

# **Geometric frustration and competing interactions in selected chalcogenide spinels**

A Dissertation Presented for the  
Doctor of Philosophy  
Degree

The University of Tennessee, Knoxville

Ganesh Pokharel

August 2020

Copyright © by Ganesh Pokharel, 2020  
All Rights Reserved.

*dedication to my parents*

# Acknowledgments

I would like to express my sincere thank to my dissertation advisors Prof. David Mandrus and Dr. Andrew D. Christianson for providing me the opportunity to work with them. They are great advisors for me. They supervised me not only in conducting the research, but also provided many opportunities in developing my overall skills. They trained me to become an independent researcher providing unlimited support and suggestions at the time of need. I greatly appreciate Dr. Christianson for his guidance to continue this project and also for the generosity to share his knowledge and experience. Dr. Mandrus is an excellent guiding figure whose inspirations and motivation always added energy to me to deal with the problems over the course of this long project. I greatly appreciate their time and trust in me.

I am thankful to Dr. Lekh Poudel for his help in material synthesis, neutron scattering measurements, and for all the personal assistance during my graduate school. I owe sincere thanks to Dr. Joseph A M Paddison for his great help to analyze the neutron scattering data. Also, thanks to Dr. Michael Koehler and Dr. Amanda Hugland for sharing the ideas and procedures for material synthesis. I would like to thank Dr. Liusuo Wu and Dr. Alice Taylor for their help to understand the neutron scattering experiments. Thank you to all the members of Prof. Mandrus's group at UTK who I've had the great pleasure of working with.

I am grateful for all my collaborators for the fruitful collaboration and their great contribution in making this project successful. Many thanks to Hasitha Suria Arachchige for his great help on neutron scattering measurements and muon spin resonance study. Thanks to Dr. Andrew F May and Dr. Michael McGuire for the help with x-ray and heat capacity measurements; to Dr. Travis Williams for muon spin resonance study; to Dr. Stuart Calder and Dr. Clarina De la Cruz for helping me neutron diffraction measurements; to Dr. David Parker, Hao Zhang and Dr. Randy S Fishman for theoretical understanding and calculations; to Dr. Georg Ehlers, Dr.



Seunghwan Do, Dr. Matthew B Stone, Dr. Mark D Lumsden and Dr. Gabriele Sala for the help on neutron scattering measurements and data visualization. I want to acknowledge all the instrument scientists, scientific associates, and sample environment staff at SNS, HFIR, and NCNR for their assistance to carry out the experiments. Thanks to Dr. Ashfia Huq, Dr. Simon. A. J. Kimber, Dr. Ovidiu Garlia, Dr. Barry Winn, Nathon Milton, Dr. Victor R. Fanelli, Lacy L. Jones, Dr. Tao Hong, Dr. Huibo Cao, Dr. Yiming Qiu, Dr. Jose A Rodriguez for helping me on neutron scattering experiments.

I would like to express my heartfelt thanks to my dissertation committee members Dr. Cristian Batista, Dr. Haidong Zhao, and Dr. Steven Johnston for their time and useful suggestions. I would also express my sincere thanks to Dr. Marianne Breinig and physics department administrative specialist Chrisanne Romeo for their help and advice throughout my graduate studies at the University of Tennessee.

Thank you to my parents and wife for your continuous love, support, and inspiration. Your continuous love and support made it possible for me to complete this big task successfully. I would also like to thank my lovely kids 'Elianna' and 'Evin' for their beautiful smiles. Although I couldn't spend as much time as you want, I think of you frequently and want to say love you a lot.

The work presented here is an output of a huge collaboration with many people from The University of Tennessee, Oak Ridge National Laboratory, Argonne National Laboratory, NIST Center for Neutron Research, and Centre for Molecular and Materials Science at TRIUMF. Most of the works in this dissertation were supported by Gordon and Betty Moore Foundation's EPIQS Initiative through Grant GBMF4416 and the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. The neutron scattering user facilities HFIR and SNS were supported by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE). The use of the advanced photon source at Argonne National Laboratory was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

# Abstract

Quantum materials often exhibit exotic ground states that are of fundamental interest with potential application in next generation technologies. Particularly important emerging areas of interest are skyrmion lattices, quantum spin liquids, and spin singlets. These quantum phases of matter originate with frustrated interactions, the interplay of spin and lattice degree of freedom, and quantum fluctuations. These properties are readily found in  $AB_2X_4$  spinels, that constitute the basic materials from which the model systems studied in this dissertation are derived. In chalcogenide spinel compounds, the A-sites form a diamond lattice structure that can exhibit frustration due to the competing nearest-neighbor and next-nearest-neighbor exchange interactions. Moreover, the B sites form a pyrochlore lattice which is a prototype for geometrical frustration. The interactions within the pyrochlore sublattice can be tuned by introducing an alternating ordered vacancy on the A-site or by the ordered substitution of two inequivalent ions on the A-site. For example, in  $LiGaCr_4S_8$  the different size of the  $Li^+$  and  $Ga^{3+}$  ions results in the formation of an alternating array of larger and smaller  $Cr_4$  tetrahedra or a breathing pyrochlore lattice.

Understanding the physical properties of the breathing pyrochlore lattice material,  $LiGaCr_4S_8$ , is a focus of this dissertation. Comprehensive neutron scattering measurements of  $LiGaCr_4S_8$  are presented along with X-ray diffraction, magnetic susceptibility, muon spin resonance and heat capacity measurements. The neutron diffraction and synchrotron X-ray diffraction data reveal negative thermal expansion (NTE) below 111(4) K. The magnetic susceptibility deviates from Curie-Weiss behavior with the onset of NTE. At low temperature a broad peak in the magnetic susceptibility at 10.5(5) K is accompanied by the return of normal thermal expansion. These results indicate strong magnetoelastic coupling in  $LiGaCr_4S_8$ . The fitting of magnetic diffuse scattering to a Heisenberg model indicates that the spin-spin couplings are ferromagnetic ( $J = -7.7(1)$  K,  $J' = -12.2(1)$  K) within the small and large  $Cr_4$  tetrahedra, but longer range exchange interactions

are essential for a reasonable description of the data. Inelastic neutron scattering measurements reveal an unconventional spin excitation spectrum with a separation of high and low-energy spin dynamics in the correlated paramagnetic regime. Our results show that emergent tetrahedral  $\text{Cr}_4$  spin clusters occupy a face-centered cubic lattice and interact with each other via net antiferromagnetic couplings, yielding cluster frustration in  $\text{LiGaCr}_4\text{S}_8$ .

Additionally, I present the growth techniques and neutron scattering study of single crystals of the skyrmion host lacunar spinel  $\text{GaV}_4\text{S}_8$ . In  $\text{GaV}_4\text{S}_8$ , the interplay of spin, charge, and orbital degrees of freedom results in a complex phase diagram that includes cycloidal, ferromagnetic, ferroelectric, orbitally ordered and skyrmion phases. Below 13 K,  $\text{GaV}_4\text{S}_8$  exhibits a cycloidal state at zero field and a Néel type skyrmion spin structure with the application of field. To understand the physics driving the formation of these novel phases, we have carried out inelastic neutron scattering measurements on  $\text{GaV}_4\text{S}_8$  single crystals above and below the ordering temperature of 13 K. Dispersive spin excitations with a zone boundary energy of 5.7 meV are observed along the (100), and (110) directions within the magnetically ordered phase. Using a Heisenberg model with nearest neighbor exchange couplings and Dzyaloshinskii-Moria (DM) interactions, the excitation spectra are calculated. Simulation shows ferromagnetic inter-tetrahedral couplings with  $J = -0.70(3)$  meV. The modeling further indicates that the DM interactions are around 15% of the nearest neighbor exchange interactions.

# Table of Contents

|          |                                                                           |           |
|----------|---------------------------------------------------------------------------|-----------|
| <b>1</b> | <b>Introduction</b>                                                       | <b>1</b>  |
| 1.1      | Exchange interactions . . . . .                                           | 2         |
| 1.1.1    | Dzyaloshinskii–Moriya (DM) interactions . . . . .                         | 2         |
| 1.2      | Magnetic frustration . . . . .                                            | 3         |
| 1.3      | Chalcogenide spinels . . . . .                                            | 6         |
| <b>2</b> | <b>Realizing a breathing pyrochlore lattice from the spinel structure</b> | <b>11</b> |
| 2.1      | Cr-breathing pyrochlore . . . . .                                         | 12        |
| 2.1.1    | Oxygen-based Cr-breathing pyrochlore . . . . .                            | 12        |
| 2.1.2    | Ground state in Cr-breathing pyrochlore . . . . .                         | 14        |
| 2.1.3    | Sulfur-based Cr-breathing pyrochlore . . . . .                            | 16        |
| 2.2      | Lacunar spinels . . . . .                                                 | 18        |
| 2.2.1    | Prototype lacunar spinel $\text{GaV}_4\text{S}_8$ . . . . .               | 19        |
| <b>3</b> | <b>Research Techniques</b>                                                | <b>23</b> |
| 3.1      | Materials synthesis . . . . .                                             | 23        |
| 3.1.1    | Solid state synthesis . . . . .                                           | 23        |
| 3.1.2    | Chemical vapor transport (CVT) . . . . .                                  | 24        |
| 3.2      | Neutron Scattering . . . . .                                              | 26        |
| 3.2.1    | Magnetic Scattering . . . . .                                             | 30        |
| 3.3      | Instrumentation . . . . .                                                 | 32        |
| 3.3.1    | Neutron powder diffractometer (HB-2A) . . . . .                           | 32        |
| 3.3.2    | Time-of-flight spectrometer . . . . .                                     | 34        |

|          |                                                                                                                                                   |           |
|----------|---------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| <b>4</b> | <b>Negative thermal expansion and magnetoelastic coupling in the breathing pyrochlore lattice material <math>\text{LiGaCr}_4\text{S}_8</math></b> | <b>36</b> |
| 4.1      | Introduction . . . . .                                                                                                                            | 37        |
| 4.2      | Experimental Details . . . . .                                                                                                                    | 40        |
| 4.3      | Results . . . . .                                                                                                                                 | 41        |
| 4.3.1    | Neutron Diffraction and X-ray Diffraction . . . . .                                                                                               | 41        |
| 4.3.2    | Magnetic Properties . . . . .                                                                                                                     | 49        |
| 4.3.3    | Heat Capacity . . . . .                                                                                                                           | 51        |
| 4.3.4    | Electrical Resistivity . . . . .                                                                                                                  | 53        |
| 4.4      | First Principles Calculations - Magnetoelastic Coupling . . . . .                                                                                 | 54        |
| 4.5      | Discussion . . . . .                                                                                                                              | 55        |
| 4.6      | Conclusion . . . . .                                                                                                                              | 57        |
| <b>5</b> | <b>Cluster frustration in the breathing pyrochlore lattice material <math>\text{LiGaCr}_4\text{S}_8</math></b>                                    | <b>58</b> |
| 5.1      | Introduction . . . . .                                                                                                                            | 59        |
| 5.2      | Methods . . . . .                                                                                                                                 | 61        |
| 5.2.1    | Synthesis and measurements . . . . .                                                                                                              | 61        |
| 5.2.2    | Modeling . . . . .                                                                                                                                | 62        |
| 5.3      | Results . . . . .                                                                                                                                 | 65        |
| 5.3.1    | Diffuse magnetic scattering . . . . .                                                                                                             | 65        |
| 5.3.2    | Spin excitation spectra . . . . .                                                                                                                 | 65        |
| 5.3.3    | Magnetic interaction modeling . . . . .                                                                                                           | 70        |
| 5.3.4    | Cluster frustration . . . . .                                                                                                                     | 72        |
| 5.3.5    | Muon spin resonance . . . . .                                                                                                                     | 75        |
| 5.3.6    | Calculation of Mydosh parameter . . . . .                                                                                                         | 77        |
| 5.4      | First principles calculations . . . . .                                                                                                           | 78        |
| 5.5      | Discussion and Conclusions . . . . .                                                                                                              | 79        |
| <b>6</b> | <b>Spin dynamics in skyrmion host lacunar spinel <math>\text{GaV}_4\text{S}_8</math></b>                                                          | <b>81</b> |
| 6.1      | Introduction . . . . .                                                                                                                            | 81        |
| 6.2      | Experimental details . . . . .                                                                                                                    | 84        |

|          |                                                                              |            |
|----------|------------------------------------------------------------------------------|------------|
| 6.3      | Results and discussion . . . . .                                             | 85         |
| 6.3.1    | Powder average spin excitation spectrum . . . . .                            | 85         |
| 6.3.2    | Measurement of the spin excitation spectra in single crystal samples . . . . | 88         |
| 6.3.3    | Spin model . . . . .                                                         | 90         |
| 6.4      | Conclusion . . . . .                                                         | 94         |
| <b>7</b> | <b>Conclusions</b>                                                           | <b>95</b>  |
|          | <b>Bibliography</b>                                                          | <b>97</b>  |
|          | <b>Appendix</b>                                                              | <b>114</b> |

# List of Figures

|     |                                                                                                                                                                                                                                                                                                                                                                                                        |    |
|-----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 1.1 | (a) Antiferromagnetically interacting spins showing geometric frustration on a triangular geometry. (b) Geometrical frustration in antiferromagnetic tetrahedral geometry. . . . .                                                                                                                                                                                                                     | 4  |
| 1.2 | (a) AFM square lattice. (b) Diamond lattice structure. The exchange interactions between NN and NNN are labeled by $J_1$ and $J_2$ respectively. . . . .                                                                                                                                                                                                                                               | 5  |
| 1.3 | (a) Arrangement of $AX_4$ tetrahedra and $BX_6$ octahedra in the $AB_2X_4$ spinel structure. (b) Arrangement of A and B sublattices in a spinel structure. A-sublattice form a diamond lattice and B-sublattice form a pyrochlore lattice structure. . . . .                                                                                                                                           | 8  |
| 1.4 | (a) Illustration of possible magnetic interaction pathways within the B sublattices. $B_0$ is a reference atom; $B_1$ , $B_2$ and $B_3$ represent the 1 <sup>st</sup> , 2 <sup>nd</sup> and 3 <sup>rd</sup> NN respectively (b) Schematic of superexchange magnetic interaction path governed by sublattice A. (c) Illustration of B-B NN of a pyrochlore lattice in a B-site spinel material. . . . . | 9  |
| 2.1 | Cr-breathing pyrochlore structure. $J$ and $J'$ represent the exchange couplings within the small and large tetrahedra respectively. . . . .                                                                                                                                                                                                                                                           | 13 |
| 2.2 | Classical phase diagram of the breathing pyrochlore lattice reproduced from the Ref. [47]. $J$ and $J'$ represent the exchange couplings within the small and large tetrahedra respectively. . . . .                                                                                                                                                                                                   | 15 |
| 2.3 | Elastic neutron scattering data in $CuInCr_4S_8$ at different temperatures (image reproduced from Ref. [51]). . . . .                                                                                                                                                                                                                                                                                  | 17 |
| 2.4 | (a) Arrangement of $AX_4$ and $M_4X_4$ structures in lacunar spinel compounds. (a) Large and small $M_4$ clusters in $AM_4X_8$ compounds. . . . .                                                                                                                                                                                                                                                      | 20 |
| 2.5 | Phase diagram of $GaV_4S_8$ (image reproduced from Ref. [65]). . . . .                                                                                                                                                                                                                                                                                                                                 | 21 |

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |    |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 2.6 | Néel type skyrmion in $\text{GaV}_4\text{S}_8$ (image reproduced from Ref. [1]). . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 22 |
| 3.1 | (a) Mortar and pestle under inert atmosphere, (b) tube sealing process, (c) sealed tube with a sample inside a furnace. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 24 |
| 3.2 | Sketch of experimental set up of chemical vapor transport crystal growth technique (image reproduced from Ref. [69]). . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 25 |
| 3.3 | Images of single crystals of selected chalcogenide spinel materials that are grown through CVT. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 25 |
| 3.4 | Scattering triangles representing the scattering process in neutron scattering. (a) represents the elastic scattering, (b) and (c) represent the inelastic scattering [71]. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 27 |
| 3.5 | Layout of the HB-2A powder diffractometer at HFIR, ORNL (image reproduced from Ref. [73]). . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 33 |
| 3.6 | General layout of Cold Neutron Chopper Spectrometer (CNCS) at the SNS, ORNL (image reproduced from Ref. [76]). . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 35 |
| 4.1 | Crystal structure of $\text{LiGaCr}_4\text{S}_8$ depicting the breathing pyrochlore Cr sublattice. The exchange interactions within the small and large tetrahedra are labeled $J_1$ and $J'_1$ respectively. $J_2$ denotes the next nearest neighbor exchange interaction. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                              | 38 |
| 4.2 | (a) Synchrotron X-ray diffraction data with $\lambda = 0.4146 \text{ \AA}$ collected at 300 K. The inset displays a limited region of reciprocal space so that the presence of a weak $\text{Cr}_3\text{S}_4$ can be compared to the intensity of the main phase. The impurity phase is indicated by arrows. The axis labels are the same as the main panel, but note the logarithmic y-axis scale. Neutron diffraction data collected with POWGEN with $0.167 \leq \lambda \leq 1.233 \text{ \AA}$ at 300 K and 1.5 K are shown in panel (b) and (c) respectively. The Rietveld refinement of the structural model described in the text with space group $F\bar{4}3m$ is indicated by the solid line through the data. . . . . | 42 |
| 4.3 | Lattice parameter of $\text{LiGaCr}_4\text{S}_8$ as a function of temperature obtained by neutron diffraction. Negative thermal expansion is observed below 111(4) K. The inset shows the estimated temperature dependence of $\Delta a(T)/a_0$ determined as explained in the text. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                     | 43 |



|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |    |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 4.4 | Temperature dependence of peak width (Full Width Half Maximum of a standard Lorentzian function) of selected diffraction peaks determined from the laboratory X-ray diffraction data. All peaks broaden with cooling at low temperature. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 45 |
| 4.5 | Temperature dependent Cr-Cr bond lengths in the small and large Cr <sub>4</sub> -tetrahedra (filled squares, left scale) and $B_r$ (filled circles, right scale). These bond lengths and $B_r$ s are obtained from the neutron diffraction data collected with POWGEN. .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 47 |
| 4.6 | Variation of selected bond angles with temperature in LiGaCr <sub>4</sub> S <sub>8</sub> . Cr-S-Cr bonds are close to 90° and are responsible for the NN superexchange interaction. S-Li-S and S-Ga-S bonds are insensitive to the change in temperature whereas other bonds show a weak anomaly with the onset of NTE. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 48 |
| 4.7 | Magnetic susceptibility measurements of LiGaCr <sub>4</sub> S <sub>8</sub> . (a, b) Show the temperature dependent dc susceptibility, $\chi$ and (c) shows the temperature dependent inverse dc susceptibility, $1/\chi$ of LiGaCr <sub>4</sub> S <sub>8</sub> . (d) Displays the in-phase part of the ac susceptibility, $\chi'$ around the magnetic transition, measured with $H_{ac} = 5$ Oe with frequencies 29 Hz, 127 Hz, 1129 Hz, 2336 Hz, 4832 Hz and 10000 Hz. The arrow in (d) indicates the direction of increasing applied frequency. The inset of (c) displays $M(H)$ loops measured at selected temperatures. A peak in the susceptibility occurs at 10.5(5) K and deviation from Curie-Weiss behavior is observed below 110 K. Small shift in the peak of $\chi'$ towards higher temperature is noticed with the increase in frequency. Weak hysteresis in the $M$ vs. $H$ data is observed at 3 K. . . . . | 50 |
| 4.8 | Temperature dependent heat capacity, $C_P$ , of LiGaCr <sub>4</sub> S <sub>8</sub> at zero magnetic field. (a) Displays the $C_P$ from 2 to 200 K. (b) Shows $C_P/T$ and the estimated entropy, $S$ , at low temperatures. The theoretical value of magnetic entropy for spin 3/2 system is indicated by the horizontal line in (b). The change in slope of $C_P$ around at 120 K and a broad hump at 10.9(4) K look coincident with the bounding temperatures of NTE. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                             | 52 |
| 4.9 | Temperature dependent resistivity, $\rho$ of LiGaCr <sub>4</sub> S <sub>8</sub> . The fitting function is described in the text. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 53 |

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |    |
|-----|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 5.1 | (a) Breathing pyrochlore lattice of $S = 3/2$ $\text{Cr}^{3+}$ ions (black circles) in $\text{LiGaCr}_4\text{S}_8$ , showing large (small) tetrahedra (colored green (grey)), and the connectivity of the exchange interactions $J$ , $J'$ , $J_2$ , $J_{3a}$ , and $J_{3b}$ . $J_{3a}$ and $J_{3b}$ span the same distance but have different symmetry. (b) Emergent tetrahedral clusters generated by strong ferromagnetic $J'$ interactions, coupled by a net antiferromagnetic interaction $J_{\text{AFM}} \propto J + 4J_2 + 2J_{3a} + 2J_{3b} (> 0)$ . . . . .                                                                                                                                                                                                                                                                                                                                                                     | 60 |
| 5.2 | Neutron diffraction data with $\lambda = 2.41 \text{ \AA}$ collected at 4 K. The solid line through the data represents the Rietveld refinement of the lattice structural model with space group $F\bar{4}3m$ . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 64 |
| 5.3 | Inelastic neutron scattering spectra of $\text{LiGaCr}_4\text{S}_8$ measured at temperatures indicated in the panels. High energy excitation spectra measured with $E_i = 25 \text{ meV}$ at 3 K (panel (a)), 20 K (panel(b)), 60 K (Panel (c)) and 200 K (Panel (d)). . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 66 |
| 5.4 | Inelastic neutron scattering spectra of $\text{LiGaCr}_4\text{S}_8$ measured at temperatures indicated in the panels. Low energy spin excitations measured with $E_i = 3.32 \text{ meV}$ at 1.5 K (panel (a)), 20 K (panel(b)), 60 K (Panel (c)) and 200 K (Panel (d)). . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 67 |
| 5.5 | (a) Wavevector dependence of constant $E$ -cuts ( $10 \leq E \leq 11 \text{ meV}$ ) of the scattering measured at different temperatures labeled on the plot. (b) Energy dependence of high-energy scattering for cuts integrated over $0.4 \leq Q \leq 2 \text{ \AA}^{-1}$ at different temperatures. (c) Energy dependence of quasielastic scattering for cuts integrated over $0.4 \leq Q \leq 1 \text{ \AA}^{-1}$ at temperatures of 1.7 K (black), 20 K (red), 60 K (green), 100 K (blue) and 200 K (cyan). (d) Measured (black squares) and fitted (red lines) dynamical susceptibility $\chi''$ at 1.7, 4, 15, 30, 60, and 100 K. The arrow in (d) indicates the direction of increasing temperature. (e) Temperature-dependent $\Gamma$ (green circle), $E_0$ (red sphere), $\gamma$ (black open square) and $\chi'$ (blue solid square) of the damped-harmonic oscillator model corresponding to the fits shown in (d). . . . . | 69 |
| 5.6 | width=2 . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 71 |

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |    |
|-----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 5.7 | (a) Spin-pair correlation $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ as a function of distance $r$ between spins. The normalization is such that $\langle \mathbf{S}(0) \cdot \mathbf{S}(0) \rangle = 1$ . Results were obtained from classical Monte Carlo simulations driven by interaction parameters optimized to our neutron data. (b) Calculated temperature dependence of the spin-spin correlation function at $r = r'$ , the distance between neighboring spins in large tetrahedra. (c) Calculated single-crystal diffuse-scattering pattern $I(\mathbf{Q})$ of $\text{LiGaCr}_4\text{S}_8$ in the $(hk0)$ plane at 20 K. (d) Calculated $I(\mathbf{Q})$ from the emergent FCC lattice of cluster spins, defined as $\mathbf{S}' = \sum_{i=1}^4 \mathbf{S}_i$ on each tetrahedron of the breathing-pyrochlore lattice. (e) Calculated $I(\mathbf{Q})$ for spins on the FCC lattice with antiferromagnetic nearest-neighbor exchange interactions $J_{\text{AFM}} = 0.43$ K. (f) Experimentally-measured spin excitation spectrum at 20 K. (g) Calculated spin excitation spectrum of an isolated tetrahedral cluster. (h) Spin excitation spectrum calculated using linear spin-wave theory assuming a proximate ordered ground state with propagation vector $\mathbf{k} = [0, 0, 1]$ [123]. . . . . | 73 |
| 5.8 | (a) ZF- $\mu$ SR data measured at $T = 100$ K (black squares) and 1.9 K (red squares) and fitted curves (blue lines). (b) Temperature dependence of relaxation rates for ZF- $\mu$ SR scans. The inset indicates the shift of the weight between the two relaxation rates with temperature. (c) The damping of the relaxation rate corresponding to the magnetism with the longitudinal field at 1.9 K. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 76 |
| 6.1 | (a) Formation of $\text{M}_4$ clusters in a lacunar spinel structure from an ideal cubic spinel structure. (b) Molecular orbital diagrams of $\text{V}_4$ cluster in $\text{GaV}_4\text{S}_8$ with and without Jahn-Teller distortion. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 83 |
| 6.2 | Spin excitation in 5 g polycrystalline sample of $\text{GaV}_4\text{S}_8$ measured at (a) 5 K with $E_i = 40$ meV (b) 5 K with $E_i = 18$ meV (c) 20 K with $E_i = 18$ meV. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 86 |
| 6.3 | (a) Single crystal of $\text{GaV}_4\text{S}_8$ . (b) Co-aligned array of single crystals along the scattering plane (HHL) horizontal. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 87 |
| 6.4 | (a) elastic neutron scattering pattern in the (HHL) plane from co-aligned single crystals of $\text{GaV}_4\text{S}_8$ (b) (220) peak showing the mosaic from the co-aligned single crystals. (c) temperature dependence of (-1-11) peak intensity. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 89 |

|     |                                                                                                                                                                                                                                                                                                                           |    |
|-----|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 6.5 | Spin wave dispersion along the (a) (-1-1L) (b) (HH-1) directions. (c) Constant energy slice ( $E = 3$ meV) of spin excitation spectrum in (HHL) plane. Simulated spin wave excitation spectrum along the (d) (-1-1L) (e) (HH-1) direction. (f) Simulated constant energy slice at $E = 3$ meV in the (HHL) plane. . . . . | 91 |
| 6.6 | Experimental and calculated constant E-cuts at temperature of 1.7 K (a) along (-1-1L) direction (b) along (HH-1) direction. (c) Constant $ Q $ -cuts at different regions along the (-1-1L) direction. (d) Constant energy cuts as a function of temperature along (HH-1) direction. . . . .                              | 92 |
| 6.7 | Unit cell of an FCC lattice of $V_4$ tetrahedra in $GaV_4S_8$ . . . . .                                                                                                                                                                                                                                                   | 93 |

# Chapter 1

## Introduction

Quantum materials possess number of exotic ground states that are of fundamental interest and may also be of use for next generation technological applications. Particularly interesting quantum phases are topological spin textures, such as skyrmions [1, 2], spin spirals [3], spin-liquid [4], spin ices [5], spin nematic phase [3], etc. These phases originate with the complex interplay of spin and lattice degree of freedom, magnetic frustration, and quantum fluctuations. Of particular interest in this dissertation is the concept of frustration as it appears to be an essential ingredient in almost all of the aforementioned quantum phases of matter. Frustration originates with competing exchange interactions. This can either be through the geometry of the lattice normally termed geometric frustration or through the competition of exchange interactions such as nearest neighbor and next nearest neighbor exchange interactions. The goal of my dissertation work is to understand the dual roles of geometric frustration and competing interactions and how they are related to and generate novel quantum phases in pyrochlore, breathing pyrochlore, and related lattice geometries as found in chalcogenide spinel materials.

To gain insight to the mechanism of magnetic frustration, we need to first understand the magnetic interactions that exist in the magnetic material under consideration. A brief introduction to exchange interactions relevant to this dissertation is given below.

## 1.1 Exchange interactions

Magnetic exchange interaction determines the type of magnetic ordering in a magnetic material. It is a quantum mechanical effect between two spins that occurs due to the Coulomb interactions and Pauli exclusion principle. The direct exchange interaction is usually expressed in the form of spin Hamiltonian as:

$$H = J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1.1)$$

where  $\mathbf{S}_i$  and  $\mathbf{S}_j$  are the spin operators located at the lattice sites  $i$  and  $j$ ,  $J_{ij}$  measures the strength of exchange interaction and is called the exchange constant (or exchange coupling constant).  $J_{ij}$  is negative for ferromagnetic spin exchange interactions, whereas its value is positive for antiferromagnetic interactions. Direct exchange interactions are due to the overlap of electronic wave functions between different magnetic sites. As the wave functions of d and f electrons decrease exponentially with the increase in distance, the value of the direct overlap integral becomes smaller for the couplings between d and f electrons. In such cases, strong exchange interactions can still occur and are mediated by non-magnetic ions or by conduction electrons. Such interactions are called indirect exchange interactions. Well known indirect interactions are superexchange interactions (mediated by non-magnetic ion), Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions (mediated by conduction electrons), Dzyaloshinskii–Moriya (DM) interactions and double exchange interactions [6]. As this dissertation focuses on the materials with non-centrosymmetric structure, the DM interaction, which usually results incommensurate magnetic structure, can provide an important contribution to the energy landscape.

### 1.1.1 Dzyaloshinskii–Moriya (DM) interactions

The Dzyaloshinskii–Moriya interaction is an anisotropic exchange interaction arising through spin-orbit coupling. The DM interaction between two spins  $S_i$  and  $S_j$  has the following form

$$H = \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j \quad (1.2)$$

Where the DM vector,  $\mathbf{D}_{ij}$ , measures the strength of DM interaction. The resulting magnetic structure is determined by the direction of  $\mathbf{D}_{ij}$  and it depends on the way inversion symmetry is

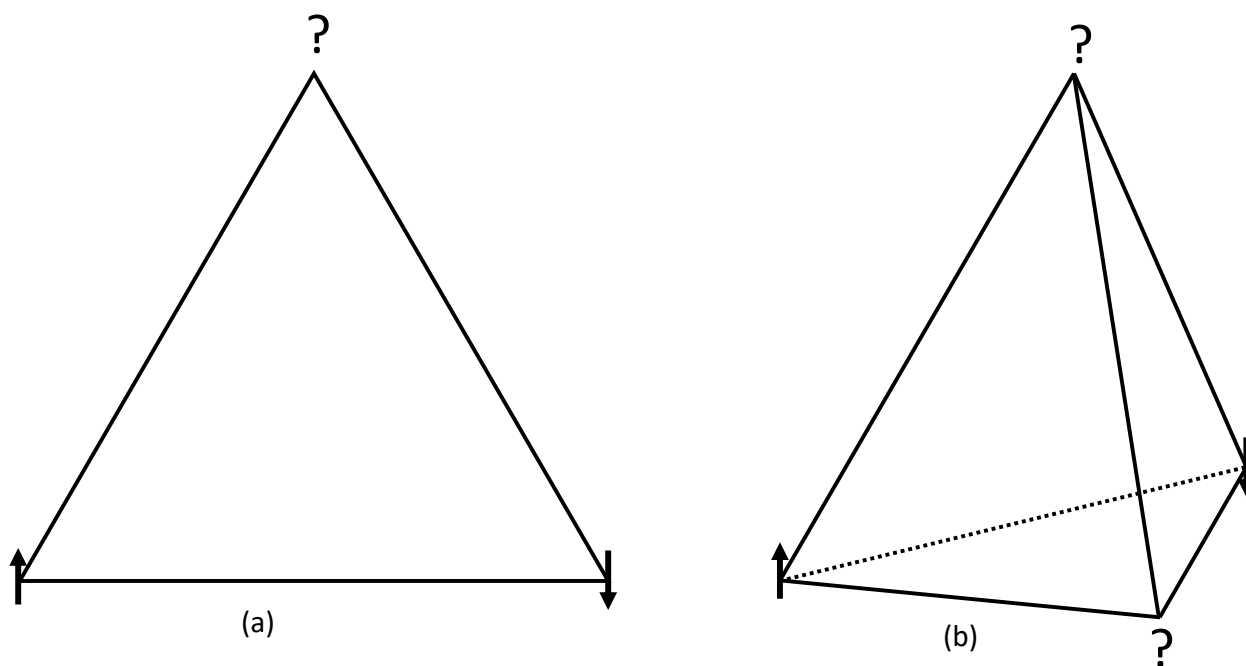
broken in the system. The DM vector vanishes for structures having inversion symmetry with respect to the center of the magnetic ions [6]. The DM interaction acts in such a way that it prefers  $\mathbf{S}_i$  and  $\mathbf{S}_j$  to be at  $90^\circ$  in the plane perpendicular to the plane of DM vector, favoring canting to a collinear spin orientation. The DM interaction is often the source of helicity in magnetic structures.

## 1.2 Magnetic frustration

Frustrated magnetism typically arises from competing exchange interactions between the localized magnetic moments that cannot be satisfied simultaneously [7]. Magnetic frustration generally destabilizes the Néel order in a conventional magnetic system and introduces degeneracy to the energy landscape. In many cases, this leads to an arrangement in which the spins are correlated at temperatures much higher than the temperature at which long range order occurs.

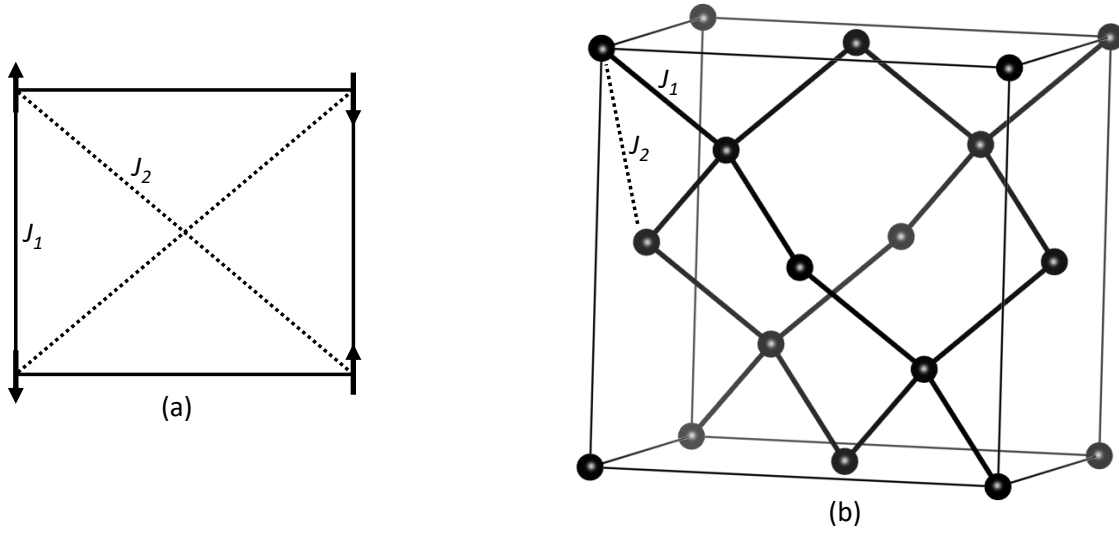
The spin frustration generated by the competing nearest neighbor (NN) interactions is called geometric frustration. An antiferromagnetic (AFM) triangular lattice is the simplest example of a geometrically frustrated magnet. An AFM triangular lattice consisting of classical Ising spins at each corner is shown in Fig. 1.1(a). If the spins at two of the corners satisfy the AFM exchange interaction and align antiparallel to one another, the third spin is unable to satisfy the AFM exchange interaction with the other two spins. Hence, the spins of an AFM triangular lattice can not simultaneously exist in their lowest energy state and thus exhibit multiple degenerate magnetic ground states [8]. Another example of a geometrically frustrated lattice is an AFM tetrahedral lattice with four classical Ising spins at the four corners (Fig. 1.1(b)). After the spins at two corners of tetrahedra are antiferromagnetically coupled, the third and fourth spins can no longer align opposite to the other two neighboring spins simultaneously. In a lattice constructed from the corner-sharing antiferromagnetic triangles in 2D kagome lattice or tetrahedra in 3D pyrochlore structure, the local moment is associated with each corner and the exchange interactions between all the local moments are in equal strength.

To illustrate the magnetic frustration generated by competing NN and NNN exchange interactions, let us consider an AFM square lattice which consists of antiparallel Ising spins at each corner. Frustration can then arise if the NN interaction ( $J_1$ ) along the side of square competes



**Figure 1.1:** (a) Antiferromagnetically interacting spins showing geometric frustration on a triangular geometry. (b) Geometrical frustration in antiferromagnetic tetrahedral geometry.





**Figure 1.2:** (a) AFM square lattice. (b) Diamond lattice structure. The exchange interactions between NN and NNN are labeled by  $J_1$  and  $J_2$  respectively.

with the diagonal NNN interaction ( $J_2$ ) as shown in Fig. 1.2(a). An AFM diamond lattice is another example of frustrated structure due to such competing interactions (Fig. 1.2(b)). In a diamond lattice, the similarity in exchange paths to NN and NNN sites can yield interactions of nearly equal strength. If the couplings are antiferromagnetic and the values of  $J_1$  and  $J_2$  are comparable, the interactions are frustrated.

The classical Heisenberg Hamiltonian representing the NN and NNN spin interactions, also referred to as  $J_1 - J_2$  model, is written as [9]:

$$H = J_1 \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle\langle ij \rangle\rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1.3)$$

where the angle brackets  $\langle \rangle$  and  $\langle\langle \rangle\rangle$  represent the NN and NNN, which are coupled with exchange constants  $J_1$  and  $J_2$ , respectively. The ground state in  $J_1 - J_2$  model depends on the value of  $J_1$  and  $J_2$  in diamond lattice [7]. Based on this model, the competition between  $J_1$  and  $J_2$  leads to a highly degenerate spin liquid ground state [9]. Theoretical calculations emphasize the presence of a large ground state degeneracy consisting of spin spirals in a frustrated diamond

lattice if the ratio of exchange couplings ( $J_2/J_1$ ) is greater than the critical value of  $1/8$ . On the other side, Néel phase is predicted theoretically in a frustrated magnet with  $J_2/J_1 < 1/8$ .

A consequence of magnetic frustration is the suppression of the magnetic ordering temperature,  $T_N$ , relative to the energy scale of the exchange interactions. An experimental way to estimate the strength of the interactions is through the Curie-Weiss temperature. In some instances the Curie-Weiss temperature can be related to size of the exchange interactions ( $J_n$ ) through  $\theta_{CW} = -\sum_n S(S+1)Z_n J_n/3$  [10, 11]. This can be compared to the ordering temperature as a means of estimating the impact of frustration on a particular system. This is often done with a frustration parameter defined as  $f = |\theta_{CW}/T_N|$ . A system with a frustration parameter above 5-10 is generally considered highly frustrated [9]. In this picture, a spin system fluctuates between many low energy configurations for the temperature range  $T_N \leq T \leq \theta_{CW}$ . In a highly frustrated magnet, the low-temperature physics is extremely sensitive to degeneracy-breaking-perturbations such as spin-orbit coupling, Dzyaloshinskii-Moria interactions, and extrinsic effects such as disorder [12, 1]. In many cases, the characteristic features of frustrated magnets are evident in neutron scattering measurements. In the temperature range  $T_N \leq T \leq \theta_{CW}$ , the neutron scattering data exhibit a broad and diffuse magnetic signal at finite wave-vector  $|Q|$ , revealing the existence of short-range spin correlations in a frustrated magnet [7].

### 1.3 Chalcogenide spinels

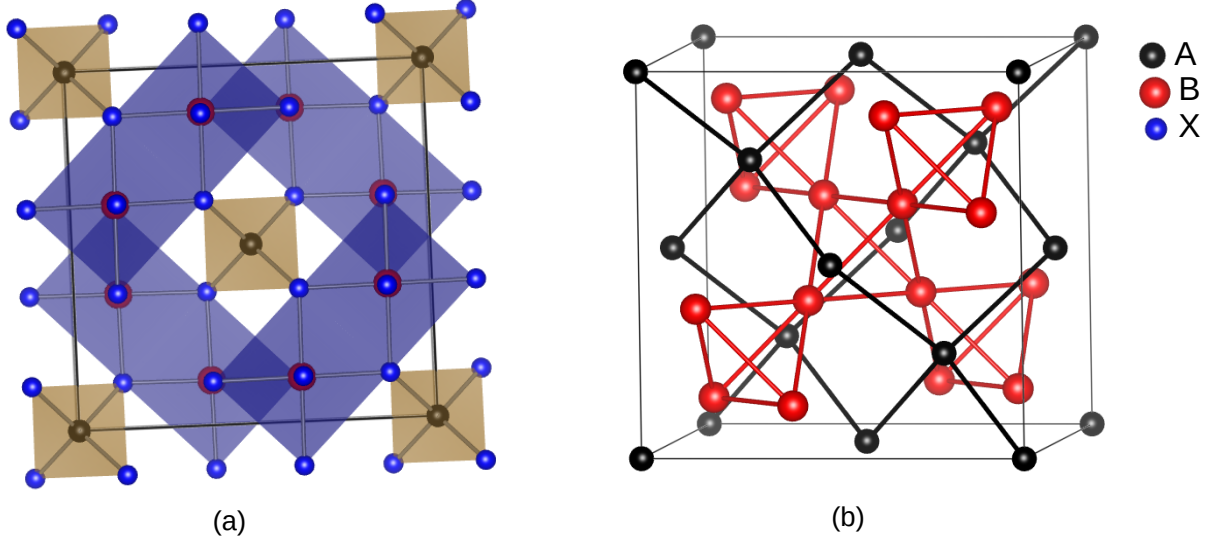
The chalcogenide spinels constitute the basic materials from which the model systems studied in this dissertation are derived. As such a brief introduction to these materials is given below.

The  $AB_2X_4$  structure represents one of the most studied transition metal ternary chalcogenides that provide a surprisingly rich category of phenomena, including multiferroicity [13, 14], metal-insulator transition [15, 16], superconductivity [17, 18], colossal magnetoresistance [19], helimagnetism [3], negative thermal expansion [20], and quantum criticality [21]. Recently, these materials have attracted growing interest as a material platform for the study of physics associated with magnetic frustration [22, 23, 24]. For example, the presence of strong magnetic frustration in  $FeSc_2S_4$  suppresses the spin ordering down to 50 mK.  $FeSc_2S_4$  is one of the strongest frustrated materials, with a frustration ratio above 900, that exhibits a quantum critical point

between the spin-orbital singlet and antiferromagnetic ground state [25]. In another chalcogenide spinel material  $\text{MnSc}_2\text{S}_4$ , the spin frustration induces spin-liquid behavior in the temperature range of 2-23 K, before undergoing a long-range antiferromagnetic ordering [24]. Similarly, the bond frustration ( $90^\circ$  superexchange interaction) in  $\text{ZnCr}_2\text{Se}_4$  yields a helical magnetic ground state below the antiferromagnetic transition at 21 K [26]. Apart from conventional Goldstone magnons with ordering vector  $(0\ 0\ q)$ ,  $\text{ZnCr}_2\text{Se}_4$  exhibits soft helimagnon modes, also referred as pseudo-Goldstone magnon modes, that emerge from two orthogonal wave vectors  $(q\ 0\ 0)$  and  $(0\ q\ 0)$  where no magnetic Bragg peaks exist. Hence, chalcogenide spinels are the potential candidates to study the rich physics associated with frustrated magnetism.

