Final Technical Report

Sponsoring Organization: Department of Energy, Office of Basic Energy Sciences

1) Award Number: DE-FG02-07ER46134

Recipient: Massachusetts Institute of Technology

2) Project Title: A United Effort for Crystal Growth, Neutron Scattering, and X-ray Scattering Studies of Novel Correlated Electron Materials

Lead PI: Young S. Lee, Professor of Physics, MIT

3) Date: February 11, 2015

Period covered: 5/01/2004-11/30/2013

4) Research accomplishments

Our research accomplishments during the award involved experimental studies of correlated electron systems and quantum magnetism. The techniques of crystal growth, neutron scattering, x-ray scattering, and thermodynamic & transport measurements were employed, and seven graduate students and three postdoctoral research associates were trained in these techniques. Our research lead to several significant results. These results highlight the complementary and fruitful relationship between crystal growth and scattering studies. The following is a listing of the papers resulting from the research:

Publications resulting from DOE award, funding period 5/1/2004 – 11/30/2013:

25) T.Asaba, T.H. Han, B. J. Lawson, F Yu, C Tinsman, Z Xiang, G Li, Y.S. Lee, and L. Li, *High-field magnetic ground state in S= 1/2 kagome lattice antiferromagnet* $ZnCu_3(OH)_6Cl_2$, Physical Review B 90, 064417 (2014).

24) D.V. Pilon, C.H. Lui, T.-H. Han, D.B. Shrekenhamer, A.J. Frenzel, W.J. Padilla, Y.S. Lee and N. Gedik, *Spin Induced Optical Conductivity in the Spin Liquid Candidate Herbertsmithite*, Phys. Rev. Lett. ***111,*** 127401 (2013).

23) T.-H. Han, J.S. Helton, S. Chu, D.G. Nocera, J.A. Rodriguez-Rivera, C. Broholm, and Y.S. Lee, *Fractionalized excitations in the spin liquid state of a kagome lattice antiferromagnet*, Nature **492**, 406 (2012).

22) D.K. Singh and Y.S. Lee, *Nonconventional Spin Glass Transition in a Chemically Ordered Pyrochlore*, Phys. Rev. Lett. **109**, 247201 (2012).

21) T.H. Han, S. Chu, and Y.S. Lee, *Refining the spin Hamiltonian in the spin-1/2 kagome lattice antiferromagnet* $ZnCu_3(OH)_6Cl_2$ *using single crystals*, Phys. Rev. Lett. **108**, 157202 (2012).

20) Z.-H. Pan, A. V. Fedorov, D. Gardner, Y.S. Lee, S. Chu, and T. Valla*, Measurement of an Exceptionally Weak Electron-Phonon Coupling on the Surface of the Topological Insulator* Bi_2Se_3 *Using Angle-Resolved Photoemission Spectroscopy*, Phys. Rev. Lett. **108**, 187001 (2012).

19) T. Valla, Z.H. Pan, D. Gardner, Y.S. Lee, and S. Chu, *Photoemission spectroscopy of magnetic and nonmagnetic impurities on the surface of the* Bi_2Se_3 *topological insulator*, Phys. Rev. Lett. **108**, 117601 (2012).

18) D.E. Freedman, R. Chisnell, T.M. McQueen, Y.S. Lee, C. Payen, and D.G. Nocera, *Frustrated magnetism in the S=1 kagome lattice* $BaNi_3(OH)_2(VO_4)_2$, Chem. Comm. **48**, 64-6 (2012).

17) T.M. McQueen, T.H. Han, D.E. Freedman, P.W. Stephens, Y.S. Lee, and D.G. Nocera, $CdCu_3(OH)_6Cl_2$*: A New Layered Hydroxide Chloride*, J. Sol. St. Chem. **184**, 3319-23 (2011).

16) T. Imai, M. Fu, T.H. Han, and Y.S. Lee*, Local Spin Susceptibility of the S=1/2 Kagome Lattice in* $ZnCu_3(OD)_6Cl_2$, Phys. Rev. B **84**, 020411 (2011).

15) Z.-H. Pan, E. Vescovo, A.V. Fedorov, D. Gardner, Y.S. Lee, S. Chu, G.D. Gu, and T. Valla*, Electronic Structure of the Topological Insulator* Bi_2Se_3 *Using Angle-Resolved Photoemission Spectroscopy: Evidence for a Nearly Full Surface Spin Polarization*, Phys. Rev. Lett. **106**, 257004 (2011).

