our data in Fig. 5.3d show that the CEF levels exhibit no significant variation in intensity with $\mathbf{Q}$, and are therefore dispersion-less to a good approximation and correspond to an excitation that is localized on the Pr ion. Thus, changes in the CEF intensity simply render a shift in the background on which the sharply localized excitations at $(0.5, 0.5, 0)$ rest. Since our detailed $\mathbf{Q}$ -scans around the resonance position indicate that this background intensity does not change from 2 K to 30 K, the influence of the CEF levels changing intensity is negligible in this temperature range. Additionally, as we have done in Figure 5.4d, the background term (comprising both nonmagnetic and CEF contributions) has been explicitly removed and only the localized resonance signal remains. Hence, the observed integrated intensity gain in Fig. 5.4d on cooling from 30 K to 2 K cannot be due to the temperature dependence of the CEF levels.

In principle, the CEF levels at 6 and 18 meV should exhibit some slight T-dependence and both become more intense at 2 K compared to 30 K due to an increase in the ground state electron population. However, our realistic temperature dependent CEF calculations using experimentally determined transition probabilities at 6 and 18 meV reveal that such a decrease is within the statistics of our measurements (see CEF model 1 calculations in Fig. 5.5a), consistent with unchanged background scattering levels in constant energy scans at 10 meV (Figs. 5.3c, 5.4e) and constant- $\mathbf{Q}$ scans at $\mathbf{Q} = (0.6, 0.6, 0)$ (Fig. 5.4a). This small change relative to the enhancement observed at the resonance position further precludes its effect on our measurements.

5.6 Absolute unit calibration of resonance mode

It is of considerable interest to determine the absolute magnitude of the fluctuating moment involved with the resonance mode. The magnitude of the resonance mode in this PLCCO system can then be compared with other known resonance's observed in various classes of hole-doped cuprates. In order to determine this, we take advantage of the fact that upon cooling through T_c in zero field, the only change in the spectral weight of $S(\mathbf{Q}, \omega)$ in the spin fluctuations is the disappearance of the resonance mode. In order to put the resonance mode itself on an absolute scale, we measured a low energy, transverse acoustic phonon and used the known scattering function to determine

the spectrometer-dependent constants. We then removed this constant and measured the momentum and energy integrated cross section of the resonance mode to determine its magnitude in μ_B^2/Cu .

The differential cross-section for coherent one phonon emission is [29, 30]:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{k_f}{k_i} \frac{(2\pi)^3}{2v_0} \sum_{\tau, s} \frac{1}{\omega_s} \left| \sum_d \frac{\bar{b}_d}{\sqrt{M_d}} e^{-2W} e^{i\mathbf{\kappa} \cdot \mathbf{d}} (\mathbf{\kappa} \cdot \vec{\xi}_{ds}) \right|^2 (n(\omega) + 1) \partial(\omega - \omega_s) \partial(\mathbf{\kappa} - \mathbf{q} - \boldsymbol{\tau}) \quad (5-2)$$

This becomes for a phonon mode at a given $(\mathbf{\kappa}, \omega)$ simply:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = A \frac{\hbar^2 N}{2E(\mathbf{q})} \frac{k_f}{k_i} (n(\omega) + 1) (\mathbf{\kappa} \cdot \vec{\xi}_{qs})^2 e^{U^2} |F(\boldsymbol{\tau})|^2 \partial(E - E(\mathbf{q})) \quad (5-3)$$

Here $\mathbf{\kappa} = \boldsymbol{\tau} + \mathbf{q}$ is the momentum transfer of the neutron, N is the number of unit cells, k_f and k_i are the incident and final wavelengths of the neutron, $(n(\omega) + 1) = (1 - \exp(\hbar\omega/k_B T))^{-1}$, $\vec{\xi}_{qs}$ is the polarization vector of the phonon, e^{U^2} is again the Debye-Waller factor, A is a spectrometer dependent constant, and $E(\mathbf{q})$ is the energy of the phonon mode. $F(\boldsymbol{\tau})$ is the weighted nuclear structure factor for the nuclear zone center wavevector $\boldsymbol{\tau}$, where

$$|F(\boldsymbol{\tau})|^2 = \left| \sum_d \frac{\bar{b}_d}{\sqrt{M_d}} e^{i\boldsymbol{\tau} \cdot \mathbf{d}} \right|^2 \text{ summed over sites in the unit cell.}$$

Approximating this cross section in the long wavelength limit, it becomes [124]:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = A \frac{\hbar^2 N}{2E(\mathbf{q})} \frac{k_f}{k_i} (n(\omega) + 1) (\mathbf{\kappa} \cdot \hat{\mathbf{e}}_{qs})^2 e^{-2W} \frac{1}{M} |G(\boldsymbol{\tau})|^2 \partial(E - E(\mathbf{q})), \quad (5-4)$$

where M is the mass of the unit cell, $\hat{\mathbf{e}}_{qs}$ is now instead a unit vector in the direction of atomic displacement for the phonon mode, and $G(\boldsymbol{\tau})$ is the nuclear structure factor. This expression allows the spectrometer-dependent constant, A , to then be determined through the measurement of a known phonon in the material.

The cross section for paramagnetic spin fluctuations is [29]:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = A \frac{(\gamma r_o)^2}{4} \frac{k_f}{k_i} N |f(\mathbf{\kappa})|^2 e^{-2W} (n(\omega) + 1) \frac{2}{\pi \mu_B^2} \chi''(\mathbf{\kappa}, \omega), \quad (5-5)$$

where $f(\mathbf{\kappa})$ is the isotropic, magnetic form factor for Cu^{2+} . The local susceptibility

$$\chi''_{local}(\omega) = \frac{\int \chi''(Q, \omega) \partial^3 Q}{\int \partial^3 Q} \text{ can then be calculated about the } \mathbf{Q}_{\text{plane}} = (0.5, 0.5) \text{ in-plane}$$

wave vector via $\mathbf{Q}$ -scans performed at specific energies.

For our experiment, we measured a transverse acoustic phonon at $\mathbf{Q} = (0.12, 2, 0)$ and determined A using the long-wavelength limit relation stated above. The raw data for the phonon intensity (collected on the IN-8 spectrometer) is shown in Fig. 5.6, and the phonon peak was well fit by a Gaussian lineshape on a linear background. The scan was performed on the focusing side for the neutron resolution ellipsoid relative to the phonon dispersion as shown in the schematic insert in Fig. 5.6.

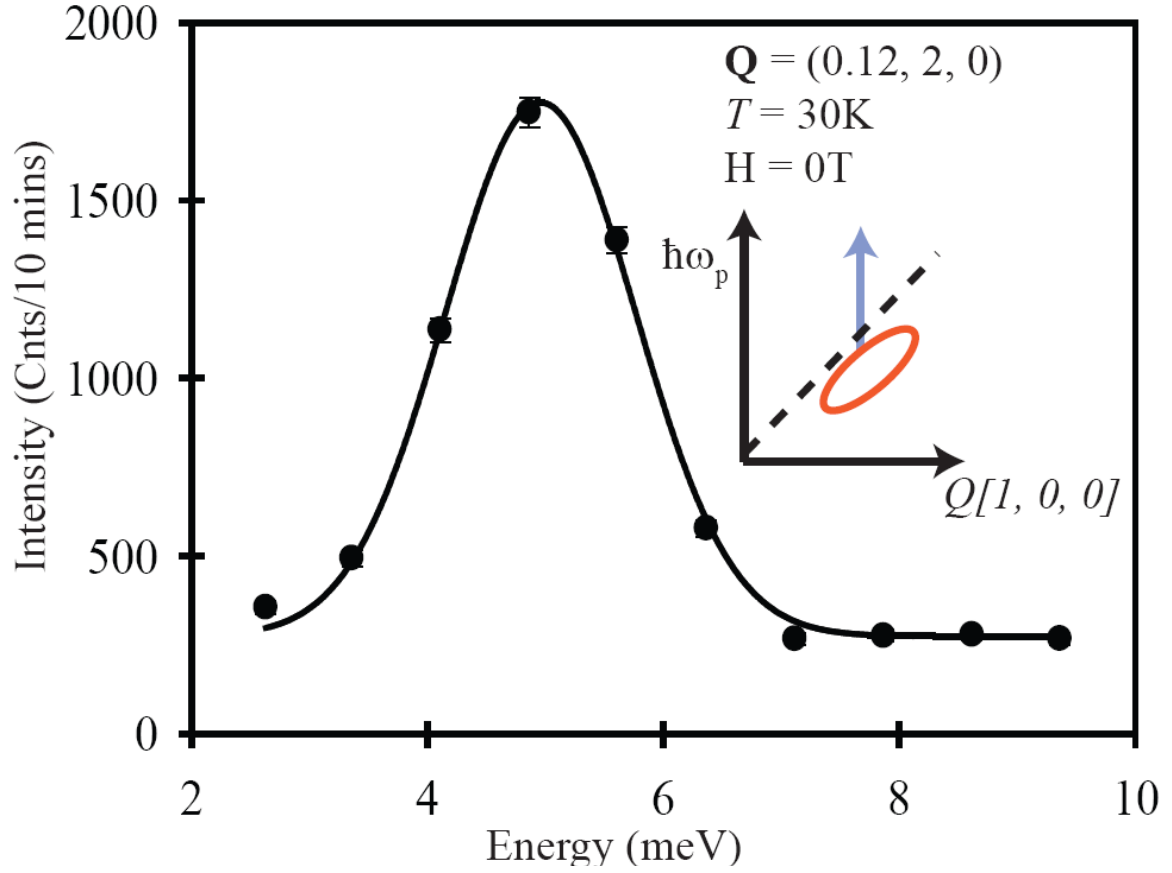


Fig. 5.6 Transverse acoustic phonon measured at $\mathbf{Q}=(0.12, 2, 0)$ and $T=30\text{K}$. Raw data collected on the IN-8 spectrometer with $E_f=14.7$ meV and 60'-40'-60'-open collimation (experimental details in section 6.2). The phonon peak was fit to a Gaussian on a linear background. The inset shows the scan direction in energy with the neutron resolution ellipsoid orientated in the focusing direction relative to the low- $\mathbf{Q}$ phonon dispersion relation.

Before calculating the integrated susceptibility for the magnetic excitations, the nonmagnetic background was removed through subtracting the measured nonmagnetic signal away from the correlated (0.5, 0.5) position as shown in Ref. [67]. All data was corrected for $\lambda/2$ contamination in the monitor, and in our calculations for data at both 2 K and 30 K, the Debye-Waller factor was assumed to be one. In correcting for the $\lambda/2$ contamination in the monitor counts, the actual measured and fit spectrum for the HB-1 spectrometer was used, whereas the calculated spectrum using the known moderator temperature was used in corrections for the other spectrometers whose data was utilized (SPINS, IN8, and BT-9). This calculated correction is simply a multiplicative factor

[124]: $C = \sum_{n=1}^{\infty} n^2 e^{-\frac{(n^2-1)E_i}{k_B T}}$, where $k_B T$ is the moderator temperature for the neutron source (typically ~ 25 meV for thermal neutrons), E_i is the incident energy, and n is the order of the monochromator reflection.

Following the subtraction of nonmagnetic background and correction for higher order contamination in the monitor, we first calculated the momentum integrated susceptibility at $\hbar\omega = 10$ meV in absolute units. This was done initially for the 10 meV spin excitation peak measured on the IN-8 spectrometer (see section 6.2 for experimental details on how this data was obtained) which was the same spectrometer and experimental conditions on which the transverse phonon in Fig. 5.6 was measured. In order to obtain a fuller picture of the dynamic susceptibility, we then cross-normalized the resulting absolute units value for $\chi''_{\text{local}}(10 \text{ meV})$ from data collected on the IN-8 spectrometer to the data collected in section 5.4 on HB-1 and reported in Ref. [67]. The data collected on the IN-8 spectrometer was obtained within a magnet sample environment that decreases the overall neutron flux and increases the nonmagnetic background levels. Since data from the HB-1 experiments in section 5.4 was not collected in a magnet, the increased signal intensities and relative intensity changes are easier to gauge along with the structure of $\chi''(\mathbf{Q}, \omega)$. For energies below 5 meV and above 10 meV, SPINS data and BT-9 data were respectively cross-normalized again using the momentum integrated susceptibility to the now absolute values of the HB-1 data using constant scale factors.

Looking first at energies below 5 meV, the measured $\mathbf{Q}$ -widths along $[H, H]$ were broader than the spectrometer resolution (Fig. 5.2), whereas scans at all higher energy transfers showed resolution limited widths (along $[H, H]$ in Figs. 5.3 and 5.4). In estimating the local susceptibility, the magnetic signal was assumed to be a two-dimensional Gaussian within the $[H, K]$ plane and rod-like out of the plane. This neglects the rotation of the resolution ellipsoid at energy transfers away from the resonance position and results in a slight underestimation of the integrated magnetic scattering at energies below the resonance. This estimation however is systematic and does not influence relative changes as a function of temperature in the local susceptibility as the system enters the superconducting phase. For points in E -scans with $\hbar\omega > 5$ meV in which no $\mathbf{Q}$ -scan data was available, the calculated resolution value used was projected along the $[H, H]$ direction.

The local susceptibility $\chi''_{\text{local}}(\omega)$ can now be plotted for the spin fluctuations observed from $\hbar\omega = 0.5$ to 16 meV both below (2K) and above (30K) T_c . This is shown

in Fig. 5.7 where there is a peak in the local susceptibility at the resonance energy. The cross-normalized data from BT-9, SPINS, and HB-1 are plotted at various energies, and data for which a full $\mathbf{Q}$ -scan was collected are plotted with open symbols (open circles for HB-1 and open triangles for SPINS data). Upon cooling into the superconducting phase, the primary change in the spectrum of excitations is a decrease in the local susceptibility at the energy of the resonance mode (11 meV). Taking this picture of the local susceptibility, the total fluctuating moment of the resonance can now be inferred.

In taking the difference between the local susceptibility determined at both 2K and 30K from 5 to 16 meV and integrating along energy, the resonance mode's total spectral weight can be determined. Performing this integration yields the value of $\langle m^2 \rangle = .0035 \pm .0014 \mu_B^2$ with the large error bar resulting mainly from uncertainty in the energy width of the resonance mode. At lower energies ($\hbar\omega = 0.5 - 4$ meV), $S(\mathbf{Q}, \omega)$ is actually unaffected by increases in temperature for T much greater than T_c . This results in a smooth decrease in $\chi''(\mathbf{Q}, \omega)$ at these energies due to removal of the Bose population factor. The spin fluctuations in these channels, however, show no evidence of being coupled to T_c and instead have been speculated to result from a QCP in the phase diagram of this system. Therefore, we have ignored the change in $\chi''_{\text{local}}(\omega)$ associated with these energies in the difference spectra taken between 2k and 30K data and only integrated changes due to the resonance mode's disappearance and not the Bose population factor (by integrating only from $\hbar\omega = 5$ to 16 meV).

5.7 Discussion and conclusions

To summarize the neutron scattering results from Figs. 5.2-5.4, we plot the dispersion of the observed magnetic excitations in Fig. 5.8a and re-plot the resonance energy as a function of T_c in Fig. 5.8b with our PLCCO resonance data point added. Although the magnetic excitations are broader than the instrumental resolution for $\hbar\omega \leq 3.5$ meV and resolution-limited for $\hbar\omega \geq 4.5$ meV, they are commensurate and centered at $\mathbf{Q}=(0.5, 0.5, 0)$ at all measured energies. This differs from the hole-doped materials, where incommensurate spin fluctuations below the resonance merge into it [42, 96, 115, 116]. On the other hand, the resonance energy of 11 meV ($E_r \approx 5.3 k_B T_c$) for the PLCCO is remarkably close to the universal value of $E_r \approx 5.8 k_B T_c$ for all materials (Fig. 5.8b).

Our results reveal several important conclusions for the electron-hole symmetry of the magnetic excitations in high- T_c copper oxides. First and foremost, the discovery of the magnetic resonance in electron-doped PLCCO with $E_r \approx 5.3 k_B T_c$ suggests that the resonance is a common feature for high- T_c superconductors irrespective of electron- or hole-doping. Second, the observation of commensurate spin fluctuations below the resonance (Fig. 5.8d) implies that the intimate connection between incommensurate spin fluctuations and the resonance in hole-doped materials is not a universal feature. Third, the magnetic excitations ($0.5 \leq \hbar\omega \leq 16$ meV) in the electron-doped PLCCO system are gapless, decrease monotonically with increasing energy, and are virtually temperature independent between $2 \leq T \leq 30$ K except for the appearance of the resonance below T_c (Figs. 5.2-5.4). Although such behavior differs from optimally hole-doped YBCO [43, 49, 98, 99] and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [48], the temperature independent low-energy

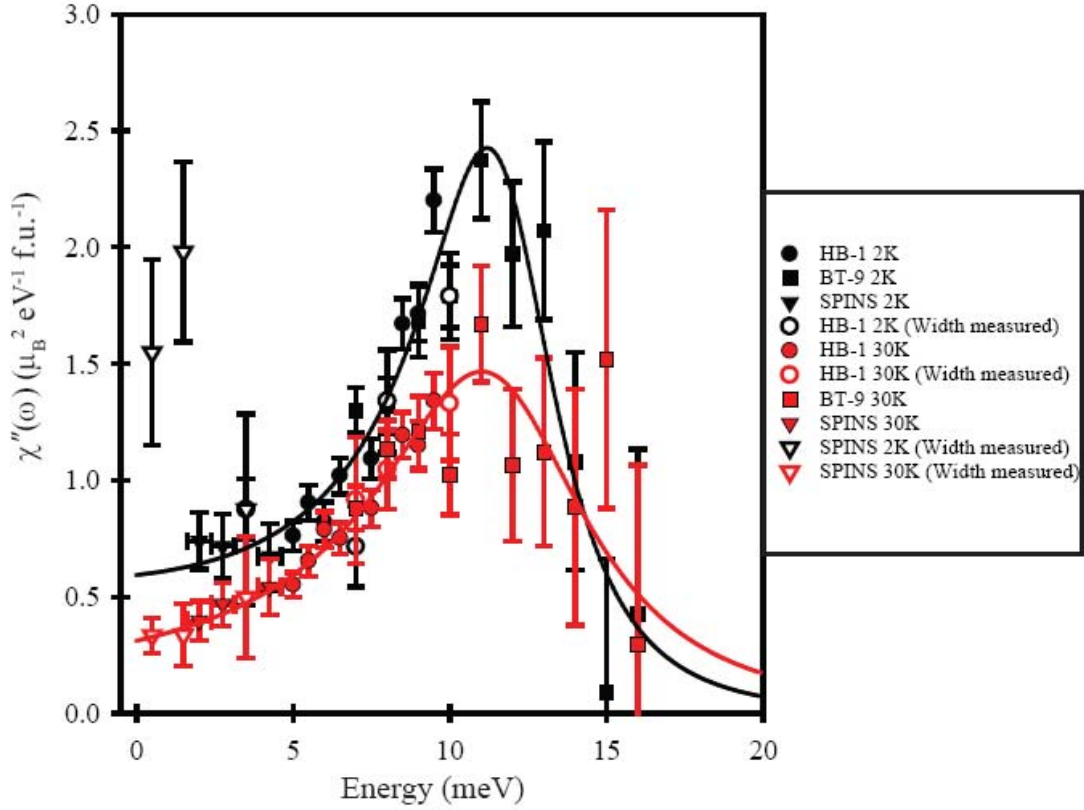


Fig. 5.7 Local susceptibility plot for PLCCO ($T_c=24\text{K}$) with resonance mode peak in absolute units. Magnetic signal was integrated over the first magnetic Brillouin zone. Black symbols show $T=2\text{K}$ data collected below T_c and red symbols collected for $T > T_c$ (30K). The momentum integration was carried out as described in the text and open symbols show energies where full $\mathbf{Q}$ -scans were performed along $[H, H]$. Solid symbols show energies at which the momentum integration was performed using the peak magnetic intensity values and the calculated momentum widths. Circles show data collected on HB-1, squares on BT-9, and triangles on the SPINS spectrometer.

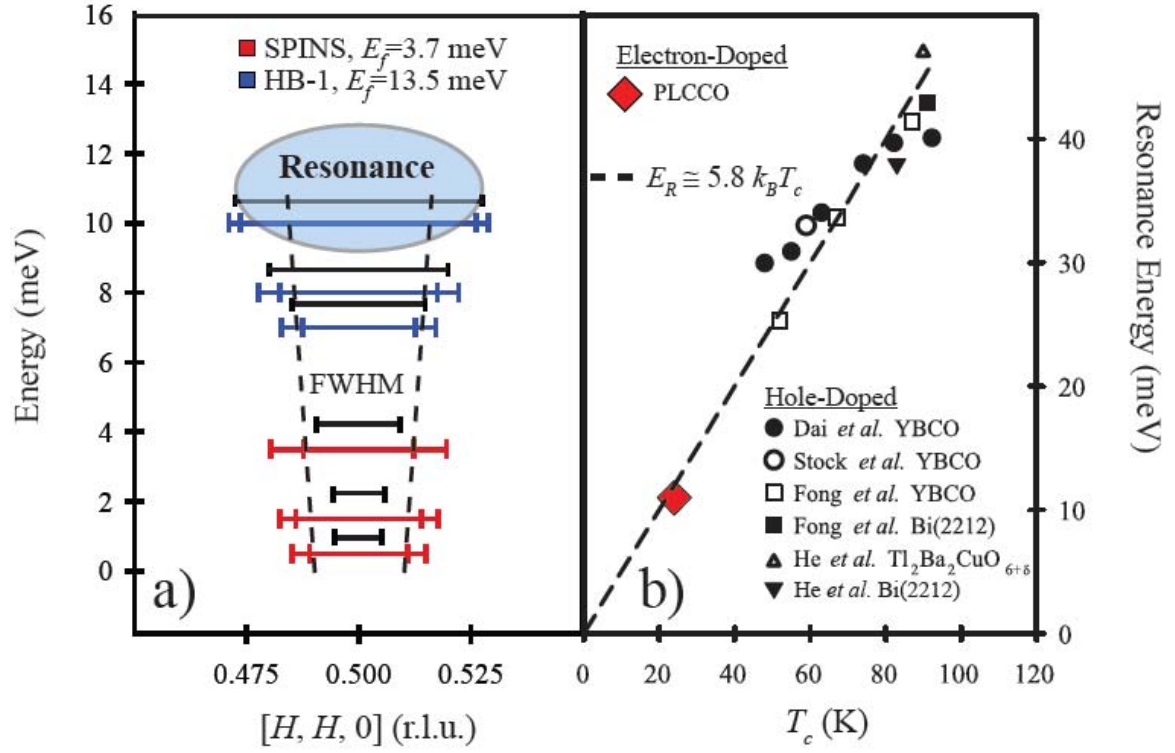


Fig. 5.8 Magnetic dispersion below the resonance and E_R vs. $k_B T_c$ for both hole- and electron-doped cuprates. a) The full-width at half maximum (FWHM) of the magnetic response at various energies with the instrumental resolution marked as black horizontal bars. Solid red lines are FWHM's measured on the SPINS spectrometer and solid blue lines are FWHM's measured on HB-1. The dashed lines are guides to the eye. b) Summary of the resonance energy as a function of T_c for hole-doped YBCO, Bi(2212), $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$, and electron-doped PLCCO. The dashed line is the best fit with $E_R = 5.8 k_B T_c$.

($0.5 \leq \hbar\omega \leq 4.5$ meV) magnetic scattering is remarkably similar to the quantum critical scattering in heavy Fermion $\text{UCu}_{5-x}\text{Pd}_x$ (see chapter 3.8) [85]. Finally, the discovery of the magnetic resonance in electron-doped PLCCO, where charged quasiparticles can also be probed by photoemission [125], allows a systematic comparison of their properties in the same bulk sample hitherto not possible for any other high- T_c superconductors. This should open new avenues of research to understand the exotic properties of high- T_c copper oxides.

Chapter 6: Field effect on the resonance mode and field induced magnetic order in PLCCO ($T_c=24K$)

6.1 Introduction and motivation

From its inception in 1986, research in the field of high temperature superconductivity (high- T_c) in the layered copper oxides has recognized the importance of magnetism in understanding the unconventional superconducting mechanism of these high- T_c cuprates. In conventional or BCS (Bardeen-Cooper-Schrieffer) superconductors, the superconducting phase forms when charge carriers are bound into pairs with long-range phase coherence via interactions mediated by lattice vibrations in the solid (phonons) [3]. An analogous pairing interaction driven instead by magnetic excitations (magnons) originating from a magnetically ordered spin system has been envisioned within this new class of high- T_c copper oxides [126, 127, 128, 129]; however, the precise role played by magnetism remains a topic of considerable debate. In order to resolve this debate, extensive neutron scattering experiments mapping out the detailed magnetism in a variety of cuprate classes have subsequently been conducted [37, 56, 65]. The most prominent feature observed within the magnetic spectrum of these high- T_c systems is a collective spin excitation centered in momentum space at the commensurate in-plane antiferromagnetic (AF) wavevector, ($\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$) known as the resonance mode. The mode itself is strongly coupled to the superconducting phase, appearing only below T_c in optimally doped cuprates, and its characteristic energy (E_R) has been shown to be directly proportional to the onset temperature of superconductivity [37, 67]. Following its discovery first in the bilayer cuprate $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ (YBCO) [49], this resonance excitation has since been observed universally in all classes of high- T_c cuprates (see Chapter 2.4 and Chapter 5.7) and stands as the lone unifying feature present in the spin spectra of the cuprates regardless of doped carrier type [67].

Despite the ubiquitous connection between the resonance mode and the superconducting phase within the cuprates, the influence of the resonance on the charge carriers themselves and quasiparticle excitations is a contentious issue [130, 131, 132, 133]. The primary cause of this controversy is that although inelastic neutron scattering experiments present the sole avenue of directly measuring the resonance mode, they also possess a fundamental inability to probe the electronic charge degrees of freedom. One way of resolving this issue is to study the behavior of the resonance mode as superconductivity (SC) is suppressed in a cuprate system via a tuning parameter, such as magnetic field, whose effect on quasiparticle and charge properties is well known. Previous experiments on the $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ system attempted such a study through observing the suppression of the resonance mode under the application of a c -axis aligned magnetic field [134]. Despite the fact that the upper critical field H_{c2} necessary for completely suppressing SC in the YBCO system was not experimentally reachable, it was known that the condensation energy of the system could be sizably reduced with relatively modest field strength, thus suggesting a possible connection between the superconducting condensation energy as measured by specific heat and the spectral weight of the resonance mode. However, the conclusions of this study, along with those

of all other neutron experiments claiming field-induced changes in magnetism in the hole-doped cuprates [135, 136, 137, 138], suffer from a large degree of uncertainty due to a primary inability to access the extremely high magnetic fields necessary to drive these systems in their true nonsuperconducting groundstates (where H_{c2} can be the order of 40-60T).

Motivated by this promising connection between the energy of the superconducting condensate and the magnitude of the resonance, we decided to study the field dependence of the magnetism in the electron-doped cuprate $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ (PLCCO $T_c=24\text{K}$) over a range of energies ($0 \leq \hbar\omega \leq 18$ meV) with particular focus given to the newly discovered resonance mode in this system [67], a system with a now experimentally reachable H_{c2} of 7T. This study presents, to the best of our knowledge, the first measurement of the evolution of the spin dynamics in a cuprate compound as it is driven into its field suppressed groundstate. Our results, which will be detailed in the sections that follow, find that under the application of a magnetic field, the relative magnitude of the resonance tracks the suppression of the condensation energy in PLCCO all the way to H_{c2} . Above the upper critical field, the resonance mode vanishes, and, as the mode is suppressed, static spin density wave (SDW) order appears at the commensurate wavevector $\mathbf{Q} = (0.5, 0.5, 0)$. The growth of this competing static SDW order as the SC phase is destroyed suggests a transfer of spectral weight from the resonance mode into the newly established SDW order in this PLCCO system.

6.2 Experimental Details

We used inelastic neutron scattering experiments to map out the evolution of the magnetic scattering function, $S(\mathbf{Q}, \omega)$, over a range of energies in the nearly optimally electron-doped cuprate $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$ with $T_c=24\text{K}$ ($a = b = 3.98$ Å, $c = 12.27$ Å; space group: $I4/mmm$) as the system is driven into its field-suppressed, nonsuperconducting groundstate. The fluctuation dissipation theorem then allows for the determination of the imaginary component of the dynamic susceptibility as a function of field through the relation $\chi''(\mathbf{Q}, \omega) \propto (n(\omega)+1)S(\mathbf{Q}, \omega)$, where $(n(\omega)+1) = (1-\exp(-\hbar\omega/k_B T))^{-1}$. Neutron experiments were performed at a variety of sources with measurements in the thermal neutron range performed on the IN-8 spectrometer at the Institute Laue Langevin and on the BT-9 spectrometer at the NIST Center for Neutron Research. Cold neutron data was collected on the V2 beamline at the Hahn Meitner Institute. For experiments on the IN-8 spectrometer, final neutron energies of $E_f=14.7$ and 35 meV were used along with collimation values of 60'-40'-60'-open. Experiments on V2 utilized a fixed $k_f=1.5$ Å⁻¹ and open-open-open-open collimation (with a horizontally focusing analyzer). For BT-9 data, final energies of $E_f=14.7$ and 28.0 meV were used with a collimation of 40'-48'-40'-80'. For these experiments (unless otherwise stated) we coaligned the same 3 PLCCO ($T_c = 24\text{K}$) samples from Ref. 67 and measured the magnetic scattering about the commensurate AF ordering wavevector $\mathbf{Q} = (0.5, 0.5, 0)$.

Here I will again denote positions in momentum space using $\mathbf{Q}$ [r. l. u.] = (H, K, L) notation in which $\mathbf{Q}$ [Å⁻¹] = ($H 2\pi/a, K 2\pi/b, L 2\pi/c$). For our experiments, the copper oxygen layers of the compound were aligned within the neutron spectrometers'

scattering plane, and the magnetic field was applied perpendicular to the copper oxygen sheets (Fig. 6.1a). Later experiments performed in section 6.6 mounted a separate PLCCO crystal in both the $[H, H, L]$ and $[H, K, 0]$ scattering planes in order to observe the anisotropy effect of the magnetic field on the static magnetic order. This case, however, will be described in detail in the text of Section 6.6.

6.3 Specific heat measurements

A small piece from one of the crystals used in the neutron experiments was later mounted in a Quantum Design PPMS system, and the entropy change upon entering the SC phase was measured. Measurements of the specific heat under various field strengths (Fig. 6.1c) then allowed the condensation energy of the superconducting phase to be determined (blue line in Fig. 6.1d) along with the upper critical field, H_{c2} , necessary for the complete suppression of the SC phase (again with $H \parallel c$). Turning to Fig. 6.1b the field subtracted C/T data ($H - 8T$) shows a clearly defined jump at the onset of the superconducting phase for low field strengths. For data with a field strength H applied greater than 8T, there was no observable increase in the value of C/T indicative of the second order superconducting phase transition at any temperature when higher strength field data was subtracted. This suggests that for this $T_c = 24K$ PLCCO system, H_{c2} was measured to be an easily accessible 7T and that data for $H \geq 7T$ represents the normal state electronic specific heat.

Now returning to Fig. 6.1 b, the field subtracted measurements of the specific heat now represent $\frac{C_{sc} - C_N}{T}$, versus temperature, T . This subtraction allows background contributions from the normal state, electronic specific heat to be removed, and the resulting entropy loss upon entering the superconducting phase,

$S_N(T) - S_{SC}(T) = \int_0^T \frac{C_{sc} - C_N}{T'} dT'$, can then be calculated. From this, the condensation

energy, U_c , can be determined for the superconducting phase under a given magnetic

field H through the relation $U_c(T) = \int_{T=2K}^{T_c+15K} (S_N(T') - S_{SC}(T')) dT'$ and plotted as a function

of temperature for various field strengths (Fig. 6.1c). The condensation energy at an accessible temperature for neutron experiments ($T=5K$) is plotted in Fig. 6.1d as a function of field strength. This measurement of the superconducting condensation energy now provides the basis from which to compare the quasiparticle/charge properties with the observed spin dynamics in this PLCCO system as it is driven into its field-suppressed nonsuperconducting groundstate.

