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Collective dynamics in the Heisenberg pyrochlore antiferromagnet $Gd_2Sn_2O_7$

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$Gd_2Sn_2O_7$ is believed to be a good approximation to a Heisenberg antiferromagnet on a pyrochlore lattice with exchange and dipole-dipole interactions. The system is known to enter a long-range ordered ground state (the "Palmer Chalker" state) below $T_c=1$ K with $\boldsymbol{k}_{\mathrm{ord}}=(000)$. However, persistent electronic spin fluctuations have been observed as $T \rightarrow 0$. Using inelastic neutron scattering, we have studied the buildup of short-range spin-spin correlations as the temperature is lowered, and the eventual formation of a gapped long-range ordered state that is able to sustain spin waves below T_c. As a magnetic field is applied, new magnetic phases develop and the gap widens. These measurements show that $Gd_2Sn_2O_7$ completely relieves itself of frustration, but the self-selected ground state is very delicate.

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A system that cannot minimize its total classical ground-state energy while simultaneously minimizing each of its pairwise interactions individually is said to be frustrated.[1,2] Frustrated interactions are ubiquitous in condensed matter and can lead to many different and complex phenomena, including the intricate structure of solid nitrogen (N_2), protein folding, and stripes in cuprate superconductors. In the context of magnetism, frustration occurs because of random interactions (e.g., in dilute spin glasses) or by virtue of the underlying crystal structure as in the case of geometric frustration. Geometric frustration commonly occurs in compounds made up of triangular or tetrahedral units with antiferromagnetic (AFM) interactions. In particular the study of rare-earth pyrochlore oxides has elucidated many of the exotic behaviors possible through geometric frustration. Examples of these exotic ground states include, but are not limited to, an unconventional anomalous Hall effect in $A_2Mo_2O_7$,[3] freezing in the topological spin glass $Y_2Mo_2O_7$,[4] spin liquid behavior in $Tb_2Ti_2O_7$,[5] and the spin ice ground state in Ho and Dy pyrochlores.[6]

Antiferromagnetically coupled Heisenberg spins on the pyrochlore lattice are particularly interesting and expected to be highly frustrated. Mean-field theory finds a massive degeneracy of soft modes with no preferred state chosen at finite temperature,[7–9] but perturbations are often expected to select a unique ordered state.[7,10,11] In the insulating pyrochlore systems $A_2B_2O_7$, where A^{3+} is a rare-earth ion possessing a large magnetic moment and B^{4+} is a nonmagnetic ion, the leading perturbation is the long-range magnetic dipole-dipole interaction. Due to its long-range nature one might naively expect this interaction to select a unique ordering wave vector $\boldsymbol{k}_{\mathrm{ord}}$. Indeed, the dipolar spin ice model predicts an ordered ground state,[12] which has not been realized experimentally, yet.

In $Gd_2Sn_2O_7$ and $Gd_2Ti_2O_7$, the Gd^{3+} ions are in a $^8S_{7/2}$ ground state ($S=7/2, L=0$) and only a small single-ion anisotropy is expected.[13] These systems are, therefore, reasonably good realizations of antiferromagnetically coupled Heisenberg spins on a pyrochlore lattice with dipolar interactions. Raju *et al.*[9] determined that the long-range magnetic dipole-dipole interaction is approximately 20% of the nearest-neighbor AFM exchange. This study went on to show that the exchange and dipolar interactions give rise to a line of degenerate soft modes along the cubic $\langle 111 \rangle$ directions. Palmer and Chalker[14] later argued, in another mean-field calculation, that including quartic terms leads to the selection of a four-sublattice Néel ordered state with $\boldsymbol{k}_{\mathrm{ord}}=(000)$.

Experimentally one finds considerable differences between $Gd_2Sn_2O_7$ and $Gd_2Ti_2O_7$, although at first glance they should be quite similar. Both B-site ions are nonmagnetic, the room-temperature lattice parameters are comparable [10.46(1) and 10.18(1) Å for $Gd_2Sn_2O_7$ and $Gd_2Ti_2O_7$, respectively], and the effective paramagnetic moments are the same ($\sim 7.9\ \mu_B$).