14) S. Chu, P. Müller, D.G. Nocera, and Y.S. Lee, *Hydrothermal growth of single crystals of the quantum magnets: Clinoatacamite, paratacamite, and herbertsmithite*, Appl. Phys. Lett. **98**, 092508 (2011).

13) T.H. Han, S. Chu, J.S. Helton, A. Prodi, D.K. Singh, C. Mazzoli, P. Muller, D.G. Nocera, and Y.S. Lee, *Synthesis and Characterization of Single Crystal Samples of Spin-1/2 Kagome Lattice Antiferromagnets in the Zn-Paratacamite Family* $Zn_xCu_{4-x}(OH)_6Cl_2$, Phys. Rev. B **83**, 100402(R) (2011).

12) D. Wulferding, P. Lemmens, P. Scheib, J. Roder, P. Mendels, S.Y. Chu, T.H. Han, Y.S. Lee, *Interplay of thermal and quantum spin fluctuations in the kagome lattice compound herbertsmithite,* Phys. Rev. B **82**, 144412 (2010).

11) D.E. Freedman, T.H. Han, A. Prodi, P. Muller, Q.-Z. Huang, Y-S. Chen, S.M. Webb, Y.S. Lee, T.M. McQueen, and D.G. Nocera, *Site Specific X-ray Anomalous Dispersion of the Geometrically Frustrated Kagome Magnet, Herbertsmithite,* $ZnCu_3(OH)_6Cl_2$, J. Am. Chem. Soc., **132** (45), 16185 (2010).

10) A. Prodi, J. S. Helton, Yejun Feng, and Y. S. Lee, *Pressure-induced spin-Peierls to incommensurate charge-density-wave transition in the ground state of TiOCl*, Phys. Rev. B **81**, 201103(R) (2010).

9) S. Chu, T. M. McQueen, R. Chisnell, D. E. Freedman,‡ P. Muller, Y. S. Lee, and D. G. Nocera, *A* Cu^{2+}*(S= 1/2) Kagome´ Antiferromagnet:* $Mg_xCu_{4-x}(OH)_6Cl_2$, J. Am. Chem. Soc. *132*, 5570–5571 (2010).

8) J.S. Helton, K. Matan, M.P. Shores, E. A. Nytko, B. M. Bartlett, Y. Qiu, D. G. Nocera, and Y. S. Lee, *Dynamic Scaling in the Susceptibility of the Spin- 1/2 Kagome Lattice Antiferromagnet Herbertsmithite*, Phys. Rev. Lett. 104, 147201 (2010).

7) K. Matan, J.S. Helton, D. Grohol, D.G. Nocera, S. Wakimoto, K. Kakurai, Y.S. Lee, *Polarized neutron scattering studies of the kagomé lattice antiferromagnet* $KFe_3(OH)_6(SO_4)_2$, Physica-B Condensed Matter 404, 2529 (2009).

6) D.K. Singh, J.S. Helton, S. Chu, T.H. Han, C.J. Bonnoit, S. Chang, H.J. Kang, J.W. Lynn, and Y.S. Lee, *Spin correlations in the geometrically frustrated pyrochlore* $Tb_2Mo_2O_7$**,** Phys. Rev. B (Rapid Comm.) 78, 220405(R) (2008).

5) E.T. Abel, K. Matan, F.C. Chou, E.D. Isaacs, D.E. Moncton, H. Sinn, A. Alatas, and Y.S. Lee, *X-ray scattering study of the spin-Peierls transition and soft phonon behavior in TiOCl*, Phys. Rev. B 76, 214304 (2007).

4) G.J. Shu, A. Prodi, S.Y. Chu, Y.S. Lee, H.S. Sheu, and F.C. Chou, *Searching for stable Na-ordered phases in single crystal samples of* □-Na_xCoO_2, Phys. Rev. B 76, 184115 (2007).

3) L. Balicas, J.G. Analytis, Y.J. Jo, K. Storr, H. Zandbergen, Y. Xin, N.E. Hussey, F.C. Chou, and P.A. Lee, *Shubnikov–de Haas Effect in the Metallic State of* $Na_{0.3}CoO_2$, Phys. Rev. Lett. **97**, 126401 (2006).

2) G. Gasparovic, R. Ott, F.C. Chou, J.H. Cho, J.W. Lynn, and Y.S. Lee, *Neutron scattering study of novel magnetic order in* $Na_{0.5}CoO_2$, Phys. Rev. Lett. **96**, 046403 (2006).

1) F.C. Chou, E. Abel, J.H. Cho and Y.S. Lee, *Electrochemical de-intercalation, oxygen non-stoichiometry, and crystal growth of* $Na_xCoO_{2-\delta}$, J. Phys. Chem. Solids **66**, 155 (2005).

PhD students supported by the project:

6) Gardner, Dillon (PhD, in progress).
5) Chisnell, Robin (PhD July 2014).
4) Bonnoit, Craig (PhD May 2013).
3) Han,Tianheng (PhD August 2012).
2) Helton, Joel (PhD May 2009).
1) Abel, Eric (PhD May 2007).

Postdocs supported by the project:

3) Deepak Singh, worked on neutron scattering and susceptibility studies of the spin glass behavior of single crystal $Tb_2Mo_2O_7$
2) Andrea Prodi, worked in high pressure x-ray scattering of spin Peierls physics in TiOCl using diamond anvil cells
1) Goran Gasparovic, worked in neutron scattering of magnetic phases in Na_xCoO_2

The main objective of the project was research using scattering techniques and crystal growth to understand the physics of several important correlated electron and quantum spin systems. A better understanding of these materials may eventually lead to their use in superconducting applications or in quantum information. From a basic science point of view, the idea that the supeconducting copper-oxides may be on the verge of quantum disorder has led to great interest in the possibility of quantum disordered spin ground states (called the spin liquid). It is expected that such systems will have remarkable new properties such as the fractionalization of the spin quantum number. For example, the usual S=1 spin wave excitation may be broken up into a pair of S=1/2 excitations (called spinons). This phenomenon is well known in one-dimensional spin chains, but has so far been elusive in two-dimensional systems, even though some recent reports are strongly suggestive. Since the kagome lattice tends to frustrate spin ordering, this is an especially promising place to look for a spin liquid.

One highlight of the research resulting from this award has been the recent work "*Fractionalized excitations in the spin liquid state of a kagome lattice antiferromagnet"* (T.-H. Han, et al, Nature **492**, 406 (2012)). This work has generated much excitement in the community of quantum magnetism. It also highlights the power of neutron scattering to discover new physics. One can summarize the result as a triumphant experimental "triple play"--1) making large, high-quality single crystals, 2) performing inelastic neutron scattering, 3) testing a hallmark prediction of quantum spin liquids for the first time. Neutron scattering can uniquely probe the spin excitations, and thereby test the fundamental idea that the excitations are "fractionalized". The reason this couldn't be done previously was the lack of crystals of sufficient size. Our recent breakthrough in crystal growth, combined with the new neutron scattering capabilities, have enabled this exciting discovery.

The experimental realization of quantum spin liquids has been a long-sought goal in physics, as they represent new states of matter. Quantum spin liquids cannot be described by the broken symmetries associated with conventional ground states. In fact, the interacting magnetic moments in these systems do not order; however, they are highly entangled with one another over long ranges. Spin liquids play a prominent role in theories describing high-T_C superconductors, and the topological properties of these state may have applications in quantum information. A key feature of spin liquids is that they support exotic excitations carrying fractional quantum numbers. However, detailed measurements of these "fractionalized excitations" have been lacking. Our neutron scattering measurements on single crystal samples of the spin-1/2 kagome lattice antiferromagnet $ZnCu_3(OD)_6Cl_2$ (also called herbertsmithite) provide striking evidence for this hallmark signature of spin liquids. At low temperatures, we find that the spin excitations form a continuum, in contrast to the conventional spin-waves expected in ordered antiferromagnets. The observation of such a continuum in a two-dimensional magnet is a remarkable first. The results also serve as a key fingerprint of the quantum spin liquid state in herbertsmithite.

In addition to the neutron project on herbertsmithite, we are involved in collaborations which use our single crystals for a variety of other important measurements. In the past year, we have grown new herbertsmithite crystals which are partially enriched with ^{18}O for NMR studies with T. Imai (McMaster University). This allows for deeper studies of the magnetic fluctuations at the NMR time scale, where one can distinguish the influence of impurity moments on the intrinsic spins. We have been collaborating with N. Gedik (MIT) who has performed optical conductivity on our samples. These measurements can indirectly probe the effects of the emergent gauge field which is another signature of the spin liquid. We find a power law to the frequency dependence that has been predicted in theories for spin liquid ground states (D.V. Pilon, et al, Phys. Rev. Lett. ***111,*** 127401 (2013)). We have also collaborated with the group of L. Li (University of Michigan) to perform measurements of the magnetization in high field. We find that above ~10 Tesla, the susceptibility of herbertsmithite becomes temperature independent below 10 K. This indicate that high fields may close any intrinsic gap in the spin fluctuations (T.Asaba, et al, Phys. Rev. B 90, 064417 (2014)).

We have also studied an S=1/2 organic-inorganic hybrid kagomé compound named Cu(1,3-bdc). Again, using hydrothermal synthesis methods, small single crystals of

Cu(1,3-bdc) as large as 2.2 mg in mass have been grown. Single crystal specific heat measurements indicate an ordering transition taking place at T_N = 1.8 K. Elastic neutron diffraction has revealed that the kagome planes order ferromagnetically below T_N, with an antiferromagnetic order between planes. Hence, Cu(1,3-bdc) appears to be a good realization of a *ferromagnetic* S=1/2 kagome material (with weak interlayer coupling). In fact, initial inelastic neutron scattering on a partially aligned crystal sample reveals a strikingly flat magnon mode, which is separated from the other magnon modes by a small energy gap. By comparing to the equivalent model of bosons with nearest neighbor hopping on a kagome lattice plus the addition of a spin-orbit coupling term, the magnon structure factor can be well described. Interestingly, it is believed that this isolated flat band is characterized by a non-trivial Chern number. In fact, there are strong analogies between what we see and theoretical models for obtaining the fractional quantum hall effect at room temperature. A manuscript on this work has been submitted.

We have synthesized and studied other compounds with spins on highly frustrated lattices. This allows us to probe different phases in frustrated magnets which do not have spin liquid ground states. Such states may be characterized by glassy behavior, such as on the pyrochlore lattice composed of corner-sharing tetrahedra (D.K. Singh, et al, Phys. Rev. Lett. **109**, 247201 (2012)). For larger spin in the kagome lattice, such as S=1, there are various theoretical proposals for interesting physical states, but there are not good samples. We have synthesized such a S=1 kagome lattice and find that competing interactions leads to glassy behavior upon cooling (D.E. Freedman,et al, Chem. Comm. **48**, 64-6 (2012)).

We have also grown many single crystals in the family of Bi_2Se_3 compounds, which are well-known examples of “topological insulators.” In these materials, spin-orbit coupling leads to insulating behavior in the bulk, while the surface state is conducting. The surface state is protected by time-reversal symmetry and should be immune to disorder which does not break this symmetry. We have collaborated with photoemission scientists at Brookhaven National Lab (T. Valla and Z. Pan) to study the effects of magnetic dopants on the surface as well as the effects of electron-phonon coupling (Z.-H. Pan, et al, Phys.

Rev. Lett. 106, 257004 (2011), Z.-H. Pan, et al, Phys. Rev. Lett. 108, 187001 (2012), T. Valla, et al, Phys. Rev. Lett. 108, 117601 (2012)).

Prior to 2010, the research in this project had focused on materials which exemplified unconventional superconductivity and quantum magnetism in a one-dimensional system. We performed several studies single crystals of Na_xCoO_2, which is an S=1/2 triangular lattice material that can be doped to become a superconductor. We found that for the doping level of x=0.5, there exists a charge ordered and spin ordered state at low temperatures. Using polarized neutron scattering, we could determine the spin ordering in the form of a pattern of stripes (G. Gasparovic, et al, Phys. Rev. Lett. **96**, 046403 (2006)). For TiOCl, we showed that this material was the best example of the famous spin-Peierls state. Using inelastic x-ray scattering, we measured the dynamics of the soft phonon for the first time (E.T. Abel, et al, Phys. Rev. B 76, 214304 (2007)). We also performed single crystal diffraction in a diamond anvil cell to measure the structural phase transition which occurs simultaneously with the insulator-to-metal transition above 13 GPa (Phys. Rev. B **81**, 201103(R) (2010)).