The building blocks of an  $\text{AB}_2\text{X}_4$  material are  $\text{AX}_4$  tetrahedra and  $\text{BX}_6$  octahedra (Fig. 1.3(a)). The A-site cations,  $\text{A}^{2+}$ , occupy one-eighth of the tetrahedrally coordinated interstices and the B-site cations,  $\text{B}^{3+}$ , occupy one-half of the octahedrally coordinated interstices [22]. The X-site anions form a close-packed face-centered cubic (fcc) lattice structure such that the different sublattices occupy the Wyckoff positions: A at 8a, B at 16d and X at 32e. The  $\text{AB}_2\text{X}_4$  compounds contain 8 formula units per unit cell with a total of 56 atoms (32 anions and 24 cations) [27]. The tetrahedrally coordinated cations form a cubic diamond structure with the repeat unit cell equal to the lattice parameter (Fig. 1.3(b)), whereas the octahedrally coordinated cations follow a network of corner-sharing tetrahedra and form a pyrochlore lattice structure. A magnetic ion may occupy either A-site or B-site or both forming a spinel structure. Based on the occupation of magnetic ions either in A-sites or in B-sites, the material is referred to as A-site or B-site spinel.

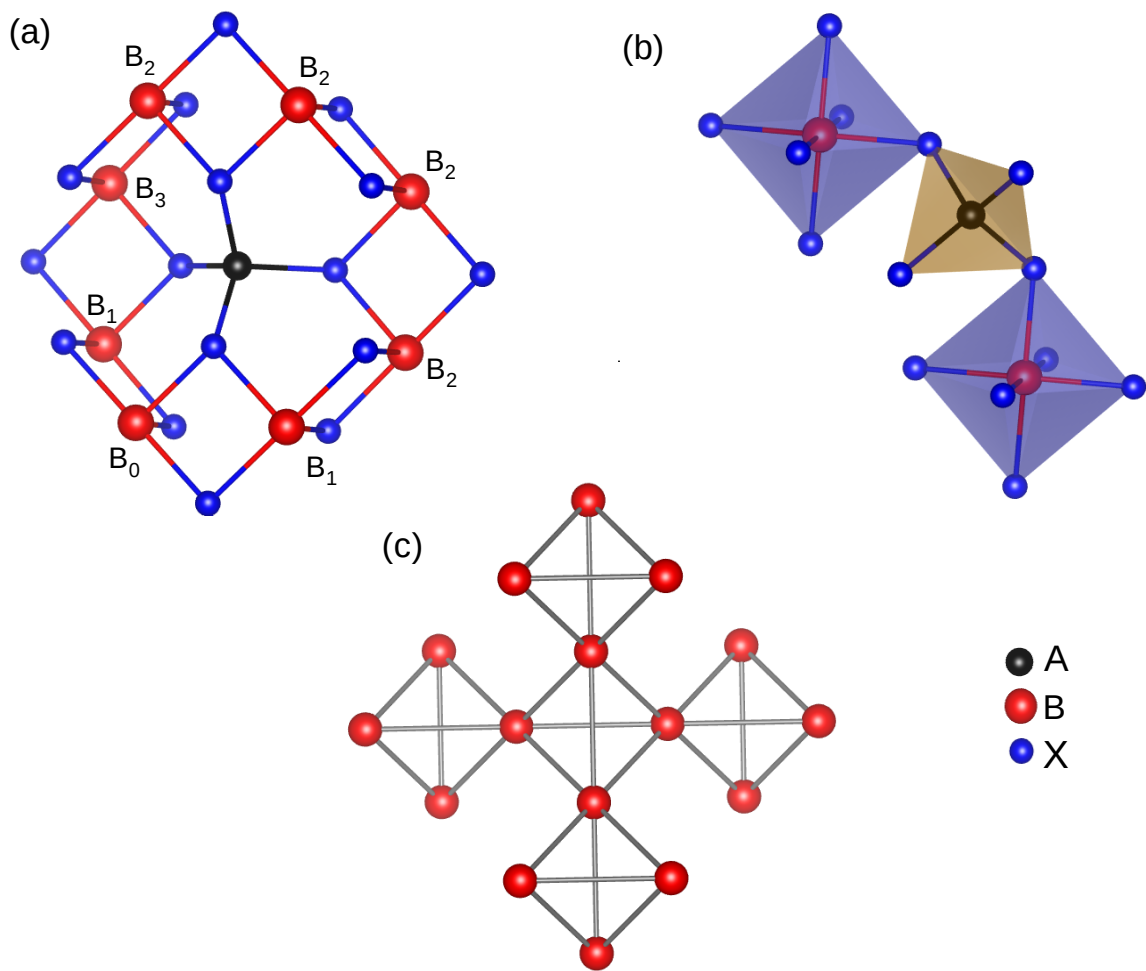
There are many magnetic exchange pathways that can play a crucial role to control the interactions in an  $\text{AB}_2\text{X}_4$  material. For example, either direct exchange or  $90^\circ$  superexchange or both may contribute to the NN B-B couplings in a B-site spinel. Accounting for the NN interactions only is usually insufficient to determine the energy landscape in these materials. The interactions beyond NN are mediated by the A-site ions or conduction electrons as shown in Fig. 1.4(a) [26, 28]. The NNN interaction between the B-site magnetic ions normally propagate through the exchange path B-X-A-X-B (Fig. 1.4(b)) [26, 29]. The exchange interactions extending to  $3^{rd}$  NN contribute significantly to the ground state energy in these materials. For a B-site spinel, there are 6 NN, 12  $2^{nd}$  NN, 12  $3^{rd}$  NN B sites [26, 29]. Due to the presence of a large number



**Figure 1.3:** (a) Arrangement of  $AX_4$  tetrahedra and  $BX_6$  octahedra in the  $AB_2X_4$  spinel structure. (b) Arrangement of A and B sublattices in a spinel structure. A-sublattice form a diamond lattice and B-sublattice form a pyrochlore lattice structure.

of interactions contributing to the classical Hamiltonian, many interaction conditions have to be satisfied simultaneously by the magnetic ions in these materials.

The large ligand size increases the distance between the magnetic ions in a thiospinel material,  $AB_2S_4$ , compared to the oxide version. The increase in inter-atomic separation limits the direct overlap of d-orbitals between two NN magnetic ions. Therefore, the dominant exchange interactions are often the indirect exchange interaction pathways in these materials [29]. The origin of magnetism in an  $AB_2S_4$  compound is generally governed by the type of A and B sublattices. With the magnetic ion  $Cr^{3+}$  in the B-sites,  $ACr_2S_4$  compounds exhibit complex interplay of spin and orbital degrees of freedom that yields fascinating low-temperature physics associated with frustrated magnetism [12, 22]. For example, strong spin fluctuations in the short-range order structure of  $CdCr_2S_4$  and  $HgCr_2S_4$  [30], spin-superfluid and spin-supersolid phases in  $MnCr_2S_4$  [31], Spin-glass behavior in ferromagnetic phase of  $CdCr_2S_4$  [32], multiferroicity and orbital glass state in  $FeCr_2S_4$  [12], etc. The lattice geometry of  $ACr_2S_4$  structure can be tuned if each alternating A-sites are occupied by inequivalent metal ions. In a mixed A-site Cr-spinel material, the pyrochlore lattice network of  $Cr^{3+}$  ions in the B-sites of a normal spinel structure distorts into a network of corner-sharing large and small  $Cr_4$  tetrahedra, forming a breathing pyrochlore lattice



**Figure 1.4:** (a) Illustration of possible magnetic interaction pathways within the B sublattices. B<sub>0</sub> is a reference atom; B<sub>1</sub>, B<sub>2</sub> and B<sub>3</sub> represent the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> NN respectively (b) Schematic of superexchange magnetic interaction path governed by sublattice A. (c) Illustration of B-B NN of a pyrochlore lattice in a B-site spinel material.

[33]. As these materials are recently discovered as the breathing pyrochlore materials, the tuning of exchange interactions and frustrated magnetism by the addition of inequivalent metal ions in A-sites need to be explored. There are limited previous experimental works that measure the spin interactions in such types of frustrated materials. Therefore, the central idea of this dissertation is to study the exchange interactions in one of such breathing pyrochlore lattices,  $\text{LiGaCr}_4\text{S}_8$ , and then explore the physics associated with the frustrated magnetism.

## Chapter 2

# Realizing a breathing pyrochlore lattice from the spinel structure

Breathing pyrochlore lattice materials have recently been realized as a fascinating route to insight into various aspects of frustrated magnetism [1, 33, 34, 35, 36, 37]. Interesting frustrated physics associated with breathing pyrochlores are enhanced stability of the quantum spin ice state [38], spin nematics [39], formation of a quantum spin-singlet state [40], the predicted appearance of a "Weyl magnon" (a bosonic analog of weyl fermion) [41, 42] etc. As described in Chapter 1, a breathing pyrochlore lattice is characterized by the periodic expansion and contraction of corner sharing tetrahedra of an underlying pyrochlore lattice (Fig. 2.1). The tetrahedral size difference in a breathing pyrochlore material yields an additional control parameter called the breathing ratio, ratio of the lengths characterizing the large and small tetrahedra ( $B_r$ ). The tetrahedral size alternation is static and breaks inversion symmetry. The presence of two unequally sized tetrahedra yields a distinct nearest neighbor (NN) exchange interaction within each tetrahedra. The degree to which the NN exchange interactions between these tetrahedra vary can be visualized through the breathing factor ( $B_f$ ), which is defined as the ratio of the NN exchange interactions between the small and large tetrahedra. In the Cr-based breathing pyrochlore material  $\text{LiGaCr}_4\text{O}_8$ , the large and small tetrahedra are strongly coupled with each other due to small  $\sim 10\%$  variation in the size of the tetrahedra. On the other hand, the individual tetrahedra are decoupled in  $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$  due to the large intertetrahedral distance. Here, we look into the materials that lie within the interacting limit of breathing pyrochlore lattice.

A breathing pyrochlore lattice in the strongly interacting limit can be realized by tuning the pyrochlore structure in normal spinel materials [33]. If each alternating A-site cation in an  $AB_2X_4$  lattice are occupied by two different metal ions, the lattice geometry is tuned into a periodic arrangement of large and small tetrahedra. As a consequence, the centrosymmetric cubic space group  $Fd\bar{3}m$  loses its inversion symmetry resulting the lower symmetry space group  $F\bar{4}3m$ . A breathing pyrochlore lattice structure is also realized in the related lacunar spinel crystal structure due to the vacancy of a metal ion at alternating A sites [1, 43]. The result of the above alterations of the normal spin structure is the periodic expansion and contraction of the tetrahedra forming a breathing pyrochlore lattice structure of B sites.

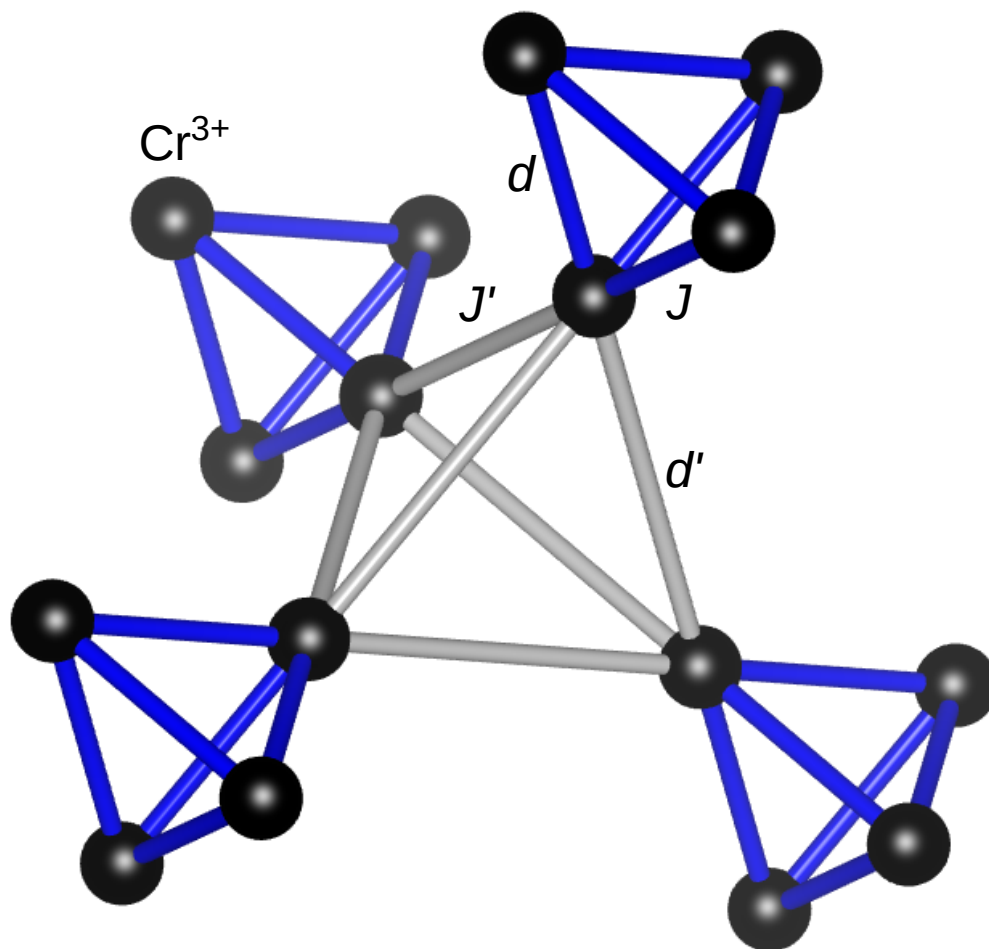
## 2.1 Cr-breathing pyrochlore

Cr-breathing pyrochlore lattices,  $AA'Cr_4X_8$ , were first reported over a half a century ago in terms of mixed A-site spinels with ordered A site cations [44]. A and A' in the chemical formula represent the monovalent and trivalent metal ions that occupy the A-sites of a spinel structure. The ligands ( $X = O, S, Se$ ) are bonded to the A- and B- sublattices of spinel structure providing tetrahedral and octahedral environments surrounding these cations. The ordering of metal ions on the A-sites exert different local chemical pressure to the alternating  $Cr_4$  tetrahedra tuning the size of tetrahedra. Recent experimental and theoretical studies reveal that Cr-breathing pyrochlores exhibit correlated paramagnetic states above the magnetic ordering temperature with new forms of nontrivial spin correlations characterized by ground state manifolds of different dimensions [45, 39, 46]. The competing exchange interactions in some of the pyrochlore materials lead to unconventional magnetic ground states with complex magnetic order like spiral spin liquid, Coulomb phase, and emergent effective antiferromagnet on FCC lattice [9, 45, 47].

### 2.1.1 Oxygen-based Cr-breathing pyrochlore

The Cr-breathing pyrochlore oxides such as  $LiGaCr_4O_8$ ,  $LiInCr_4O_8$  have attracted much attention recently, after several mixed A-site spinel materials were realized to be hosts of a breathing pyrochlore lattice [33, 46, 48, 49]. The magnetic properties of these materials have been extensively studied. Relative to the change in Cr-Cr bond lengths between two sets of  $Cr_4$  tetrahedra, a





**Figure 2.1:** Cr-breathing pyrochlore structure.  $J$  and  $J'$  represent the exchange couplings within the small and large tetrahedra respectively.

large enhancement of the strength of NN exchange interactions have been observed in the Cr-breathing pyrochlore oxides. This results the breathing factors around 0.6 and 0.1 to  $\text{LiGaCr}_4\text{O}_8$  and  $\text{LiInCr}_4\text{O}_8$  respectively [33, 46]. The individual tetrahedra in these breathing pyrochlores are strongly coupled with each other. The direct orbital overlap of Cr-3d orbitals yields strong antiferromagnetic couplings between Cr-ions within each  $\text{Cr}_4$  tetrahedra. So,  $\text{LiGaCr}_4\text{O}_8$  and  $\text{LiInCr}_4\text{O}_8$ , respectively, exhibit an antiferromagnetic ground state below 14 and 16 K [33, 46, 49]. Neutron scattering studies on  $\text{LiInCr}_4\text{O}_8$  indicate an additional complex magnetostructural order, possibly a spin nematic state, in a narrow temperature range just above the ordering temperature [46]. A spin nematic state is also observed in  $\text{LiGa}_{0.95}\text{In}_{0.05}\text{Cr}_4\text{O}_8$  below the magnetic transition at 11 K [39]. However,  $\text{LiGa}_{1-x}\text{In}_x\text{Cr}_4\text{O}_8$  ( $0.05 < x < 0.75$ ) loses long-range order and exhibit a frustrated spin-glass state at low temperature [49]. The large chemical disorder generated by A-site cations provides a major contribution for glassy behavior in the breathing pyrochlore series  $\text{LiGa}_{1-x}\text{In}_x\text{Cr}_4\text{O}_8$ .

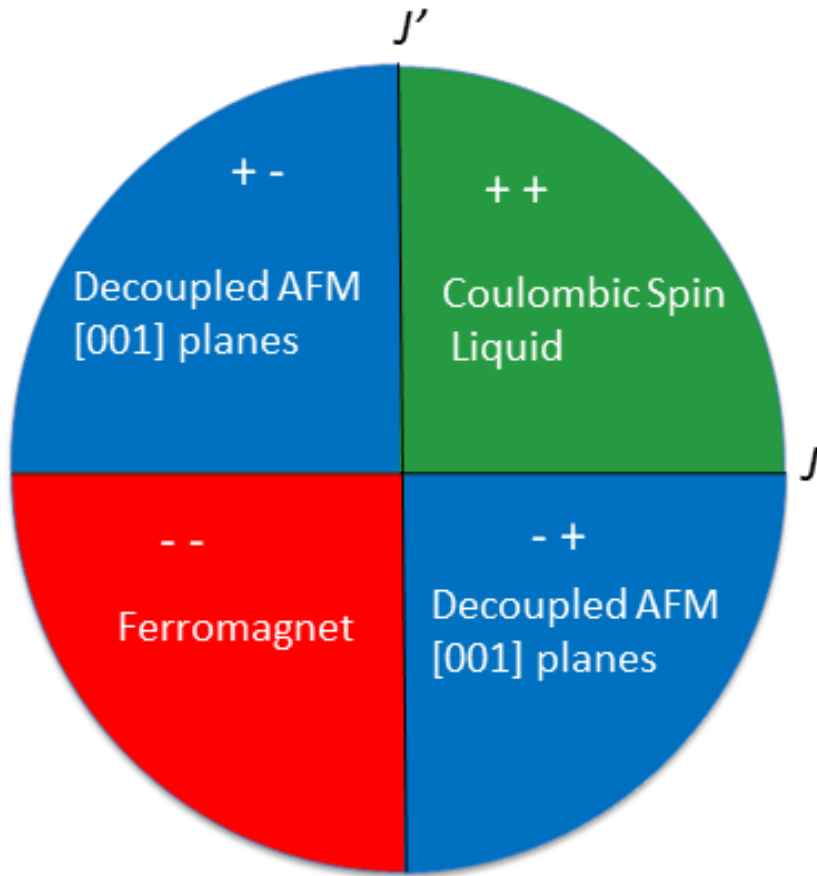
### 2.1.2 Ground state in Cr-breathing pyrochlore

To illustrate the basic physics of the Cr-breathing pyrochlore materials, we consider a Heisenberg Hamiltonian of the form [47]

$$H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \quad (2.1)$$

Where the summation over  $ij$  runs to the NN Cr-Cr bonds of small and large tetrahedra.  $J$  and  $J'$ , respectively, in equation (2.1) represent the NN exchange couplings within the small and large  $\text{Cr}_4$  tetrahedra as shown in Fig. 2.1. According to the classical ground state phase diagram (Fig. 2.2) of the breathing pyrochlore lattice [47], the magnetic ground state in these materials is determined by the sign of the exchange constants. Based on the same phase diagram:

- (I) When both the exchange constants are positive, strong antiferromagnetic couplings within the tetrahedra suppresses the ordering temperature and then the material enters into a coulombic liquid state.
- (II) When the couplings are ferromagnetic ( $J$  and  $J'$  both negative), the material orders with ferromagnetic ground state.



**Figure 2.2:** Classical phase diagram of the breathing pyrochlore lattice reproduced from the Ref. [47].  $J$  and  $J'$  represent the exchange couplings within the small and large tetrahedra respectively.

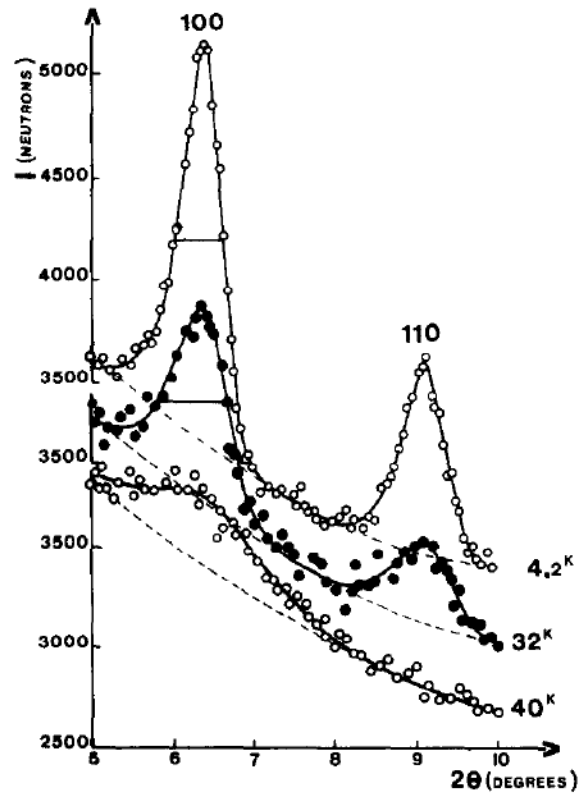
(III) For the case of opposite signs of exchange constants, the ground state manifold lowers its dimensionality following an order-by-disorder mechanism and form decoupled antiferromagnetic (AFM) (001) planes at low temperature below the AFM transition.

Recently density functional theory (DFT) calculations by Ghosh et al. indicate the significance of further neighbor exchange interactions in Cr-breathing pyrochlore materials [45]. We examine the importance of further neighbor interactions in Chapter 5.

### 2.1.3 Sulfur-based Cr-breathing pyrochlore

The Cr-Cr distances in sulfur-based Cr-breathing pyrochlores are larger than the oxide versions due to the increase in the size of the ligands. So, the breathing ratio of these breathing pyrochlores lies potentially in between the breathing ratio of oxygen-based Cr-breathing pyrochlores, where the individual tetrahedra are strongly coupled, and  $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$ , where the individual tetrahedra are completely decoupled. The increase in NN distance reduces the direct couplings between  $\text{Cr}^{3+}$  ions in sulfur-based Cr-breathing pyrochlores. So, NN antiferromagnetic couplings corresponding to the orbital overlap of Cr 3d-orbitals within the  $\text{Cr}_4$  tetrahedra reduces in  $\text{Li}(\text{Ga}, \text{In})\text{Cr}_4\text{S}_8$  in comparison with the oxide analog. The modulation of bond length results in dominant ferromagnetic exchange interactions within the large  $\text{Cr}_4$  tetrahedra due to  $90^\circ$  superexchange interactions in  $\text{Li}(\text{Ga}, \text{In})\text{Cr}_4\text{S}_8$  [28, 37, 50]. The direct exchange couplings may still exist predominantly in small  $\text{Cr}_4$  tetrahedra due to the small value of Cr-Cr bond length. In this case, the exchange couplings become opposite to each other in two sets of tetrahedra. Hence, the sulfur-based Cr-breathing pyrochlores are potentially interesting examples where the exchange couplings are the same or opposite to each other in two sets of tetrahedra.

There are limited previous studies on sulfur-based Cr-breathing pyrochlores. Although the literature [44, 51, 52] pointed out interesting observations of the magnetic ground states about a half-century ago, there are not many recent studies on these materials that investigate the static and dynamic spin correlations. Pinch et al. in reference [44] reported that the mixed A-site chromium thiospinel materials order antiferromagnetically at low temperatures. Pinch, et al. Reported that the Néel temperature of the  $\text{A}_{1/2}^{1+}\text{A}_{1/2}^{3+}\text{Cr}_2\text{S}_4$  compounds vary in the range 6 - 31 K depending upon the A-site diamagnetic ions. Around the same time, the neutron scattering



**Figure 2.3:** Elastic neutron scattering data in  $\text{CuInCr}_4\text{S}_8$  at different temperatures (image reproduced from Ref. [51]).

measurements carried out on  $\text{Cu}_{1/2}\text{In}_{1/2}\text{Cr}_2\text{S}_4$  [51] shows unusual magnetic ordering with the first-order transition from short-range order magnetic structure to long-range order structure at 35 K. The temperature-dependent neutron scattering data in  $\text{Cu}_{1/2}\text{In}_{1/2}\text{Cr}_2\text{S}_4$  is shown in Fig. 2.3 [51]. Three magnetic transitions are reported at a low temperature below 160 K in  $\text{Cu}_{1/2}\text{In}_{1/2}\text{Cr}_2\text{S}_4$ . Above 160 K, it is paramagnetic. The short-range spin correlations that exist in the temperature range 35 - 160 K persist to third nearest neighbors. The long-range antiferromagnetic correlations in  $\text{CuInCr}_4\text{S}_8$  extends up to 200 Å. According to Plumier et al. [51], the NN exchange couplings in  $\text{CuInCr}_4\text{S}_8$  are ferromagnetic with three neighbors and antiferromagnetic with the remaining other three neighbors. Hence,  $\text{CuInCr}_4\text{S}_8$  exhibits complex low-temperature physics associated with unusual magnetic ground states. No such studies are available to other sulfur-based Cr-breathing pyrochlore materials, which are potential candidates for exhibiting rich frustrated physics.

Here, we study a sulfur-based Cr-spinel material  $\text{LiGaCr}_4\text{S}_8$ . The metal ions  $\text{Li}^{1+}$  and  $\text{Ga}^{3+}$  occupy the A-sites of spinel structure. The ionic radii of  $\text{Li}^{1+}$  and  $\text{Ga}^{3+}$  are 76 and 62 pm respectively. The difference in the ionic size of A-site metal ions creates a large difference in local chemical pressure around  $\text{Cr}_4$  tetrahedra. So,  $\text{LiGaCr}_4\text{S}_8$  is a potential candidate for breathing pyrochlore lattice with a larger breathing ratio. Pinch et al. [44] studied  $\text{LiGaCr}_4\text{S}_8$  first time in 1970 and reported that this material orders antiferromagnetically at low temperature. But, this argument was made based solely on vibrating sample magnetometer measurements. No comprehensive studies have been made to understand the intrinsic spin behavior. Many physical properties of  $\text{LiGaCr}_4\text{S}_8$  have remained unexplored. The effect of breathing distortion in  $\text{LiGaCr}_4\text{S}_8$  has not been the focus of the study yet. How the increase in the breathing ratio in  $\text{LiGaCr}_4\text{S}_8$ , compared to the oxide versions, affects the spin static and dynamic structures serves as the motivation for the studies presented in Chapters 4 and 5.

## 2.2 Lacunar spinels

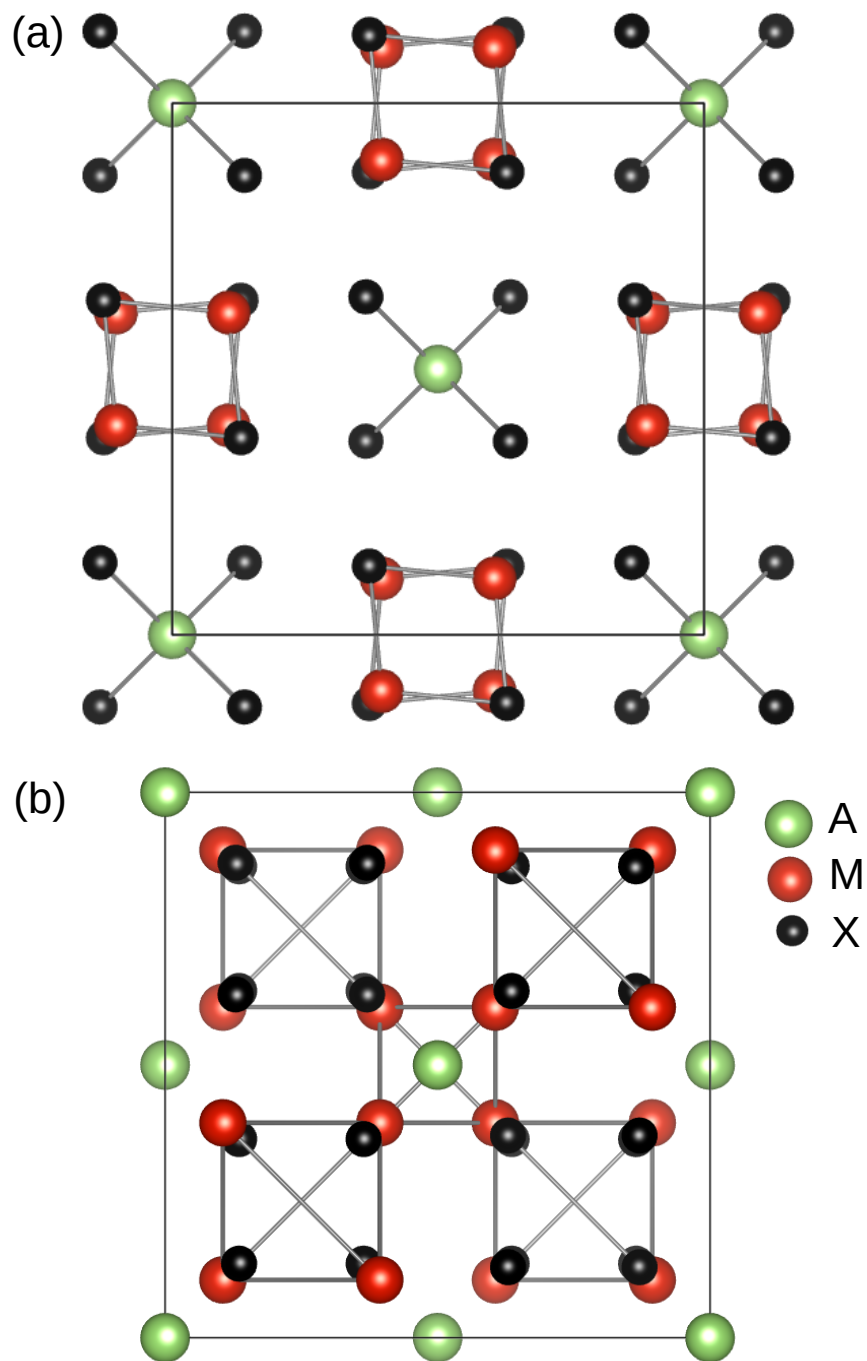
The cubic spinel structure remains same if the alternating A-site cations are absent in a regular  $\text{AB}_2\text{X}_4$  structure. These materials are represented by chemical formula  $\text{AM}_4\text{X}_8$  and are referred to as lacunar spinels. The name "lacunar" means the lack of every second A-site cations compared to the regular spinel structure. The structural building blocks of these ternary chalcogenides,

$AM_4X_8$  ( $A = \text{Ga, Ge}$ ;  $M = \text{Mo, V, Nb, Ta}$ ,  $X = \text{S, Se}$ ) compounds, are  $(AX_4)^{n-}$  tetrahedra and  $(M_4X_4)^{n+}$  cubanes, which are weakly linked with each other in a periodic arrangement (Fig. 2.4(a)).  $(M_4X_4)^{n+}$  cubane in  $AM_4X_8$  compounds forms a molecular unit that arranges in an fcc lattice network with a well-described unique electron density in the molecular orbital scheme [53, 54].

Lucunar spinels have a non-centrosymmetric crystal structure. The lowering of symmetry from space group  $Fd\bar{3}m$  to  $F\bar{4}3m$ , occurs through the removal of interpenetrating FCC A-sublattices in a normal spinel structure. The rearrangement of bond lengths results in a formation of new  $M_4$  tetrahedral clusters. So, the pyrochlore lattice structure in a regular spinel material, formed by the corner-sharing  $M_4$  tetrahedra, is tuned by the deficiency of alternating A-site metal ions as shown in Fig. 2.4(b). In most of the lacunar spinel materials, the tetrahedral  $M_4$  metallic clusters are characterized by partially filled electronic orbitals. Due to the partly filled electronic shell, these materials are Jahn-Teller active and exhibit ferroelectric polarization at low temperature [53, 55, 56, 57]. Recently, a plethora of physical phenomena originated by spin correlations have been observed in lacunar spinel materials. Examples include multiferroicity [53, 57, 58], pressure-induced superconductivity [59], bandwidth-controlled metal-to-insulator transitions [60], large negative magnetoresistance [61], resistive switching via an electric-field induced transition [62], skyrmion lattices [1, 53, 63], a two-dimensional topological insulating state [64]. More excitement about this class of materials has been created by the skyrmion host material  $GaV_4S_8$ , which exhibits a rich phase diagram with multiple exciting ground states as shown in Fig. 2.5.

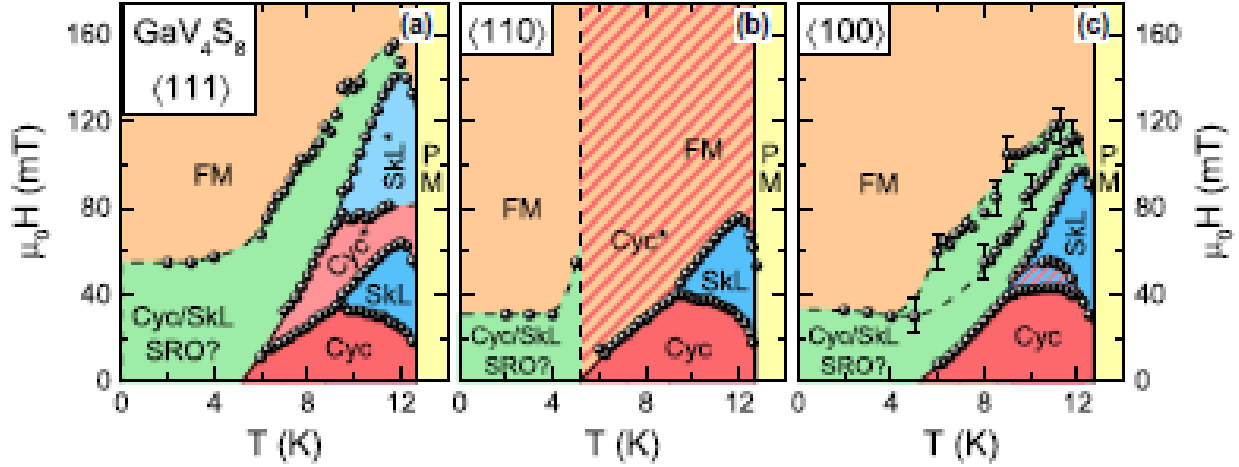
### 2.2.1 Prototype lacunar spinel $GaV_4S_8$

The lacunar spinel  $GaV_4S_8$  is a magnetic semiconductor where the ordered vacancy on the Ga-sites breaks the inversion symmetry. The hybridization of atomic orbitals on  $V_4$  tetrahedra leads to seven valence electrons per tetrahedra in  $GaV_4S_8$  [54]. Based on the molecular orbital picture, only one valence electron is unpaired and occupies the triply degenerate  $t_2$  molecular orbitals. So, each  $V_4$  cluster shares a local spin 1/2 moment in  $GaV_4S_8$ . Due to the presence of a single electron in the triply degenerate molecular orbitals,  $GaV_4S_8$  is an orbitally active material. Below 44 K, a cooperative Jahn-Teller distortion lifts the orbital degeneracy, driving a cubic to



**Figure 2.4:** (a) Arrangement of  $AX_4$  and  $M_4X_4$  structures in lacunar spinel compounds. (a) Large and small  $M_4$  clusters in  $AM_4X_8$  compounds.



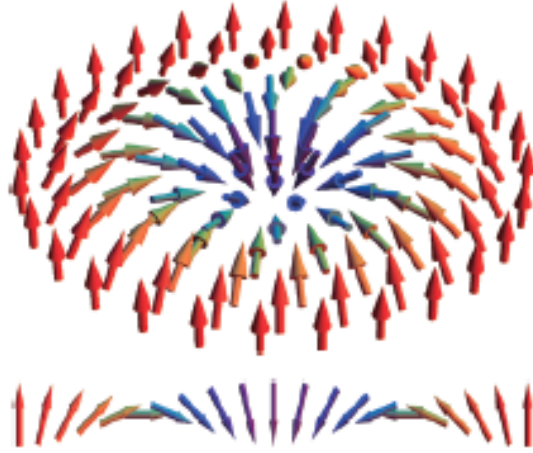


**Figure 2.5:** Phase diagram of GaV<sub>4</sub>S<sub>8</sub> (image reproduced from Ref. [65]).

rhombohedral structural phase transition in GaV<sub>4</sub>S<sub>8</sub> [53]. The structural transition is characterized by the elongation of V<sub>4</sub> tetrahedra along one of the four easy axes [111] directions [1, 53]. The orbital ordering in GaV<sub>4</sub>S<sub>8</sub> induces rhombohedral ferroelectric polarization with the direction of polarization in each structural domain aligning parallel to the direction of structural distortion [66].

GaV<sub>4</sub>S<sub>8</sub> exhibits interesting magnetic structures, including cycloidal and skyrmion lattice (SKL) below the magnetic ordering temperature of 13 K [65]. A lattice structure consisting of a periodic array of spin vortices, whirl-like spin textures, is referred to as SKL. The skyrmion lattice in GaV<sub>4</sub>S<sub>8</sub> is a Néel-type (Fig. 2.6), where the spins rotate in a radial plane from the core of skyrmion to the periphery. This is unusual as GaV<sub>4</sub>S<sub>8</sub> is the only a non-chiral polar bulk crystal with  $C_{nv}$  symmetry that hosts Néel-type SKL. The SKL phase exist in an unusually wider range of temperature in GaV<sub>4</sub>S<sub>8</sub> compared to the other bulk crystals [67, 1]. The DM interaction plays an important role in the stabilization of the novel magnetic phases in GaV<sub>4</sub>S<sub>8</sub>. Small-angle neutron scattering (SANS) measurements show magnetic satellite peaks in cycloid and SKL phases with three possible  $q$ -vectors that are perpendicular to the easy axis ([111] direction). In GaV<sub>4</sub>S<sub>8</sub>, the pitch of a cycloid is around 177 Å and the size of a skyrmion is close to 220 Å [1].

While the physical behavior of GaV<sub>4</sub>S<sub>8</sub> has been studied extensively in recent years [1, 53, 54, 65], experimental investigations of the spin dynamics has been limited. One of the key reasons for the unavailability of such studies is the lack of a large single crystals of GaV<sub>4</sub>S<sub>8</sub> of sufficient



**Figure 2.6:** Néel type skyrmion in  $\text{GaV}_4\text{S}_8$  (image reproduced from Ref. [1]).

size for inelastic neutron scattering experiments. The experimentally measured ordered moment in  $\text{GaV}_4\text{S}_8$  is  $0.8 \mu_B/\text{f.u.}$  [53]. As the moment size is small, a relatively large size single crystal is needed for inelastic neutron scattering measurements. A significant achievement of the research described here is the growth of large  $\text{GaV}_4\text{S}_8$  single crystals. Large crystals are essential for inelastic neutron scattering measurements of the spin dynamics. I will explore how the spins are interacting with each other in  $\text{GaV}_4\text{S}_8$  at base temperature of 1.7 K to generate a complex phase shown by the phase diagram in Fig. 2.5.

# Chapter 3

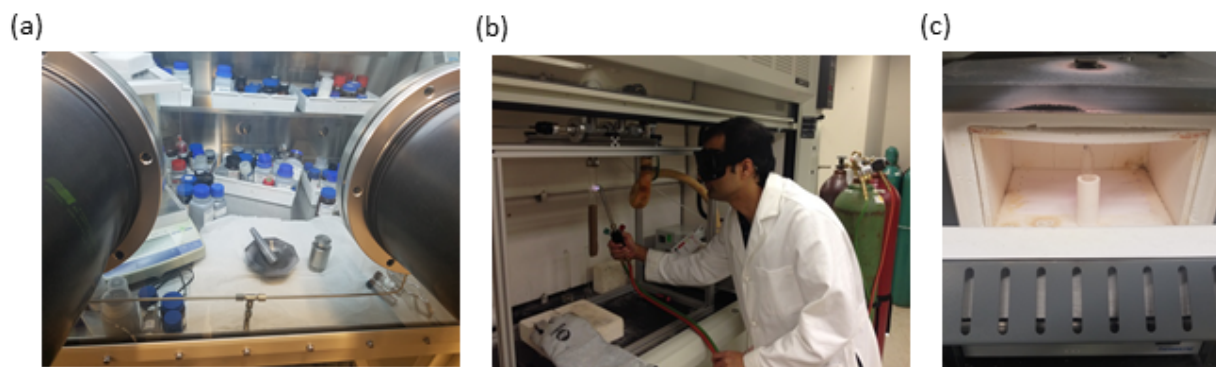
## Research Techniques

This chapter emphasizes the fundamentals of sample preparation and neutron scattering measurement techniques. The polycrystalline samples of  $\text{LiGaCr}_4\text{S}_8$  and  $\text{GaV}_4\text{S}_8$  were prepared using conventional solid state reaction. After the powders were successfully synthesized, chemical vapor transport (CVT) technique was used to grow the single crystal of  $\text{GaV}_4\text{S}_8$ . The details of the materials synthesis techniques are described in the following sections. Later, the basics of neutron scattering are discussed with a brief introduction of neutron scattering instruments used in this research.

### 3.1 Materials synthesis

#### 3.1.1 Solid state synthesis

In the conventional solid state synthesis technique, an appropriate amount of starting materials are ground together into a fine powder, typically with a mortar and pestle. If the sample ingredients are sensitive to air, the grinding process is normally carried out under an inert atmosphere. The fine ground powder is pelletized into desired diameter and thickness using a press. The resulting pellet is sealed inside a quartz tube and heated to high temperature to complete the solid state reaction. Fig 3.1 depicts the three steps of the solid state synthesis technique.



**Figure 3.1:** (a) Mortar and pestle under inert atmosphere, (b) tube sealing process, (c) sealed tube with a sample inside a furnace.

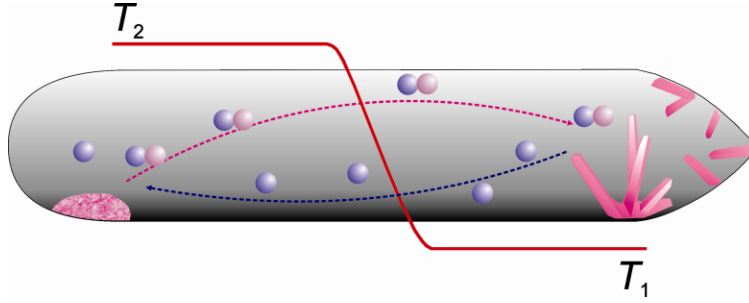
### 3.1.2 Chemical vapor transport (CVT)

Chemical vapor transport is a synthesis and purification process of a solid material where a condensed phase is first volatilized and then deposited elsewhere, usually in the form of single crystal. Due to the temperature gradient inside the tube, the volatile derivative reverts back to the single crystals of the parent solid as the transport agent releases it at the opposite end. Generally halogens or halogen compounds are used as transport agents. For the set up, the reactants and the transport agent are sealed in an ampoule and then kept in a two zone furnace for the duration of the growth (see sketch in Fig. 3.2). The overall reaction is represented as [68]:

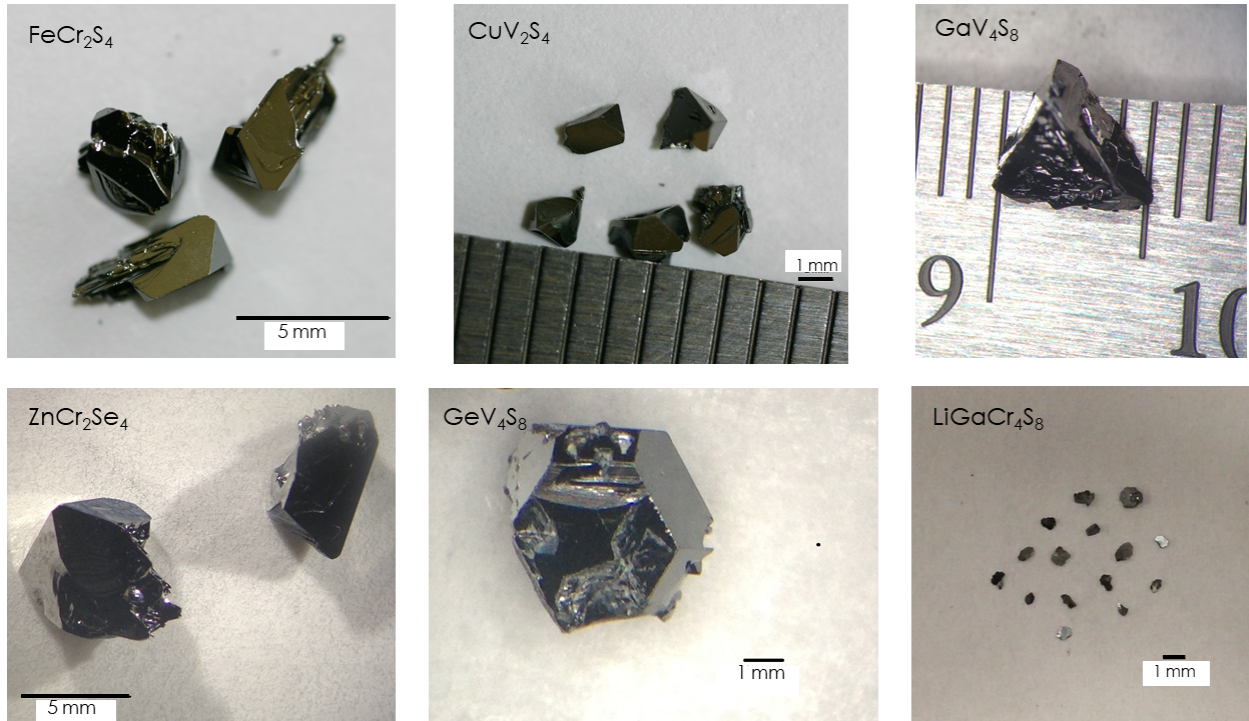


Where the condensed phase 'A' volatilized into 'C' at high temperature due to the influence of transport agent 'B'. The product is in a gaseous state after the chemical vapor transport reaction. Usually there are three steps for the growth process;

- (1) Forward reaction where the transport agent reacts with the reactants.
- (2) Gas flow inside the ampoule.
- (3) Back reaction where the transport agent releases the condensed phase.



**Figure 3.2:** Sketch of experimental set up of chemical vapor transport crystal growth technique (image reproduced from Ref. [69]).



**Figure 3.3:** Images of single crystals of selected chalcogenide spinel materials that are grown through CVT.

The gas flow by diffusion is assumed to be the rate determining step to predict the amount of transported condensed phase. For this process, the gas pressure inside the ampoule is typically in the range  $10^{-3} - 3$  bar. The amount of transported condensed phase can be approximated by "Schafer's transport equation" which is written as [68]:

$$\dot{n}(A) = n(A)/t' = \frac{a}{c} \cdot \frac{\Delta p(C)}{\sum p} \frac{T^{0.75} \cdot q}{s} \cdot 0.6 * 10^{-4} \quad (3.2)$$

$\dot{n}(A)$  = Transport rate (mol.h<sup>-1</sup>)

$t'$  = total growth time

$a, c$  = Stoichiometric coefficients in the transport equation

$\Delta p(C)$  = partial pressure difference of species C

$\sum p$  = total pressure

$T$  = mean temperature between hot and cold end of sealed tube

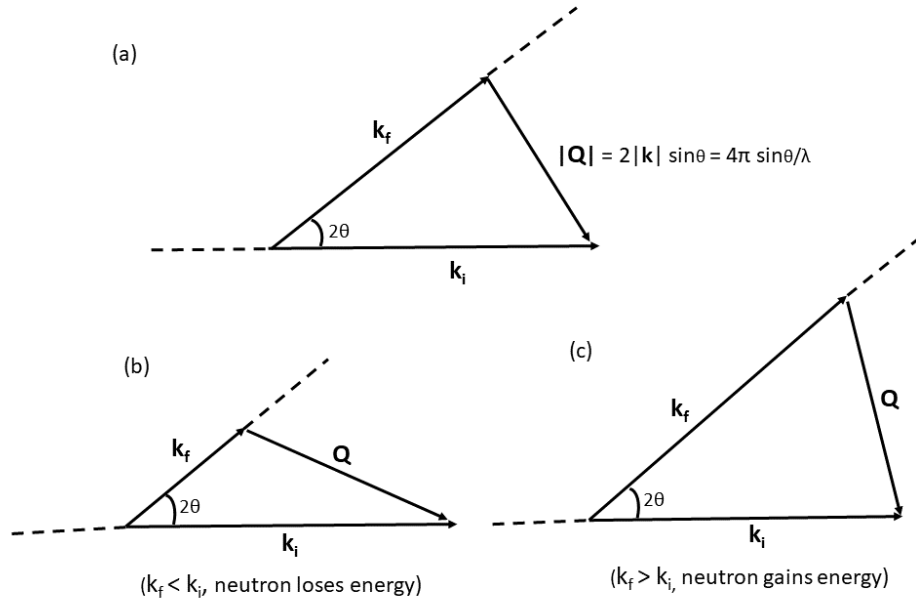
$q$  = cross section of diffusion path

$s$  = length of diffusion path

The images of single crystals of selected chalcogenide spinel materials that are grown through CVT are shown in Fig. 3.3

## 3.2 Neutron Scattering

The neutron scattering technique is used to study the static and dynamic behavior of spin-spin correlations in the materials investigated in this dissertation. The use of neutron scattering has many advantages over the other similar measurement techniques [70]. The neutron is a chargeless, spin 1/2 particle with magnetic moment  $-1.913 \mu_N$  and mass 1 amu. It can interact with the nuclear spin and moment of unpaired electrons. The wavelength and energy of thermal neutrons are comparable to the inter-atomic distance and energy of elementary excitation in solids, respectively. Therefore, neutron scattering is a powerful technique to obtain information about the structure and dynamics of materials. The high penetrating power of neutrons is useful to carry out a neutron scattering experiment in various sample environments such as pressure cells, magnets, and cryostats. The neutron scattering cross-section varies by element and between different isotopes of



**Figure 3.4:** Scattering triangles representing the scattering process in neutron scattering. (a) represents the elastic scattering, (b) and (c) represent the inelastic scattering [71].

same element. Consequently, the experimental study of different isotopes and lighter elements is possible with neutron scattering measurements.

A neutron scattering measurement requires a beam or pulse of the incident neutrons to scatter from a target sample exchanging momentum and energy with each other. The momentum and energy gained or lost by the neutron is equal to the momentum and energy of an excitation inside the sample. In a neutron scattering experiment, the momentum and energy change of scattered neutrons are detected using either a single detector or detector banks. The scattered neutrons carry the information about the spin static and dynamic structures in a target sample. If the scattering process does not involve a change in energy, then the scattered neutrons carry the information about the spin static structure. On the other hand, if the scattering process involve both energy and momentum change, then the scattered neutron carries the information about the spin dynamics.

Consider a basic neutron scattering measurement in which a beam of neutrons with wave vector  $\mathbf{k}_i$  incident on a target nucleus and then scatter with wave vector  $\mathbf{k}_f$ . The scattering process is represented by Fig. 3.4. The scattered neutrons are detected in terms of momentum and energy

change. The conservation laws for momentum and energy, governing the scattering process, are as follows [71]:

$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f, \quad (3.3)$$

$$\Delta E = \hbar^2/2m_n(k_i^2 - k_f^2), \quad (3.4)$$

where  $\hbar\mathbf{Q}$  = change in momentum,  $\Delta E$  = change in energy,  $\hbar = h/2\pi$ ,  $k = 2\pi/\lambda$  (wave vector magnitude),  $\lambda$  = wavelength of neutron,  $m_n$  = mass of the neutron. As the neutron has a finite mass, the energy of neutron follows the dispersion relation  $E = \hbar^2 k^2/2m_n$

The angle of scattering  $2\theta$  is calculated as

$$|\mathbf{Q}| = k_i^2 + k_f^2 - 2k_i k_f \cos(\theta). \quad (3.5)$$

The probability of effective scattering of neutrons from a sample is expressed in terms of the scattering cross section,  $\sigma$ , which is defined as the ratio of number of neutrons scattered per second to the incident neutron flux per unit area,

$$\sigma = \frac{\text{number of scattered neutrons in one second}}{\text{incident neutron flux}} \quad (3.6)$$

$$= \frac{\text{number of scattered neutrons in one second}}{\left( \frac{\text{number of incident neutrons in one second}}{\text{area perpendicular to incident beam}} \right)}. \quad (3.7)$$

The angular dependence of scattering is defined by the partial differential scattering cross section as [71]:

$$\frac{d^2\sigma}{d\Omega dE} = \frac{N_{\theta,\phi}}{\psi d\Omega dE} \quad (3.8)$$

Where  $d\Omega$  is the solid angle into which the neutrons with energies  $E$  and  $E + dE$  are scattered,  $N_{\theta,\phi}$  represents the number of neutrons scattered in solid angle  $d\Omega$  with the scattering angles  $\theta$  and  $\phi$ ,  $\psi$  represents the incident neutron flux.

The differential scattering cross-section is obtained by integrating over all energy.



$$\frac{d\sigma}{d\Omega} = \int \frac{N_{\theta,\phi}}{\psi d\Omega dE} dE. \quad (3.9)$$

Therefore, the total scattering cross-section is

$$\sigma = \int \int \frac{N_{\theta,\phi}}{\psi d\Omega dE} dE d\Omega \quad (3.10)$$

Let us consider a scattering process in which an incident neutron in quantum state  $|\mathbf{k}_i \lambda_i\rangle$  is scattered from a target nucleus to a final quantum state  $|\mathbf{k}_f \lambda_f\rangle$ . If  $E_i$  and  $E_f$  represent the energies of incident and scattered neutron, respectively, then the partial differential scattering cross section can be obtained using the Fermi-Gorden rule as

$$\left( \frac{d^2\sigma}{d\Omega dE} \right)_{k_i \rightarrow k_f} = \frac{k_f}{k_i} \left( \frac{m_n}{2\Pi\hbar^2} \right)^2 |\langle \mathbf{k}_f \lambda_f | V | \mathbf{k}_i \lambda_i \rangle|^2 \delta(\hbar\omega + E_i - E_f), \quad (3.11)$$

where  $V$  represents an interaction potential operator between the target nucleus and scattered neutron for the particular scattering process. The energy conservation law in scattering process is described by the delta function. According to the Born approximation, neutrons can be described as plane waves:

$$|\mathbf{k}_i \lambda_i\rangle \propto e^{i\mathbf{k}_i \cdot \mathbf{r}} \quad (3.12)$$

$$|\mathbf{k}_f \lambda_f\rangle \propto e^{i\mathbf{k}_f \cdot \mathbf{r}}. \quad (3.13)$$

Then the interaction between the neutron and the target nucleus can be expressed as

$$V(r) = \frac{2\Pi\hbar^2}{m_n} b \delta(r - R) \quad (3.14)$$

Where  $b$  represents the scattering length which generally depends on the target nucleus,  $r$  and  $R$  are the positions of neutron and target nucleus.

Substituting these values, the partial differential scattering cross section becomes

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_f}{k_i} \sum_{\lambda_i, \lambda_f} P(\lambda_i) |\langle \lambda_f | b \sum_l e^{i\mathbf{Q} \cdot \mathbf{r}_l} | \lambda_i \rangle|^2 \delta(\hbar\omega + E_i - E_f) \quad (3.15)$$

Where  $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$  and  $P(\lambda_i)$  is statistical population factor of initial state  $|\lambda_i\rangle$ . Equation (3.15) was evaluated after averaging all the initial states and summing the final states.

The double scattering cross section is related to the scattering function  $S(\mathbf{Q}, \omega)$  as [71]

$$\frac{d^2\sigma}{d\Omega dE} = N \frac{k_f}{k_i} b^2 S(\mathbf{Q}, \omega), \quad (3.16)$$

where

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi\hbar N} \sum_{nn'} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q}\cdot\mathbf{r}'_n(0)} e^{-i\mathbf{Q}\cdot\mathbf{r}_n(t)} \rangle e^{-i\omega t} dt. \quad (3.17)$$

Here,  $N$ ,  $t$  and angle bracket  $\langle \dots \rangle$  represent the numbers of nuclei, time and average over all the initial states respectively. The above equation (3.17) shows that the scattering function  $S(\mathbf{Q}, \omega)$  depends on the momentum and energy transfer between the sample and the scattered neutrons.  $S(\mathbf{Q}, \omega)$  contains the information about the position and motion of atoms in the target sample. Therefore, all neutron scattering experiments measure the scattering function  $S(\mathbf{Q}, \omega)$  in order to study the static and dynamic properties of different system of atoms.

### 3.2.1 Magnetic Scattering

The interaction of the magnetic moment of a neutron with the field produced by unpaired electrons in the sample results in magnetic neutron scattering. Neutrons interact with the moment of unpaired d or f electrons via dipole-dipole interactions. If the net spin magnitude of an atom is  $S$ , then the amplitude of magnetic scattering is written as  $pS$  [71], where

$$p = (\gamma r_0/2) g f(\mathbf{Q}) \quad (3.18)$$

Where  $\gamma r_0/2 = 0.2695 \times 10^{-12}$  cm;  $r_0$  is the classical electron radius and  $g$  is Lande splitting factor.

The Fourier transform of normalized spin density  $\rho(\mathbf{r})$ , magnetic form factor  $f(\mathbf{Q})$ , is

$$f(\mathbf{Q}) = \int \rho(\mathbf{r}) e^{-i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} \quad (3.19)$$

Where  $f(0) = 1$ . The cross section of magnetic scattering depends not only on the initial and final wave vectors but also on the spin states  $s_i$  and  $s_j$ . Using these equations, the differential cross-section (equation (3.15)) can be written as [71]

$$\frac{d^2\sigma}{d\Omega dE}|_{s_i s_j} = \frac{k_f}{k_i} \sum_{i,f} P(\lambda_i) |\langle \lambda_f | b \sum_l e^{i\mathbf{Q}\cdot\mathbf{r}_l} U_l^{s_i s_f} | \lambda_i \rangle|^2 \delta(\hbar\omega + E_i - E_f) \quad (3.20)$$

with

$$U_l^{s_i s_j} = \langle s_f | |b_l - p_l \mathbf{S}_{\perp l} \cdot \boldsymbol{\sigma} + B_l \mathbf{I}_l \cdot \boldsymbol{\sigma}| |s_i \rangle \quad (3.21)$$

where  $b$  = nuclear coherent scattering amplitude,  $B$  = spin dependent nuclear amplitude,  $\mathbf{I}$  = nuclear spin operator,  $\mathbf{S}_{\perp}$  = magnetic interaction vector [71]. Equation (3.21) represents the atomic scattering amplitude from the initial spin state  $s_i$  to the final state  $s_j$  of the atomic site  $l$ . The magnetic interaction vector in reciprocal space is [71, 72]

$$\mathbf{S}_{\perp} = \hat{\mathbf{Q}} \times (\mathbf{S} \times \hat{\mathbf{Q}}) \quad (3.22)$$

$$\mathbf{S}_{\perp} = \mathbf{S} - \hat{\mathbf{Q}}(\hat{\mathbf{Q}} \cdot \mathbf{S}) \quad (3.23)$$

Equation (3.23) indicates that the component of  $\mathbf{S}$  perpendicular to the unit vector along  $\mathbf{Q}$  contribute to the magnetic scattering amplitude. Using Ref. [71]

$$|\mathbf{S}_{\perp}|^2 = \sum_{m,n} (\delta_{m,n} - \hat{\mathbf{Q}}_m \hat{\mathbf{Q}}_n) S_m^* S_n \quad (3.24)$$

Using equation (3.24), differential cross section of magnetic scattering becomes

$$\frac{d^2\sigma}{d\Omega dE} = \frac{N}{\hbar} \frac{k_f}{k_i} p^2 e^{-2W} \sum_{m,n} (\delta_{m,n} - \hat{\mathbf{Q}}_m \hat{\mathbf{Q}}_n) S^{mn}(\mathbf{Q}, \omega) \quad (3.25)$$

Where

$$S^{mn}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \cdot \sum_l e^{-i\mathbf{Q}\cdot\mathbf{r}_l} \langle S_0^m(0) S_l^n(t) \rangle dt \quad (3.26)$$

The angle bracket in equation (3.26) represents the average over all the spin states. Equation (3.25) represents the differential cross-section for magneto-vibrational scattering.

The fluctuation dissipation theorem relates the the scattering function  $S(\mathbf{Q}, \omega)$  to the imaginary part of dynamic susceptibility as

$$\chi''(\mathbf{Q}, \omega) = (1 - e^{-\frac{\hbar\omega}{k_B T}})S(\mathbf{Q}, \omega) \quad (3.27)$$

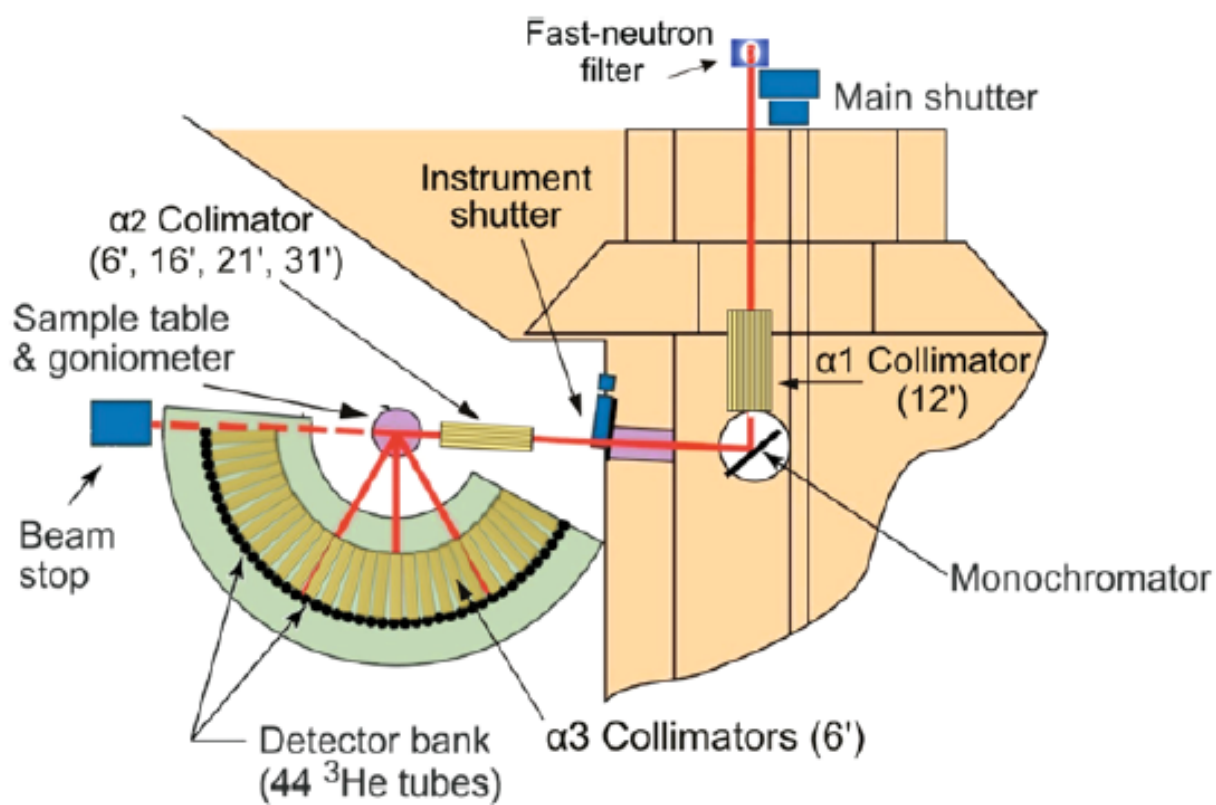
Where  $\chi''$  is the imaginary part of dynamic susceptibility and  $(1 - e^{-\frac{\hbar\omega}{k_B T}})$  is the Bose factor.

### 3.3 Instrumentation

Neutron scattering measurements were carried out at the neutron scattering user facilities at Oak Ridge National Laboratory (ORNL) and NIST Center of Neutron Research (NCNR). Two different neutron sources, i.e. reactor-based neutron source and accelerator-based neutron sources, were used to produce the neutrons for the scattering experiments performed on this dissertation. In a reactor-based neutron source, neutrons are generated by the nuclear fission inside a reactor. On the other hand, an accelerator based source typically uses an intense proton pulse that impinge upon a target (liquid mercury at the SNS) and neutrons are generated from the neutrons spalling off of the heavy metal nucleus. A wide variety of neutron scattering instruments have been designed to achieve diverse scientific goals. A brief description of the selected instruments used in this research is given in the following sections.

#### 3.3.1 Neutron powder diffractometer (HB-2A)

Neutron powder diffraction is a powerful technique to study static structural and magnetic properties. The neutron powder diffractometer (HB-2A) at HFIR is designed to provide a balance between high resolution and high neutron flux for neutron diffraction measurements [73]. HB-2A works on the principle of Debye-Scherrer geometry (Fig. 3.5). HB-2A uses a vertically focusing germanium wafer-stack monochromator that provides one of the three wavelengths: 2.41 Å, 1.54 Å, and 1.12 Å. The monochromatic beam then passes through a collimator before illuminating the sample. The diffracted neutron beam from the sample passes through a different another set of collimators and then to 44  $^3\text{He}$  detectors. The entire detector bank, which are spaced by  $\sim 2.5^\circ$  in  $2\theta$ , are movable and provide a coverage from 2 to  $154^\circ$ .

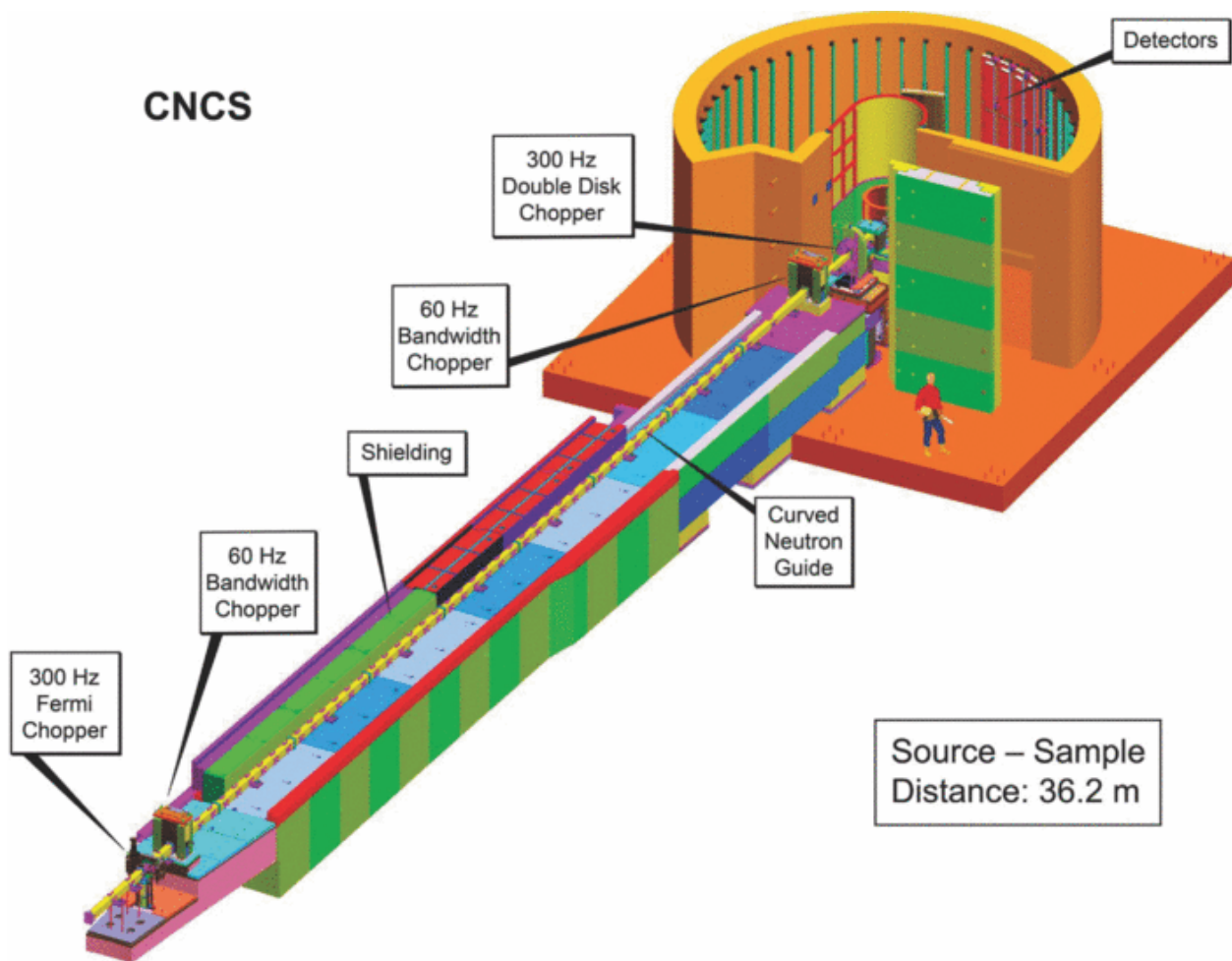


**Figure 3.5:** Layout of the HB-2A powder diffractometer at HFIR, ORNL (image reproduced from Ref. [73]).

### 3.3.2 Time-of-flight spectrometer

Multiple neutron time-of-flight (TOF) spectrometers including the Wide Angular-Range Chopper Spectrometer (ARCS), Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA), and Cold Neutron Chopper Spectrometer (CNCS) at the SNS, ORNL have been used to perform the neutron scattering measurements in this dissertation. In the TOF spectrometers used in this research, the energy of the incident neutrons is controlled by passing the pulse of neutrons through a series of choppers [74, 75, 76]. The choppers are made of neutron-absorbing cylinders or discs with each having a window or slits. The change in energy of neutron after impacting with the sample directly affects the velocity of scattered neutrons and hence the time to reach the detector. If a neutron losses energy after interacting with the sample, it takes a longer time to reach the detector. On the other hand, the scattered neutron reaches the detector faster if it absorbs energy from the sample. In either case, the time-of-flight of incident and scattered neutron is measured. The time-of-flight of incident and scattered neutrons are used to calculate the energy loss/gain in the scattering process.

The general layout of CNCS is shown in Fig. 3.6. CNCS is a direct-geometry inelastic neutron TOF spectrometer, designed to provide energy resolution in the range 10 – 500  $\mu\text{eV}$  for the neutron scattering experiments in the cold and thermal energy ranges [76]. It consists of two high-speed choppers that can be coupled in several ways to control the incident energy and the instrumental resolution. There are two additional disk choppers to remove frame overlap of neutron pulses. CNCS consists of a 36.2 m long neutron guide that has a curved section in the middle to eliminate high energy neutrons from reaching the sample. The detector array consists of 400 position-sensitive two-meter long  $^3\text{He}$  tubes that provide a solid angle coverage of 1.7 sr around the sample [76]. The detector array is 3.5 m away from the sample stage and is situated inside a detector enclosure.



**Figure 3.6:** General layout of Cold Neutron Chopper Spectrometer (CNCS) at the SNS, ORNL (image reproduced from Ref. [76]).

## Chapter 4

# Negative thermal expansion and magnetoelastic coupling in the breathing pyrochlore lattice material $\text{LiGaCr}_4\text{S}_8$

A similar version of this chapter is published as, “Negative thermal expansion and magnetoelastic coupling in the breathing pyrochlore lattice material  $\text{LiGaCr}_4\text{S}_8$ ”, G. Pokharel, A. F. May, D. S. Parker, S. Calder, G. Ehlers, A. Huq, S. A. J. Kimber, H. Suriya Arachchige, L. Poudel, M. A. McGuire, D. Mandrus, and A. D. Christianson, Phys. Rev. B. 97, 134117 (2018) (Reference [77]).

In this chapter, the physical properties of the spinel  $\text{LiGaCr}_4\text{S}_8$  have been studied with neutron diffraction, X-ray diffraction, magnetic susceptibility and heat capacity measurements. The neutron diffraction and synchrotron X-ray diffraction data reveal negative thermal expansion (NTE) below 111(4) K. The magnetic susceptibility deviates from Curie-Weiss behavior with the onset of NTE. At low temperature a broad peak in the magnetic susceptibility at 10.5(5) K is accompanied by the return of normal thermal expansion. First principles calculations find a strong coupling between the lattice and the simulated magnetic ground state. These results indicate strong magnetoelastic coupling in  $\text{LiGaCr}_4\text{S}_8$ .

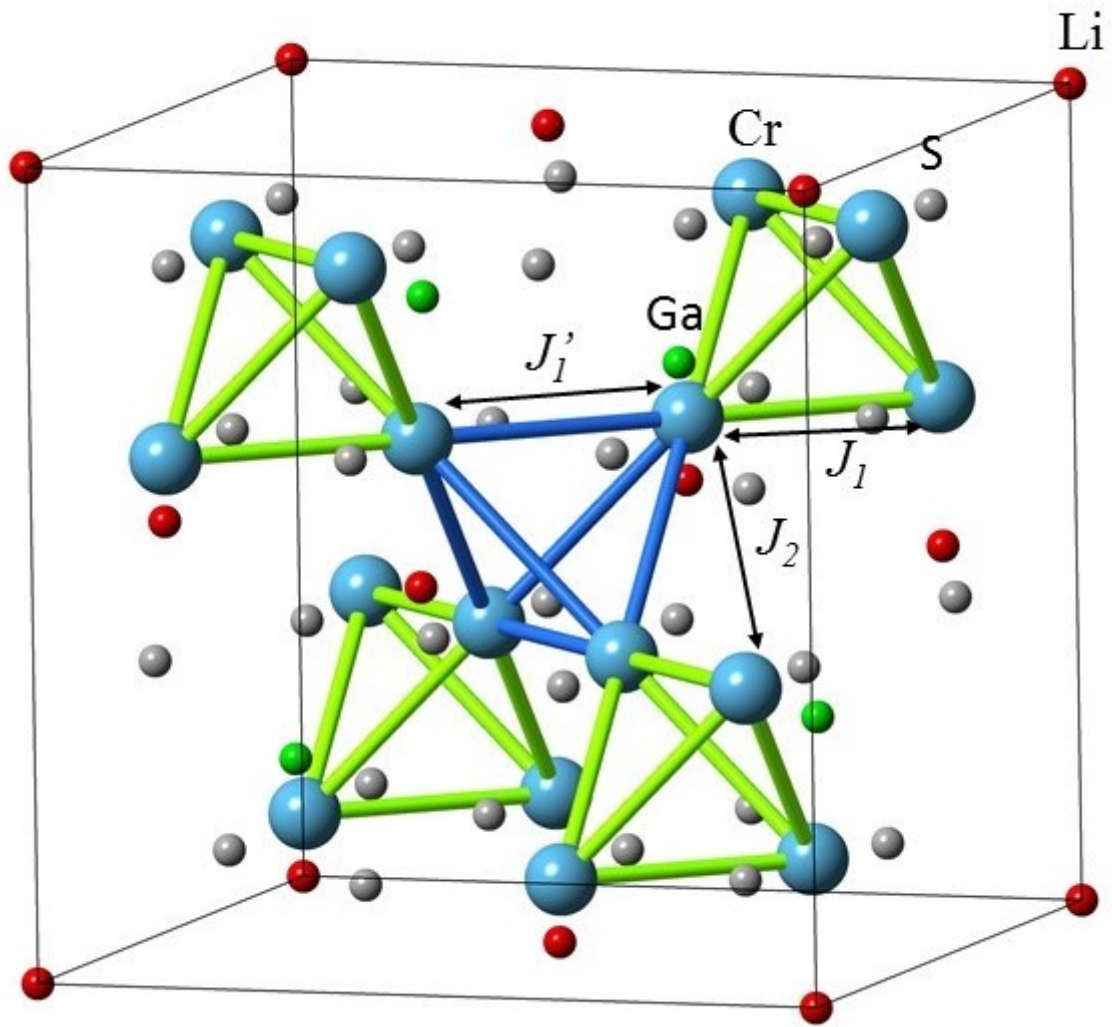


## 4.1 Introduction

Breathing pyrochlore lattices have emerged as an important structural motif for the realization of novel quantum phases of matter [1, 33, 38, 42]. A breathing pyrochlore lattice is an alteration of the pyrochlore lattice consisting of alternating large and small tetrahedra (see Fig. 4.1). The modulation of the size can result in dramatically different exchange interactions connecting the magnetic atoms within the differently sized tetrahedra. Recently studied examples include  $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$  [34, 38, 40, 78] and  $\text{Li}(\text{In},\text{Ga})$  [33]. These materials exist in the opposite limits of the breathing pyrochlore lattice:  $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$  is in the noninteracting limit where the individual tetrahedra are uncoupled, whereas in  $\text{Li}(\text{In},\text{Ga})\text{Cr}_4\text{O}_8$  the individual tetrahedra are strongly coupled. The investigation of model systems between these limits is a current challenge.

One starting point for the realization of a breathing pyrochlore lattice is the chromium containing chalcogenide compounds,  $\text{ACr}_2\text{X}_4$  ( $\text{X} = \text{S}, \text{Se}$ ). These materials crystallize into a spinel structure with centrosymmetric space group  $Fd\bar{3}m$  and provide a remarkably versatile playground to study the physics emerging from frustrated magnetic interactions [24, 28, 79]. In these materials, the metal ions  $\text{A}^{2+}$  occupy the tetrahedral sites forming a diamond like structure and the magnetic ions  $\text{Cr}^{3+}$  occupy the octahedral sites forming a pyrochlore lattice with corner sharing  $\text{Cr}_4$  tetrahedra. These materials are often multifunctional and exhibit interesting phenomena such as multiferrocity [12], large magnetocapacitance/magnetoresistance [19], negative thermal expansion [20], helical magnetism [3], strong magnetoelastic coupling [80, 81], spin nematics [3], and spin/orbital glasses [22, 82, 83]. This rich physical behavior is derived from the interplay of spin, charge and lattice degrees of freedom [12].

Of particular interest here are Cr-based spinels with a non-magnetic A-site cation, which often exhibit strong magnetoelastic effects [20, 80, 81, 84]. For example, the source of structural instability in chalcogenide spinels such as  $\text{ZnCr}_2\text{S}_4$  [80] and  $\text{ZnCr}_2\text{Se}_4$  [20] has been identified as an effect of competing ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions due to the presence of strong bond frustration. Additionally, in  $\text{CdCr}_2\text{O}_4$  [85], and  $\text{ZnCr}_2\text{Se}_4$  [20], the presence of strong magnetoelastic coupling drives a region of negative thermal expansion (NTE). Hence, one of the motivations of this paper is to determine if similar physics is present



**Figure 4.1:** Crystal structure of  $\text{LiGaCr}_4\text{S}_8$  depicting the breathing pyrochlore Cr sublattice. The exchange interactions within the small and large tetrahedra are labeled  $J_1$  and  $J_1'$  respectively.  $J_2$  denotes the next nearest neighbor exchange interaction.

in structurally-related quaternary spinels that also possess a breathing pyrochlore lattice of the magnetic species.

A breathing pyrochlore lattice can be realized through substitution of inequivalent cations on the A-site of the aforementioned family of ternary spinels. This path has been recently explored in Cr-spinel oxides,  $\text{ACr}_2\text{O}_4$ , by substituting two inequivalent metal ions with different oxidation states such as  $\text{Li}^+$  and  $\text{Ga}^{3+}/\text{In}^{3+}$  [33, 86]. When the substituted cations are ordered the resulting breathing pyrochlore lattice is described by non-centrosymmetric space group  $F\bar{4}3m$ . For example, in  $\text{LiGaCr}_4\text{O}_8$  the cations  $\text{Li}^+$  and  $\text{Ga}^{3+}$  alternatively occupy the A-sites of the  $\text{ACr}_2\text{O}_4$  spinel structure and exert an unequal local chemical pressure on the  $\text{Cr}_4$  tetrahedra [33]. Thus, a breathing pyrochlore lattice forms by the arrangement of larger and smaller  $\text{Cr}_4$  tetrahedra in a corner sharing network. Oxide breathing pyrochlores have been reported to order antiferromagnetically at low temperature with complex magnetostructural order [33, 46] and multistage symmetry breaking [86]. Related S-based materials including  $\text{LiGaCr}_4\text{S}_8$  were studied by H.L. Pinch et.al [44] who reported that they order antiferromagnetically with Neel temperature between 6 K and 31 K, yet many of the basic physical properties remain unknown. Recently, additional studies of  $\text{LiInCr}_4\text{S}_8$ ,  $\text{LiGaCr}_4\text{S}_8$  and  $\text{CuInCr}_4\text{S}_8$  have been reported [37] further demonstrating the rich physics of breathing pyrochlore lattice systems.

In this chapter, we study the chalcogenide spinel  $\text{LiGaCr}_4\text{S}_8$ , where the A site of spinel structure is occupied by the two metal ions  $\text{Li}^+$  and  $\text{Ga}^{3+}$ . As in the oxide-based spinel  $\text{LiGaCr}_4\text{O}_8$ , the metal atoms Li and Ga are ordered and occupy the tetrahedral sites alternately with a diamond like arrangement [44] and Cr ions form a breathing pyrochlore lattice as shown in Fig. 4.1. The presence of two unequally sized  $\text{Cr}_4$  tetrahedra yields a distinct nearest neighbor (NN) exchange interaction for each (here denoted by  $J_1$  and  $J'_1$  to allow for comparison to normal spinel counterparts). One means of understanding the degree to which the different sizes of the tetrahedra may modify the physical behavior is through the breathing ratio ( $B_r$ ), defined as the ratio of the Cr-Cr bond length within the larger and smaller  $\text{Cr}_4$  tetrahedra,  $B_r = d'/d \geq 1$ . For the A-site ordered quaternary spinels, the breathing ratio can be determined from the  $x$ -coordinate of the  $\text{Cr}^{3+}$  ion via  $B_r = |(2x - 1)/(2x - 0.5)|$ . Importantly, this shows that the breathing ratio is independent of the lattice parameter.

We use neutron and X-ray diffraction to study the structural properties of polycrystalline  $\text{LiGaCr}_4\text{S}_8$ . We find a  $B_r$  of 1.077(2) which represents a modest increase over the value of 1.035(1) for  $\text{LiGaCr}_4\text{O}_8$  [33]. Below 111(4) K, we find a region of NTE that extends down to 10 K. This behavior is similar to that observed in the spinel [20], however, a similar region of NTE has not been observed in related oxide-based breathing pyrochlores such as  $\text{LiGaCr}_4\text{O}_8$ . The changes in lattice expansion are accompanied by the departure from Curie-Weiss behavior of the magnetic susceptibility and a peak in both the magnetic susceptibility and specific heat at 10.5(5) K. This indicates that magnetic and lattice degrees of freedom are strongly coupled in  $\text{LiGaCr}_4\text{S}_8$ . Additionally, first principles calculations presented here also find strong coupling between magnetism and the lattice.

## 4.2 Experimental Details

Polycrystalline samples of  $\text{LiGaCr}_4\text{S}_8$  were synthesized by solid state reaction. Stoichiometric amounts of Ga (99.999%),  $\text{Li}_2\text{S}$  (99.9%), Cr (99.95%), S (99.9995%), purchased from Alfa Aesar, were ground together inside a glove box and then pressed into a 0.5 inch diameter pellet. The resulting pellet was heated to 1175 K for 3 days. This process was repeated until laboratory X-ray diffraction patterns indicated a phase pure sample.

Synchrotron X-ray diffraction measurements were performed at 11-BM the Advanced Photon Source (APS) at Argonne National Laboratory (ANL) using X-rays of wavelength  $\lambda = 0.4146 \text{ \AA}$ . For the measurements, a finely ground polycrystalline sample was packed inside a Kapton tube with a diameter of 0.8 mm, which was mounted on the cold finger of an Oxford helium cryostat. The sample was spun at the frequency of 50 Hz to ensure proper powder randomization. The Rietveld refinement packages FullProf [87] and GSAS/EXPGui [88] were used to refine the crystal structure against the X-ray diffraction data.

Neutron diffraction data were collected using the HB-2A powder diffractometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory (ORNL). Measurements were made at HB-2A in the temperature range 1.5 K to 300 K using incident neutrons with wavelength  $\lambda = 1.5396 \text{ \AA}$ . Additional neutron diffraction measurements were made with POWGEN at the Spallation Neutron Source, ORNL using a band of incident neutrons with  $0.167 \leq \lambda \leq 1.233 \text{ \AA}$ . The Rietveld

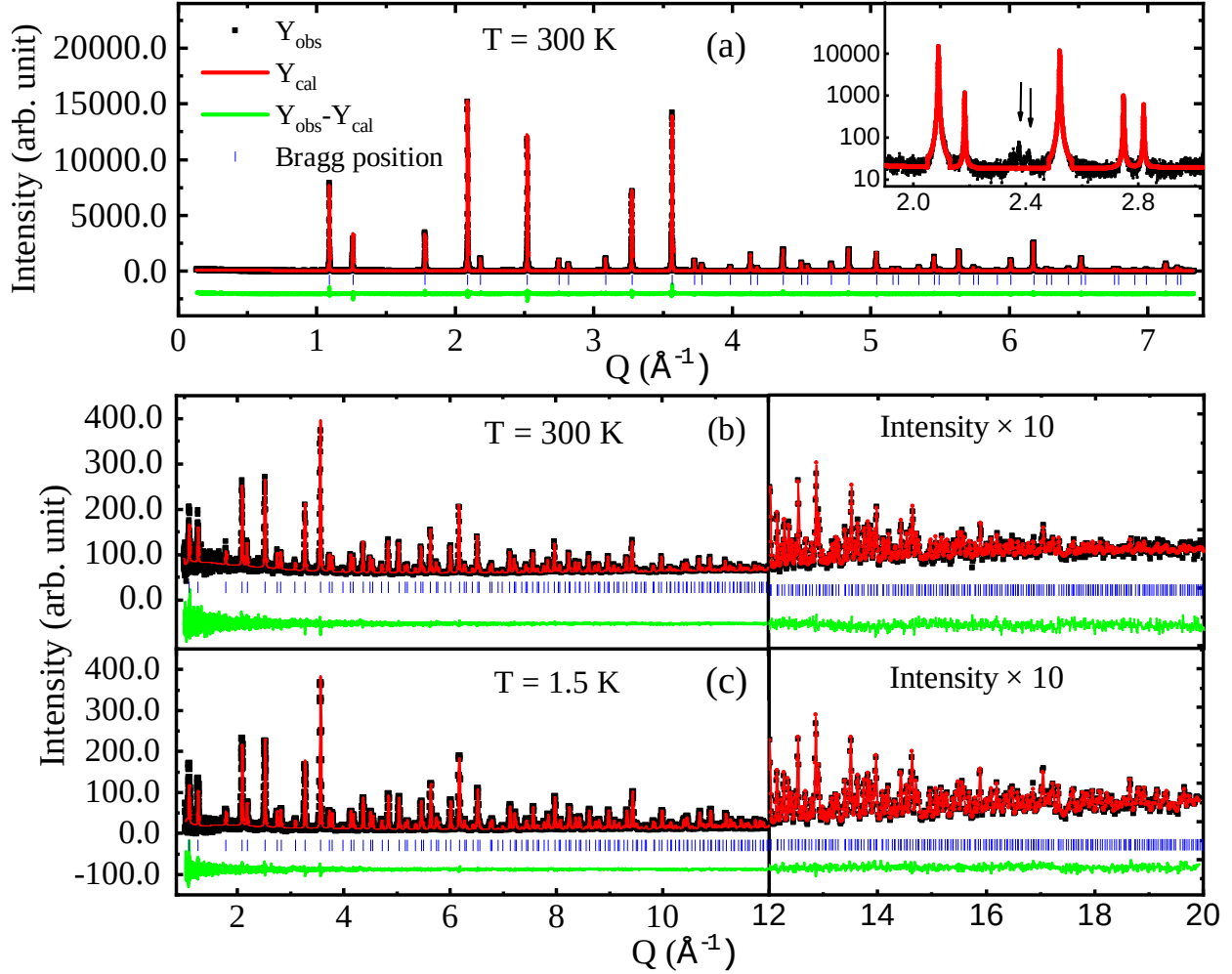
refinement packages FullProf [87] and GSAS/EXPGui [88] were used to refine the crystal structure against the neutron diffraction data.

Field cooled (FC) and zero field cooled (ZFC) dc susceptibility measurements with applied magnetic fields  $H$  ranging from  $\mu_0 H$  of 0.01 to 5 T in the temperature range 2 K to 300 K were carried out using a Quantum Design magnetic property measurement system (MPMS). AC magnetic susceptibility measurements were performed in a Quantum Design physical property measurement system (PPMS). These measurements were performed with a static field of  $H_{dc} = 0$ , using an ac amplitude of  $H_{ac} = 5$  Oe. The frequency  $f$  dependence of the in-phase component  $\chi'$  was examined by performing measurements as a function of  $f$ . Data were collected upon cooling from 30 to 2 K. Heat capacity was measured using a Quantum Design PPMS in the temperature range 2 K to 300 K. Measurement of the electrical resistivity was carried out on a sintered sample with a Quantum Design PPMS using the four-point measurement technique with gold wires attached to the sample using silver paint.

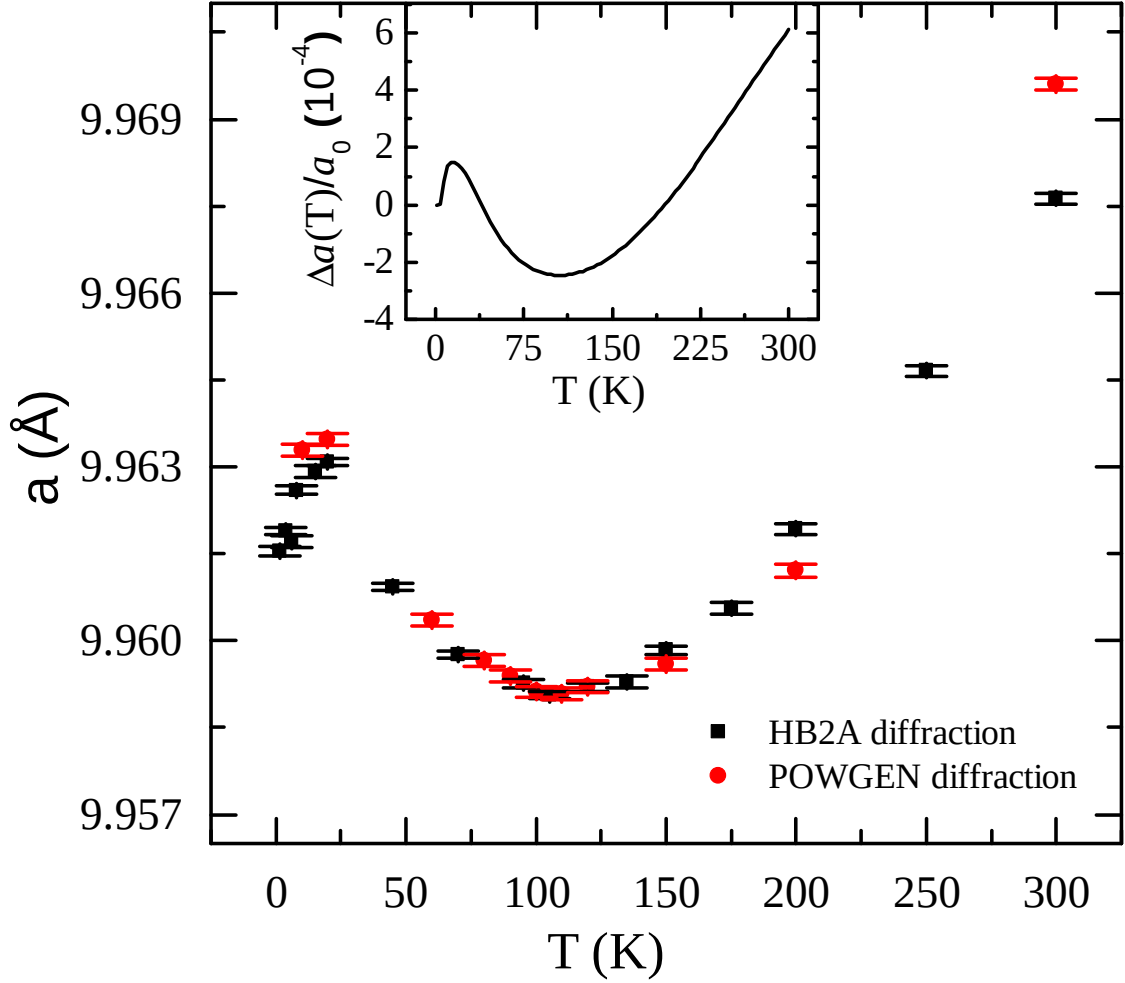
## 4.3 Results

### 4.3.1 Neutron Diffraction and X-ray Diffraction

We begin with a discussion of the crystallography and lattice behavior of  $\text{LiGaCr}_4\text{S}_8$ . Neutron and synchrotron X-ray diffraction patterns are shown in Fig. 4.2. Unlike the diffraction pattern corresponding to a normal spinel structure with space group  $Fd\bar{3}m$  (No. 227), additional reflections, such as 002 are observed as expected for space group  $F\bar{4}3m$  (No. 216) [44]. The space group  $F\bar{4}3m$  is a subgroup of space group  $Fd\bar{3}m$ . The number of symmetry operations are reduced by half, including the loss of inversion symmetry in  $F\bar{4}3m$  compared to the parent space group. The diffraction patterns are consistent with those of the oxides of related breathing pyrochlore lattice materials  $\text{LiGaCr}_4\text{O}_8$  and  $\text{LiInCr}_4\text{O}_8$  [33] and studies of  $\text{LiGaCr}_4\text{S}_8$  in Ref. [37]. We find only weak impurity phases:  $\text{Cr}_3\text{S}_4$  and an even less significant unidentified phase (see Inset of Fig. 4.2(a)). We estimate the impurity phase fraction to be less than one percent of the main phase based upon taking ratios of Bragg peak intensities. On the other hand, Ref. [37] finds impurity phases of less than a few percent of  $\text{Cr}_2\text{S}_3$  and an additional unknown phase.



**Figure 4.2:** (a) Synchrotron X-ray diffraction data with  $\lambda = 0.4146$   $\text{\AA}$  collected at 300 K. The inset displays a limited region of reciprocal space so that the presence of a weak  $\text{Cr}_3\text{S}_4$  can be compared to the intensity of the main phase. The impurity phase is indicated by arrows. The axis labels are the same as the main panel, but note the logarithmic y-axis scale. Neutron diffraction data collected with POWGEN with  $0.167 \leq \lambda \leq 1.233$   $\text{\AA}$  at 300 K and 1.5 K are shown in panel (b) and (c) respectively. The Rietveld refinement of the structural model described in the text with space group  $F\bar{4}3m$  is indicated by the solid line through the data.



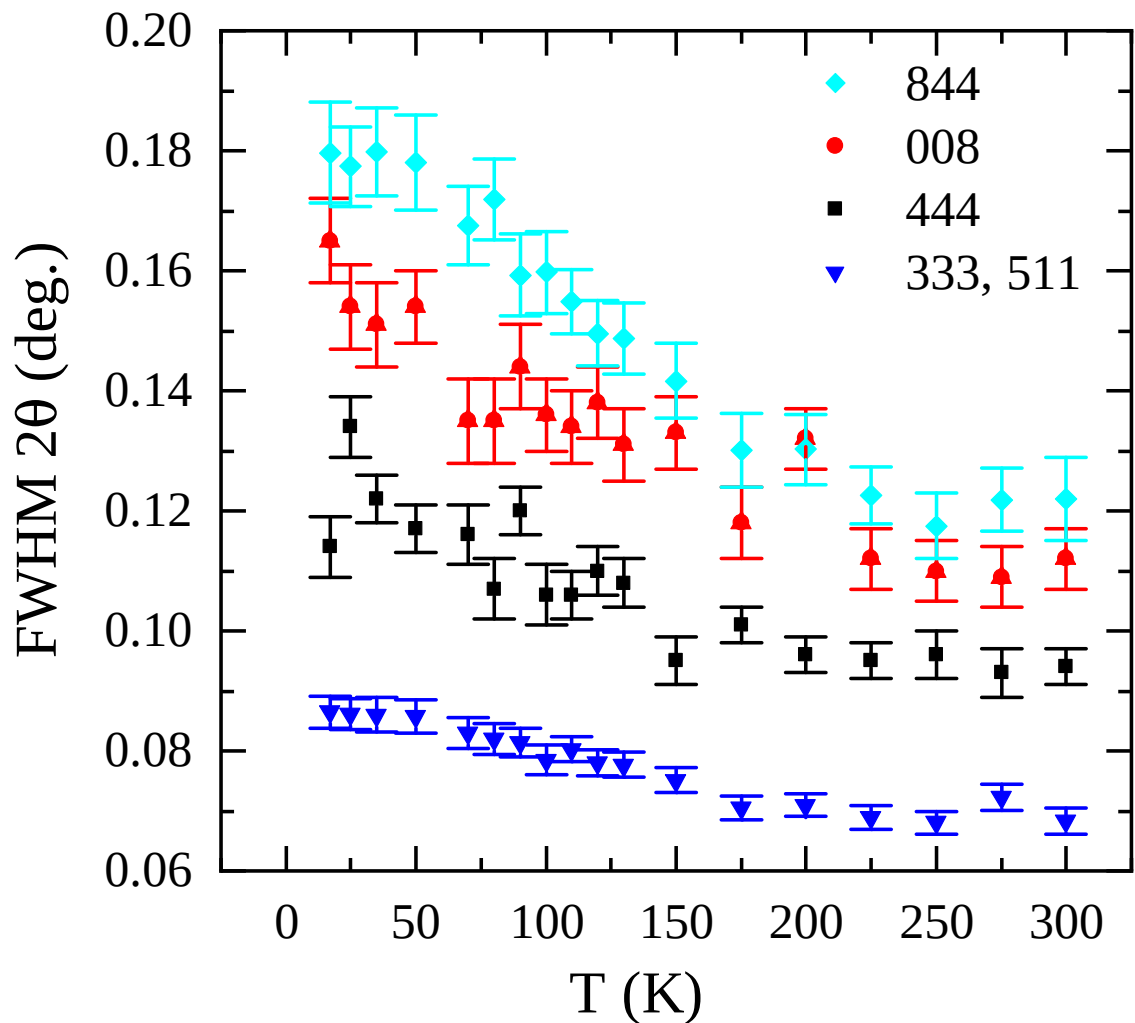
**Figure 4.3:** Lattice parameter of  $\text{LiGaCr}_4\text{S}_8$  as a function of temperature obtained by neutron diffraction. Negative thermal expansion is observed below 111(4) K. The inset shows the estimated temperature dependence of  $\Delta a(T)/a_0$  determined as explained in the text.

Rietveld refinement of the structural model against the X-ray data, as well as the neutron diffraction data discussed below, confirms that the metal ions  $\text{Li}^+$  and  $\text{Ga}^{3+}$  occupy the A-sites of the spinel structure with occupancies close to the ideal values of equivalent sites in the standard spinel structure ( $\text{Fd}\bar{3}\text{m}$ ). Initial refinements assumed these 4a and 4d sites were fully occupied by Li and Ga, respectively. Better agreement with the data was obtained by allowing Li and Ga site interchange, and this approach was informed by the complementary nature of neutron and x-ray diffraction data. The best refinements indicate the Ga site is fully occupied by Ga and in final refinements the occupancy of this site was fixed. The Li site was found to have some Ga, however, and refinements suggest a  $\approx 5\%$  deficiency of Li in the samples studied here. The refined composition of  $\text{Li}_{0.956}\text{Ga}_{1.043}\text{Cr}_4\text{S}_8$  is obtained from a combined refinement of both the neutron and synchrotron x-ray data, and the additional refinement results are presented in Table 4.1.

Initial x-ray diffraction data indicated a region of NTE. To examine this behavior over a broader temperature range, neutron powder diffraction measurements were performed and the lattice parameter as a function of temperature was extracted. The variation of lattice parameter with temperature is shown in Fig. 4.3. Cooling from room temperature, the lattice parameter decreases until 111(4) K. Further cooling results in lattice expansion (NTE) until  $\approx 10$  K where the NTE terminates. Parameters obtained by a combined refinement of the structural model to the synchrotron X-ray and POWGEN neutron diffraction data are shown in Table 4.1 (a). The refined parameters at 10 K obtained from POWGEN neutron diffraction are also shown in Table 4.1 (b). No direct evidence for a distortion from cubic symmetry was detected in any of our diffraction data, including the high-resolution synchrotron data. However, below  $\sim 200$  K a temperature-dependent broadening of the Bragg peaks was observed in the x-ray diffraction data upon cooling (see Fig.4.4), likely indicating the development of microstrain.

This behavior can be compared to other NTE materials such as  $\text{ZnCr}_2\text{Se}_4$  [20] by comparing the relative change in lattice parameter as a function of temperature,  $\Delta a(T)/a_0$ . Here  $\Delta a(T)/a_0$  of  $\text{LiGaCr}_4\text{S}_8$  has been estimated using a cubic spline interpolation of the data. For this estimation, the lattice parameter at 1.5 K is taken as the standard initial value,  $a_0$ .  $\Delta a(T)/a_0$  increases up to  $\sim 12$  K. Fitting the downturn and upturn of data to the Gaussian function reveals that  $\Delta a(T)/a_0$  exhibits NTE in the temperature range 12(2) - 111(4) K.





**Figure 4.4:** Temperature dependence of peak width (Full Width Half Maximum of a standard Lorentzian function) of selected diffraction peaks determined from the laboratory X-ray diffraction data. All peaks broaden with cooling at low temperature.

**Table 4.1:** Parameters of LiGaCr<sub>4</sub>S<sub>8</sub> obtained from combined refinement of the structural model to the synchrotron X-ray and POWGEN neutron diffraction data.

$$T = 300 \text{ K}, R_p = 6.9 \%, R_{wp} = 4.2 \%$$

$$\chi^2 = 1.4, a = 9.9696(1) \text{ \AA}$$

| atom                 | $x = y = z$ | $B_d (\text{\AA}^2)$ | $B_{nd} (\text{\AA}^2)$ | occupancy |
|----------------------|-------------|----------------------|-------------------------|-----------|
| S <sub>1</sub> (16e) | 0.1342(1)   | 0.69(2)              | 0.08(2)                 | 1         |
| S <sub>2</sub> (16e) | 0.616(1)    | 0.61(2)              | -0.06(2)                | 1         |
| Cr(16e)              | 0.370(1)    | 0.60(1)              | 0.00(2)                 | 1         |
| Ga <sub>1</sub> (4d) | 0.75        | 0.63(1)              | 0                       | 1         |
| Li(4a)               | 0           | 1.24(7)              | 0                       | 0.953(1)  |
| Ga <sub>2</sub> (4a) | 0           | 1.24(7)              | 0                       | 0.046(1)  |

Refined parameters of LiGaCr<sub>4</sub>S<sub>8</sub> obtained from  
POWGEN neutron diffraction.

$$T = 10 \text{ K}, R_p = 5.8 \%, R_{wp} = 1.9 \%$$

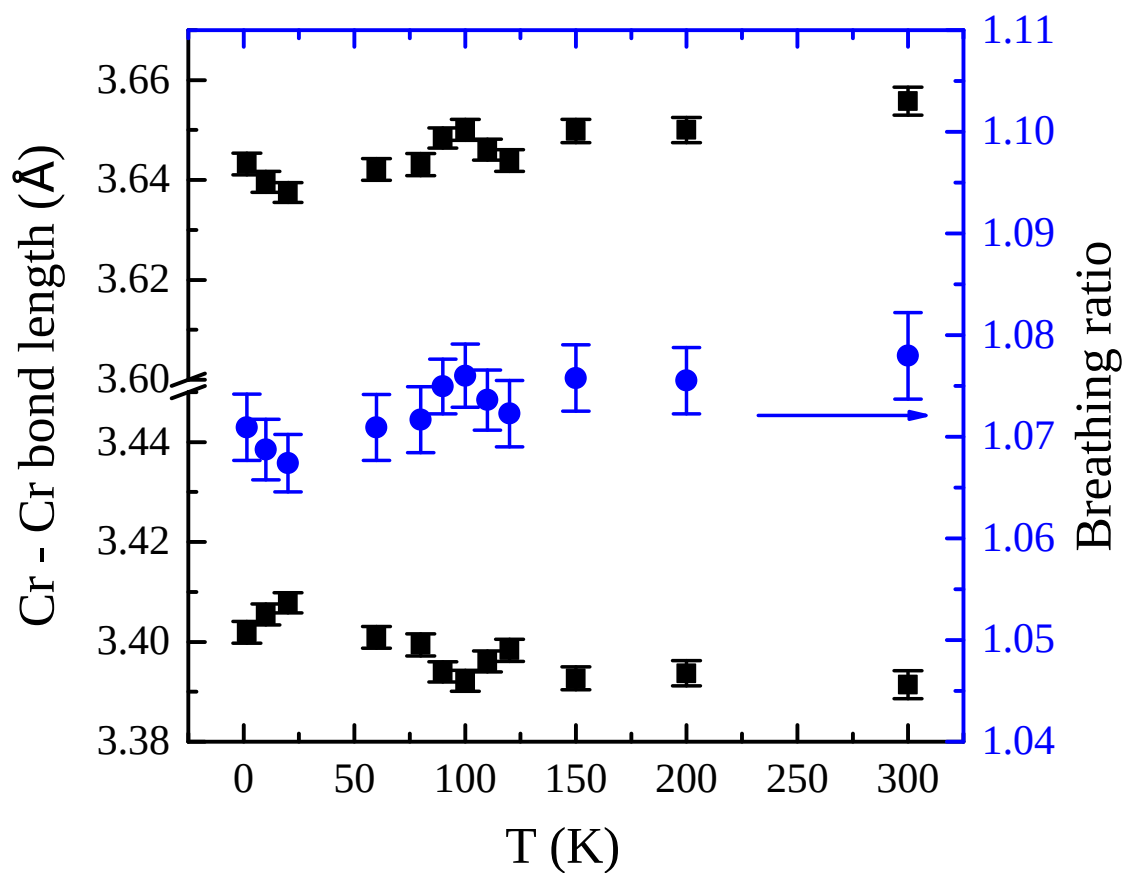
$$\chi^2 = 1.6, a = 9.9633(3) \text{ \AA}$$

| atom                 | $x = y = z$ | $B_d (\text{\AA}^2)$ | $B_{nd} (\text{\AA}^2)$ | occupancy |
|----------------------|-------------|----------------------|-------------------------|-----------|
| S <sub>1</sub> (16e) | 0.1345(1)   | 0.33(2)              | 0.02(1)                 | 1         |
| S <sub>2</sub> (16e) | 0.6167(1)   | 0.25(1)              | -0.02(1)                | 1         |
| Cr(16e)              | 0.3708(1)   | 0.29(1)              | 0.04(1)                 | 1         |
| Ga <sub>1</sub> (4d) | 0.75        | 0.23(2)              | 0                       | 1         |
| Li(4a)               | 0           | 1.10(8)              | 0                       | 0.953     |
| Ga <sub>2</sub> (4a) | 0           | 1.10(8)              | 0                       | 0.046     |

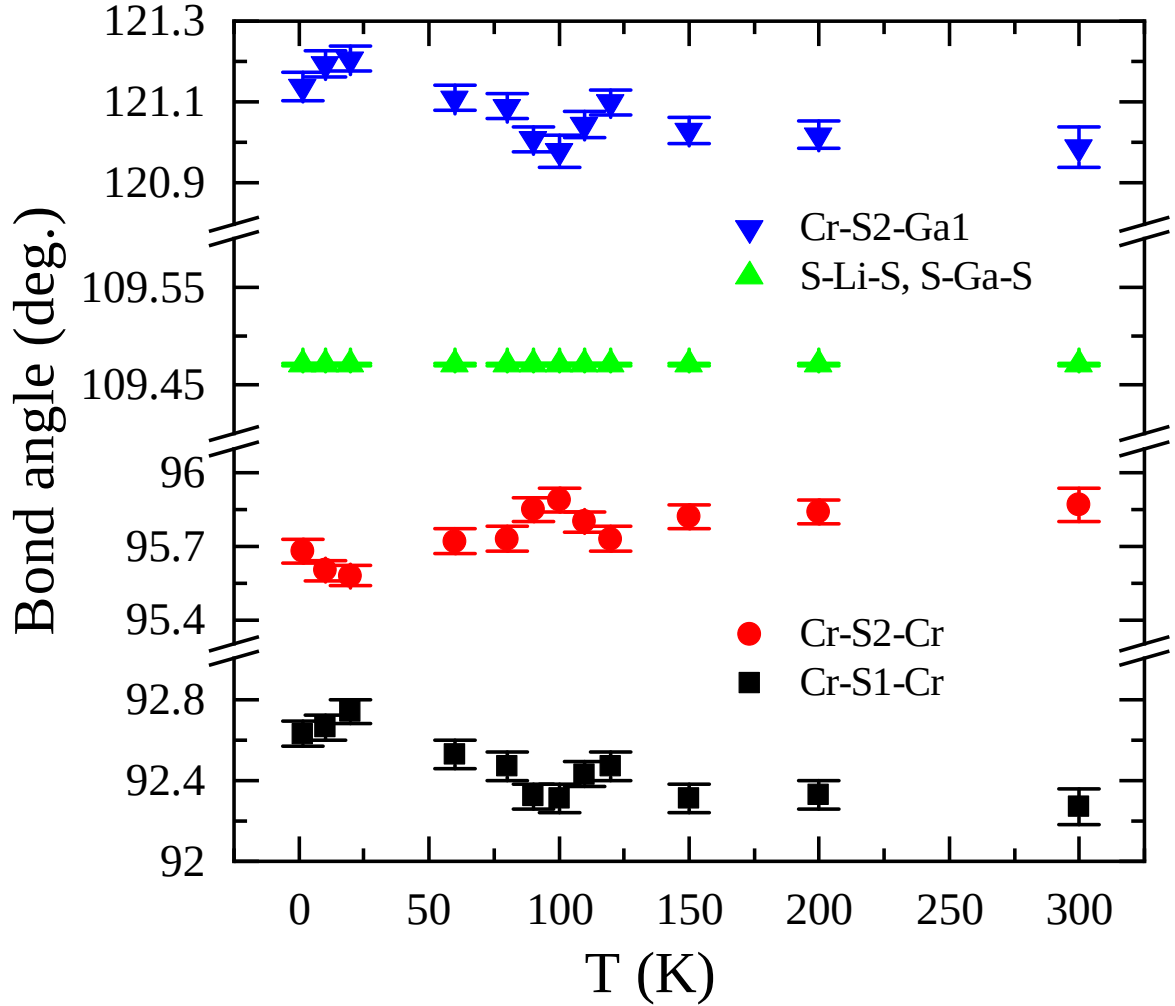
$B_d$  = Anisotropic diagonal thermal parameter  
 $B_{nd}$  = Anisotropic non-diagonal thermal parameter

The onset of NTE is reflected in the internal degrees of freedom of the unit cell. The effect is evident in bond lengths and bond angles involving Cr. The two Cr-Cr bond lengths show a weak anomaly near the onset of negative thermal expansion (Fig. 4.5). Changes in the two Cr-S-Cr bond angles are also observed (Fig. 4.6). Both the Cr-Cr distances and Cr-S-Cr bond angles are expected to play an important role in the magnetic exchange interactions in LiGaCr<sub>4</sub>S<sub>8</sub> and the observations of changes in these quantities appear correlated with the changes in magnetic behavior that are discussed in following sections.

As described in the Introduction, the difference between the two Cr-Cr bond lengths is driven by the inequivalent ionic radii (59 pm and 47 pm [89]) of the Li<sup>1+</sup> and Ga<sup>3+</sup> ions respectively.



**Figure 4.5:** Temperature dependent Cr-Cr bond lengths in the small and large Cr<sub>4</sub>-tetrahedra (filled squares, left scale) and  $B_r$  (filled circles, right scale). These bond lengths and  $B_r$ s are obtained from the neutron diffraction data collected with POWGEN.



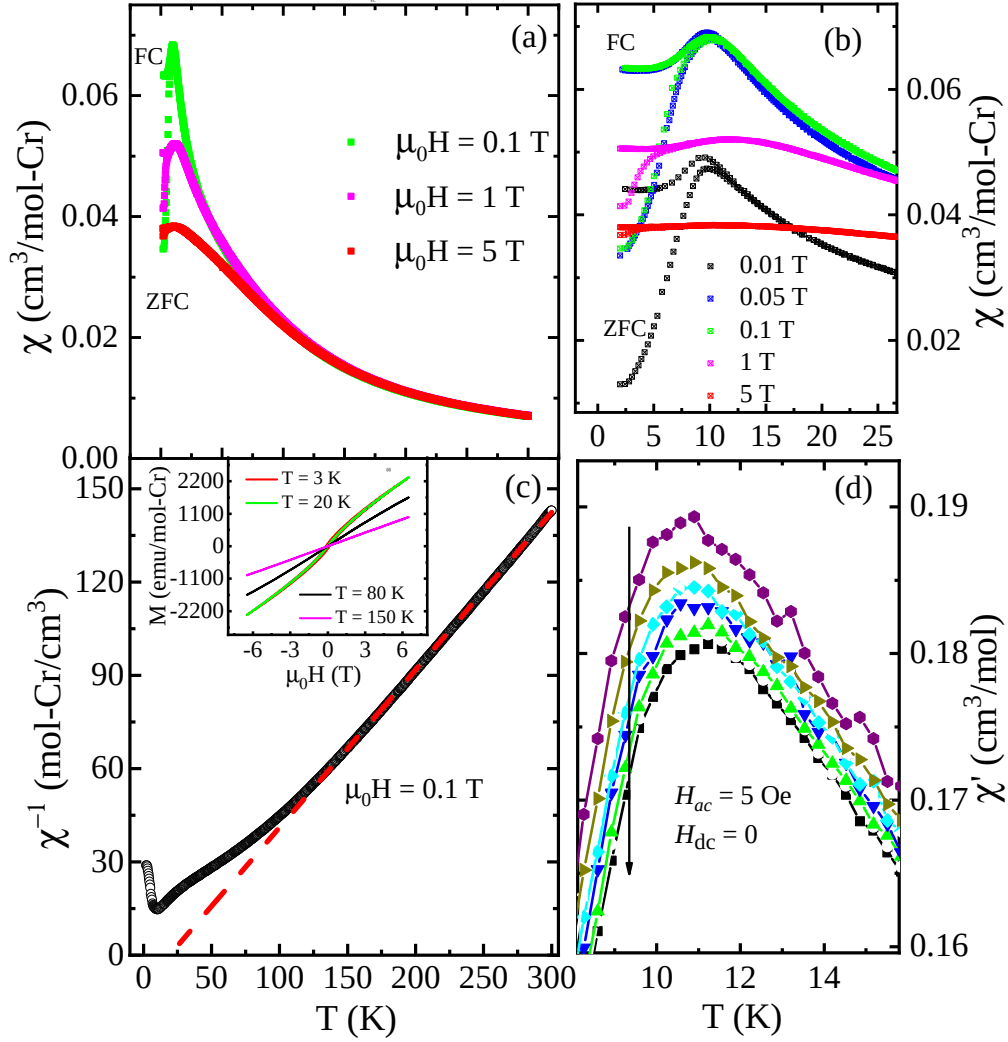
**Figure 4.6:** Variation of selected bond angles with temperature in  $\text{LiGaCr}_4\text{S}_8$ . Cr-S-Cr bonds are close to  $90^\circ$  and are responsible for the NN superexchange interaction. S-Li-S and S-Ga-S bonds are insensitive to the change in temperature whereas other bonds show a weak anomaly with the onset of NTE.

This difference in bond lengths is quantified by  $B_r$ . At 300 K the larger and smaller Cr-Cr bond lengths  $d'$  and  $d$  extracted from the neutron diffraction data are found to be 3.655(2) Å and 3.394(2) Å yielding a breathing ratio  $B_r = 1.077(2)$ . The value of  $B_r$  as a function of temperature is shown in Fig. 4.5. The value  $B_r$  in LiGaCr<sub>4</sub>S<sub>8</sub> is somewhat larger than the values of 1.035(1) and 1.051(1) for LiGaCr<sub>4</sub>O<sub>8</sub> and CuInCr<sub>4</sub>O<sub>8</sub> respectively [33]. However, the breathing ratio is considerably less than in Ba<sub>3</sub>Yb<sub>2</sub>Zn<sub>5</sub>O<sub>11</sub>, where  $B_r=1.90(2)$  is observed [40]. The value of  $B_r$  and, the thermodynamic measurements presented in the following sections, places LiGaCr<sub>4</sub>S<sub>8</sub> in the interacting limit of the breathing pyrochlore lattice.

### 4.3.2 Magnetic Properties

To study the magnetic properties of LiGaCr<sub>4</sub>S<sub>8</sub>, temperature-dependent magnetization  $M$  measurements were performed under applied fields  $\mu_o H$  ranging from 0.01 to 5 T, and the results are summarized in Fig. 4.7. A cusp in the susceptibility  $\chi = M/H$  is evident at 10.5(5) K (Fig. 4.7 (a)), indicating a magnetic transition. The zero field cooled and field cooled curves bifurcate below the cusp, and the temperature where bifurcation ceases is inversely proportional to applied field (Fig. 4.7(b)). This behavior is commonly observed in systems with glassy spin dynamics, and such spin freezing transitions are often observed in the spinel family due to the strong frustration and competing interactions. The weak hysteresis observed in the field-dependence of the magnetization is also consistent with glassy-dynamics below  $\approx 10$  K (inset, Fig. 4.7(c)). To verify that the cusp near 10 K is associated with a transition involving glassy spin dynamics, we performed a time-dependent measurement below 10 K and observed that the remanent moment does indeed decrease with increasing time. In addition, we have performed ac susceptibility measurements which show a weak frequency dependence of the peak in the in-phase part of the susceptibility,  $\chi'$  (see Fig. 4.7(d)). Thus, the cusp in  $\chi$  near 10 K is likely associated with some type of spin freezing transition, the nature of which is still under investigation.

From 150 to 300 K,  $1/\chi$  is linear in  $T$  (Fig. 4.7(c)) and thus the Curie-Weiss law provides an excellent description of the data. However, at temperatures below 125 K, the susceptibility does not increase as fast as expected from Curie-Weiss behavior, and this may reflect the increasing



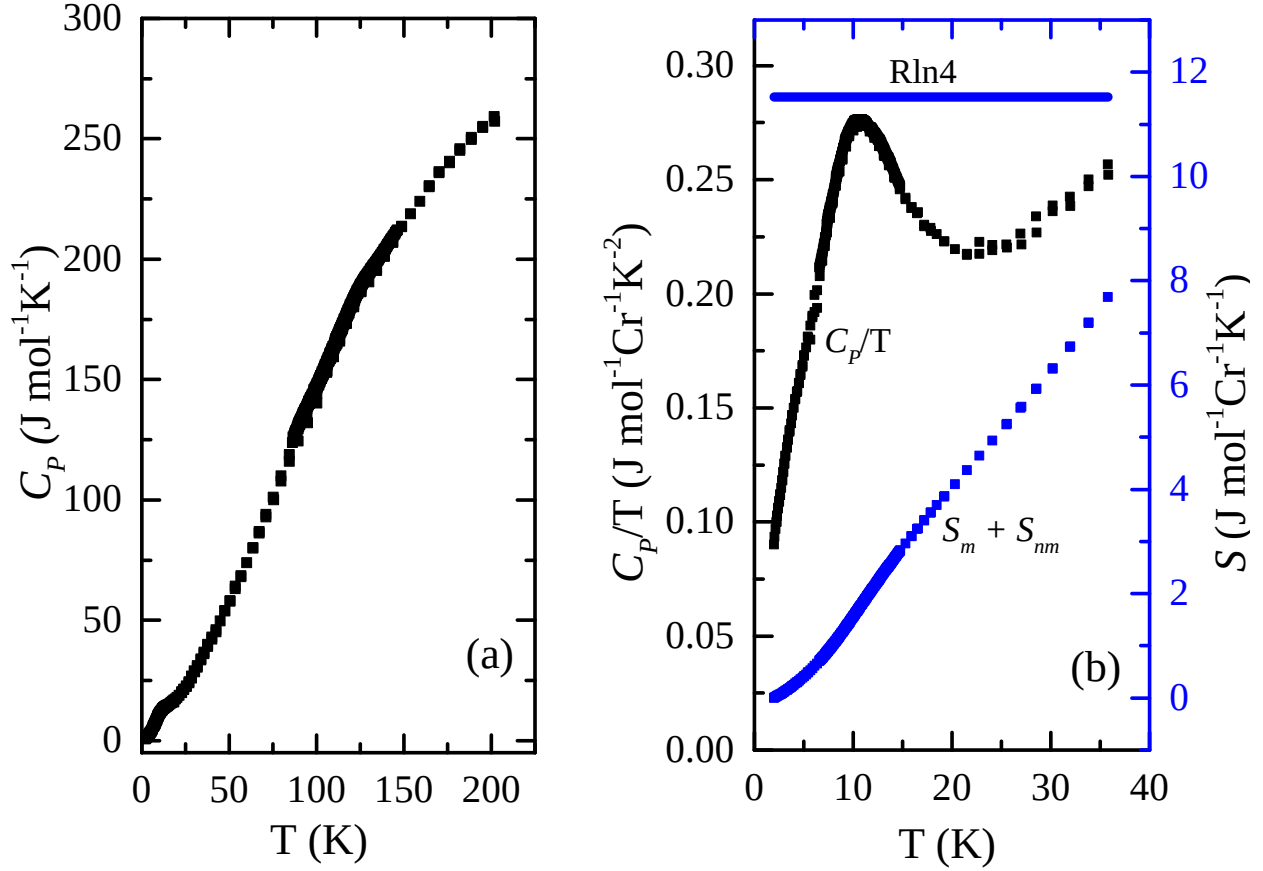
**Figure 4.7:** Magnetic susceptibility measurements of LiGaCr<sub>4</sub>S<sub>8</sub>. (a, b) Show the temperature dependent dc susceptibility,  $\chi$  and (c) shows the temperature dependent inverse dc susceptibility,  $1/\chi$  of LiGaCr<sub>4</sub>S<sub>8</sub>. (d) Displays the in-phase part of the ac susceptibility,  $\chi'$  around the magnetic transition, measured with  $H_{ac} = 5$  Oe with frequencies 29 Hz, 127 Hz, 1129 Hz, 2336 Hz, 4832 Hz and 10000 Hz. The arrow in (d) indicates the direction of increasing applied frequency. The inset of (c) displays  $M(H)$  loops measured at selected temperatures. A peak in the susceptibility occurs at 10.5(5) K and deviation from Curie-Weiss behavior is observed below 110 K. Small shift in the peak of  $\chi'$  towards higher temperature is noticed with the increase in frequency. Weak hysteresis in the  $M$  vs.  $H$  data is observed at 3 K.

importance of antiferromagnetic correlations upon cooling. Importantly, the departure from Curie-Weiss behavior appears to coincide with the onset of NTE. Fitting the data above 150 K to the Curie-Weiss law,  $\chi = C/(T - \Theta_{CW})$ , produces a Curie constant  $C$  that yields an effective moment of  $\mu_{eff} = 3.96(1) \mu_B/\text{Cr}$ , and a Weiss Temperature  $\Theta_{CW} = 19.5(1)$  K. The value of  $\mu_{eff}$  is slightly larger than the theoretical value of  $3.86 \mu_B$  for  $S = 3/2$ . The positive  $\Theta_{CW}$  indicates ferromagnetic correlations dominate in the high- $T$  regime. We note that including a diamagnetic contribution in the fitting procedure still results in a positive  $\Theta_{CW}$  of  $\sim 10$  K. In their studies of  $\text{LiGaCr}_4\text{S}_8$ , Ref. [37] obtained a negative  $\Theta_{CW}$  of -20 K. The reason for the difference with the results presented here is not readily apparent but may be due to different impurity levels in the samples or differing amounts of Li-deficiency. The results presented here along with the presence of the short range or glassy magnetic order below 10.5 K, indicate substantial competition between AFM and FM interactions in  $\text{LiGaCr}_4\text{S}_8$ .

### 4.3.3 Heat Capacity

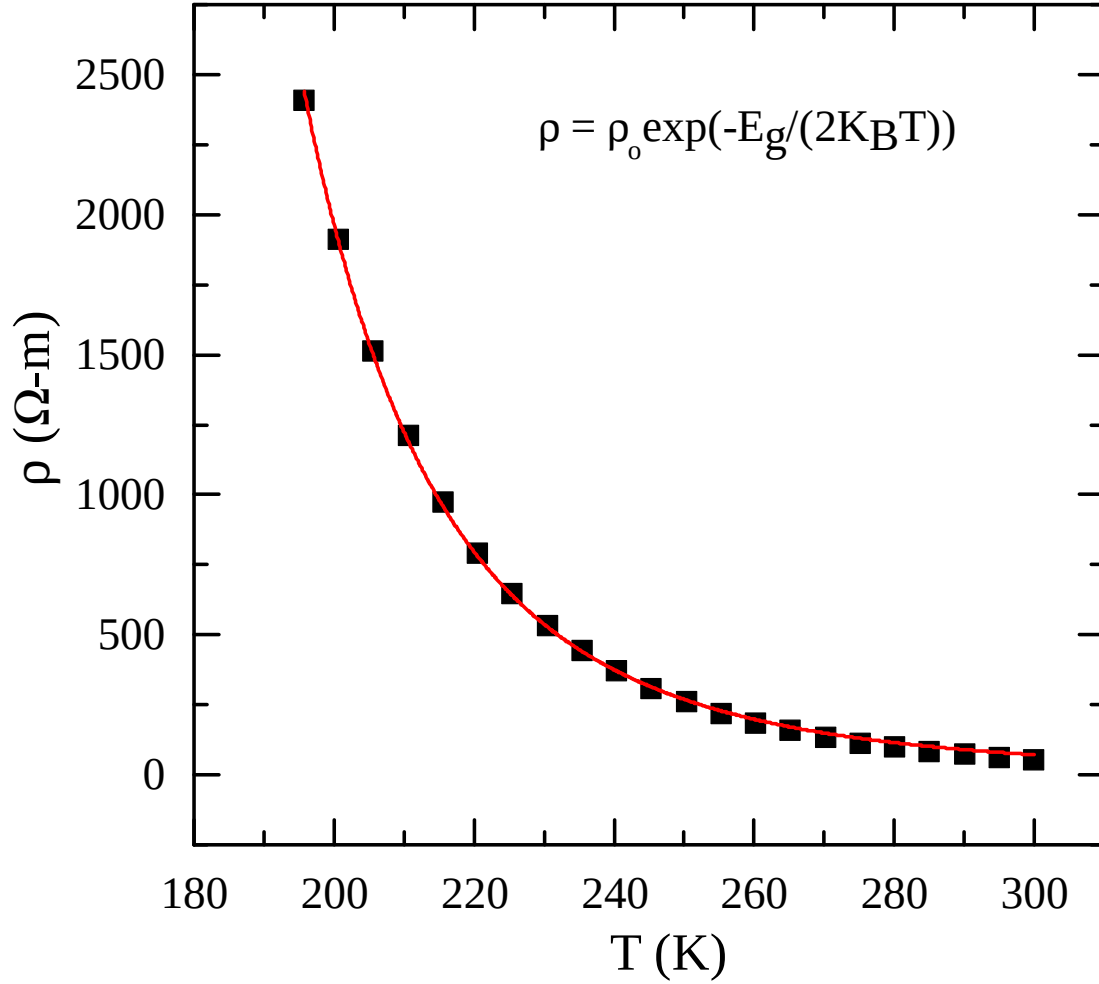
The temperature dependent specific heat,  $C_P$ , of  $\text{LiGaCr}_4\text{S}_8$  is displayed in Fig. 4.8. A broad hump in  $C_P$  occurs with a maximum near 10.9(4) K. A very weak anomaly is also observed around 120 K. While a feature is visible, and occurs near the change in thermal expansion behavior, it is too weak to provide any additional information. This observation is consistent with the inability of our synchrotron diffraction data to detect a structural transition near the onset of the negative thermal expansion.

The anomaly in the specific heat capacity that is associated with the magnetic transition at low  $T$  is best observed in a plot of  $C_P/T$  vs.  $T$  (Fig. 4.8(b)). From these data, the entropy as a function of temperature is obtained by integrating  $C_P/T dT$  (4.8(b)) starting at  $T = 2$  K. Note that this estimate of the entropy includes all contributions to  $C_P$  and represents an upper limit to the magnetic contribution to the entropy,  $S_{mag}$  (no baseline is utilized as a non-magnetic analogue is not present). In this context, it is noteworthy that the entropy determined is dramatically reduced from the value of  $R\ln(4)$  expected from a magnetic order-disorder transition involving  $S=3/2 \text{ Cr}^{3+}$ . This could be caused by the presence of residual entropy due to the glassy phase. However, a



**Figure 4.8:** Temperature dependent heat capacity,  $C_p$ , of  $\text{LiGaCr}_4\text{S}_8$  at zero magnetic field. (a) Displays the  $C_p$  from 2 to 200 K. (b) Shows  $C_p/T$  and the estimated entropy,  $S$ , at low temperatures. The theoretical value of magnetic entropy for spin 3/2 system is indicated by the horizontal line in (b). The change in slope of  $C_p$  around at 120 K and a broad hump at 10.9(4) K look coincident with the bounding temperatures of NTE.





**Figure 4.9:** Temperature dependent resistivity,  $\rho$  of  $\text{LiGaCr}_4\text{S}_8$ . The fitting function is described in the text.

substantial portion of the entropy may be lost at higher temperatures, corresponding to the likely interplay of magnetic and lattice degrees of freedom with an onset near 111 K.

#### 4.3.4 Electrical Resistivity

The electrical resistivity,  $\rho$  of  $\text{LiGaCr}_4\text{S}_8$  measured in the temperature range 195 to 300 K is shown in Fig 4.9. Below 195 K, the resistance was too large for the instruments utilized. From 300 K, the resistivity increases exponentially with decreasing temperature indicating typical semiconducting

behavior. To estimate the band gap,  $E_g$ , the equation  $\rho(T) = \rho_0 \exp(-E_g/2k_B T)$  is fitted to the resistivity data, where  $k_B$  is the Boltzmann constant. This yields  $E_g=0.37(3)$  eV.

## 4.4 First Principles Calculations - Magnetoelastic Coupling

To understand the observed behavior, first principles calculations of the structure and magnetic behavior were performed, using the all-electron planewave density functional theory (DFT) code WIEN2K [90]. The generalized gradient approximation of Perdew, Burke and Ernzerhof [91] was employed, with an  $RK_{max}$  of 7.0. Here  $RK_{max}$  is the product of the smallest muffin-tin radius (that for S) and the largest planewave expansion wavevector. We assume an ordered structure with crystallographically separate Li and Ga sites, generally consistent with the experimental refinements showing only a few percent of Li and Ga mixing on these sites.

The experimental results suggest a strong coupling of magnetism and structure in  $\text{LiGaCr}_4\text{S}_8$ , in particular with the inverse susceptibility first deviating from linear behavior at nearly the same temperature as the onset of the NTE. While we do not directly address the NTE here, these calculations also find evidence for magnetoelastic coupling.

First principles calculations were performed for two configurations: a non-magnetic configuration, and a simple ferromagnetic (FM) configuration. While the presence of chromium, the highly electronegative sulfur, and the complex geometric frustration may argue against a simple ferromagnetic ground state, for the purposes of discussing magnetoelastic coupling this structure appears to be sufficient. For both calculations, the internal coordinates were optimized, and a cubic lattice parameter of  $a = 9.9675$  Å was utilized.

The optimized FM calculation finds a Cr coordinate of 0.3791, which leads to a nearest-neighbor Cr-Cr distance of 3.408 Å, in excellent agreement (within 0.5 percent) with the experimental value of 3.390 Å. However, the optimized non-magnetic configuration finds a Cr coordinate of 0.3956, and thereby a nearest-neighbor Cr-Cr distance of just 2.86 Å, which differs from the experiment by more than 0.5 Å. This is more than an order of magnitude beyond any possible error associated with the inherent approximations in DFT. Rather, it is suggestive that even at 300 K that the magnetism is affecting and possibly determining the structure. While it has long been known that signatures of magnetism often persist well above the ordering point, a

factor of 30 here is unusual. This is likely due to the effective suppression of the ordering point by geometric and magnetic frustration, as well as the strength of the magnetic interactions involved. We find the ferromagnetic state (with a Cr moment of approximately  $3 \mu_B$ ) to fall some  $\sim 500$  meV per Cr below the non-magnetic state.

This is a relatively large energy compared with the 300 K thermal energy  $k_B T$  of just 25 meV, and speaks to the likelihood of “disordered local moments” persisting up to and even beyond room temperature. By this we mean that while long-range magnetic order is absent above the ordering temperature, the individual Cr atoms likely carry a moment of approximately  $3 \mu_B$ , but these moments are essentially randomly oriented in spatial direction, with relatively little moment direction correlation between neighboring Cr atoms. Detailed discussions of this scenario applied to iron can be found in Ref. [92]. In this context the observed anomalous structural behavior, such as the NTE, can be considered to arise from the detailed temperature dependence of the ordering energy (via competing interactions) and its interactions with the lattice.

## 4.5 Discussion

As described above, the magnetic properties of  $\text{LiGaCr}_4\text{S}_8$  are strongly reflected in the behavior of the lattice. NTE appears when the susceptibility deviates from Curie-Weiss behavior. The lattice continues to expand with decreasing temperature until the magnetic transition at 10 K after which the lattice contracts to the lowest temperatures measured (1.5 K). These observations along with the first principles calculations presented in Sec. 4.4 are compelling evidence that magnetoelastic coupling is strong in  $\text{LiGaCr}_4\text{S}_8$ . As noted above, neither the neutron diffraction data nor the synchrotron X-ray data provide direct evidence of a departure from cubic symmetry. This appears to be one of the distinctions between  $\text{LiGaCr}_4\text{S}_8$  and  $\text{LiGaCr}_4\text{O}_8$ , where two different phases either tetragonal or orthorhombic along with a cubic phase are reported below the ordering temperature of 12 K [46, 93].

The existence of NTE in magnetically frustrated Cr-spinel compounds has been explained as a consequence of magnetoelastic coupling [20, 94]. This mechanism relies on competing AFM and FM exchange interactions [80]. This situation is likely realized in  $\text{LiGaCr}_4\text{S}_8$  as the competition between antiferromagnetic and ferromagnetic exchange interactions is evident in the

magnetic properties. The bond angle for the Cr-S-Cr nearest neighbor superexchange paths are close to  $90^\circ$  (see Fig. 4.6) which can yield a ferromagnetic exchange interaction. This is in accord with the fitting of  $\chi$  with the Curie-Weiss law in the paramagnetic region from 150 to 300 K, which yields a positive  $\Theta_{CW}=19.5$  K. This indicates that ferromagnetic interactions dominate the magnetic properties at high temperature. This is another distinction between the oxide counterparts of  $\text{LiGaCr}_4\text{S}_8$  where antiferromagnetic correlations dominate at high temperature as evidenced by the reported  $\Theta_{CW}$  values of -658.8 K and -331.9 K for  $\text{LiGaCr}_4\text{O}_8$  and  $\text{LiInCr}_4\text{O}_8$  respectively [33].

At lower temperatures, antiferromagnetic correlations become important in  $\text{LiGaCr}_4\text{S}_8$ . In particular, the magnetic phase transition at  $\sim 10$  K exhibits glassy behavior that would only be expected with the presence of antiferromagnetic couplings, and the deviation from Curie-Weiss behavior near the onset of NTE can be considered to have AFM-like character (relative decrease in  $\chi$ ). We note that the glassy behavior could be promoted by the deviation from perfect  $\text{LiGaCr}_4\text{S}_8$  stoichiometry, which was demonstrated via diffraction data that revealed our samples possess excess Ga.

There are at least two possible sources for antiferromagnetic exchange in Cr-spinel compounds [28, 50]. One is direct Cr-Cr exchange, which can be relevant in oxides where significantly smaller Cr-Cr distances are found. In  $\text{LiGaCr}_4\text{S}_8$  the minimum Cr-Cr distance is 3.39 Å and thus direct exchange is not likely to be the dominate source of antiferromagnetic interactions. A second and likely more relevant set of interactions are between 2nd and 3rd nearest neighbors [23, 28]. In contrast to  $J_1$  and  $J'_1$  where there are 3 NN, there are 12 NNN each for  $J_2$  and  $J_3$ . Inelastic neutron scattering experiments could be useful to provide greater details to the various terms in the spin Hamiltonian.

Finally, we comment on the nature of the low temperature phase. Glassy dynamics likely plays an important role in the low temperature physical properties as evidenced from the following experimental observations: The bifurcation of the field cooled and zero field cooled susceptibility and the weak frequency dependence of the ac susceptibility. Likewise, the observed hysteresis in the field-dependence of the magnetization is likely associated with time-dependent relaxation of the moments. Additionally, the anomaly in the heat capacity is rather broad and analysis of this data result in a small fraction of the entropy expected for a  $S = 3/2$  system. This behavior may be

explained as a consequence of the chemical disorder induced by the deficiency of Li and associated occupation of the Li site by Ga (see Tables 4.1). Such disorder may be particularly important for exchange interactions beyond NN. Additional efforts to understand the low temperature phase are underway.

## 4.6 Conclusion

In summary, we find that the chalcogenide spinel  $\text{LiGaCr}_4\text{S}_8$  forms a breathing pyrochlore lattice with the tetrahedral A sites alternately occupied by metal ions  $\text{Li}^+$  and  $\text{Ga}^{3+}$ . Negative thermal expansion is observed from 10 to 110 K and appears along with the deviation from Curie-Weiss behavior of the magnetic susceptibility. At lower temperatures a magnetic transition to a phase with slow dynamics occurs at 10.5(5) K and is accompanied by the return to normal thermal expansion. Together these experimental observations along with first principles calculations point to strong magnetoelastic coupling in  $\text{LiGaCr}_4\text{S}_8$ .

# Chapter 5

## Cluster frustration in the breathing pyrochlore lattice material $\text{LiGaCr}_4\text{S}_8$

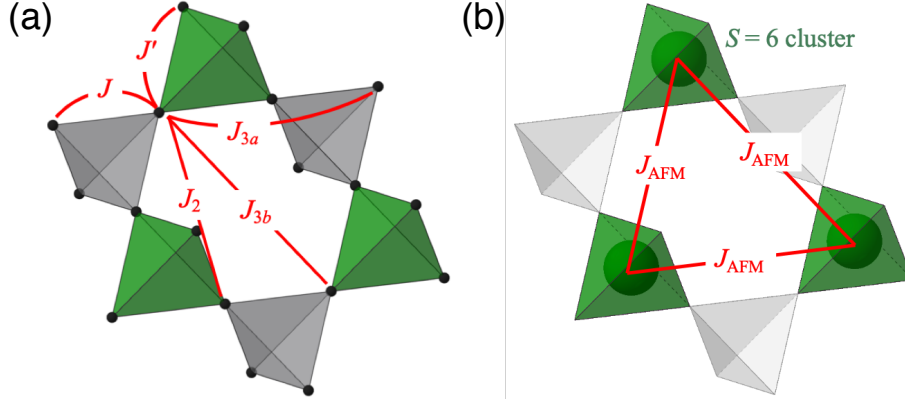
A similar version of this chapter is submitted for publication as, “Cluster frustration in the breathing pyrochlore magnet  $\text{LiGaCr}_4\text{S}_8$ ”, Ganesh Pokharel, Hasitha Suriya Arachchige, Travis J. Williams, David. S. Parker, Andrew F. May, Stuart Calder, Georg Ehlers, Gabriele Sala, Tao Hong, Randy S. Fishman, Andrew Wildes, David Mandrus, Joseph A. M. Paddison, and A. D. Christianson. arXiv:2002.09749 (2020) (Reference [95]).

In this chapter, we present a comprehensive neutron scattering study of the breathing pyrochlore magnet  $\text{LiGaCr}_4\text{S}_8$ . We observe an unconventional magnetic excitation spectrum with a separation of high and low-energy spin dynamics in the correlated paramagnetic regime above a spin-freezing transition at 12(2) K. By fitting to magnetic diffuse-scattering data, we parameterize the spin Hamiltonian. We find that interactions are ferromagnetic within the large and small tetrahedra of the breathing pyrochlore lattice, but antiferromagnetic further-neighbor interactions are also essential to explain our data, in qualitative agreement with density-functional theory predictions [Ghosh *et al.*, *npj Quantum Mater.* **4**, 63 (2019)]. We explain the origin of geometrical frustration in  $\text{LiGaCr}_4\text{S}_8$  in terms of net antiferromagnetic coupling between emergent tetrahedral spin clusters that occupy a face-centered lattice. Our results provide insight into the emergence of frustration in the presence of strong further-neighbor couplings, and a blueprint for the determination of magnetic interactions in classical spin liquids.

## 5.1 Introduction

Geometrical frustration—the inability to satisfy all interactions simultaneously due to geometrical constraints—can generate unusual magnetic states in which long-range magnetic ordering is suppressed but strong short-range spin correlations endure [96]. Canonical models of frustrated magnetism often consider spins coupled by antiferromagnetic nearest-neighbor (NN) interactions, which generate a macroscopic degeneracy of magnetic ground states on lattices such as the pyrochlore network of corner-sharing tetrahedra [97, 98, 99]. This ground-state degeneracy is not symmetry-protected, and in general is expected to be broken by perturbations such as further-neighbor interactions or spin-lattice coupling. Remarkably, however, some materials exhibit highly-frustrated behavior, despite having complex magnetic interactions that deviate strongly from canonical frustrated models [100, 101, 102]. These states are of fundamental interest because they can reveal novel frustration mechanisms.

A modification of the pyrochlore lattice with potential to realize such states is an alternating array of small and large tetrahedra [Fig. 5.1(a)]. This lattice is conventionally called a “breathing pyrochlore”, although the size alternation is static, and corresponds to a symmetry lowering from  $Fd\bar{3}m$  to  $F\bar{4}3m$  [33]. Different exchange interactions can occur within the small and large tetrahedra ( $J$  and  $J'$ , respectively; see Fig. 5.1(a)), increasing the richness of the phase diagram [47]. Neglecting further-neighbor interactions, conventional ordering is expected only if both  $J$  and  $J'$  are ferromagnetic. If  $J$  and  $J'$  are both antiferromagnetic, the ground state is a classical spin liquid, whereas if  $J$  and  $J'$  are of opposite sign, the ground-state manifold is dimensionally reduced [47]. Further-neighbor interactions ( $J_2$ ,  $J_{3a}$ , and  $J_{3b}$ ; see Fig. 5.1(a)) can generate further exotic phases. Perhaps the most intriguing of these is predicted [45] to occur when  $J$  or  $J'$  is large and ferromagnetic, and further-neighbor interactions are antiferromagnetic. The dominant ferromagnetic interactions drive the formation of ferromagnetic tetrahedral clusters, and inter-cluster interactions are frustrated because these clusters occupy a face-centered cubic (FCC) lattice [Fig. 5.1(b)] [45]. This model provides a notable example of the concept of emergent frustration—the frustration of multi-spin degrees of freedom that occupy a different lattice to the spins themselves [101, 102].



**Figure 5.1:** (a) Breathing pyrochlore lattice of  $S = 3/2$   $\text{Cr}^{3+}$  ions (black circles) in  $\text{LiGaCr}_4\text{S}_8$ , showing large (small) tetrahedra (colored green (grey)), and the connectivity of the exchange interactions  $J$ ,  $J'$ ,  $J_2$ ,  $J_{3a}$ , and  $J_{3b}$ .  $J_{3a}$  and  $J_{3b}$  span the same distance but have different symmetry. (b) Emergent tetrahedral clusters generated by strong ferromagnetic  $J'$  interactions, coupled by a net antiferromagnetic interaction  $J_{\text{AFM}} \propto J + 4J_2 + 2J_{3a} + 2J_{3b} (> 0)$ .

Experimental realizations of the breathing pyrochlore model include the spinel derivatives  $AA'\text{Cr}_4X_8$ , in which the  $A$ -site is occupied by an ordered arrangement of  $\text{Li}^+$  and  $\text{In}^{3+}/\text{Ga}^{3+}$ ;  $X = \text{O}, \text{S}$  or  $\text{Se}$ ; and the  $\text{Cr}^{3+}$  ions occupy a breathing pyrochlore lattice [33]. Since  $J \sim J'$  in these materials, collective magnetic behavior is expected, in contrast to the breathing pyrochlore material  $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$  in which tetrahedra are decoupled [34, 35, 78, 103]. Series members with  $X = \text{O}$  have antiferromagnetic  $J$  and  $J'$  and exhibit magnetostructural phase transitions and nematic spin ordering [33, 39, 48, 49, 86]. Replacement of  $\text{O}$  with  $\text{S}$  or  $\text{Se}$  ligands is predicted to cause two key differences: suppression of direct exchange relative to superexchange, which is expected to be ferromagnetic because the  $\text{Cr-X-Cr}$  bond angles are near to  $90^\circ$ ; and enhancement of further-neighbor interactions [45]. Hence, series members with  $\text{S}$  or  $\text{Se}$  ligands [37, 51, 104, 82] are promising candidates to realize models of frustration driven by further-neighbor interactions. However, no experimental determination of the magnetic interactions in such systems exists.

Here, we use neutron scattering measurements to study the breathing pyrochlore  $\text{LiGaCr}_4\text{S}_8$ . While the Weiss constant of  $\text{LiGaCr}_4\text{S}_8$  is relatively small,  $\theta_{\text{CW}} \approx 20$  K [37, 44], its bulk magnetic susceptibility  $\chi$  shows strong deviations from Curie-Weiss behavior below  $\sim 100$  K, suggesting the development of strong spin correlations above its spin-freezing transition at  $T_f = 12(2)$  K [37]. Spin freezing is probably driven by a small amount of off-stoichiometry, as approximately



4% of Li sites are occupied by Ga. Our three key results explain the nature and origin of spin correlations in  $\text{LiGaCr}_4\text{S}_8$ : we experimentally parameterize the spin Hamiltonian to reveal the importance of further-neighbor couplings; we confirm recent theoretical predictions (Ref. [45]) of cluster frustration; and we observe a direct signature of cluster formation in its magnetic excitation spectrum. These results show that  $\text{LiGaCr}_4\text{S}_8$  realizes the frustration of tetrahedral clusters on an emergent FCC lattice.

Our paper is structured as follows. We begin by summarizing our experimental methodology. We then present a comprehensive survey of the temperature evolution of the magnetic excitation spectrum of  $\text{LiGaCr}_4\text{S}_8$ . We model our experimental results by fitting interaction parameters in a Heisenberg Hamiltonian to magnetic diffuse-scattering data. We use this model to explain the frustration of the system in terms of cluster formation, and to explain the key features of its magnetic excitation spectrum. In conclusion, we discuss the general implications of our results.

## 5.2 Methods

### 5.2.1 Synthesis and measurements

A finely ground polycrystalline sample of  $\text{LiGaCr}_4\text{S}_8$  was loaded in a cylindrical vanadium holder of diameter 9 mm for neutron powder diffraction measurements on the HB-2A powder diffractometer at the High Flux Isotope Reactor, Oak Ridge National Laboratory (ORNL). The sample was mounted in a Janis top loader closed-cycle refrigerator (CCR) and data were collected at 4, 20, 45, 70, 95, 120, and 150 K. In order to study the low temperature properties of the sample, the sample environment was replaced by an Orange cryostat and an additional measurement was performed at 1.5 K after loading the powder in a cylindrical Al holder. Incident neutrons of wavelength 2.41 Å, obtained from the (113) reflection of a vertically-focused germanium wafer-stack monochromator, were used. For these measurements, the instrumental resolution  $\Delta Q/Q$  is  $\sim 0.015$ .

Inelastic neutron-scattering measurements were carried out on the Wide Angular-Range Chopper Spectrometer (ARCS) [74] and the Cold Neutron Chopper Spectrometer (CNCS) [76] at the Spallation Neutron Source (SNS) at ORNL. Preliminary data was also collected with the

cold triple-axis instrument CTAX at the high flux isotope reactor at ORNL. The same sample as used for the neutron diffraction measurements was mounted in a CCR and inelastic scattering data were collected at 3, 20, 30, 60, 100 and 200 K on ARCS. Incident energies,  $E_i$ , of 10, 25, 50 and 120 meV were used. The Fermi and  $T_0$  choppers were operated at 240, 240, 420, 460 Hz and 60, 60, 60, 90 Hz, respectively. The elastic energy resolution of these measurements was 3.5-5% of  $E_i$  (0.36 meV for  $E_i = 10$  meV and 5.9 meV for  $E_i = 120$  meV). To increase the energy resolution,  $E_i = 3.32$  meV (elastic energy resolution  $\sim 0.1$  meV) was used at CNCS. An empty holder was also measured to subtract the background scattering on CNCS. Scattering from sample and background were collected over the temperature range 1.7 to 200 K. All inelastic scattering data were reduced with the Mantid software package using vanadium standard calibration files [105] and then analyzed using the DAVE software suite [106]. Data were normalized on an absolute intensity scale (units of barn sr<sup>-1</sup>meV<sup>-1</sup>Cr<sup>-1</sup>) *via* refinement of the nuclear Bragg profile using the Fullprof program [107].

For the  $\mu$ SR experiments, a finely ground and homogenized polycrystalline sample of mass 1 g with a surface area 1 cm<sup>2</sup> was measured. Measurements were performed on the M20 surface muon beamline at the TRIUMF Center of Molecular and Materials Science. The sample was loaded in a He flow cryostat with a base temperature of 1.9 K, utilizing muons polarized with their initial spin antiparallel to the muon beam direction. ZF- $\mu$ SR scans were performed in the temperature range 1.9 to 250 K, followed by a series of longitudinal field scans with fields ranging from 0 to 0.3 T while holding the sample at 1.9 K.

### 5.2.2 Modeling

The magnetic diffuse scattering is calculated in the Onsager reaction-field approximation (MFO) [108, 109, 110]. In the MFO, we consider the primitive pyrochlore unit cell that contains  $N = 4$  sites at positions  $\mathbf{r}_i$ . The Fourier transform of the magnetic interactions between sites  $i$  and  $j$  separated by a lattice vector  $\mathbf{R}$  is given by  $J_{ij}(\mathbf{Q}) \equiv -\sum_{\mathbf{R}} J_{ij}(\mathbf{R}) \exp(-i\mathbf{Q} \cdot \mathbf{R})$ , where  $J_{ij}(\mathbf{R}) \in \{J, J', J_2, J_{3a}, J_{3b}\}$  is an interaction shown in Fig. 5.1. The  $J_{ij}(\mathbf{Q})$  are elements of a  $4 \times 4$  matrix whose eigenvalues  $\lambda_\mu(\mathbf{Q})$  and eigenvector components  $U_{i\mu}(\mathbf{Q})$  ( $\mu \in \{1, N\}$ ) are obtained by numerical diagonalization using EISPACK routines [111]. The magnetic diffuse scattering

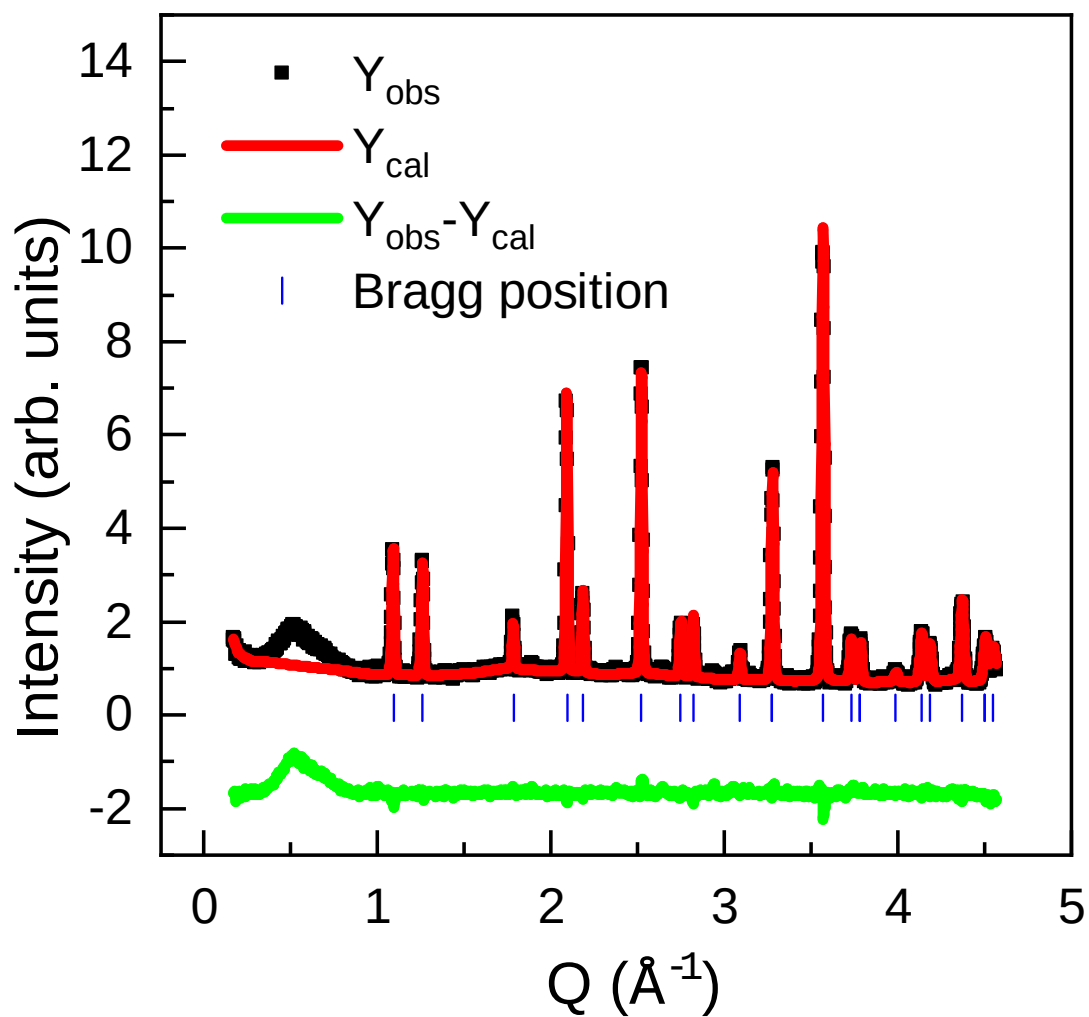
intensity in the paramagnetic phase (i.e., above any ordering or freezing transition) is given in the MFO by

$$I_{\text{MFO}}(\mathbf{Q}) \propto [f(Q)]^2 \sum_{\mu=1}^N \frac{|s_{\mu}(\mathbf{Q})|^2}{1 - \chi_0 [\lambda_{\mu}(\mathbf{Q}) - \lambda]}, \quad (5.1)$$

where  $f(Q)$  is the  $\text{Cr}^{3+}$  magnetic form factor [112],  $\chi_0 = S(S+1)/3T$  is the Curie susceptibility, and  $s_{\mu}(\mathbf{Q}) = \sum_i U_{i\mu}(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{r}_i)$ . Eq. (5.1) is equivalent to the mean-field expression [113] except for the presence of the reaction field  $\lambda$ , which is evaluated self-consistently by requiring that  $\sum_{\mu, \mathbf{q}} [1 - \chi_0 (\lambda_{\mu}(\mathbf{q}) - \lambda)]^{-1} = NN_{\mathbf{q}}$  for a grid of  $N_{\mathbf{q}} = 16^3$  wavevectors in the Brillouin zone. The spherical (powder) average of Eq. (5.1) is performed numerically to obtain  $I_{\text{MFO}}(Q = |\mathbf{Q}|)$ . where  $\mu = g\sqrt{S(S+1)}$  is the paramagnetic moment, and  $C = 0.07265 \text{ bn}$  is a constant

In fits to the experimental  $I(Q)$ , an overall intensity scale factor and flat-in- $Q$  intensity offset are refined to match the experimental data at each temperature. These parameters are included to account for small errors in absolute intensity normalization and/or temperature-dependent energy integration. In fits to the bulk susceptibility data, only an overall intensity scale factor is refined. In co-refinements to  $I(Q)$  and  $\chi T$  data, the  $\chi T$  are weighted such that they contribute approximately one quarter of the overall sum-of-squared residuals when the values of all the interaction parameters are set to zero.

Given the relatively large number of interaction parameters in our  $\{J, J', J_2, J_{3a}, J_{3b}\}$  model, it is necessary to check that our refinements reaches the global minimum in the sum of squared residuals. To achieve this, we performed 50 separate fits starting from different initial parameter values, where each interaction parameter is initially set to a random value in the range  $\{-10 : 10\}$  K. Each fit is performed using the nonlinear least-squares algorithm implemented in the MINUIT program [114]. The parameter values correspond to the optimal solution detected from this procedure, which is obtained in 20% of cases. A local minimum, with a worse fit, is also detected, which essentially corresponded to swapping the values of  $J$  and  $J'$  obtained for the global minimum; the relative similarity in the fits for these two parameter sets are anticipated because of the small difference between  $r$  and  $r'$  distances.



**Figure 5.2:** Neutron diffraction data with  $\lambda = 2.41 \text{ \AA}$  collected at 4 K. The solid line through the data represents the Rietveld refinement of the lattice structural model with space group  $F\bar{4}3m$ .

## 5.3 Results

### 5.3.1 Diffuse magnetic scattering

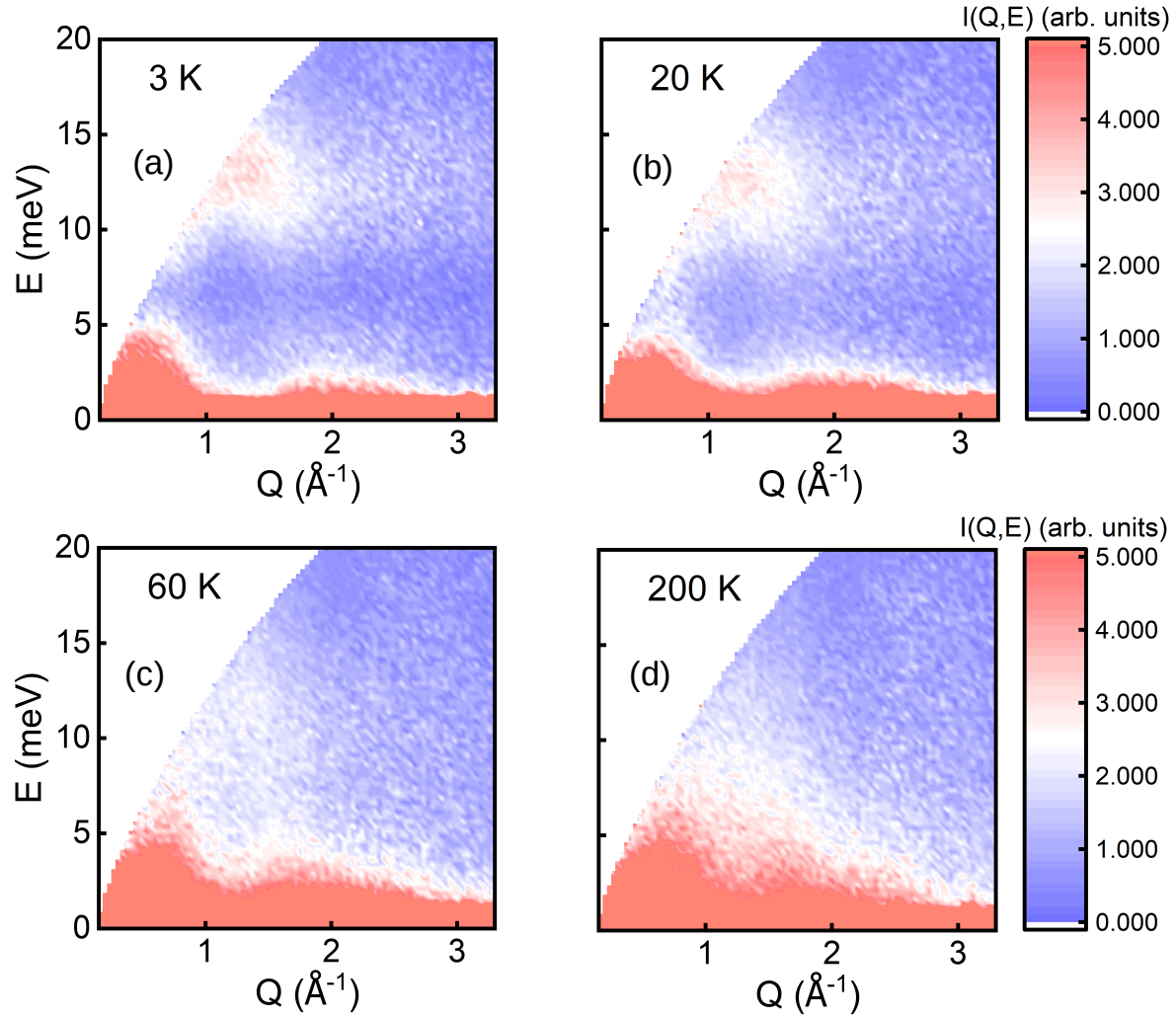
The neutron diffraction pattern at 4 K measured with incident neutron wavelength 2.41 Å is shown in Fig. 5.2. Rietveld refinement [107] of diffraction pattern to a structural model with space group  $F\bar{4}3m$  fits all the structural peaks except the diffuse magnetic scattering centered around  $Q \approx 0.5 \text{ Å}^{-1}$ . The diffuse scattering persists to fairly high temperature above the magnetic transition observed in bulk susceptibility measurements.

Powder neutron diffraction data collected on the HB-2A diffractometer are corrected for absorption and then background is subtracted using a measurement of an empty vanadium container. To estimate the magnetic diffuse scattering, the calculated nuclear Bragg profile obtained from a Rietveld refinement is subtracted, and placed the data on an absolute intensity scale (units of barn  $\text{sr}^{-1}\text{Cr}^{-1}$ ) by normalizing them to the nuclear Bragg profile. The comprehensive analysis and modeling of diffuse scattering data are presented in the section 5.3.3.

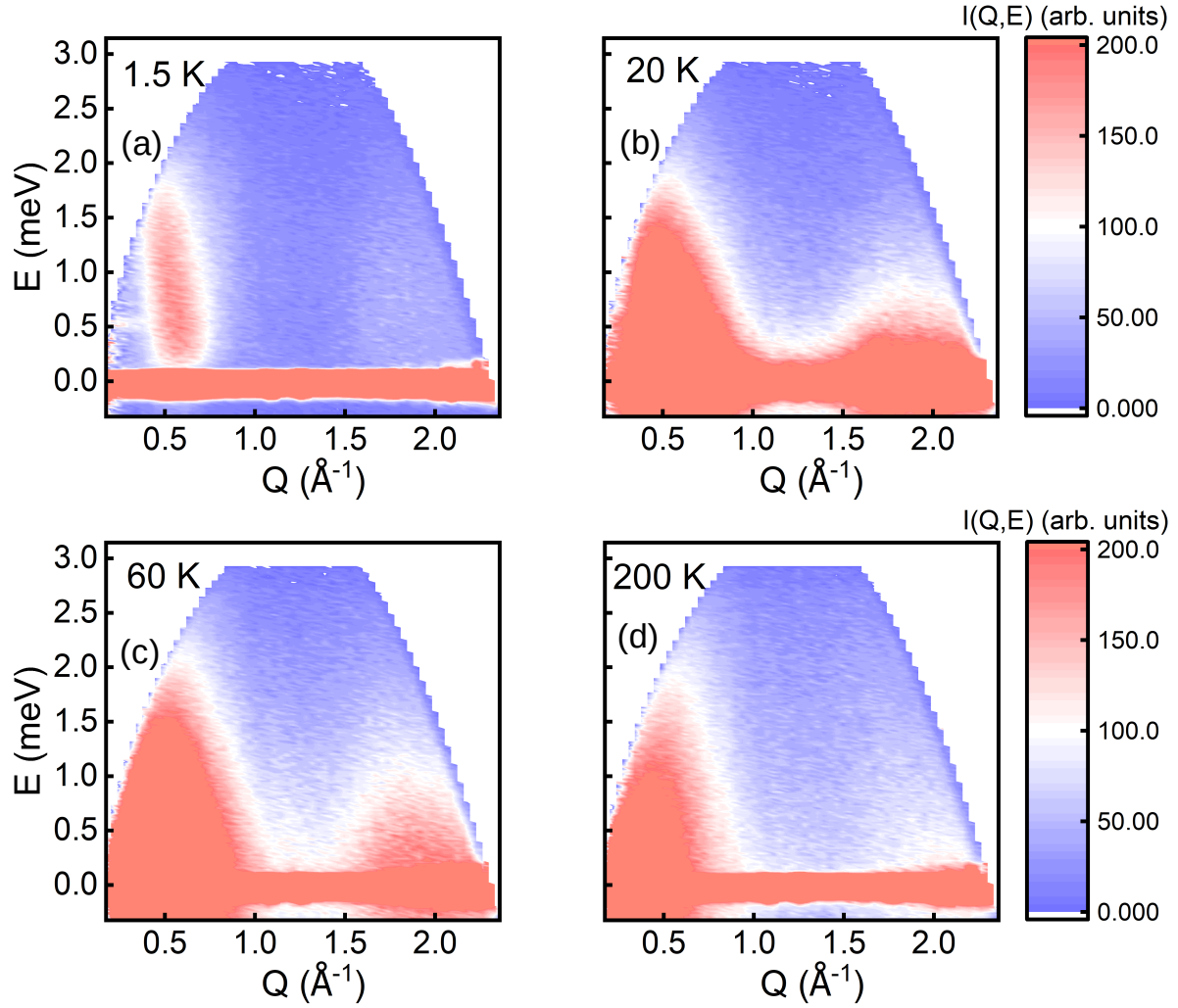
### 5.3.2 Spin excitation spectra

Fig. 5.3 presents an overview of the temperature dependence of the excitation spectrum as a function of wavevector transfer  $Q = |\mathbf{Q}|$  and energy transfer  $E$ , with intensity shown by color. Data from two neutron-scattering spectrometers are shown: Fig. 5.3 shows high-energy data measured using the ARCS spectrometer with  $E_i = 25 \text{ meV}$ , and Fig. 5.4 shows low-energy data measured using the CNCS spectrometer with  $E_i = 3.32 \text{ meV}$ .

The dependence of the inelastic scattering shown in Fig. 5.3 on  $Q$  and temperature suggests that its origin is very likely to be magnetic. The bandwidth of the magnetic excitation spectrum is about 15 meV, which is much larger than  $\theta_{\text{CW}} \approx 20 \text{ K}$  (2 meV). Since  $\theta_{\text{CW}} = -\sum_n S(S+1)Z_n J_n/3$  is a measure of the net interaction strength, whereas the bandwidth is related to the largest interaction, this result suggests that both ferromagnetic and antiferromagnetic exchange interactions are significant. At 100 K and above, the spectrum is broad, as expected for a conventional paramagnet. In contrast, between 20 K and 100 K, the spectrum shows both a high-energy band at approximately 12 meV and low-energy quasielastic excitations. The low-energy



**Figure 5.3:** Inelastic neutron scattering spectra of  $\text{LiGaCr}_4\text{S}_8$  measured at temperatures indicated in the panels. High energy excitation spectra measured with  $E_i = 25$  meV at 3 K (panel (a)), 20 K (panel(b)), 60 K (Panel (c)) and 200 K (Panel (d)).



**Figure 5.4:** Inelastic neutron scattering spectra of  $\text{LiGaCr}_4\text{S}_8$  measured at temperatures indicated in the panels. Low energy spin excitations measured with  $E_i = 3.32$  meV at 1.5 K (panel (a)), 20 K (panel(b)), 60 K (Panel (c)) and 200 K (Panel (d)).

scattering is much more intense than the high-energy scattering, and has a more pronounced wavevector dependence. On cooling the sample, the quasielastic scattering moves increasingly towards low energy. At base temperature, below  $T_f$ , most of the quasielastic spectral weight shifts to the elastic line, which is consistent with the expected dramatic slowing-down of spin dynamics associated with spin freezing. Interestingly, however, the intensity of the high-energy band does not change appreciably compared to 20 K.

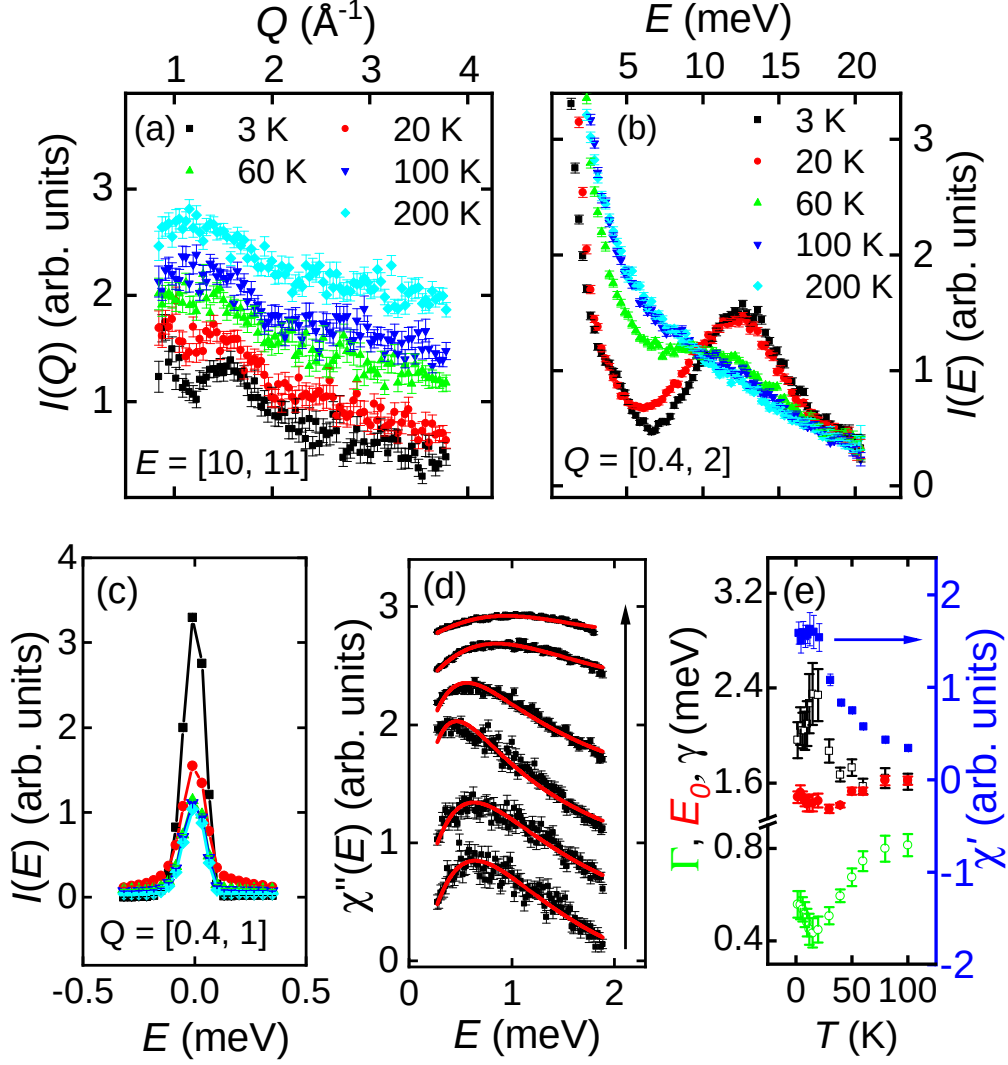
Fig. 5.5 shows line plots that explore the excitation spectrum in detail. Fig. 5.5(a) shows the wavevector dependence of the high-energy excitation, integrated over  $10 \leq E \leq 11$  meV, at different temperatures. At lower temperatures, this excitation does not monotonically decrease with increasing  $Q$ ; i.e., it does not follow the magnetic form factor for independent  $\text{Cr}^{3+}$  ions. Fig. 5.5(b) shows the energy dependence of the high-energy spectrum, integrated over  $0.4 \leq Q \leq 2.0 \text{ \AA}^{-1}$ , and demonstrates that the high-energy excitation emerges as a distinct contribution between 20 and 60 K. Fig. 5.5(c) shows the energy dependence of the low-energy spectrum, integrated over  $0.4 \leq Q \leq 1.0 \text{ \AA}^{-1}$ , and demonstrates that the intensity of the elastic scattering increases sharply between 20 K and 3 K, as the spin-freezing transition at  $T_f$  is traversed. Fig. 5.5(d) shows the imaginary part of the dynamical susceptibility  $\chi''(Q, E)$ , obtained from the CNCS neutron data *via* the fluctuation-dissipation theorem,  $I(Q, E) \propto [1 - e^{-E/k_B T}]^{-1} \chi''(Q, E)$ . For these data, the  $Q$ -integration ( $\Delta Q$ ) is  $\pm 0.025 \text{ \AA}^{-1}$  around the most intense  $Q$  for the low-energy inelastic spectrum. We model the low-energy susceptibility phenomenologically using the damped harmonic-oscillator (DHO) model [46, 115, 116],

$$\chi''(E; T) = \frac{2\chi'(T)\gamma(T)E}{[E^2 - E_0(T)^2]^2 + 4\gamma^2(T)E^2} \quad (5.2)$$

where  $\chi'(T)$  is proportional to the real part of the susceptibility,  $\gamma(T)$  is the damping rate, and  $E_0(T)$  is the resonance energy of the undamped oscillation. The temperature dependence of  $E_0$ ,  $\gamma$ ,  $\chi'$  and the characteristic damping energy (also referred to as the inverse relaxation time)  $\Gamma = E_0^2/2\gamma$  are shown in Fig. 5.5(e). We find that  $\gamma > E_0$  at low temperatures, which suggests that  $\chi''(Q, E)$  does not vanish at finite energy and a spin gap is not present.

The value of  $\chi'$  increases monotonically with decreasing temperature and then saturates near the magnetic transition, consistent with the bulk susceptibility data reported previous chapter 4.





**Figure 5.5:** (a) Wavevector dependence of constant  $E$ -cuts ( $10 \leq E \leq 11$  meV) of the scattering measured at different temperatures labeled on the plot. (b) Energy dependence of high-energy scattering for cuts integrated over  $0.4 \leq Q \leq 2 \text{\AA}^{-1}$  at different temperatures. (c) Energy dependence of quasielastic scattering for cuts integrated over  $0.4 \leq Q \leq 1 \text{\AA}^{-1}$  at temperatures of 1.7 K (black), 20 K (red), 60 K (green), 100 K (blue) and 200 K (cyan). (d) Measured (black squares) and fitted (red lines) dynamical susceptibility  $\chi''$  at 1.7, 4, 15, 30, 60, and 100 K. The arrow in (d) indicates the direction of increasing temperature. (e) Temperature-dependent  $\Gamma$  (green circle),  $E_0$  (red sphere),  $\gamma$  (black open square) and  $\chi'$  (blue solid square) of the damped-harmonic oscillator model corresponding to the fits shown in (d).

The  $\Gamma$  decreases with decreasing temperature above  $T_f$ , reaches a minimum close to  $T_f$ , and increases below  $T_f$ . Above  $T_f$ , we find  $\Gamma \propto T^\delta$  with  $\delta \approx 0.41$ , in contrast to the linear temperature dependence expected for isotropic pyrochlore lattices [97, 117]. A similar reduction in  $\delta$  has been observed in  $\text{LiGa}_{0.95}\text{In}_{0.05}\text{Cr}_4\text{O}_8$ , for which  $\delta \approx 0.66$  [48].

### 5.3.3 Magnetic interaction modeling

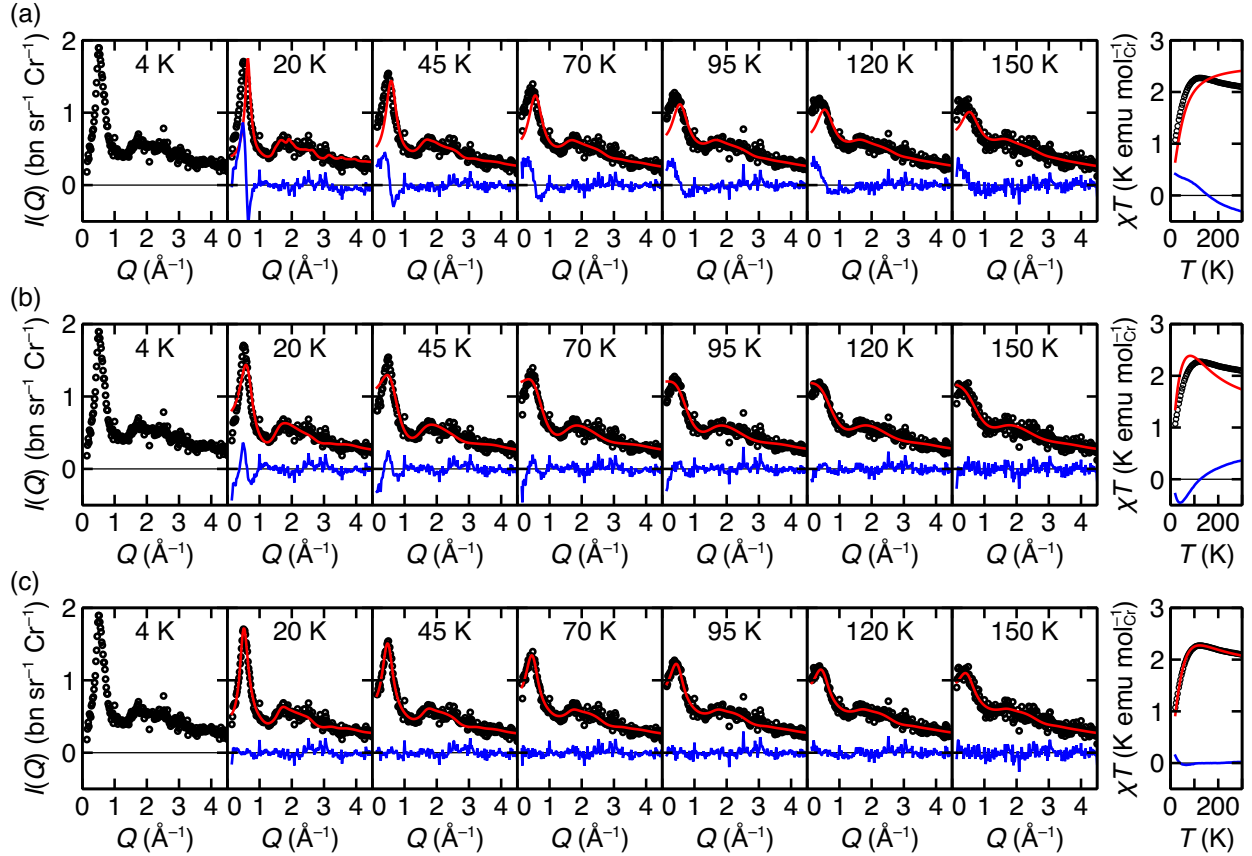
We now obtain an experimental estimate of the magnetic interactions relevant to  $\text{LiGaCr}_4\text{S}_8$ . We expect that its spin Hamiltonian has the Heisenberg form,

$$H = \frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (5.3)$$

which has previously been applied successfully to other  $\text{Cr}^{3+}$ -based spinels [118]. In equation (5.3),  $J_{ij} \in \{J, J', J_2, J_{3a}, J_{3b}\}$  denotes a magnetic interaction shown in Fig. 5.1, and  $S$  denotes a classical vector of magnitude  $\sqrt{S(S+1)}$  with  $S = 3/2$  for  $\text{Cr}^{3+}$ . We expect this classical approximation to be reasonable for  $S = 3/2$ .

Because  $\text{LiGaCr}_4\text{S}_8$  does not exhibit long-range magnetic ordering, it is not possible to employ the conventional approach of fitting magnetic interactions to spin-wave spectra in an ordered state. Therefore, we consider instead the magnetic diffuse scattering intensity,  $I(Q) = \int I(Q, E) dE$ , which is sensitive to the equal-time (instantaneous) spin-pair correlation function [119, 120]. The powder-diffraction data collected on HB-2A provide an approximation to  $I(Q)$ , where the upper limit of the energy integral is given by  $E_i \approx 14$  meV. For a given set of interaction parameters in equation (5.3), we calculate  $I(Q)$  and the bulk magnetic susceptibility (expressed as a product of susceptibility and temperature,  $\chi T$ ) using Onsager reaction field theory [108, 109, 110], which is a self-consistent modification of mean-field theory equivalent to the self-consistent Gaussian approximation (SCGA) used elsewhere [47, 118, 121]. This approximation has been shown to give accurate results for frustrated classical Heisenberg models on the pyrochlore lattice [122].

We tested three interaction models against our diffuse-scattering data and the bulk susceptibility data. An overall intensity scale factor and flat-in- $Q$  intensity offset were refined to match the  $I(Q)$  data at each temperature, and an overall intensity scale factor was refined to match the  $\chi T$  data. These factors correct for small inaccuracies in background subtraction and absolute intensity



**Figure 5.6:** Neutron diffraction data (black circles), model fits (red lines), and data-fit (blue lines) for (a) the DFT model, (b) the  $J$ - $J'$  model, and (c) the  $J$ - $J'$ - $J_2$ - $J_{3a}$ - $J_{3b}$  model discussed in the text. The left-hand panels of (a), (b) and (c) represent the neutron scattering data at temperatures indicated in each panel, and the right-hand panel represents the bulk susceptibility. Fits were performed in the correlated paramagnetic regime at  $T \geq 20$  K.

normalization, as well as high-energy ( $E > 14$  meV) spectral weight outside the energy window of our measurements.

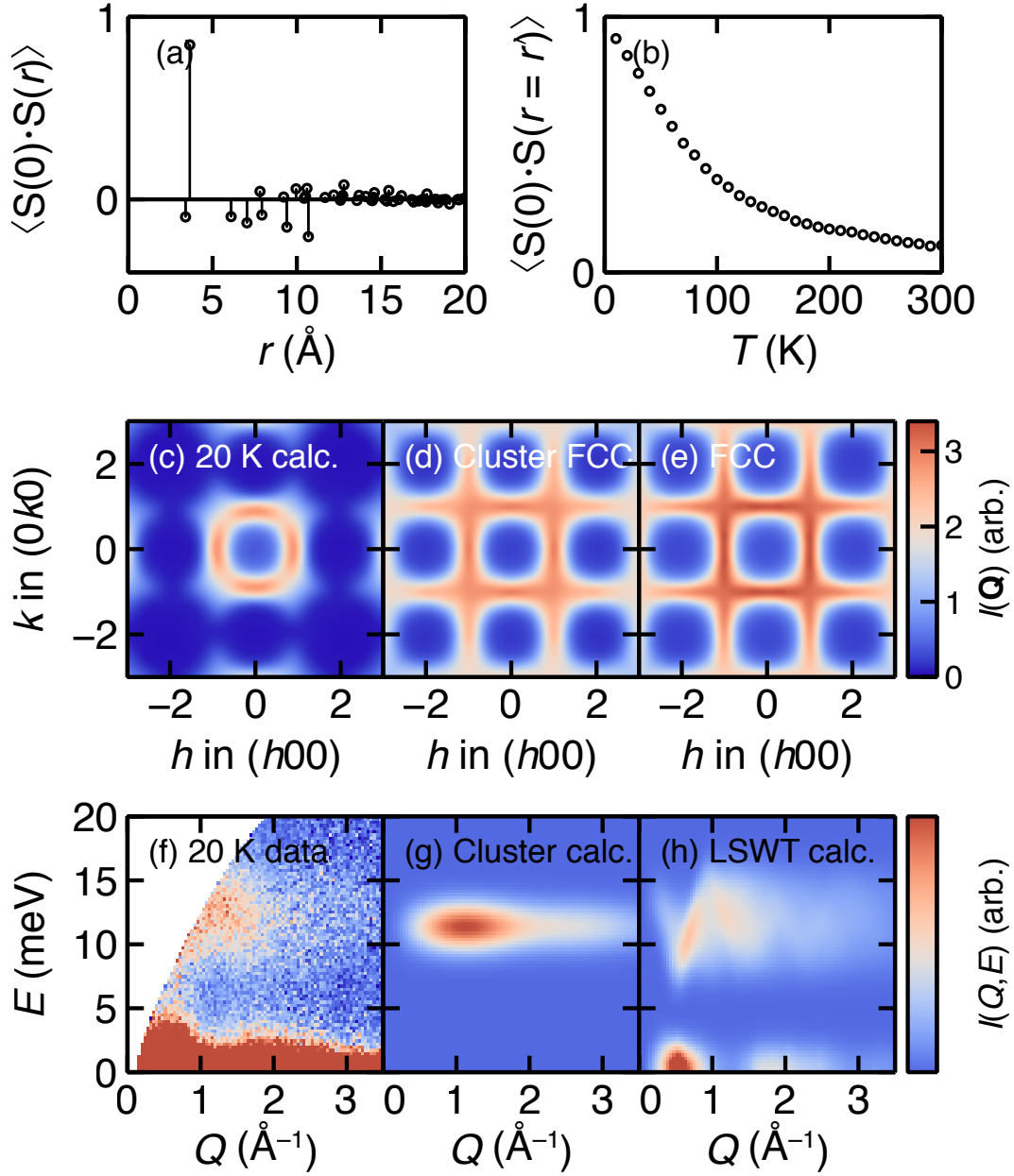
First, we considered the parameter set reported in Ref. [45], which was obtained using density-functional theory (DFT). This “DFT model” contains five interaction parameters whose values are reproduced in Table 5.1. Calculations of  $I(Q)$  and  $\chi T$  for this model are compared with experimental data in Fig. 5.6(a). While some features of the calculation are broadly consistent with experiment, the calculated position of the main diffuse peak disagrees markedly.

Second, we attempted to fit to  $I(Q)$  using a simpler model that included  $J$  and  $J'$  interactions only (“ $J$ - $J'$  model”). Fits are shown in Fig. 5.6(b) and optimized parameter values are given in Table 5.1. These fits also do not agree well with the neutron data at low  $Q$ , and are inconsistent with the bulk susceptibility data. Importantly, this result indicates that longer-ranged interactions beyond  $J$  and  $J'$  are necessary to account for our experimental data.

Finally, we fitted all five interaction parameters to our experimental data (“ $J$ - $J'$ - $J_2$ - $J_{3a}$ - $J_{3b}$  model”). This fit included both the neutron data and the bulk susceptibility data. We were aware that our data might not be sufficient to determine the values of five parameters, and of the possibility of shallow local minima in the sum of squared residuals. To assess the extent of these potential problems, we performed multiple refinements initialized from different (randomly-chosen) parameter sets. Remarkably, our data robustly determines a unique optimal solution. Fits are shown in Fig. 5.6(c) and optimized parameter values are given in Table 5.1. This model gives a good fit to both neutron and bulk susceptibility data. We find that  $J'$  is the largest interaction,  $J$ ,  $J'$  are both ferromagnetic,  $J_{3a}$  is antiferromagnetic, and  $J_2$  and  $J_{3b}$  are both small. These qualitative trends are consistent with the DFT model [45], suggesting that our results are physically reasonable.

### 5.3.4 Cluster frustration

With a model of the magnetic interactions in hand, we consider the origin of frustration in  $\text{LiGaCr}_4\text{S}_8$  and its effects on the excitation spectrum. The strongest interaction is  $J'$ , which is ferromagnetic and couples spins within large tetrahedra [Fig 5.1(a)]. We therefore hypothesize that, at low temperature, spins are essentially aligned within the large tetrahedra, forming  $S' \approx 6$



**Figure 5.7:** (a) Spin-pair correlation  $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$  as a function of distance  $r$  between spins. The normalization is such that  $\langle \mathbf{S}(0) \cdot \mathbf{S}(0) \rangle = 1$ . Results were obtained from classical Monte Carlo simulations driven by interaction parameters optimized to our neutron data. (b) Calculated temperature dependence of the spin-spin correlation function at  $r = r'$ , the distance between neighboring spins in large tetrahedra. (c) Calculated single-crystal diffuse-scattering pattern  $I(\mathbf{Q})$  of  $\text{LiGaCr}_4\text{S}_8$  in the  $(hk0)$  plane at 20 K. (d) Calculated  $I(\mathbf{Q})$  from the emergent FCC lattice of cluster spins, defined as  $\mathbf{S}' = \sum_{i=1}^4 \mathbf{S}_i$  on each tetrahedron of the breathing-pyrochlore lattice. (e) Calculated  $I(\mathbf{Q})$  for spins on the FCC lattice with antiferromagnetic nearest-neighbor exchange interactions  $J_{\text{AFM}} = 0.43$  K. (f) Experimentally-measured spin excitation spectrum at 20 K. (g) Calculated spin excitation spectrum of an isolated tetrahedral cluster. (h) Spin excitation spectrum calculated using linear spin-wave theory assuming a proximate ordered ground state with propagation vector  $\mathbf{k} = [0, 0, 1]$  [123].

**Table 5.1:** Values of magnetic interaction parameters for different models. Parameter values held fixed in fits are denoted by an asterisk (\*).

| Model                                          | $J$ (K) | $J'$ (K) | $J_2$ (K) | $J_{3a}$ (K) | $J_{3b}$ (K) | $R_{wp}^{neutron}$ (%) | $R_{wp}^{bulk}$ (%) |
|------------------------------------------------|---------|----------|-----------|--------------|--------------|------------------------|---------------------|
| DFT model (Ref. [45])                          | -7.7(1) | -12.2(1) | 1.2(1)    | 6.1(1)       | 3.0(1)       | 20.3                   | 11.6                |
| $J$ - $J'$ model                               | 3.07(3) | -29.9(4) | 0*        | 0*           | 0*           | 12.5                   | -                   |
| $J$ - $J'$ - $J_2$ - $J_{3a}$ - $J_{3b}$ model | -7.8(6) | -22.1(3) | -1.6(4)   | 9.6(1)       | 0.8(4)       | 9.8                    | 1.5                 |

clusters. The lattice occupied by these clusters is FCC [Fig. 5.1(b)], and the net interaction between such clusters is given by  $J_{AFM} = (J + 4J_2 + 2J_{3a} + 2J_{3b})/16 = 0.43$  K; [45] i.e., it is antiferromagnetic for our optimized interaction parameters. We therefore also hypothesize that the suppression of  $T_f$  compared to  $J'$  occurs because of the frustration of antiferromagnetic inter-cluster interactions on the FCC lattice, as proposed based on computational modeling in Ref. [45].

To test the hypothesis of ferromagnetic cluster formation, we performed classical Monte Carlo simulations driven by our fitted interaction parameters. Our simulations employed a simulated annealing routine with single-spin-flip Metropolis dynamics; results were averaged over 40 independent periodic configurations, each containing  $6 \times 6 \times 6$  cubic unit cells. Fig. 5.7(a) shows that, at 20 K, the normalized spin correlation function  $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$  extracted from our simulations is close to its maximum value of unity at the distance  $r'$  between neighboring spins within large tetrahedra. This result shows that large tetrahedral clusters are essentially ferromagnetic at 20 K. Fig. 5.7(b) shows the calculated temperature dependence of  $\langle \mathbf{S}(0) \cdot \mathbf{S}(r = r') \rangle$ , and reveals that the clusters develop rapidly as temperature decreases below 100 K.

To test the hypothesis of antiferromagnetic frustration of  $S' \approx 6$  cluster spins, we calculated single-crystal neutron scattering patterns from our Monte Carlo model using the program Scatty [124]. For a Heisenberg model, this quantity  $I(\mathbf{Q}) \propto \langle \mathbf{S}(0) \cdot \mathbf{S}(\mathbf{r}) \rangle \exp(i\mathbf{Q} \cdot \mathbf{r})$  measures the Fourier transform of the equal-time spin-pair correlation function. Fig. 5.7(c) shows the calculated  $I(\mathbf{Q})$  for LiGaCr<sub>4</sub>S<sub>8</sub> at 20 K. Fig. 5.7(d) shows the calculated  $I(\mathbf{Q})$  from the FCC lattice of “cluster spins”, defined on each tetrahedron of the breathing-pyrochlore lattice as  $\mathbf{S}' = \sum_{i=1}^4 \mathbf{S}_i$ . Figs. 5.7(c) and (d) are different because the former includes the structure factor of the tetrahedral cluster, whereas the latter does not. Fig. 5.7(e) shows the calculated  $I(\mathbf{Q})$  for spins on the FCC

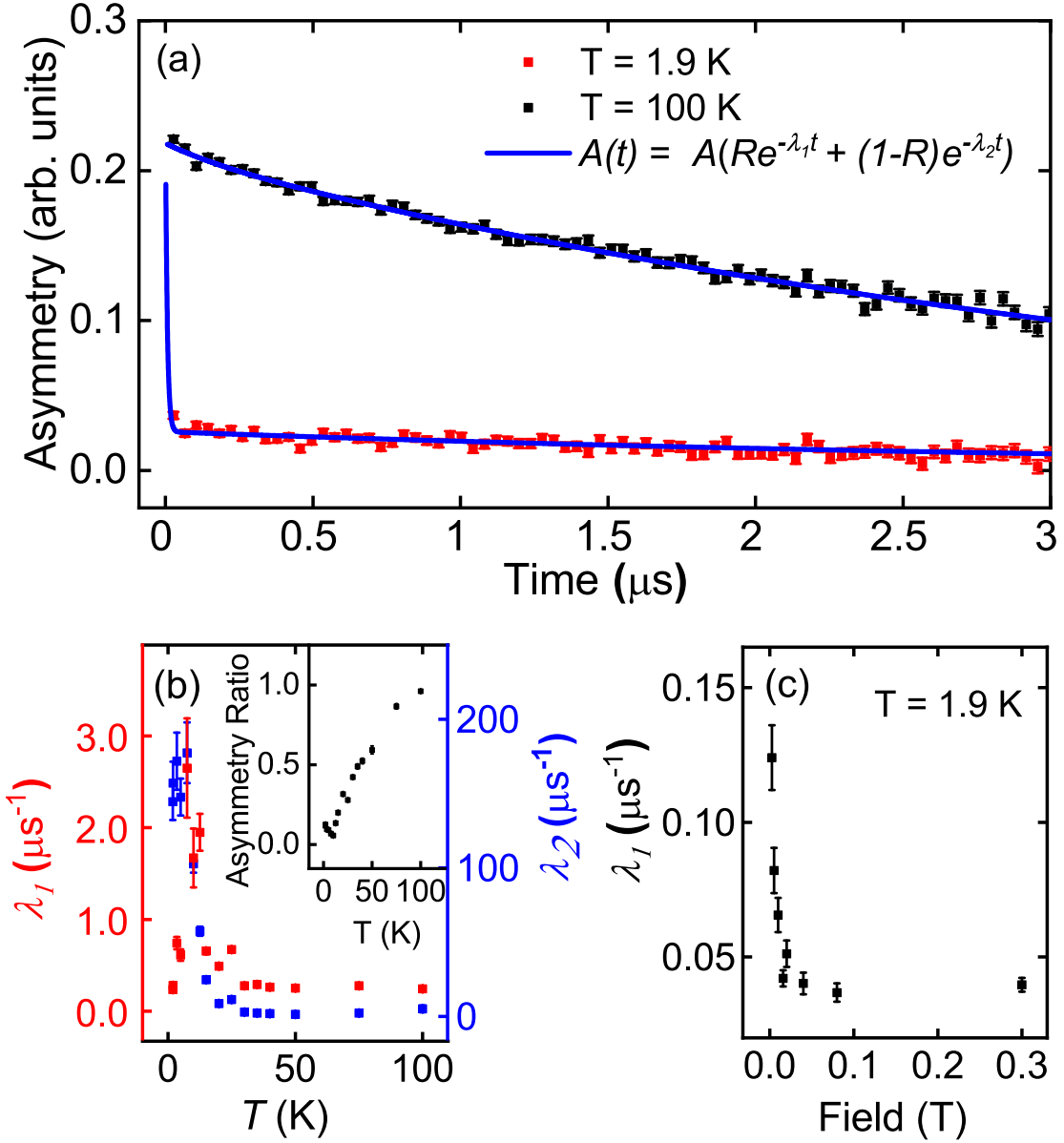
lattice coupled by nearest-neighbor interactions  $J_{\text{AFM}}$ . The strong similarity between Figs. 5.7(d) and (e) demonstrates that antiferromagnetic interactions between cluster spins in  $\text{LiGaCr}_4\text{S}_8$  are frustrated in the same way as individual spins on the FCC lattice.

The cluster model helps to explain our low-temperature inelastic neutron-scattering data. Our 20 K experimental data are shown on a linear intensity scale in Fig. 5.7(f). From ferromagnetic-cluster spin-wave theory [123, 125], we calculate that the excitation spectrum of an isolated tetrahedral cluster with interaction  $J'$  contains a single flat mode at  $E = 4J'S$ , whose intensity shows a broad peak centered at a wavevector of approximately  $1.1 \text{ \AA}^{-1}$  [Fig. 5.7(g)]. Despite the simplicity of this calculation, it is in qualitative agreement with both the energy and wavevector dependence of the high-energy excitation observed experimentally. The single-cluster approximation neglects the effect of coupling between the tetrahedra and consequently contains no low-energy excitations. A different approximation is obtained by optimizing an ordered magnetic ground state using the SpinW software [123]: this state again has ferromagnetic spins within large tetrahedra, but they are now ordered with propagation vector  $\mathbf{k} = [0, 0, 1]$ . The assumption of a proximate ordered ground state allows the spin-wave spectrum to be calculated from conventional linear spin-wave theory, but overestimates the effect of coupling between tetrahedra [Fig. 5.7(h)].

### 5.3.5 Muon spin resonance

Muon spin resonance ( $\mu\text{SR}$ ) is a local, real space, probe that is used to understand the magnetic properties of a material. Muon spins precess about the local magnetic field once they stop in the sample. These precessing muons stochastically decay to a positron, an electron neutrino, and an anti-muon neutrino, with the positron emitted preferentially along the muon spin direction at the time of decay.

We measured the muon spectrum of  $\text{LiGaCr}_4\text{S}_8$  in zero applied field (ZF- $\mu\text{SR}$ ) and with a field applied longitudinally along the direction of the initial muon spin polarization (LF- $\mu\text{SR}$ ). Plots of the ZF- $\mu\text{SR}$  spectrum at  $T = 100 \text{ K}$  and  $1.9 \text{ K}$  are shown in Fig. 5.8(a), where the absence of an oscillatory signal indicates that there is no long range order present on the  $\mu\text{SR}$  timescale at either temperature. All of the ZF- $\mu\text{SR}$  curves were fitted to a two-component exponential fitting function



**Figure 5.8:** (a) ZF- $\mu$ SR data measured at  $T = 100\text{ K}$  (black squares) and  $1.9\text{ K}$  (red squares) and fitted curves (blue lines). (b) Temperature dependence of relaxation rates for ZF- $\mu$ SR scans. The inset indicates the shift of the weight between the two relaxation rates with temperature. (c) The damping of the relaxation rate corresponding to the magnetism with the longitudinal field at  $1.9\text{ K}$ .



described by

$$A(t) = A [Re^{-\lambda_1 t} + (1 - R) e^{-\lambda_2 t}] . \quad (5.4)$$

Here, the total asymmetry,  $A(t)$ , was fixed by measuring in a weak transverse field at 300 K, but the asymmetry ratio between the two components,  $R$ , was allowed to be temperature dependent. The two components were required due to a fast-relaxing component described by the relaxation rate  $\lambda_2$  that was present at all temperatures. This relaxation occurs on a timescale  $\sim 1\%$  of the muon time scale which could typically correspond to a dephasing of muons due to inhomogeneity and other sample-specific issues.

The slower-relaxing component,  $\lambda_1$ , is on a timescale comparable to the muon lifetime and peaks at a temperature that corresponds to the magnetic transition seen by neutron scattering. This suggests that this component of the  $\mu$ SR signal is related to the magnetism within the sample, and while no indication of long-range order is seen by  $\mu$ SR, the peak in the relaxation rate at  $T_f$  suggests that the measurement is sensitive to the magnetic transition. The magnetic state that is present at low temperature likely has a dynamic or disordered component that precludes the observation of oscillations in the ZF- $\mu$ SR measurements on the muon timescale.

In order to probe the dynamic magnetic properties, we performed LF- $\mu$ SR measurements at 1.9 K using fields of up to 0.3 T. The field dependence of the relaxation rate is shown in Fig. 5.8(c) and shows that the muon signal is decoupled in relatively small ( $< 0.05$  T) fields. This suggests that the spins are static on the muon time scale in agreement with the occurrence of spin freezing at low temperature in LiGaCr<sub>4</sub>S<sub>8</sub>.

### 5.3.6 Calculation of Mydosh parameter

The Mydosh parameter,  $\delta T_f$ , refers to the relative shift in freezing temperature with respect to the change in input a.c. frequency in an a.c. susceptibility measurement. Mathematically,  $\delta T_f = \Delta T_f / T_f \Delta[\log_{10}(\nu)]$ , where  $\Delta T_f = T_f(\nu_1) - T_f(\nu_2)$  and  $\Delta[\log_{10}(\nu)] = \log_{10}(\nu_1) - \log_{10}(\nu_2)$ . From the frequency dependence of the magnetic transition in LiGaCr<sub>4</sub>S<sub>8</sub> reported in chapter 4, we obtained the Mydosh parameter  $\sim 0.012$  for the input frequencies of 1129 Hz and 127 Hz. The value of Mydosh parameter is consistent with the value classical cluster glass system such as Zn<sub>3</sub>V<sub>3</sub>O<sub>8</sub> [126], and LiMn<sub>2</sub>O<sub>4</sub> [127].

## 5.4 First principles calculations

First principles calculations, using the generalized gradient approximation [91] within the all-electron linearized augmented plane-wave density functional theory code WIEN2K [90], were performed for a ferromagnetic configuration as well as several antiferromagnetic configurations. Internal coordinates not symmetry-dictated were relaxed within each magnetic state; spin-orbit coupling was not included and no Hubbard  $U$  was employed. An  $RK_{max}$  value of 8.0 was employed—this is the product of the smallest “muffin-tin” radius and the largest plane-wave vector. Sphere radii of 1.91, 1.95, 2.22 and 2.28 Bohr were used, respectively, for the S, Li, Ga, and Cr atoms.

All antiferromagnetic states modeled were insulating, with gaps ranging from 0.65 to 0.92 eV, while the ferromagnetic state was found a semi-metal, with band overlap of approximately 150 meV. All Cr local moments corresponded to  $S = 3/2$ , i.e. an ordered moment of  $3 \mu_B$ , although the (necessarily understated) moment within the spheres ranged between 2.67 and  $2.77 \mu_B$ . The energetics of all these states were mapped to the same Heisenberg model as in the work of Ghosh *et al.* [45].

We find the following respective values (in units of K) for  $J$ ,  $J'$ ,  $J_2$  and  $J_3$  (we have not attempted to distinguish  $J_{3a}$  and  $J_{3b}$  using DFT):  $-4.0$ ,  $-9.6$ ,  $+2.6$  and  $+6.0$ , where a  $-$  sign indicates ferromagnetic coupling. As observed experimentally, the first two exchange interactions are ferromagnetic but the latter antiferromagnetic, and in particular the large magnitude of  $J_3$ , along with its multiplicity of 12, overwhelms the ferromagnetic short-range interactions and precludes a long-range ferromagnetic order. This is reminiscent of our previous work on MnBi [128, 129, 130], where a short-range *antiferromagnetic* interaction is overwhelmed by longer-ranged, higher multiplicity ferromagnetic interactions, yielding a ferromagnetic ground state.

The strongly ferromagnetic short-range interactions offer strong support for the “ferromagnetic cluster” hypothesis advanced in the section 5.3.4, and we note that the strength of these interactions is comparable to the temperature of the susceptibility maximum in our earlier work on  $\text{LiGaCr}_4\text{S}_8$ , though we do not observe long-range order in the experiment.

Also noteworthy is that, as in the fits to experimental neutron-scattering data in the main text, very different results are obtained if one truncates the expansion at  $J$  and  $J'$ , with one being

ferromagnetic in sign and the other antiferromagnetic. This is indicative of the importance of long-range interactions, in particular  $J_3$ , at a distance of more than 7 Å.

## 5.5 Discussion and Conclusions

We have determined the magnetic interactions of the breathing-pyrochlore magnet  $\text{LiGaCr}_4\text{S}_8$  using neutron-scattering measurements. We find that further-neighbor interactions are large compared to oxide spinels [118], and play a crucial role in  $\text{LiGaCr}_4\text{S}_8$ . This behavior was predicted by DFT calculations [45]: our results broadly confirm these predictions, but also suggest how the accuracy of the DFT models may be improved. The comprehensive parameterization of further-neighbor interactions that we have obtained sets a benchmark for the quantitative interpretation of neutron-scattering data from polycrystalline samples. In particular, by fitting a physically-motivated interaction model simultaneously to temperature-dependent neutron-scattering data and to bulk susceptibility data, we obtain a robust solution despite the spherical averaging inherent to powder data.

Our results indicate that the origin of frustration in  $\text{LiGaCr}_4\text{S}_8$  is the formation of tetrahedral clusters due to a dominant ferromagnetic  $J'$  interaction, and the frustration of net antiferromagnetic inter-cluster interactions. The formation of the clusters is directly observed in inelastic neutron-scattering measurements *via* the development of a high-energy excitation that we identify as an essentially intra-cluster mode. We speculate that such high-energy modes may also be present in other materials where emergent clusters are coupled by frustrated interactions: examples include the quantum-spin-liquid candidate  $\text{Ca}_{10}\text{Cr}_7\text{O}_{28}$ , in which ferromagnetic interactions convert a stacked kagome lattice of spins into a triangular lattice of triangular clusters,[100] and the metallic frustrated magnet  $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$ , in which ferromagnetic interactions convert a hyperkagome lattice of spins into intersecting triangular rod lattices [101]. The observation of distinct low and high-energy excitations, associated respectively with inter-cluster and intra-cluster dynamics, may also present an analogy with the rotational and translational molecular dynamics in nonmagnetic phases such as plastic crystals [131].

The nature of the frozen magnetic phase in  $\text{LiGaCr}_4\text{S}_8$  below  $T_f$  is particularly intriguing. Frequency dependence of the magnetic transition in ac susceptibility measurements results the

value of Mydosh parameter  $\sim 0.02$ . This value is an order of magnitude larger than that of canonical spin-glass systems such as AuMn [132] and CuMn [133], but is compatible with the values for cluster-glass systems such as  $\text{Cr}_{0.5}\text{Fe}_{0.5}\text{Ga}$  [134],  $\text{Zn}_3\text{V}_3\text{O}_8$  [126], and  $\text{LiMn}_2\text{O}_4$  [127], suggesting that the thermodynamic behavior of  $\text{LiGaCr}_4\text{S}_8$  is cluster-glass-like. Given this, the evolution of our neutron-scattering measurements on traversing  $T_f$  is intriguing: the high-energy mode does not change intensity, whereas the low-energy excitations shift to the elastic line. This result suggests that the timescale of inter-cluster dynamics is greatly enhanced  $T_f$ , while that of the intra-cluster dynamics is unchanged. To the best of our knowledge, the observation of persistent intra-cluster dynamics in a cluster-glass-like state has not previously been reported. An interesting avenue for future research would, therefore, involve determining if such excitations occur in traditional cluster-glass materials, in which strong structural disorder typically generates clusters with a broad size distribution.

# Chapter 6

## Spin dynamics in skyrmion host lacunar spinel $\text{GaV}_4\text{S}_8$

In this chapter, the spin excitations in the lacunar spinel  $\text{GaV}_4\text{S}_8$  are studied using inelastic neutron scattering measurements in polycrystalline and single crystalline samples. The characteristic features of spin waves propagating along the high symmetry directions (110) and (001) are described. A spin model with competing symmetric and assymetric exchange (DM) interactions including Zeeman interaction explains the experimental data. The finding of the interaction parameters in  $\text{GaV}_4\text{S}_8$  provides an important information about the magnetic ground state in  $\text{GaV}_4\text{S}_8$ .

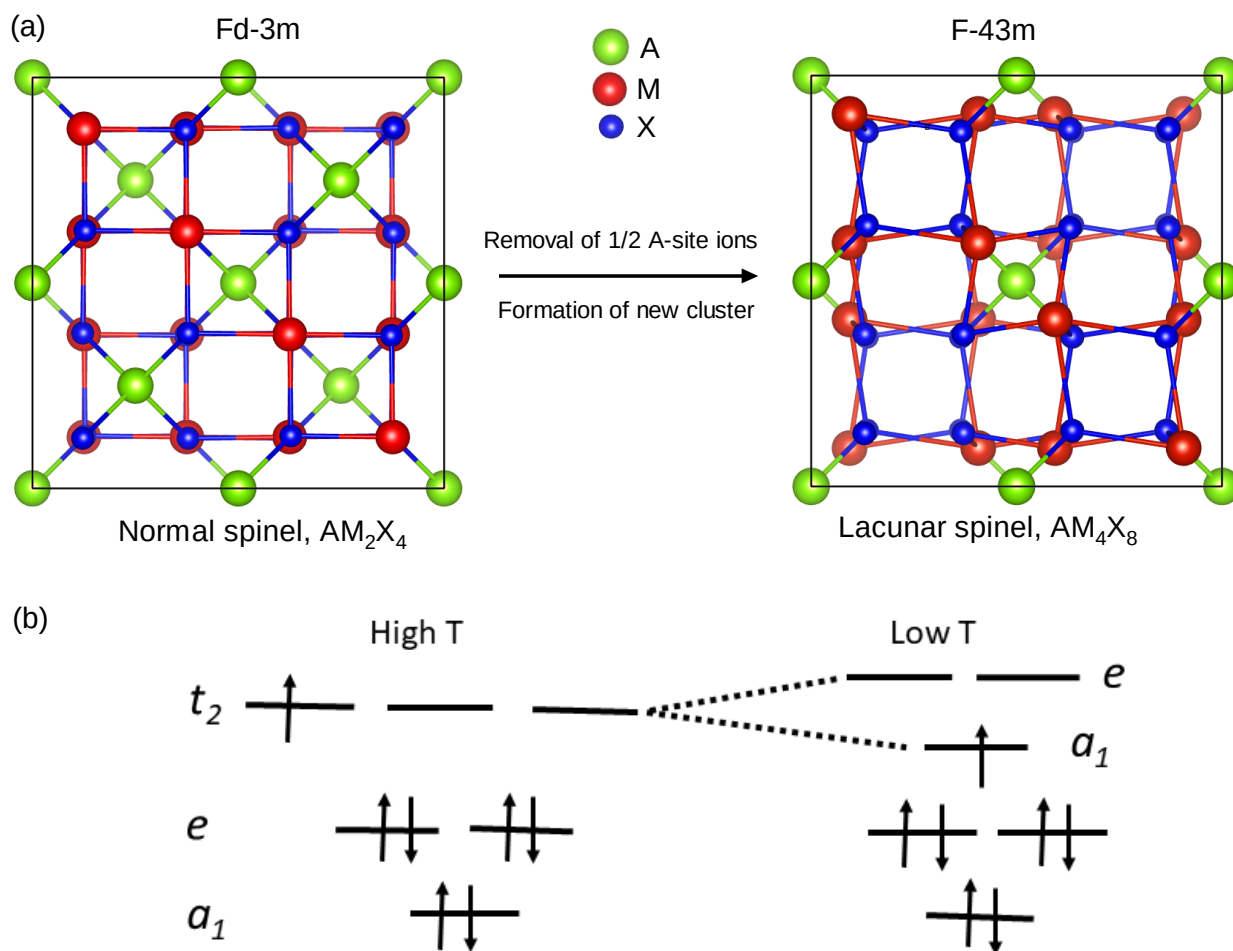
### 6.1 Introduction

The lacunar spinel compounds,  $\text{AM}_4\text{X}_8$  ( $\text{A} = \text{Ga, Ge}$ ;  $\text{M} = \text{V, Mo, Nb, and Ta}$ ;  $\text{X} = \text{S and Se}$ ), have attracted much attention in recent years due to their interesting and tunable properties such as multiferroicity [53, 57, 58], pressure induced superconductivity [59], large negative magnetoresistance [61], bandwidth-controlled metal-to-insulator transitions [60], skyrmion lattices [1, 53, 63], resistive switching via an electric-field induced transition [62], and a two-dimensional topological insulating state [64]. The main reason for such properties is the presence of weakly linked  $\text{M}_4\text{X}_4$  cubanes with orbital overlaps in between. The magnetism in  $\text{AM}_4\text{X}_8$  compounds is controlled by  $\text{M}_4$  tetrahedral metal clusters. As mentioned in chapter 2, the crystal structure of

lacunar spinel materials is derived by removing one-half of the cations in the alternating A-sites of the normal spinel structure (Fig. 6.1(a)). Due to the the ordered voids, the pyrochlore sublattices in the M-sites of a normal spinel material rearrange into a network of corner sharing large and small  $M_4$  tetrahedra in an  $AM_4X_8$  compound.

$GaV_4S_8$  is one of the exciting, intensively investigated lacunar spinels that exhibits a rich phase diagram with unconventional magnetic structures as shown in Fig. 2.5. Multiple ground states including the Néel-type skyrmion lattice (SKL), have been uncovered in the bulk crystalline state of  $GaV_4S_8$ . The SKL structure in  $GaV_4S_8$  nucleates out from the modulated cycloidal phase with the increase of the applied magnetic field, and it exists in a wider magnetic field and temperature range compared to the conventional SKL hosts. The vortices of the magnetic skyrmion in  $GaV_4S_8$  are confined along the easy axis of magnetization [1, 65]. The field stability range of the skyrmion and cycloidal phases depend on the direction of the magnetic field with respect to the rhombohedral axis. Multiple SKL and cycloidal phases can be supported in  $GaV_4S_8$  because of the different projections of the field along the four easy axis in rhombohedral symmetry [65, 135]. The experimental realization of bulk skyrmion ordering in  $GaV_4S_8$ , outside from typical helical magnets, provides a new opportunity to investigate the formation, manipulation and stabilization of such non-trivial spin textures.

The magnetic building block of  $GaV_4S_8$  is a  $V_4$  tetrahedral cluster, which has been described by the molecular orbital picture [54]. Due to the short V-V metal bond in the small  $V_4$  tetrahedra, V 3d-bands hybridize with each other, forming triply degenerate molecular  $t_2$  orbitals in the cubic phase at room temperature.  $GaV_4S_8$  exhibits  $t_2^1$  occupancy, suggesting strong orbitally active behavior. Below 44 K, the triply degenerate molecular  $t_2$  orbitals split into two sets of orbitals,  $a_1$  and  $e$ , following a collective Jahn-Teller distortion (Fig. 6.1(b)). The orbital  $a_1$  is more stable and is occupied by the unpaired electron in the emergent low temperature  $GaV_4S_8$  rhombohedral structure [136]. This molecular picture implies that the unpaired spin is distributed across the tetrahedral  $V_4$  cluster rather than localized on an individual V-site. The complex interplay of the spin, charge and lattice degree of freedom yields multiple magnetic phases below 13 K ( $T_c$ ) as described in previous paragraph. The material becomes multiferroic with the presence of spin-driven excess polarization in each magnetic state and the direction of the ferroelectric polarization overlaps with the direction of easy axis anisotropy [1]. Due to the absence of inversion symmetry in



**Figure 6.1:** (a) Formation of  $M_4$  clusters in a lacunar spinel structure from an ideal cubic spinel structure. (b) Molecular orbital diagrams of  $V_4$  cluster in  $GaV_4S_8$  with and without Jahn-Teller distortion.

the crystal structure, the allowed anisotropic exchange interactions compete with the ferromagnetic exchange interactions, stabilizing the modulated spin cycloidal state in  $\text{GaV}_4\text{S}_8$ .

The complex phase diagram and the presence of unconventional magnetic ground states in  $\text{GaV}_4\text{S}_8$  signify the importance of understanding spin dynamic properties as such properties enable understanding of the underlying spin-spin interactions. Here neutron scattering measurements are used to study the spin dynamics in powder and single crystals of  $\text{GaV}_4\text{S}_8$ . The powder averaged spin excitation spectrum shows a dispersive mode with the bandwidth of  $\sim 6$  meV. Single crystal inelastic neutron scattering data provided additional freedom to map the spin waves along the high symmetry directions (110) and (001). The spin excitation spectrum is modeled using a classical Heisenberg Hamiltonian including Dzyaloshinskii-Moria (DM) interactions in zero applied field. We observe a strong inter-tetrahedral ferromagnetic couplings between neighboring  $\text{V}_4$ -tetrahedra at 1.7 K. The modeling further indicates a significant contribution of DM interactions to the energy landscape of  $\text{GaV}_4\text{S}_8$ .

This chapter is structured as follows. I begin with a description of the experimental details of the sample synthesis. I then discuss the powder average spin excitation data as a function of temperature and incident energy. The sample co-alignment and the spin waves in the single crystals are described for the comprehensive understating of spin dynamics. Finally, I discuss the structural model to explain the key features of the magnetic excitation spectrum. In conclusion, I explain the general implication of my results.

## 6.2 Experimental details

Polycrystalline samples of  $\text{GaV}_4\text{S}_8$  were synthesized by solid state reaction. Stoichiometric amounts of Ga (99.999%), V (99.5%), and S (99.9995%), purchased from Alfa Aesar, were ground together inside a glove box and then pressed into a 0.5-inch diameter pellet. The pellet was heated at 1073 K for 24 hours. The heating rate was slow due to the vapor pressure of sulfur. The heating process was repeated until the laboratory X-ray diffraction patterns revealed a phase pure sample.

The single crystal growth was carried out using the chemical vapor transport (CVT) technique. An approximate five-weight percentage of iodine as a transport agent was mixed with a 2.5 gm polycrystalline sample of  $\text{GaV}_4\text{S}_8$  and then sealed in a quartz tube. The tube was placed inside a



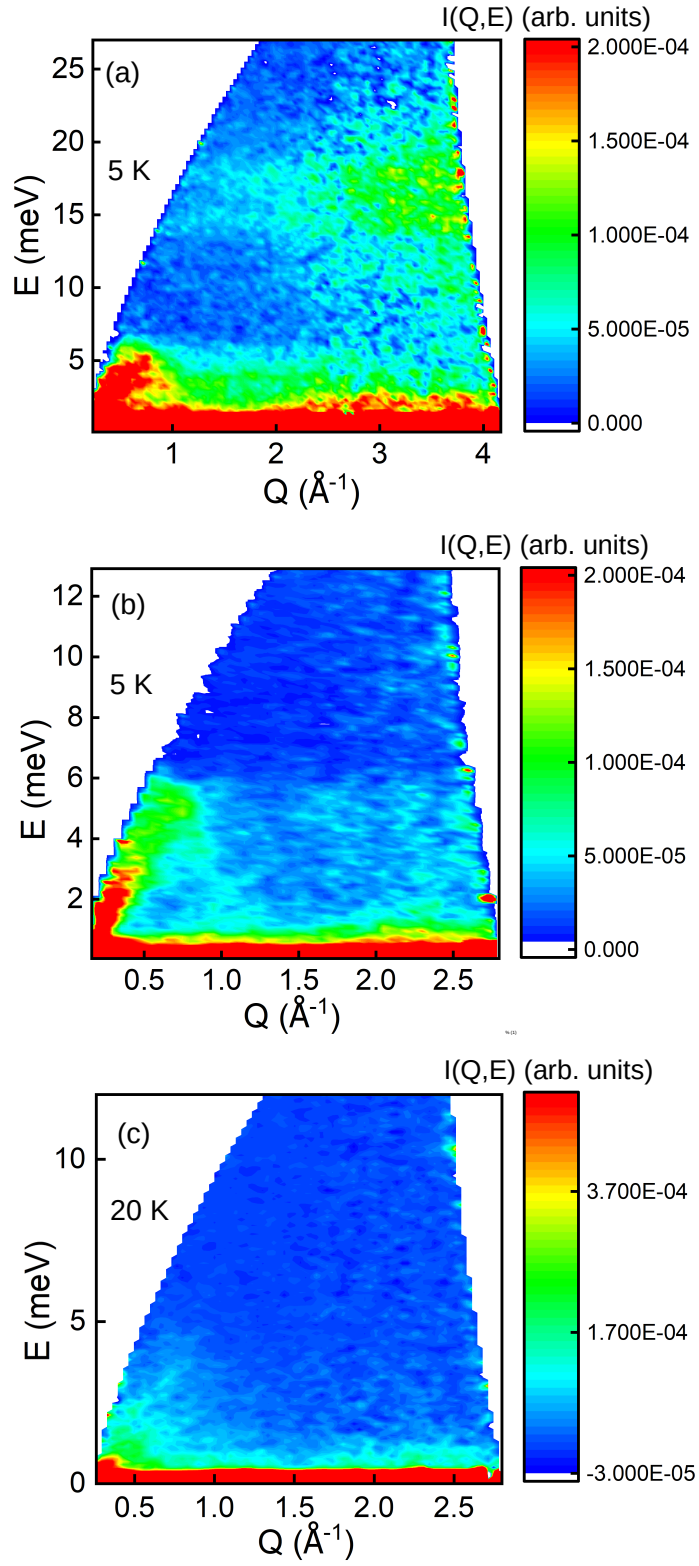
two-zone furnace for single crystal growth and then the temperature gradient maintained around 50 K. The growth period was kept about eight weeks.

Inelastic neutron scattering measurements on powder were performed with the Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA) [75] at Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL) with incident neutrons of energies  $E_i = 18$  and 40 meV. For the measurements, a finely ground polycrystalline sample with a mass of 5 g was packed inside an aluminum cylinder of  $\sim 9$  mm in diameter and then mounted on the sample holder of a closed-cycle refrigerator. The measurement was carried out in high-resolution mode with the frequency of the  $T_0$  chopper set to 60 Hz. The frequency of the Fermi chopper was fixed at 300 and 240 Hz for  $E_i = 40$  and 18 meV respectively. Single crystal inelastic neutron scattering data with a sample mass of 1.2 g were collected using the Multi-Axis Chopper Spectrometer (MACS) [137], NIST center for neutron research (NCNR). The details of the experiment for the single crystal measurements are discussed in the section 6.3.2.

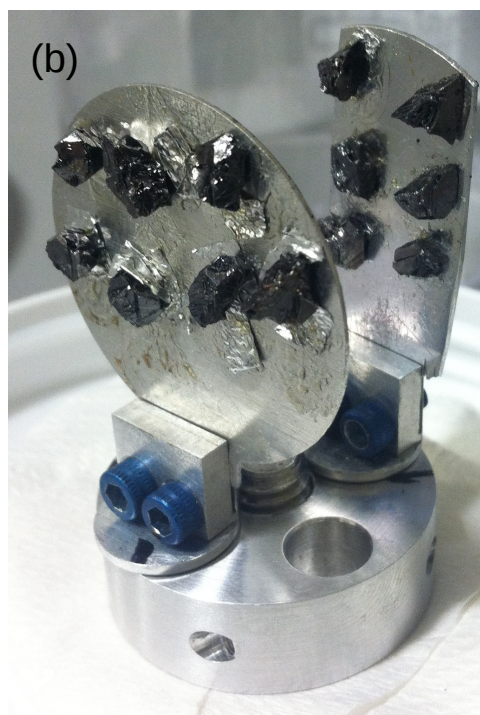
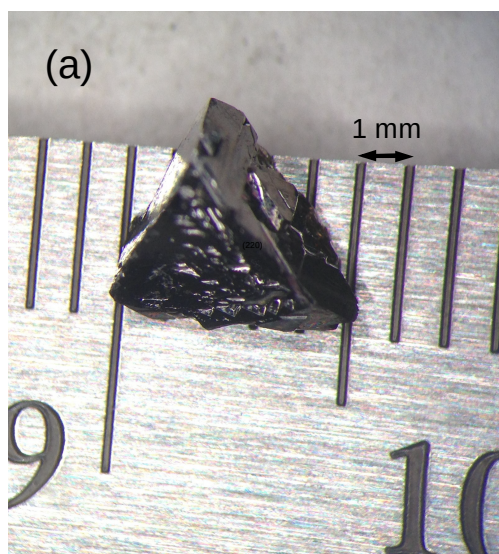
## 6.3 Results and discussion

### 6.3.1 Powder average spin excitation spectrum

The powder averaged inelastic neutron scattering (INS) spectra of  $\text{GaV}_4\text{S}_8$ , measured on the SEQUOIA instrument with  $E_i = 40$  and 18 meV at a temperature of 5 K, are shown in Fig. 6.2. The energy resolution of these measurements is approximately 3% of  $E_i$ . The data at 5 K shows a spin wave like excitation with energies ranging from 0 to 6 meV. The higher incident energy scattering data with  $E_i = 40$  meV is helpful for checking the possible existence of higher energy modes. No additional modes at higher energy were detected in these measurements. At 20 K, the spin wave like excitation disappears (Fig. 6.2(c)). However, weak diffuse inelastic scattering is observed at 20 K. This indicates that a weakly correlated paramagnetic state with diffusive spin dynamics exists in  $\text{GaV}_4\text{S}_8$  near to the ordering temperature. Achieving a comprehensive understanding of the spin wave spectrum challenging with only powder averaged data. Hence, the single crystal measurements are performed to gain further insight into the spin dynamics.



**Figure 6.2:** Spin excitation in 5 g polycrystalline sample of  $\text{GaV}_4\text{S}_8$  measured at (a) 5 K with  $E_i = 40$  meV (b) 5 K with  $E_i = 18$  meV (c) 20 K with  $E_i = 18$  meV.



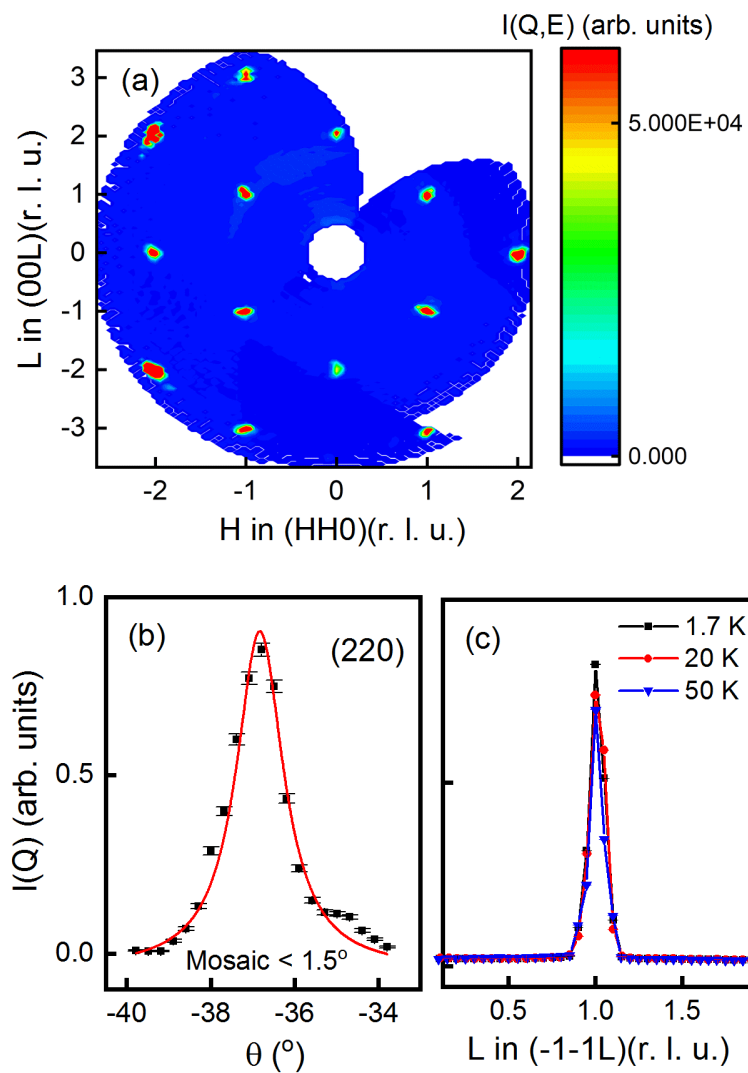
**Figure 6.3:** (a) Single crystal of GaV<sub>4</sub>S<sub>8</sub>. (b) Co-aligned array of single crystals along the scattering plane (HHL) horizontal.

### 6.3.2 Measurement of the spin excitation spectra in single crystal samples

Single crystals with an average mass of approximately 100 mg were grown via the CVT technique. An image of a laboratory-grown  $\text{GaV}_4\text{S}_8$  single crystal is shown in Fig. 6.3(a). A larger sample mass is necessary to achieve an adequate intensity of inelastically scattered neutrons since the ordered moment of each  $\text{V}_4$  tetrahedra in  $\text{GaV}_4\text{S}_8$  is small ( $0.8 \mu_B/\text{f.u.}$ ). Therefore, we co-aligned our 14 best single crystals making the total sample mass around 1.2 g (Fig. 6.3(b)). The crystals were co-aligned on two parallel plates with the scattering plane (HHL) horizontal using the neutron diffractometer CG-1B at HFIR, ORNL and then inelastic neutron scattering (INS) measurements were carried out at MACS, NCNR [137]. The wide  $|Q|$ -coverage of MACS along the scattering plane allows mapping of the spin excitation spectrum as a function of momentum transfer  $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$  and energy transfer  $E = E_i - E_f$  in a broad range of momentum space. At MACS, The sample was mounted in an orange cryostat with the (HHL) scattering plane horizontal and then cooled to 1.7 K. A Be-filter was inserted in the path of scattered neutrons before analyser. To cover a large momentum space, the sample was rotated about the vertical axis with steps of  $2^\circ$  over a range of  $120^\circ$ . The measurements were performed with a fixed final energy,  $E_f$ , of 5 meV. The energy of the incident neutrons was varied in the range of 5-12 meV to capture the complete excitation spectrum. An empty holder data set was also collected with the same experimental configuration. The energy resolution of these measurements varies in the range of  $\sim 0.5$ -1.8 meV based on the value of incident neutron energy. All the scattering data are analyzed after subtracting the empty holder measurements using Dave software [106].

Elastic scattering peaks, obtained from the co-aligned single crystals at MACS in the (HHL) scattering plane, are shown in Fig. 6.4(a-c). The elastic neutron scattering pattern at 300 K shows no additional scattering outside from the expected Bragg diffraction peaks. The overall crystal mosaic of the co-aligned single crystals is  $\leq 1.5^\circ$ . The temperature dependence of (-1-11) peak intensity, 6.4(c), reveals that the elastic scattering intensity increases slightly at 1.7 K compared to 20 K and 50 K.

The inelastic neutron scattering data at 1.7 K are summarized in Fig. 6.5 and 6.6. The typical energy-momentum slices along the high symmetry axes in  $Q$  space, which are parallel to the (001) and (110) directions, are shown in Fig. 6.5(a) and 6.5(b). Spin waves emanating from the magnetic



**Figure 6.4:** (a) elastic neutron scattering pattern in the (HHL) plane from co-aligned single crystals of  $\text{GaV}_4\text{S}_8$  (b) (220) peak showing the mosaic from the co-aligned single crystals. (c) temperature dependence of (-1-11) peak intensity.

peaks which are either overlapping with lattice Bragg peaks or extremely close to the lattice Bragg peaks are observed. The bandwidth of the spin excitation spectrum is approximately 5.7 meV. The spin excitations are somewhat broad, but this is consistent with the energy resolution of the measurements. The spin wave propagating along the (-1-1L) direction rises smoothly to a peak at the zone boundary whereas along the (HH-1) direction a broad sloped maximum occurs. A constant energy slice at 3 meV of the spin wave spectrum in the (HHL) plane is shown in Fig. 6.5(c).

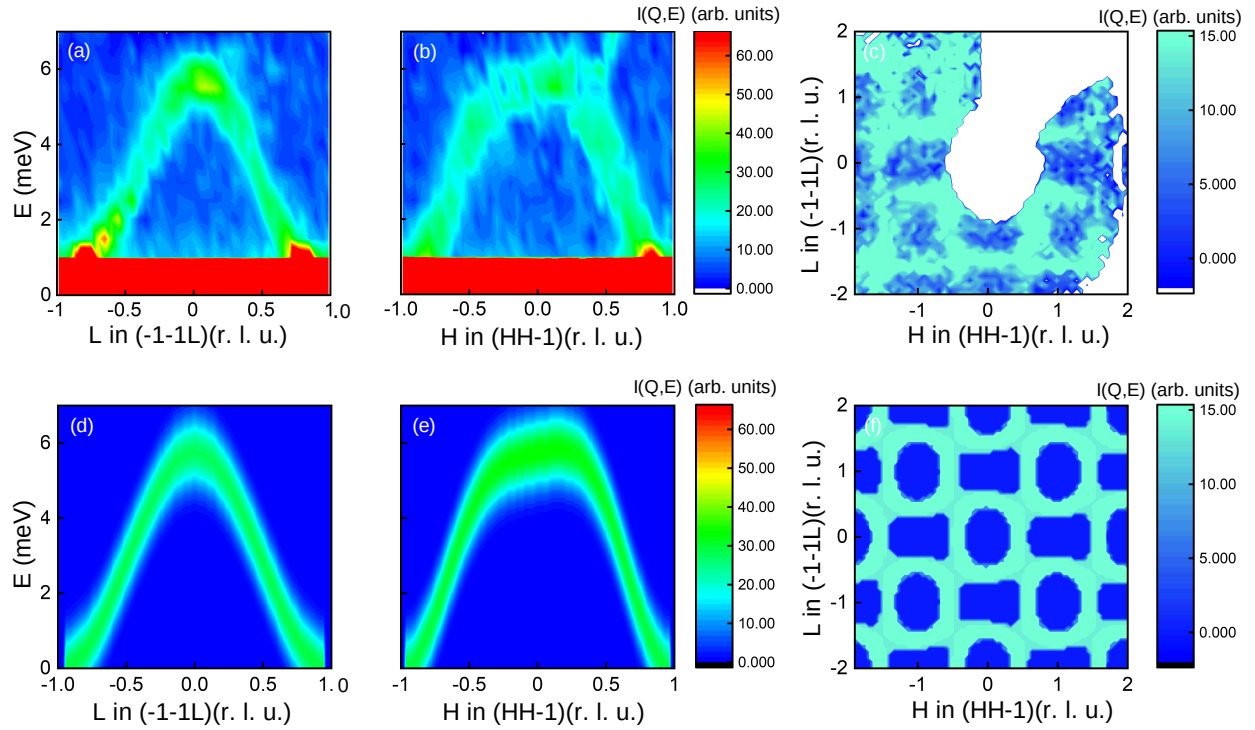
The line-cuts of the spin excitation spectrum as a function of energy and momentum, parallel to the (001) and (110) directions, are shown in Fig. 6.6(a-d). The line-cuts as a function of energy show a single inelastic peak at the zone boundary. Away from the zone boundary, there are two inelastic peaks at all energies. These peaks are non-symmetric about the high symmetry point X (Brillouin-zone boundary) in reciprocal space for the spin waves propagating along (110) direction. But the inelastic peaks corresponding to the spin waves propagating parallel to (001) direction are completely symmetric about X. Fig. 6.6(c) shows the constant  $|Q|$ -cuts of the spin wave spectrum along the (-1-1L) direction. Additionally, the temperature-dependent constant energy cuts in Fig. 6.6(d) show that the spin wave excitation no longer exists at 20 K and above.

### 6.3.3 Spin model

To determine the values of the exchange constants in  $\text{GaV}_4\text{S}_8$ , we compare our data to the spin-dynamic structure factor calculations performed under the assumptions of linear spin wave theory using the SpinW software package [123]. The spin excitation spectrum is calculated for an FCC lattice including the nearest-neighbor (NN) exchange and DM interactions:

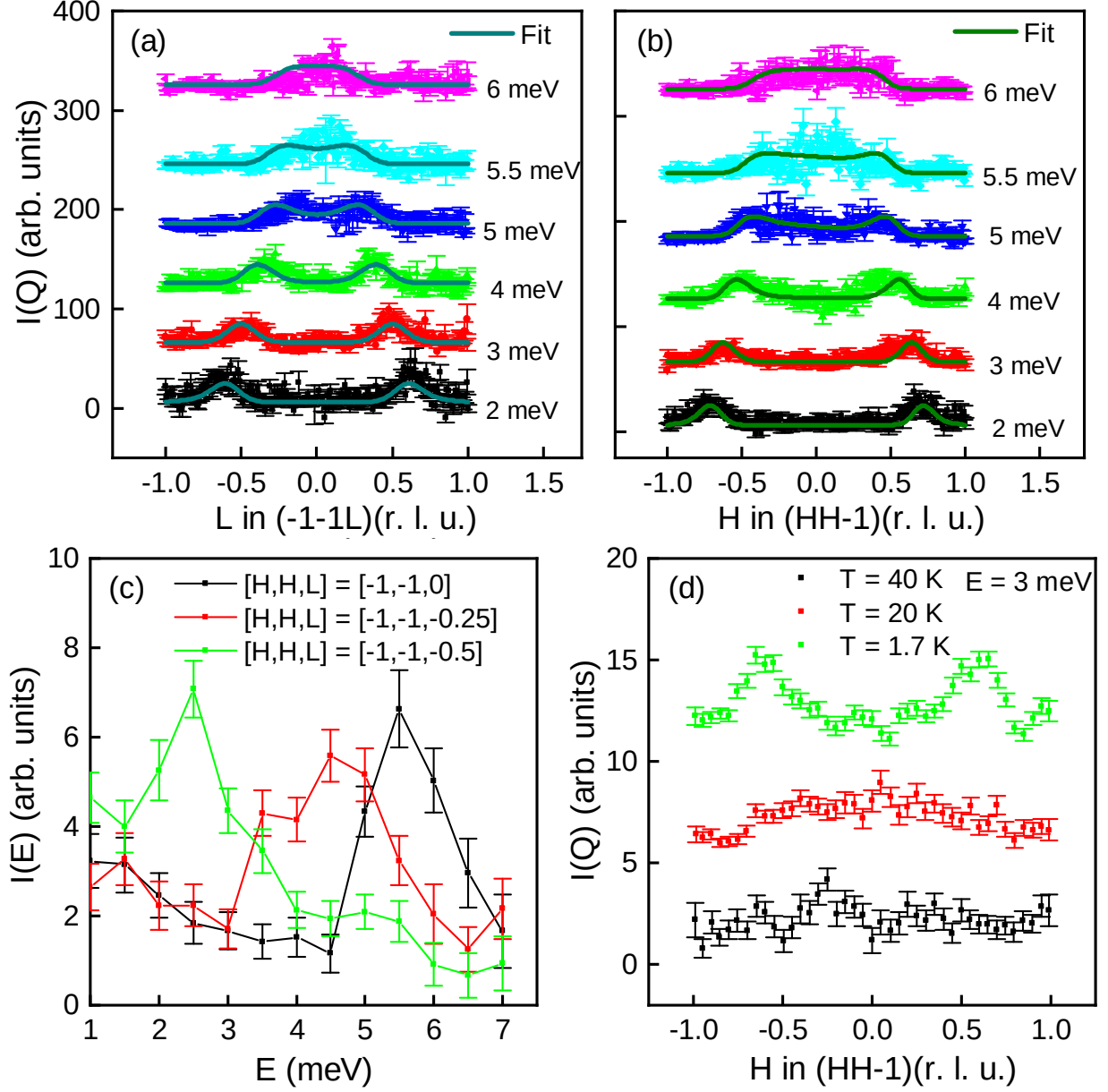
$$H = \sum_{\langle ij \rangle} J \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{\langle ij \rangle} \mathbf{D}(\mathbf{S}_i \times \mathbf{S}_j) \quad (6.1)$$

Where the angle bracket  $\langle \rangle$  represents the NN.  $i$  and  $j$  in equation (6.1) are the lattice sites representing the center of mass of the neighboring  $\text{V}_4$  tetrahedra. The lattice formed by the small  $\text{V}_4$  tetrahedra in  $\text{GaV}_4\text{S}_8$  is a face-centered cubic as shown in Fig. 6.7. Our model assumes that a single spin is distributed uniformly across the  $\text{V}_4$  entire tetrahedra, hence we consider a spin-1/2 moment localized at the center of mass of each tetrahedra in the linear spin wave calculations.



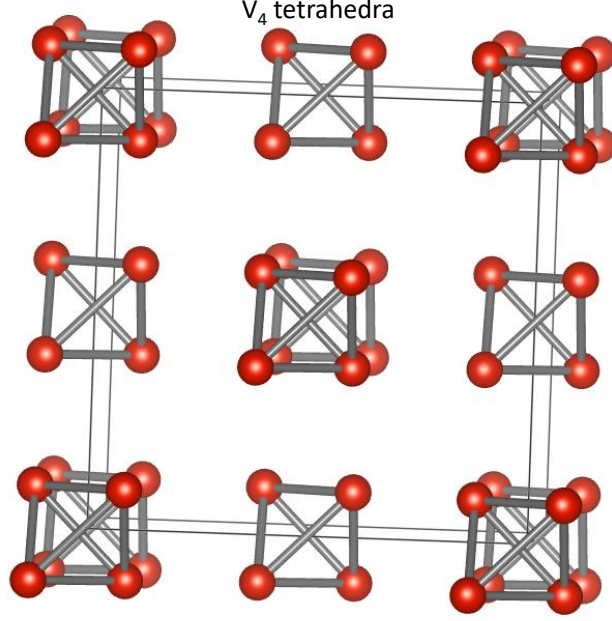
**Figure 6.5:** Spin wave dispersion along the (a)  $(-1-1L)$  (b)  $(HH-1)$  directions. (c) Constant energy slice ( $E = 3$  meV) of spin excitation spectrum in  $(HHL)$  plane. Simulated spin wave excitation spectrum along the (d)  $(-1-1L)$  (e)  $(HH-1)$  direction. (f) Simulated constant energy slice at  $E = 3$  meV in the  $(HHL)$  plane.





**Figure 6.6:** Experimental and calculated constant E-cuts at temperature of 1.7 K (a) along  $(-1-1L)$  direction (b) along  $(HH-1)$  direction. (c) Constant  $|Q|$ -cuts at different regions along the  $(-1-1L)$  direction. (d) Constant energy cuts as a function of temperature along  $(HH-1)$  direction.





**Figure 6.7:** Unit cell of an FCC lattice of  $V_4$  tetrahedra in  $GaV_4S_8$ .

While the molecular orbital picture provides some basis for this approach [54, 138], there are in principle deviations due to the orbital ordering transition at 44 K [53, 65]. However, the transition at 44 K results in structural domains such that deviations from the above picture are averaged over with the result that the model provides a reasonable parameterization of the data. The simulated spin excitation spectra are shown in the lower panels of Fig. 6.5. The energy scale and the features of the calculated excitation spectrum are consistent with the experimental data. Fitting the calculated values to the experimental data using  $\chi^2$ -minimization technique, we obtain the following optimized parameters:

$$J = -0.70(3) \text{ meV} \quad \text{and} \quad D = 0.10(3) \text{ meV} \quad (6.2)$$

The optimized value of  $J$  indicates that the neighboring  $V_4$  tetrahedra are coupled with each other ferromagnetically, as expected for a ground state that is ferromagnetic or very nearly so. Additionally, a significant DM interaction is indicated by the modeling of  $GaV_4S_8$  at 1.7 K. As the existence of a ferromagnetic ground state is reported in some literature at zero applied magnetic field [54, 139], we checked our calculations without adding DM interaction in the classical NN

Heisenberg Hamiltonian. With this simplification, the model is unable to reproduce the weakly sloped feature along (110) direction.

## 6.4 Conclusion

In summary, we have successfully grown large single crystals of  $\text{GaV}_4\text{S}_8$  of sufficient size for the experimental investigation of the spin dynamics with inelastic neutron scattering. Inelastic neutron scattering measurements in polycrystalline and single-crystalline sample of  $\text{GaV}_4\text{S}_8$  reveals a well-defined spin excitation spectrum with a zone boundary energy of 5.7 meV. A structural model with competing symmetric and antisymmetric exchange interactions reproduces the experimentally measured spin excitation spectra in zero magnetic field. We find ferromagnetic couplings ( $J = -0.70(3)$  meV) between neighboring  $\text{V}_4$  tetrahedra. The simulation further reveals that the DM interactions are around 15% of the NN exchange interactions.

# Chapter 7

## Conclusions

This dissertation presents a comprehensive study of physical and magnetic properties of the Cr-spinel material  $\text{LiGaCr}_4\text{S}_8$ . Additionally, this dissertation describes an investigation of the spin dynamics in the lacunar spinel  $\text{GaV}_4\text{S}_8$ . Both these materials crystallize in a non-centrosymmetric cubic spinel structure at room temperature.

The Cr-based spinel material  $\text{LiGaCr}_4\text{S}_8$  is successfully synthesized using a conventional solid-state reaction technique. A thorough investigation of this material is completed using neutron scattering measurements along with X-ray diffraction, magnetic susceptibility, muon spin resonance, and heat capacity measurements. We find that the Cr-spinel material  $\text{LiGaCr}_4\text{S}_8$  forms a breathing pyrochlore lattice with the tetrahedral A-sites alternately occupied by the inequivalent cations  $\text{Li}^+$  and  $\text{Ga}^{3+}$ . The ordering of A-site cations modifies the NN Cr-Cr distance by 7.5% in the large and small  $\text{Cr}_4$  tetrahedra. Negative thermal expansion (NTE) is observed in the temperature range 111(4) K to 12(2) K. The magnetic susceptibility deviates from Curie-Weiss behavior around 110 K and is accompanied by the departure from normal thermal expansion. Below 12(2) K, a magnetic transition appears with the bifurcation of field-cooled and zero field-cooled susceptibility. A phase with slow dynamics exists below 12(2) K and is accompanied by the return to normal thermal expansion. All these experimental observations indicate the presence of strong magnetoelastic coupling in  $\text{LiGaCr}_4\text{S}_8$ .

Neutron scattering measurements are used to determine the magnetic interactions in the breathing-pyrochlore magnet  $\text{LiGaCr}_4\text{S}_8$ . We obtain a ground state solution by fitting a spin model simultaneously to the temperature-dependent diffuse magnetic scattering and magnetic

susceptibility. We find that the nearest neighbor interactions within the large and small tetrahedra are ferromagnetic and are insufficient to completely describe the energy landscape in  $\text{LiGaCr}_4\text{S}_8$ . Further-neighbor interactions to  $3^{rd}$  NN are significant and play a crucial role to control the ground state in  $\text{LiGaCr}_4\text{S}_8$ . Our structural model is consistent with the DFT calculation. The strongest interaction is a ferromagnetic interaction within the large  $\text{Cr}_4$  tetrahedra. While smaller, the interaction within the smaller tetrahedra is also ferromagnetic. Despite this,  $\text{LiGaCr}_4\text{S}_8$  does not exhibit long range order. Rather it appears that the spins within the large tetrahedra essentially align with each other forming a  $S' \approx 6$  cluster. The emergent cluster occupies the FCC lattice positions and couples with each other antiferromagnetically due to the presence of strong further neighbor antiferromagnetic interactions. The cluster frustration, as a consequence of inter-cluster antiferromagnetic couplings in FCC lattice, yields a phase with slow spin dynamics below 12(2) K. Therefore, our investigation offers an important insight into the influence of further neighboring interactions driving the formation of frustrated spin clusters.

Another important result of this dissertation is the successful growth of single crystals of skyrmion host lacunar spinel material  $\text{GaV}_4\text{S}_8$ . Using the CVT growth technique, I have grown large single crystals of  $\text{GaV}_4\text{S}_8$ . To investigate the spin dynamic structure, inelastic neutron scattering measurements were carried out on the polycrystalline and single-crystalline samples of  $\text{GaV}_4\text{S}_8$ . We observe well-defined spin excitations propagating along the high symmetry directions (001) and (110) at the 1.7 K. We use a spin Hamiltonian with nearest-neighbor exchange and DM interactions to simulate the experimentally observed spin excitation spectrum. The optimized spin model shows strong ferromagnetic inter-tetrahedral couplings between  $\text{V}_4$  tetrahedra in  $\text{GaV}_4\text{S}_8$ . A careful analysis of spin fluctuations in single-crystal reveals that the presence of DM interaction introduces asymmetry about the high symmetry point X to the spin waves along the (110) direction.

# **Bibliography**

- [1] I. Kézsmárki, S. Bordács, P. Milde, E. Neuber, L. M. Eng, J. S. White, H. M. Rønnow, C. D. Dewhurst, M. Mochizuki, K. Yanai, H. Nakamura, D. Ehlers, V. Tsurkan, and A. Loidl. Néel-type skyrmion lattice with confined orientation in the polar magnetic semiconductor  $\text{GaV}_4\text{S}_8$ . *Nature Materials*, 14(1116), 2015. [xi](#), [1](#), [6](#), [11](#), [12](#), [19](#), [21](#), [22](#), [37](#), [81](#), [82](#)
- [2] Taro Nakajima, Hiroshi Oike, Akiko Kikkawa, Elliot P. Gilbert, Norman Booth, Kazuhisa Kakurai, Yasujiro Taguchi, Yoshinori Tokura, Fumitaka Kagawa, and Taka-hisa Arima. Skyrmion lattice structural transition in MnSi. *Science Advances*, 3(6), 2017. [1](#)
- [3] A S Cameron, Y V Tymoshenko, P Y Portnichenko, J Gavilano, V Tsurkan, V Felea, A Loidl, S Zherlitsyn, J Wosnitza, and D S Inosov. Magnetic phase diagram of the helimagnetic spinel compound  $\text{ZnCr}_2\text{Se}_4$  revisited by small-angle neutron scattering. *Journal of Physics Condensed Matter*, 28(14):146001, 2016. [1](#), [6](#), [37](#)
- [4] Shang Gao, Oksana Zaharko, Vladimir Tsurkan, Yixi Su, Jonathan S. White, Gregory S. Tucker, Bertrand Roessli, Frederic Bourdarot, Romain Sibille, Dmitry Chernyshov, Tom Fennell, Alois Loidl, and Christian Rüegg. Spiral spin-liquid and the emergence of a vortex-like state in  $\text{MnSc}_2\text{S}_4$ . *Nature Physics*, 13:pp. 157–161, 2017. [1](#)
- [5] Steven T. Bramwell and Michel J. P. Gingras. Spin ice state in frustrated magnetic pyrochlore materials. *Science*, 294(5546):1495–1501, 2001. [1](#)
- [6] stephen blundell. Magnetism in condensed matter. (Oxford University Press, New York), 2001. [2](#), [3](#)
- [7] Frédéric Mila Philippe Mendels, Claudine Lacroix. Introduction to frustrated magnetism. *Springer Series in Solid-State Sciences*, 164, 2011. [3](#), [5](#), [6](#)
- [8] G. H. Wannier. Antiferromagnetism. the triangular ising net. *Phys. Rev.*, 79(2):357–364, 1950. [3](#)
- [9] Doron Bergman, Jason Alicea, Emanuel Gull, Simon Trebst, and Leon Balents. Order-by-disorder and spiral spin-liquid in frustrated diamond-lattice antiferromagnets. *Nature Physics*, 3:487–491, 2007. [5](#), [6](#), [12](#)

- [10] Arvind Yogi, A. K. Bera, Ashwin Mohan, Ruta Kulkarni, S. M. Yusuf, A. Hoser, A. A. Tsirlin, M. Isobe, and A. Thamizhavel. Zigzag spin chains in the spin-5/2 antiferromagnet  $\text{Ba}_2\text{Mn}(\text{PO}_4)_2$ . *Inorg. Chem. Front.*, 6(10):2736–2746, 2019. [6](#)
- [11] E. S. Klyushina, B. Lake, A. T. M. N. Islam, J. T. Park, A. Schneidewind, T. Guidi, E. A. Goremychkin, B. Klemke, and M. Månsson. Investigation of the spin-1 honeycomb antiferromagnet  $\text{BaNi}_2\text{V}_2\text{O}_8$  with easy-plane anisotropy. *Phys. Rev. B*, 96:p. 214428, 2017. [6](#)
- [12] J. Bertinshaw, C. Ulrich, A. Günther, F. Schrettle, M. Wohlaue, S. Krohns, M. Reehuis, A. J. Studer, M. Avdeev, D. V. Quach, J. R. Groza, V. Tsurkan, A. Loidl, and J. Deisenhofer.  $\text{FeCr}_2\text{S}_4$  in magnetic fields: possible evidence for a multiferroic ground state. *Scientific Reports*, 4(6079), 2014. [6](#), [8](#), [37](#)
- [13] K. Dey, A. Indra, A. Karmakar, and S. Giri. Multicaloric effect in multiferroic sulpho spinel  $\text{MCr}_2\text{S}_4$  (M=Fe Co). *Journal of Magnetism and Magnetic Materials*, 498:166090, 2020. [6](#)
- [14] J. Bertinshaw, C. Ulrich, A. Günther, F. Schrettle, M. Wohlaue, S. Krohns, M. Reehuis, A. J. Studer, M. Avdeev, D. V. Quach, J. R. Groza, V. Tsurkan, A. Loidl, and J. Deisenhofer.  $\text{FeCr}_2\text{S}_4$  in magnetic fields: possible evidence for a multiferroic ground state. *Scientific Reports*, 4:6079, 2014. [6](#)
- [15] H. Okada, K. Koyama, M. Hedo, Y. Uwatoko, and K. Watanabe. Pressure-induced metal insulator transition in spinel compound  $\text{CuV}_2\text{S}_4$ . *Physica B: Condensed Matter*, 403(5): 1612 – 1613, 2008. [6](#)
- [16] H. Ishibashi, T. Sakai, and K. Nakahigashi. X-ray diffraction study on spinel compound  $\text{CuIr}_2\text{S}_4$  with metal insulator transition. *Journal of Magnetism and Magnetic Materials*, 226-230(1):233 – 234, 2001. [6](#)
- [17] Huixia Luo, Tomasz Klimczuk, Lukas Muehler, Leslie Schoop, Daigorou Hirai, M. K. Fuccillo, C. Felser, and R. J. Cava. Superconductivity in the  $\text{Cu}(\text{Ir}_{1-x}\text{Pt}_x)_2\text{Se}_4$  spinel. *Phys. Rev. B*, 87(21):214510, 2013. [6](#)

- [18] Weiwei Xie and Huixia Luo. Magnetic spinels - synthesis, properties and applications, chapter-6. *InTech*, 2017. [6](#)
- [19] S. Weber, P. Lunkenheimer, R. Fichtl, J. Hemberger, V. Tsurkan, and A. Loidl. Colossal magnetocapacitance and colossal magnetoresistance in  $\text{HgCr}_2\text{S}_4$ . *Phys. Rev. Lett.*, 96: 157202, 2006. [6](#), [37](#)
- [20] J. Hemberger, H.-A. Krug von Nidda, V. Tsurkan, and A. Loidl. Large magnetostriction and negative thermal expansion in the frustrated antiferromagnet  $\text{ZnCr}_2\text{Se}_4$ . *Phys. Rev. Lett.*, 98:147203, 2007. [6](#), [37](#), [40](#), [44](#), [55](#)
- [21] Gang Chen, Leon Balents, and Andreas P. Schnyder. Spin-orbital singlet and quantum critical point on the diamond lattice:  $\text{FeSc}_2\text{S}_4$ . *Phys. Rev. Lett.*, 102:096406, 2009. [6](#)
- [22] N Bättgen, J Hemberger, V Fritsch, A Krimmel, M Mücksch, H-A Krug von Nidda, P Lunkenheimer, R Fichtl, V Tsurkan, and A Loidl. Orbital physics in sulfur spinels: ordered, liquid and glassy ground states. *New Journal of Physics*, 6(1):191, 2004. [6](#), [7](#), [8](#), [37](#)
- [23] Hidenori Takagi and Seiji Niitaka. *Highly Frustrated Magnetism in Spinels*, pages 155–175. springer Berlin Heidelberg, 2011. [6](#), [56](#)
- [24] V. Fritsch, J. Hemberger, N. Büttgen, E.-W. Scheidt, H.-A. Krug von Nidda, A. Loidl, and V. Tsurkan. Spin and orbital frustration in  $\text{MnSc}_2\text{S}_4$  and  $\text{FeSc}_2\text{S}_4$ . *Phys. Rev. Lett.*, 92: 116401, 2004. [6](#), [7](#), [37](#)
- [25] L. Mittelstädt, M. Schmidt, Zhe Wang, F. Mayr, V. Tsurkan, P. Lunkenheimer, D. Ish, L. Balents, J. Deisenhofer, and A. Loidl. Spin-orbiton and quantum criticality in  $\text{FeSc}_2\text{S}_4$ . *Phys. Rev. B*, 91:125112, 2015. [7](#)
- [26] Y. V. Tymoshenko, Y. A. Onykienko, T. Müller, R. Thomale, S. Rachel, A. S. Cameron, P. Y. Portnichenko, D. V. Efremov, V. Tsurkan, D. L. Abernathy, J. Ollivier, A. Schneidewind, A. Piovano, V. Felea, A. Loidl, and D. S. Inosov. Pseudo-goldstone magnons in the frustrated  $S=3/2$  heisenberg helimagnet  $\text{ZnCr}_2\text{Se}_4$  with a pyrochlore magnetic sublattice. *Phys. Rev. X*, 7:041049, 2017. [7](#)



- [27] Kurt E. Sickafus, John M. Wills, and Norman W. Grimes. Structure of spinel. *Journal of the American Ceramic Society*, 82(12):3279–3292, 1999. [7](#)
- [28] A. N. Yaresko. Electronic band structure and exchange coupling constants in  $\text{ACr}_2\text{X}_4$  spinels ( $\text{A}=\text{Zn}, \text{Cd}, \text{Hg}$ ;  $\text{X}=\text{O}, \text{S}, \text{Se}$ ). *Phys. Rev. B*, 77:115106, 2008. [7](#), [16](#), [37](#), [56](#)
- [29] Brent C. Melot. Phd dissertation entitled "competing magnetic interactions in complex oxides". *UNIVERSITY of CALIFORNIA, Santa Barbara*, 2010. [7](#), [8](#)
- [30] Ola Hartmann, Georg Michael Kalvius, Roger Wäppling, Axel Günther, Vladimir Tsurkan, Alex Krimmel, and Alois Loidl. Magnetic properties of the multiferroic chromium thio-spinels  $\text{CdCr}_2\text{S}_4$  and  $\text{HgCr}_2\text{S}_4$ . *The European Physical Journal B*, 86(4), 2013. [8](#)
- [31] Alexander Ruff, Zhaosheng Wang, Sergei Zherlitsyn, Joachim Wosnitza, Stephan Krohns, Hans-Albrecht Krug von Nidda, Peter Lunkenheimer, Vladimir Tsurkan, and Alois Loidl. Multiferroic spin-superfluid and spin-supersolid phases in  $\text{MnCr}_2\text{S}_4$ . *Phys. Rev. B*, 100: 014404, 2019. [8](#)
- [32] Suguru Kitani, Makoto Tachibana, and Hitoshi Kawaji. Spin-glass-like behavior in ferromagnetic phase of  $\text{CdCr}_2\text{S}_4$ . *Solid State Communications*, 179:16 – 19, 2014. [8](#)
- [33] Yoshihiko Okamoto, Gøran J. Nilsen, J. Paul Attfield, and Zenji Hiroi. Breathing pyrochlore lattice realized in  $a$ -site ordered spinel oxides  $\text{LiGaCr}_4\text{O}_8$  and  $\text{LiInCr}_4\text{O}_8$ . *Phys. Rev. Lett.*, 110:097203, 2013. [10](#), [11](#), [12](#), [14](#), [37](#), [39](#), [40](#), [41](#), [49](#), [56](#), [59](#), [60](#)
- [34] J. G. Rau, L. S. Wu, A. F. May, L. Poudel, B. Winn, V. O. Garlea, A. Huq, P. Whitfield, A. E. Taylor, M. D. Lumsden, M. J. P. Gingras, and A. D. Christianson. Anisotropic exchange within decoupled tetrahedra in the quantum breathing pyrochlore  $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$ . *Phys. Rev. Lett.*, 116:257204, 2016. [11](#), [37](#), [60](#)
- [35] J G Rau, L S Wu, A F May, A E Taylor, I-Lin Liu, J Higgins, N P Butch, K A Ross, H S Nair, M D Lumsden, M J P Gingras, and A D Christianson. Behavior of the breathing pyrochlore lattice  $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$  in applied magnetic field. *J. Phys.: Condens. Matter*, 30(45):455801, 2018. [11](#), [60](#)

- [36] T. Haku, M. Soda, M. Sera, K. Kimura, J. Taylor, S. Itoh, T. Yokoo, Y. Matsumoto, D. Yu, R. A. Mole, T. Takeuchi, S. Nakatsuji, Y. Kono, T. Sakakibara, L.-J. Chang, and T. Masuda. Neutron scattering study in breathing pyrochlore antiferromagnet  $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$ . *Journal of Physics: Conference Series*, 828(1):012018, 2017. [11](#)
- [37] Yoshihiko Okamoto, Masaki Mori, Naoyuki Katayama, Atsushi Miyake, Masashi Tokunaga, Akira Matsuo, Koichi Kindo, and Koshi Takenaka. Magnetic and structural properties of a-site ordered chromium spinel sulfides: Alternating antiferromagnetic and ferromagnetic interactions in the breathing pyrochlore lattice. *Journal of the Physical Society of Japan*, 87(3):034709, 2018. [11](#), [16](#), [39](#), [41](#), [51](#), [60](#)
- [38] Lucile Savary, Xiaoqun Wang, Hae-Young Kee, Yong Baek Kim, Yue Yu, and Gang Chen. Quantum spin ice on the breathing pyrochlore lattice. *Phys. Rev. B*, 94:075146, 2016. [11](#), [37](#)
- [39] R. Wawrzyńczak, Y. Tanaka, M. Yoshida, Y. Okamoto, P. Manuel, N. Casati, Z. Hiroi, M. Takigawa, and G. J. Nilsen. Classical spin nematic transition in  $\text{LiGa}_{0.95}\text{In}_{0.05}\text{Cr}_4\text{O}_8$ . *Phys. Rev. Lett.*, 119:087201, 2017. [11](#), [12](#), [14](#), [60](#)
- [40] K. Kimura, S. Nakatsuji, and T. Kimura. Experimental realization of a quantum breathing pyrochlore antiferromagnet. *Phys. Rev. B*, 90:060414, 2014. [11](#), [37](#), [49](#)
- [41] Shao-Kai Jian and Wenxing Nie. Weyl magnons in pyrochlore antiferromagnets with an all-in-all-out order. *Phys. Rev. B*, 97:115162, 2018. [11](#)
- [42] Fei-Ye Li, Yao-Dong Li, Yong Baek Kim, Leon Balents, Yue Yu, and Gang Chen. Weyl magnons in breathing pyrochlore antiferromagnets. *Nature communications*, 7:12691, 2016. [11](#), [37](#)
- [43] Regina Pocha, Dirk Johrendt, Bingfang Ni, and Mohsen M. Abd-Elmeguid. Crystal structures, electronic properties, and pressure-induced superconductivity of the tetrahedral cluster compounds  $\text{GaNb}_4\text{S}_8$ ,  $\text{GaNb}_4\text{Se}_8$ , and  $\text{GaTa}_4\text{Se}_8$ . *Journal of the American Chemical Society*, 127(24):8732–8740, 2005. [12](#)

- [44] H.L. Pinch, M.J. Woods, and E. Lopatin. Some new mixed a-site chromium chalcogenide spinels. *Materials Research Bulletin*, 5(6):425 – 429, 1970. [12](#), [16](#), [18](#), [39](#), [41](#), [60](#)
- [45] Pratyay Ghosh, Yasir Iqbal, Tobias Müller, Ravi T. Ponnaganti, Ronny Thomale, Rajesh Narayanan, Johannes Reuther, Michel J. P. Gingras, and Harald O. Jeschke. Breathing chromium spinels: a showcase for a variety of pyrochlore heisenberg hamiltonians. *npj Quantum Mater.*, 4(1):63, 2019. [12](#), [16](#), [59](#), [60](#), [61](#), [72](#), [74](#), [78](#), [79](#)
- [46] Gøran. J. Nilsen, Yoshihiko Okamoto, Takatsugu Masuda, Juan Rodriguez-Carvajal, Hannu Mutka, Thomas Hansen, and Zenji Hiroi. Complex magnetostructural order in the frustrated spinel  $\text{LiInCr}_4\text{O}_8$ . *Phys. Rev. B*, 91:174435, 2015. [12](#), [14](#), [39](#), [55](#), [68](#)
- [47] Owen Benton and Nic Shannon. Ground state selection and spin-liquid behaviour in the classical heisenberg model on the breathing pyrochlore lattice. *J. Phys. Soc. Jpn.*, 84(10): 104710, 2015. [x](#), [12](#), [14](#), [15](#), [59](#), [70](#)
- [48] Yu Tanaka, Rafal Wawrzyńczak, Manh Duc Le, Tatiana Guidi, Yoshihiko Okamoto, Takeshi Yajima, Zenji Hiroi, Masashi Takigawa, and GÅ\_ran J. Nilsen. Inelastic neutron scattering study of the spin dynamics in the breathing pyrochlore system  $\text{LiGa}_{0.95}\text{In}_{0.05}\text{Cr}_4\text{O}_8$ . *J. Phys. Soc. Jpn.*, 87(7):073710, 2018. [12](#), [60](#), [70](#)
- [49] Yoshihiko Okamoto, GÅ\_ran J. Nilsen, Taishi Nakazono, and Zenji Hiroi. Magnetic phase diagram of the breathing pyrochlore antiferromagnet  $\text{LiGa}_{1-x}\text{In}_x\text{Cr}_4\text{O}_8$ . *J. Phys. Soc. Jpn.*, 84(4):043707, 2015. [12](#), [14](#), [60](#)
- [50] P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin. Exchange interactions in ferromagnetic chromium chalcogenide spinels. *Phys. Rev.*, 151:367–377, 1966. [16](#), [56](#)
- [51] R. Plumier, M. Sougi, and M. Lecomte. Observation of an unusual short range magnetic ordering in spinel  $\text{Cu}_{1/2}\text{In}_{1/2}\text{Cr}_2\text{S}_4$ . *Physics Letters A*, 60(4):341 – 344, 1977. [x](#), [16](#), [17](#), [18](#), [60](#)
- [52] R. Plumier, M. Sougi, M. Lecomte, and A. Miedan-Gros. High magnetic field study of sulphur spinel  $\text{Cu}_{1/2}\text{In}_{1/2}\text{Cr}_2\text{S}_4$ . *Zeitschrift für Physik B Condensed Matter*, 40, 1980. [16](#)

- [53] Eugen Ruff, Sebastian Widmann, Peter Lunkenheimer, Vladimir Tsurkan, Sandor Bordács, Istvan Kézsmárki, and Alois Loidl. Multiferroicity and skyrmions carrying electric polarization in  $\text{GaV}_4\text{S}_8$ . *Science Advances*, 1(10), 2015. [19](#), [21](#), [22](#), [81](#), [93](#)
- [54] Regina Pocha, Dirk Johrendt, and Rainer Pöhlitz. Electronic and structural instabilities in  $\text{GaV}_4\text{S}_8$  and  $\text{GaMo}_4\text{S}_8$ . *Chemistry of Materials*, 12(10):2882–2887, 2000. [19](#), [21](#), [82](#), [93](#)
- [55] E. Ruff, A. Butykai, K. Geirhos, S. Widmann, V. Tsurkan, E. Stefanet, I. Kézsmárki, A. Loidl, and P. Lunkenheimer. Polar and magnetic order in  $\text{GaV}_4\text{Se}_8$ . *Phys. Rev. B*, 96:165119, 2017. [19](#)
- [56] Kiran Singh, Charles Simon, Elena Cannuccia, Marie-Bernadette Lepetit, Benoit Corraze, Etienne Janod, and Laurent Cario. Orbital-ordering-driven multiferroicity and magnetoelectric coupling in  $\text{GaV}_4\text{S}_8$ . *Phys. Rev. Lett.*, 113:137602, 2014. [19](#)
- [57] K. Geirhos, S. Krohns, H. Nakamura, T. Waki, Y. Tabata, I. Kézsmárki, and P. Lunkenheimer. Orbital-order driven ferroelectricity and dipolar relaxation dynamics in multiferroic  $\text{GaMo}_4\text{S}_8$ . *Phys. Rev. B*, 98:224306, 2018. [19](#), [81](#)
- [58] Matthew T. Warren, G. Pokharel, A. D. Christianson, D. Mandrus, and R. Valdés Aguilar. Terahertz dielectric analysis and spin-phonon coupling in multiferroic  $\text{GaV}_4\text{S}_8$ . *Phys. Rev. B*, 96:054432, 2017. [19](#), [81](#)
- [59] M. M. Abd-Elmeguid, B. Ni, D. I. Khomskii, R. Pocha, D. Johrendt, X. Wang, and K. Syassen. Transition from mott insulator to superconductor in  $\text{GaNb}_4\text{Se}_8$  and  $\text{GaTa}_4\text{Se}_8$  under high pressure. *Phys. Rev. Lett.*, 93:126403, 2004. [19](#), [81](#)
- [60] V. Ta Phuoc, C. Vaju, B. Corraze, R. Sopracase, A. Perucchi, C. Marini, P. Postorino, M. Chligui, S. Lupi, E. Janod, and L. Cario. Optical conductivity measurements of  $\text{GaTa}_4\text{Se}_8$  under high pressure: Evidence of a bandwidth-controlled insulator-to-metal mott transition. *Phys. Rev. Lett.*, 110:037401, 2013. [19](#), [81](#)
- [61] Eugen Dorolti, Laurent Cario, Benoît Corraze, Etienne Janod, Cristian Vaju, Hyun-Joo Koo, Erjun Kan, and Myung-Hwan Whangbo. Half-metallic ferromagnetism and large negative

- magnetoresistance in the new lacunar spinel  $\text{GaTi}_3\text{VS}_8$ . *Journal of the American Chemical Society*, 132(16):5704–5710, 2010. [19](#), [81](#)
- [62] Pablo Stoliar, Laurent Cario, Etienne Janod, Benoit Corraze, Catherine Guillot-Deudon, Sabrina Salmon-Bourmand, Vincent Guiot, Julien Tranchant, and Marcelo Rozenberg. Universal electric-field-driven resistive transition in narrow-gap mott insulators. *Advanced Materials*, 25(23):3222–3226, 2013. [19](#), [81](#)
- [63] Hui-Min Zhang, Jun Chen, Paolo Barone, Kunihiro Yamauchi, Shuai Dong, and Silvia Picozzi. Possible emergence of a skyrmion phase in ferroelectric  $\text{GaMo}_4\text{S}_8$ . *Phys. Rev. B*, 99:214427, 2019. [19](#), [81](#)
- [64] Myung Joon Han Hosub Jin Heung-Sik Kim, Jino Im. Spin-orbital entangled molecular jeff states in lacunar spinel compounds. *Nature Communications volume 5, Article number: 3988 (2014)*, 5:3988, 2014. [19](#), [81](#)
- [65] S. Widmann, E. Ruff, A. Günther, H.-A. Krug von Nidda, P. Lunkenheimer, V. Tsurkan, S. Bordács, I. Kézsmárki, and A. Loidl. On the multiferroic skyrmion-host  $\text{GaV}_4\text{S}_8$ . *Philosophical Magazine*, 97(36):3428–3445, 2017. [x](#), [21](#), [82](#), [93](#)
- [66] Ádám Butykai, Sándor Bordács, István Kézsmárki, Vladimir Tsurkan, Alois Loidl, Jonathan Döring, Erik Neuber, Peter Milde, Susanne C. Kehr, Lukas M. Eng, and et al. Characteristics of ferroelectric-ferroelastic domains in néel-type skyrmion host  $\text{GaV}_4\text{S}_8$ . *Scientific Reports*, 7:44663, 2017. [21](#)
- [67] T. Adams, A. Chacon, M. Wagner, A. Bauer, G. Brandl, B. Pedersen, H. Berger, P. Lemmens, and C. Pfleiderer. Long-wavelength helimagnetic order and skyrmion lattice phase in  $\text{Cu}_2\text{OSeO}_3$ . *Phys. Rev. Lett.*, 108:237204, 2012. [21](#)
- [68] Michael Binnewies, Robert Glaum, Marcus Schmidt, and Peer Schmidt. Chemical vapor transport reactions – a historical review. *Zeitschrift für anorganische und allgemeine Chemie*, 639(2):219–229, 2013. [24](#), [26](#)
- [69] Peer Schmidt, Michael Binnewies, Robert Glaum, and Marcus Schmidt. Chemical vapor transport reactions-methods, materials, modeling. 2013. [xi](#), [25](#)

- [70] A. R. Rennie. Mechanical properties and testing of polymers: Neutron scattering. pages 171–173, 1999. [26](#)
- [71] Gen Shirane, S Shapiro, and John Tranquada. Neutron scattering with a triple-axis spectrometer. 2002. [xi](#), [27](#), [28](#), [30](#), [31](#)
- [72] Introduction to the theory of thermal neutron scattering. [31](#)
- [73] Vasile O Garlea, Bryan C Chakoumakos, Scott A Moore, Gerald Brent Taylor, Timothy Chae, Ron G Maples, Richard A Riedel, Gary W Lynn, and Douglas L Selby. The high-resolution powder diffractometer at the high flux isotope reactor. *Appl. Phys. A*, 99(3): 531–535, 2010. [xi](#), [32](#), [33](#)
- [74] D. L. Abernathy, M. B. Stone, M. J. Loguillo, M. S. Lucas, O. Delaire, X. Tang, J. Y. Y. Lin, and B. Fultz. Design and operation of the wide angular-range chopper spectrometer arcs at the spallation neutron source. *Rev. Sci. Instrum.*, 83(1):015114, 2012. [34](#), [61](#)
- [75] G E Granroth, A I Kolesnikov, T E Sherline, J P Clancy, K A Ross, J P C Ruff, B D Gaulin, and S E Nagler. SEQUOIA: A newly operating chopper spectrometer at the SNS. *Journal of Physics: Conference Series*, 251:012058, 2010. [34](#), [85](#)
- [76] Georg Ehlers, Andrey A Podlesnyak, Jennifer L Niedziela, Erik B Iverson, and Paul E Sokol. The new cold neutron chopper spectrometer at the spallation neutron source: design and performance. *Rev. Sci. Instrum.*, 82(8):085108, 2011. [xi](#), [34](#), [35](#), [61](#)
- [77] G. Pokharel, A. F. May, D. S. Parker, S. Calder, G. Ehlers, A. Huq, S. A. J. Kimber, H. Suriya Arachchige, L. Poudel, M. A. McGuire, D. Mandrus, and A. D. Christianson. Negative thermal expansion and magnetoelastic coupling in the breathing pyrochlore lattice material  $\text{LiGaCr}_4\text{S}_8$ . *Phys. Rev. B*, 97:134117, 2018. [36](#)
- [78] T. Haku, K. Kimura, Y. Matsumoto, M. Soda, M. Sera, D. Yu, R. A. Mole, T. Takeuchi, S. Nakatsuji, Y. Kono, T. Sakakibara, L.-J. Chang, and T. Masuda. Low-energy excitations and ground-state selection in the quantum breathing pyrochlore antiferromagnet  $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$ . *Phys. Rev. B*, 93:220407, 2016. [37](#), [60](#)

- [79] V. Felea, S. Yasin, A. Günther, J. Deisenhofer, H.-A. Krug von Nidda, S. Zherlitsyn, V. Tsurkan, P. Lemmens, J. Wosnitzer, and A. Loidl. Spin-lattice coupling in the frustrated antiferromagnet  $\text{ZnCr}_2\text{Se}_4$  probed by ultrasound. *Phys. Rev. B*, 86:104420, 2012. [37](#)
- [80] J. Hemberger, T. Rudolf, H.-A. Krug von Nidda, F. Mayr, A. Pimenov, V. Tsurkan, and A. Loidl. Spin-driven phonon splitting in bond-frustrated  $\text{ZnCr}_2\text{S}_4$ . *Phys. Rev. Lett.*, 97:087204, 2006. [37](#), [55](#)
- [81] J.-H. Chung, M. Matsuda, S.-H. Lee, K. Kakurai, H. Ueda, T. J. Sato, H. Takagi, K.-P. Hong, and S. Park. Statics and dynamics of incommensurate spin order in a geometrically frustrated antiferromagnet  $\text{CdCr}_2\text{O}_4$ . *Phys. Rev. Lett.*, 95:247204, 2005. [37](#)
- [82] H. Duda, E. Maciażek, T. Groń, S. Mazur, A. W. Pacyna, A. Waśkowska, T. Mydlarz, and A. Gilewski. Spin-glass-like behavior in single-crystalline  $\text{Cu}_{0.44}\text{In}_{0.48}\text{Cr}_{1.95}\text{Se}_4$ . *Phys. Rev. B*, 77:035207, 2008. [37](#), [60](#)
- [83] R. Fichtl, V. Tsurkan, P. Lunkenheimer, J. Hemberger, V. Fritsch, H.-A. Krug von Nidda, E.-W. Scheidt, and A. Loidl. Orbital freezing and orbital glass state in  $\text{FeCr}_2\text{S}_4$ . *Phys. Rev. Lett.*, 94:027601, 2005. [37](#)
- [84] A. B. Sushkov, O. Tchernyshyov, W. Ratcliff II, S. W. Cheong, and H. D. Drew. Probing spin correlations with phonons in the strongly frustrated magnet  $\text{ZnCr}_2\text{O}_4$ . *Phys. Rev. Lett.*, 94:137202, 2005. [37](#)
- [85] Suguru Kitani, Makoto Tachibana, Naoya Taira, and Hitoshi Kawaji. Thermal study of the interplay between spin and lattice in  $\text{CoCr}_2\text{O}_4$  and  $\text{CdCr}_2\text{O}_4$ . *Phys. Rev. B*, 87:064402, 2013. [37](#)
- [86] S. Lee, S.-H. Do, W.-J. Lee, Y. S. Choi, M. Lee, E. S. Choi, A. P. Reyes, P. L. Kuhns, A. Ozarowski, and K.-Y. Choi. Multistage symmetry breaking in the breathing pyrochlore lattice  $\text{Li}(\text{Ga},\text{In})\text{Cr}_4\text{O}_8$ . *Phys. Rev. B*, 93:174402, 2016. [39](#), [60](#)
- [87] Juan Rodríguez-Carvajal. *An introduction to the program Fullprof 2000*, 2001. [40](#), [41](#)
- [88] B. H. Toby. A graphical user interface for *gsas*. *J. Appl. Cryst.*, 34:210–213, 2001. [40](#), [41](#)

- [89] R. D. Shannon. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*, 32(5):751–767, 1976. [46](#)
- [90] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz. *WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*, 2017. [54, 78](#)
- [91] Perdew J.P., K. Burke, and M. Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 77:3865, 1996. [54, 78](#)
- [92] F. J. Pinski, J. Staunton, B. L. Gyorffy, D. D. Johnson, and G. M. Stocks. Ferromagnetism versus antiferromagnetism in face-centered-cubic iron. *Phys. Rev. Lett.*, 56:2096–2099, 1986. [55](#)
- [93] Rana Saha, Francois Fauth, Maxim Avdeev, Paula Kayser, Brendan J. Kennedy, and A. Sundaresan. Magnetodielectric effects in A-site cation-ordered chromate spinels  $\text{LiMCr}_4\text{O}_8$  ( $\text{M} = \text{Ga}$  and  $\text{In}$ ). *Phys. Rev. B*, 94:064420, 2016. [55](#)
- [94] Chuanchuan Gu, Zhaorong Yang, Xuliang Chen, LI Pi, and Yuheng Zhang. Negative thermal expansion and magnetostriction in the frustrated spinel  $\text{ZnCr}_2(\text{Se}_{1-x}\text{S}_x)_4$  ( $0 \leq x \leq 0.1$ ). *Journal of Physics: Condensed Matter*, 28(18), 2016. [55](#)
- [95] Ganesh Pokharel, Hasitha Suriya Arachchige, Travis J. Williams, Andrew F. May, Randy S. Fishman, Gabriele Sala, Stuart Calder, Georg Ehlers, David S. Parker, Tao Hong, Andrew Wildes, David Mandrus, Joseph A. M. Paddison, and Andrew D. Christianson. Cluster frustration in the breathing pyrochlore magnet  $\text{LiGaCr}_4\text{S}_8$ . *arXiv*, 2002.09749, 2020. [58](#)
- [96] Leon Balents. Spin liquids in frustrated magnets. *Nature*, 464(7286):199–208, 2010. [59](#)
- [97] R. Moessner and J. T. Chalker. Low-temperature properties of classical geometrically frustrated antiferromagnets. *Phys. Rev. B*, 58(18):12049–12062, 1998. [59, 70](#)
- [98] R. Moessner and J. Chalker. Properties of a classical spin liquid: The heisenberg pyrochlore antiferromagnet. *Phys. Rev. Lett.*, 80:2929–2932, 1998. [59](#)



- [99] B. Canals and C. Lacroix. Pyrochlore antiferromagnet: A three-dimensional quantum spin liquid. *Phys. Rev. Lett.*, 80:2933–2936, 1998. [59](#)
- [100] Christian Balz, Bella Lake, Johannes Reuther, Hubertus Luetkens, Rico Schönmann, Thomas Herrmannsdörfer, Yogesh Singh, A. T. M. Nazmul Islam, Elisa M. Wheeler, Jose A. Rodriguez-Rivera, Tatiana Guidi, Giovanna G. Simeoni, Chris Baines, and Hanjo Ryll. Physical realization of a quantum spin liquid based on a complex frustration mechanism. *Nature Physics*, 12:942–949, 2016. [59](#), [79](#)
- [101] Joseph A. M. Paddison, J. Ross Stewart, Pascal Manuel, Pierre Courtois, Garry J. McIntyre, Brian D. Rainford, and Andrew L. Goodwin. Emergent frustration in co-doped  $\beta$  Mn. *Phys. Rev. Lett.*, 110:267207, 2013. [59](#), [79](#)
- [102] Jörn W. F. Venderbos, Maria Daghofer, Jeroen van den Brink, and Sanjeev Kumar. Macroscopic degeneracy and emergent frustration in a honeycomb lattice magnet. *Phys. Rev. Lett.*, 107:076405, 2011. [59](#)
- [103] Sang-Youn Park, S.-H. Do, K.-Y. Choi, J.-H. Kang, Dongjin Jang, B. Schmidt, Manuel Brando, B.-H. Kim, D.-H. Kim, N. P. Butch, and et al. Spin–orbit coupled molecular quantum magnetism realized in inorganic solid. *Nature Communications*, 12912, 2016. [60](#)
- [104] R. Plumier, F. Lotgering, and R. Van Stapele. Magnetic properties of  $\text{Cu}_{1/2}\text{In}_{1/2}\text{Cr}_2\text{S}_4$  and some related compounds. *Journal de Physique Colloques*, 32(C1):C1–324–C1–325, 1971. [60](#)
- [105] O. Arnold, J.C. Bilheux, J.M. Borreguero, A. Buts, S.I. Campbell, L. Chapon, M. Doucet, N. Draper, R. Ferraz Leal, M.A. Gigg, V.E. Lynch, A. Markvardsen, D.J. Mikkelsen, R.L. Mikkelsen, R. Miller, K. Palmen, P. Parker, G. Passos, T.G. Perring, P.F. Peterson, S. Ren, M.A. Reuter, A.T. Savici, J.W. Taylor, R.J. Taylor, R. Tolchenov, W. Zhou, and J. Zikovsky. Mantid-data analysis and visualization package for neutron scattering and  $\mu\text{sr}$  experiments. *Nucl. Instr. Meth. Phys. Res. A*, 764:156 – 166, 2014. [62](#)

- [106] R. T. Azuah, L. R. Kneller, Y. Qiu, P. L. W. Tregenna-Piggott, C. M. Brown, J. R. D. Copley, and R. M. Dimeo. Dave: A comprehensive software suite for the reduction, visualization, and analysis of low energy neutron spectroscopic data. *J. Res. Natl. Inst. Stan. Technol.*, 114:341, 2009. [62](#), [88](#)
- [107] Juan Rodriguez-Carvajal. Fullprof. 2k, version 4.6 c-mar 2002. *Physica B*, 55:192, 1993. [62](#), [65](#)
- [108] R. Brout and H. Thomas. Molecular field theory, the onsager reaction field and the spherical model. *Physics Physique Fizika*, 3:317–329, 1967. [62](#), [70](#)
- [109] D. E Logan, Y. H Szczec, and M. A Tusch. Onsager reaction field theory of the heisenberg model. *Europhys. Lett.*, 30(5):307–312, 1995. [62](#), [70](#)
- [110] Dietmar Hohlwein, Jens-Uwe Hoffmann, and Rainer Schneider. Magnetic interaction parameters from paramagnetic diffuse neutron scattering in mno. *Phys. Rev. B*, 68:140408, 2003. [62](#), [70](#)
- [111] Burton S. Garbow. Eispack — a package of matrix eigensystem routines. *Comp. Phys. Commun.*, 7(4):179 – 184, 1974. [62](#)
- [112] P. J. Brown. International tables for crystallography. C:454–460, 2004. [63](#)
- [113] Matthew Enjalran and Michel J. P. Gingras. Theory of paramagnetic scattering in highly frustrated magnets with long-range dipole-dipole interactions: the case of the  $\text{Tb}_2\text{Ti}_2\text{O}_7$  pyrochlore antiferromagnet. *Phys. Rev. B*, 70:174426, 2004. [63](#)
- [114] F. James and M. Roos. Minuit - a system for function minimization and analysis of the parameter errors and correlations. *Comp. Phys. Commun.*, 10(6):343 – 367, 1975. [63](#)
- [115] S.-H. Lee, J. M. Tranquada, K. Yamada, D. J. Buttrey, Q. Li, and S.-W. Cheong. Freezing of a stripe liquid. *Phys. Rev. Lett.*, 88:126401, 2002. [68](#)
- [116] Y. Y. Peng, E. W. Huang, R. Fumagalli, M. Minola, Y. Wang, X. Sun, Y. Ding, K. Kummer, X. J. Zhou, N. B. Brookes, B. Moritz, L. Braicovich, T. P. Devereaux, and G. Ghiringhelli. Dispersion, damping, and intensity of spin excitations in the monolayer

- (Bi,Pb)<sub>2</sub>(Sr,La)<sub>2</sub>(CuO)<sub>6+δ</sub> cuprate superconductor family. *Phys. Rev. B*, 98:144507, 2018. [68](#)
- [117] P. H. Conlon and J. T. Chalker. Spin dynamics in pyrochlore heisenberg antiferromagnets. *Phys. Rev. Lett.*, 102:237206, 2009. [70](#)
- [118] X. Bai, J. A. M. Paddison, E. Kapit, S. M. Koohpayeh, J.-J. Wen, S. E. Dutton, A. T. Savici, A. I. Kolesnikov, G. E. Granroth, C. L. Broholm, J. T. Chalker, and M. Mourigal. Magnetic excitations of the classical spin liquid MgCr<sub>2</sub>O<sub>4</sub>. *Phys. Rev. Lett.*, 122:097201, 2019. [70](#), [79](#)
- [119] W Marshall and R D Lowde. Magnetic correlations and neutron scattering. *Rep. Prog. Phys.*, (2):705, 1968. [70](#)
- [120] I. A. Blech and B. L. Averbach. *Physics*, 1:31–44, 1964. [70](#)
- [121] K. W. Plumb, Hitesh J. Changlani, A. Scheie, Shu Zhang, J. W. Krizan, J. A. Rodriguez-Rivera, Yiming Qiu, B. Winn, R. J. Cava, and C. L. Broholm. Continuum of quantum fluctuations in a three-dimensional S = 1 heisenberg magnet. *Nature Physics*, 15(1):54–59, 2019. [70](#)
- [122] P. H. Conlon and J. T. Chalker. Absent pinch points and emergent clusters: Further neighbor interactions in the pyrochlore heisenberg antiferromagnet. *Phys. Rev. B*, 81:224413, 2010. [70](#)
- [123] S. Toth and B. Lake. Linear spin wave theory for single-q incommensurate magnetic structures. *J. Phys.: Condens. Matter*, 27(16):166002, 2015. [xiv](#), [73](#), [75](#), [90](#)
- [124] Joseph A. M. Paddison. Ultrafast calculation of diffuse scattering from atomistic models. *Acta Crystallogr. A*, 75(1):14–24, 2019. [74](#)
- [125] Krunoslav Prša and Oliver Waldmann. Ferromagnetic cluster spin wave theory: Concepts and applications to magnetic molecules. *Inorganics*, 6(2), 2018. [75](#)
- [126] T Chakrabarty, A V Mahajan, and S Kundu. Cluster spin glass behavior in geometrically frustrated Zn<sub>3</sub>V<sub>3</sub>O<sub>8</sub>. *J. Phys.: Condens. Matter*, 26(40):405601, 2014. [77](#), [80](#)

- [127] X. K. Zhang, J. J. Yuan, Y. M. Xie, Y. Yu, F. G. Kuang, H. J. Yu, X. R. Zhu, and H. Shen. Phase coexistence and exchange-bias effect in  $\text{LiMn}_2\text{O}_4$  nanorods. *Phys. Rev. B*, 97:104405, 2018. [77](#), [80](#)
- [128] T. J. Williams, A. E. Taylor, A. D. Christianson, S. E. Hahn, R. S. Fishman, D. S. Parker, M. A. McGuire, B. C. Sales, and M. D. Lumsden. Extended magnetic exchange interactions in the high-temperature ferromagnet mnbi. *Appl. Phys. Lett.*, 108(19):192403, 2016. [78](#)
- [129] K. V. Shanavas, David Parker, and David J. Singh. Theoretical study on the role of dynamics on the unusual magnetic properties in MnBi. *Sci. Rep.*, 4(1):7222, 2014. [78](#)
- [130] Michael A. McGuire, Huibo Cao, Bryan C. Chakoumakos, and Brian C. Sales. Symmetry-lowering lattice distortion at the spin reorientation in mnbi single crystals. *Phys. Rev. B*, 90:174425, 2014. [78](#)
- [131] R. Brand, P. Lunkenheimer, and A. Loidl. Relaxation dynamics in plastic crystals. *J. Chem. Phys.*, 116(23):10386–10401, 2002. [79](#)
- [132] C. A. M. Mulder, A. J. van Duynveldt, and J. A. Mydosh. Frequency and field dependence of the ac susceptibility of the AuMn spin-glass. *Phys. Rev. B*, 25:515–518, 1982. [80](#)
- [133] C. A. M. Mulder, A. J. Van Duynveldt, and J. A. Mydosh. Susceptibility of CuMn spin glass. *Phys. Rev. B*, 23, 1981. [80](#)
- [134] Pallab Bag, P. R. Baral, and R. Nath. Cluster spin-glass behavior and memory effect in  $\text{Cr}_{0.5}\text{Fe}_{0.5}\text{Ga}$ . *Phys. Rev. B*, 98:144436, 2018. [80](#)
- [135] P. Padmanabhan, F. Sekiguchi, R. B. Versteeg, E. Slivina, V. Tsurkan, S. Bordács, I. Kézsmárki, and P. H. M. van Loosdrecht. Optically driven collective spin excitations and magnetization dynamics in the néel-type skyrmion host  $\text{GaV}_4\text{S}_8$ . *Phys. Rev. Lett.*, 122, 2019. [82](#)
- [136] Yiqun Wang, Danilo Puggioni, and James M. Rondinelli. Assessing exchange-correlation functional performance in the chalcogenide lacunar spinels  $\text{GaM}_4\text{S}_8$  ( $\text{M}=\text{Mo}, \text{V}, \text{Nb}, \text{Ta}$ ;  $\text{Q}=\text{S}, \text{Se}$ ). *Phys. Rev. B*, 100:115149, 2019. [82](#)

- [137] J A Rodriguez, D M Adler, P C Brand, C Broholm, J C Cook, C Brocker, R Hammond, Z Huang, P Hundertmark, J W Lynn, N C Maliszewskyj, J Moyer, J Orndorff, D Pierce, T D Pike, G Scharfstein, S A Smee, and R Vilaseca. MACS—a new high intensity cold neutron spectrometer at NIST. *Measurement Science and Technology*, 19(3):034023, 2008. [85](#), [88](#)
- [138] Helen Müller, Winfried Kockelmann, and Dirk Johrendt. The magnetic structure and electronic ground states of mott insulators  $\text{GeV}_4\text{S}_8$  and  $\text{GaV}_4\text{S}_8$ . *Chemistry of Materials*, 18(8):2174–2180, 2006. [93](#)
- [139] J. T. Zhang, J. L. Wang, X. Q. Yang, W. S. Xia, X. M. Lu, and J. S. Zhu. Magnetic properties and spin-driven ferroelectricity in multiferroic skyrmion host  $\text{GaV}_4\text{S}_8$ . *Phys. Rev. B*, 95: 085136, 2017. [93](#)

# **Appendix**

# List of Publications

- G. Pokharel, A. F. May, D. S. Parker, S. Calder, G. Ehlers, A. Huq, S. A. J. Kimber, H. Suriya Arachchige, L. Poudel, M. A. McGuire, D. Mandrus, A. D. Christianson "Negative thermal expansion and magnetoelastic coupling in the breathing pyrochlore lattice material  $\text{LiGaCr}_4\text{S}_8$ " Phys. Rev. B 97, 134117, 2018.
- Matthew T Warren, G Pokharel, Andrew D Christianson, David Mandrus, R Valdés Aguilar "Terahertz dielectric analysis and spin-phonon coupling in multiferroic  $\text{GeV}_4\text{S}_8$ " Phys. Rev. B 96, 054432, 2017.
- G. Pokharel, H. Suriya Arachchige, T. J. Williams, A. F. May, S Calder, G. Ehlers, G. Sala, T. Hong, A. Wildes, R. S. Fishman, D. Mandrus, J. A. M. Paddison, A. D. Christianson "Cluster frustration in the breathing pyrochlore magnet  $\text{LiGaCr}_4\text{S}_8$ " arXiv:2002.09749, 2020.
- E. M. Clements, R. Das, G. Pokharel, M. H. Phan, A. D. Christianson, D. Mandrus, J. C. Prestigiacomo, M. S. Osofsky, and H. Srikanth "Robust cycloid crossover driven by anisotropy in the skyrmion host  $\text{GaV}_4\text{S}_8$ " Phys. Rev. B 101, 094425, 2020.
- G. Pokharel, K. S. Syed Ali, S. R. Mishra "Structural, magnetic and Mossbauer studies of Ti doped  $\text{Gd}_2\text{Fe}_{17-x}\text{Ti}_x$  and  $\text{Gd}_2\text{Fe}_{16}\text{Ga}_{1-x}\text{Ti}_x$  ( $0 \leq x \leq 1$ )" Journal of Magnetism and Magnetic Materials 382, 31–42, 2015.
- G. Sala, M. B. Stone, Binod K. Rai, A. F. May, Pontus Laurell, V. O. Garlea, N. P. Butch, M. D. Lumsden, G. Ehlers, G. Pokharel, D. Mandrus, D. S. Parker, S. Okamoto, Gabor B. Halasz, and A. D. Christianson "Van Hove singularity in the magnon spectrum of the antiferromagnetic quantum honeycomb lattice" arXiv:2003.01754, 2020.

# Vita

Ganesh was born in the eastern district Morang of the south Asian country Nepal. He started his school at Kabir Secondary School located at Lalbhitti, Nepal. He graduated with a high school diploma from Vishwa Adarsha Higher Secondary school, Itahari, Nepal in 2001. He completed his Bachelor of Science (B.Sc.) and Master of Science (M.Sc.) in Physics from Tribhuvan University, Nepal. He then spent around 4 years teaching high school and undergraduate physics courses in different academic institutes in Nepal. In August 2011, Ganesh joined the University of Memphis, Memphis, TN as a Master's degree physics student. After graduating from the University of Memphis, he joined the Department of Physics and Astronomy at the University of Tennessee as a PhD student. He worked with Prof. David Mandrus and Dr. Andrew Christianson for the synthesis and neutron scattering measurements of novel magnetic materials during his PhD research. He is going to graduate with PhD degree in August 2020. After graduation, Ganesh will work as a postdoctoral research associate at the University of California, Santa Barbara.