6.4 Field induced suppression of the resonance excitation

Since the resonance mode has been experimentally shown to be fundamentally linked to the superconducting phase, it is interesting to first investigate the behavior of the resonance excitation in this PLCCO system as a magnetic field completely suppresses

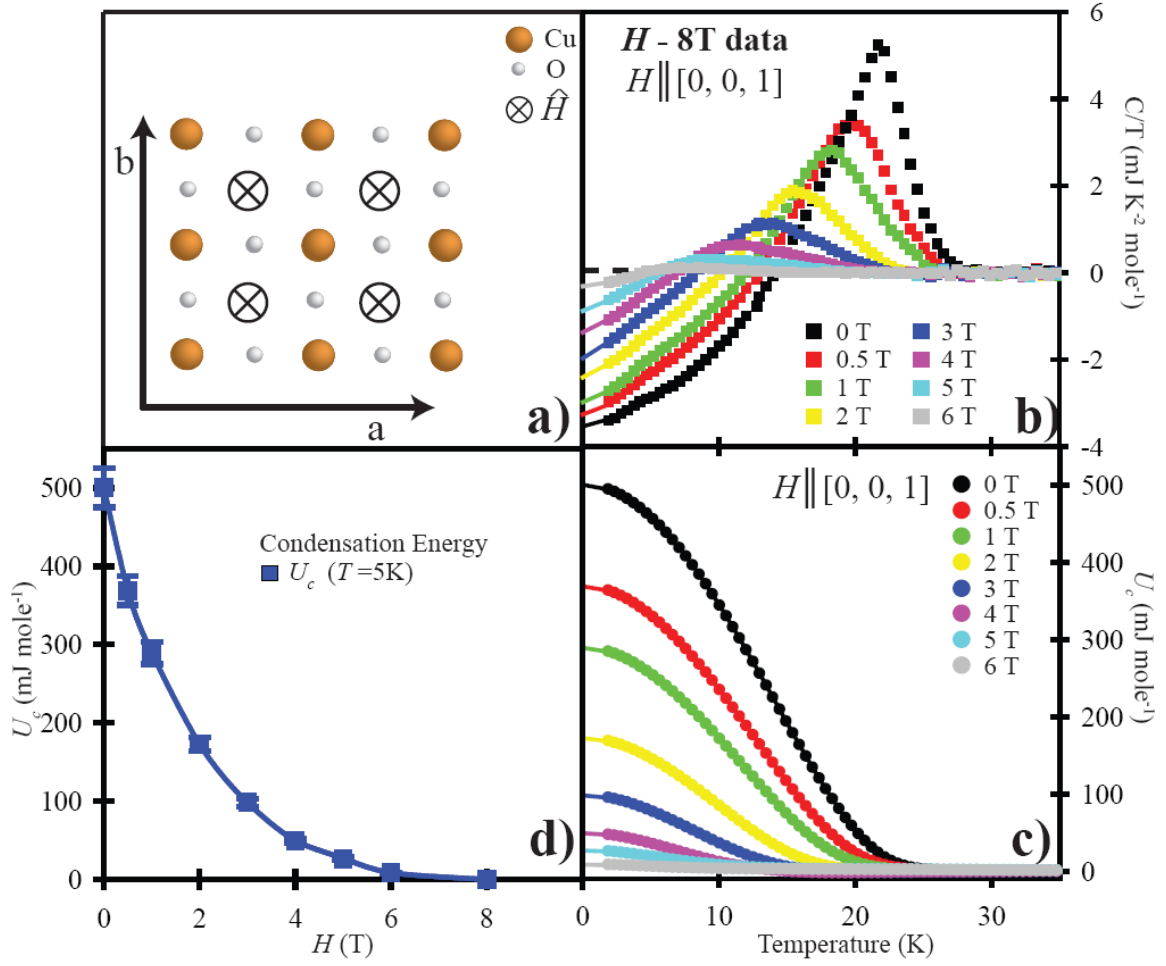


Fig. 6.1 Specific heat measurements and condensation energy for PLCCO ($T_c = 24\text{K}$). a) Schematic of the structure of the CuO_2 plane with the applied field direction orthogonal to it ($H \parallel c$). b) Superconducting state electronic specific heat (C/T) versus T with the normal state contribution subtracted (collected at $H = 8\text{T}$) for various field strengths. c) Temperature dependence of the condensation energy of the superconducting phase under various fields calculated as described in the text for magnetic field applied along the c-axis. d) Field dependence of the condensation energy at low- T ($T = 5\text{K}$).

T_c . Data collected on the IN-8 spectrometer are plotted in Fig. 6.2a, showing the resonance excitation in zero field (reproducing the effect reported in Fig. 5.3c). Momentum scans through the commensurate $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ position at the resonance energy ($E_R \approx 10$ meV) show the onset of the mode through a clear enhancement in $S(\mathbf{Q}, \omega)$ upon cooling into the superconducting phase. After applying a field greater than H_{c2} ($H=10$ T), these same $\mathbf{Q}$ -scans show that the resonance mode has now completely vanished (Fig. 6.2b). The data collected on BT-9, where a slightly lower field of $H = H_{c2}$ was applied to the sample and identical scans were performed, shows that the resonance excitation, while clearly visible in 0T (Fig. 6.2c), again completely disappears with the destruction of bulk SC in the system (Fig. 6.2d). These $\mathbf{Q}$ -scans clearly demonstrate that the resonance excitation is completely destroyed for $H \geq H_{c2}$.

Alternatively, the resonance mode's behavior can be resolved through measuring $S(\mathbf{Q}, \omega)$ at a fixed momentum transfer, $\mathbf{Q} = (0.5, 0.5, 0)$, and varying the specified energy, $\hbar\omega$, of the measured neutrons. Plotting these energy scans collected on the IN-8 spectrometer at fixed $\mathbf{Q}$ in Figs. 6.2e-i, shows again the unambiguous suppression of the resonance mode under fields $H \geq H_{c2}$. Looking first at Fig. 6.2e, the application of $H \approx H_{c2}$ illustrates that, while the magnetic field has no influence on the nonmagnetic background along with the effective background 6 meV crystalline electric field excitation (see Chapter 5.5), a clear suppression of scattering at the resonance energy, E_R , is seen. The resonance mode at $T = 2$ K, $H = 8$ T is in fact suppressed completely to the zero field normal state value observed at $T=30$ K. This is more plainly demonstrated through the temperature subtraction of superconducting (2K) and normal state (30K) values in the energy scans of Figs. 6.2f and 6.2g. These scans, due to the higher fixed final neutron energy of $E_f=35$ meV, can scan higher in $\hbar\omega$ and resolve changes in the resonance mode throughout the mode's entire energy distribution. In the zero field case, the resonance peak appears centered at 11 meV and identical to the resonance mode observed in earlier experiments [67] (Fig. 6.2h); however, under 10T this well-defined resonance mode vanishes (Fig. 6.2i). It is of importance to note also that from Figs. 6.2e-g, the resonance mode retains its characteristic energy, E_R , under field, and therefore the suppression observed in $\mathbf{Q}$ -scans of Figs. 6.2a-d is not due to a trivial shifting of the mode's energy as a function of applied field.

Having observed the resonance mode's complete suppression under fields H greater than H_{c2} , the detailed field dependence of the resonance excitation in this PLCCO system can now be measured. Figure 6.3a shows the measured field dependence of the resonance intensity at low- T (5K). Data collected from the peak value of the resonance excitation at $\hbar\omega = 11$ meV, with the normal state magnetic intensity subtracted, are plotted as red triangles, and open circles show the observed resonance intensity (for fields greater than 7T) at 10 meV collected in $\mathbf{Q}$ -scans originally plotted in Figs. 6.2a-d. Due to slight changes in the background intensity originating from the 18 meV CEF level for fields above ~ 6 T, these full $\mathbf{Q}$ -scans are necessary in resolving the true change in the resonance excitation at these high fields. Over-plotted with the field dependence of the resonance (as blue symbols connected by a solid line) is the scaled field dependence of the condensation energy of this PLCCO system (originally plotted in Fig. 6.1d). From this plot, the smooth suppression of the resonance mode parallels the relative suppression observed in the condensation energy under a c -axis aligned magnetic field at low- T

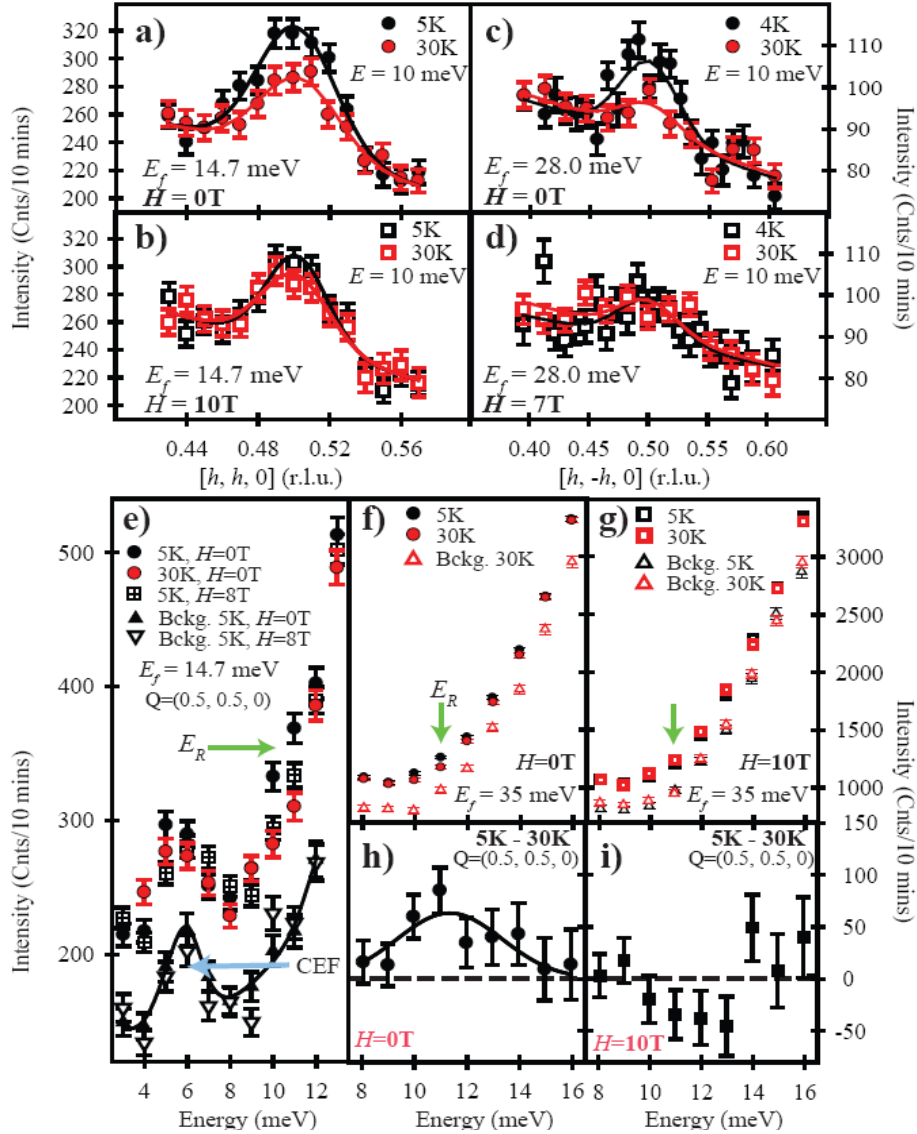


Fig. 6.2 IN-8 data showing the suppression of the resonance under field. a) Zero field Q -scans at $\hbar\omega = 10$ meV at both $T=5$ K and $T=30$ K on the IN-8 spectrometer at the ILL. b) 10T Q -scans at $\hbar\omega = 10$ meV again on IN-8 showing no difference between $T=5$ K and $T=30$ K intensities. c) Q -scans on the BT-9 spectrometer showing the presence of the resonance mode again at 10 meV in 0T. d) BT-9 Q -scans at $T=5$ K and $T=30$ K showing the disappearance of the resonance mode under $H=7$ T. e) Energy-scans at $Q_{\text{in-plane}} = (0.5, 0.5)$ taken on the IN-8 spectrometer at both 5K and 30K in 0T and 8T. Background points were collected at $Q=(0.6, 0.6, 0)$ (down triangle symbols). f) Energy scans at 5K (black circles) and 30K (red circles) at $Q_{\text{in-plane}} = (0.5, 0.5)$ in 0T and taken on IN-8. Background data collected at $Q=(0.6, 0.6, 0)$, $T=30$ K are plotted as red triangles. g) Energy scans at 5K (black squares) and 30K (red squares) at $Q_{\text{in-plane}} = (0.5, 0.5)$ in 10T, taken again on IN-8. Background data were collected at $Q=(0.6, 0.6, 0)$ at both $T=5$ K (black triangles) $T=30$ K (red triangles). h-i) Temperature subtracted ($5\text{K} - 30\text{K}$) energy scans collected at $Q_{\text{in-plane}} = (0.5, 0.5)$ under 0T and 10T, respectively.

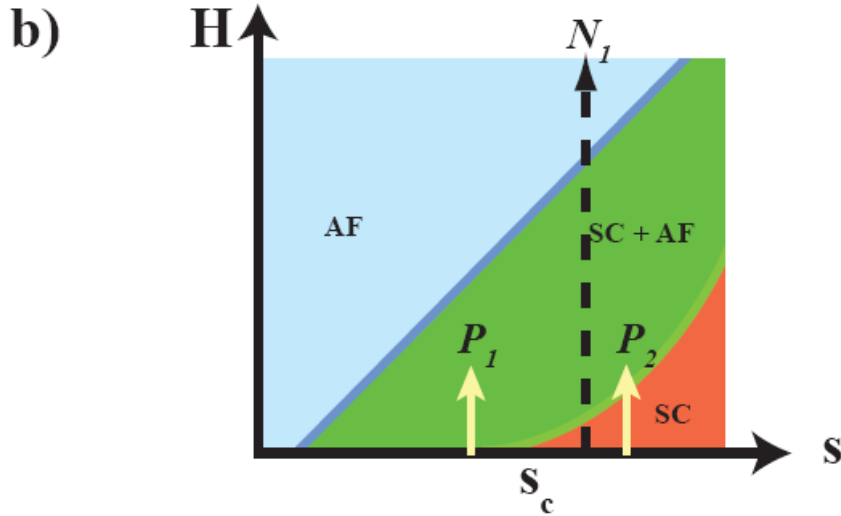
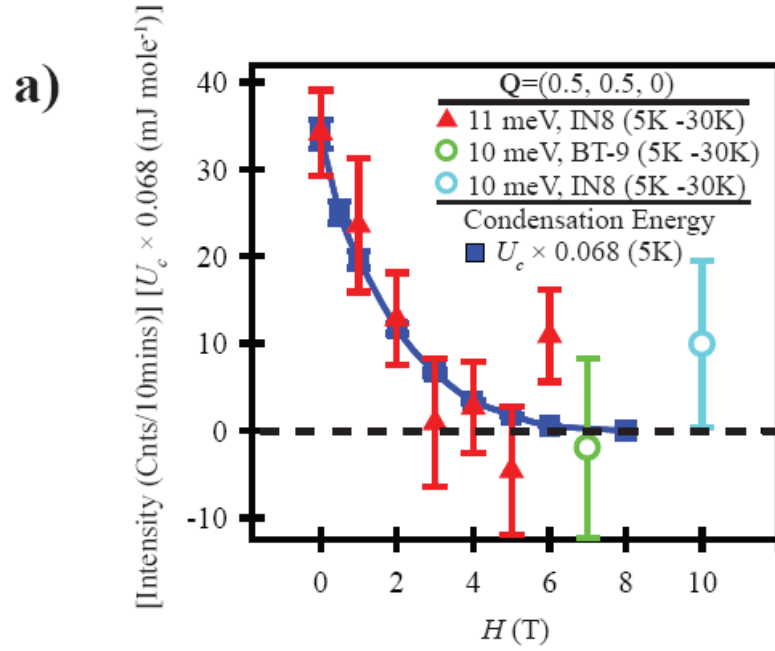


Fig. 6.3 Detailed field dependence of the resonance mode and qualitative phase diagram from Demler et al. [145] with PLCCO data point added. a) Intensity of the resonance mode plotted as a function of applied field. The corresponding condensation energy at each field is over-plotted using solid blue square symbols connected by a solid line. b) Qualitative phase diagram adapted from Ref. [144] showing the quantum critical phase transition between phase pure superconductivity and mixed phase superconductivity, where SDW order and SC coexist. P_1 and P_2 are previously reported results for hole-doped concentrations of LSCO reported in Ref.'s [135] and [143], respectively. N_1 is the point presented in our current study of PLCCO ($T_c=24$ K).

($T=5\text{K}$). This strongly suggests that the resonance mode couples to the charged quasiparticles constituting the superconducting phase and that it is intimately tied to the electron-electron pairing within the superconducting condensate.

6.5 Suppression of low frequency spin excitations under magnetic field

Now turning to the low energy spin excitations, in zero field there exists a continuum of gapless, commensurate spin excitations down to $\hbar\omega = 0.5\text{ meV}$ despite the absence of static SDW order in this system (as reported earlier [56, 67]). Though there remains no coupling of these low energy spin dynamics to the superconducting phase in zero field [67], a surprising suppression of the quasielastic magnetic scattering occurs under the application of a magnetic field, as shown in Fig. 6.4. This is most strikingly demonstrated in Fig. 6.4c in which low temperature ($T=2\text{K}$) energy scans at $\mathbf{Q} = (0.5, 0.5, 0)$ show a suppression of low energy spin fluctuations under 13T. Upon warming into the normal state at $T = 30\text{K}$, this field-induced suppression of the quasielastic scattering vanishes (Fig. 6.4d). Plots of the field-subtracted data ($13\text{T} - 0\text{T}$) at both $T = 2\text{K}$ (Fig. 6.4e) and $T = 30\text{K}$ (Fig. 6.4f) show this low energy suppression more clearly. There also exists a second, weaker component to the field induced suppression in the spin dynamics present at all energies in both the 2K and 30K field subtraction data. This is most likely due to the high magnetic field imposed on the system slightly polarizing the residual paramagnetic scattering from Pr^{3+} sites, and its magnitude is shown as an offset dashed line in both Figs. 6.4e and 6.4f. This small polarization effect is present in both 2K and 30K field subtracted data sets and is distinct from the quasielastic suppression observed only in the 2K data below 2meV, which I will now discuss further.

Scans in momentum transfer at finite energy $\hbar\omega = 1.5\text{ meV}$ are plotted in Fig. 6.4a and also show this low energy, low temperature suppression of spectral weight in a 13T field. A check of the relevance of this suppression to the superconducting phase is shown in Fig. 6.4b in which the field dependence of the 1.5 meV spin fluctuations shows a saturation at $H \approx H_{c2}$. After warming to 30K under 13T, Fig. 6.4a shows that the intensity of the spin fluctuations at 1.5 meV actually recovers its respective normal state 30K value observed in 0T. This is unexpected since T_c no longer remains a viable energy scale under the application of $H \geq H_{c2}$. Looking again at Fig 6.4d, it is clear that at $T = 30\text{K}$ and $H = 13\text{T}$, aside from the slight polarization of paramagnetic moments, the scattering completely recovers its zero field values for all energies probed. This is particularly significant at lower energies where a naïve interpretation of this temperature dependence under field as originating merely from the population of new magnon states following Bose statistics is clearly violated. For example, after warming from 2K to 30K, one would expect a factor of ~ 5 increase in scattering intensity in 0.5 meV excitations from the Bose population factor rather than the observed increase by only a factor of ~ 1.5 . This is shown explicitly through plotting both $\mathbf{Q}$ -scans and E-scans at $\hbar\omega = 0.5\text{ meV}$ under 13T in Fig. 6.5. The expected energy/temperature dependence of the Bose-population term is plotted in Fig. 6.5b showing that the departure from boson statistics upon warming is the most dramatic at low energies. Hence, the observed increase in the intensity of low energy spin fluctuations upon warming to 30K is not simply a population of bosonic magnetic excitations (such as spin waves) rooted in the stabilization of AF

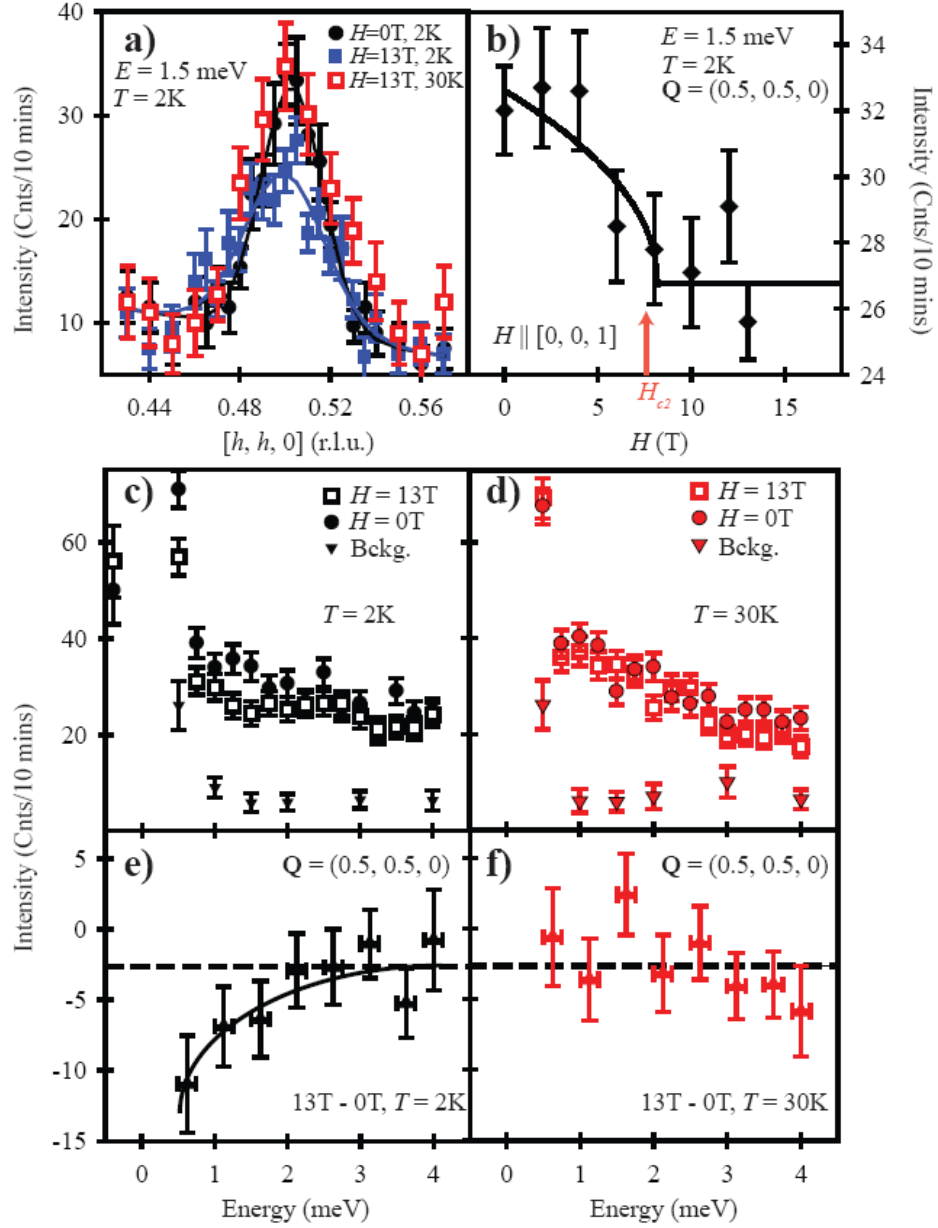


Fig. 6.4 Magnetic field effect on the low energy spin fluctuations in PLCCO ($T_c=24K$). a) Q -scans taken at $\hbar\omega = 1.5$ meV collected both under 0T (solid circles) and 13T (open squares). Data was fitted as Gaussian peak on a linear background and fit values are plotted as solid lines for 0T, 2K (black line) and 13T, 2K (blue line). b) Field dependence of scattering intensity at $\hbar\omega = 1.5$ meV, $Q=(0.5, 0.5, 0)$. Solid line is fit to the data using $I = A(H_a - H)^\alpha + B$ with $A=2.09$, $\alpha=0.488$, $B=26.77$, $H_a=8.18$. c) Energy scans at $T=2K$, in both 0T (circles) and 13T (open squares). Nonmagnetic background data collected at $T=2K$, $Q=(0.6, 0.6, 0)$ are plotted as triangles. d) Energy scans at $T=30K$, again at both 0T (circles) and 13T (open squares). Nonmagnetic background data collected at $T=2K$, $Q=(0.6, 0.6, 0)$ are plotted as triangles. e-f) Field subtracted (13T - 0T) scans from panels C and D at $T=2K$ and $T=30K$, respectively.

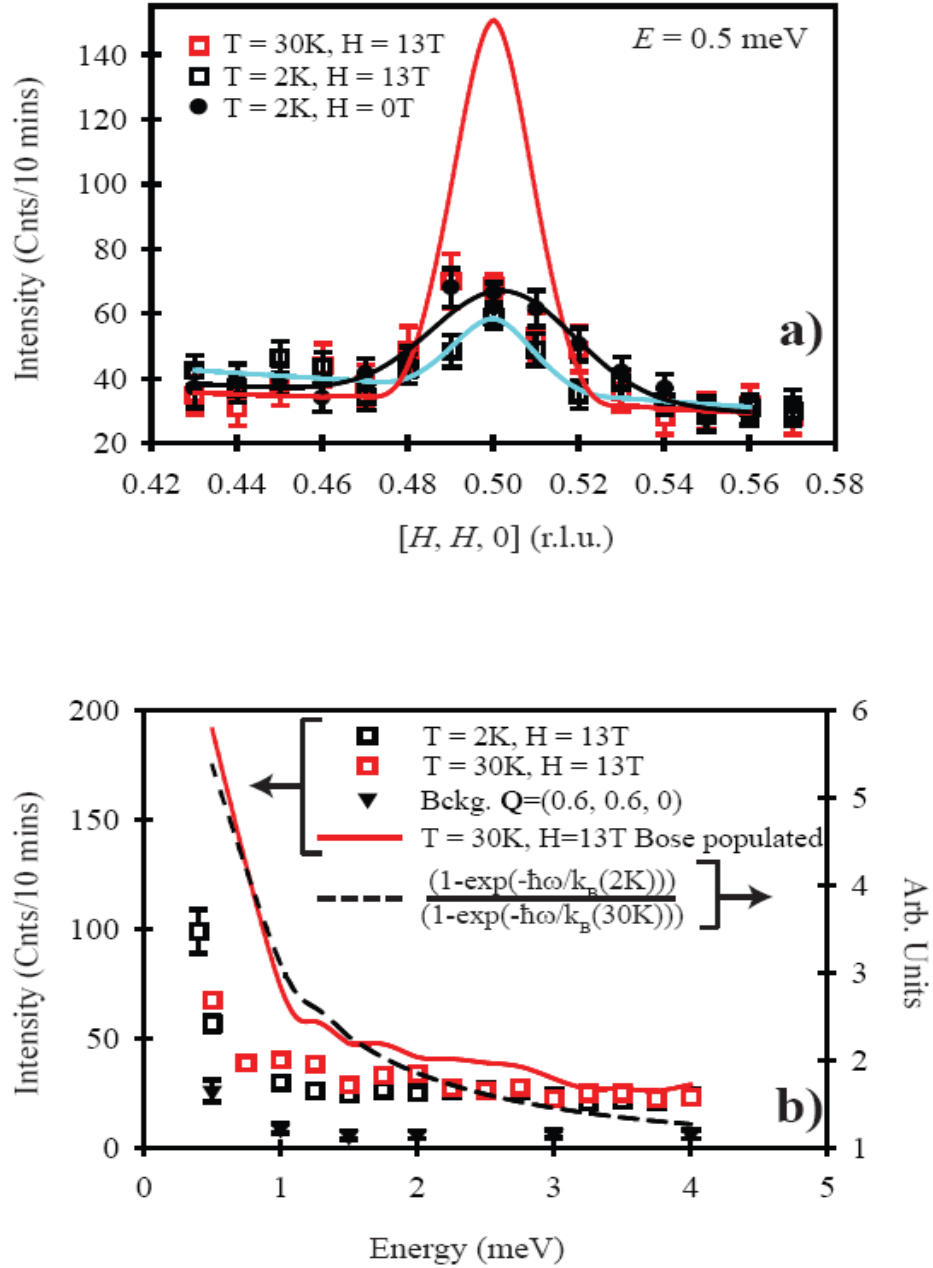


Fig. 6.5 Field effect on the $\hbar\omega=0.5$ meV spin fluctuations and projected Bose population of low energy excitations under field. a) Q -scans at $\hbar\omega=0.5$ meV along $[H, H, 0]$. Solid black line is a Gaussian fit to the scattering at $T=2$ K, $H=0$ T and $T=30$ K, $H=13$ T, and the solid teal line is a Gaussian fit to the scattering peak at $T=2$ K, $H=13$ T. The solid red line represents the expected scattering at $T=30$ K intensity from simply populating the $T=2$ K, $H=13$ T observed scattering intensities using Bose statistics. b) E -scans at $T=2$ K and 30 K under 13 T field collected at $Q=(0.5, 0.5, 0)$ plotted at square symbols. Triangle symbols are background intensities collected at $Q=(0.6, 0.6, 0)$. The solid red line is expected scattering from Bose populating the $T=2$ K, $H=13$ T observed intensities. The dashed black line is the ratio of the Bose factor at $T=2$ K and $T=30$ K at various energies.

order under field but rather appears to be a recovery of the normal state zero field scattering intensity. This suggests the persistence of the zero field SC energy scale in the magnetism of the system, despite the complete suppression of SC, and paralleling earlier results reported for field-induced static SDW order in the hole-doped cuprate $\text{La}_{1.9}\text{Sr}_{1.0}\text{CuO}_4$ ($T_c = 30\text{K}$) [135].

6.6 Magnetic field induced quasi-two-dimensional AF order

Despite the fact that previous muon measurements have observed the emergence of field induced AF order throughout the volume of optimally-doped PLCCO and $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4.8}$ samples [139, 140], early neutron experiments, possibly due to small signal strength, have failed to detect such a signal [62, 141]. The suppression of magnetism in the low energy and quasielastic scattering channels in a magnetic field in our PLCCO, however, is suggestive of a possible spectral weight transfer into the elastic channel. In order to test this possibility, we also measured the elastic scattering at the in-plane SDW ordering wavevector $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ for a series of magnetic fields. Surprisingly, the results, shown in Figure 6.6, demonstrate the unambiguous appearance of field-induced elastic SDW order at the commensurate $\mathbf{Q}=(0.5, 0.5, 0)$ position, similar to that observed in underdoped PLCCO systems.

Earlier experiments have already established that this $T_c = 24\text{K}$ PLCCO system possesses no static SDW order in zero field [67], and this is verified through $\mathbf{Q}$ -scans at both 2K and 30K in 0T plotted in Figs. 6.6b and 6.6g. Now looking at Fig. 6.6a, the application of a c-axis aligned field of 8T is clearly shown to induce magnetic intensity centered at the $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ position. The field subtraction (8T - 0T) data at $T = 2\text{K}$ displayed in Fig. 6.6c shows this induced order without the presence of the residual nonmagnetic structural peak at $\mathbf{Q}=(0.5, 0.5, 0)$. Examining the temperature dependence of this induced order (Fig. 6.6g) shows that the onset of the induced quasi-two-dimensional order appears only below the zero field T_c (dashed vertical line in Fig. 6.6g). The appearance of the induced AF signal below 24K in a 7T field, where T_c itself has been completely suppressed, again mirrors earlier results from hole-doped LSCO [135]. For fields greater than 7T, there is also a component of the induced magnetic intensity at the $\mathbf{Q}=(0.5, 0.5, 0)$ position resulting from field-driven polarization of paramagnetic Pr^{3+} ions similar to the polarization effect observed in the low energy excitations under high field shown in Fig. 6.4e-f. This is most likely due to the polarization of paramagnet Pr^{3+} moments along a structural superlattice rod of scattering at the $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$ position (first reported by Kang et al. [62]); however, it is important to stress that there exists no field effect originating from the nonmagnetic $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{O}_3$ impurity phase created during the annealing process. The field effect of this three-dimensionally ordered impurity phase has been well documented in PLCCO [61, 62], and the absence of induced magnetism from this phase was verified in our experiments by checking alternate reflections in $\mathbf{Q}$ -space away from $(0.5, 0.5, 0)$, which will be presented later in section 6.8.