In $Gd_2Sn_2O_7$, one phase transition has been detected at $T_c=1$ K (Refs. 15–17) and it is believed that the ground state is the one anticipated by the Palmer-Chalker model. On the other hand, in $Gd_2Ti_2O_7$ two successive magnetic transitions at $T_{c1} \sim 1$ K and $T_{c2} \sim 0.7$ K have been observed.[17–20] Neutron diffraction by Champion *et al.*[21] and Stewart *et al.*[22] confirmed these as transitions to an ordered state. In the latter work it was shown, using neutron polarization analysis of the diffuse scattering, that the spin structure is a four-k structure with $\boldsymbol{k}_{\mathrm{ord}}=(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. Between T_{c1} and T_{c2} the structure is partially ordered with 1/4 of the spin ensemble remaining fully dynamic but spatially correlated over 3.5 Å, the near neighbor (Gd-Gd) distance. The long-range ordered moments are aligned parallel to $\langle 110 \rangle$ in a 120° arrangement. At 250 mK, deep in the second phase, the dynamic spins align collinearly within the [111] plane but with less than 30% of the expected moment, that is, a significant paramagnetic component remains. This does not correspond to the Palmer and Chalker model and Wills *et al.*[16] suggested that a third-neighbor interaction is the origin of the differences between $Gd_2Sn_2O_7$ and $Gd_2Ti_2O_7$.

The presence of "persistent spin dynamics" has been invoked to explain the low-temperature muon spin relaxation[23,24] and specific-heat data in both compounds[20] and Mössbauer[17,20] data from the stannate. In $Gd_2Ti_2O_7$, where 1/4 of the spin system is not fully ordered at 250 mK, persistent spin-dynamics could be expected and has been seen in a neutron spin-echo experiment.[25] Surprisingly, Mössbauer studies saw a system static on a time scale of about 100 MHz and equivalent Gd sites.[17,20] This discrepancy has not been resolved to date. Bonville *et al.*[17] found a T^2 dependence to the specific heat of $Gd_2Sn_2O_7$ below the ordering temperatures. Such a power law is not expected for an ordered three-dimensional (3D) magnet and a band of low-energy excitations was invoked to explain the data. A more recent lower temperature study by Quilliam *et al.*[15] showed that $Gd_2Sn_2O_7$ has the characteristics of an ordered system with a gapped spin-wave spectrum. Del Maestro and Gingras[26] reported some detailed calculations for $Gd_2Sn_2O_7$ in which they described the specific heat and predicted a gapped spin-wave excitation spectrum.

A 750 mg polycrystalline sample of $Gd_2Sn_2O_7$ was prepared at the NIST Center for Neutron Research (NCNR) by firing, in air at 1350 °C, $^{160}Gd_2O_3$ and SnO_2 for several days with intermittent grindings to ensure a complete reaction. Enriched $^{160}Gd_2O_3$ was used in order to reduce neutron attenuation by the sample. X-ray powder diffraction and bulk susceptibility confirmed that the sample was phase pure with bulk properties identical to those reported earlier.[9,17] Time-of-flight neutron-scattering measurements were performed at the disk chopper spectrometer (DCS) at the NCNR with an incident wavelength of between 2.3 and 7 Å, providing an energy resolution of between 1140 and 42 μeV full width at half maximum. The sample was mounted in a dilution refrigerator within a 11.5 T vertical field superconducting magnet to obtain 50 mK. Additional high-temperature measurements above 1.2 K were performed in a helium bath cryostat.

The buildup of short-ranged spin correlations below 20 K is shown in the inset of Fig. 1. The low-Q upturn is temperature independent and is likely to be associated with instrumental background and grain-boundary scattering. The data at 1.2 K and above show a broad maximum at $|\mathbf{Q}| \sim 1.05$ Å^{-1} indicating predominantly AFM near neighbor correlations. Cooling below T_c the diffuse scattering is quenched and sharp Bragg peaks appear which can be indexed with a propagation vector $\boldsymbol{k}_{\mathrm{ord}}=(000)$. Elastic scattering data, over a wider range, are shown at 50 mK in the main figure. The data have been fitted using the Rietveld refinement program FULLPROF (Ref. 27) and are described well by the Palmer-Chalker model, as discussed earlier by Wills *et al.*[16] In this ground state, two pairs of spins will collinearly align antiparallel to each other and parallel to the opposite Gd-Gd line of contact in the tetrahedron. From our data we find that all Gd moments are identical with (6.7 ± 0.2) μ_B at 50 mK. The accuracy of this magnetic moment derived from our Rietveld refinement is greatly improved compared to the value of (6 ± 1) μ_B found by Wills *et al.* due to the lower neutron attenuation of our sample. This value is consistent with the low-temperature calculated moment in Ref. 26 of 6.8 μ_B and close to the full moment (7 μ_B) which is often reduced by crystalline electric field and other effects.

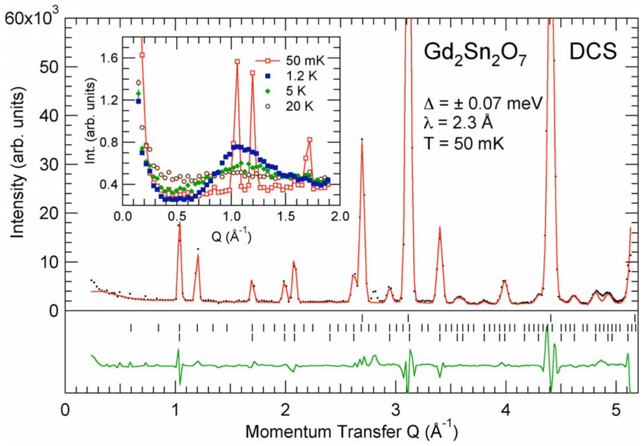

FIG. 1. (Color online) Elastic scattering and Rietveld refinement of $Gd_2Sn_2O_7$ at 50 mK. Scattering from the Al sample can was included in the refinement (upper row of tic marks). The middle and bottom rows of tic marks show the magnetic and nuclear Bragg-peak positions of $Gd_2Sn_2O_7$, respectively. Inset shows the diffuse scattering centered on 1.05 Å^{-1} as a function of temperature. The peak at ≈2.8 Å^{-1} comes from the sample environment.

Representative constant-Q cuts, taken under several instrumental conditions, are shown in Fig. 2. In this range one expects to observe four spin-wave modes, as discussed by Del Maestro and Gingras.[26] By considering several ratios between second and third nearest neighbors they expect the first two, relatively flat, modes to be between 0.09 and 0.18 meV (1 meV ≡ 11.6 K) with all four modes within 0.5 meV. With low energy resolution (top panel Fig. 2) one can see some quasielastic scattering and a dearth of scattering out to ≈10 meV. Improving the energy resolution reveals multiple modes within the first 0.5 meV, as shown in the lower two panels of Fig. 2. In the lowest panel, a gap of $\hbar\omega \approx 0.13(1)$ meV is seen unambiguously. This is in the middle of the range anticipated in Ref. 26 and compares well to the value from specific heat.[15] From the size of the measured gap the ratio of the second and third near neighbors to the nearest-neighbor exchange is less than 3%, again consistent with the 1% found by modeling the specific heat.

Other Q-dependent modes are seen at higher energy transfer. The powder averaging, unavoidable in the data from a polycrystalline sample, makes it hard to define all four expected levels, but at least three modes are clearly identified. A summary of the magnetic modes is given in the inset of the top panel. The gap is Q independent and drawn as a dotted line. The other modes have some degree of softening and resemble conventional spin-wave modes with a quadratic dependence in Q.

We have initiated an exploration of the ground state and elementary excitations in $Gd_2Sn_2O_7$ when subjected to a magnetic field. The field dependence of the intensities of several magnetic Bragg reflections is shown in Fig. 3. Although it is difficult to determine exactly the number of field dependent phases seen at 50 mK, two phase boundaries appear to occur around 2.5 and 5.25 T, as indicated by significant intensity changes in different magnetic Bragg peaks. In comparison, four phases were observed at base temperature

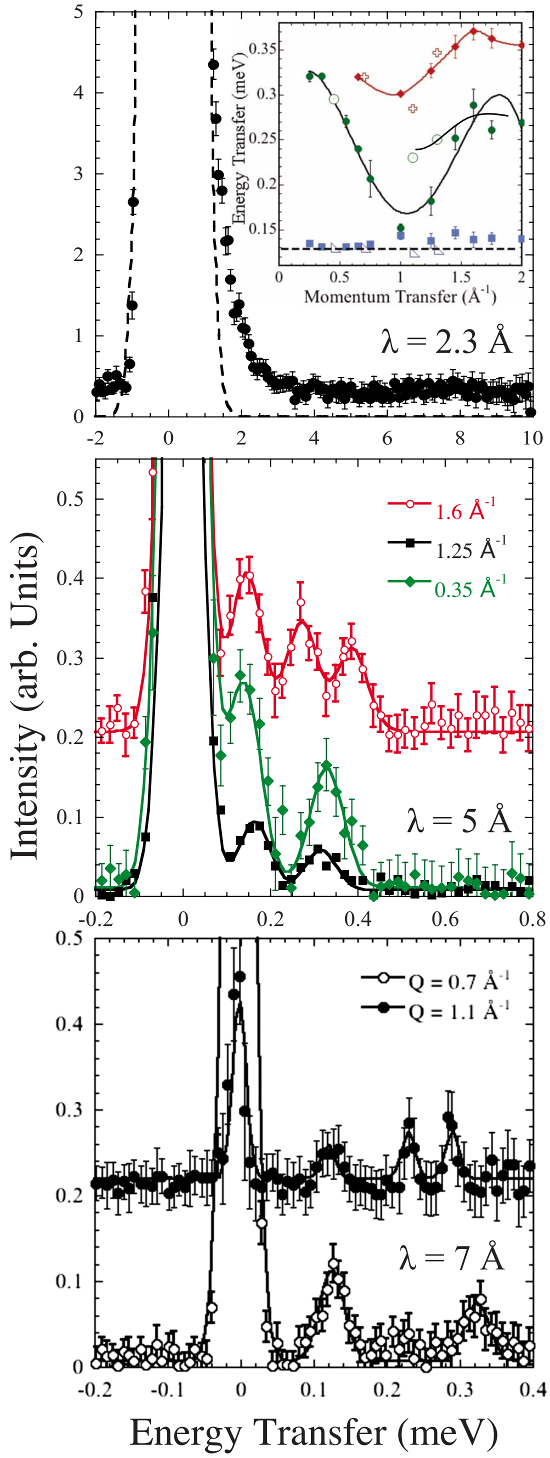

FIG. 2. (Color online) Cuts through $S(|\mathbf{Q}|,\omega)$ space under three different instrument setups. For clarity, the data at 1.6 and 1.1 Å^{-1} in the center and bottom panels have been vertically shifted, and the statistical errors associated with the data are not shown for all curves. The dotted line in the top panel shows the instrument resolution at 2.3 Å. Lines are Gaussian fits to the data, which are summarized in the dispersion relationship shown as an inset to the top panel with open and closed symbols representing 7 and 5 Å data sets, respectively. Lines are guides to the eyes, with a Q-independent gap (dotted line) at 0.13 meV above the ground state.

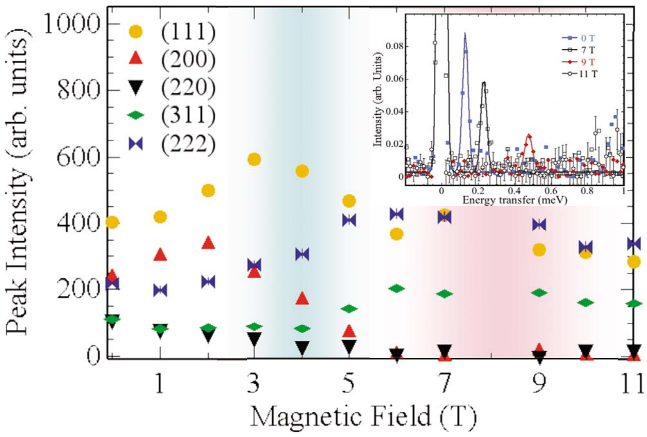

FIG. 3. (Color online) Peak intensity of several magnetic Bragg reflections at 50 mK as a function of applied field. Three possible phases are depicted by the shading. Inset shows the low energy spectrum, summed over all $|\mathbf{Q}|$, revealing the gap to the first low lying spin wave.

in $Gd_2Ti_2O_7$,[19] but as discussed earlier, the ground state of that system is not the "Palmer Chalker" state. With the availability of single crystals of $Gd_2Ti_2O_7$, Petrenko *et al.*[28] were able to identify the direction of the magnetic field that had to be applied to observe these transitions. However as in our experiment, polycrystalline samples observe all the transitions, assuming that the signal-to-noise ratio is appropriate. A similar number of field induced phases has been measured in another frustrated gadolinium magnet, namely, $Gd_3Ga_5O_{12}$, where three or four phases have been reported.[29,30] It could be argued that the infinite degrees of spin freedom allowed in these Heisenberg magnets along with the delicate balance between exchange and dipolar interactions allow an external field to partially pin the moments along many directions. Indeed, a recent mean-field study[31] showed that $Gd_3Ga_5O_{12}$ can be understood once the long-ranged nature of the dipole interactions was considered along with balanced exchange interactions out to J_3. We have shown that the strength of the further neighbor interactions in $Gd_2Sn_2O_7$ is a small percent of the nearest-neighbor interaction. Such a delicately balanced system will easily be perturbed by an external field of a few Teslas. In the inelastic spectrum, shown in the inset of Fig. 3, the Q-independent gap is seen to increase with field, lying outside the 1 meV range by 11 T. These initial field dependent studies will hopefully stimulate future studies, including the field dependent magnetic structure determination, single-crystal investigations, and further theoretical studies to explore the complex phenomena displayed by $Gd_2Sn_2O_7$.

To summarize, we have performed a detailed neutron-scattering study of $Gd_2Sn_2O_7$. In zero field the frustration is relieved and the spin-spin correlations that start to develop around 20 K order at 1 K in a manner consistent with the PC model.[14] This *static* state has the full ordered moment, with little room for spin fluctuations as observed by Mössbauer spectroscopy.[17,20,23] We have measured for the first time long-range propagating spin waves in this ordered phase, which are gapped by ≈1.5 K. As one might expect, although the system has satisfied itself and picked a unique ground state, this Heisenberg spin system is delicately balanced and multiple magnetic phases can be induced by applying moderate magnetic fields. These results raise the questions: why do muon and Mössbauer spectroscopies[17,20,23] suggest $Gd_2Sn_2O_7$ is dynamic and what is the origin of the ubiquitous temperature independent persistent spin dynamics seen in many rare-earth oxide pyrochlores by muons. We hope that these measurements will stimulate further studies to address these two very important questions.

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[1] *Magnetic Systems with Competing Interactions*, edited by H. T. Diep (World Scientific, Singapore, 1994).

[2] *Frustrated Spin Systems*, edited by H. T. Diep (World Scientific, Singapore, 2004).

[3] T. Katsufuji, H. Y. Hwang, and S.-W. Cheong, Phys. Rev. Lett. **84**, 1998 (2000).

[4] J. E. Greedan, M. Sato, Xu Yan, and F. S. Razavi, Solid State Commun. **59**, 895 (1986).

[5] J. S. Gardner, S. R. Dunsiger, B. D. Gaulin, M. J. P. Gingras, J. E. Greedan, R. F. Kiefl, M. D. Lumsden, W. A. MacFarlane, N. P. Raju, J. E. Sonier, I. Swainson, and Z. Tun, Phys. Rev. Lett. **82**, 1012 (1999).

[6] S. T. Bramwell and M. J. P. Gingras, Science **294**, 1495 (2001).

[7] J. N. Reimers, A. J. Berlinsky, and A.-C. Shi, Phys. Rev. B **43**, 865 (1991).

[8] M. J. P. Gingras and B. C. den Hertog, Can. J. Phys. **79**, 1339 (2001).

[9] N. P. Raju, M. Dion, M. J. P. Gingras, T. E. Mason, and J. E. Greedan, Phys. Rev. B **59**, 14489 (1999).

[10] R. Moessner and S. L. Sondhi, Phys. Rev. Lett. **86**, 1881 (2001).

[11] A. B. Harris, C. Kallin, and A. J. Berlinsky, Phys. Rev. B **45**, 2899 (1992).

[12] B. C. den Hertog and M. J. P. Gingras, Phys. Rev. Lett. **84**, 3430 (2000).

[13] V. N. Glazkov, M. E. Zhitomirsky, A. I. Smirnov, H.-A. Krug von Nidda, A. Loidl, C. Marin, and J.-P. Sanchez, Phys. Rev. B **72**, 020409(R) (2005).

[14] S. E. Palmer and J. T. Chalker, Phys. Rev. B **62**, 488 (2000).

[15] J. A. Quilliam, K. A. Ross, A. G. Del Maestro, M. J. P. Gingras, L. R. Corruccini, and J. B. