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Physical Properties of Unconventional Superconductors

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Valentina Anatolyevna Kuznetsova

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Abstract

In the following development, we attempt to obtain basic physical properties of majority of unconventional superconductors through a Bardeen-Cooper-Schrieffer-type weak-coupling approach. The method we adopted in our study is model-independent. The weak-coupling approach depends only on the *symmetry* of the coupling, not on its origin. It is known that a general analysis of physical properties of unconventional superconductors is possible, but has not been done yet. The goal of our work is to develop and test such analysis, using available experimental data.

Since paramagnetic limiting for spin-singlet superconductors can be suppressed in superconductors with broken inversion symmetry of crystal lattice, a possibility for triplet-pairing opens up. However, it contradicts a P.W. Anderson theorem that spin-triplet is unlikely to occur in a material without an inversion center. Nevertheless, experimental evidence (in CePt₃Si, for example) strongly supports the *p*-wave pairing mechanism in A12 (non-centrosymmetric) compounds. In our research, we found Re₃W to be the most attractive material from the A12 family for experimental investigation and decided to concentrate on it. Although theoretically favorable in many aspects for some degree of *p*-wave superconductivity, annealed bulk Re₃W exhibited no evidence for triplet pairing upon experimental study. Instead, we discovered behaviors usually attributed to BCS-like *s*-wave pairing in SC state, such as $\Delta C_{el} / C_{el} \approx \text{BCS value}$, exponential *T*-dependence of the specific heat and dirty-limit BCS-like normalized superfluid density, $\lambda^2(0) / \lambda^2(T)$, at low temperatures. We report remarkably large (up to 60% of the upper critical magnetic field H_{c2}) reversible and linear in field magnetization, $M(H)$, in Re₃W. Subsequent magnetic measurements with application of modified flux line lattice relaxation method allowed us to construct/determine a reliable SC state phase diagram in this mildly hysteretic material, that includes data for the lower critical field $H_{c1}(T)$, penetration field $H_p(T)$, and thermodynamic critical field $H_c(T)$. The developed technique is fast, reliable and requires virtually no processing time.

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1. Introduction

Superconductivity is a macroscopic quantum phenomenon that manifests itself through exclusion of magnetic flux from the interior of a bulk sample, along with disappearance of normal state resistivity as the material enters superconducting state below the characteristic transition temperature, T_c , for that material. Discovered in 1911 by Kamerlingh Onnes,¹ superconductivity became a rich field of scientific study and discovery for almost a century. The phenomenon itself promises indisputable benefits to humankind, especially if it could be obtained near room temperature: transfer and storage of electric energy nearly with no or minimal losses, induction of huge magnetic fields with relatively small electromagnets, possibility of minimization of generators and motors, utilization of magnetic levitation, and other remarkable applications.² To date, room-temperature superconductors are not known, but there is a variety of superconducting materials that look very promising. For example, high temperature superconductors (HTS) have transition temperatures that are quite achievable with liquid nitrogen refrigeration, and range³ from 90 K for YBCO to 138 K for $\text{Hg}_{0.2}\text{Tl}_{0.8}\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}$. Furthermore, an intriguing direction in search for room-temperature T_c 's is currently developing in superconducting polymers.

Conventionally, all (bulk) superconductors are divided in two classes: the Type I and the Type II superconductors. Difference between them lies in the ratio of characteristic lengths, also known as the Ginzburg-Landau (GL) parameter κ : materials with $\kappa < 1/\sqrt{2}$ belong to the Type I, and those with $\kappa \geq 1/\sqrt{2}$ - to the Type II. The GL

parameter is determined as $\kappa = \lambda_{GL} / \xi_{GL}$, where λ_{GL} is the GL penetration depth (or, the characteristic depth within which a magnetic field applied to the superconductor falls off from its value at the surface of the superconductor to effectively zero inside it), and ξ_{GL} is the correlation length (or, the average size of the Cooper pair in the superconductor). The Type II materials were not recognized until A.A. Abrikosov predicted their existence.

In any material in SC state, superconducting order can be suppressed by application of sufficiently large magnetic field. Macroscopically, the Type I materials exhibit only one such characteristic magnetic field, H_c (also known as the thermodynamic critical field), at which the material undergoes the normal/superconducting state transition; below H_c (while also below T_c) these materials exclude magnetic flux from their interior (Meissner state). Unlike them, the Type II superconductors have two critical fields: the lower critical field, H_{c1} (below this field a Type II superconductor is in Meissner state), and the upper critical field H_{c2} (between H_{c1} and H_{c2} a Type II material is in a so called mixed state, in which magnetic flux partially penetrates the superconductor interior in form of magnetic vortices). The thermodynamic critical field, H_c , is related to the condensation energy of the Cooper pairs: $H_c^2(8\pi)^{-1} = F_{\text{cond}}$. Although the physical meaning of H_c is clear for the Type I SCs, it becomes vague for the Type II materials, since no obvious manifestation of this field has been experimentally detected so far. Theoretical developments in references [4, 5] suggest a physical meaning for H_c in the Type II materials, and we believe that our experimental study supports their hypothesis, as will be discussed in Chapter 5, "Test by Experiment: Re_3W ."

The first materials found to superconduct, such as pure mercury, tin, or lead, had very low transition temperatures. In fact, it was believed for several decades that the transition temperatures must have a limit of about 30 Kelvin. The necessity of expensive refrigeration made early superconductors unattractive for industrial purposes. Then, a breakthrough in 1986 by G. Bednorz and A. Müller⁶ – the discovery of superconductivity in lanthanum-barium copper oxide just below 35 K – rejuvenated interest in superconductivity. As result of stimulated activity in the field, many so-called high-temperature superconductors (HTS) were found. These materials, as well as others like heavy fermion and organic superconductors, exhibit physical properties that could not be universally accounted for within the existing theoretical framework.

Many superconductors are very well (or can be sufficiently well) described by the Bardeen-Cooper-Schrieffer (BCS) weak-coupling theory. The major hypothesis of this theory suggests⁷ that the BCS Hamiltonian becomes unstable against formation of Cooper pairs (coherent electrons in SC state) in presence of however small attractive potential between the electrons in a pair. In this theory, the attraction between electrons is indirect, and is mediated by oscillations of the crystalline lattice (phonons) of the SC material. A BCS Cooper pair is formed out of two electrons with opposite spins and orbital momenta. If an external magnetic field is sufficiently large for paramagnetic alignment of all spins of electrons forming Cooper pairs, it destroys the coherent BCS SC state (thus, it is referred to as the paramagnetic limit, H_{para}). In the BCS picture, density of the superconducting electrons, which is proportional to the square of the collective coherent wave function of the SC electrons, can serve as the order parameter. We give a more complete analytical description of this theory in Chapter 2, "Theoretical Aspects."

The BCS theory gives an order parameter that is totally symmetric with respect to rotations, i.e. s -wave symmetry. The low-energy excitation spectrum of these materials has a gap (which also can be treated as a SC order parameter), with exception of the gapless superconductors (SC) that have magnetic impurities. The presence of the gap in the excitation spectrum leads to an exponential temperature dependence at low temperatures of the specific heat, the NMR T_1 relaxation rate, and Knight shift.

However, not all materials have the conventional (s -wave) pairing state. The order parameter in an unconventional superconductor may have lines or points of zeroes (nodes) and therefore not to possess spherical symmetry. It turns out that the density of states at low temperatures depends on the topology of the gap nodes,⁸ and, consequently, some of the above-mentioned physical properties have power-law dependence on temperature instead of the exponential dependence of conventional superconductors, as presented in Table 1.

Unconventional superconductors (USCs) exhibit power-law behaviors at low temperatures of other physical properties as well: ultrasonic attenuation, thermal conductivity, and London penetration depth. There is a pronounced peak in the

Table 1. Power law dependencies in unconventional superconductors.

Gap topology	Specific heat, C	NMR relaxation rate, $1/T_1$
Gapless	$\sim T$	$\sim T$
Point zeroes	$\sim T^2$	$\sim T^3$
Line zeroes	$\sim T^3$	$\sim T^5$

ultrasonic attenuation just below the T_c in UBe_{13} , a heavy fermion superconductor – a feature similar to that of liquid ^3He , which is a p -wave superfluid. Some have double transitions detectable in ultrasonic attenuation experiments.^{9,10} Non-zero orbital momentum and/or spin of the Cooper pair often give rise to a multidimensional wave function. Many interesting effects are possible in the multidimensional USCs, such as domains, fractionally quantized vortices on domain walls and stable non-axial vortices in SCs with multidimensional order parameter, coexistence of superconductivity and magnetism, and others.^{8,11} Similar to bulk ferromagnets, a pairing state which breaks time-reversal symmetry tends to form a domain structure, with magnetic moments arising from circulating electric currents in the domain walls. Thus, there is no net magnetic moment in the bulk. Perhaps the most interesting phenomena for multicomponent USCs arise in magnetic field. An obvious consequence of applied magnetic field in some direction is the change of phase, which has to do with the symmetry of the superconducting state.^{11,12} This gives rise to very unusual topological excitations and vortex lattices,^{8,13,14} and a peculiar $H - T$ phase diagram (for example, see Figure 1), reflecting the possibility of many different phases,^{15,16} or an abrupt change of slope for $H_{c2}(T)$.^{17,18} Another interesting detectable property is the splitting of T_c under uniaxial stress.¹⁹ For such phases, phenomena similar to textures are expected to be observed, although the topological properties are rather simple, since only discrete degeneracy exists below the superconducting phase transition. For example, fractional vortices can appear in a lattice in a small applied magnetic field, and also non-uniaxial stable vortices are a possibility.⁸ Any combination of these exotic properties may signal the unconventional character of superconductivity in a material, and, inversely, complex

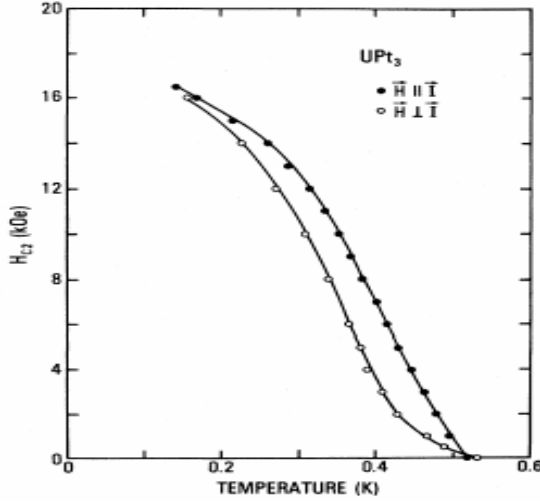


Figure 1. Anisotropy of H_{c2} in UPt_3 (figure taken from ref. [8]).

symmetry of the order parameter of a superconductor usually allows those interesting properties to arise.

Since the discovery of HTS, it was clear that pairing symmetry of superconducting electrons plays very important role in determination of physical properties of a superconductor. Standard BCS theory, accounting for s -wave superconductivity, basically rules out the high T_c values observed in HTS. The crystalline field in HTS is very anisotropic, and superconductivity occurs predominantly within copper-oxide planes, thus making the SC order parameter quasi-2D. It is now generally accepted that the symmetry of the superconducting state in HTS is d -wave, with spin-singlet ($S = 0$) parity of the superconducting state.

In the classic BCS picture, the order parameter is assumed to be spherically symmetric, and the total spin of the condensate of Cooper pairs to be zero. Alternatively, an anisotropic order parameter can accommodate spin-triplet (total spin $S = 1$) states in

UNi₂Al₃,²⁰ and some organic superconductors, such as²¹ (TMTSF)₂PF₆ (under 7 kbar of pressure).

In centrosymmetric crystals, the 3D inversion symmetry insures two-fold degeneracy of the energy spectrum as required for the formation of Cooper pairs in SC state, throughout the Brillouin zone both in the normal and in superconducting states. Below the superconducting transition, presence of inversion symmetry of crystalline structure of the material allows a separation of spin-triplet and spin-singlet components of the superconducting state, and consequently a classification of Cooper pairs by their parity, as discussed in Chapter 2, "Theoretical Aspects." In these materials, either spin-singlet or spin-triplet SC state is naturally chosen. However, when 3D inversion is broken by some inhomogeneity of the order parameter (as it happens in surface SC and in bulk materials that lack inversion symmetry), mixing of states of different parity becomes possible. Early studies of non-centrosymmetric superconductors addressed 2D systems, such as surfaces, interfaces, and thin films.^{23,24,25,26} Quite recently, bulk superconductors without inversion symmetry CePt₃Si (a heavy fermion, where SC coexists with anti-ferromagnetism²⁷) and UIr (a heavy fermion ferromagnetic superconductor²⁸) have been discovered. The microscopic theory of superconductivity in metals without inversion center of space group had been developed by V.M. Edelstein²³ in late 1980's, and the general symmetry approach to the SC in materials with space parity violation has been developed several years ago.^{29,30}

In a time-reversal invariant system, absence of spatial inversion symmetry is connected with presence of antisymmetric spin-orbit coupling (ASOC). ASOC is detrimental for most spin-triplet pairing states,³¹ except for those whose *d*-vector lies

parallel to $\mathbf{g}_k$. Thus SC states of mixed parity are rather stable against magnetic destruction of Cooper pairs in parallel magnetic field, and paramagnetic limiting of superconductivity can be lifted³² in some instances, allowing for higher upper critical field values than predicted within the classical approach. Particularly, formation of an inhomogeneous SC state similar to Fulde-Ferrell-Larkin-Ovchinnikov^{33,34} phase in ferromagnetic SCs is an intriguing possibility. We give a general overview of the theoretical developments in the field of non-centrosymmetric superconductors in Chapter 4, "Non-centrosymmetric Superconductors," and also outline physical properties anticipated in these exotic materials.

Experimental evidence (in CePt₃Si, for example)³⁵ strongly supports the possibility of the *p*-wave pairing mechanism in non-centrosymmetric compounds. Recently, CePt₃Si has been studied extensively due to its unconventional properties (particularly, it is a heavy fermion (HF) compound, with $H_{c2} \gg H_{para}$). These exciting findings inspired an investigation of the properties of other non-centrosymmetric materials (Re₃W, Re₃Mo, Re₃Ta, Re₃Zr, OsTa and other A12 materials with T_d point group) for the presence of unconventional superconductivity. We found Re₃W to be the most convenient material from this family for our research purposes and decided to concentrate on it. Re₃W is a non-centrosymmetric compound, found to superconduct below 9 K. In this research, we synthesized high-purity polycrystalline samples of this refractory material; then studied transport, magnetic and thermodynamic properties of Re₃W, as well as several properties of off-stoichiometric Re-W alloys close to 3:1 stoichiometry, and finally compared results with those for known non-centrosymmetric superconductors and with existing theoretical predictions.

During our experimental investigation, we developed new methods of direct measurement of the lower critical field H_{c1} and penetration field H_p , and confirmed the suggestion^{36,37} that H_p traces H_c , in specimens with weak bulk pinning and good surface. Detailed discussion of the method, its origin, and our contribution to its development are offered in section 5.4 "Experimental Results" of Chapter 5 of this thesis.

This thesis is organized as follows. Following Chapter 1 "Introduction," we give a brief overview of the BCS theory in Chapter 2, "Theoretical Aspects." Chapter 3, "Weak Coupling Method," presents an original theoretical development of the microscopic theory in multi-component superconductors in a weak coupling BCS approximation. Chapter 4, "Non-centrosymmetric Superconductors," offers an overview of the theoretical and experimental developments in the field of non-centrosymmetric superconductors, - materials, where mixing of singlet and triplet components is likely to occur, and thus a multicomponent SC order parameter is anticipated. Chapter 5, "Test by experiment: Re_3W ," describes a number of experimental investigations of Re_3W materials and some surprising findings. The work concludes with a summary and some suggestions for further directions of study.