The only way to unambiguously separate this polarization effect from the true field-induced AF intensity at $\mathbf{Q}_{\text{plane}}=(0.5, 0.5)$ is to test the anisotropy of the effect by applying the magnetic field both perpendicular to and along the CuO_2 sheets. Magnetic

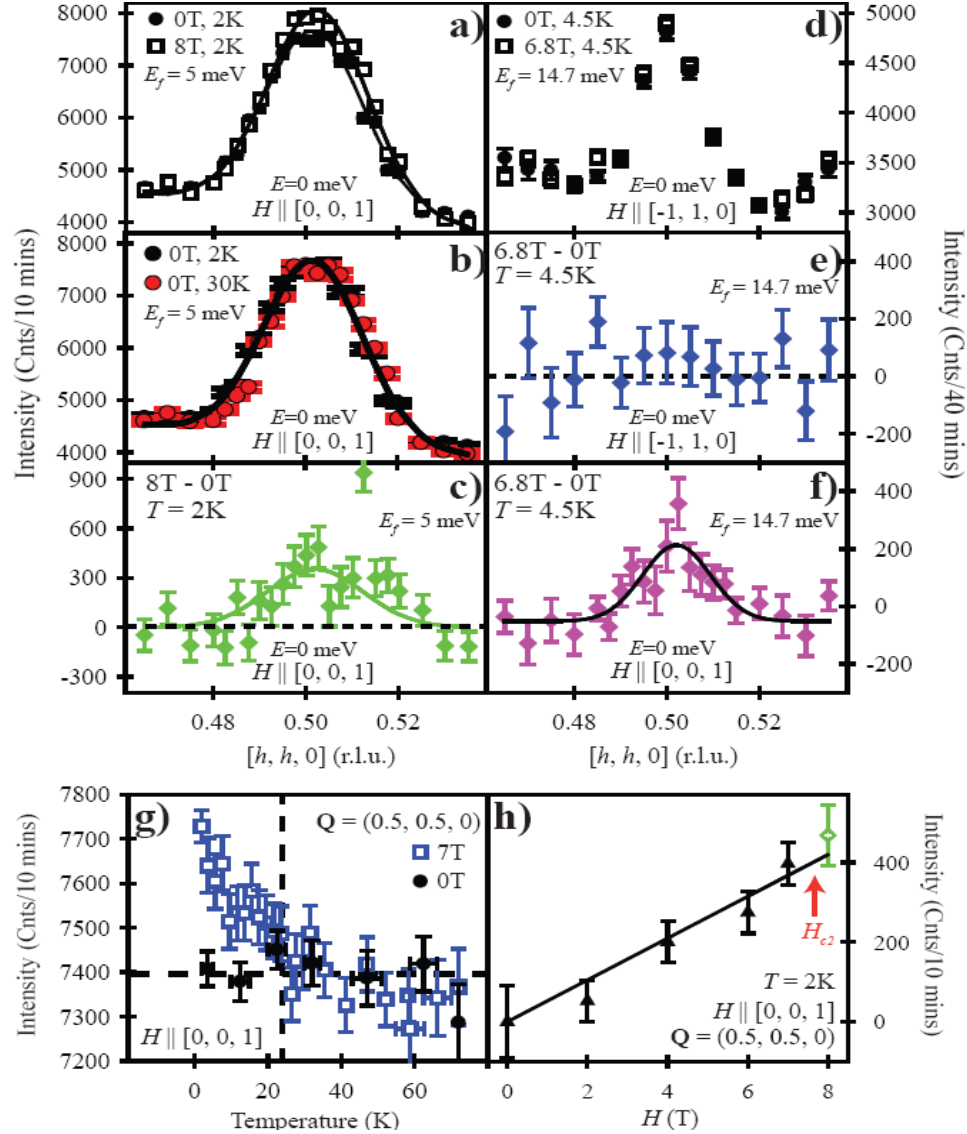


Fig. 6.6 Field-induced static magnetic order in PLCCO ($T_c=24K$). a) Elastic Q -scans through $Q=(0.5, 0.5, 0)$ in both 0T and 8T at $T=2K$. Fits to the data are Gaussian lineshapes on a linear background. b) Elastic Q -scans under 0T at both $T=2K$ and $30K$. c) $T=2K$ Field (8T - 0T) subtraction of data shown originally in panel A. d) Low- T elastic Q -scans through $Q=(0.5, 0.5, 0)$ under 0T and 6.8T applied parallel to the $[-1, 1, 0]$ direction. e) Q -scans at the elastic channel at both 4K and 30K and under 6.8T applied along the $[-1, 1, 0]$ direction. f) Field subtraction (6.8T - 0T) of low temperature Q -scans with the field applied parallel to $[-1, 1, 0]$ shown in panel D. (G) Temperature dependence of elastic intensity under both 0T and 7T. T_c is denoted by the vertical dashed line. h) Field dependence of peak intensity values measured at $T=2K$, $Q=(0.5, 0.5, 0)$, $\hbar\omega = 0$ meV with the $H=0T$, $T=30K$ measured background value subtracted (plotted as black triangles). The peak intensity value obtained via a Gaussian fit to the 8T data shown in panel A is plotted as well (green crossed diamond). The field dependence is modeled by a linear fit, $f = \beta x$ with $\beta = 52.44 \pm 3.11$ and plotted as a straight black line.

signal resulting from a simple polarization of paramagnetic Pr^{3+} moments should be independent of the applied field direction, whereas the signal originating from AF order, stabilized by the suppression of SC in the system, should exhibit an enhanced response with the field applied perpendicular to the copper-oxygen planes. In order to test this, an identical PLCCO ($T_c = 24\text{K}$) sample was aligned such that the field ($H \approx 7\text{T}$) was applied along the in-plane wavevector $[-1, 1, 0]$, and the elastic measurements were repeated on the BT-9 spectrometer. The results, shown in Figs. 6.6d-e, show that there exists no induced magnetic signal at 2K for $H \parallel ab$ where $H \ll H_{c2(ab)}$ and stands in contrast to the clear enhancement observed when $H \parallel c$ and $H = H_{c2(c)}$ (shown in Fig. 6.6a and c). To further verify this, we then realigned this *same* single PLCCO ($T_c=24\text{K}$) sample into the $[H, K, 0]$ scattering plane and measured it in the *same* spectrometer setup and sample environment. The results of this measurement are plotted in Fig. 6.6f, and a clear signal from induced AF order from the sample in this geometry is now observed. Anisotropy in the field induced effect for this single PLCCO sample further proves that the field induced magnetic order observed when the field is applied parallel to the c -axis is intrinsic to the suppression of superconductivity and not simply due to the polarization to Pr^{3+} paramagnetic moments in the PLCCO system.

The data presented in Figs. 6.6a-f effectively demonstrates that for fields up to $\sim 7\text{T}$ there exists a negligible contribution from the polarization effect within the induced magnetism observed at $\mathbf{Q}_{\text{plane}} = (0.5, 0.5)$. However, for fields greater than 7T, the contribution to the magnetic scattering at $(0.5, 0.5, 0)$ from field polarized paramagnetism can no longer be ignored, rendering the data at these high fields unreliable.

Looking at the field dependence of the induced SDW order in Fig. 6.6h, the induced order is seen to increase approximately linearly with increasing field all the way to H_{c2} . This stands in contrast to the $H/H_{c2} \ln(H_{c2}/H)$ behavior observed in underdoped LSCO and suggests the linear increase in the induced SDW moment could simply reflect AF order in the vortex cores [142], whose density increases linearly with H . The correlated peak obtained from the induced order in Fig. 6.6f, however, gives a minimum correlation length of $\xi_{\text{min}}=123 \text{ \AA}$ that, similar to the case of induced order in LSCO [135], lies outside of the radius of the vortex cores. This is assuming that the in-plane superconducting coherence length is $\xi_{sc} = \sqrt{\frac{\theta_0}{2\pi B_{c2}}} = 69 \text{ \AA}$ for PLCCO ($T_c=24\text{K}$).

Alternatively, the observed linear increase also parallels the approximately linearly induced moment seen in nearly optimally doped LSCO ($x = 0.144$) [143], which is thought to be near a quantum critical point (QCP) between the so called “mixed-phase” (with SC and SDW order coexisting) and phase-pure SC [144]. Interestingly, both hole-doped LSCO ($x=0.144$) and electron-doped PLCCO ($T_c = 24\text{K}$) exhibit a transition from phase-pure SC to the microscopic coexistence of SC and SDW order under field, suggesting this feature is something generic to high- T_c irrespective of the doped carrier type. The fact that the induced order in PLCCO is observed—even at the lowest fields measured—potentially reflects an extremely close proximity to the QCP in this $T_c = 24\text{K}$ PLCCO system (Fig. 6.3b); however, more comprehensive data at lower fields is required to assess this.

6.7 Calculation of moment of field-induced order in absolute units

Although the precise spin structure for the induced spin order in PLCCO remains a topic for future experiments, we can for the moment speculate the spin structure for this quasi-two dimensional AF phase. The simplest model is to simply assume AF checkerboard-type order within the Cu-O layers with no correlation between neighboring copper-oxygen planes (Fig. 6.7). We also assume that ordered moments on the Pr^{3+} sites are negligibly small and that ordered spins are only present on the Cu^{2+} sites. For this model, we are simply calculating the magnetic response for random CuO_2 sheets within the PLCCO matrix. Rocking scans through a magnetic Bragg reflection yield an integrated intensity [29, 30]:

$$P_{mag} = N \frac{(2\pi)^3}{v_0} \Phi \left(\frac{\gamma r_0}{2\mu_B} \right)^2 \langle M^2 \rangle \frac{g}{2} f^2(Q) \frac{|G_M|^2}{k^3 \sin(2\theta)}, \quad (6-1)$$

where $G_M = \sum_d e^{i\mathbf{Q} \cdot \mathbf{d}} e^{U_d^2} [\hat{\mathbf{Q}} \times [\hat{\mathbf{s}}_d \times \hat{\mathbf{Q}}]]$ is summed over all sites, $\mathbf{d}$, in the unit cell, and

$e^{U_d^2}$ is the Debye Waller factor (approximated as 1). In the above cross section: N is the number of unit cells, v_0 is the volume of the unit cell, $\gamma r_0 = 5.39 \text{E-}15 \text{ m}$, g is assumed to be 2, $f^2(Q)$ is the isotropic Cu^{2+} form factor, $k = \sqrt{\frac{E_i}{2.072}}$, Φ is the incident neutron flux, M

is the magnitude of the ordered moment on each Cu site, θ is the scattering angle, and $\hat{\mathbf{s}}$ is a unit vector in the direction of the spin on site $\mathbf{d}$. In assuming that the moment direction in each CuO_2 plane is randomly oriented with respect to the neighboring plane, we take the average over all possible spin orientations within the each plane giving $\left\{ 1 - (\hat{\mathbf{Q}} \cdot \hat{\mathbf{s}})^2 \right\}_{avg} = 1/2$.

The magnetic cross section can then be compared to the measured intensity of a known nuclear Bragg peak. Rocking curves through a nuclear reflection give an integrated neutron intensity of

$$P_{nucl} = N \frac{(2\pi)^3}{v_0} \Phi \frac{|F_N|^2}{k^3 \sin(2\theta)}, \quad (6-2)$$

where $F_N = \sum_d e^{i\mathbf{Q} \cdot \mathbf{d}} e^{U_d^2} \bar{b}_d$, and $\bar{b}_d$ is the coherent scattering length of the atom on site $\mathbf{d}$.

Since the nuclear structure factor F_N is readily calculated, the ratio of the integrated intensities of the nuclear and magnet peaks gives an estimate of the magnitude of the ordered moment. This ratio also removes spectrometer-dependent prefactors in the cross sections if both the nuclear and magnetic peaks were collected under identical experimental conditions.

For the $\mathbf{Q}=(1, 1, 0)$ reflection, $|F_N|^2 = 4.4295 \times 10^{-24} \text{ cm}^2$ and the integrated intensity, P_{nucl} , was 134773 Cnts/30 secs. Now looking at the induced order at $\mathbf{Q}=(0.5, 0.5, 0)$ in Fig. 6.6a, there is substantial contamination due to the residual nuclear peak at this position. In order to get the integrated intensity, we subtract from the integrated

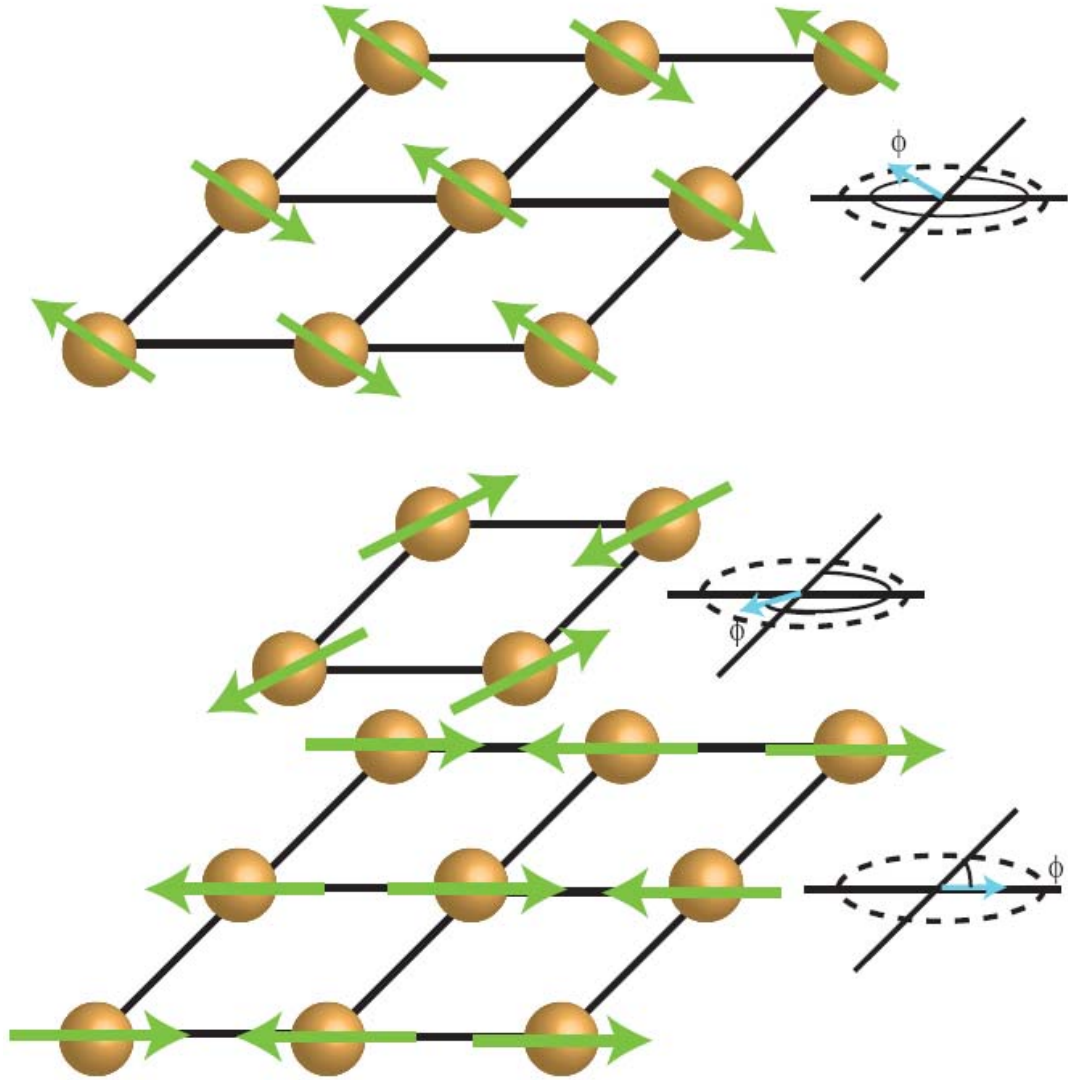


Fig. 6.7 Schematic of the assumed spin structure for the field-induced magnetism in PLCCO ($T_c=24\text{K}$) in a single magnetic unit cell. The arrows represent the AF ordered moment direction within a single CuO_2 plane. The structure assumes that the relative orientation of the ordered moment in a single plane, Φ , is randomly distributed and completely uncorrelated with the neighboring CuO_2 planes.

intensity observed under 8T (nuclear + induced magnetic moment) the 0T integrated intensity, which has no magnetic contribution. Performing this yields $P_{mag}=23.3$ Cnts/30 secs. Using the above relations, the ordered moment can then be approximated to be $\langle M^2 \rangle = .0005 \mu_B^2$. Unfortunately, this method of determining the ordered moment is highly dependent on the assumed spin structure and the current calculation is only valid for assumption structure of randomly oriented CuO_2 planes; however, in the present context the calculated moment is also valid for a collinear-type AF structure with spins oriented along the bond directions and a random stacking sequence between neighboring CuO_2 planes. I have also neglected absorption effects and the Lorentz factor correction in the above calculation. It is only intended to provide an order of magnitude estimate, and hopefully future experiments can resolve the precise induced AF spin structure and corresponding ordered moment.

6.8 Field effect on the elastic scattering from the impurity phase in PLCCO

In order to acquire a superconducting phase, electron-doped high- T_c cuprates require a post-growth annealing process in an oxygen poor environment. This annealing process has been shown to create a small volume fraction ($\sim 1\%$) of a cubic impurity phase within the crystalline matrix of the N -type cuprates [58, 62]. For PLCCO, this impurity phase is $(\text{Pr}_{1-x}\text{LaCe}_x)\text{O}_3$, whose cubic structure has a lattice constant mismatch with the host lattice ($a_{\text{impurity}}=2\sqrt{2} a$; $a = 3.98 \text{ \AA}$), thereby generating a three dimensional nuclear Bragg reflection at the $\mathbf{Q}=(0.5, 0.5, 0)$ position [59]. Since this is the wave vector where static SDW order appears in PLCCO, it is vital to differentiate between effects intrinsic to this impurity phase and the field-induced effects originating from bulk SC phase of PLCCO. Fortunately, this is possible due to a c -axis lattice mismatch of $\sim 10\%$ between the imbedded impurity phase and the host lattice, where impurity reflections are also resolvable at $(0, 0, 2.2)$, $(0, 0, 4.4)$, ... positions. This allows any potential field effect on the impurity phase to be observed independently of the field-induced SDW order at the $(0.5, 0.5, 0)$ position.

For our experiments, we studied the field dependence of the impurity $\mathbf{Q} = (0, 0, 2.2)$ reflections in a PLCCO ($T_c=24\text{K}$) sample (the same sample studied in Section 6.6) with the magnetic field applied parallel to the $[-1, 1, 0]$ direction in order to minimize the suppression of the SC phase. This allows for the direct observation of any potential field-induced order from the polarization of the paramagnetic Pr^{3+} ions originating from the impurity phase exclusively. The results, shown in Fig. 6.8, confirm that there is no field-induced order originating from the $(\text{Pr}_{1-x}\text{LaCe}_x)\text{O}_3$ impurity phase in this PLCCO system. Elastic $\mathbf{Q}$ -scans show no difference between scans taken in 0T or 6.8T in either the normal state (30K) or the SC state (5K). This observation confirms previous measurements by Kang et al. [62], in which no field effect on the impurity phase in PLCCO was observed over a series of doping levels.

The absence of field-induced magnetic scattering originating from the impurity phase in PLCCO, however, does not entirely exclude spurious field-induced magnetism from the polarization of Pr^{3+} ions at the $(0.5, 0.5, 0)$ position. There also exists a quasi-two dimensional structural superlattice rod of reflection present at $\mathbf{Q}=(0.5, 0.5, 0)$ that

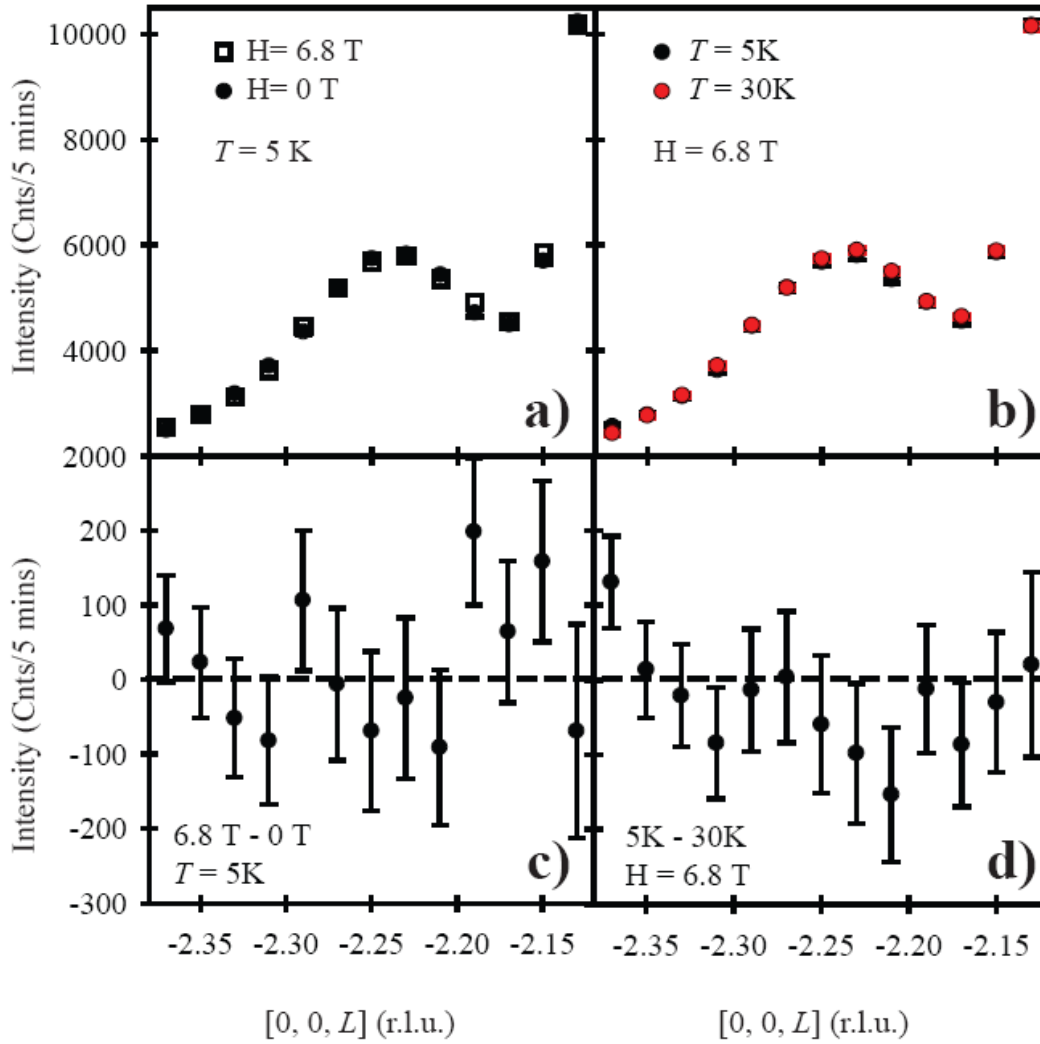


Fig. 6.8 Field effect on the impurity phase in PLCCO ($T_c=24\text{K}$). a) $T=5\text{K}$ elastic scans along $[0, 0, L]$ through the $\mathbf{Q}=(0, 0, 2.2)$ impurity reflection under both $H=0\text{T}$ and 6.8T . b) $H=6.8\text{T}$ elastic scans through the $\mathbf{Q}=(0, 0, 2.2)$ impurity peak along the $[0, 0, L]$ direction. Scans were collected at both $T=5\text{K}$ and 30K . c) Field subtracted ($6.8\text{T} - 0\text{T}$) data at $T=5\text{K}$ from panel (a) showing the absence of any field induced magnetic intensity at the impurity position $\mathbf{Q}=(0, 0, 2.2)$. d) Temperature subtracted data ($5\text{K} - 30\text{K}$) from panel (b) collected under $H=6.8\text{T}$ showing the absence of any temperature dependent magnetic scattering at the $\mathbf{Q}=(0, 0, 2.2)$ impurity reflection.

was first reported by Kang et al. [62]. In order to ascertain at which magnetic fields paramagnet Pr^{3+} ions are polarized from this superlattice component, identical $\mathbf{Q}$ -scans, both with the magnetic field applied parallel to the c -axis and with the magnetic field applied within the ab -plane, were taken through the (0.5, 0.5, 0) elastic position. The results of these scans were described in the Section 6.7 and demonstrate that for $H < 7\text{T}$ no contribution to the signal originating from the polarization of Pr^{3+} sites is observed.

6.9 Bulk susceptibility measurements and polarization of Pr^{3+} under field

Even though the rare-earth Pr^{3+} ions in PLCCO possess a nonmagnetic singlet groundstate [70], there exists a pseudo-dipolar interaction between Cu- and Pr- sites creating an effective exchange between the Cu^{2+} moments and the Pr^{3+} moments. A small moment may be induced within the Pr^{3+} sites through this interaction at low temperatures. As a result there exists a strong anisotropy in the low temperature response of the paramagnetic Pr^{3+} sites with respect to the applied field direction. The resulting easy-axis for the polarization of the Pr moments is observed to be within the ab -plane and is ~ 3 times stronger than the field-induced response for a magnetic field applied parallel to the c -axis. This is shown in Fig. 6.9a where bulk susceptibility measurements show the measured moment under a 7T magnetic field applied both parallel and perpendicular to the CuO_2 planes. The fact that the easy-axis for polarization resides in the ab -plane of PLCCO is further evidence that the field-induced effect, which we observe in the elastic channel at $\mathbf{Q}=(0.5, 0.5, 0)$ with $H \parallel c$ but absent when $H \parallel ab$ -plane, is unlikely to arise from any polarization effect of Pr^{3+} -sites and must be associated with the suppression of superconductivity in the system.

6.10 Discussion and conclusions

Now referring to Figs. 6.9b-c, we are able to qualitatively form a complete picture of the influence of a magnetic field on the spin dynamics in this PLCCO system. Our first main result is the simultaneous observation of the destruction of the resonance mode and the stabilization of SDW order under a SC suppressing field. In contrast to previous studies reporting either field-induced SDW order in LSCO [135] or the suppression of the resonance excitation in YBCO [134] without knowledge of the origin of the observed change in spectral weight, we can now suggest that in PLCCO the spectral weight lost during the suppression of the resonance reappears in the SDW order established under field. The simultaneous tradeoff in magnetic intensities between the newly formed AF order and the suppression of the resonance mode is contrary to theoretical predictions of a “softening” of the resonance mode [145] and instead suggests that these two features compete with one another.

Our second major finding, plotted in Fig. 6.3a, is that the relative magnitude of the resonance mode tracks the superconducting condensation energy as a function of field. This provides a fundamental connection between the resonance mode and quasiparticle states within the superconducting condensate. A further check of this claim can be carried out by comparing the total moment of the resonance mode observed in a different class of cuprates and contrasting the relative magnitude of the condensation

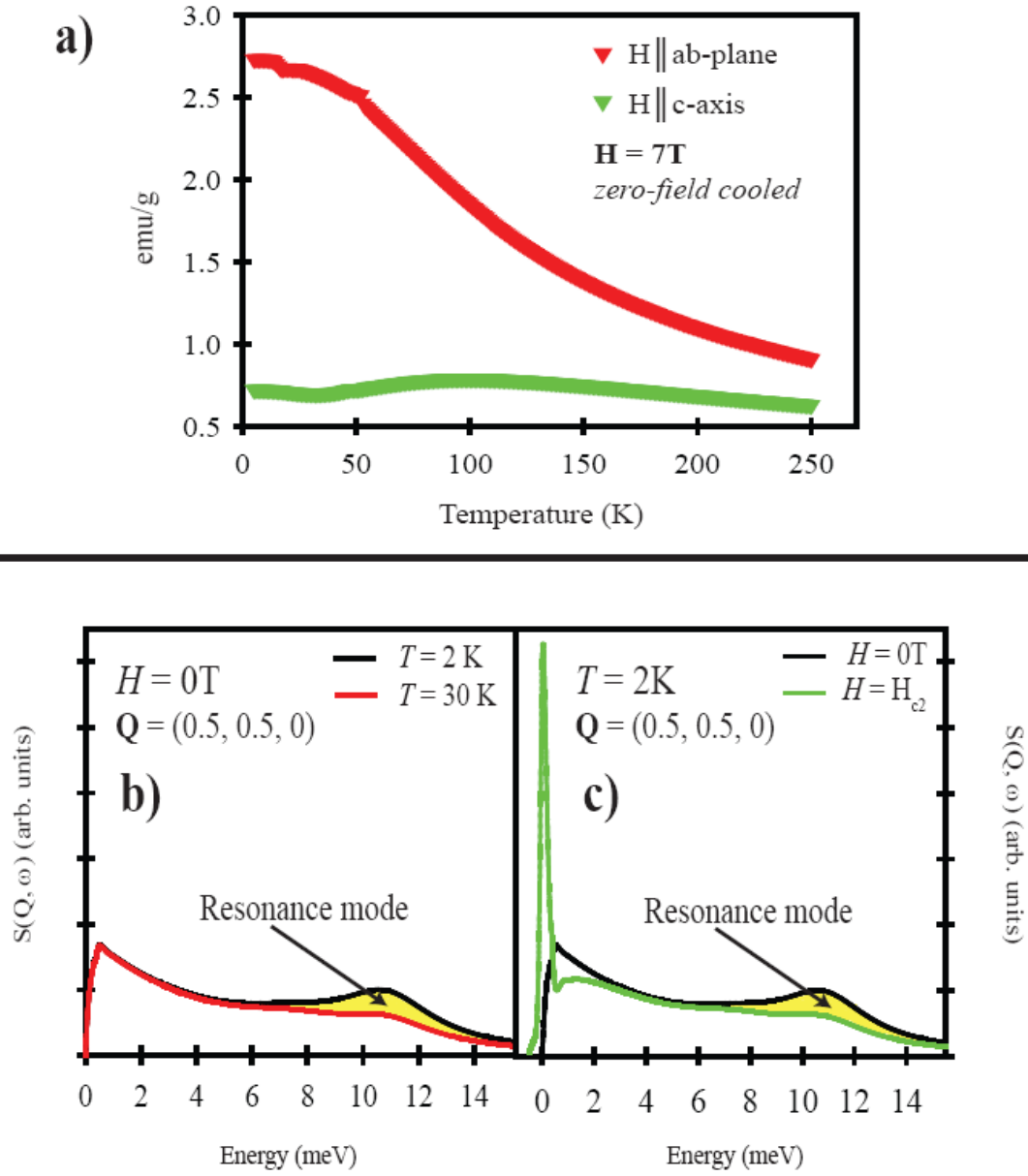


Fig. 6.9 Bulk susceptibility measurements and schematic of the field-induced changes in $S(\mathbf{Q}, \omega)$ for PLCCO ($T_c = 24\text{K}$). a) Bulk susceptibility measurements performed in a SQUID magnetometer with the field applied parallel to the ab -plane (red line) and parallel to the c -axis (green line). The sample was cooled under zero field prior to all temperature sweeps. b) Schematic showing the evolution of the measured neutron scattering function $S(\mathbf{Q}, \omega)$ both at $T = 2\text{K}$ and 30K under zero field. c) Schematic of measured scattering function $S(\mathbf{Q}, \omega)$ for both $H = 0\text{T}$ and $H = H_{c2}$ in the superconducting phase ($T = 2\text{K}$). The resonance mode is highlighted in yellow and is completely suppressed either through warming from the superconducting state into the normal state or through applying a magnetic field greater than H_{c2} . Under a c -axis aligned magnetic field, AF order is also observed in the elastic channel.

energy in these systems. Looking at the recent result from $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ [47], the total moment change in the spin fluctuations upon cooling through T_c in both acoustic and optical channels was $\langle m^2 \rangle_{\text{Res}} = 0.09 \pm 0.014 \mu_B^2/\text{Cu}$ and the condensation energy was measured to be $U_c = 1.5\text{K}/\text{Cu}$, giving a ratio of $\langle m^2 \rangle_{\text{Res}}/U_c = 0.06 \pm 0.009 \mu_B^2/\text{K}$. In our PLCCO system, the total moment of the resonance is a much weaker $\langle m^2 \rangle_{\text{Res}} = 0.0035 \pm 0.0014 \mu_B^2/\text{Cu}$ (see Section 5.6); however, the condensation energy is also a much smaller value of $U_c = 0.0687 \text{K}/\text{Cu}$ (shown in Fig. 6.1), rendering, within experimental uncertainty, a similar ratio of $\langle m^2 \rangle_{\text{Res}}/U_c = 0.0510 \pm 0.02 \mu_B^2/\text{Cu}$. This is consistent with Scalapino and White's treatment of the superconducting condensation energy originating from the change in the spin fluctuation spectrum in the cuprates upon entering the superconducting state [126].

In conclusion, we have presented the first ever comprehensive report of the evolution of the spin dynamics in a high- T_c cuprate as the system is driven into the normal state via the application of a magnetic field. This picture of the precise evolution of spin fluctuations along with the emergence of static AF order in the field-suppressed nonsuperconducting groundstate should allow for more robust theoretical modeling and predictions toward the role magnetism occupies within the underlying mechanism of high- T_c superconductivity.

Chapter 7: Introduction to non-Fermi liquid behavior in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$

7.1 Introduction to Fermi-Liquid theory

One of the greatest accomplishments in the history of condensed matter physics is the formulation of Landau-Fermi liquid theory. Its ability to renormalize the complicated system of electron-electron interactions in metals into a system of non-interacting quasiparticles above an inert Fermi-sea constitutes a cornerstone in the modern understanding of electronic behavior in metals. The applications of the Fermi-liquid formalism and its predictive power extend over a broad range of systems, and it even provides the basis necessary for the formulation of BCS theory [3]. In this section, I will present a very general and qualitative overview of the assumptions and consequences of the Landau-Fermi-liquid treatment. Most of the key ideas I will discuss will be referenced from Ref. [146].

The basis for Fermi-liquid theory is that for a system of a given symmetry, a simple/manageable Hamiltonian can be chosen as a starting point and then the complicated components of the intractable Hamiltonian may be perturbatively introduced. The low energy and long wavelength properties between the two Hamiltonians (the manageable one and the impossible one) can be connected adiabatically via this perturbation since there exists a one-to-one correspondence between the analytic properties of the two [146]. Of course the initial hurdle in applying this formalism is the nontrivial task of choosing the correct simple Hamiltonian that can reproduce the appropriate physics. For the case of interacting electrons in systems with metallic electron densities, the choice of a starting Hamiltonian is surprisingly simple: the noninteracting electron gas. When interactions are turned on in this system, there is a one-to-one correspondence between the quantum numbers of the noninteracting electrons and those in the interacting case simply with renormalized parameters.

Starting with the Hamiltonian $H = \sum_{k,\sigma} \epsilon_k c_{k,\sigma}^\dagger c_{k,\sigma}$, one obtains the energy of the noninteracting electron gas where ϵ_k is the energy of an electron state with momentum k and $c_{k,\sigma}^\dagger c_{k,\sigma}$ is a standard second-quantized number operator that counts the number of electrons occupying the state (k, σ) . Electrons only occupy states up to the Fermi-momentum k_f (with Fermi energy ϵ_f), and the momentum distribution is $n(k) = \Theta(\epsilon_f - \epsilon_k)$. Now in allowing interactions between electrons, the Hamiltonian can be expressed as $H = \sum_{k,\sigma} \epsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{k,k',q,\sigma,\sigma'} V_{k,k',q} c_{k+q,\sigma}^\dagger c_{k'-q,\sigma'}^\dagger c_{k,\sigma} c_{k',\sigma'}$ in which the pairwise interactions between scattered electrons, $V_{k,k',q}$, have been introduced and depend on both the initial electron states (k and k') and on the momentum transfer q of the elastic collisions [147]. The application of the Landau-Fermi-liquid treatment to this problem famously demonstrates that in the long-wavelength, low-energy limit, electronic excitations above the Fermi-sea can be renormalized into quasiparticle states that, near the Fermi-energy, are long-lived and effectively noninteracting. This picture of noninteracting quasiparticles and the notion that electrons at the Fermi-level have infinitely long lifetimes stems from the Pauli exclusion principle that severely restricts the phase-space

channels for any one particular electron-electron scattering event. A qualitative plot of the momentum distribution for electron states between the noninteracting electron gas (before interactions are allowed) and a Fermi-liquid (after interactions are added) is reproduced in Fig. 7.1. Hence, even in systems with strong electron-electron interactions, the low energy excitations will behave qualitatively the same as in the noninteracting electron case. Only the parameters for the corresponding low energy excitations will be strongly renormalized, and this will be discussed further in the following sections.

7.2 non-Fermi-liquid behavior in heavy-Fermion metals

An example of the renormalization of low energy excitations is best illustrated by first considering the predictions of Landau-Fermi-liquid theory at sufficiently low temperatures. For example, the electronic specific heat is predicted to be linear in temperature at low- T with $C \approx \gamma T$ and C/T roughly a constant for a given system. The resistivity of a system can be described as $\rho = \rho_0 + AT^2$, and the magnetic susceptibility is independent of temperature entirely, $\chi \approx \beta$. Often the renormalization in the parameters of these electronic properties (i.e. γ , A , β , ...) is envisioned simply as a renormalization of the bare electron mass.

Now for instance, in the f -electron system CeAl_3 , where electronic correlations are strong, the measured behavior of the specific heat follows the linear T -dependence of Fermi-liquid theory but with a value of $\gamma \sim 1000$ times larger than that expected from the density of states for a typical metal at ε_f ($N(0) = \frac{m_e k_f}{\pi^2 \hbar^2}$) [146, 148]. In this estimate for the typical metallic density of states, the free electron mass, m_e , is used. In order to account for the increased density of states observed in this system, the effective mass of the electron is envisioned to be renormalized to a value m^* such that the density of states is now $N(0) = \frac{m^* k_f}{\pi^2 \hbar^2}$. This results in an effective electron mass that is ~ 1000 greater than the free electron mass for Fermions in this system. Such systems with sufficiently large renormalized electron mass are referred to as heavy-Fermion (HF) systems and have provided very rich avenues in discovery of new physics phenomena.

The discovery of deviations from Fermi-liquid (FL) predictions of low- T electronic behavior was first publicized through work on the f -electron, heavy-Fermion system $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ (YUPd) [149, 150]. This overshadowed earlier reports of similar behavior in the spin-glass compound AuFe [151], and the discovery of similar “marginal Fermi-liquid” behavior in the normal state of the d -electron, high- T_c cuprates soon followed. As the $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ system is the most widely studied example of a non-Fermi liquid (NFL) metal, it is useful to first focus on it and review how its low- T electronic properties deviate from FL predictions. The resistivity reported in YUPd by Seaman et al. [149] follows $\rho \sim \rho_0 + AT^{1/2}$, and the specific heat displayed a logarithmic divergence from linearity following $C/T \sim -\ln(T)$. The susceptibility also deviated from the T -independent FL prediction and instead was observed to follow $\chi \sim \alpha - \beta T^{1/2}$. Theories leveraging only the influence of the Kondo interaction in this material have failed to explain this divergence, and an extensive amount of theoretical work has been published

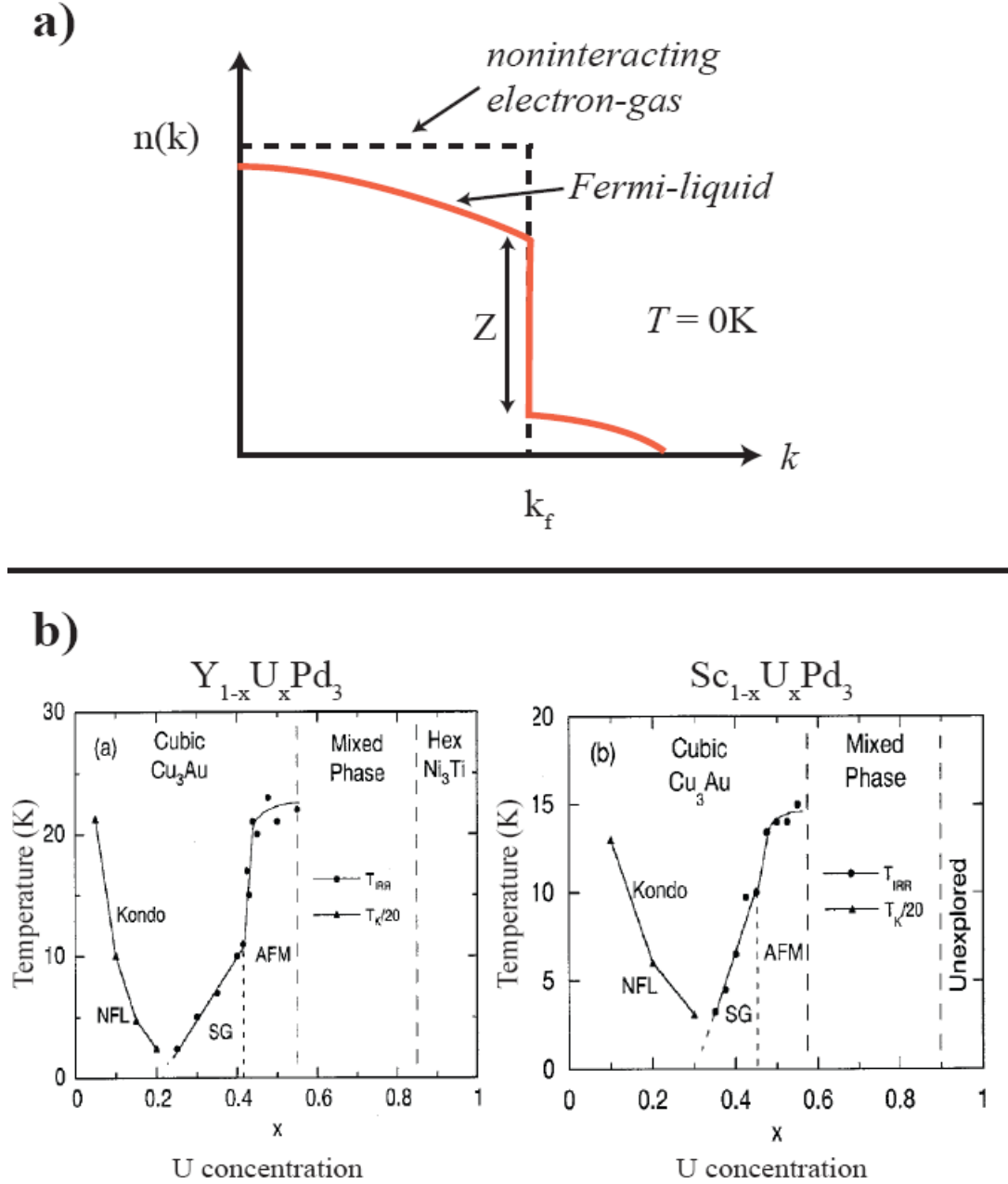


Fig. 7.1 Momentum distribution for electron gas with and without interactions at $T = 0K$ and phase diagrams for $(Y,Sc)_xU_xPd_3$ systems. a) Momentum distribution for a noninteracting electron system shown as a dashed line with a normalized discontinuity of $Z=1$. Red line shows the modified momentum distribution when interactions are turned on. A renormalized discontinuity remains at the same wave vector k_f with quasiparticle states pushed above k_f at $T=0K$. b) Phase diagrams for the $Sc_{1-x}U_xPd_3$ and $Y_{1-x}U_xPd_3$ systems [158]. Both systems show qualitatively similar phase diagrams with a low- T NFL phase at low U -doping and a potential SG QCP, which evolves into an AF phase at higher U -doping levels.

attempting to explain how the electron-electron correlations in this alloy prevent the stabilization of the Fermi-liquid groundstate [88].

Experimental efforts have since uncovered a large array of other f -electron systems that exhibit NFL electronic properties ranging from NFL alloys (e.g. $\text{UCu}_{5-x}\text{Pd}_x$ [152]) to pressure tuned NFL behavior (e.g. CePd_2Si_2 [153]) to NFL stoichiometric systems simply in the proximity of a quantum critical point (e.g. CeCu_2Si_2 [154]). Unconventional superconductivity is also observed to form in a large number of these NFL compounds in which the SC phase transition develops out of heavy band of quasiparticles. These systems are known as heavy-Fermion (HF) superconductors in which the interaction between localized f -electron moments with itinerant conduction-band electrons renders an effective mass for the conduction electrons 100-1000 times greater than the bare electron mass [88].

One of the components of theoretical models seeking to explain NFL behavior and also a pervasive feature in the myriad of uncovered NFL systems is the presence of a magnetic quantum critical point in the phase diagrams of these compounds. A quantum critical point (QCP) occurs when a second order phase transition occurs at $T=0\text{K}$. The quantum phase transition itself then is driven by quantum fluctuations rather than the thermal fluctuations in a classically-driven phase transition. At $T=0$ near this QCP, the long wavelength fluctuations and resulting long-range interaction between electrons inhibit Fermi-liquid behavior and can continue to couple to the low energy electronic properties over a large range of temperatures when extended to finite T [155]. The resulting magnetic singularity on the phase diagram can have dramatic consequences and is thought to constitute the origin of NFL behavior in a number of heavy Fermion systems [88, 146]. This in fact was precisely the case argued by Andraka et al. [150], following their initial discovery of NFL behavior in the $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ system.

7.3 Phase Diagram of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$

Returning to the properties of the $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$, there are several complicating factors when analyzing the physics of this system. The primary of these is the effect of U-ion inhomogeneity introduced in the alloying process during the samples' creation. This is an intrinsic disorder effect, and substantial U-clustering has been directly observed in these systems [156]. The influence of this disorder has in some cases been utilized to explain the NFL behavior in this class of systems [157], and its effect on quantum critical phenomena is also an issue of considerable complexity. Recently however, an isostructural compound, $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ (ScUPd), with smaller Sc-sites replacing Y-sites in the cubic lattice has been synthesized and shown to possess a nearly homogenous distribution of U-sites, thereby substantially reducing the influence of disorder in this system [158]. This fact combined with the discovery that Sc- and Y-doped variants both exhibit qualitatively identical phase diagrams (plotted in Fig. 7.1) possessing a low- T NFL phase, makes this ScUPd system an attractive candidate system for research on NFL phenomena. The onset of an AF phase at $x \sim 0.45$ in ScUPd and a potential spin-glass (SG) quantum critical point at $x \sim 0.3$ in the phase diagram also

presents exciting avenues for studying how magnetism couples to the electronic properties in this system.

The NFL phase of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ again shows a logarithmic divergence in the quantity C/T (where $C/T \sim -\ln(T)$) and resistivity values follow $\rho \sim a(1-bT^{1/2})$ for $x=0.3$ and 0.35 concentrations. Theories based on a multichannel-quadropolar-Kondo effect have also been proposed to account for behavior of the electronic properties in both this system and in $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$; however, continued uncertainty concerning the nature of the crystal electric field groundstate (CEF) in these systems has made this a subject of continued debate [88]. The details of this controversy will be discussed in the next chapter; however, they provide a key motivation for studying the magnetic excitations in the ScUPd system with now cleaner metallurgical properties. The still unresolved CEF groundstate in this class of systems combined with the importance of determining the evolution of magnetic excitations in understanding the origin of NFL behavior in this system provides the key motivation for our neutron scattering studies presented in Chapters 8 and 9.

Chapter 8: Quantum critical scaling in the spin excitations of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$

Portions of the data and discussion in the following sections have been published recently and can be found in Ref. 87.

8.1 Introduction and Motivation

The breakdown of Fermi-liquid theory has been observed in many classes of strongly correlated f -electron materials, following the initial attraction of the so-called non-Fermi-liquid (NFL) behavior in the $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ pseudobinary alloy in 1991 [88, 149, 150, 159]. In spite of intensive theoretical and experimental efforts over the past decade [160, 161, 162, 163, 164, 165, 166, 167, 168], it is still unclear whether the observed NFL behavior is an intrinsic property [158, 169] or an extrinsic property associated with metallurgical inhomogeneity in these materials [156]. Models describing this anomalous NFL behavior include single-ion physics of noninteracting local magnetic moments [160, 161], close proximity to a $T=0$ K second-order phase transition or quantum critical point (QCP) [162, 163, 164, 165], and disorder induced effects [166, 167, 168].

In this chapter, I will present our recent studies of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ because this system has a phase diagram and NFL properties similar to $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ (Fig. 7.1), but with a nearly homogeneous U distribution in the ScPd_3 matrix [158] (as discussed in Chapter 7.3). The U-inhomogeneity in $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ is unlikely the main cause of the NFL behavior [169], but neutron scattering experiments seeking to provide constraints on various microscopic models have reached different conclusions. According to Lea, Leask, and Wolf [170], the cubic crystalline electric field (CEF) of ScPd_3 splits the $\text{U}^{4+} J=4$ multiplet into Γ_4 and Γ_5 triplets, a Γ_1 singlet, and a Γ_3 doublet. If the single-ion based two-channel quadrupolar Kondo effect (QKE) is responsible for the NFL behavior in $\text{Y}_{0.8}\text{U}_{0.2}\text{Pd}_3$ [149], the U^{4+} ground state should be a nonmagnetic Γ_3 with magnetic Γ_5 and Γ_4 excited states [160]. In contrast, polarized neutron-scattering experiments on $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ reveal a magnetic ground state for $x=0.45$ and possibly for $x=0.2$, thus precluding the possibility of a QKE [171]. However, based on subsequent neutron time-of-flight measurements, Bull et al. [172] argue that the Γ_3 doublet ground state is more consistent with the $x=0.45$ data and the $x=0.2$ compound has a degenerate Γ_3 and Γ_5 ground state. In this case, the QKE could be the predominant cause of NFL behavior [169].

In the following sections, experiments attempting to address this discrepancy in the CEF groundstate for this class of systems in the now more homogenous ScUPd system will be presented. Inelastic neutron scattering experiments on $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ ($x=0.0, 0.25, 0.35$) will be discussed, and the data presented will instead show that magnetic excitations at the NFL concentration ($x=0.35$) do not form the distinct CEF excitations seen in $\text{Y}_{0.55}\text{U}_{0.45}\text{Pd}_3$. Instead, the susceptibility $\chi''(\mathbf{Q}, \omega, T)$ at all probed wave vectors ($\mathbf{Q}$), temperatures (T), and energies ($\hbar\omega$) obeys ω/T scaling indicative of a $T=0$ K second order phase transition. Whereas such behavior is also observed in the NFL compounds $\text{CeCu}_{6-x}\text{Au}_x$ [173], $\text{UCu}_{5-x}\text{Pd}_x$ [85, 174], and $\text{Ce}(\text{Rh}_{0.8}\text{Pd}_{0.2})\text{Sb}$ [175] near antiferromagnetic (AF) QCPs, $\chi''(\mathbf{Q}, \omega, T)$ in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ ($x=0.35$) is wave vector

independent with no spatial correlations and obeys ω/T scaling over a much wider energy range and with a different critical exponent. Therefore, the following will demonstrate that the dynamics of isolated U ions are responsible for the temperature and energy scaling, suggestive that the NFL behavior originates from the spin-glass phase transition suppressed to near zero temperature.

8.2 Experimental details

For our experiments on this system, 18 g of polycrystalline samples of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ ($x=0, 0.25, 0.35$) were grown through arc-melting techniques by Dr. Brian Maple's group at the University of California at San Diego [158]. The crystal symmetry of this system is cubic with the cubic Cu_3Au structure with lattice parameters $a = b = c = 4.01 \text{ \AA}$ for the $x=0.35$ concentration and $3.99 \text{ \AA}$ for the $x=0.25$ concentration. Since these samples are polycrystalline powders, in the discussion of the data in the following sections, locations in momentum space will simply be referred to by the modulus of the wave vector transfer, $Q [\text{\AA}^{-1}]$.

The time-of-flight data presented in the following sections was collected on the HET spectrometer at the ISIS spallation neutron source. The HET data was collected with incident beam energies (E_i) of both 18 meV and 65 meV over a range of temperatures, and a vanadium standard was used to normalize the scattering intensity to absolute units (similar to that described in Chapter 4.2). The magnetic scattering in the U-doped materials was determined by directly comparing the scattering intensity with that of the nonmagnetic ScPd_3 parent compound ($x = 0$) for 18 meV data, and by a subtraction of a parent-compound-generated mapping background for 65 meV data [172,176]. This mapping background accounts for phonon and nonmagnetic scattering at higher energies through a ratio of the scattering observed in low angle detector banks and that observed at the identical energies in high angle detector banks. It was generated through multiplying the ratio of scattering high angle divided by low angle data at a fixed energy for the magnetic compound by the low angle data at the same energy of the nonmagnetic reference system. This process is able to account for slight shifts in phonon intensities and frequencies in the phonon spectrum of the magnetic system relative to the $x = 0$ reference compound and provides a useful reference spectra for filtering out the nonmagnetic scattering in the data.

In order to study the low-energy spin dynamics, we used the SPINS cold neutron triple-axis spectrometer at the NIST Center for Neutron Research (NCNR) with a final neutron energy fixed at $E_f = 5 \text{ meV}$. An incident beam collimation of $80'$ was used, followed by a cold Be filter and a radial collimator after the sample. In addition, a horizontally focusing analyzer was used following the radial collimator. In this experiment, both the $x=0.35$ sample and the $x=0$ parent reference system were studied.

Data was also collected using polarized neutrons on BT-2 at the NCNR in order to separate the magnetic signal from nuclear spin incoherent scattering in the elastic channel. Due to the low intensity of the scattering strength, magnetic signal was measured only in the $x=0.35$ system using this polarized setup and only over a limited range of (Q, ω) space.

8.3 Inelastic neutron scattering measurements of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ ($x = 0.2, 0.35$)

Looking first at the spin excitations mapped out on the HET spectrometer in this ScUPd system, Figure 8.1 summarizes the results with $E_i=18$ meV for $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ at $x=0, 0.25, 0.35$, where probed excitations in the energy range between 3 and 13 meV were probed. The scattering for $x=0.35$ in the energy-momentum ($\hbar\omega$, $\mathbf{Q}$) space probed (Fig. 8.1a) shows a broad continuum of intensity with no peak at the expected AF ordering wave vector for $\text{Y}_{0.55}\text{U}_{0.45}\text{Pd}_3$ and is marked as the vertical dashed line [171]. This is, of course, calculated assuming that the magnetic ordering of the two isostructural YUPd and ScUPd systems is the same (a direct measurement of the static AF order parameter in ScUPd has yet to be performed). Different energy-integrated cuts at 5 K (see inset of Fig. 8.1a) show no modulation at any wave vector, different from that of $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ (Fig. 10 of Ref. 172). In order to determine if the scattering in Fig. 8.1a is magnetic, the $\mathbf{Q}$ -integrated energy cuts for all three concentrations at 5 K are compared in Fig. 8.1b. Despite the fact that the outcome shows clear magnetic response for the two doped systems, the scattering is broad and featureless with no evidence for localized CEF states. In addition, the magnetic scattering does not follow a simple U concentration scaling. If the magnetism in this system is assumed to arise from a naïve picture of localized U-ions, then the resulting magnetic intensity is expected to scale linearly with the U-doping concentration. Assuming that the magnetic fluctuations in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ scale linearly with the U solute concentration, one would expect scattering for $x=0.25$ as the dashed line in Fig. 8.1b. The actual scattering from the $x=0.25$ concentration instead almost lies directly on top of the nonmagnetic parent background with much less magnetic signal. We note that similar behavior has also been observed in $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ [172], where the buildup of magnetic intensity is a nonlinear function of U-concentration.

Since the $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ $x=0.25$ compound is nearly nonmagnetic and does not exhibit strong NFL features [169], it is more informative to instead focus on the NFL $x=0.35$ compound and study the temperature evolution of the magnetic scattering. The most striking feature of the data is the temperature independence on the neutron energy loss side of the spectra, while the neutron energy gain side obeys detailed balance as shown in Fig. 8.1c. To confirm that such behavior indeed arises from the U magnetic moment, a careful study of the temperature dependence of the nonmagnetic ScPd_3 was performed, and it was found that the nonmagnetic scattering is temperature independent below 100 K and increases only slightly at 300 K as shown in Fig. 8.1c.

In order to determine the magnetic excitations of the $x=0.35$ compound above 13 meV, the incident energy on the sample was increased to $E_i=65$ meV on the HET spectrometer. Fig. 8.2a shows the scattering at $T=5$ K for both the $x=0.35$ compound and the nonmagnetic background [172, 176] in this new experimental configuration. The resulting difference spectra at several temperatures are shown in Fig. 8.2b. Similar to Fig. 8.1c, the magnetic excitations are broad, temperature independent, and extend up to 50 meV. If excitations from the U moments in the $x=0.35$ compound have localized states at $\hbar\omega \sim 6$ meV and $\hbar\omega \sim 36$ meV as in the AF ordered $\text{Y}_{0.55}\text{U}_{0.45}\text{Pd}_3$ [171, 172], one can calculate the expected temperature dependence of the CEF levels, assuming either Γ_5 [171] or Γ_3 [172] as the zero-energy ground state. Performing these calculations and simulating the resulting magnetic cross sections for both groundstates using resolution-

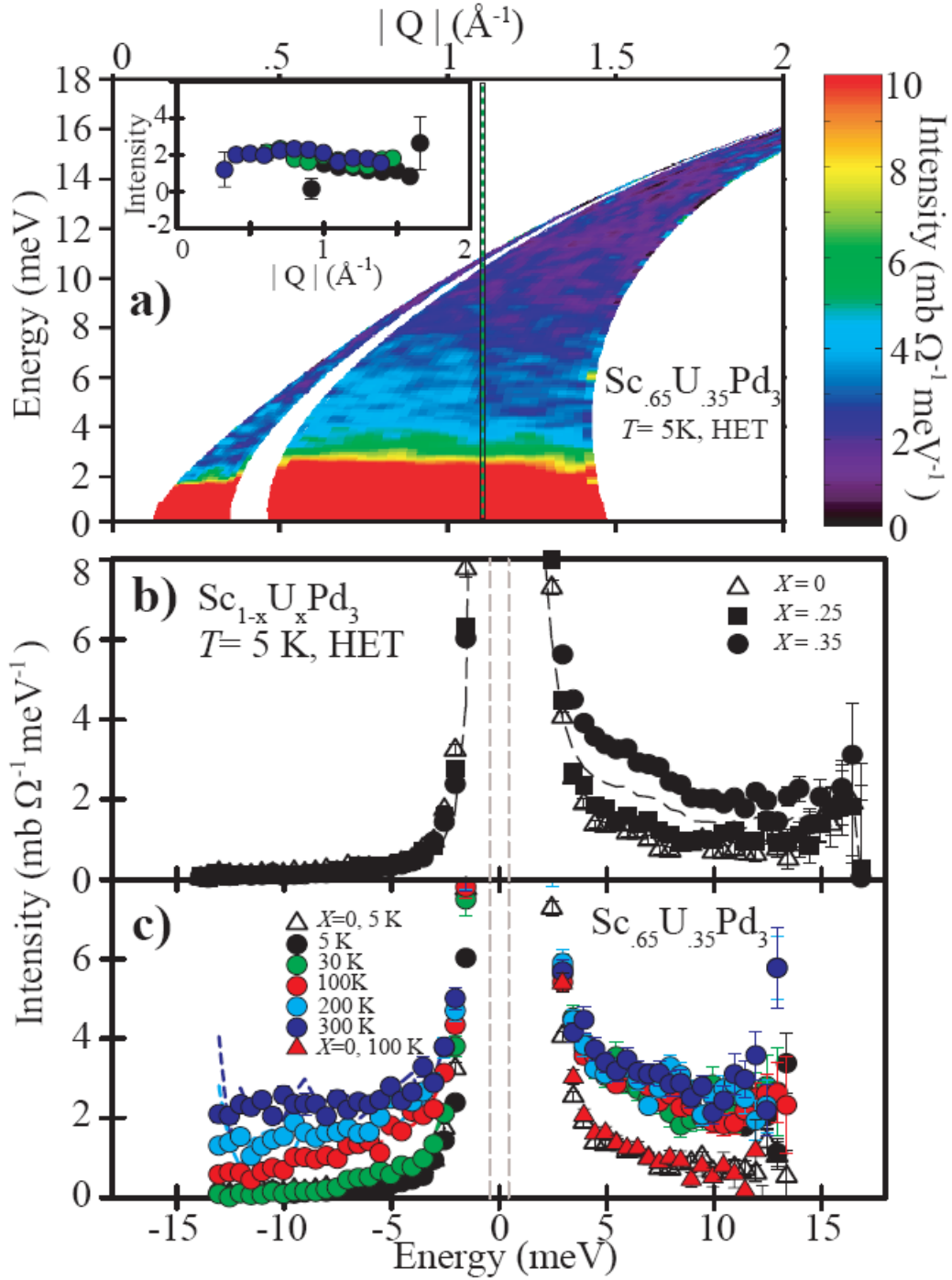


Fig. 8.1 $E_i=18\text{ meV}$ HET data for ScUPd ($x=0.35, 0.25$, and 0) a) E - Q image of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ ($x=0.35$) at 5 K . The inset shows E -integrated [$E=3\text{--}6\text{ meV}$ (blue); $6\text{--}9\text{ meV}$ (green); $9\text{--}12\text{ meV}$ (black)] Q -cuts at 5 K . b) The Q -integrated ($0 < Q < 2.5 \text{ \AA}^{-1}$) $S(\omega, T)$ for $x=0.0, 0.25$, and 0.35 . The dashed line shows the expected magnetic scattering for $x=0.25$ assuming simple U-concentration scaling. c) The Q -integrated ($0 < Q < 1.5 \text{ \AA}^{-1}$) $S(\omega, T)$ for $x=0.35$ at various temperatures. Dashed lines on the $E < 0$ side reflect detailed balance expectations. Vertical dashed-lines show the resolution half-width of 0.433 meV .

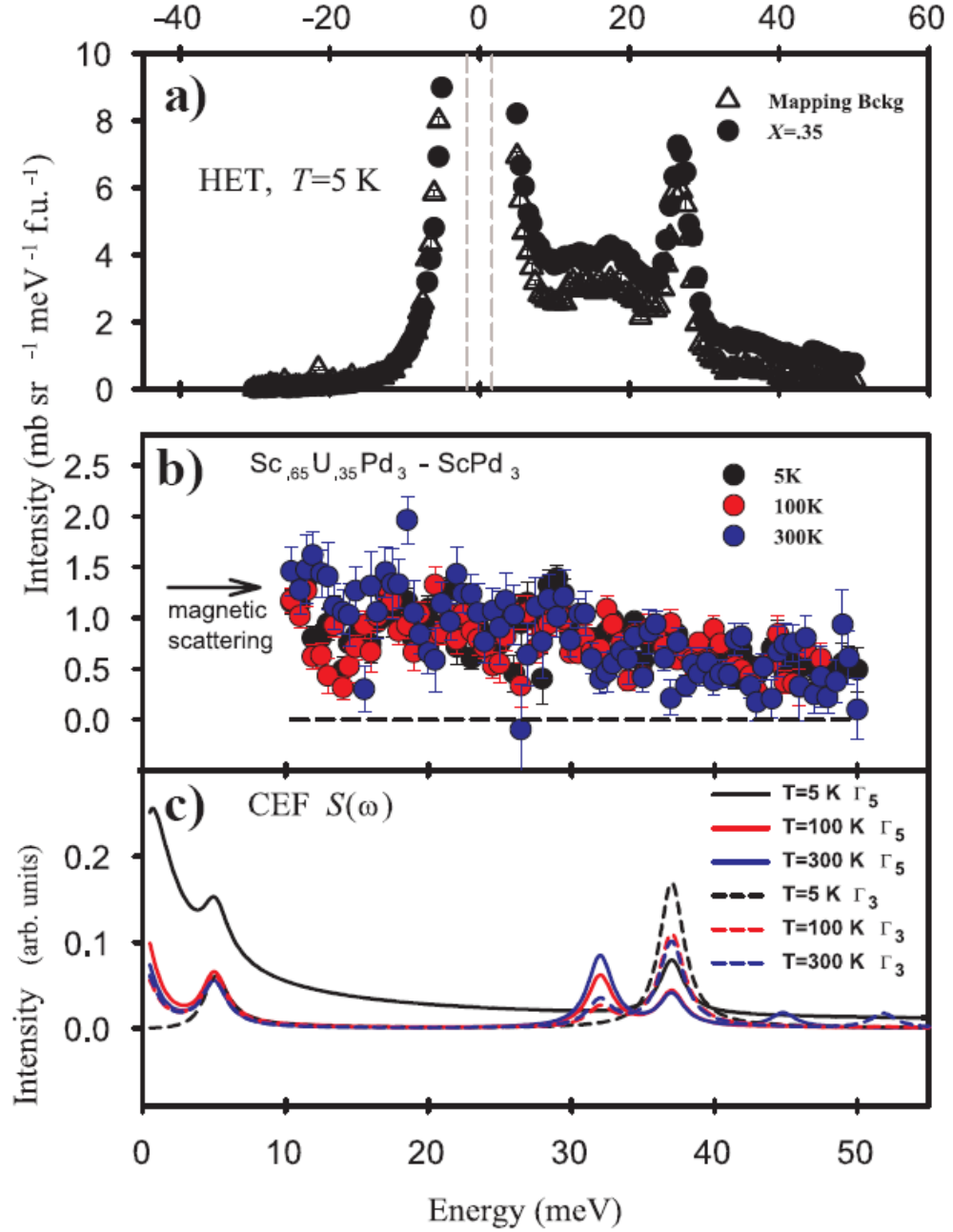


Fig. 8.2 $E_i=65\text{ meV}$ HET data and model CEF calculations for Γ_5 and Γ_3 groundstates. a) $\mathbf{Q}$ -integrated ($0 < \mathbf{Q} < 2.5\text{\AA}^{-1}$) $S(\omega, T)$ for $x=0.35$. Open triangles show the mapping background (discussed in Section 8.2), and vertical dashed lines are the resolution half-width of 1.65 meV. b) Net magnetic scattering at various temperatures. c) Calculated CEF $S(\omega, T)$ for two possible ground states: magnetic Γ_5 and nonmagnetic Γ_3 .

limited lineshapes constituting the CEF excitations yields the simulated spectra plotted in Fig. 8.2c. The comparison of Figs. 8.2b and 8.2c reveals that both CEF models are incompatible with the data. Instead there exists no clear evidence of either a localized excitation in energy or any clear indication of the temperature dependence predicted in the CEF models.

If excitations in the NFL $x=0.35$ are indeed nonlocalized in energy, one would expect to find magnetic scattering at energies much less than 3 meV. Figure 8.3a shows energy scans at $Q=1.3 \text{ \AA}^{-1}$ for $x=0.35$ and $x=0.0$ samples using the SPINS spectrometer at NCNR. Consistent with results at higher energies (Figs. 8.1 and 8.2), magnetic excitations between 0.4 meV and 8 meV are broad, featureless, and temperature independent from 1.4 K to 300 K. In order to test if the magnetic scattering in the $x=0.35$ sample peaks at the same AF wave vector observed in $Y_{0.55}U_{0.45}Pd_3$ [171], we carried out a series of energy scans at different wave vectors at $T=1.4$ K. The outcome shows no enhancement along any wave vectors probed, thus confirming the localized or single ion nature of the magnetic scattering (Fig. 8.3b).

Now in order to probe if there exists any magnetic scattering at an arbitrary ($Q = 1.95 \text{ \AA}^{-1}$) elastic position, we performed polarized neutron beam measurements on the $x=0.35$ ScUPd system at $T=5$ K using the BT-2 spectrometer at NCNR. The flipping ratios for both horizontal and vertical guide fields were measured to be ~ 20 . (See Chapter 3.2 for a review of polarized neutron techniques.) By subtracting the vertical field scattering intensity from the intensity measured under horizontal field in the spin-flip

scattering channels, $\frac{\partial^2 \sigma^{(+)}}{\partial \Omega \partial E}$, the presence of elastic magnetic scattering was observed.

The actual measured intensities for horizontal and vertical fields are 679.7 ± 8.2 and 655.7 ± 7.4 counts/hour, respectively at $Q=1.97 \text{ \AA}^{-1}$ and $\hbar\omega = 0$ meV. The net elastic magnetic scattering for $x=0.35$ is then 48 ± 22 counts/hour at $T=5$ K and $Q=1.95 \text{ \AA}^{-1}$. This was determined through using the following cross sections for magnetic scattering in the spin-flip channel for a paramagnetic system [43, 63]:

$$\frac{\partial^2 \sigma^{(+)}}{\partial \Omega \partial E_{HF}} = \frac{R_H}{R_H + 1} \left(M + \frac{2}{3} NSI + BG \right) + \frac{1}{R_H + 1} \left(N + \frac{1}{3} NSI + BG \right) \quad (8-1)$$

$$\frac{\partial^2 \sigma^{(+)}}{\partial \Omega \partial E_{VF}} = \frac{R_V}{R_V + 1} \left(\frac{1}{2} M + \frac{2}{3} NSI + BG \right) + \frac{1}{R_V + 1} \left(N + \frac{1}{2} M + \frac{1}{3} NSI + BG \right) \quad (8-1)$$

Formula (8-1) is the case for a horizontal field configuration, and (8-2) is the cross section for the case of a vertically applied field. In these expressions for the neutron spin-flip cross sections, the terms R_H and R_V represent the flipping ratios measured for each respective field configuration, and ratios involving these terms are broken up into two parts: the true polarized scattering process ($R_H/(R_H+1)$) and the bleed-through scattering due to imperfect polarization and flipping of the incident neutrons ($1/(R_H+1)$). The M term represents the neutron intensity from paramagnetic spin scattering, the NSI represents the scattering due to nuclear-spin-incoherent scattering, and the BG term represents scattering from nonmagnetic background processes. If the flipping ratio is large, then the ($1/(R_H+1)$) term may be neglected and the subtraction of the horizontal

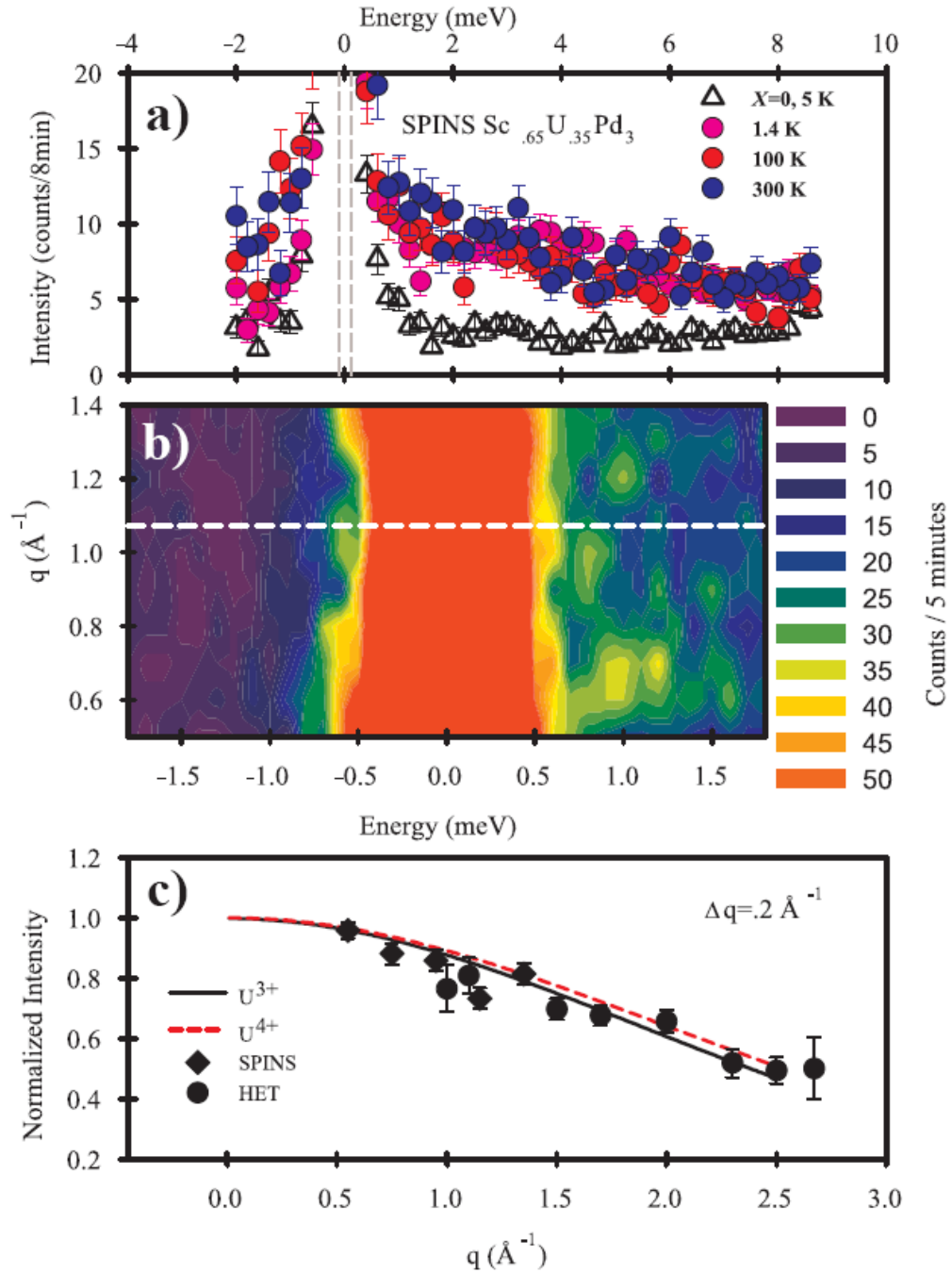


Fig. 8.3 SPINS data and form factor dependence for ScUPd ($x=0.35$) a) Energy scans at fixed $Q=1.3 \text{ \AA}^{-1}$ for $x=0.35$ and 0.0 on SPINS. Dashed vertical lines show the resolution halfwidth of 0.12 meV . b) (Q, E) map of magnetic fluctuations for $x=0.35$ at 1.4 K . The dashed grey line shows the AF ordering wave vector of $Q=(0.5, 0.5, 0)$ for $\text{Y}_{0.55}\text{U}_{0.45}\text{Pd}_3$ [171]. c) Q -dependence of magnetic excitations. Solid lines show calculated magnetic form factors for U^{3+} and U^{4+} ions which are responsible for the spin scattering observed.

and vertical field cross sections should yield a cross section of $\sim 1/2 M$, thereby providing a measure of the magnitude of the magnetic intensity at a given point in reciprocal space.

As a further check that the observed excitations are from U moments, the wave vector dependence of the magnetic scattering from both HET and SPINS experiments is normalized to the expected U^{4+} and U^{3+} magnetic form factors and plotted in Fig. 8.3c. The simple dependence on the magnetic form factor for U-ions shown by the magnetic scattering in this system is a clear indication that the origin of the scattering is magnetic and originates from the U-sites.

8.4 Dynamic (ω/T) scaling analysis $Sc_{1-x}U_xPd_3$ ($x = 0.35$)

The absence of any characteristic Q and E scale in the magnetic excitations of the $x = 0.35$ compound suggests that isolated U ions are responsible for the observed spin dynamical behavior. The unique temperature independent form of the magnetic scattering in $S(Q, \omega, T)$ (Figs. 8.1 and 8.2) bears a remarkable resemblance to that of $UCu_{5-x}Pd_x$, where the excitations at all Q and for the limited temperatures and energies ($\hbar\omega < 25$ meV) accessed display a form of NFL ω/T scaling [85, 174]. The similarities in the T -independent behavior of $S(Q, \omega)$ between the in the NFL concentrations of the $UCu_{5-x}Pd_x$ and $Sc_{1-x}U_xPd_3$ systems seems to suggest that a similar scaling treatment of the data in ScUPd system is viable. The measured $S(Q, \omega, T)$ can be related to the imaginary part of the dynamical susceptibility, $\chi''(Q, \omega, T)$, via the relation $S(Q, \omega, T) \propto \chi''(Q, \omega, T)/[1 - \exp(-\hbar\omega/k_B T)]$, where $[n(\omega) + 1] = 1/[1 - \exp(-\hbar\omega/k_B T)]$ is the Bose population factor. In calculating $\chi''(Q, \omega, T)$ in the $Sc_{0.65}U_{0.35}Pd_3$ system under various temperatures, a universal scaling collapse results when $\chi''(\omega/T)$ multiplied by $T^{1/5}$ falls onto a single curve for all data sets as a function of ω/T .

Turning now to Figure 8.4, the outcome of the scaling analysis can be seen. In this plot the SPINS data have been scaled to the absolute scale of the HET data through normalizing the elastic incoherent scattering of the $x=0.0$ and 0.35 ScUPd samples. Also in this final plot (Fig. 8.4), all data have been corrected for their magnetic form factor dependence, which is critical for the time-of-flight data due to the coupled E - Q values. The obtained scaling exponent of $z = 1/5$ represents a purely empirical analysis; however, slight deviations from this value induce substantial discontinuities in the resulting ω/T scaling plot. For comparison, the scaling exponent of $UCu_{5-x}Pd_x$ is $z = 1/3$ [174]. The solid line in Fig. 8.4 shows the theoretically proposed spin susceptibility scaling function $\chi''(Q, \omega/T) = 1/[A T^\alpha F(\omega/T)]$ with $\alpha=1/5$ and $F(\omega/T)=\exp[\alpha\Psi(1/2-i\omega/2\pi T)]$ [165]. Although notable deviations with the opposite sign from $UCu_{5-x}Pd_x$ are seen for small ω/T [174], the model accurately describes the data over a remarkable ω/T range (Fig. 8.4). Though this model is not intended to model scaling behavior arising from the influence of a spin-glass QCP (but instead localized quantum criticality from the competition between Kondo screening and RKKY interactions in the heavy Fermion Kondo systems), the similarity between the scaling prediction and the behavior observed in this ScUPd $x=0.35$ system is quite surprising.

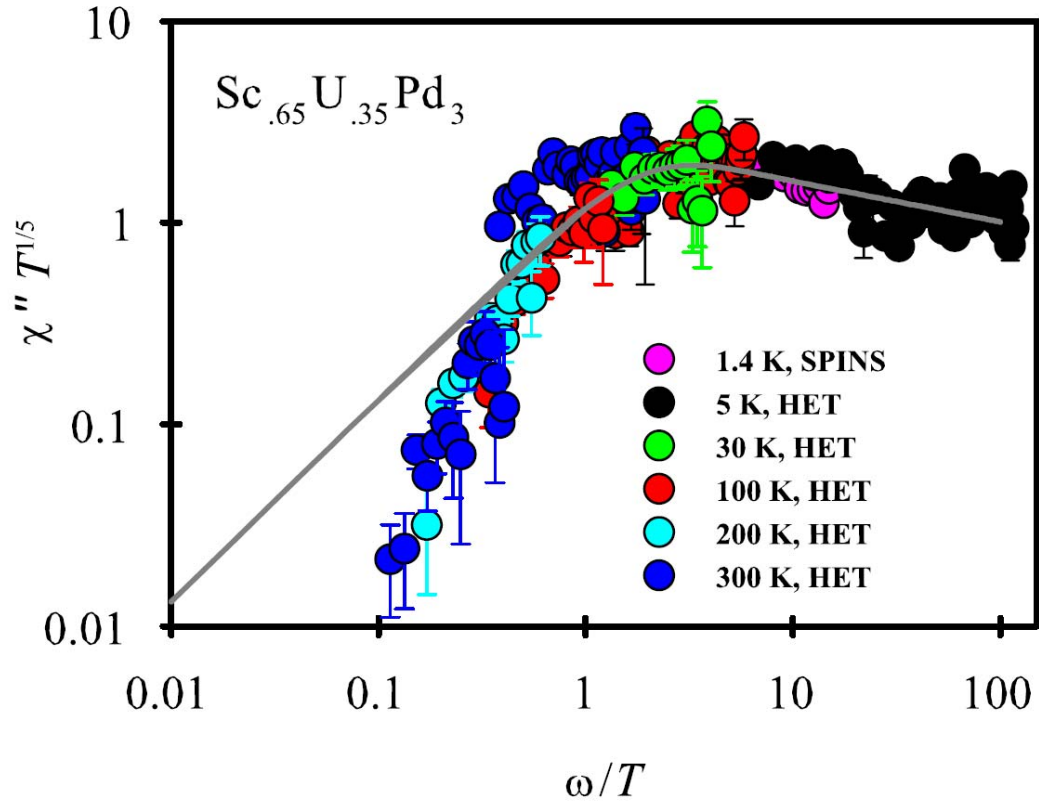


Fig. 8.4 ω/T Scaling plot for $\text{Sc}_{0.65}\text{U}_{0.35}\text{Pd}_3$. Data showing the collapse of $\chi''(\omega/T)T^{1/5}$ onto a universal curve for all temperatures and energies probed ($T=5\text{K}$ to 300K , $E=0.4\text{ meV}$ to 55 meV). The 300K HET data exhibit a slight deviation due possibly to underestimation of phonon contributions.

This discovery of the validity of ω/T scaling in the NFL $x = 0.35$ compound strongly suggests that the magnetic fluctuations in this system arise from the close proximity to a $T = 0$ K phase transition. Similar ω/T scaling was first identified in the NFL $\text{UCu}_{5-x}\text{Pd}_x$ system, but over a much smaller energy range (the (E, T) range of scaling validity) [174]. One key difference, however, is that $\text{Sc}_{0.65}\text{U}_{0.35}\text{Pd}_3$ exhibits no enhancement in its magnetic scattering spectra around the expected AF ordering vector of higher U concentrations [171]. Although the antiferromagnetism in $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ compounds with $x \geq 0.41$ may not control the spin dynamics for $\text{Sc}_{0.65}\text{U}_{0.35}\text{Pd}_3$, the scaling results presented here are consistent with the observation that the spin-glass transition temperatures of the NFL $x = 0.35$ and 0.3 compounds are suppressed close to $T=0$ K [169]. Since NFL behavior has previously been attributed exclusively to the proximity of an AF QCP at $T=0$ K such as in $\text{CeCu}_{5.9}\text{Au}_{0.1}$ [173], the observation of quantum critical dynamics due to a SG QCP in the presence of the NFL phase in ScUPd suggests that details of the $T=0$ K phase transition are unimportant for the NFL behavior.

8.5 Discussion and Conclusions

From the scaling analysis presented in Section 8.4, the spin dynamics seem to obey scaling behavior indicative of the close proximity of a QCP in the phase diagram of ScUPd. The only viable candidate for such a QCP in the phase diagram of ScUPd ($x=0.35$) is the nearby spin-glass QCP at $x \sim 0.3$ in which the spin glass freezing temperature is suppressed to $T = 0$ K. Theoretically, the NFL behavior may arise from the proximity to a $T=0$ K spin-glass quantum phase transition, although models in their present forms do not forecast the observed ω/T scaling [162, 163, 164]. Recent experiments on $\text{Ce}(\text{Ru}_{0.5}\text{Rh}_{0.5})_2\text{Si}_2$ [177] have attributed the NFL behavior to the disorder near a spin glass QCP [166, 167, 168]. On the other hand, disorder was found not to be the main cause for the NFL behavior in the quantum spin-glasses $\text{UCu}_{5-x}\text{Pd}_x$ at $x = 1.0$ and 1.5 [178, 179]. Assuming that disorder does not play a major role, one can envision three different microscopic scenarios for the NFL behavior in $(\text{Y,Sc})_{1-x}\text{U}_x\text{Pd}_3$. The first is the QKE [160], where one would expect localized spin excitations with nonmagnetic Γ_3 as the ground state. Inspection of previous data for $\text{Y}_{0.8}\text{U}_{0.2}\text{Pd}_3$ [172] as well as Figs. 8.1-8.3 for $\text{Sc}_{0.65}\text{U}_{0.35}\text{Pd}_3$ reveals no convincing evidence for localized states. The analysis of Bull et al. for lightly doped YUPd, in which a CEF level scheme is assigned, is predicated on the resolution of a well defined, low energy, localized CEF mode at a given momentum transfer that is then claimed to be weakly dispersive. Our data reveals no such localized mode at any energy, and thus precludes any assumption of a clearly defined CEF level scheme from the outset of our analysis. In addition, there is clear magnetic scattering at $E=0$ meV indicated through our polarized measurements on the ScUPd $x=0.35$ sample, and the temperature dependence of magnetic excitations does not follow the expectations of a simple CEF scheme (Figs. 8.1-8.3). The second scenario is possible influence of the $T=0$ K AF phase transition [165]. However, the maps of magnetic scattering in $(\mathbf{Q}, \omega)$ and the resulting picture of $\chi''(\mathbf{Q}, \omega, T)$ display localized moment dynamics with no evidence for U-U correlations (Fig. 8.1a). Instead, the data are consistent with ω/T scaling analogous to $\text{UCu}_{5-x}\text{Pd}_x$, and therefore can be understood

as manifestations of single-impurity critical scaling associated with a spin-glass phase transition suppressed to near 0 K [180].

In conclusion, the results presented in this chapter have shown that magnetic excitations in the NFL $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ ($x=0.35$) compound are broad and featureless in wave vector and energy. The absence of any characteristic energy scale, other than the temperature itself, suggests that the microscopic origin of the NFL behavior lies with individual U ions near a $T=0$ K spin-glass phase transition. Therefore, the NFL properties in a wide variety of f -electron systems including $(\text{Y},\text{Sc})_{1-x}\text{U}_x\text{Pd}_3$, $\text{UCu}_{5-x}\text{Pd}_x$, $\text{CeCu}_{6-x}\text{Au}_x$, and $\text{Ce}(\text{Rh}_{0.8}\text{Pd}_{0.2})\text{Sb}$ can be unified and be described by a common physical picture: proximity to a $T=0$ K quantum phase transition. Although the intrinsic disorder in these systems is essential for establishing the spin-glass ground state, it is unlikely to constitute main cause of the NFL behavior.

Chapter 9: Evolution of the spin excitations in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$

9.1 Introduction and Motivation

The precise origin of the non-Fermi liquid behavior in the electronic properties of a variety of the *f*-electron heavy Fermion compounds remains an issue of considerable debate [146, 165, 167]. This debate is especially poignant in modeling the properties of U- and Ce-doped non-Fermi liquid alloys. At the heart of this controversy is the role of disorder in the low-frequency electron dynamics of these systems and the extent to which it contributes to the NFL behavior [167]. One of the most widely studied and prototypical NFL compounds, $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$, has been shown to contain a large degree of U-inhomogeneity that was thought to play a role in its NFL behavior [158]. The subsequent discovery of greatly reduced U-disorder in the $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ system, which possesses a qualitatively similar phase diagram and NFL properties to those observed in $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$, implied that the influence of disorder on the fundamental properties of NFL mechanism in this class of systems was minimal. Instead, the presence of a 0 K magnetic instability in the phase diagram of this class of alloys has been put forth as the origin of the anomalous electronic behavior [146]. Specifically, for the case of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$, previous work suggests that the presence of a spin-glass (SG) quantum critical point (QCP) influences the electronic behavior near the NFL phase boundary [56].

Previous experiments on NFL liquid concentrations of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ have shown that the magnetic spectra of this compound in the proximity of the SG QCP exhibits a localized, single-ion type magnetic response distributed over a broad range of energies [56]. This contrasts the distinct CEF levels observed in the more disordered YUPd system; however, it appears as a striking parallel to the magnetic behavior observed in another NFL alloy, $\text{UCu}_{5-x}\text{Pd}_3$ (UCuPd) [85]. In both of these systems (ScUPd and UCuPd), the magnetic excitations exhibit little **Q**-dependence (other than the magnetic form factor) and a power-law-like decay as a function of energy. The most surprising feature, however, appears as the nearly *T*-independent magnetic response over vast ranges of energies and temperatures probed. Over these regions a form of hyperscaling known as ‘ ω/T ’ scaling has been shown to exist in the resulting dynamic susceptibility $\chi''(\mathbf{Q}, \omega)$, and the presence of this scaling is a well established consequence of a nearby singularity or QCP in the phase diagram of a system. In nonstoichiometric systems, this quantum critical interpretation of the magnetic behavior must naturally confront the influence of disorder on the resulting spin dynamics. Aside from the scaling behavior potentially resulting from a nearby QCP, there have therefore also been proposals that the magnetism in these systems is dominated by the presence of disorder due to the inherent alloying of these U-based materials. Both systems, ScUPd and UCuPd, in fact exhibit glassy ordered phases [88] and, despite the presence of a long-range ordered antiferromagnetic phase in their phase diagrams, also demonstrate uncorrelated magnetic excitations whose local nature may be attributed to disorder.

One way of resolving the precise role of disorder in the spin dynamics of the ScUPd system is to systematically map out the evolution of magnetism in this system as it is doped away from the SG QCP (and NFL regime) in its phase diagram. ScUPd offers a unique advantage over UCuPd in this regard through its ability to probe the role of

disorder resulting from rare-earth actinide site, U. The localized $4f$ electrons on the U-sites in this system constitute the most relevant source of magnetic disorder, which is dictated by the alloying process and the intrinsic properties of the sample. Within ScUPd, the U-concentration can be varied over an appreciable region (from $x=0$ -0.5) and can therefore provide a unique window into the relation between U-site disorder and the broad, featureless, magnetic spectrum observed near the SG QCP in this system. Since the detailed electronic phase diagram over these U-concentrations has also been recently reported, the evolution of magnetism in ScUPd as it is tuned across the NFL regimes in its phase diagram can also be analyzed.

In this chapter, I will present recent neutron scattering measurements that map out both the static and fluctuating magnetic order in the ScUPd system as it is tuned across its phase diagram. Unfortunately, only polycrystalline samples of this material are currently available, and this constrains the subsequent analysis of the magnetic signal. However, the results do allow for a general picture of how magnetism in this system evolves as it is tuned toward the SG QCP. The picture that appears is one of local, uncorrelated magnetic excitations observed about the SG QCP in this system evolving into weakly correlated spin excitations coupled to the appearance of the SG phase. The uncorrelated response, however, persists in all doping concentrations, and the newly developed magnetic correlations simply appear on top of this featureless magnetic signal.

9.2 Experimental Overview

For the following experiments, six concentrations of $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ were synthesized using arc-melting techniques with U concentrations of $x=0, 0.25, 0.35, 0.42, 0.45$, and 0.48 by M. B. Maple's group at the University of California, San Diego. The samples used for U concentrations of $x=0, 0.25$, and 0.35 are the identical 18g polycrystalline samples discussed in Chapter 8. The newly synthesized $x=0.42$ and 0.45 samples each have a mass of 18.6g. Finally, two different samples for $x=0.48$ were used: one polycrystalline ingot with a mass of $\sim 6\text{g}$ grown in a mirror-image furnace, and one 30.46g polycrystalline sample grown via arc-melting.

Due to the uncorrelated nature of the magnetic excitations previously observed in this ScUPd system and their distribution over large energy regions (as discussed in Chapter 8), neutron time-of-flight spectrometers were utilized to collect large regions of magnetic scattering over a broad energy spectrum simultaneously. For $\hbar\omega \geq 3 \text{ meV}$, data was collected on the HET spectrometer at the ISIS spallation neutron source at the Rutherford Appleton laboratory. Both $E_i=18 \text{ meV}$ and $E_i=65 \text{ meV}$ incident energies were used in order to map out the energy spectrum from $3 \text{ meV} \leq \hbar\omega \leq 55 \text{ meV}$. All samples were mounted within a closed-cycle refrigerator and temperatures from $T=5\text{K}$ to 300K were accessed.

For energies below $\hbar\omega=3 \text{ meV}$, the DCS chopper time-of-flight spectrometer was utilized at the NIST Center for Neutron Research. Using the superior resolution afforded via the cold neutrons available at DCS, the elastic ($\hbar\omega=0$) channel and energy range $0.2 \text{ meV} \leq \hbar\omega \leq 3 \text{ meV}$ could be studied. For these DCS measurements, samples were mounted within the liquid-He cooled cryostat and magnetism within the temperature range of $T=2\text{K}$ to $T=200\text{K}$ was probed. Although all 6 ScUPd concentrations were

studied using the HET spectrometer, only the $x=0.42$ and $x=0.48$ samples were measured at the DCS spectrometer. For the DCS experiments, the 30.46g $x=0.48$ sample grown via arc-melting was used, whereas for HET experiments, the ~6g floating-zone grown $x=0.48$ crystal was used.

9.3 Static order in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$

In order to first probe the static order in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ ($x=0.42$ and 0.45), spectra were collected on the DCS spectrometer at both 2K (below T_{SG} , T_{N}) and 30K (above T_{SG} , T_{N}). The relevant changes in the elastic spectra were isolated through the subtraction of high temperature data at equivalent $\mathbf{Q}$ positions. This allows for the removal of spurious signals, such as are caused by sample environment and air scattering, and remains viable as long as the chosen high-temperature data set does not exhibit appreciable differences in background from the low- T scans. The resulting elastic scans are shown in Fig. 9.1 for both the $x=0.48$ and 0.42 concentrations.

Turning first to the results for the $x=0.48$ concentration shown in Fig. 9.1a, the low temperature difference (2K-100K) spectra at the elastic position show four clear correlated magnetic components that were well fit by Gaussian lineshapes and an uncorrelated overall magnetic intensity shift that is modeled by a $\mathbf{Q}$ -independent constant term. The global fit to the 2K-100K spectra in Fig. 9.1a is plotted as a solid black line, whereas the individual constituent components are plotted as solid and dashed green lines. Two broad magnetic peaks (whose fits values are plotted as dashed green lines) appear centered at $\mathbf{Q}=0.865 \text{ \AA}^{-1}$ and $\mathbf{Q}=1.894 \text{ \AA}^{-1}$ with short coherence lengths of $\xi_{\text{min}}=16.2 \pm 1.5 \text{ \AA}$ and $\xi_{\text{min}}=14.7 \pm 1.5 \text{ \AA}$, respectively. In addition to this, two sharply correlated peaks (whose fit values are plotted as solid green lines) appear centered at $\mathbf{Q}=1.10 \text{ \AA}^{-1}$ and $\mathbf{Q}=1.91 \text{ \AA}^{-1}$ with $\xi_{\text{min}}=110 \pm 16 \text{ \AA}$ and $\xi_{\text{min}}=143 \pm 21 \text{ \AA}$, respectively. A further component, which is $\mathbf{Q}$ -independent within the scan range probed, is also necessary to model the magnetic scattering that appears in the elastic channel. This is plotted as a solid green line with an overall magnitude of 1.93 Cnts/monitor. Now when taking the temperature difference between 30K and 100K, all of the correlated components observed in the low- T spectra disappear. Instead, only a slight featureless $\mathbf{Q}$ -independent shift is observed with a magnitude of 0.39 Cnts/monitor. This minor shift between the 30K and 100K spectra may be attributed to either a small amount of residual incoherent magnetic scattering or a slight shift in the nonmagnetic background; however, in either case the only slight difference between the 30K and 100K spectra validates the use of the 100K spectra as a background reference for the elastic channel.

Looking again at the low- T spectra, the two long-range magnetic peaks can be attributed to the appearance of AF order in this $x=0.48$ U-concentration (consistent with the phase diagram plotted in Fig. 7.1b). For a cubic lattice with $a=4.017 \text{ \AA}$, the $\mathbf{Q}=1.10 \text{ \AA}^{-1}$ peak position corresponds to the $(\pi, \pi, 0)$ AF Bragg reflection, and the $\mathbf{Q}=1.91 \text{ \AA}^{-1}$ peak corresponds to the $(\pi, \pi, 1)$ AF Bragg position. These long-range AF peaks appear below 15K (Fig. 9.2a) and are also consistent with the previous phase diagram determined via susceptibility measurements (Fig. 7.1b). The position of the AF Bragg peaks is also consistent with magnetic structure determined from the detailed measurements of Dai et al. on the isostructural $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$. In their measurements, the

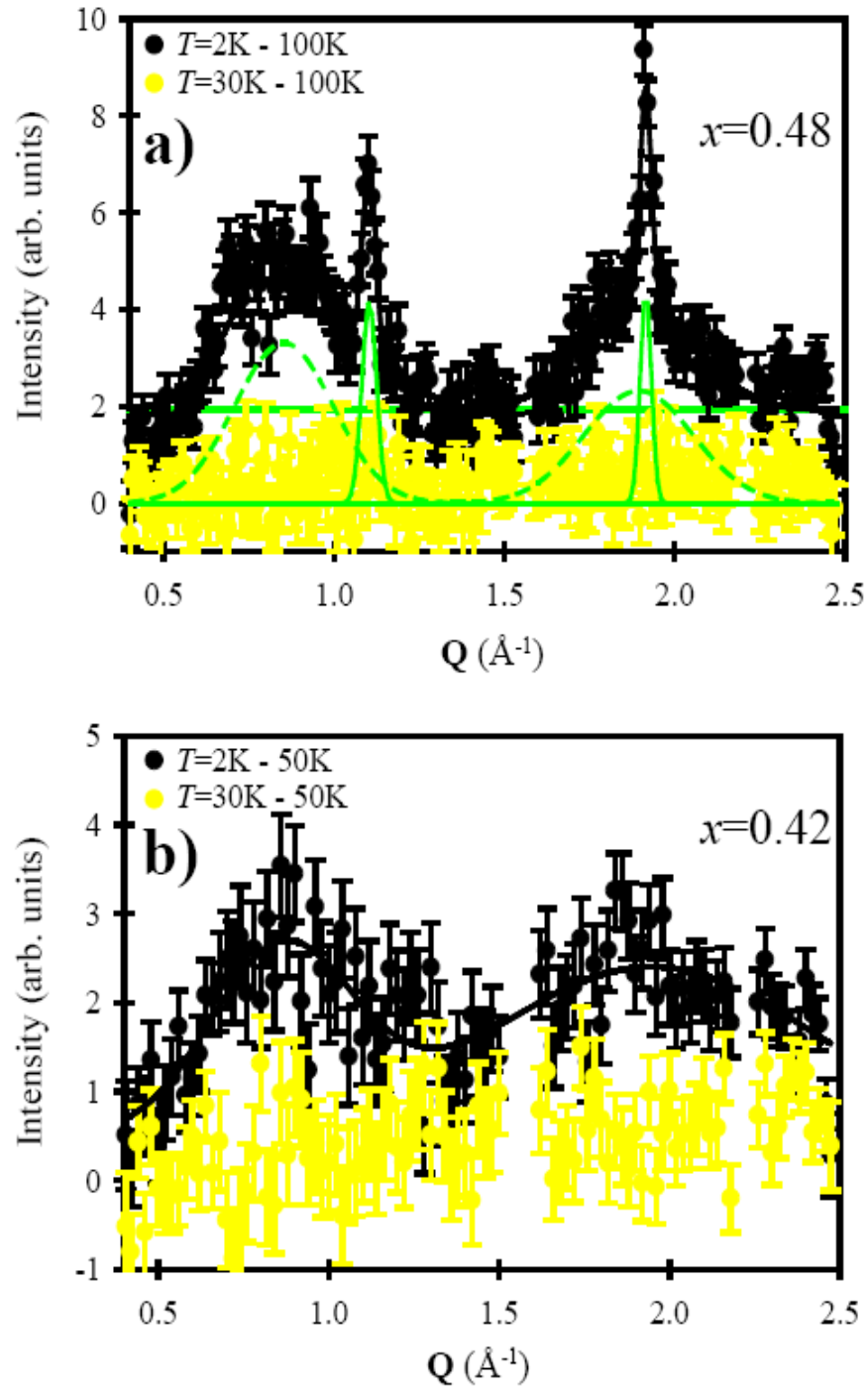


Fig. 9.1 Static order in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ ($x=0.42$ and 0.48). a) Temperature subtracted elastic scans averaged over $-0.1 \leq \hbar\omega \leq 0.1$ meV for $x=0.48$ sample. Solid green lines show the various global fit constituents as described in the text. b) Temperature subtracted elastic scans averaged over $-0.1 \leq \hbar\omega \leq 0.1$ meV for $x=0.42$ sample. The solid black line represents two Gaussian lineshapes used to fit the modulation along Q in the 2K-50K data.

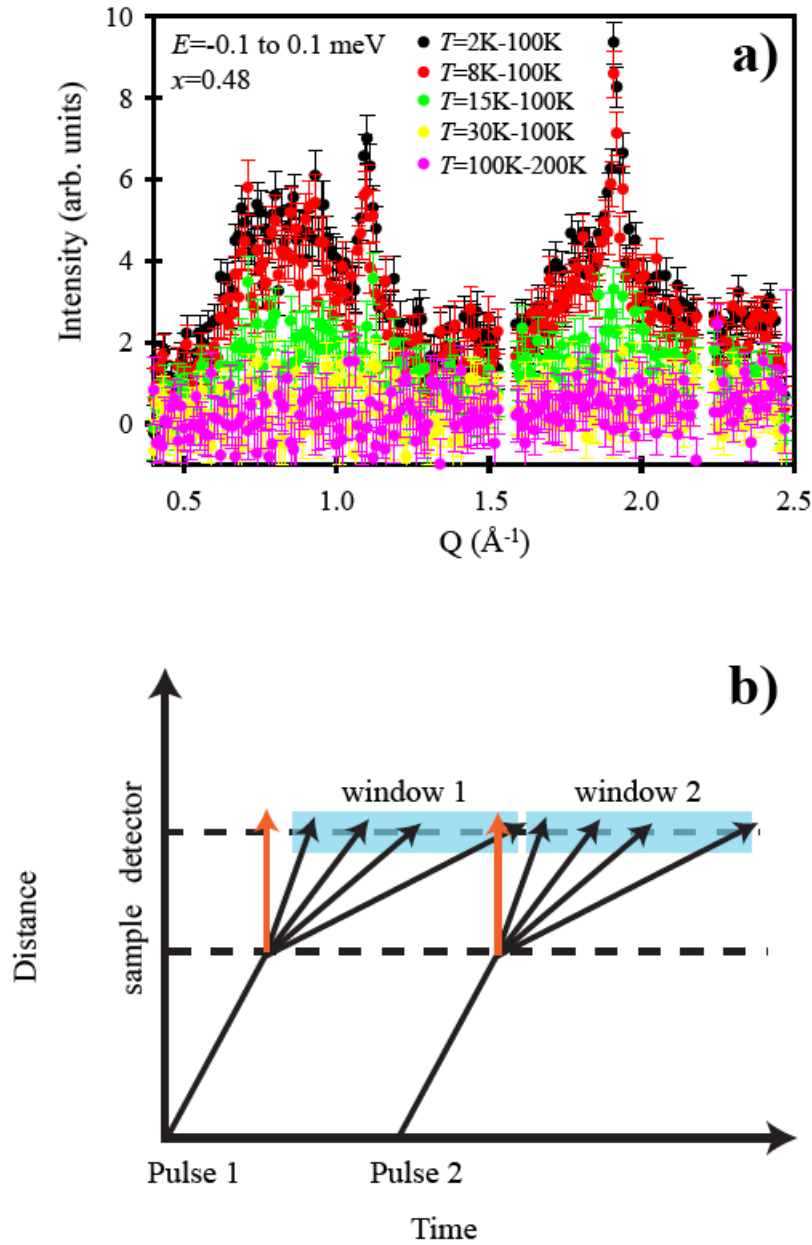


Fig. 9.2 Temperature dependence of the elastic order in $\text{ScUPd}(x=0.48)$ and (Time, Distance) diagram for the spurious fast neutron peak in time-of-flight spectra. a) Detailed T -dependence of the elastic scattering in $x=0.48$ ScUPd averaged over $-0.1 \leq \hbar\omega \leq 0.1$ meV. The persistence of weakly correlated peaks at 15K is clear from the 15K-100K data. b) Qualitative time and distance diagram for the time-of-flight scattering process. Black lines show the neutrons path both before and after scattering from the sample. The measurement window for scattering processes is extended in order to maximize the measurement's dynamic range for neutron energy loss. Once fast neutrons (red lines) are created; however, they may be fast enough to enter the measurement window of the previous neutron pulse. This creates spurious scattering signal at a given energy.

magnetic unit cell doubled the chemical unit cell in the *ab*-plane and is commensurate with it along the *c*-axis, thus yielding the first allowable magnetic Bragg reflections at $(\pi, \pi, 0)$ and $(\pi, \pi, 1)$. In ScUPd, the short ranged correlations observed centered at $\mathbf{Q}=0.865 \text{ \AA}^{-1}$ and $\mathbf{Q}=1.894 \text{ \AA}^{-1}$, however, do not match up well with the magnetic structure discussed above. The closest reflections lying to the peak centers are the disallowed $(\pi, 0, 0)$ at $0.782 \text{ \AA}^{-1}$ and $(\pi, \pi, 1)$ at $1.91 \text{ \AA}^{-1}$. The second peak may be attributed to shortrange AF clusters forming in certain regions of the sample; however, the first peak at $\mathbf{Q}=0.865 \text{ \AA}^{-1}$ fails to match up to the $(\pi, \pi, 0)$ reflection at $1.1 \text{ \AA}^{-1}$ and seems to preclude this interpretation. Both peaks should have a similar origin given their similar correlation lengths and onset temperatures, and it is therefore unlikely that the second peak is attributed to short-ranged AF clusters, whereas the first is not. The persistence of these short-ranged peaks above the T_N (Fig. 9.2a) also implies that the magnetic coupling of this ordered phase is more robust against thermally induced disorder.

One possible origin of this secondary ordered phase is the spin glass phase within the phase diagram of ScUPd. Whereas the phase diagram in Fig. 7.1b seems to imply that the low-*T* SG phase in this system evolves into an AF ordered phase, there most likely continue to exist glassy clusters within the AF-ordered concentrations that are electronically phase separated from the AF order. In this scenario, modulations along the SG ordering wave vectors would continue to be present in the AF ordered samples of ScUPd and may constitute an ordering distinct from that of the AF phase. Without knowing the precise nature of the possibly phase separate SG phase in this AF-ordered concentration, the most definitive check of this possibility is to look for identical magnetic ordering in a purely SG ordered system without coexisting AF order. In order to check this, we next studied a system now tuned to a slightly lower doping level at $x=0.42$ in the SG regime of the phase diagram.

Turning now to Fig. 9.1b, the resulting static order in the $x=0.42$ concentration can be seen. Temperature subtracted spectra at $T=2\text{K}-50\text{K}$ and $T=30\text{K}-50\text{K}$ are plotted as black and yellow symbols, respectively. The low-*T* subtraction data immediately reveal that the long-range AF order has disappeared in this sample. Instead only the two weakly correlated peaks remain with a $\mathbf{Q}$ -independent overall shift similar to that observed in the $x=0.48$ concentration. The two peaks are well fit by Gaussian lineshapes with peaks centered at $\mathbf{Q}=0.862 \text{ \AA}^{-1}$ and $\mathbf{Q}=1.95 \text{ \AA}^{-1}$ and with $\xi_{\min}=11 \text{ \AA}$ and $\xi_{\min}=5 \text{ \AA}$, respectively. The peak positions of these two broad magnetic peaks correspond approximately to those observed in the $x=0.48$ concentration with slightly broadened lineshapes; however, the larger $\mathbf{Q}$ -peak's fit value is shifted slightly higher. This is most likely due to the uncertainty in fitting the spectra due to the weaker intensity and broadening of the magnetic response in this concentration. The scattering intensity and resulting statistics observed within the $x=0.42$ spectra are considerably lower than that in the $x=0.48$, primarily due to the difference in sample masses studied (see section 9.2). The $T=30\text{K}-50\text{K}$ subtracted data reveal that these two weakly correlated peaks disappear from the elastic channel with only a weak $\mathbf{Q}$ -independent intensity shift remaining by 30K. All static magnetic features in this system seem to vanish above $T=15\text{K}$ with only $\mathbf{Q}$ -independent features (within the window available) persisting above this temperature (Fig. 9.1b).

The presence of short-range magnetic ordering along the identical wave vectors in this SG ordered ScUPd($x=0.42$) concentration as those observed in the AF-ordered ScUPd($x=0.48$) concentration implies that these peaks are intrinsic to the SG ordering in the ScUPd system and that this SG ordering persists into the AF ordered region of the phase diagram. In addition, the relative spectral weight along each ordering wave vector can give a gauge of the ordered moment attributed to each phase. A qualitative inspection reveals that even within the AF-ordered concentration ($x=0.48$), the majority of the moments remain in the SG phase rather than the AF phase, as evidenced by the vastly larger spectral weight of the short-ranged SG peaks (Fig. 9.1a). The persistence of the SG peaks at 15K in the $x=0.48$ sample also suggests that the SG phase persists above the indexed AF ordering temperature reported through susceptibility measurements in Fig. 7.1b. In order to further investigate the interplay between the SG and AF phases in these two ScUPd concentrations, we also probed the low-energy spin excitations about the relevant ordering wave vectors.

9.4 Low energy spin excitations in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$

The low energy excitations from $0.2 \leq \hbar\omega \leq 2$ meV were mapped out for both the $x=0.42$ and $x=0.48$ ScUPd concentrations over a variety of temperatures with an incident neutron wave length of $\lambda=4.8\text{\AA}$. The resulting spectra at low temperatures are plotted in Figs. 9.3a-d. There exist a variety of spurious features universally present in each $(\mathbf{Q}, \omega)$ spectrum, and it is beneficial to first discuss these before proceeding to the measured magnetic signal.

Since each sample studied contains U, there exists the low probability that each U-site will capture an incident neutron, fission, and emit fast neutrons. This probability is minimized by the use of depleted- U^{238} ions in the sample's composition; however, there remains a small isotopic abundance of U^{235} present in the sample. This minority isotope has a large cross section for fission, and the resulting fast neutrons emitted interfere with the timing resolution of time-of-flight spectrometers. This process is illustrated in Fig. 9.2b in which the measurement frame of a preceding neutron pulse inadvertently measures the fast neutrons emitted during a subsequent neutron pulse. This generates a high intensity neutron peak that is $\mathbf{Q}$ -independent although fortunately present only over a small spread of neutron energies. The energy where this spurious peak appears is highly dependent of the specific setup and measurement parameters of the spectrometer; however, the position of the fast neutron peak will shift dramatically as a function of incident neutron energy, and it is easy to identify. For the case of $\lambda=4.8\text{\AA}$, the fast neutron peak is clearly visible at $\hbar\omega=1.2$ meV with a tail extending up to 1.7 meV (Fig. 9.3a-b). Above this energy, there remains a large amount of spurious scattering due to air and spectrometer-intrinsic scattering processes. Additionally, since the DCS spectrometer does not have an evacuated detector chamber, at low energies and low momentum transfers there appears a substantial amount of small angle air scattering. For momentum transfers above $Q=0.4\text{\AA}^{-1}$, this spurious signal can be largely avoided as shown in Fig. 9.3a-b.

Looking at Figs. 9.3a and b, the $T=2\text{K}$ low-temperature magnetic spectra of both the $x=0.42$ and 0.48 samples both show a featureless magnetic response similar to that

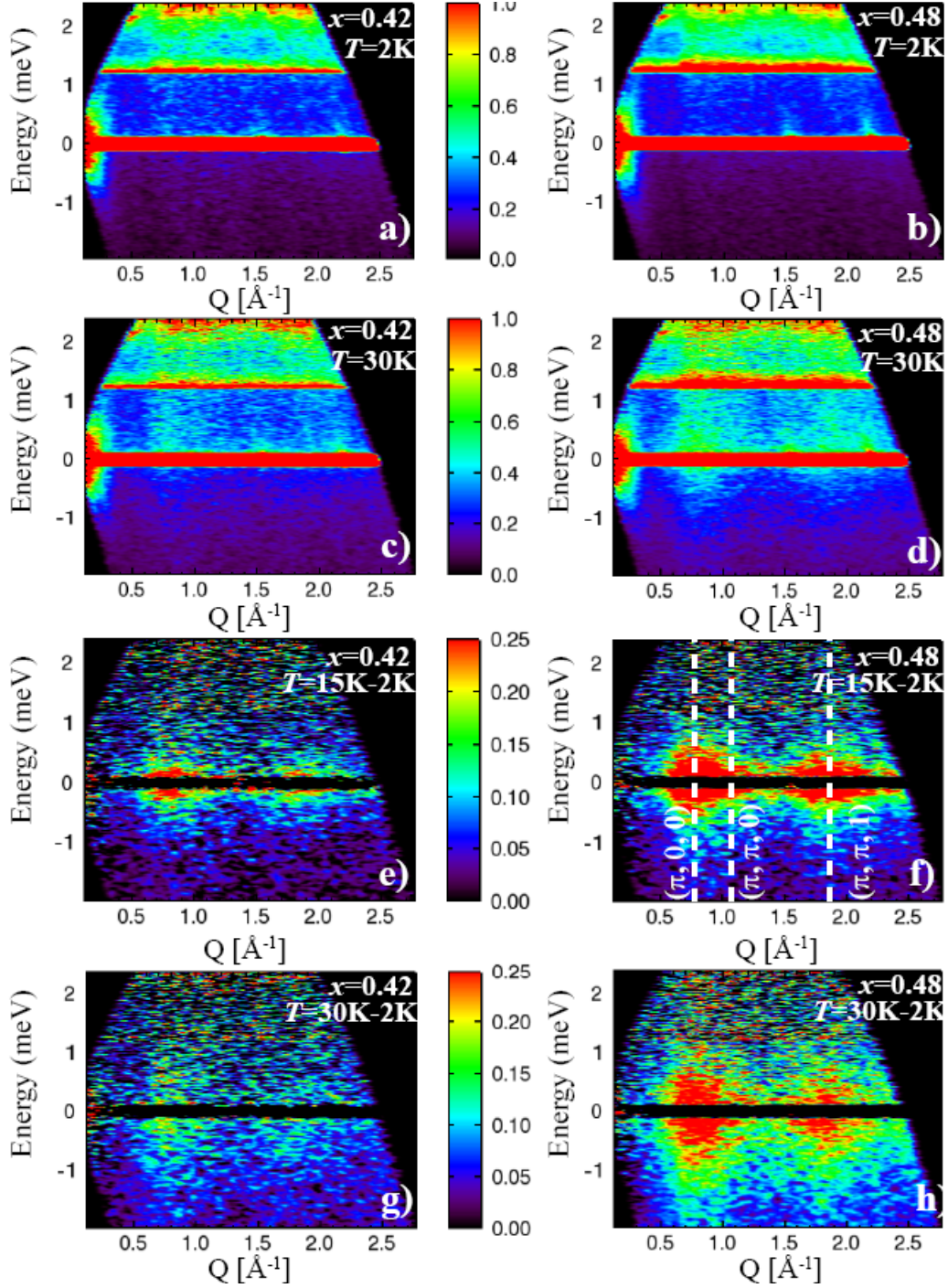


Fig. 9.3 Low- T DCS ($\lambda_i=4.8\text{\AA}$) spectra for both $x=0.42$ and 0.48 ScUPd. a-b) $T=2\text{K}$ spectra collected for the $x=0.42$ and 0.48 samples, respectively. c-d) $T=30\text{K}$ spectra collected for the $x=0.42$ and 0.48 samples, respectively. e-f) $T=15\text{K}-2\text{K}$ scans for $x=0.42$ and 0.48 samples. Dashed lines denote wave vector positions for reference. g-h) $T=30\text{K}-2\text{K}$ $S(Q, \omega)$ spectra for $x=0.42$ and 0.48 samples, respectively.

observed in the ScUPd($x=0.35$) system (see Chapter 8). The details and proof of the magnetic response at $T=2\text{K}$ will be discussed later in this section; however, it becomes clear that when the system is warmed to 30K the magnetic intensity is enhanced and develops a localized response along two distinct wave vectors (Figs. 9.3c-d). This can be demonstrated more clearly through taking the temperature subtraction of the featureless 2K spectra from the spectra at slightly higher temperatures that display a strengthened and correlated magnetic response. A temperature subtraction also allows the T -independent spurious scattering components to be removed and also allows any T -dependent magnetic processes to be clearly resolved. The results of this subtraction are plotted in Figs. 9.3e-h where both the $T=15\text{K}-2\text{K}$ spectra for the $x=0.42$ and 0.48 samples show a correlated quasielastic response along two wave vectors. The corresponding wave vectors for the $(\pi, 0, 0)$, $(\pi, \pi, 0)$, and $(\pi, \pi, 1)$ positions are plotted in Fig. 9.3f for reference. Upon warming to 30K, the $T=30\text{K}-2\text{K}$ subtraction spectra in Figs. 9.3g-h show that this localized enhancement is substantially diminished for the $x=0.42$ concentration and only slightly reduced in the $x=0.48$ sample. The enhanced quasielastic response also broadens in energy upon further warming from $T=15\text{K}$ to $T=30\text{K}$.

In order to examine the spectra in more detail, both constant- $\mathbf{Q}$ spectra and constant- E spectra can be plotted as one dimensional cuts across the intensity maps in Figs. 9.3e-h. The results for the $x=0.48$ spectra are shown in Fig. 9.4 where the magnetic response at a variety of wave vectors is plotted. Looking first at Fig. 9.4a, cuts taken along E at three different wave vectors $\mathbf{Q}_{\text{avg}}=0.8\text{\AA}^{-1}$, $\mathbf{Q}_{\text{avg}}=1.3\text{\AA}^{-1}$, and $\mathbf{Q}_{\text{avg}}=1.9\text{\AA}^{-1}$ show an identical intensity spectrum. The cuts in all three cases have had the nonmagnetic background scattering due to the aluminum sample can and air scattering removed. This was done via measuring the identical spectra with only an empty sample can in the spectrometer and subtracting the measured response from the sample data. The three cuts shown in Fig. 9.4a demonstrate that there exists a nearly $\mathbf{Q}$ -independent magnetic response at $T=2\text{K}$, as shown by the overlap of all three E -cuts for all three $\mathbf{Q}$ -vectors. The finite scattering amplitude at all energies on the neutron energy loss side of the spectrum shows this magnetic intensity relative to the measured background indicated by the data on the neutron energy gain side (where excitations are suppressed by a factor of $\exp(-\hbar\omega/1.7234)$). The solid line in Fig. 9.4a shows a linear fit to the scattering at all wave vectors within the energy window available. This uncorrelated magnetic response is similar to that observed in the low- T response of lower U-concentrations of ScUPd($x=0.25$ and 0.35) as discussed in Chapter 8.

Looking now instead at Fig. 9.4b, it becomes clear that once the $x=0.48$ system is warmed to $T=30\text{K}$ the response becomes much different. The scattering observed is no longer wave vector independent as evidenced by the enhanced intensities observed at $\mathbf{Q}_{\text{avg}}=0.8\text{\AA}^{-1}$ (black symbols) above the weakest observed at $\mathbf{Q}_{\text{avg}}=1.3\text{\AA}^{-1}$ (red symbols). The solid black line shows the measured fit to the isotropic $T=2\text{K}$ spectrum first plotted in Fig. 9.4a. From this data, it becomes clear that the magnetic excitations are strengthened at all wave vectors probed upon warming to $T=30\text{K}$ with a larger enhancement along the SG ordering wave vectors $\mathbf{Q}_{\text{avg}}\sim 0.8\text{\AA}^{-1}$ and $\mathbf{Q}_{\text{avg}}\sim 1.9\text{\AA}^{-1}$ than along the uncorrelated static position $\mathbf{Q}_{\text{avg}}=1.3\text{\AA}^{-1}$. In order to investigate the emergence of a $\mathbf{Q}$ -dependence to the magnetic scattering at $T=30\text{K}$, constant- E cuts can also be taken along $\mathbf{Q}$ at various temperatures.

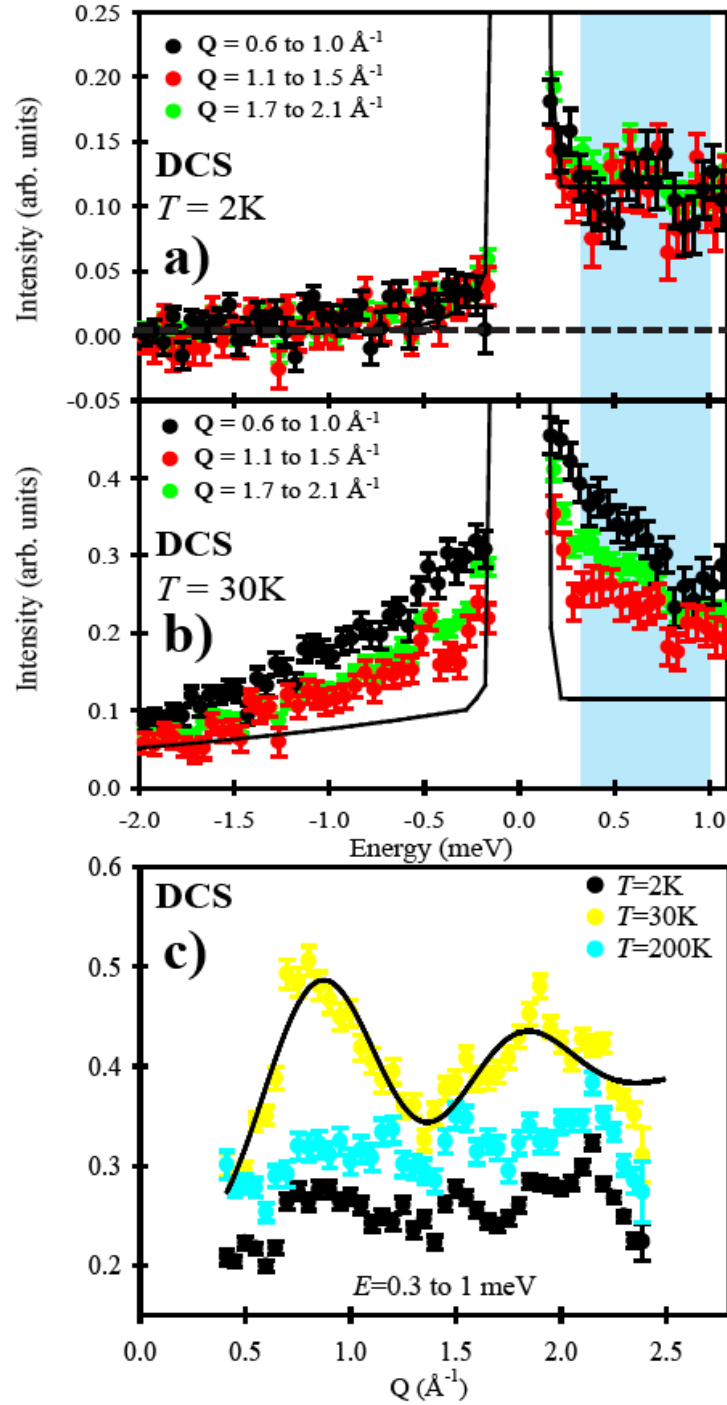


Fig. 9.4 Q -dependence of the low- E excitations in ScUPd($x=0.48$). a) $T=2\text{K}$ energy collected along the three wave vectors $Q_{\text{avg}}=0.8 \text{ \AA}^{-1}$, $Q_{\text{avg}}=1.3 \text{ \AA}^{-1}$, and $Q_{\text{avg}}=1.9 \text{ \AA}^{-1}$. b) $T=30\text{K}$ energy spectra collected along the same three wave vectors. c) Q -scans taken with E averaged from 0.3 to 1.0 meV at $T=2\text{K}$, 30K, and 200K. The solid black line is a fit to the function $I = C + A \sin(Qr)/Qr$.

Since the distribution of the correlated scattering shown in the intensity maps from Fig. 9.3e-h is quasielastic, the response should in principle be stronger at lower energies. However, in order to improve the statistics of a constant- E cut, a range of energies must be chosen, which in the present case is optimal for $\hbar\omega=0.3$ to 1 meV (shown as the blue shaded region in Figs. 9.4a-b). Performing cuts averaged over this energy range renders the $\mathbf{Q}$ -cuts plotted in Fig. 9.4c with $\hbar\omega_{\text{avg}}=0.65$ meV. The black symbols in this plot show data collected at $T=2\text{K}$ and confirm the presence of the nearly $\mathbf{Q}$ -independent low- T response of this system evidenced first in Figs. 9.3b and 9.4a.

Upon warming to $T=30\text{K}$, however, the data (yellow symbols) show two clear peaks in the now strengthened magnetic signal centered at approximately the ordering wave vectors for the SG magnetic ordered phase. These two peaks appear on top of a weakly $\mathbf{Q}$ -dependent magnetic enhancement present at all wave vectors probed and are strikingly similar to the structure of the magnetic order observed in the 2K static channel of this system. After warming to 200K, the modulation along $\mathbf{Q}$ completely vanishes and only a $\mathbf{Q}$ -independent enhancement above the 2K magnetic signal remains (as shown by teal symbols in Fig. 9.4c).

In Fig. 9.5a energy scans are plotted along the peak position $\mathbf{Q}_{\text{avg}}=0.8\text{\AA}^{-1}$ at both 2K and 15K using a smaller incident neutron wave length. One fundamental question yet to be addressed is the extent to which the elevated scattering amplitudes on the neutron energy loss side of the 2K spectra in Figs. 9.3a-b and 9.4a are magnetic. By looking now at both the neutron energy loss (positive E) and the neutron energy gain (negative E) sides of this low- T spectra over the broader range afforded by a higher incident neutron energy (Fig. 9.5a), the 2K energy loss scattering signal is seen to decrease approximately linearly with increasing E (black symbols) and is again observed to reside above the neutron energy gain background. By warming to 15K, where a known localized magnetic response appears along this wave vector $\mathbf{Q}_{\text{avg}}=0.8\text{\AA}^{-1}$ (as shown in Fig. 9.4), the extent to which the $\mathbf{Q}$ -independent signal at 2K constitutes an excitation can be resolved. The 15K data in this figure (green symbols) demonstrate that a strong magnetic enhancement appears along this wave vector above the 2K scattering signal. This 15K-2K response in a naïve picture leaves two scenarios: 1) scattering at 2K is simply a background process which the localized magnetic signal at 15K resides on top of, or, 2) the scattering at 2K also consists of excitations separate from the induced magnetic signal at 15K. By examining the neutron energy gain side of the spectrum, the answer to this becomes clear. Since excitations necessarily obey the principle of detailed balance in which the measured $S(\mathbf{Q}, \omega)=S(-\mathbf{Q}, -\omega)\exp(-\hbar\omega/k_{\text{B}}T)$, the expected scattering intensity at a value of $(-\mathbf{Q}, -\hbar\omega)$ can be forecasted via the measured response of the corresponding excitations at $(\mathbf{Q}, \hbar\omega)$. The resulting detailed balance forecasts for both scenarios 1) and 2) are plotted as solid yellow and blue lines, respectively. The excellent agreement between the blue line and the measured 15K energy gain intensities shows conclusively that the scattering observed in the 2K spectrum is intrinsically an excitation. Given that a qualitatively identical form of scattering in the $x=0.35$ ScUPd concentration was determined to be magnetic and that a similar phenomenon does not exist in the isostructural parent system ScPd₃, these 2K excitations are most likely magnetic in nature.

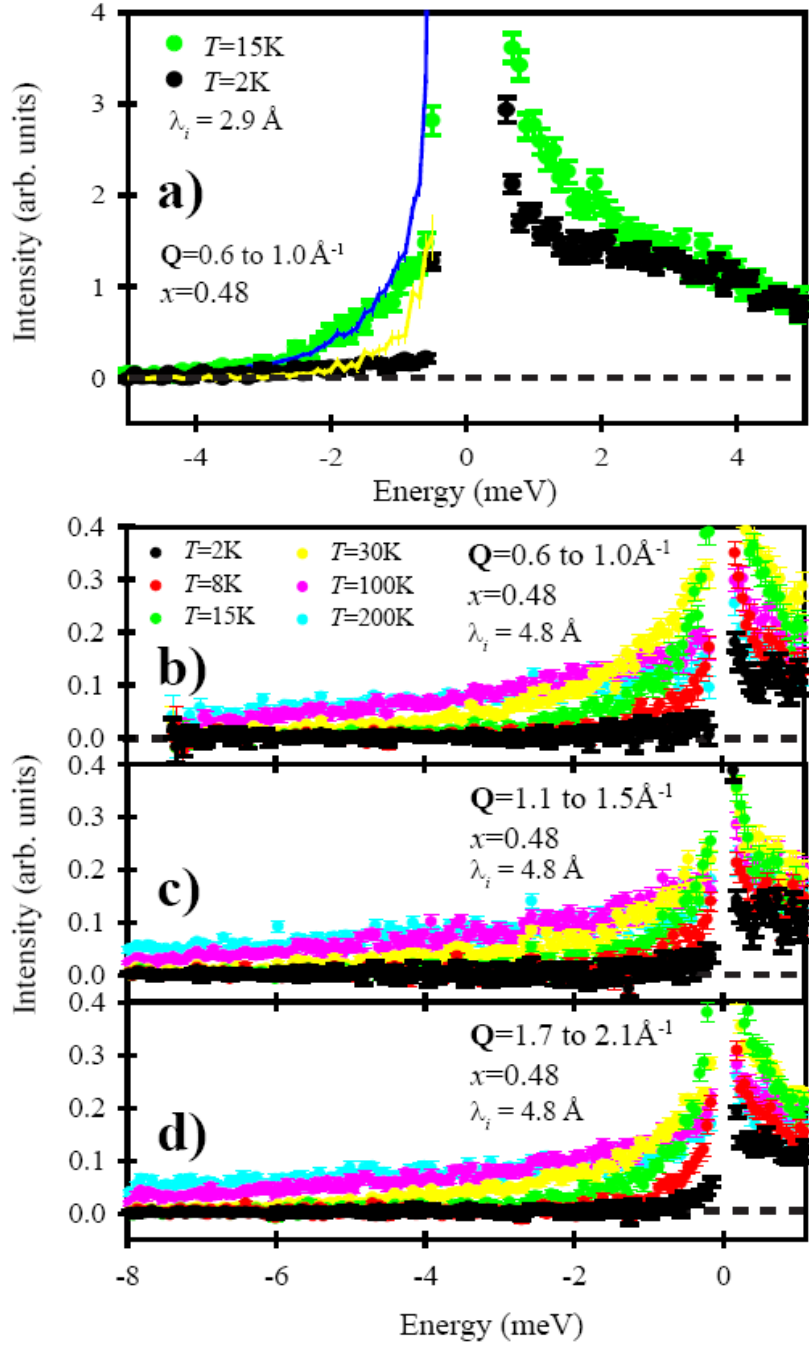


Fig. 9.5 Detailed balance comparison and T-dependence along $Q_{\text{avg}}=0.8\text{\AA}^{-1}$, $Q_{\text{avg}}=1.3\text{\AA}^{-1}$, and $Q_{\text{avg}}=1.9\text{\AA}^{-1}$ for ScUPd($x=0.48$). a) $\lambda_i=2.9 \text{ \AA}$ data taken at 2K and 15K. Solid blue and yellow lines are detailed balance calculations following scenarios outlined in the text. The excellent agreement between the blue line and the measured 15K data proves that the 2K energy loss signal corresponds to excitations within the system. b-d) $\lambda_i=4.8 \text{ \AA}$ data showing the detailed T -dependence of the E -spectra collected along the $Q_{\text{avg}}=0.8\text{\AA}^{-1}$, $Q_{\text{avg}}=1.3\text{\AA}^{-1}$, and $Q_{\text{avg}}=1.9\text{\AA}^{-1}$ wave vectors, respectively.

Now returning to the detailed T -dependence of the magnetic excitations along the three $\mathbf{Q}_{\text{avg}}=0.8\text{\AA}^{-1}$, $\mathbf{Q}_{\text{avg}}=1.3\text{\AA}^{-1}$, and $\mathbf{Q}_{\text{avg}}=1.9\text{\AA}^{-1}$ wave vectors, Figs. 9.5b-d plot the scattering via E -scans. These energy scans again confirm the uniform presence of an enhanced magnetic response upon warming to 30K in all wave vector channels with stronger enhancements observed in the SG ordering channels, $\mathbf{Q}_{\text{avg}}=0.8\text{\AA}^{-1}$ and $\mathbf{Q}_{\text{avg}}=1.9\text{\AA}^{-1}$. The quasielastic lineshape for $8\text{K} \leq T \leq 100\text{K}$ shows a continuous broadening with increasing T until the magnetic intensity degrades into the featureless and linearly E -dependent lineshape at 200K. A general feel for the temperature evolution of the magnetic scattering can be obtained through examining the energy gain side of the spectrum where it becomes clear that a sizable single-ion-type magnetic signal persists even at 200K. Although the data in this figure have not been corrected for detailed balance, at 200K the 2 meV intensity should only be suppressed by $\sim 10\%$ and the 4 meV intensity only by $\sim 20\%$ from its nominal value.

The extent over which the modulation in $\mathbf{Q}$ of the spin excitations persists at 15K was investigated through again using a higher incident neutron energy in order to collect a larger dynamic range. Using $\lambda_i=2.9\text{\AA}$, energies from $\hbar\omega=0.5$ to 5 meV can be probed and are plotted in Fig. 9.6a-b. In order to resolve the correlated magnetic scattering at 15K, the temperature difference spectrum was plotted for $T=15\text{K}-2\text{K}$ in Fig. 9.6b. The modulation along $\mathbf{Q}$ observed is similar to that in Fig. 9.4 with an extended modulation observed to higher $\mathbf{Q}$ values. The precise structure of this modulation is difficult to resolve due to the low scattering intensities and the form factor loss at higher- $\mathbf{Q}$ values. A cut along $\mathbf{Q}$ with an average energy of $\hbar\omega_{\text{avg}}=1$ meV ($\hbar\omega=0.5$ to 1.5 meV range highlighted as cut 1 in Fig. 9.6b) is plotted in Fig. 9.6a as red symbols fit by a solid green line. The two prominent peaks again confirm the previous result at lower incident energies; however, higher order peaks are not resolvable due to statistics. At higher energies, $\mathbf{Q}$ -cuts with $\hbar\omega_{\text{avg}}=4$ meV ($\hbar\omega=3$ to 5 meV range highlighted as cut 2 in Fig. 9.6b) show no sign of any correlated magnetic scattering. This clearly demonstrates that by 4 meV all resolvable contributions from the magnetic scattering localized at the SG ordering wave vectors vanishes.

An identical type of magnetic behavior is observed in the low energy spin excitations of the $x=0.42$ sample. Although the intensity is weaker due to a smaller sample mass and intrinsic U-concentration, clear enhancements and correlated scattering in the low energy spin response appear in the 15K spectra as evidenced in Figs. 9.7a-b. Fig. 9.7b also seems to suggest that a small residual amplitude of the correlated spin excitations at $\mathbf{Q}_{\text{avg}}=0.8\text{\AA}^{-1}$ may still be present at 2K, although the statistics make it difficult to determine conclusively. In addition, the second peak at $\mathbf{Q}_{\text{avg}}=1.9\text{\AA}^{-1}$ is barely visible in this concentration, and the data may suggest that the $\mathbf{Q}$ -modulation itself has shifted to a slightly higher $\mathbf{Q}$ than in the $x=0.48$ sample. To resolve this definitely, however, better statistics and a broader $\mathbf{Q}$ -range are required.

The overall trend in the inelastic signal, therefore, appears as a combination of 3 components: a single-ion type magnetic response, and two correlated components along the SG ordering wave vectors. The first, single-ion type, component is a $\mathbf{Q}$ -independent response similar to that observed in the $x=0.35$ concentrations. This response is present at the lowest T probed and is enhanced upon warming out of the SG/AF ordered phase. Above T_{SG} the precise T -dependence of this $\mathbf{Q}$ -independent response is difficult to

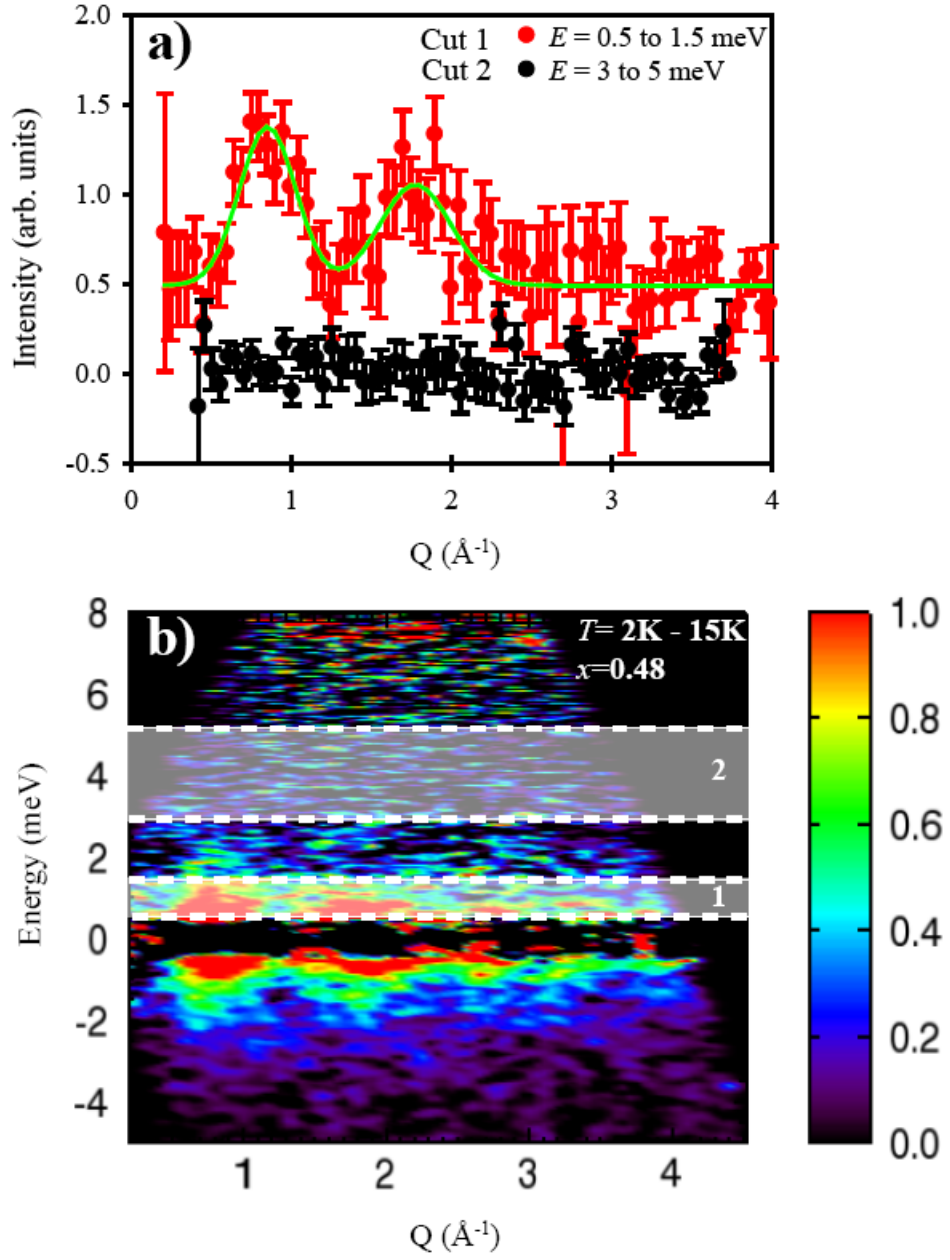


Fig. 9.6 $T=15\text{K}-2\text{K}$ $\lambda_i=2.9\text{\AA}$ DCS spectra for ScUPd($x=0.48$). a) Constant- E cuts along Q with both $\hbar\omega_{\text{avg}}=1.0$ meV (cut 1) and $\hbar\omega_{\text{avg}}=4.0$ meV (cut 2). The green line is a fit to two Gaussians on a linear background. b) (Q, ω) map at $T=15\text{K}-2\text{K}$ with the energy regions and paths of cut 1 and cut 2 highlighted.

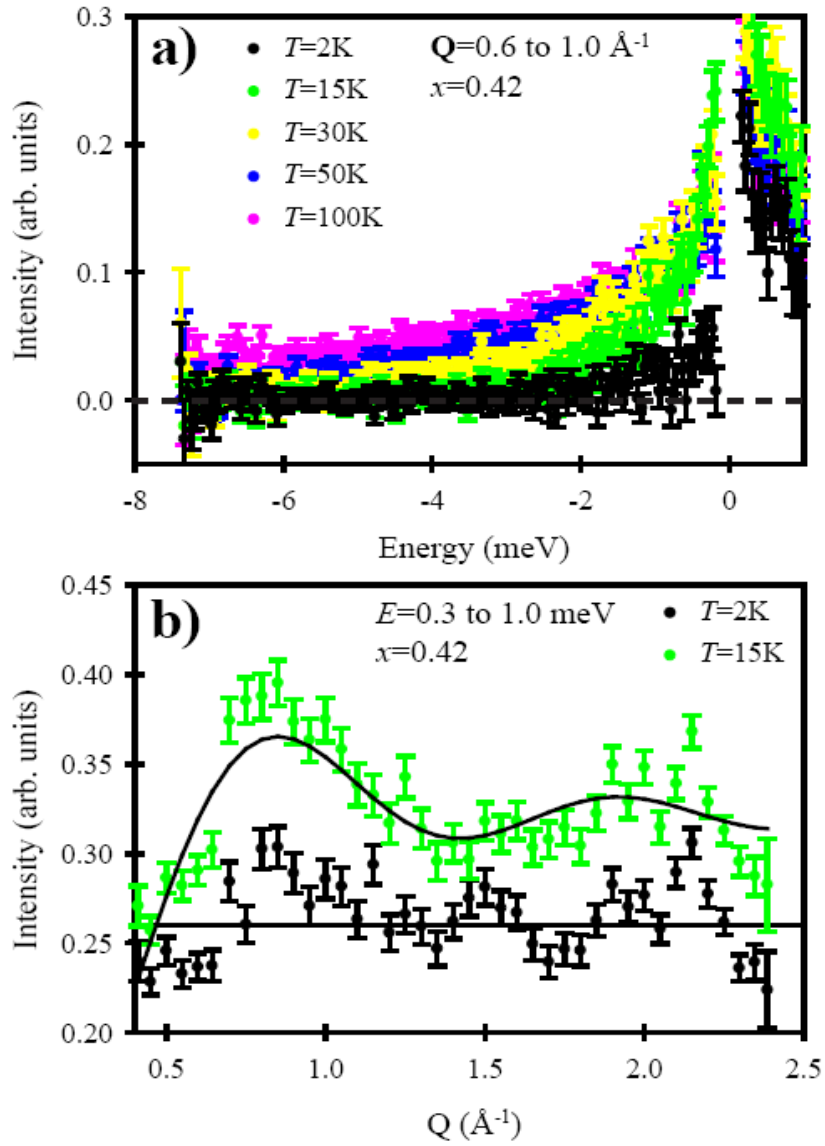


Fig. 9.7 Detailed T -dependence and Q -dependence of the low- E excitations in ScUPd($x=0.42$). a) Energy spectra collected at $T=2\text{K}$, 15K , 30K , 50K , and 100K with $Q_{\text{avg}}=0.8 \text{ \AA}^{-1}$. b) Q -cuts with $\hbar\omega_{\text{avg}}=0.65 \text{ meV}$ at both 2K and 15K . The solid black line modeling the 15K response is a fit to the functional form $I = C + A \sin(Qr)/Qr$.

precisely determine due to the substantial correlated scattering that appears along the SG ordering wave vectors. However, it is clear that the T -dependence of this single-ion scattering is extremely weak, and a substantial component of the signal remains even at 200K. The overall picture of this single-ion response is then one of extremely weak T -dependence from 200K to 30K, below which, the single-ion magnetism is rapidly suppressed (although some signal remains even at 2K). The two correlated components centered near the SG ordering $\mathbf{Q}$'s behave in a qualitatively similar fashion in which their peak intensities (and peak spectral weight) are reached around 30K. Below 30K, the peaks are sharply suppressed and vanish by 2K, and, above 30K, they slowly degrade until they are no longer resolvable by 200K.

The correlation between the elastic and inelastic components of the scattering from the $x=0.48$ sample are plotted as a function of temperature in Fig. 9.8a. The integrated fluctuating moments from $0.3 \leq \hbar\omega \leq 1$ meV along the three previously discussed wave vectors $\mathbf{Q}_{\text{avg}}=0.8\text{\AA}^{-1}$, $\mathbf{Q}_{\text{avg}}=1.3\text{\AA}^{-1}$ and $\mathbf{Q}_{\text{avg}}=1.9\text{\AA}^{-1}$ are plotted along with the static moment ($-0.1 \leq \hbar\omega \leq 0.1$ meV) integrated over $Q=0.5$ to $2.5 \text{\AA}^{-1}$. While the total static moment decreases sharply at 15K (above which all correlated peaks disappear) and slowly decreases above 30K, the inelastic spin fluctuations at all three wave vectors increase sharply at 15K and slowly taper off above 30K. The fluctuations measured at $\mathbf{Q}_{\text{avg}}=0.8\text{\AA}^{-1}$ and $\mathbf{Q}_{\text{avg}}=1.9\text{\AA}^{-1}$ primarily probe the correlated response of the spin spectrum below 30K while the fluctuations measured at $\mathbf{Q}_{\text{avg}}=1.3\text{\AA}^{-1}$ probe consist mainly of the single-ion-type magnetic signal. The qualitatively identical response of all three wave vectors suggest that the generalized behavior of both the correlated magnetism at the SG ordering wave vectors and single-ion type magnetism are controlled by the appearance of the corresponding static moments (ordered or disordered).

9.5 High energy spin excitations in $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$

After the low-energy response which couples strongly to the SG phase had been mapped out, experiments were performed on the HET time-of-flight spectrometer so that the magnetic excitations could be put on an absolute scale and in order to extend window of magnetic excitations to higher energies. In addition to this, previous data discussed earlier (and collected under identical experiment conditions) for $x=0$, 0.25, and 0.35 concentrations can now be compared directly to the newly synthesized samples $x=0.42$, 0.45, and 0.48. As a reminder, in this section the $x=0.48$ sample now has a substantially reduced mass of $\sim 6\text{g}$ (see section 9.2). Before examining the inelastic magnetic spectra for these systems, it is helpful to first verify the behavior of the static magnetic order in these concentrations. Fig. 9.8b shows the temperature subtracted (5K – 15K) magnetic spectra integrated from $\hbar\omega=-1$ to 1 meV for 4 different concentrations of ScUPd . Even though analyzing the elastic spectrum with the poorer resolution of the HET spectrometer is not ideal, the qualitative properties of the static magnetic order in these samples are verified. The $x=0.48$ sample again shows a AF Bragg reflection at $(\pi, \pi, 0)$ on top of a broader magnetic response which is also present in the $x=0.42$ sample. For $x=0.35$ and 0.25 concentrations no static magnetic signal can be resolved which is consistent with the substantially lower SG ordering temperatures of these systems ($T_{\text{SG}} < 5\text{K}$). Having verified the appearance of static AF and SG order in the $x=0.48$ concentration and SG

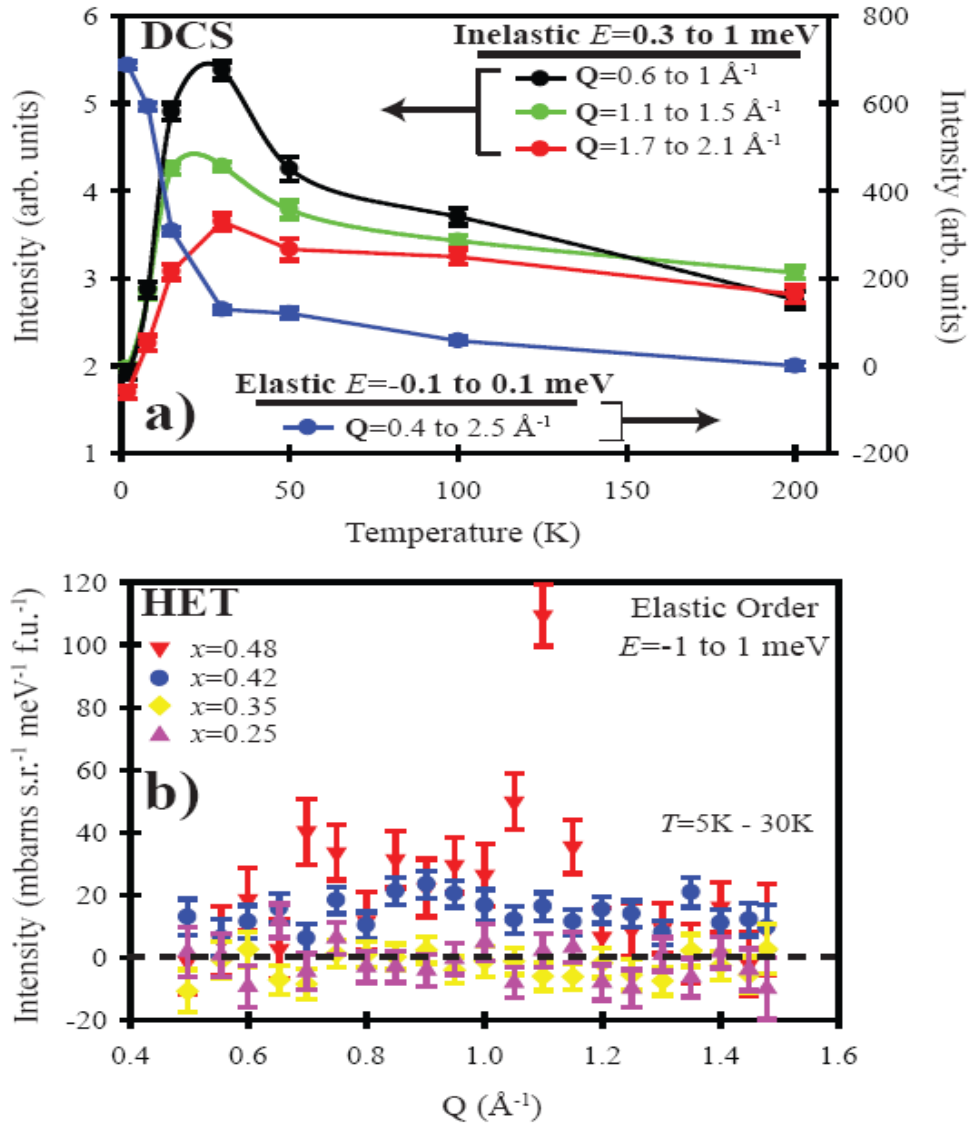


Fig. 9.8 Correlation between the static ordered moment and the fluctuating low-E moments in ScUPd($x=0.48$) and HET data probing the doping evolution at static order in ScUPd. a) T -dependence of the integrated fluctuating moments of the low- E inelastic response along three wave vectors ($Q_{\text{avg}}=0.8 \text{ \AA}^{-1}$, $Q_{\text{avg}}=1.3 \text{ \AA}^{-1}$, $Q_{\text{avg}}=1.9 \text{ \AA}^{-1}$). In addition, the temperature dependence of the integrated static magnetic response is overplotted as blue symbols. b) HET data resolving the static order in $x=0.25$, 0.35 , 0.42 , and 0.45 ScUPd samples. Data was integrated from $\hbar\omega=-1$ meV to $\hbar\omega=1$ meV.

order in the $x=0.42$ sample, it is now interesting to turn to the resulting inelastic spectra for these systems.

Initially an incident neutron energy of $E_i=18\text{meV}$ was utilized to study the evolution of the low- T spin excitations from $3 \leq \hbar\omega \leq 11$ meV as the ScUPd system is tuned from the undoped parent ScPd₃ compound into the AF/SG-ordered Sc_{0.52}U_{0.48}Pd₃ system. Figures 9.9a-f show the resulting spectra collected at $T=5\text{K}$ for all 6 U-concentrations studied. While comparing panels a) and b) for concentrations $x=0$ and $x=0.25$ shows no noticeable magnetic scattering at any energy, looking at panel 9.9 c) shows the clear emergence of a single-ion type magnetic scattering distributed over a broad range of energies for the $x=0.35$ sample. Upon further doping, the $x=0.42$ sample displays a large enhancement at all available energies and the uncorrelated, quasielastic nature of the magnetic response becomes clearer. For the $x=0.45$ sample, the single-ion type magnetic signal is further enhanced and some weakly resolvable correlations become evident for $\hbar\omega < 5$ meV. The emergence of weak correlation in the inelastic spin signal is consistent with the much clearer DCS data and will be discussed again later in this section. Finally, looking at the $x=0.48$ sample the spectrum shows a dramatic enhancement at all wave vectors and energies; however any correlation in the signal is difficult to resolve due to poor statistics. There also appears a slight background shift in the energy gain side of the $x=0.48$ sample's spectrum relative to the other concentrations, although this fails to account for the large increase observed in the magnetic signal.

In order to examine the doping evolution of inelastic response for $\hbar\omega \leq 10$ meV, constant- $\mathbf{Q}$ cuts were taken along E for the low- T spectra and overplotted in Fig. 9.10a. The $\mathbf{Q}$ values were averaged over a significant range (the entire low-angle detector banks) in order to compare the relative magnitude of the inelastic response between the various U-concentrations. This effectively allows the single-ion type magnetic response spread over all $\mathbf{Q}$'s to dominate the averaged intensity and provides a gauge of its doping dependence. The most significant change in the magnetic spectra in Fig. 9.10a is simply the overall intensity which increases dramatically with increased U-doping; however the slope of the approximately linear energy dependence of the intensity seems to systematically increase as the system is tuned from the $x=0.35$ to the $x=0.48$ concentration. This may have significant implications regarding the power-law-like type time dependence of magnetic correlations. It also implies at a cursory level that the scaling behavior observed in the $x=0.35$ concentration will break down in these higher doping regimes.

Now examining the constant- E scans of the low- T spectra for each U-concentration in Fig. 9.10b, reveals the systematic evolution of spin correlations in the inelastic response with increased doping. $\mathbf{Q}$ -scans were taken at $\hbar\omega_{\text{avg}}=5$ meV ($3 < \hbar\omega < 5$ meV) as indicated by the shaded region in Fig. 9.9f. The featureless inelastic response observed in the $x=0.35$ concentration evolves into a weakly correlated peak at $\mathbf{Q} \sim 0.86\text{\AA}^{-1}$ in the $x=0.42$ sample consistent with the results presented in section 9.3. The presence of the resolvable peak in the low energy response of the $x=0.42$ sample in the $T=5\text{K}$ HET data, while it is absent in the 2K DCS data, may be due to the slight T -difference between the two scans or the coarsened resolution of the HET spectrometer. The coarser resolution fundamentally alters the apparent behavior of the SG phase which also controls the T -dependence of the low- E spin dynamics. Continued U-doping shows that the peak

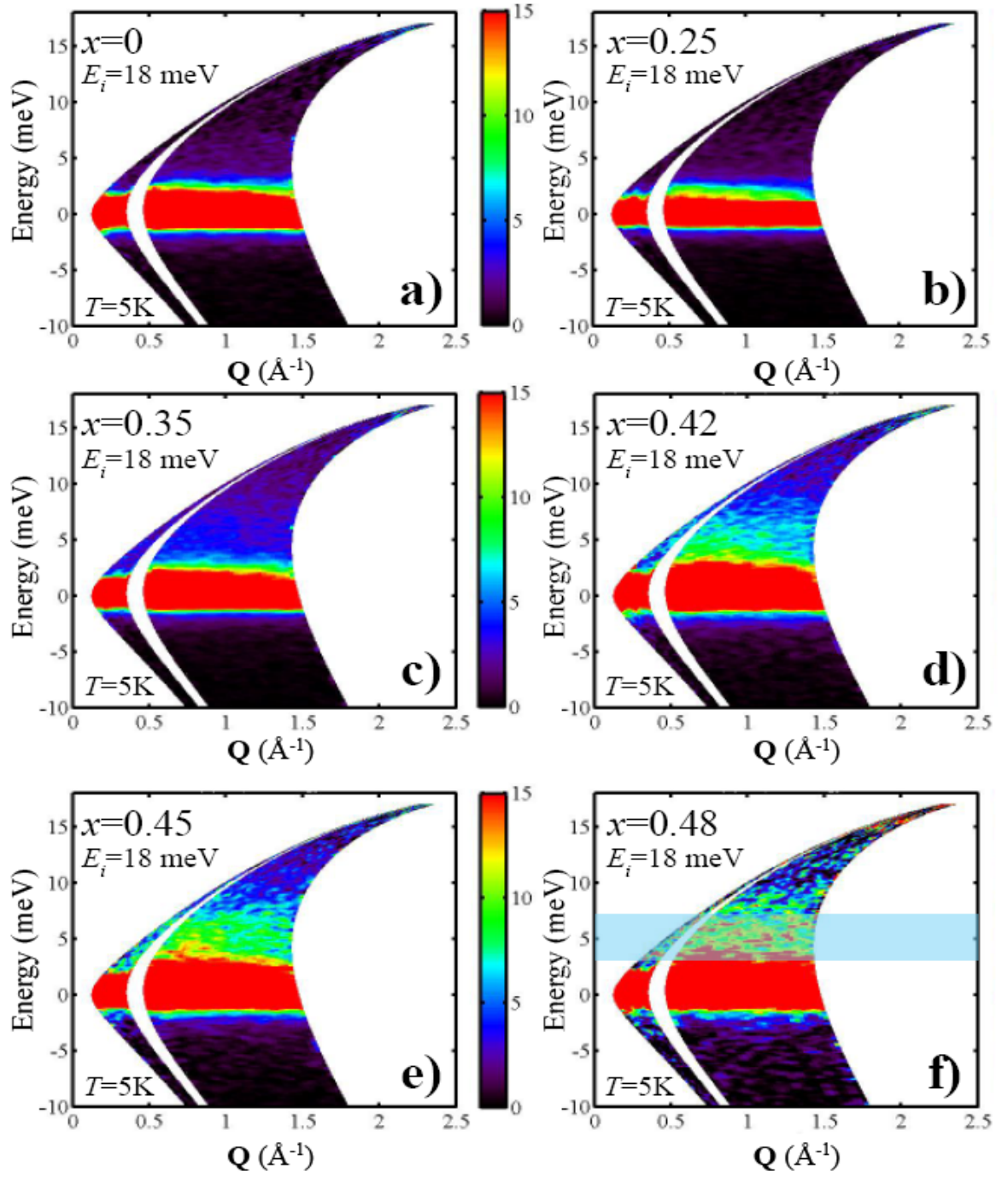


Fig. 9.9 $E_i=18$ meV HET spectra taken at $T=5$ K showing the doping evolution of the spin excitations in ScUPd. a-f) $T=5$ K ($\mathbf{Q}$, ω) maps of scattering intensities for the $x=0, 0.25, 0.35, 0.42, 0.45$, and 0.48 ScUPd samples, respectively. The shaded region in panel f) denotes the energies averaged over and the path of the constant- E cuts in Fig. 9.10.

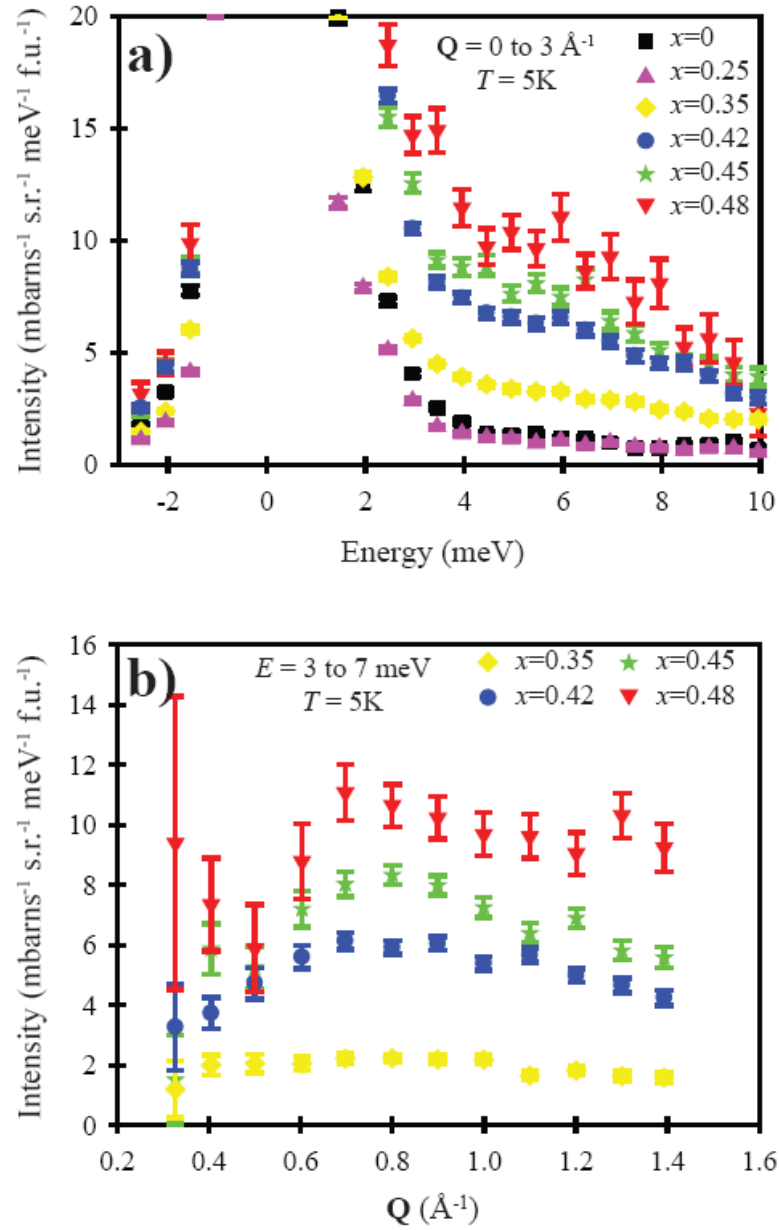


Fig. 9.10 ScUPd doping dependence of $T=5\text{K}$ constant- E and constant- Q scans from HET data. a) Energy scans for all 6 ScUPd concentrations which have been averaged over all momentum transfers available in the low angle detector banks of HET. b) Q -scans averaged over $\hbar\omega=3$ to $\hbar\omega=7$ meV. All scans in this plot were collected at $T=5\text{K}$.

at $Q \sim 0.86 \text{ \AA}^{-1}$ continues to strengthen in the $x=0.45$ and $x=0.48$ samples. The fact that high- Q portion of the peak retains a significant tail which also strengthens with doping suggests that this Q structure in the spin spectra is perhaps better described as a liquid-structure-like modulation due to short-range correlated spin clusters similar those observed in frustrated magnetic systems (and in the low- E spectra of UCuPd [85]). This formalism would also apply to the DCS low- E data presented in section 9.3 where the next Q -peak of the modulation is accessible. In fact, the Q -modulation presented in the inelastic data of Figs. 9.4c and 9.7b is well fit by a simple short range correlation model of $I \sim \sin(Qr)/Qr$ [181] as shown by the solid fit lines in these plots. In this model, r is simply the real space distance of the relevant correlated magnetic ions. At the moment however, a more thorough analysis with a larger experimental Q -range is required to accurately test this model.

The temperature dependence of the peak at $Q \sim 0.86 \text{ \AA}^{-1}$ in the $x=0.42$ sample is plotted in Fig. 9.11a. In this figure, the nonmagnetic scattering has been removed via the subtraction of the measured nonmagnetic parent spectrum under identical experimental conditions. Upon warming to $T=30\text{K}$, the $T=5\text{K}$ peak in the spin spectrum decreases slightly and continues a slow suppression with temperature until it completely vanishes by 200K . This is again consistent with the earlier DCS results in section 9.3. The 200K and 300K data show the persistence of the weakly T -dependent single-ion type magnetic response to extremely high temperatures. Fig. 9.11b also displays the T -dependence of the spin scattering via constant- Q scans averaged over $Q=0$ to $3 \text{ \AA}^{-1}$. The magnetic nature of the resulting signal is also verified by the detailed balance forecast plotted as solid lines on the energy gain side of the spectrum for all temperatures. Hence, again, both the Q -modulated and constant- Q scattering signals comprise magnetic excitations in this system.

The doping evolution of the inelastic excitations in all doping levels measured at $T=5\text{K}$, 100K and 300K is plotted in Figs. 9.12a-c. All of the plots in this figure have again had the nonmagnetic background removed through the subtraction of the corresponding parent scattering spectrum. In order to generate a more comprehensive picture of the Q -dependence, a larger energy range was integrated over with $\hbar\omega_{\text{avg}} = 8.5 \text{ meV}$ (from $\hbar\omega = 3$ to 14 meV), which allows larger Q -vectors to be reached. Due to the intrinsic coupling between energy transfer and momentum transfer in time-of-flight, spectra, each Q value is weighted by different energy ranges. Therefore, this plot is only useful as a qualitative overview. At $T=5\text{K}$, increased U-concentration again shows the development of a peak around $Q \sim 0.86 \text{ \AA}^{-1}$. At $T=100\text{K}$, the peak is significantly damped for the $x=0.42$ and $x=0.48$ concentrations, and by 300K the response for all doping concentrations is suppressed to an identical Q -independent magnetic signal. The only difference between doping levels at this temperature is an overall intensity shift.

The dominance of the single-ion-type spin excitations at high temperatures suggests that the high energy magnetic response will be similar. In order to investigate this, an incident energy of $E_i=65 \text{ meV}$ was used to probe magnetism at energies from $10 \leq \hbar\omega \leq 55 \text{ meV}$. The resulting spectra collected at $T=2\text{K}$ are plotted in Fig. 9.13. One observation that becomes quickly apparent is that the nonmagnetic parent system fails as a phonon reference system for dopings greater than $x=0.35$. The large U-concentrations sufficiently perturb the lattice dynamics of the ScPd_3 host matrix and make the removal

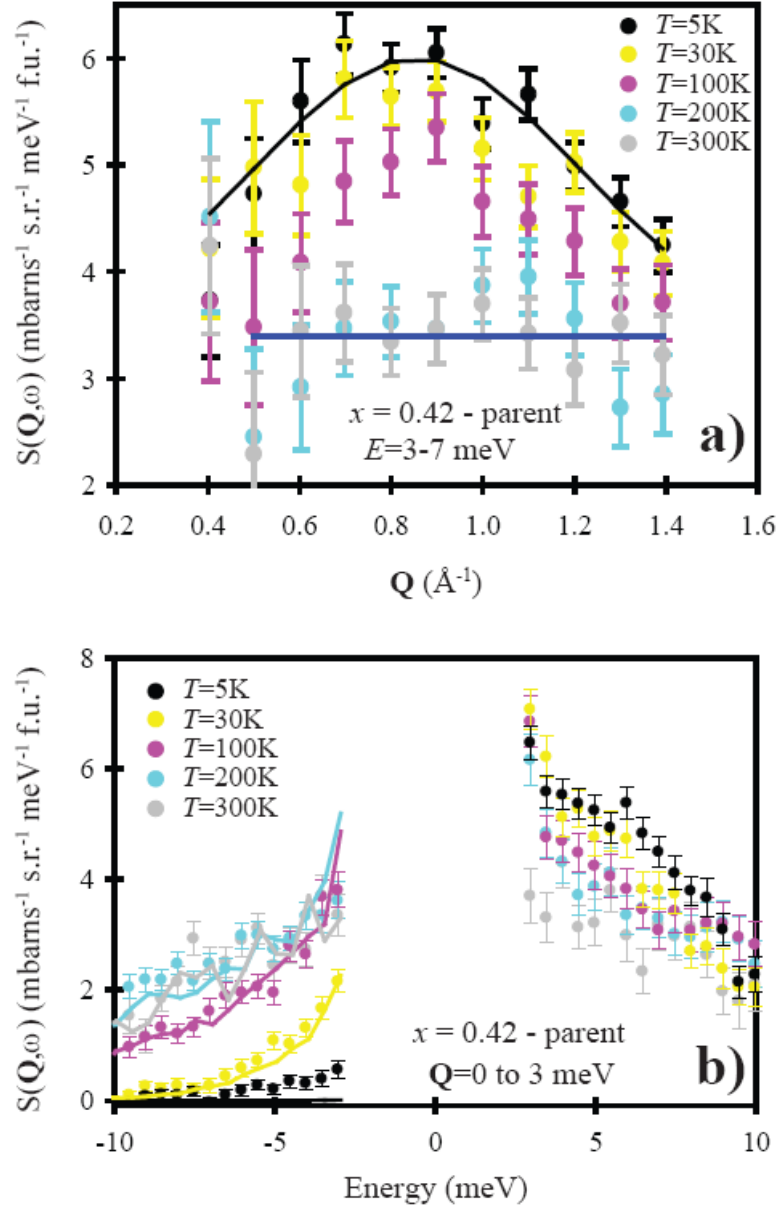


Fig. 9.11 HET data showing T -dependence of Q -scans and E -scans for ScUPd($x=0.42$). a) Q -scans averaged over $\hbar\omega=3$ to $\hbar\omega=7$ meV with the nonmagnetic parent spectra of ScPd $_3$ subtracted. Solid lines are guides to the eye only. b) E -scans averaged over the entire low angle detector banks. Solid lines on the energy gain side of the spectrum show the detailed balance calculations given the scattering measured on the corresponding neutron energy loss side of the spectrum. The forecast agrees with the data reasonably well.

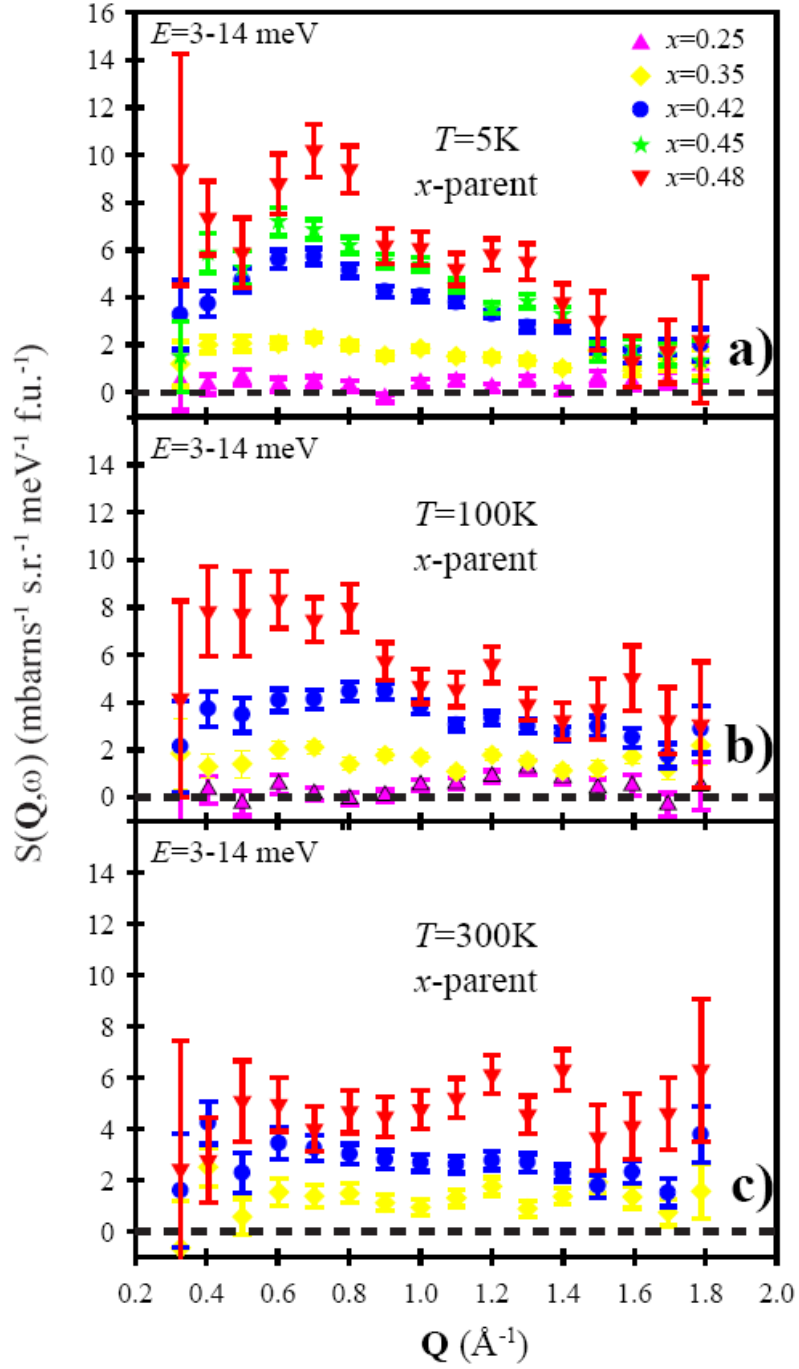


Fig. 9.12 Doping and temperature dependence of Q -scans collected on HET ($E_i=18\text{meV}$). a-c) Q -scans averaged over $\hbar\omega=3$ to $\hbar\omega=14 \text{ meV}$ with the nonmagnetic parent compound subtracted for $T=5\text{K}$, 100K , and 300K , respectively.

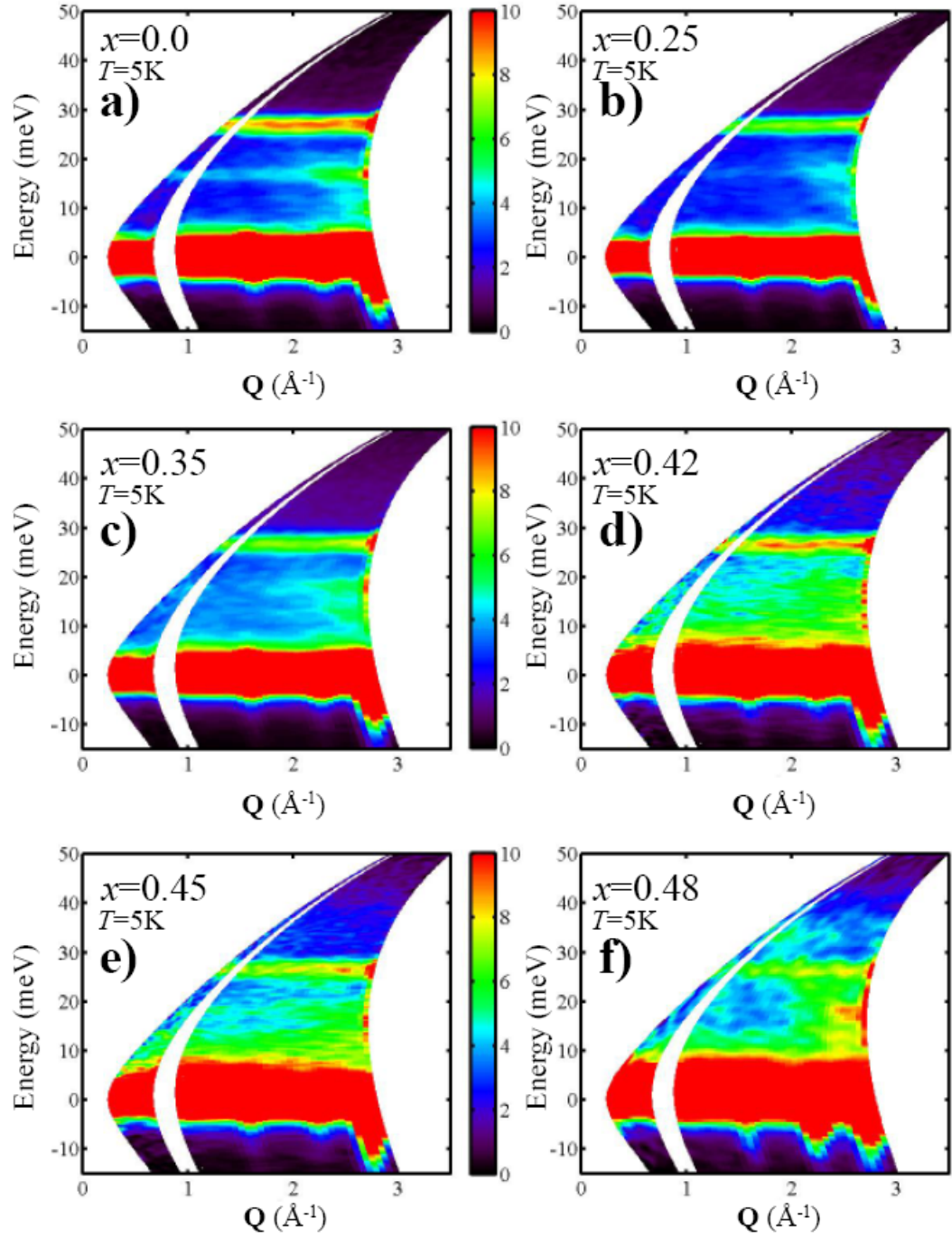


Fig. 9.13 $E_i=65$ meV HET spectra taken at $T=5\text{K}$ showing the doping evolution of the spin excitations in ScUPd. a-f) $T=5\text{K}$ (Q , ω) maps of scattering intensities for the $x=0$, 0.25, 0.35, 0.42, 0.45, and 0.48 ScUPd samples, respectively.

of phonon contributions from the neutron spectra problematic. Hence, even though there exists a large increase in magnetic signal visible in the energy window $10 \leq \hbar\omega \leq 30$ meV with U-doping (Fig. 9.13), this magnet signal will be neglected due to contamination from phonon scattering in this energy regime. Instead, I will focus on the magnetic scattering in the region above the prominent 27 meV phonon where the magnetic scattering in the $35 \leq \hbar\omega \leq 45$ meV window can be cleanly isolated.

Figure 9.14a shows low- T constant- $\mathbf{Q}$ cuts averaged over the entire low detector banks for all U-concentrations measured. As a function of increased U doping, the spectra show an increase in the magnetic scattering at all energies along with a simultaneous softening of the 27meV phonon mode. In addition, the 17 meV phonon mode in the parent system is split into two separate phonon energies by the U-concentration of $x=0.35$ and both modes are blurred at increased doping levels. This is possibly due to the large increase in quasielastic magnetic scattering in these higher dopings. Another prominent change in the phonon spectrum appears in the $x=0.48$ concentration, where a well defined mode is present at 35 meV in both the low and high angle detector banks. One curious point about this mode is the intensity arises from the lowest $\mathbf{Q}$ position in the low angle detector banks as shown in Fig. 9.13f. However, with the exception of this 35 meV mode in the $x=0.48$ concentration, the energy window from $35 \leq \hbar\omega \leq 45$ meV is reasonably clean and clear of phonon contamination for all samples studied (as highlighted in Fig. 9.14a).

Now plotting constant energy scans at low- T averaged over the range $35 \leq \hbar\omega \leq 45$ meV in Fig.9.14b, the magnetic scattering in this energy range is featureless and increases rapidly with increased U-concentration. The integration of the edge of the 35 meV mode for the $x=0.48$ sample is primarily reflected in the increase in the low- $\mathbf{Q}$ values for data from this concentration (Fig. 9.13f). When this is taken into account, it can be seen that the response at high energies is qualitatively identical between the $x=0.35, 0.42, 0.45$, and 0.48 concentrations with only an overall shift in the magnetic intensity dependent on the U-doping of the sample. The fluctuating moment in this energy and momentum range was calculated for the various U concentrations and plotted in Fig. 9.14c. The data reveal an exponential increase in the magnetic intensity with U-doping that is well fit by the function $e^{x/\tau}$ with $\tau = 10 \pm 0.35$. This is particularly surprising given the single-ion nature of the magnetic response where one would naively expect a linear scaling of the magnetic intensity with U-concentration.

9.6 Discussion and conclusions

In this chapter a systematic study of the evolution of the spin dynamics and static magnetic order in the ScUPd system was presented. Samples doped across the SG QCP in the phase diagram and into the AF ordered regime were studied over a dynamic range of $0.1 \leq \hbar\omega \leq 55$ meV and a temperature range of $2\text{K} \leq T \leq 300\text{K}$. The elastic magnetic signal in the highly U-doped samples $x=0.42$ and 0.48 exhibited three distinct components. The first component appears only in the AF ordered phase of the $x=0.48$ sample and consists of simple AF Bragg reflections consistent with the magnetic structure determined for the YUPd system. The second component appears as a short-range correlated modulation in $\mathbf{Q}$ that appears only below the SG ordering temperature in

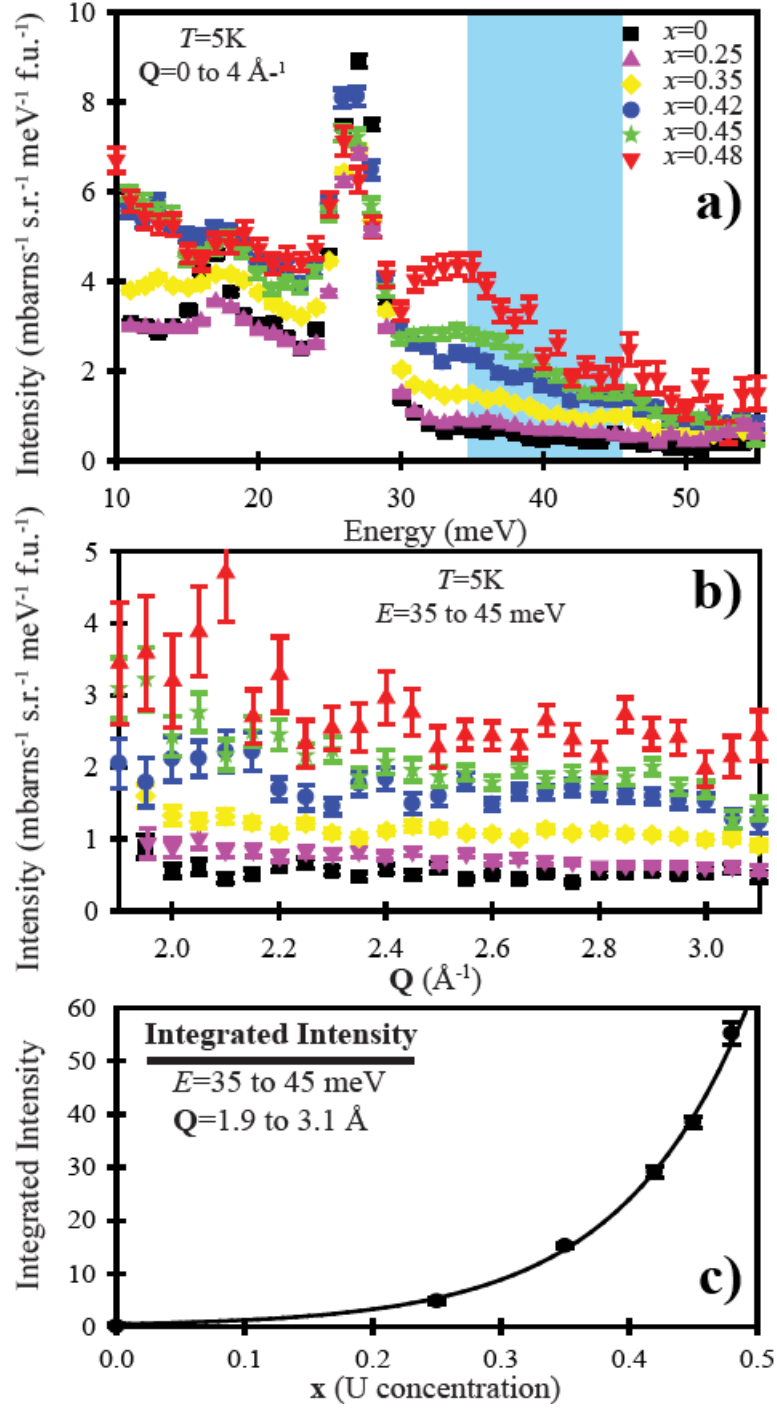


Fig. 9.14 HET $E_i=65\text{ meV}$ doping dependence of constant- Q and constant- E scans at $T=5\text{K}$. a) Energy scans averaged over the entire low angle detector banks. b) Q -scans collected with E averaged over $\hbar\omega=35$ to $\hbar\omega=45\text{ meV}$ (shown by shaded region in panel a) for all ScUPd concentrations. c) Inelastic signal integrated from 1.9 to 3.1 $\text{\AA}^{-1}$ and averaged over $\hbar\omega=35$ to $\hbar\omega=45$, plotted as a function of U-doping.

the $x=0.42$ and 0.48 samples. Samples with $x=0.35$ and 0.25 were unable to be cooled to sufficiently low temperatures in order to access their respective SG regimes; hence, no corresponding peaks were observed in these concentrations. The third component is present as a $\mathbf{Q}$ -independent, incoherent magnetic scattering signal that is greatly enhanced below the SG ordering temperature. Within the $x=0.48$ sample, the majority of the spectral weight resides in both the incoherent magnetic signal and within the liquid-like modulated signal intrinsic to the SG order, rather than within the AF Bragg peaks. This implies that a majority of the U-ions reside in short-range correlated clusters and only a small minority of these clusters freeze into long-range AF order. The electronic phase separation of these two magnetic phases could easily be overlooked in the previously established phase diagram that was generated via bulk susceptibility measurements.

The low energy inelastic response in the $x=0.42$ and 0.48 samples is strongly coupled to the onset of the SG phase, and the intensity of the spin fluctuations are maximal at the onset of the SG order. For temperatures distributed about T_{SG} , there are two corresponding components to the low energy inelastic response. The first of these components corresponds to the SG order and mirrors the $\mathbf{Q}$ -modulation observed when the SG order freezes into the elastic channel. The second component is the identical single-ion response observed in lower U-concentrations and discussed initially in Chapter 8. This single-ion response dominates the magnetic signal at high temperatures or for sufficiently high energies. At higher energies, the weakly $\mathbf{Q}$ - and T -dependent magnetic signal is fundamentally similar for all U-concentrations with only increasing overall intensities with increased U-doping. This seemingly single-ion type magnetic response, however, surprisingly increases exponentially with U-doping, and this contradicts any simple picture of the magnetic scattering as arising from a simple dilute mixture of noninteracting U-ions. Although future studies are needed to fully explore the $\mathbf{Q}$ -modulation of both the elastic and inelastic scattering in this system, the overall picture appears as one of the ScUPd system evolving into a regime of single-ion type physics as it is doped toward the SG QCP and NFL behavior.

Chapter 10: Conclusions

The still contentious pairing mechanism of high-temperature superconductors continues to fuel a colossal experimental effort in studying these materials. The intriguing possibility that magnetism may play a fundamental role in the formation of Cooper-pairs in the high- T_c cuprates has led to thorough investigations of the magnetism of these systems as they are doped from antiferromagnetic insulators into paramagnetic superconductors. Magnetic behavior in these systems has unveiled properties never before witnessed by science, and the appearance of new phenomena continues to intrigue researchers today. The quasi-two-dimensional nature and confinement of the spin/charge degrees of freedom in the CuO_2 planes of the cuprates has provided a fascinating playground for the exploration of charge/spin ordering in an effectively two-dimensional environment, exploration of the quantum two-dimensional antiferromagnetic Hamiltonian, and a variety of other rich physics avenues. Most importantly, magnetic properties fundamentally linked to the superconductivity in the high- T_c cuprates have been universally observed and are likely integral to the superconducting pair formation.

The vast experimental effort to map out the magnetism in the hole-doped high- T_c cuprates (reviewed in Chapter 2) has no parallel in the electron-doped systems. For this reason our systematic studies of the doping evolution of the magnetism in n -type cuprate $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_{4-\delta}$, along with the previous work of Kang *et al.*, represents the first such comprehensive study for the electron-doped cuprates. The magnetic phase diagram previously determined by Kang *et al.* uncovered the presence of two competing antiferromagnetic magnetic groundstates with superconductivity in PLCCO. At optimal doping where the antiferromagnetic order is completely suppressed, there potentially exists a magnetic quantum critical point in this system's phase diagram. Our studies of the spin dynamics in this PLCCO system revealed a variety of interesting phenomena. For samples that exhibit a coexisting AF order with the superconducting phase, the low energy spin dynamics couple to the onset of the AF order. As the AF order is continually weakened with increased doping, this coupling is also weakened until at optimal doping (where no zero field AF order is present) the spin excitations are only very weakly temperature dependent.

For all samples studied in the low energy and temperature regimes greater than the energy scale of the AF order, a systematic ' ω/T ' scaling behavior is observed in the low energy spin dynamics. The dynamic range of the scaling validity therefore increases with increased doping until optimal doping is obtained. This suggests that there exists a magnetic quantum critical point at or near optimal doping in the PLCCO system; however, the correlation lengths for the fluctuating magnetic order fail to diverge as the system is tuned closer to this QCP. This excludes the presence of a prototypical AF QCP, but perhaps not one arising from an intrinsically disordered phase such as spin-glass order.

In order to form a more complete picture of the magnetic dispersion in the n -type cuprates, we conducted high-energy mapping measurements of the magnon dispersion in PLCCO up to 300 meV. The resulting high-energy dispersion is vastly different from the hourglass-type dispersion observed universally within the hole-doped cuprates. Instead the dispersion is spin-wave-like at high energies and exhibits a weakly dispersive and

broadened commensurate response at low energies. The measured nearest neighbor exchange coupling, J , was unusually large, and in fact the dispersion appears sharper than that observed in the undoped parent system, Pr_2CuO_4 . It would be advantageous for future experiments to map out the precise doping evolution of the high-energy spin dynamics in PLCCO in order to better resolve the relevance of these high energy modes to the electronic behavior of the system.

The most important component of the spin spectrum in PLCCO is the newly discovered magnetic resonance mode, and it is analogous to the resonance excitations observed in a broad spectrum of classes of hole-doped cuprates. This mode was observed in the optimally-doped PLCCO concentration with $T_c=24\text{K}$, and it is intimately coupled to the superconducting phase in this material. Given the global picture of the spin dynamics and the established magnetic dispersion in the electron-doped cuprates, there exist large differences in the structure of magnetic excitations between hole- and electron-doped high- T_c systems. The resonance mode, however, is fundamentally identical in both classes of n - and p -type cuprates, thereby establishing it as the lone unifying feature present in the magnetism of the high- T_c cuprates, regardless of the doped carrier type.

The discovery of the resonance mode in PLCCO now provides a unique experimental window into the underlying, universal properties of the mode itself. Since PLCCO, and n -type cuprates in general, can be driven into their field-suppressed, nonsuperconducting groundstates much more easily than hole-doped cuprates, the link between the resonance mode and superconductivity can be further tested. Specifically, experiments previously not possible in hole-doped systems, due to the inaccessible upper critical fields necessary to destroy superconductivity, are now possible in the PLCCO system. The most important of these experiments, is exploring the relation between the resonance mode and superconductivity as the PLCCO system is continuously driven from superconducting to the normal state via the application of a magnetic field. Our results demonstrate that the resonance mode is smoothly suppressed as a c -axis aligned magnetic field is applied and vanishes above the upper critical field H_{c2} . The suppression of the mode itself tracks the suppression of the condensation energy of the system, further establishing the fundamental link between the resonance mode and the superfluid density present in the system. The application of a c -axis aligned magnetic field and the suppression of superconductivity also induces the appearance of competing AF order in optimally-doped PLCCO.

Previous experiments by Kang *et al.* have shown that in samples with coexisting zero field AF order with superconductivity such a competition exists; however, they were unable to resolve the appearance of field induced AF order in a sample with no zero-field antiferromagnetism. The competition previously argued by Kang *et al.* was countered by some as a simple modification of the coexisting AF order under field and unrelated to the suppression of the superconducting phase; however, the discovery now of field-induced AF order in an optimally doped PLCCO sample with no zero-field antiferromagnetism further proves the arguments of Kang *et al.* correct. The anisotropy of the field-induced effect, measured via the application of different magnetic field directions, further confirms that this effect is related to the suppression of superconductivity. In addition, the discovery of both field-induced AF order and the suppression of the resonance mode

under field suggest that there perhaps exists a smooth transfer of the resonance's spectral weight in to the static AF channel as magnetic field is applied. Future measurements that will place these field induced changes on an absolute scale are necessary to confirm this scenario.

Studies were also presented on the non-Fermi-liquid f -electron alloy $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$. For the $\text{ScUPd}(x=0.35)$ concentration, the spin excitations in this system differ greatly from those explored in the isostructural $\text{Y}_{1-x}\text{U}_x\text{Pd}_3$ system. Instead of clearly defined crystal electric field excitations, a featureless single-ion-type magnetic response was observed distributed over a broad range of energies. This spin signal was also weakly T -dependent and no resolvable temperature dependence could be observed from $T=5\text{K}$ to $T=300\text{K}$. Given that this system is in the close proximity of a spin-glass quantum critical point on the phase diagram, a scaling analysis was performed, and it was found that this system obeys ' ω/T ' scaling over all temperature and energy ranges measured. This is a strong indication that the spin dynamics couple to the quantum critical fluctuations from the nearby SG QCP, and the behavior is strikingly similar to that observed in the $\text{UCu}_{5-x}\text{Pd}_x$ system (also a U-based NFL alloy).

The systematic, doping-evolution of the magnetism in this $\text{Sc}_{1-x}\text{U}_x\text{Pd}_3$ system was carried out over a broad range of U-concentrations (for $x=0, 0.25, 0.35, 0.42, 0.45$, and 0.48). These concentrations cover both the regions about the SG QCP in the phase diagram and the region where this SG order freezes into long-range antiferromagnetic order. Our results show that concentrations previously thought to be AF ordered ($x=0.48$) are in fact electronically phase separated with only a minority of spins freezing into the AF ordered state. The majority of the moments retain the response observed to be characteristic of the spin-glass phase with short-range correlations best fit by a liquid-like structure factor modulation. Low energy spin excitations in higher U-doping concentrations of this system couple to the onset of the spin glass phase; however, at higher energies the single-ion type magnetic response dominates. Spin fluctuations observed at low U-doping levels ($x=0.25$ and 0.35) are also dominated exclusively by this same broad, local magnon response scaled only in intensity due to the variable U-concentration.

Though there remains substantial work to be done in order to completely resolve the underlying origin of both high- T_c superconductivity or the precise mechanism of non-Fermi liquid behavior, the field of strongly-correlated electron systems continues to provide a seemingly endless avenue of new phenomena. The physics it provides represents some of the most interesting and fundamentally challenging problems to modern condensed matter physics and undoubtedly will continue to do so for many years to come. In order to develop a robust theoretical framework for any of these phenomena, comprehensive experimental mapping of the relevant systems must first be performed, which I sincerely hope has been contributed to by my work presented here.

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Vita

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