2. Theoretical Aspects

In the following development, we attempt to obtain basic physical properties of all USCs through a BCS-type weak-coupling approach. The BCS theory is based on the discovery that the degenerate state of a normal Fermi gas is unstable against formation of electronic bound states (Cooper pairs) if any attractive potential, however small, between the electrons in a pair is present. The electrons' pairing effectively appears in momentum space, not in the real space. In the original BCS theory, the attraction between electrons in a pair is mediated by phonons of the superconductor, and appears only in a thin layer near the Fermi surface in the momentum space. The electron-phonon mechanism leads to the formation of spherically-symmetric pairs in spin-singlet configuration (*s*-wave symmetry). Other pairing mechanisms lead to different pair configurations. Nevertheless, the nature of the electron-electron attraction is not important in the BCS theory, only the symmetry of the coupling is.⁸

The effective BCS Hamiltonian has the form:

$$H = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} a_{\mathbf{k}\alpha}^\dagger a_{\mathbf{k}\alpha} + \frac{1}{2} \sum_{\mathbf{k}, \mathbf{k}'} V_{\alpha\beta, \lambda\mu}(\mathbf{k}, \mathbf{k}') a_{-\mathbf{k}\alpha}^\dagger a_{\mathbf{k}\beta}^\dagger a_{\mathbf{k}'\lambda} a_{-\mathbf{k}'\mu}, \quad (1)$$

where $\varepsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m^* - \varepsilon_F$ is the energy of the excitations measured with respect to the Fermi level, and m^* is effective mass. The summation over repeating spin indices is assumed hereafter. V is a general electron-electron interaction potential, attractive in a small range near the Fermi surface, and $V_{\alpha\beta, \lambda\mu}(\mathbf{k}, \mathbf{k}')$ denotes $\langle -\mathbf{k}, \alpha; \mathbf{k}, \beta | V | \mathbf{k}, \lambda; -\mathbf{k}', \mu \rangle$, with the

following symmetry properties: $V_{\alpha\beta,\lambda\mu}(\mathbf{k},\mathbf{k}') = -V_{\beta\alpha,\lambda\mu}(-\mathbf{k},\mathbf{k}') = -V_{\alpha\beta,\mu\lambda}(\mathbf{k},-\mathbf{k}') = V_{\mu\lambda\beta\alpha}(\mathbf{k},\mathbf{k}')$. In cases when spin-orbit coupling is negligible, we can rewrite

$$V_{\alpha\beta,\lambda\mu}(\mathbf{k},\mathbf{k}') = V(\mathbf{k},\mathbf{k}')\Gamma_{\alpha\beta,\lambda\mu}. \quad (2)$$

And $V(\mathbf{k},\mathbf{k}')$ can be expanded in terms of spherical harmonics:

$$V(\mathbf{k},\mathbf{k}') = V_l(k,k') \sum_{m=-l}^l Y_{lm}(\underline{\mathbf{k}}) Y_{lm}^*(\underline{\mathbf{k}'}); \quad \underline{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$$

Here the interaction component $V_l(k,k')$ is responsible for the highest T_c .

The spin-dependent part of the interaction potential is expressed in terms of matrices $\Gamma_{\alpha\beta,\lambda\mu}$, antisymmetric under permutation of spin indices $\alpha\beta(\lambda\mu)$ for even l and symmetric for odd l :

$$\Gamma_{\alpha\beta,\lambda\mu} = \frac{1}{2} g_{\alpha\beta} g_{\lambda\mu}^\dagger, \quad (l \text{ even}), \quad \text{with } g_{\alpha\beta} = (i\sigma_y)_{\alpha\beta} \quad (3)$$

$$\Gamma_{\alpha\beta,\lambda\mu} = \frac{1}{2} \mathbf{g}_{\alpha\beta} \mathbf{g}_{\lambda\mu}^\dagger, \quad (l \text{ odd}), \quad \text{with } \mathbf{g}_{\alpha\beta} = (i\boldsymbol{\sigma}\sigma_y)_{\alpha\beta} \quad (4)$$

In solids, the interaction must be invariant with respect to the crystal point symmetry and the interaction potential for singlet and triplet pairing with weak spin-orbit (SO) coupling assumes the following form:

$$V_{\alpha\beta,\lambda\mu}(\mathbf{k},\mathbf{k}') = V_l(k,k')\Gamma_{\alpha\beta,\lambda\mu} \sum_{i=1}^{d\Gamma} \psi_i^\Gamma(\underline{\mathbf{k}}) \psi_i^{*\Gamma}(\underline{\mathbf{k}'}), \quad (5)$$

Here V_Γ is the interaction corresponding to the irreducible representation Γ with basis functions $\psi_i^\Gamma(\mathbf{k})$, and gives rise to the highest T_c . For the case of strong SO and spin $S = 1$ we have:

$$V_{\alpha\beta,\lambda\mu}(\mathbf{k},\mathbf{k}') = \frac{1}{2} V_\Gamma(k,k') \sum_{i=1}^{d_\Gamma} (\psi_i^\Gamma(\mathbf{k}) \mathbf{g}_{\alpha\beta}) (\psi_i^{*\Gamma}(\mathbf{k}') \mathbf{g}_{\lambda\mu}^\dagger), \quad (6)$$

$$\text{where} \quad \psi_i^\Gamma(\mathbf{k}) = \psi_i^x(\mathbf{k})\mathbf{x} + \psi_i^y(\mathbf{k})\mathbf{y} + \psi_i^z(\mathbf{k})\mathbf{z}. \quad (7)$$

To account for the instability of the Hamiltonian against formation of Cooper pairs we take the wave function as follows:

$$\Psi = \prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} a_{\mathbf{k}\uparrow}^\dagger a_{-\mathbf{k}\downarrow}^\dagger) |\text{vac}\rangle. \quad (8)$$

Here $v_{\mathbf{k}}(u_{\mathbf{k}})$ corresponds to the probability that the state $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ is occupied (vacant), and

$$|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$$

In a normal metal, for all $|\mathbf{k}| < k_F$ $u_{\mathbf{k}}=0$ while $v_{\mathbf{k}}=1$, and for all $|\mathbf{k}| > k_F$, $u_{\mathbf{k}}=1$ while $v_{\mathbf{k}}=0$, which constitutes the Fermi sea at zero temperature. In a superconductor, however, there is a finite probability for a state with *any* $\mathbf{k}$ to be vacant. This gives the superconducting ground state that is a superposition of states with different amounts of Cooper pairs in them. As a consequence, we get non-vanishing anomalous averages:

$$F_{\mathbf{k},\uparrow\downarrow} = \langle \Psi | a_{\mathbf{k}\uparrow} a_{-\mathbf{k}\downarrow} | \Psi \rangle; \quad F_{\mathbf{k},\uparrow\downarrow}^\dagger = \langle \Psi | a_{\mathbf{k}\uparrow}^\dagger a_{-\mathbf{k}\downarrow}^\dagger | \Psi \rangle \quad (9)$$

or, at arbitrary temperature:

$$F_{\mathbf{k},\alpha\beta} = \langle a_{\mathbf{k}\alpha} a_{-\mathbf{k}\beta} \rangle; F_{\mathbf{k},\alpha\beta}^\dagger = \langle a_{\mathbf{k}\alpha}^\dagger a_{-\mathbf{k}\beta}^\dagger \rangle. \quad (10)$$

Assuming that deviations of operators $a_{\mathbf{k}\alpha} a_{-\mathbf{k}\beta}$ and $a_{\mathbf{k}\alpha}^\dagger a_{-\mathbf{k}\beta}^\dagger$ from their average values are small, the effective Hamiltonian can be rewritten in the following way:

$$H = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}\alpha}^\dagger a_{\mathbf{k}\alpha} + \frac{1}{2} \sum_{\mathbf{k}, \mathbf{k}'} V_{\alpha\beta, \lambda\mu}(\mathbf{k}, \mathbf{k}') (-F_{\mathbf{k}, \alpha\beta}^\dagger F_{\mathbf{k}', \lambda\mu} + F_{\mathbf{k}', \lambda\mu} a_{\mathbf{k}\alpha}^\dagger a_{\mathbf{k}\beta}^\dagger + F_{\mathbf{k}, \alpha\beta}^\dagger a_{\mathbf{k}'\lambda} a_{\mathbf{k}'\mu}). \quad (11)$$

To simplify the Hamiltonian, let's introduce the functions

$$\Delta_{\mathbf{k}, \alpha\beta} = -\sum_{\mathbf{k}'} V_{\alpha\beta, \lambda\mu}(\mathbf{k}, \mathbf{k}') F_{\mathbf{k}', \lambda\mu} \quad (12)$$

$$\Delta_{\mathbf{k}, \lambda\mu}^\dagger = -\sum_{\mathbf{k}'} V_{\alpha\beta, \mu\lambda}(\mathbf{k}', \mathbf{k}) F_{\mathbf{k}', \alpha\beta}^\dagger \quad (13)$$

These functions can be shown to obey: $\Delta_{\mathbf{k}, \alpha\beta} = -\Delta_{-\mathbf{k}, \beta\alpha}$. Parity of the interaction potential $V_{\alpha\beta, \lambda\mu}$ should be the same as parity of $\Delta_{\mathbf{k}, \alpha\beta}$ and $F_{\mathbf{k}', \lambda\mu}$. So, for $V_{\alpha\beta, \lambda\mu}$ even in $\mathbf{k}$ (singlet pairing) we get

$$\Delta_{\mathbf{k}, \alpha\beta} = \Delta g(\mathbf{k}) (i\sigma_y)_{\alpha\beta}, \quad \text{with } g(\mathbf{k}) = g^l(\mathbf{k}) = \sum_{m=-l}^l a_{lm}(k) Y_{lm}(\underline{\mathbf{k}}); \int d\Omega (4\pi)^{-l} |g^l(\mathbf{k})|^2 = 1.$$

And for $V_{\alpha\beta, \lambda\mu}$ odd in $\mathbf{k}$ (triplet pairing) we get

$$\Delta_{\mathbf{k}, \alpha\beta} = \Delta \mathbf{d}(\mathbf{k}) (i\sigma_y)_{\alpha\beta}, \quad \text{with } \mathbf{d}(\mathbf{k}) = \mathbf{d}^l(\mathbf{k}) = \sum_{m=-l}^l \mathbf{b}_{lm}(k) Y_{lm}(\underline{\mathbf{k}}); \int d\Omega (4\pi)^{-l} |\mathbf{d}(\mathbf{k})|^2 = 1.$$

Coefficients a_{lm} and $\mathbf{b}_{lm}$ in the above equations play role of the order parameter. After diagonalization of the Hamiltonian using the unitary Bogoliubov transformation ($a_{\mathbf{k}\alpha}^\dagger a_{\mathbf{k}\alpha} \rightarrow b_{\mathbf{k}\alpha}^\dagger b_{\mathbf{k}\alpha}$) we obtain:

$$H = E_0 + \sum_{\mathbf{k}} E_{\mathbf{k}} b_{\mathbf{k}\alpha}^\dagger b_{\mathbf{k}\alpha}, \quad (14)$$

$$\text{where} \quad E_0 = \frac{1}{2} \sum_{\mathbf{k}} \Delta_{\mathbf{k},\alpha\beta} F_{\mathbf{k},\alpha\beta}^\dagger + \frac{1}{2} \sum_{\mathbf{k}\alpha} (\xi_{\mathbf{k}} - E_{\mathbf{k}}) \quad (15)$$

$$\text{and} \quad E_{\mathbf{k}} = \sqrt{(\xi_{\mathbf{k}}^2 + \Delta^2 |g(\mathbf{k})|^2)} \quad (S=0) \quad (16)$$

$$E_{\mathbf{k}} = \sqrt{(\xi_{\mathbf{k}}^2 + \Delta^2 |\mathbf{d}(\mathbf{k})|^2)} \quad (S=1) \quad (17)$$

The Fermi distribution function for excitations with energy $E_{\mathbf{k}}$ is given by

$$f_{\mathbf{k}} = f(E_{\mathbf{k}}) = [\exp(E_{\mathbf{k}}/T) + 1]^{-1} \quad (18)$$

The gap in the excitation spectrum can be calculated using the so called gap equation:

$$\Delta_{\mathbf{k},\alpha\beta} = - \sum_{\mathbf{k}'} V_{\beta\alpha,\lambda\mu}(\mathbf{k},\mathbf{k}') (1 - 2f_{\mathbf{k}'}) \Delta_{\mathbf{k}',\lambda\mu} / (2E_{\mathbf{k}}). \quad (19)$$

Various physical properties at low temperatures ($T/T_c \ll 1$) can be easily derived using this theory. For example, the electronic specific heat of a superconductor can be found using $C_s = \sum_{\mathbf{k}\alpha} E_{\mathbf{k}} \partial f_{\mathbf{k}} / \partial T$, which gives $C_s \approx N_0 (\Delta_0/T)^2 \sqrt{(2\pi T \Delta_0)} e^{-\Delta_0/T}$ as $T \rightarrow 0$ for s -wave case (non-zero gap). When the pairing state is anisotropic, finding the temperature dependence of the thermodynamic and kinetic characteristics becomes a non-trivial task.

If the pairing state in an unconventional superconductor or superfluid transforms according to a multidimensional representation of the group, the order parameter is also multicomponent. For example, the p -wave order parameter in ^3He is a 3×3 complex matrix, i.e., has 9 complex components. As a result, many different phases can arise in the superfluid state, such as the A-phase,³⁸ which is not invariant with respect to rotations or time-reversal operations, and the B-phase, which is both rotationally and time-reversal invariant.

Although the details of the mechanism are essential for strong coupling Eliashberg-type calculations, knowledge of the energy spectrum and the coupling constants for quasiparticle - mediated superconductivity is not required in the weak-coupling approach, which is adopted in our work. A microscopic description of unconventional superconductors can be useful for analysis of experiments in new superconducting materials, where an unconventional pairing mechanism may be operative. The usual suspects are materials with strong Coulomb correlations, such as heavy fermions and high- T_c cuprates. In such materials the conventional phonon mechanism is suppressed.³⁹

The microscopic analysis is somewhat less general than the Ginzburg-Landau (GL) approach of Refs. [12, 40]. For example, weak coupling BCS-type theory always gives the B-phase⁴¹ of the superfluid ^3He . The non-BCS spin fluctuation feedback effect, when the interaction itself depends upon the superconducting ground state, is required to stabilize the A-phase.⁴² Most, if not all, unconventional superconductors are characterized by the presence of strong Coulomb correlations, so the applicability of the

weak-coupling approach for such materials is questionable. Nevertheless, this approach is often used theoretically as a starting point.

3. Weak Coupling Method

In what follows we analyzed multicomponent superconductors, i.e., superconductors belonging to a 2-dimensional or 3-dimensional representations of the cubic, hexagonal or tetragonal groups, where the superconducting phase is not uniquely determined by the irreducible representation. Examples of superconductors where multicomponent state is suspected are, among others, UPt_3 (hexagonal symmetry),⁴³ Sr_2RuO_4 (tetragonal symmetry),^{44,45} $\text{PrOs}_4\text{Sb}_{12}$ (cubic symmetry),¹⁷ and $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$.^{42,18} For such superconductors many phases can possibly appear, according to the GL theory.^{12,40} Only one of these phases is realized in the microscopic weak coupling theory. The analysis done below is well known,^{24,25} and has been applied to many particular cases, such as the d -wave superconductivity in high- T_c s,⁴⁶ or general multi-band phonon mechanism.⁴⁷

As usual,³⁹ we assume that electrons have a weak short-range attractive interaction, $U(\mathbf{r}, \mathbf{r}')$. Since the phonon cutoff frequency is much less than the Fermi energy, $\omega_D \ll \epsilon_F$, only the quasiparticles in the vicinity of the Fermi surface participate. Then the interaction can be expanded in a complete set of basis functions, $\chi_{lm}(\mathbf{p})$, where index l corresponds to different irreducible representations of the point group, while index m enumerates the basis functions of a given irreducible representation l . This expansion is similar to an expansion in spherical functions for an isotropic model. The interaction in momentum space then takes the following form:

$$U(\mathbf{p}, \mathbf{p}') = \sum_{lm} U_l \chi_{lm}(\mathbf{p}) \chi_{lm}(\mathbf{p}'), \quad (20)$$

Where the momenta $\mathbf{p}, \mathbf{p}'$ are on the Fermi surface. The gap equation for the superconducting order parameter takes the following form:

$$\Delta_{\alpha\beta,m}(\mathbf{p}) = |U_l| \chi_{lm}(\mathbf{p}) \int d^3p' (2\pi)^{-3} \chi_{lm}(\mathbf{p}') T \sum_{\omega_n} F_{\alpha\beta}(\mathbf{p}'; i\omega_n), \quad (21)$$

where $F_{\alpha\beta}(\mathbf{p}'; i\omega_n)$ is the Fourier component of anomalous Gor'kov function,

$$F_{\alpha\beta}(\mathbf{r} - \mathbf{r}', \tau - \tau') = -\langle T_\tau (\Psi_\alpha(\mathbf{r}, \tau) \Psi_\beta(\mathbf{r}', \tau')) \rangle, \quad (22)$$

and $U_l < 0$ is a constant in Eq.(20) corresponding to a selected pairing channel. The two fermion operators inside brackets in Eq.(22) anticommute. In the presence of a center of inversion, the behavior of $\chi_{lm}(\mathbf{p})$ with respect to inversion, $\mathbf{p} \rightarrow -\mathbf{p}$, determines the symmetry of $\Delta_{\alpha\beta}(\mathbf{p})$ - even for singlet, and odd for triplet pairing.^{12,40} The order parameter below T_c has the form:

$$\Delta_{\alpha\beta,m}(\mathbf{p}) = \Delta(T) (i\sigma_y)_{\alpha\beta} \chi_{lm}(\mathbf{p}), \quad S = 0, \quad (23)$$

$$\Delta_{\alpha\beta,m}(\mathbf{p}) = \Delta(T) (i\boldsymbol{\sigma}_{\alpha\beta} \cdot \mathbf{d}) \chi_{lm}(\mathbf{p}), \quad S = 1. \quad (24)$$

Different phases for the multi-component pairing state were determined from the GL analysis in Ref. [12, 40]. The weak coupling approach completely determines the coefficients³⁹ in the GL functional. The inhomogeneous gap equation Eq.(21) written in

the vicinity of T_c becomes the GL equation. In what follows we analyzed the GL coefficients in degenerate representations of cubic, hexagonal and tetragonal groups to determine possible phases that can arise in the microscopic theory.

The cubic group O_h – two-dimensional representations. The order parameter for $S = 0$ and $S = 1$ can be written as

$$\Delta(\mathbf{k}) = \Delta(\eta_1 \varphi^{(1)}(\mathbf{k}) + \eta_2 \varphi^{(2)}(\mathbf{k})) \quad (25)$$

where the basis functions are

$$\varphi^{(1)}(\mathbf{k}) \sim k_x^2 + \varepsilon k_y^2 + \varepsilon^2 k_z^2, \quad \varphi^{(2)}(\mathbf{k}) = \varphi^{(1)}(\mathbf{k})^*; \quad S = 0, \quad (26)$$

$$\varphi^{(1)}(\mathbf{k}) \sim x k_x + \varepsilon y k_y + \varepsilon^2 k_z, \quad \varphi^{(2)}(\mathbf{k}) = \varphi^{(1)}(\mathbf{k})^*; \quad S = 1, \quad (27)$$

Here $\varepsilon = \exp(2\pi i/3)$, and the wave functions are normalized to 1:

$$\langle |\varphi^{(i)}(\mathbf{k})|^2 \rangle_{F.S.} = 1, \quad |\eta_1|^2 + |\eta_2|^2 = 1. \quad (28)$$

For singlet order parameter, we find

$$F = N_0 \Delta^2 \ln[T/T_c] (|\eta_1|^2 + |\eta_2|^2) + \alpha N_0 \Delta^4 \zeta(3) / (16\pi^2 T_c^2) (|\eta_1|^4 + |\eta_2|^4 + 4|\eta_1|^2 |\eta_2|^2) \quad (29)$$

Here N_0 is the density of states for one spin direction, α is a coefficient determined from the Fermi surface averages:

$$\alpha = \langle |\varphi^{(I)}(\mathbf{k})|^4 \rangle_{F.S.} / \langle |\varphi^{(I)}(\mathbf{k})|^2 \rangle_{F.S.}^2 \quad (30)$$

For isotropic spherical shape of the Fermi surface we find that $\alpha = 10/7$. While α will be different for an arbitrary Fermi surface, the form of the functional F is completely determined by the cubic symmetry, since certain averages, such as $\langle \varphi^{(I)}(\mathbf{k})^4 \rangle_{F.S.}$, must vanish by symmetry (in this case, rotation about the three-fold axis). This functional leads to the phase (1, 0) with a magnetic d -wave order parameter,

$$\Delta(k) \sim k_x^2 + \varepsilon k_y^2 + \varepsilon^2 k_z^2, \quad (31)$$

which breaks $T \rightarrow -T$ symmetry, and has point nodes along the diagonals of the cube. Note that in this case higher-order terms are not necessary to determine the phase.

In the triplet case, we obtain, for the spherical Fermi surface:

$$\begin{aligned} F^{(4)-(6)} = N_0 \Delta^4 7\zeta(3) / (10\pi^2 T_c^2) (|\eta_1|^4 + |\eta_2|^4 + |\eta_1|^2 |\eta_2|^2) \\ - 93 N_0 \Delta^6 \zeta(5) / (2240\pi T_c^4) (\eta_1^3 \eta_2^{*3} + \eta_1^{*3} \eta_2^3) \end{aligned} \quad (32)$$

The 6th-order term is necessary in this case to distinguish between the two non-magnetic superconducting phases. The magnetic class turns out to be the trivial $D_4 \times R$, with the order parameter

$$d(\mathbf{k}) \sim 2xk_x - yk_y - zk_z. \quad (33)$$

This order parameter is nodeless, i.e., thermodynamic properties of this state are exponential at low temperature, similar to BCS s -wave. For a general Fermi surface we found that the sign of the 6-th order term is always negative. However, the coefficient κ in the 4-th order term,

$$F^{(4)} \sim |\eta_1|^4 + |\eta_2|^4 + \kappa |\eta_1|^2 |\eta_2|^2 \quad (34)$$

depends on the shape of the Fermi surface. We find that $-0.8 \leq \kappa \leq 4$, which makes the magnetic class $O(D_2)$ ($\kappa > 2$) also a possibility.

2. Three-dimensional representations.

For the four 3D vector representations, the basis functions can be chosen in the following form:

$$F_{1g}(S=0) : k_y k_z (k_y^2 - k_z^2), k_z k_x (k_z^2 - k_x^2), k_y k_x (k_x^2 - k_y^2); \quad (35)$$

$$F_{1u}(S=1) : yk_z - zk_y, zk_x - xk_z, xk_y - yk_x; \quad (36)$$

$$F_{2g}(S=0) : k_y k_z, k_x k_z, k_x k_y; \quad (37)$$

$$F_{2g}(S=1) : yk_z + zk_y, zk_x + xk_z, xk_y + yk_x. \quad (38)$$

The free energy can be written in the universal form:

$$F = N_0 \Delta^2 \ln[T/T_c](\boldsymbol{\eta} \cdot \boldsymbol{\eta}^*) + \beta_1 N_0 \Delta^4 (\boldsymbol{\eta} \cdot \boldsymbol{\eta}^*)^2 + \beta_2 N_0 \Delta^4 |\boldsymbol{\eta} \cdot \boldsymbol{\eta}^*|^2 + \beta_3 N_0 \Delta^4 \sum_i |\eta_i|^4 \quad (39)$$

a) $\underline{E}_{1g}$. We find the following GL coefficients in Eq.(39) for a spherical Fermi surface:

$$\beta_1 = 2205\zeta(3)/(3536\pi^2 T_c^2), \quad \beta_2 = \beta_1/2, \quad \beta_3 = 9\beta_1/22, \quad (40)$$

which gives magnetic superconducting class $D_3(E)$, with a phase $(1, \varepsilon, \varepsilon^2)$, given in terms of the above basis functions. This phase is ferromagnetic, with orbital magnetic moment pointing along the 3-fold axis of the cube. The order parameter has 2 point nodes, at the points of intersection of the spontaneous 3-fold anisotropy axis with the Fermi surface. For a general Fermi surface, the phase is not completely determined. We found that

$$\beta_1 > 0, \quad \beta_1 = 2\beta_2, \quad \beta_3 = 9\beta_1/22. \quad (41)$$

This gives a line on more general phase space for the GL theory. Thus, magnetic phases $D_3(E)$, $D_4(E)$, and a non-magnetic phase $D_4(C_4) \times R$ are possible depending on the shape of the Fermi surface.

b) $\underline{E}_{2g}$. For a spherical Fermi surface, we find:

$$\beta_1 = 5\zeta(3)/(8\pi^2 T_c^2), \quad \beta_2 = \beta_1/2, \quad \beta_3 = 0. \quad (42)$$

This case falls on the boundary between phases $(1, \varepsilon, \varepsilon^2)$ and $(1, i, 0)$, with accidental degeneracy between $D_4(E)$ and $D_3(E)$. For an arbitrary Fermi surface, we find:

$$\beta_1 = 4\beta_2, \quad \beta_2 \geq 0, \quad \beta_3 \geq -5\beta_1/4. \quad (43)$$

and the magnetic phases $D_3(E)$, $D_4(E)$, and non-magnetic $D_4^{(2)}(D_2) \times R$ are possible.

c) F_{1u} and F_{2u} . For both triplet representations we find, in case of spherical Fermi surface:

$$\beta_1 = 63\zeta(3)/(80\pi^2 T_c^2), \quad \beta_2 = -\beta_1/3, \quad \beta_3 = 0. \quad (44)$$

which falls on the boundary between 2 non-magnetic phases: (1, 1, 1) (class $D_3(C_3) \times R$ for F_{1u} , $D_3 \times R$ for F_{2u}) and (1, 0, 0) (class $D_4(C_4) \times R$ for F_{1u} , class $D_4^{(2)}(D_2) \times R$ for F_{2u}). For the general Fermi surface one of these non-magnetic phases will be realized. We find that

$$\beta_1 > \beta_2, \quad \beta_1 \geq 0, \quad \beta_3/\beta_1 + 3\beta_2/\beta_1 + 1 = 0. \quad (45)$$

The hexagonal group D_{6h} .

Multi-component order is possible in hexagonal group, if the pairing wave function transforms according to one of the 2D irreducible representations. For E_1 , the GL functional is given by Eq.(39), with the order parameter now a 2D vector:

$$E_{1g}(S = 0) : \varphi(k) \sim \eta_x k_z k_x + \eta_y k_z k_y \quad (46)$$

$$E_{1u}(S = 1) : \mathbf{d}(k) \sim \eta_x z k_x + \eta_y z k_y \quad (47)$$

For an arbitrary Fermi surface we find:

$$\beta_1 = 2\beta_2, \quad \beta_1 > 0, \quad \beta_3 = 0. \quad (48)$$

This gives rise to the phase $(1, i)$, in both singlet and triplet cases, or the symmetry class $D_6(E)$, which breaks the time-reversal symmetry, and possesses ferromagnetism. For the particular case of a spherical or cylindrical Fermi surface we find:

$$\beta_{1(sph)}=5\zeta(3)/(8\pi^2 T_c^2), \quad \beta_{1(cyl)}=7\zeta(3)/(16\pi^2 T_c^2). \quad (49)$$

For E_{2g} the GL functional is the same as for the 2D representation E_g in the cubic lattice.

The basis functions are, of course, not the same:

$$E_{2g}(S=0) : \varphi^{(1)}(\mathbf{k}) \sim (k_x + ik_y)^2, \quad \varphi^{(2)}(\mathbf{k}) = \varphi^{(1)}(\mathbf{k})^* \quad (50)$$

For an arbitrary Fermi surface we find the same form of the functional, Eq.(29), with α for the particular cases of spherical or cylindrical Fermi surface given by:

$$\alpha(sph) = 10/7, \quad \alpha(cyl) = 1. \quad (51)$$

The resulting phase $\varphi(\mathbf{k}) \sim (k_x + ik_y)^2$ belongs to the symmetry class $D_6(C_2)$, and is an orbital ferromagnet. Finally, for E_{2u} triplet representation, with basis wave functions

$$E_{2u}(S=1): \varphi^{(1)}(\mathbf{k}) = (\mathbf{x} + i\mathbf{y})(k_x + ik_y), \quad \varphi^{(2)}(\mathbf{k}) = \varphi^{(1)}(\mathbf{k})^* \quad (52)$$

we find a new result:

$$F=N_0\Delta^2\ln[T/T_c](|\eta_1|^2+|\eta_2|^2)+\alpha N_0\Delta^47\zeta(3)/(16\pi^2T_c^2)(|\eta_1|^4+|\eta_2|^4) \quad (53)$$

which gives either the p -wave phase $\mathbf{x}k_x-\mathbf{y}k_y$ (symmetry class $D_2\times R$), or $\mathbf{x}k_y+\mathbf{y}k_x$ (symmetry class $D_2(C_2)\times R$). Unfortunately, the BCS theory does not distinguish between the two phases in the 6-th order of the Ginsburg-Landau functional. Here $\alpha > 0$ is a coefficient, which depends on the shape of the Fermi surface. For the cases of a cylindrical and a spherical Fermi surface,

$$\alpha (sph) = 6/5, \quad \alpha (cyl) = 1. \quad (54)$$

The tetragonal group D_{4h} .

Since the basis functions for the 2D representations E_u and E_g of the tetragonal group are exactly the same as for hexagonal E_{1u} and E_{1g} representations, not surprisingly, the GL functionals and the resulting phases also turn out to be identical. The class in tetragonal group is $D_4(E)$, which allows ferromagnetism along z -axis. There are 2 point nodes for the singlet, and a line of nodes in the triplet case.

Our results are summarized in Table 2, where we also list specific heat jump at T_c for simple Fermi surfaces (a ratio to the BCS theory specific heat jump), such as cylindrical and spherical.

With this knowledge, we can readily classify, for example, order parameter symmetry of the heavy fermion superconductor $CeCu_2Si_2$, based on available experimental data.⁸ Its a tetragonal material, with inversion symmetry present in crystalline lattice, it exhibits $C_{el} \sim T^3$ and $\Delta C/C_n|_{T_c} \sim 5/6$ that of the BCS value, therefore

we can classify this material as a spin-triplet SC with order parameter belonging to the class $D_4(E)$, and we may expect in it ferromagnetic ordering coexisting with superconductivity. The same order parameter is to be expected in the HF material URu_2Si_2 . Recent experiments on URu_2Si_2 show that the low-pressure hidden order is non-magnetic but it nonetheless breaks time reversal invariance⁴⁸ (which is still consistent with our analysis).

In the case of recently discovered and intensively studied superconductor Sr_2RuO_4 crystallizes into a tetragonal lattice (D_4), has a T_c of 1.5 K, $C(T) \sim T^3$, and $\Delta C/C_n \sim 0.6$ BCS, thus we would expect a triplet SC state with order parameter belonging to the class $D_4(E)$. Other experimental data strongly suggests triplet pairing in this material as well.⁴⁹

The heavy fermion superconductor $PrOs_4Sb_{12}$ (crystal symmetry is cubic, O_h) has two (or a split in) SC transitions: one characterized by T_c of 1.75 K, $C(T) \sim T^3$, and $\Delta C/C_n = 0.7$ BCS and another one by T_c of 1.85 K, and $\Delta C/C_n = 0.53$ BCS (the low temperature T -dependence of specific heat cannot be determined). Also, a Schottky anomaly has been detected in this material.⁵⁰ According to our analysis, the first SC transition, occurring at 1.85 K, is likely to produce the order parameter of symmetry class $D_3(E)$ in spin-singlet pairing state. The second transition has an order parameter of different symmetry class, either $O(D_2)$ in 2D representation of the cubic group, or $D_3(E)$ in 3D representation of the cubic group, which give the spin-singlet pairing state in each case. There is currently no consensus about the pairing state symmetry in this material.

Another suitable class of materials where this analysis is applicable, is class of superconductors that crystallize in Chevrel phase symmetry (slightly distorted cubic CsCl structure with central atom substituted by a Mo_6S_8 , or similar, cluster): ternary

molybdenum chalcogenides. For example, $\text{Mo}_6\text{S}_6\text{I}_2$ has T_c of 4.8 K, $C(T) \sim T^3$, and $\Delta C/C_n \sim 0.5$ BCS.⁵¹ It follows from our theoretical analysis that the appropriate choice of the order parameter for this material would be $D_3(E)$ in the singlet pairing state. It implies that we should expect ferromagnetic ordering in this material. Experimental data from ref. [51] confirm this result.

In such a complicated system as UPt_3 , classification of the SC state may not be just as trivial. Hexagonal symmetry group and $C_{el} \sim T^2$ give a clue that we are dealing with a spin-singlet $D_6(E)$ state, however, it is known that this material undergoes an anti-ferromagnetic transition below 5 K and behaves more like a p -wave SC.

As described elsewhere,⁸ the cubic HF superconductor UBe_{13} is also difficult to classify based on the experimental data, because accuracy of most valuable, low-temperature ($T < 0.1T_c$) measurements of the thermodynamic quantities are strongly affected by self-heating due to nuclear decay processes.

For the recently discovered⁵² "first non-oxide perovskite" superconductor MgCNi_3 , categorization is yet to take place. This material has cubic (O_h) structure, $T_c = 8.5$ K, $C_{el} \sim T^3$ (above $0.25 T_c$, lower temperature data unavailable) and $\Delta C/C_n|_{T_c} = 1.9 >$ BCS value! The presence of Ni atoms suggests the possibility for some (ferro-) magnetic ordering, but such ordering has not yet been detected. London penetration depth measurements⁵³ show a power-law behavior that cannot be accounted for in conventional sense. Some reports⁵⁴ suggest that MgCNi_3 is a multigap superconductor, in which non-trivial interband coupling may accommodate s -wave BCS-like behaviors and unconventional superconductivity. Unfortunately, the presented analysis does not account for multi-band interaction, and is not applicable in the last case.

Table 2. Magnetic classes obtained in weak coupling approach for degenerate representations of cubic, tetragonal, and hexagonal point groups.

Symmetry group	Irreducible rep.	Symmetry class	(η_1, η_2) or (η_1, η_2, η_3)	Magnetic properties	$C_{\sim}$	$\Delta C/C$ Spher. FS	$\Delta C/C$ Cyl. FS
Cubic	E_g	$O(D_2)$	(1,0)	AFM	T^3	0.7 BCS	N/A
	E_u	$D_4 \times R$	(1,1)	Non-magn	$e^{-\Delta/T}$	5/6 BCS	N/A
		$O(D_2)$	(1,0)	AFM	T^3	N/A	N/A
	F_{1g}	$D_3(E)$	$(1, \varepsilon, \varepsilon^2)$	FM	T^3	~ 0.5 BCS	N/A
		$D_4(E)$	(1,i,0)	FM	T^2	N/A	N/A
		$D_4(C_4) \times R$	(1,0,0)	Non-magn	T^2	N/A	N/A
	F_{1u}	$D_3(C_3) \times R$	(1,1,1)	Non-magn	T^3	5/6 BCS	N/A
		$D_4(C_4) \times R$	(1,0,0)	Non-magn	T^3	5/6 BCS	N/A
	F_{2g}	$D_3(E)$	$(1, \varepsilon, \varepsilon^2)$	FM	T^3	0.7 BCS	N/A
		$D_4(E)$	(1,i,0)	FM	T^2	0.7 BCS	N/A
		$D_4^{(2)}(D_2) \times R$	(1,0,0)	Non-magn	T^2	N/A	N/A
	F_{2u}	$D_3 \times R$	(1,1,1)	Non-magn	$e^{-\Delta/T}$	5/6 BCS	N/A
		$D_4(D_2) \times R$	(1,0,0)	Non-magn	T^3	5/6 BCS	N/A
Hexagonal	E_{1g}	$D_6(E)$	(1,i)	FM	T^2	0.7 BCS	BCS
	E_{1u}	$D_6(E)$	(1,i)	FM	T^3	5/6 BCS	BCS
	E_{2g}	$D_6(C_2)$	(1,0)	FM	T^3	0.7 BCS	BCS
	E_{2u}	$D_2 \times R$	(1,1)	Non-magn	$e^{-\Delta/T}$	5/6 BCS	BCS
		$D_2(C_2) \times R$	(1,-1)	Non-magn	T^3	5/6 BCS	BCS
Tetragonal	E_g	$D_4(E)$	(1,i)	FM	T^2	0.7 BCS	BCS
	E_u	$D_4(E)$	(1,i)	FM	T^3	5/6 BCS	BCS

4. Non-centrosymmetric Superconductors

Superconductivity in materials with broken inversion symmetry has lately received considerable attention.⁵⁵ It is often a complicated problem to show that a crystal indeed is non-centrosymmetric, nevertheless many mirror-odd superconductors are known at present. Examples of such materials include, but not limited to, Mo_3AlC (symmetry $P4_132$), $\text{La}_5\text{B}_2\text{C}_6$ (symmetry $P4$), Mo_3P (symmetry $I-4$),⁵⁶ CeCoSi_3 , LaRhSi_3 , LaIrSi_3 (symmetry $I4mm$),⁵⁷ Na^+ -doped on surface insulator WO_3 ,⁵⁸ and others. Local breaking of mirror symmetry can occur near the interface of two different SC, or a SC and a normal metal.⁵⁹

It has been shown that broken inversion symmetry is not indiscriminately destructive for the triplet pairing states; furthermore, it actually softens the effect of the paramagnetic depairing for spin-singlet pairs.³² Lack of the inversion center leads to splitting of the energy gap in the energy spectrum of the Cooper pairs, through presence in the SC Hamiltonian of the so-called Rashba (SO coupling) term, $H_{so} = \alpha[\mathbf{p} \cdot \mathbf{c}]\vec{\sigma}$, defined as in [24], required by symmetry. The two branches of the Fermi surface, resulting from this splitting, contain states with opposite chirality of the Cooper pairs. It has been shown by Edelstein⁶⁰ that in non-centrosymmetric materials the energy necessary to destroy a Cooper pair will depend on the chirality of the pair.

Microscopic treatment of SC in non-centrosymmetric systems has been developed several decades ago by V.M. Edelstein,⁶¹ and re-visited by different authors^{26,29,30,32} recently due to the discovery of a non-centrosymmetric heavy fermion SC CePt_3Si and

other similar materials. In ref. [30] by Sergienko and Curnoe general symmetry properties of the SC state in non-centrosymmetric (NCS) crystals in presence of strong SO coupling are derived in a similar way as we conducted in the chapter above. In that work, consideration is initially restricted to one band, neglecting possible pairing in other bands and interband interactions. Symmetry properties of the SC order parameter in NCS SCs, Josephson tunneling between a conventional SC and a SC with nondegenerate bands, and limiting case of small SO coupling (with Rashba Hamiltonian) are also described. Ref. [30] concludes with analysis of applicability of the developed approach to NCS SC crystals known to date. Among the main conclusions of ref. [30] is that there exists a (theoretically anticipated) close analogy between NCS and usual centrosymmetric singlet superconductors.

Special case of NCS SC – the 2D superconductor – has been the center of attention of ref. [26] by Dimitrova and Fegel'man, which offers a theory of 2D SC with broken mirror symmetry. The focus of ref. [26] is on magnetic properties of such a system, with careful analysis of possible magnetic phase transitions, and specific attention to the LOFF phase behavior. The work is strongly theoretical, and authors, unfortunately, do not offer comparison of their theoretical results with experimental data.

The effect of suppression of the paramagnetic limiting in NCS SC was studied by Mineev³² and Frigeri *et al.*³⁵ In ref. [32], it was demonstrated that the paramagnetic suppression of a superconducting state in NCS SC exists, and the effect depends on field orientation with respect to crystal axes. It takes place due to magnetic lifting of the degeneracy of electronic states with opposite momenta of the particles forming the Cooper pairs; but it can be, in principle, absent, because the degeneracy is recreated for

some directions of applied field. The similar conclusions have been given in ref. [35] on the assumption of negligibly small gap splitting. Superconductivity in NCS systems exhibits many novel properties, especially if it occurs in materials with strong SO coupling. Examples include unusual response to Zeeman coupling, suppressed paramagnetic limiting in heavy fermion materials; coexistence of magnetic (FM or AFM) ordering with the SC phase, and other exciting properties.⁶¹

Properties characteristic of superconductors with broken inversion symmetry of crystalline lattice, but forbidden by symmetry in systems with space parity include the bulk magnetoelectric effect⁶³ – the occurrence of a spin-polarization of the current carriers induced by the supercurrent flow; difference of the magnitude of the supercurrent for two opposite directions in applied external magnetic field dependent on the sign of the mixed product $\vec{c} \times \vec{B} \cdot \hat{J}_s$; coexistence of singlet and triplet components of the SC state, and (surface) magnetoelectric effects near the interface of a mostly *s*-wave SC with a normal metal.⁵⁹

Recently, a lot of experimental activity in NCS SC was concentrated on heavy fermion and similar systems due to evidence for strong SO coupling. In these systems, triplet pairing state can be detected and manifests itself, as in CePt₃Si,³⁵ through $H_{c2}(0) \gg H_{para}$, coexistence of the SC and magnetic ordering, and other effects. Multicomponent order parameter has been predicted²⁹ in CePt₃Si, with gap structure depending on the dimensionality of the order parameter: for the 1D representation C_{4v} , the gap should have line nodes, manifested in macroscopic measurements such as $C_{el}(T) \sim T^3$ as $T \rightarrow 0$. Many NCS SC with suspected strong SO coupling have been recently

discovered, and one of them is in the focus of our experimental investigation. The motivation, description and results of this study are presented in the next chapter.

5. Test by Experiment: Re_3W

5.1. Motivation

Paramagnetic limiting for spin-singlet superconductors can be suppressed in superconductors with broken inversion symmetry of the crystal lattice.³² This opens a possibility for triplet-pairing. However, it contradicts a suggestion by P.W. Anderson³¹ that spin-triplet is unlikely to occur in a material without inversion center. Nevertheless, experimental evidence (in CePt_3Si , for example)³⁵ strongly supports the presence of p -wave pairing mechanism in non-centrosymmetric compounds. Superconductors with a crystal structure lacking inversion center, such as CePt_3Si and $\text{Li}_2\text{Pt}_3\text{B}$, are at present the subject of intense interest. Their properties can differ fundamentally from those of conventional superconductors, both low- and high-temperature.^{30,29,64,65,66,67} The subject of this investigation is superconducting Re_3W , a compound without a center of inversion. The absence of a center of inversion permits, but does not require, mixed pairing²³ and can lead to a pronounced impact by spin-orbit coupling and the possible presence of a triplet component in the order parameter.

Superconductivity in the intermetallic compound Re_3W was first reported in the 1960's.⁶⁸ The material was found to have a superconducting transition temperature, T_c , of 9 K, and to possess the crystal group symmetry $I-43m$, or $A12$, structure of $\alpha\text{-Mn}$, which does not have an inversion center. As far as we know, the present investigation of the superconducting properties of Re_3W in mixed state is the first systematic study of the material since the initial work. It is noteworthy that the original studies⁶⁸ were conducted on “as prepared” samples of this highly refractory material; annealed materials were not

investigated at the time, perhaps due to technical difficulties with processing and vacuum annealing at quite high temperatures $\sim 1500^\circ\text{C}$. Consequently, some very interesting physical properties of this material have not been discovered until now.

Experimentally, one feature of this study – “shaking” the flux line lattice (FLL) of sample's interior by a transverse *ac* magnetic field – is developed to access the equilibrium magnetization of a mildly hysteretic superconductor, one with moderately weak flux pinning. Knowledge of equilibrium magnetization allows one to calculate the thermodynamic critical field H_c . We also use this methodology to obtain estimates for the lower critical field H_{c1} from the magnetization data, which is generally a non-trivial problem for hysteretic materials.

5.2. Preparation of Samples and Other Experimental Details

The stoichiometry 3:1 in the binary phase diagram of Re_3W is approximate, with intermetallic compounds of $\sim 75\%$ Re and $\sim 25\%$ W forming in narrow χ -phase homogeneity range^{68,69} below 2573 K. In this study, Re_3W samples were prepared from elemental 99.999% Re and 99.999% W. Powdered metals were mixed in molar ratio 3:1, and the mixture was pressed into pellets using a hydraulic press. Subsequently, pellets were individually arc-melted (following the melting technique described in ref. [68]), and then annealed for 14 days at 1773 K in either an atmosphere of flowing high-purity argon or high vacuum, and then allowed to cool. Rectangular bars were then cut out of these polycrystalline pellets for measurement of their magnetic and transport properties. Synchrotron X-ray powder diffraction patterns, collected at the X7A beamline at the Brookhaven National Laboratory, confirm the non-centrosymmetric (A12, α -Mn, or *I*-

43m, in various standard notations) structure of our Re_3W samples.⁷⁰ Experimental neutron diffraction data were collected at room temperature with the HIPPO13 time-of-flight (TOF) diffractometer at the Los Alamos Neutron Science Center.

The bulk magnetic response was studied using a Quantum Design model MPMS-7 SQUID-based magnetometer equipped with a horizontal rotator for rotation of the sample about an axis perpendicular to the applied magnetic field. Electronic transport and bulk heat capacity measurements were performed on a Quantum Design PPMS-14 cryostat, equipped with a ^3He cooling option providing sample temperatures down to 0.38 Kelvin.

5.3. Structure

Synchrotron X-ray powder diffraction patterns were collected for us at the X7A beamline at the Brookhaven National Laboratory, using the wavelength of 0.70050(4) Å in flat-plate reflection geometry. The diffraction pattern of Re_3W can be almost completely indexed assuming I-centered cubic ($\alpha\text{-Mn}$) lattice (Re metal is present "on a trace level": estimated weight fraction is ~1%). Rietveld refinement yielded the results reflected in Table 3. This unit cell structure is presented on Fig. 2. Different symmetry lowering pathways were considered. There are two non-cubic maximal subgroups:

- 1) $I-42m$ - appears as isotropy subgroup for the Γ_3 (in Miller-Love notation) irreducible representation for the order parameter equal to $(a,0)$
- 2) $R3m$ - Γ_4 irreducible representation for the order parameter equal to (a, a, a)

Table 3. Re_3W : Symmetry Group $I-43m$, $a = 9.59656(5) \text{ \AA}$.

<i>Atom</i>	<i>site</i>	<i>X</i>	<i>Y</i>	<i>Z</i>
Re/W1	$2a$	0	0	0
Re/W2	$8c$	0.32184(11)	=x	=x
Re/W3	$24g$	0.35822(6)	=x	0.04383(9)
Re/W4	$24g$	0.09048(7)	=x	0.28358(9)

Tetragonal and hexagonal distortions are equally probable, based on the collected data.

The presence and degree of Re/W redistribution (i.e. deviation from stoichiometric 3:1 ratio at each crystallographic site) was established from the analysis of neutron diffraction data. Rietveld analysis was performed^{71,72} with GSAS/EXPGUI suite. No deviation from cubic symmetry was detected, consistent with the synchrotron X-ray diffraction data, Fig. 3. Refined magnitudes of the atomic displacement parameters (ADPs) and intensity distribution in the high- d -spacing region favor Re/W redistribution for the two analyzed samples. Inset of Fig. 3 shows the dependence of the integrated intensity of “superlattice” (211) reflection on the Re-occupancy of the $8c$ site calculated in the assumption of a plausible (based on ADP data) distribution model: site $8c$ W-enriched; all three other sites equally W-depleted. From this integrated intensity data it can be concluded that the $8c$ site is occupied exclusively by W; the exact distribution pattern over the three remaining sites can not be established unambiguously.

The Re/W distribution pattern varies with from sample to sample: Fig. 4 shows the same range of the normalized TOF neutron diffraction patterns for samples prepared

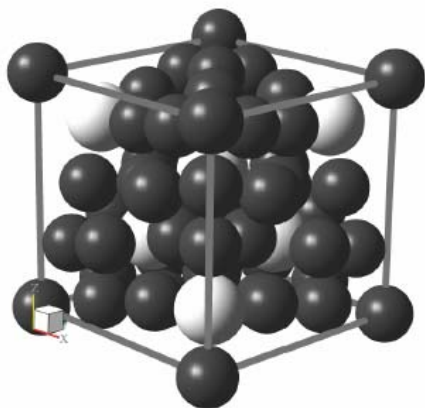


Figure 2. Crystal structure of non-centrosymmetric Re_3W . Most of rhenium and tungsten atoms are statistically distributed among crystallographic sites in this structure (black); only the position $8c$ (light gray) appears to be occupied predominantly by tungsten.

under identical conditions. These datasets were collected with different TOF diffractometers (HIPD and NPDF - this accounts for the difference in resolution). The data shown on the graph were normalized on incident spectrum, background-subtracted and normalized to the same maximum intensity. Clearly, the intensity distribution in the high- d -spacing range, especially, in the (211) reflection is markedly different, indicating different Re/W distribution patterns collected by two different methods. This variation in distribution patterns isn't surprising, taking in consideration that crystallographic site multiplicities (2, 8, 24 and 24) of the χ -phase cannot accommodate 3:1 ratio of Re to W atoms; some sites will have to show some statistics, and therefore no exact ordering of W and Re between crystallographic sites exists.

Pair Distribution Function (PDF) analysis revealed only minor deviations from the average (crystallographic) structure. Fig. 5 shows the comparison of observed PDF

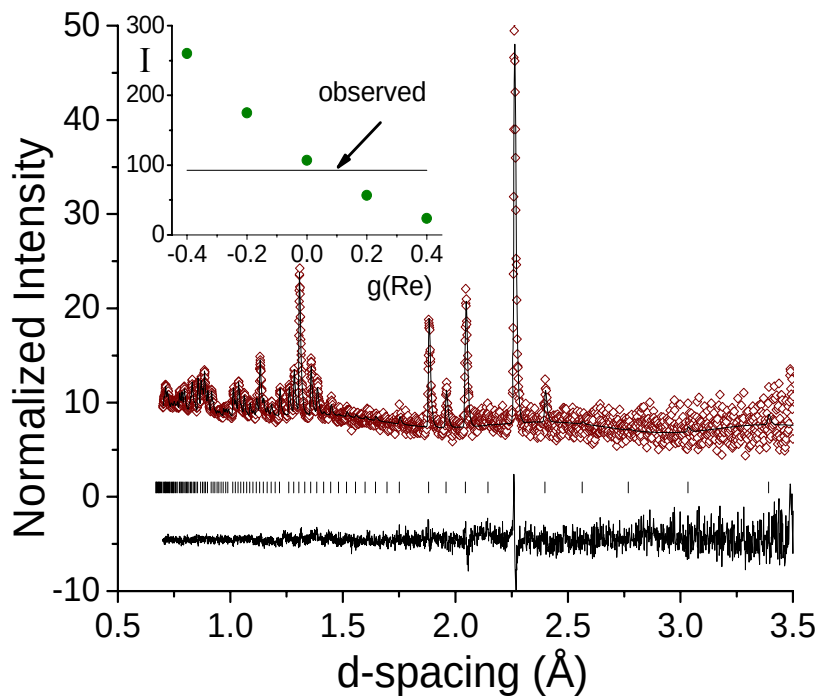


Figure 3. Normalized intensity, in arbitrary units, as function of d -spacing.

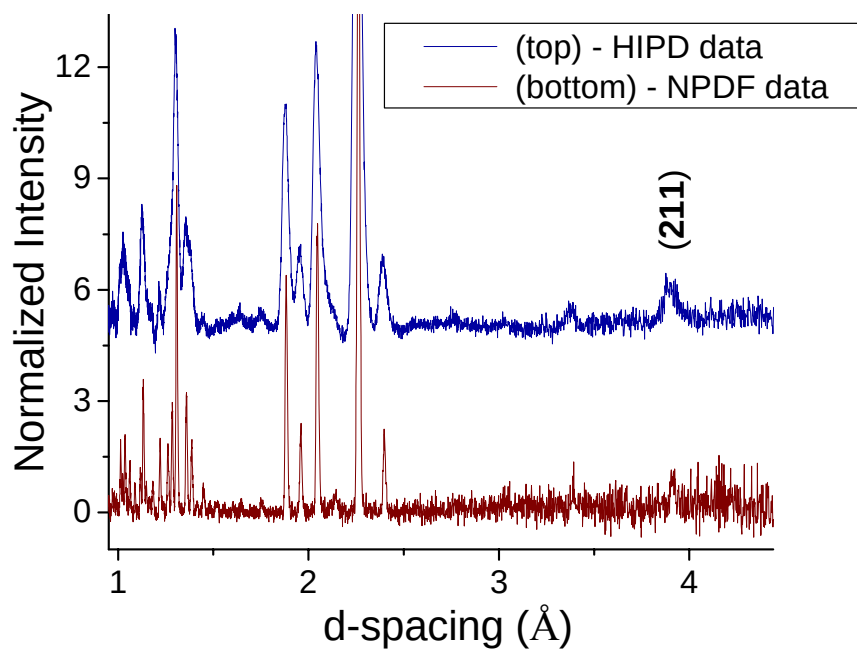


Figure 4. Normalized intensity, in arbitrary units, as function of d -spacing. Comparison of HIPD and NPFD data, collected for the same material.

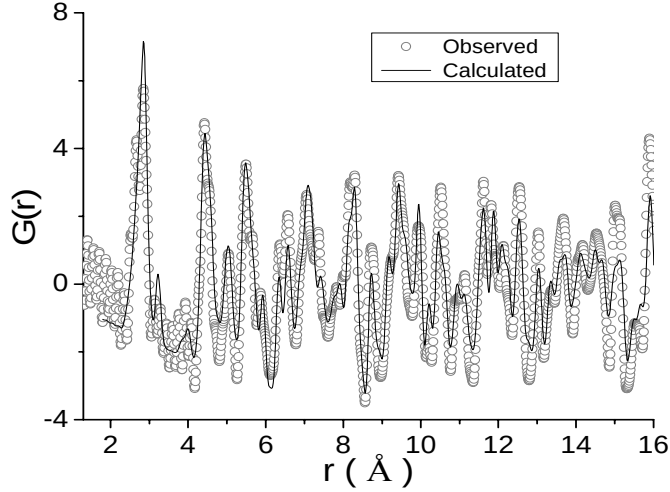


Figure 5. Comparison of the observed (circles) and calculated (solid line) Pair Distribution Functions for neutron diffraction data in annealed Re_3W .

(i.e., calculated⁷³ from NPDF data using the PDFgetN program) and calculated PDF (using PDFGUI/PDFFit2 suite, described in [74]; with lattice parameter and overall ADP as the only refinement variables). Thus, the disorder effects (e.g. reduction of l_{tr} , the transport mean free path) are associated predominantly with the compositional disorder.

5.4. Experimental Results

The superconducting transition temperature T_c was determined from the measurement of the magnetization M of rectangular samples of annealed Re_3W as a function of temperature T (Fig. 6) in an applied field H of 10 Oe, with longest dimension of the sample parallel to the field. The field-warming after zero-field-cooling curve shows that the annealed Re_3W materials exhibits 100 % screening in the Meissner state

with a T_c near 7.8 K. The field-cooled curve displays little diamagnetic signal from Meissner-like flux expulsion.

Resistivity measurements were conducted in a Quantum Design PPMS-14 on rectangular samples in standard four-wire geometry, in the range of temperatures 2 K to 300 K. Copper wires were attached to the sample by means of silver-paste epoxy. Samples became superconductive at $T_c = 7.8$ K. The width of the superconducting transition was $\Delta T = 0.1$ K at zero field, and increased with field. These results are in perfect agreement with the aforementioned measurements of magnetic susceptibility. The residual resistivity ratio for these samples was $RRR \approx 1.1$ (resistivity just above the super-conducting transition being $\rho(T_c) = 116 \mu\Omega.\text{cm}$, and resistivity at room temperature being $\rho(300 \text{ K}) = 133 \mu\Omega.\text{cm}$). Experimental data are represented on Fig. 7, with inset emphasizing the phase transition. Relatively high resistivity, compared to 18.9 (pure Re)

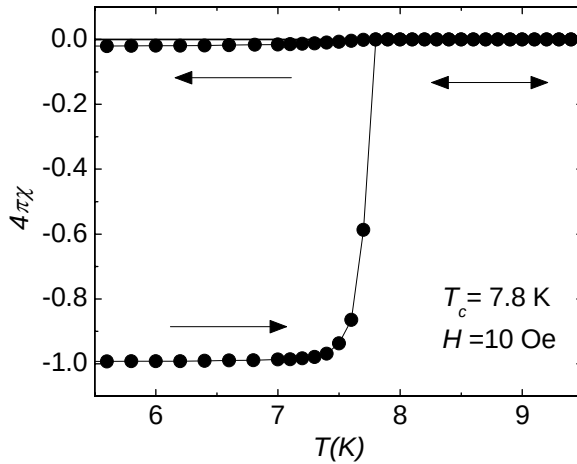


Figure 6. Magnetic susceptibility of the annealed samples of Re_3W . Data collected on heating after ZFC (lower branch), followed by field-cooling (upper branch).

and 4.9 (pure W) $\mu\Omega\cdot\text{cm}$ at 273 K, can be rationalized taking in consideration the complicated architecture of the α -Mn structure. For comparison,^{75,76} $\rho(300\text{ K}) = 710\ \mu\Omega\cdot\text{cm}$ for α -Mn (some sources list $\rho(300\text{ K}) = 185\ \mu\Omega\cdot\text{cm}$), while $\rho(300\text{ K}) = 23\ \mu\Omega\cdot\text{cm}$ for b.c.c. γ -Mn.

This high metallic resistivity can arise, for instance, from loose packing of Re and W atoms in α -Mn structure, which allows for large amplitudes of thermal vibrations and thus very strong electronic scattering. Another source of scattering is likely the disorder in distribution of Re/W atoms between the lattice sites, detected by the neutron scattering analysis, as described above. Neutron scattering analysis showed that only $8c$ sites are predominantly (at least 97%) occupied by W atoms, while other lattice sites all have some statistical distribution of Re/W showing depletion in W. Multiplicities of the crystallographic sites of the χ -phase of Re-W inhibits a completely ordered distribution of Re and W atoms between structural sites, making it very difficult to remove structural disorder, even with the extensive anneals used in this work.

Calculation of the mean free path based on the BCS approach⁷⁷ using our experimental data gave $l_{tr} = 4\ \text{\AA}$ (less than $\frac{1}{2}$ of the lattice parameter), also supporting presence of very strong electronic scattering described above. Below is the outline of the mean free path calculation.

$$M_{\text{Re}} = 186.2\ \text{g/mol}, M_{\text{W}} = 183.9\ \text{g/mol}; \text{density } \rho_{\text{Re}_3\text{W}} = 18.1\ \text{g/cm}^3$$

$$\Rightarrow \text{Molar volume } V_M = [3(186.2) + 183.9] / 18.1 = 41.0\ \text{cm}^3/\text{mol}$$

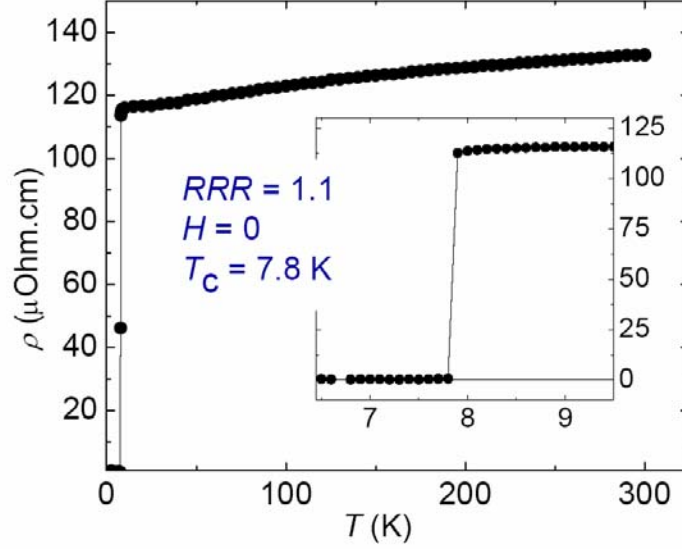


Figure 7. Resistivity of Re_3W in range 2 - 300 K, zero field. Inset shows an expanded view near T_c .

$$\text{Valence electron density } n = \frac{1}{V_M} \times (3 \cdot 7 + 1 \cdot 6) \frac{e}{u.c.} \times 6.02 \times 10^{23} \frac{u.c.}{mol} = 3.96 \times 10^{23} \frac{e}{cm^3}$$

$$\text{Fermi surface area for free electron gas: } S_F = 4\pi(3\pi^2 n)^{2/3}$$

$$\text{Mean free path } l_{tr} = \frac{1.27 \times 10^4}{\rho_{\Omega.cm} n^{2/3} (S/S_F)} = 3.5 \times 10^{-8} \text{ cm}$$

We take $S/S_F = 0.5$ ($= 1/2 \dots 2/3$ for V_3Si , Nb_3Sn). Hence, the coherence length $\xi(0) \gg l_{tr}$, and our Re_3W samples are clearly in the dirty limit.

In the mixed state, in larger magnetic fields, the total bulk magnetization is a sum of Pauli and superconductive components, as is evident from Fig. 8. The Pauli term (and

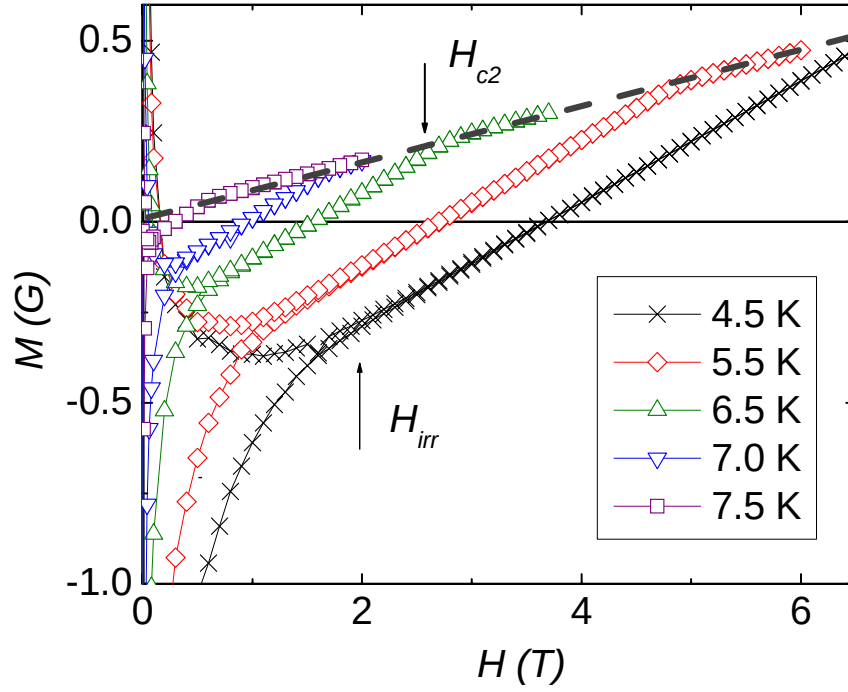


Figure 8. Magnetic hysteresis curves of bulk annealed Re_3W at various temperatures, with the longest sample dimension parallel to the applied homogeneous longitudinal field. The linear, reversible Abrikosov-like behavior of $M(H)$ spans, on average, over 60% of the superconducting region. These raw data include a significant contribution from the Pauli susceptibility (indicated by the dashed line). Arrows indicate the criteria for determining upper critical field, H_{c2} , and classical irreversibility field, H_{irr} .

also core diamagnetism) is linear-in-field with the form $M_{ns} = \chi H$ where the susceptibility χ has negligible temperature dependence near T_c . By subtracting the Pauli component (which was obtained both from the data above T_c and from the linear portion of the $M(H)$ curves above H_{c2} , the upper critical magnetic field), we obtain the superconducting component, M_{sc} . This quantity clearly goes to zero at H_{c2} , thus allowing the temperature dependence of upper critical field to be determined. The data for $H_{c2}(T)$ are nearly linear close to the transition temperature, with the slope $(dH_{c2}/dT)|_{T_c} = -2.1$ T/K, and an estimated value of the upper critical field at $T = 0$ of $H_{c2}(0) = 11.3$ T using the Werthammer – Helfand - Hohenberg relations.⁷⁸

The Ginzburg – Landau coherence length (which is, in turn, related to the vortex core size⁷⁹) is $\xi(0) = [\phi_0/(2\pi H_{c2}(0))]^{1/2} = 5.3$ nm at $T = 0$ K. Overall, these results agree very well with transport measurements on samples of the same material.

Measurements of resistivity in a series of magnetic fields from 0 T up to 10 T are shown in Fig. 9. High magnetic fields appear to promote thermal fluctuations (or mechanical vibrations) in this setup. The noisy character of normal state resistivity above 3 T, as reflected on Fig. 9, is likely due to eddy currents (especially around non-superconductive leads in contact with the sample) increasing with applied field. Note the positive magnetoresistance, $\rho_m(H) = 0.9 \mu\Omega\text{.cm/T}$, while the resistivity just above the T_c is rather large, $\rho(T_c) \sim 120 \mu\Omega\text{.cm}$. By recording the transition temperature at each static magnetic field, we found the $H_{c2}(T)$ dependence in Re_3W , with $-dH_{c2}/dT$ at T_c of 2.0 T/K, and $H_{c2}(0 \text{ K}) = 10.76$ T using the WHH formula in dirty limit. These results are nearly identical (see Fig. 10) to the $H_{c2}(T)$ finding from the magnetic measurements.

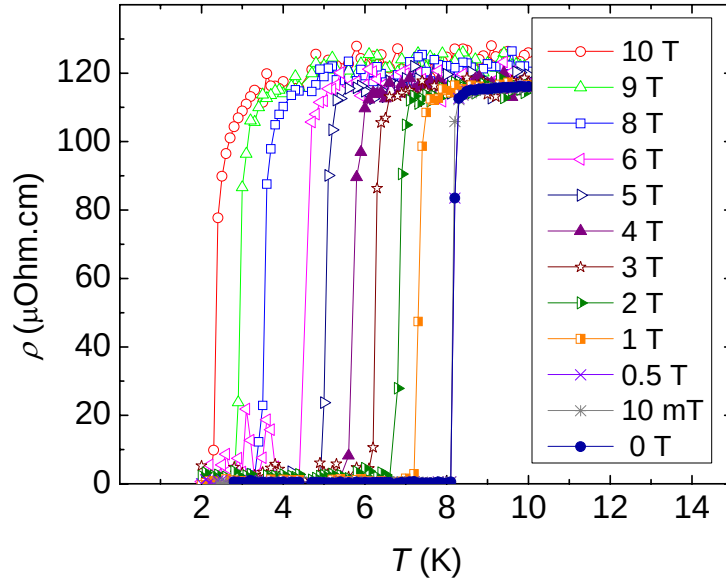


Figure 9. Resistivity of Re_3W from 2 K to 10 K in a set of magnetic fields from 0 - 10 T.

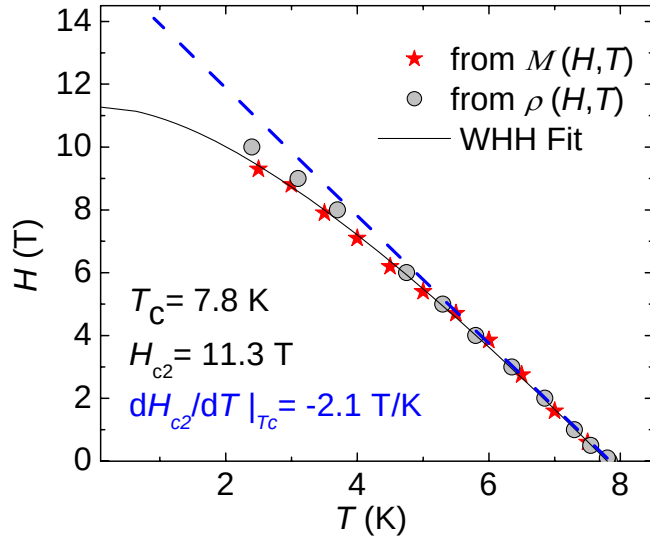


Figure 10. Phase diagrams $H_{c2}(T)$, obtained by transport and magnetic methods, are linear close to T_c and nearly coincident. Dashed line indicates the tangent of H_{c2} near T_c .

Taking into consideration percolative character of resistivity, we have taken T_c as the temperature immediately below the offset of each transition. In the mixed state, transition widths expand due to increased effect of thermal fluctuations just below a superconducting transition.

The magnetization curves $M(H)$ in the mixed state (see Fig. 8) are remarkably reversible and linear over a large range of values of the applied fields, following the Abrikosov⁸⁰ relation (for a more common triangular vortex lattice configuration):

$$-4\pi M_{sc} = (H_{c2} - H) / 1.18(2\kappa^2 - 1) \quad (55)$$

Normally, the Abrikosov formula is considered to apply only in a narrow range of fields close to H_{c2} . In contrast, the linear-in- H dependence extends over an exceptionally wide range of fields, as discussed below. Quantitatively, application of Eq.(55) gives values for the GL parameter $\kappa(0) = \lambda(0) / \xi(0) = 52$ and penetration depth $\lambda(0) = 297$ nm. Knowledge of the GL parameter also allows calculation, within the same Ginzburg-Landau-Abrikosov-Gorkov (GLAG) framework, of the lower critical field, with $H_{c1}(0) = H_c(0) \ln(\kappa) / [\kappa\sqrt{2}] \approx 8$ mT. The thermodynamic critical field is given by the familiar expression $H_c = H_{c2} / [\kappa\sqrt{2}]$. Careful examination of the data revealed that the slope of reversible linear part of M_{sc} slightly increases as temperature goes down, leading to the temperature-dependent GL parameter, $\kappa = \kappa(T)$. Thus, one can estimate the temperature dependence of the lower critical field, $H_{c1}(T) = H_{c2}(T) (2 \kappa(T))^{-2} \ln(\kappa(T))$.

Next, let us consider a somewhat unusual method to overcome irreversible effects in the magnetic response of these and similar materials. In particular, we were able to extend the reversible, equilibrium part of the magnetization curve by rocking the sample by an angle θ (typically 20°) in an applied static magnetic field H_0 . In effect, this resembles the application of a transverse *ac* field of magnitude $H_0 \sin \theta$ and frequency of about 0.2 Hz of the flux line lattice (FLL) shaking method, developed by Willemin *et al.*⁸¹ The application of a transverse alternating magnetic field to a superconductor in mixed state promotes flux motion that may overcome vortex pinning effects⁸² and cause the relaxation of the Bean critical state flux profile within the sample; thus lessening the magnetic hysteresis and allowing an approach to the equilibrium magnetic state. The longitudinal *ac* field contribution to the FLL relaxation in our setup is negligible compared to that of the transverse *ac* field.⁸³

In our setup, a rectangular parallelepiped (with dimensions, in mm, 0.63 x 0.61 x 5.01) of Re_3W was mounted with a small amount of Duco Cement on the platform in a Horizontal Rotator assembly of the Quantum Design MPMS, with the longest dimension of the sample initially parallel to the *dc* field. The effect of FLL shaking on magnetic hysteresis was investigated starting from the "virgin" state. The *dc* field was set to some fixed value, where the sample moment was measured; at that field, the sample was then rotated back and forth in an oscillatory manner using the horizontal rotator with (typical) angular setting of $+20^\circ$, -15° , $+10^\circ$, -5° , 0° ; after this, the sample moment was immediately measured again. This routine was performed at successive fields in the range 0-65-0 kOe, for both increasing and decreasing field history. Smaller field steps were used below 1.5 kOe, and magnetization loops were collected at fixed temperatures in the range of 2.5 to

7.5 K. Variation of the rotation amplitude and the number of oscillations per measurement had negligible effect on the results.

The effective frequency of oscillations, 0.2 Hz, is sufficiently low to rule out sample heating by *ac* field as a cause of the FLL relaxation. If heating were the main reason for the observed change in magnetization, $M(H)$ should have shifted up both along field-increase and field-decrease branches of the hysteresis loop. We find that, on the contrary, $M(H)$ is shifted up along the field-increase branch as result of FLLS, and is shifted down along the field decrease branch, so that hysteresis is reduced or completely eliminated. As an additional check, we have compared the magnetization immediately after rocking the sample and magnetization measured ten minutes after sample rotation. If there were significant sample heating, the measurement immediately after rocking would result in higher (more positive) value. However, in both cases magnetization was the same within the experimental resolution. Therefore we conclude that the observed relaxation is not due to sample heating by an *ac* field.

Typically, one set of oscillations appeared to be sufficient to redistribute vortices into an equilibrium configuration for a given field, as evidenced by collapse of the increasing and decreasing field branches of $M(H)$ curves to coincident values (Fig. 11). We will denote as $M^*(H)$ the magnetization of the system in its equilibrium magnetic state, and H^* - the lowest field at which the system exhibits fully reversible isothermic $M^*(H)$. Criteria for determining H^* and Meissner slope are shown on Fig. 11 and explained in the caption to the picture.

Results of FLL relaxation on samples in our study are illustrated in Fig. 12 for bulk Re_3W at $T = 3$ K. At this temperature, the fully reversible region without the FLL

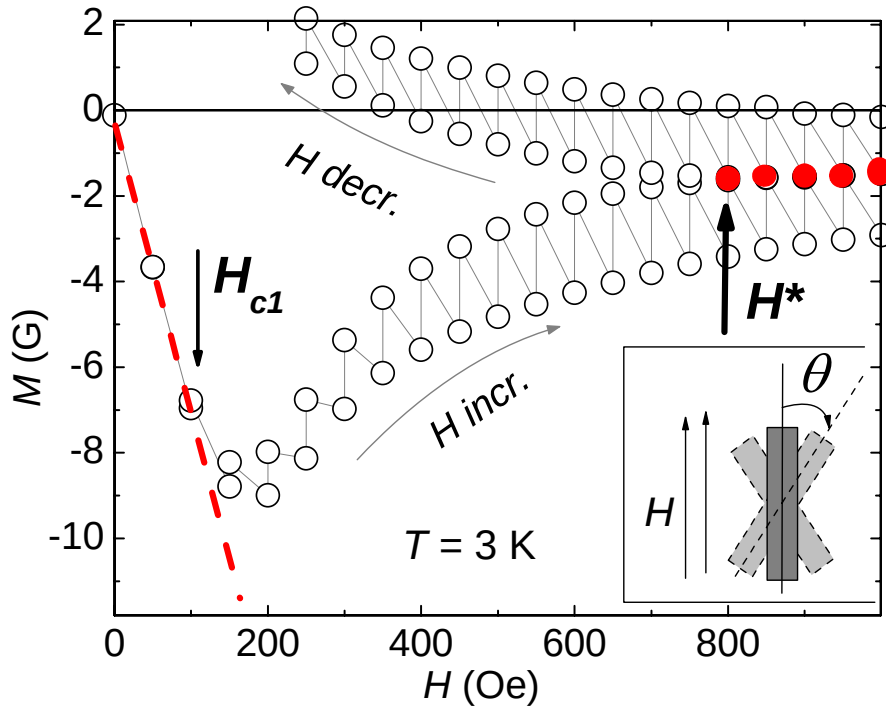


Figure 11. At a higher resolution in field steps, magnetization as a function of field before and after FLL shaking, reveals the lower irreversibility field, $H^*(T)$. Circles represent data points; the data points (filled red circles) coincidental after the FLL shaking in increasing and decreasing fields represent equilibrium magnetization, $M^*(H)$; Meissner slope (dashed red line) is obtained from the lower magnetization branch (0-100 Oe in increasing from "virgin state" field). Criterion for H_{c1} determination is also presented. Inset shows conceptual picture of shaking the sample in longitudinal applied field.

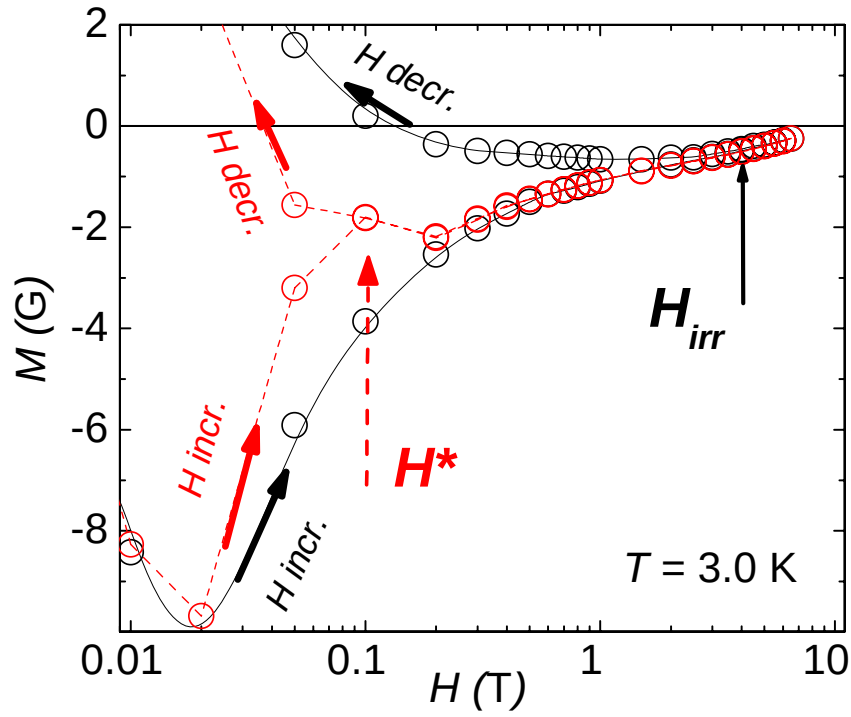


Figure 12. Effect of the FLL shaking on hysteresis curves $M(H)$ in bulk Re_3W . Open circles represent data points; solid (black) line connects data points collected immediately prior to shaking, and dashed (red) line - immediately after shaking the sample in field. Vertical arrows indicate the irreversibility field prior to the FLL relaxation, H_{irr} , and the lower irreversibility field, H^* , after the FLL relaxation obtained by application of transverse ac magnetic field to the sample.

shaking spans from $H_{\text{irr}} = 5$ T to extrapolated $H_{c2} = 8.8$ T (43% of the superconductive region); while after application of the FLL shaking to the sample, complete reversibility extends from $H^* = 0.085$ T to extrapolated $H_{c2} = 8.8$ T (over 99% of the superconducting region). With exception for fields above H_{c1} and below 1% of $H_{c2}(T)$, the nearly perfect reversibility of the measured equilibrium magnetization $M^*(H)$ allows one to calculate the thermodynamic critical field $H_c(T)$ via the following relationship:

$$F_s - F_n = \left| \int_{H^*}^{H_{c2}} M dH \right| + \left| F_H \right| = \frac{H_c^2}{8\pi} \quad (56)$$

Here F_H is the correction to the condensation energy below H^* , and can be estimated as $\frac{1}{2} \{M(H_{c1}) \cdot H_{c1} + [M(H_{c1}) + M(H^*)] \cdot [H^* - H_{c1}]\}$. We found that F_H contributes about 35% to the condensation energy at $T \sim T_c$, and about 10 % well below T_c .

Application of the FLL shaking method to annealed Re_3W samples with 5 G steps in fields up to 100 G allows one to measure the temperature-dependent lower critical field with very good precision (estimated error $\sim 5\%$). The procedure of determining lower critical field is, in principle, similar to conventional H_{c1} measurements in type II superconductors;⁸⁴ however, it possesses the benefit of virtually no processing time requirement. Also, conventional methods of lower critical field determination rely on the assumption that magnetization curve should diverge from the Meissner slope $\chi = -1/(4\pi)$ just above H_{c1} . At the same time, specimens with significant Bean-Livingston surface barrier effect and/or with strong bulk pinning typically exhibit screening by sheet currents well above H_{c1} , impeding accurate H_{c1} estimation. In Meissner state, $M(H)$ is fully reversible and linear, with the temperature- and field-independent slope of $\chi = -1/(4\pi)$.

On the other hand, as soon as magnetic flux (vortices) begins to penetrate the sample and form the mixed state, the susceptibility becomes a function of H and T : $\chi = \chi(H, T)$. Thus, magnetization is typically no longer linear in H (unless the aforementioned linearity is extended by strong surface barrier), and it also strongly depends on pinning of flux lines within the sample. Both Bean-Livingston surface barrier,⁸⁵ which prevent magnetic vortices from entering a superconductor above H_{c1} , and bulk pinning that prohibits flux lines from accessing equilibrium configuration inside superconductors enhance hysteresis and dramatically affect the correct evaluation of H_{c1} by traditional methods. However, application of a transverse alternating field in FLL shaking method assists the flux lines in moving from a metastable pinned configuration(s) into the thermodynamically stable equilibrium at given H and T . So, H_{c1} can be accurately determined as the lowest field at which the values of $M(H)$ at fixed (H, T) before and after shaking the sample in field start diverging as we increase field from the "virgin state" of the sample. This method produced values for the lower critical field for samples in our study that are in good agreement with calculation of H_{c1} from data for H_{c2} , yielding $H_{c1}(0) = 70$ Oe. Note that for this method to be applicable, FLLS must produce at least a *partial* relaxation of the non-equilibrium state at H_{c1} ; it is not necessary to realize a complete relaxation to equilibrium.

One potential scenario to account for the linearity of the hysteresis curves, in combination with the temperature - dependent κ , is a field - dependent size of the vortex cores.⁷⁹ In this picture, the vortex cores start to come in contact with each other at a relatively low field. Then, as the field is raised towards the observed H_{c2} , the vortex cores shrink, so that the degree of their overlap and the volume fraction of normal metal stay

unchanged. This would require a very strong field dependence of ξ . Having the equilibrium magnetization as a function of field, extracted with help of the FLL shaking method, allowed us to address the possibility of field-dependence of the vortex core size in Re_3W . We followed the approach described in [79]. Within the framework of this method, one can approximate reversible part of the isothermic magnetic hysteresis curve of a superconductor by a general expression:

$$M = -M_0 [\ln(\eta/b) + \alpha/b - (\ln \eta + \alpha)b], \quad (57)$$

where $b = B/H_{c2}$, $M_0 = \phi_0(32\pi^2\lambda^2)^{-1}$, η and α are fitting parameters, such that $M(H_{c2}) = 0$. Upon finding the best fit for the reversible part of magnetization, one can calculate the field-dependent vortex core size, $\xi^*(b)$, through

$$\xi^*(b) = \xi^*(B) / \xi(H_{c2}) = b^{-\alpha/2b} \exp [(\ln \eta + \alpha)(b^2 - 1)/4b] \quad (58)$$

It was found that the best fitting parameters for the equilibrium magnetization give the vortex core size in annealed Re_3W , illustrated on Fig. 13. Normally, it would be expected for a vortex core to expand with decreasing field, as observed for most materials, with rare exceptions. On the contrary, this analysis leads to an indicated decrease in core size with decreasing field for Re_3W . Core size increasing with field was observed for $H||c$ -axis in MgB_2 - an effect attributed in [79] to change in the gap structure under application of magnetic field. This hypothesis is not applicable in the case of polycrystalline samples for obvious reasons, unless the gap opens up isotropically. This comes as a surprise, since for

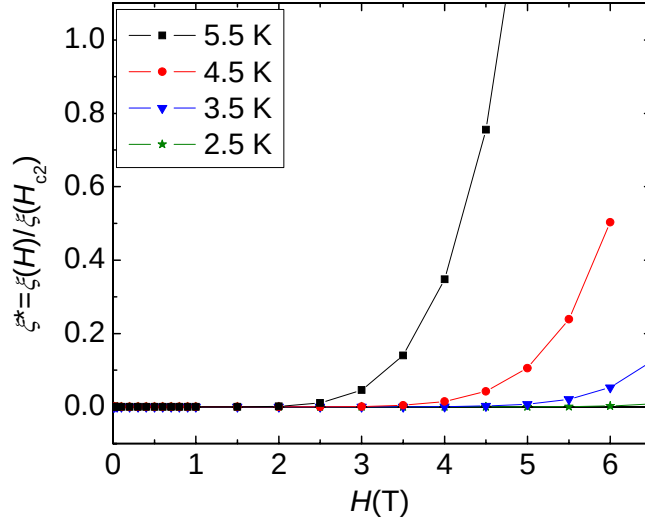


Figure 13. Coherence length field dependence at different temperatures.

superconductors in dirty limit (as Re_3W evidently is) recent analysis by Kogan and Zhelezina⁸⁶ revealed that $d\xi/dH = 0$. Thus, the scenario of field-dependent core size cannot account for extended linearity of $M(H)$ curves, at least not within the confines of present day theory. Finally, extended linearity of reversible $M(H)$ was recorded⁸⁷ by B. Andrzejewski *et al* for $\text{W}_7\text{Re}_{13}\text{X}$ ($\text{X} = \text{B}, \text{C}$) compounds, but they do not offer discussion of this phenomenon.

Next, we consider explicitly irreversible magnetization. Calculation of the critical currents based on the Bean model⁸⁸ gives results shown in Fig. 14. The values of critical

current density, given by $J_c(H, T) = \frac{15\Delta M(H, T)}{r}$ in critical state, are very low, as to be

expected from the highly reversible magnetization curves. Change in the power law on the logarithmic plot $J_c(H)$, most pronounced at low temperatures, can be interpreted as an

indication of the change in pinning mechanism. Assuming an empirical relation $J_c \sim H^{-m}$ between the critical current density and field, the magnitude of the exponent m allows one to judge the character of the vortex pinning. The field corresponding to this crossover in pinning mechanism is referred to here as H_{kink} , and indicated on Fig. 14.

A magnetic phase diagram, summarizing our findings, is presented on Fig. 15. It reflects that application of the FLL relaxation, through shaking of a long thin sample in homogeneous field, is capable of lowering the irreversibility field by at least an order of magnitude or more. A possible interpretation of the vortex states based on this diagram can be as follows. Here, the area below the $H_{cI}(T)$ curve indisputably corresponds to Meissner state. Areas between $H_{cI}(T)$ and $H^*(T)$ can be interpreted as a dynamic vortex state dominated by the surface barrier. It was shown theoretically by Burlachkov and others^{4,5} that surface barriers control penetration field H_p in superconductors with weak

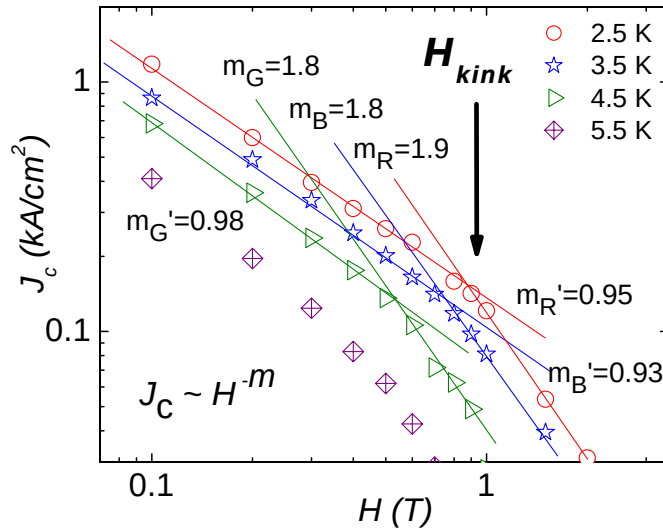


Figure 14. Critical current density in Re_3W , as calculated from the magnetic hysteresis using Bean model. H_{kink} is the field at which power law $J_c(H)$ changes.

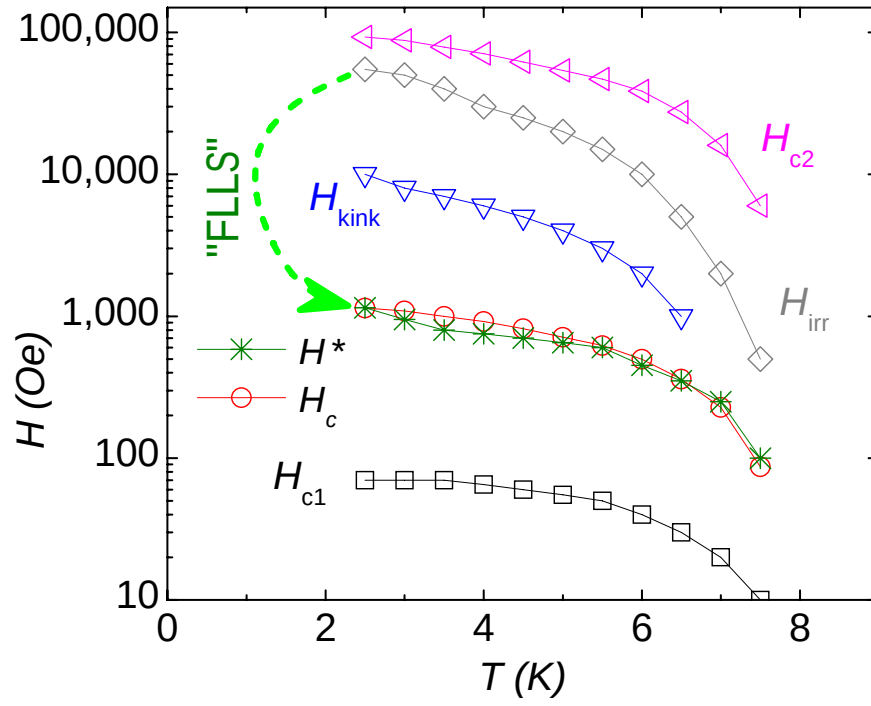


Figure 15. Vortex state diagram in decimal scale. Application of FLL shaking (FLLS) decreases the observed irreversibility field by an order of magnitude or more, and extends the reversibility region down to H^* , as indicated by the dashed arrow.

pinning, and may persist up to H_c : $H_p \approx H_c$ for an absolutely perfect surface.⁵ In this sense, H^* resembles H_p . Therefore it is not surprising that the dynamical quantity H^* traces the thermodynamic quantity H_c in bar-like samples of annealed, weakly pinning Re_3W in homogenous longitudinal field. Discovered in this work, the relationship between H_p and H^* should be tested on more specimens with variably weak pinning and well-prepared surface, and may become a practical tool for evaluation of H_p in such materials. Furthermore, in the area of the diagram on Fig. 15 corresponding to fields between H_{irr} and H_{c2} the material exhibits completely reversible magnetic behavior.

Finally, the area between H^* and H_{kink} corresponds to an FLL configuration with one pinning mechanism, and the area between H_{kink} and H_{irr} – with another pinning mechanism, as discussed above.

It appears that magnetic and electronic transport measurements provide little information about the fundamental character and pairing in superconductivity of Re_3W . When these approaches fail, probing thermal of quantities tied to superfluid electrons density, such as the London penetration depth or electronic specific heat, can provide an alternative, direct, reliable and insightful method of superconducting state study.

5.5. Penetration Depth Measurements

The London penetration depth and the superfluid density, for a fully-gapped *isotropic* pairing state, are completely connected, at low temperatures, through the following expression⁹¹:

$$\rho_s \propto \lambda^{-2}(T) \propto 1 - (2\pi\Delta(0)/T)^{1/2} \exp(\Delta(0)/k_B T) \quad (59)$$

In this case, $\lambda^{-2}(T)$ changes insignificantly below $T < 0.3T_c$. On the other hand, it is known that line nodes in the gap cause the superfluid density to display a power-law behavior, $\lambda^{-2}(T) \propto 1 - aT^n$, where $n = 1, 2$, or 3 . A nonexponential temperature dependence of $\lambda^{-2}(T)$ that implies presence of nodes in the superconducting gap has been reported for several unconventional superconductors without inversion symmetry, such as CePt₃Si and Li₂Pt₃B.⁶⁴ The model of Hayashi *et al*⁹⁰ allows calculation of $\lambda^{-2}(T)$ for a given magnitude of singlet and triplet (or *s*-wave and *p*-wave) components. It produces a good agreement with experiment in case of non-centrosymmetric Li₂Pt₃B and Li₂Pd₃B.⁶⁴

We have extracted the magnetic penetration depth $\lambda^{-2}(T)$ for Re₃W from the measurement of the *dc*-susceptibility $\chi(T)$ of a collection of small particles dispersed in epoxy, and compared our results to that of our collaborators from the Ames National Laboratory, who derive their data for $\lambda^{-2}(T)$ from the change in resonance frequency of a tunnel-diode driven oscillator operating at 10 MHz.

In the first technique, ball-milled powder of annealed Re₃W, with particle size of the order 10 μm and the average aspect ratio of 0.6 (determined by direct optical microscopy analysis), was mixed with epoxy in a gelatin capsule and cured at room temperature in a uniform applied magnetic field of 6 T. Curing in field induces alignment of the paramagnetic particles with their longest dimension parallel to the field, thereby reducing their demagnetizing ratio. Measurement of the *dc* susceptibility of this sample

was performed on a QD MPMS in the applied field of 3 Oe at temperatures down to 1.85 K ($1/4T_c$). The epoxy and other addenda showed minimal amount of diamagnetism, about 0.5% that of the actual sample in the temperature range used. Prepared in this manner, the sample showed no magnetic hysteresis in fields up to at least 10 Oe.

The magnetic susceptibility can be related to the London penetration depth and particle size by the following expression⁹²:

$$4\pi\chi = -\frac{1}{1-D} \left(1 - \frac{3\lambda}{R} \coth \frac{R}{\lambda} + \frac{3\lambda^2}{R^2}\right) \quad (60)$$

where $D = 0.22$ for the aspect ratio of 0.6. Note that Shoenberg's original derivation considered spherical particles, leading to a prefactor of $3/2$ in Eq.(60); we have replaced that prefactor by $1/(1-D)$ to produce the correct susceptibility $4\pi\chi$ for large particles with demagnetizing factor D . After averaging over the particle size and inverting Eq.60 numerically, we obtain λ . As it is λ/R that enters Eq.60, accurate knowledge of particle size is not important for determination of the normalized London penetration depth, $\lambda(T)/\lambda(0)$. The absolute value of $\lambda(0) = 300 \pm 10$ nm was determined from measurements of H_{c2} and κ , as described earlier in this work.

In the tunnel-diode resonator technique, a self-resonating LC tank is powered by a tunnel-diode.^{89,92} As a bulk polycrystalline sample is inserted into a coil, its inductance changes in response and causes the shift of the resonant frequency, $\Delta f = -4\pi \Delta f_0 \chi$, where Δf_0 is a calibration constant dependent on sample geometry. At low

temperatures $\chi = -(4\pi)^{-1}(1 - (\lambda/R)\tanh(R/\lambda))$, where R is the effective sample dimension.⁹² This technique has high stability (0.1 ppb) and small excitation field amplitude, which result in sub-Angstrom precision of measurements.

The normalized superfluid density $\lambda^2(0)/\lambda^2(T)$, extracted from the susceptibility measurements, is shown in Fig. 16 by solid squares, together with results from the resonator experiment (open circles). The agreement between the two measurements is excellent. The line through the data (symbols) was obtained through the s -wave weak coupling BCS theory in dirty limit, for which the superfluid density is given by⁹³:

$$\left[\frac{\lambda^2(0)}{\lambda^2(T)} \right]_{dirty} = \frac{\Delta(T)}{\Delta(0)} \tanh\left(\frac{\Delta(T)}{2k_B T} \right)$$

The temperature-dependent gap was obtained by solving the self-consistent gap equation in the full temperature range (Fig. 16, inset). Both datasets can be fit well by the above equation, and we obtain $(\Delta(0)/k_B T_C)_{dirty} = 1.76 \pm 0.01$, which coincides with the standard BCS value (weak coupling). Better fit can be obtained by assuming weaker electronic scattering, which requires an increase in coupling strength. Treating $\Delta(0)$ as an adjustable parameter in clean limit and fitting the low-temperature portion of the data, we obtained an essentially perfect fit with upper bound on the gap magnitude: $(\Delta(0)/k_B T_C)_{clean} = 2.1 \pm 0.1$.

Thus it appears that superfluid density in these Re_3W samples is adequately described within the BCS framework and no appreciable influence of spin-triplet pairing

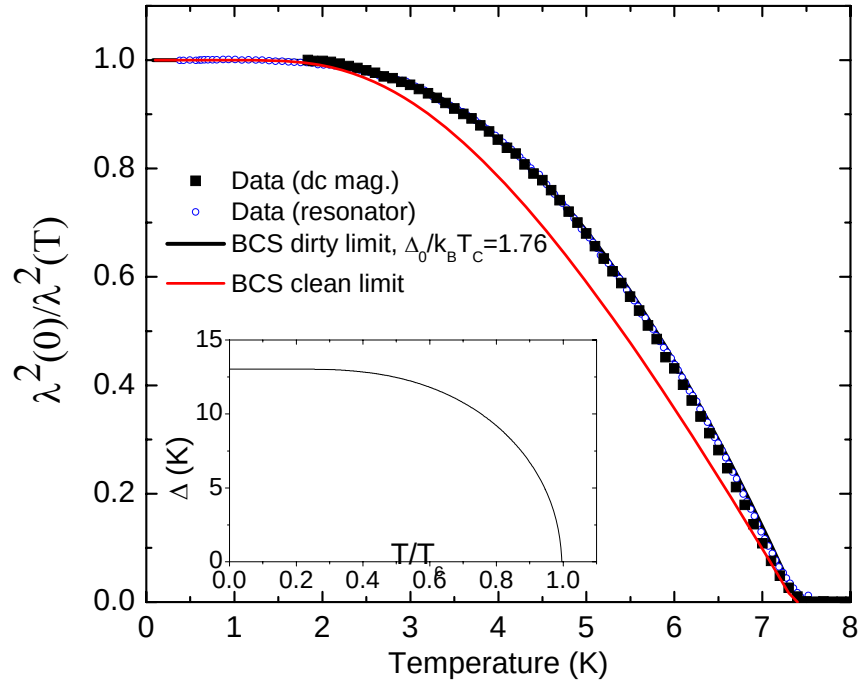


Figure 16. Temperature dependence of normalized superfluid density $\lambda^2(0)/\lambda^2(T)$. Squares represent data from dc magnetization measurements; circles – tunnel diode resonator method. Dotted line – clean limit, weak-coupling BCS curve $\lambda_L^{-2}(T)$. Solid line – dirty limit BCS calculation with $\Delta(0)/k_B T_C = 1.76$, weak-coupling value. Inset: energy gap $\Delta(T)$.

is detected. This makes Re_3W different from the heavy fermion CePt_3Si , but similar to $\text{Li}_2\text{Pd}_3\text{B}$.⁶⁴ In the latter case, spin-triplet component of the order parameter was noticed, but it was smaller than spin-singlet, thus making for a nodeless, but anisotropic gap. In our case, however, no contribution from spin-triplet is detected at all. This is somewhat surprising, as the large atomic numbers of both Re and W, can be expected to promote strong spin-orbital interactions in this material.

A possible reason for the absence of a spin-triplet component may be significant disorder stemming from statistical character of distribution of Re and W atoms among the crystallographic sites, which leads to a very irregular electronic landscape of the material. When the order parameter has nodes, even non-magnetic impurities suppress T_c very effectively. If Re_3W would possess a triplet component, scattering suppresses it in presently available materials. In references [94, 95] the effect of impurities on mixed-pairing superconductivity was considered. The conclusion of that work was that triplet-pairing channel should be suppressed by non-magnetic impurities/disorder similarly to Abrikosov-Gor'kov T_c suppression in conventional superconductors by magnetic impurities. In contrast, disorder reduces T_c in the conventional channel, but does not suppress it to zero. Finally, it is possible that strong scattering results in filling in electronic states at the gap nodes, and therefore masks a power-law behavior of $\lambda^{-2}(T)$. Materials similar to Re_3W , but with more regular crystallographic (and thus electronic) structure are needed to explore the possibility of unconventional superconductivity in representatives of the A12 family.

5.6. Thermodynamic Properties

To gain complementary insight into the superconductive state and the nature of the gap at low temperatures, measurements of the specific heat of Re_3W materials were conducted using a Quantum Design PPMS-14 with a ^3He insert, in the range of temperatures 0.4 – 15 K. The specific heat curve has a typical form for a second order phase transition discontinuity, with a single peak at 7.8 K, as can be seen on Fig. 17. The phonon part of the specific heat of our samples above the transition in zero magnetic field can be well fit by the function $C_n = 3NR(4/5)\pi^4(T/\Theta_D)^3$ (where the Debye temperature $\Theta_D = 229.8$ K, and $N = 4$ atoms per formula unit). We also measured the normal state specific heat in range 0.4 K to 15 K by suppressing superconductivity magnetically in field $H = 14$ T (following careful calibration of the PPMS thermometer in that magnetic field). As expected for normal metals, the specific heat of Re_3W in 14 T follows the same $C_n \sim (A^*T^3 + \gamma T)$ -dependence, where the last term represents the normal state electronic specific heat, $C_{n\text{ el}}$. Here 1 mol corresponds to one formula unit. Replotting the data in C/T vs T^2 axes and extrapolating the normal state $C_n(T)$ to 0 K, we obtain the Sommerfeld parameter $\gamma = 17.4$ mJ/mol.K². The jump of specific heat at the phase transition $\Delta C(T_c) = (C_s - C_n)|_{T_c} = 228.5$ mJ/mol.K, with $\Delta C/C_n|_{T_c} = 1.68$, which is 18% higher than the BCS value of 1.43.

Upon subtraction of the phonon part, the electronic part, C_s , of the specific heat data in the superconducting state follows an exponential $e^{-\Delta/T}$ dependence at $T \ll T_c$ rather well, with $\Delta = 14.5$ K (see Fig. 18). These facts can be taken as evidence of BCS-like s -wave pairing in annealed Re_3W , and such hypothesis is strongly supported by the

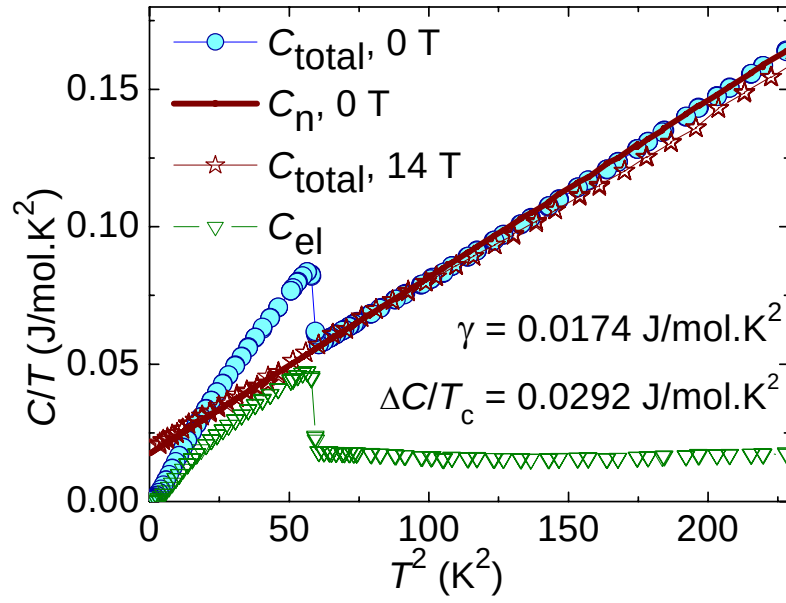


Figure 17. Heat capacity of Re_3W , represented in $C/T - T^2$ format.

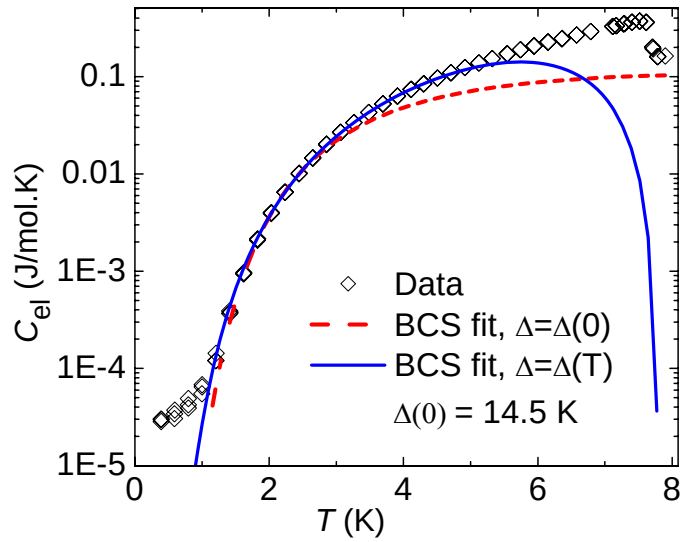


Figure 18. The low-temperature portion of the specific heat data fit. Best fit acquired with T -dependent gap $\Delta = \Delta(T)$ and $\Delta(0) = 14.5$ K. The "tail" below 1 K is instrumental.

penetration depth measurements reported by our group⁷⁰ earlier. We must note here that the exponential dependence of specific heat on temperature is a required, but not sufficient criterion to exclude a possibility of multi-dimensional order parameter. For instance, a material with an inversion center (see Table 2) and a two-dimensional order parameter belonging to the symmetry class $D_4 \times R$, or a three-dimensional order parameter belonging to the symmetry class $D_3 \times R$ can have spin-triplet pairing.

Since $\gamma = (1/3)p_F m^* / \hbar^3$, where $p_F = \hbar(3\pi)^{1/3} / a_{u.c.}$ is the Fermi momentum and $a_{u.c.} = 9.5966 \text{ \AA}$ is the Re_3W lattice parameter, the calculated effective electron mass, $m^* = 4m_e$ in Re_3W . Such magnitude of the effective mass of charge carriers is normal for superconductive alloys of transitional metals. This result completely rules out the hypothesis of Re_3W being a heavy-fermion superconductor, and further separates it from USCs like CePt_3Si and $\text{Li}_2\text{Pt}_3\text{B}$.⁶⁴

Off-stoichiometric Re-W alloys of χ -phase.

Since the stoichiometry 3:1 of Re_3W is approximate, with intermetallic compounds of ~75% Re and ~25% W forming in a narrow χ -phase homogeneity range below 2573 K,^{68,69} we studied the effect of alloy concentration variation within the limits of existence of the χ -phase in the published Re-W binary phase diagram.^{96,97} At 1500 °C, the width of the χ -phase is only 3 at. % (from 72 at. % Re to 75 at. % Re), and thus in addition to Re_3W we studied compounds $\text{Re}_{72}\text{W}_{28}$ and $\text{Re}_{73}\text{W}_{27}$, prepared by the method described above. Comparison of magnetic susceptibility $\chi(T)$ and zero-field resistivity $\rho(T)$ for all three Re-W alloys with aforementioned concentrations are presented on Fig.

19 and Fig. 20, respectively. It appears from the transport measurements that, as expected for binary Re alloys with low concentration of second element, T_c of these compounds is raised with increasing concentration of tungsten.⁹⁷ It was found⁹⁸ that strain increases T_c in Re. It is believed that strain induced by application of mechanical pressure and chemical alloying (doping) may have similar effects on critical temperature of type II superconductors.⁹⁹ Magnetic measurements were inconclusive in regard to T_c changing with W concentration trend; however they are fairly consistent with the transport measurements. Other physical properties measured and calculated in our study varied insignificantly with changes in tungsten concentration; the results are summarized in Table 4.

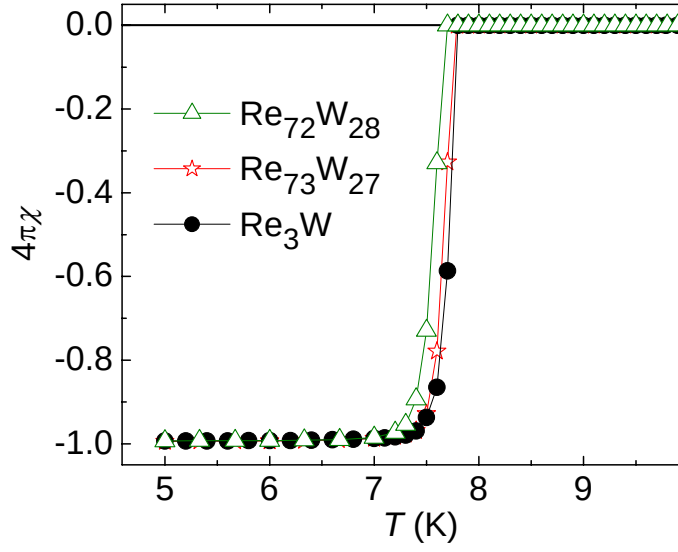


Figure 19. Susceptibility, $4\pi\chi$, of Re-W compounds of χ -phase.

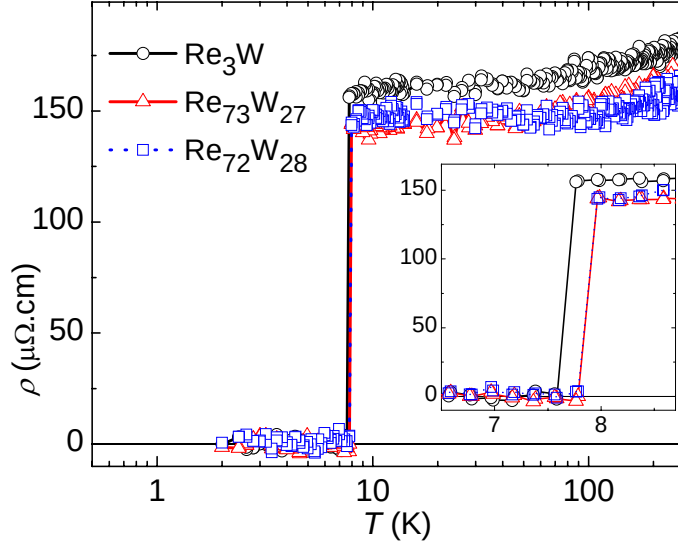


Figure 20. Resistivity of some off-stoichiometric Re-W compounds within the χ -phase.

Slight increase in T_c with W concentration is evident from the inset (T in linear scale).

Table 4. Summary of the physical properties of alloys in χ -phase of Re-W system.

Parameter	Re₃W		Re₇₃W₂₇	Re₇₂W₂₈
	Annealed		Annealed	Annealed
	In vacuum	In Argon	In vacuum	In vacuum
T_c , K	7.8	7.8	7.8	7.7
$-dH_{c2}/dT$, T/K	2.1	2.0	2.1	2.1
$H_{c2}(0)$, T	11.3	10.8	11.3	11.2
GL parameter, κ	61	52	57	56
Corr. Length, ξ_{GL} , nm	5.4	5.5	5.4	5.4
Penetr. Depth, λ_{GL} , nm	330	288	308	304
$H_{c1}(0)$ (from $H_{c2}(0)$), Oe	62	79	70	72
$H_c(0)$ (from GLAG), Oe	975	1141	911	884
$H_c(0)$ (from M^*), Oe		1390		
Resistivity, $\rho(T_c)$, $\mu\Omega\cdot\text{cm}$	156	116	143	144
$RRR = \rho_{300}/\rho_{T_c}$	1.58	1.15	1.12	1.16
$\Delta C(T_c)$, mJ/mol.K		211		
$J_c(4.5\text{K}, 0.1\text{T})$, mA/cm ²	118			
Sommerfeld γ , mJ/mol.K ²		17.35		
$\Delta C/\gamma T_c$		1.68		
$-dH_{c2}/dT(\text{transport})$, T/K	2.0	-	1.7	1.7
$H_{c2}(0)$, T (transport)	10.8	-	9.4	9.1
T_c , K (transport)	7.7	7.8	7.85	7.9

6. Conclusions

To summarize, we have considered phases realized in microscopic weak coupling theory in multi-component superconductors. We found that, for the most part, weak coupling mechanism in superconductors selects the most interesting magnetic phase, which is similar to the A-phase in superfluid ^3He . In this pairing state the time-reversal symmetry is broken. The properties of such superconductors are well known.^{8,11,40} Our results for singlet superconductors are consistent with ref. [47] by Agterberg *et al*, where the BCS mechanism for multi-pocket Fermi surfaces was considered. The main conclusion of ref. [47] was that it is the peculiar shape of the Fermi surface, such as its multi-pocketed structure, which determines the phase realized in BCS approach for a multi-component order parameter and leads to a magnetic phase. We found that this statement is only partially correct. For many degenerate representations the appearance of a magnetic phase indeed depends on the shape of the Fermi surface. However, in case of the 2D representations of the hexagonal and tetragonal groups, and the representation E_g of the cubic group, the magnetic phase chosen by the weak coupling approach is determined by *symmetry alone*, and is not influenced in any way by the shape of the Fermi surface. Another interesting observation is that exponentially T -dependent electronic specific heat is not sufficient evidence of conventional s -wave pairing – superconductors with a multicomponent order parameter and spin-*triplet* can exhibit such thermodynamic behavior just as well. In case of the cubic symmetry, the latter case can be differentiated from the s -wave pairing by careful measurement of the specific heat jump at T_c . But for materials with the symmetry class $D_2 \times R$ of the hexagonal group D_{6h}

with cylindrical Fermi surface the specific heat measurements alone are not enough to identify the pairing symmetry of the superconducting state.

In experimental studies, we have shown that annealed Re_3W exhibits unconventional magnetic behavior: linearity of $M(H)$ in large part ($\sim 80\%$) of SC region. We present the experimentally obtained vortex state diagram, $H(T)$, and show that reversibility region can be drastically extended (to over 99% of the superconducting region) using the FLL shaking technique. By extending the reversibility of $M(H)$, we could access H_c through simple thermodynamic relations. We found that the equilibrium irreversibility field $H^*(T)$ traces $H_c(T)$, and may in fact resemble the penetration field $H_p(T)$ in weak-pinning, good-surface samples. We offered and tested a new, straightforward method of measuring the lower critical field $H_{c1}(T)$, and showed that experimental data are in very good agreement with indirect calculations.

Otherwise, annealed Re_3W exhibits BCS-like superconductivity in dirty limit, characterized by T_c of 7.8 K, exponential electronic specific heat well below T_c , $C_s \sim \exp(-\Delta/T)$, $\Delta = 14.5$ K, and $\Delta C/C_{el}|_{T_c} = 1.68$, which is slightly higher than the fully-gapped weak-coupling s -wave BCS value of 1.43.

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Vita

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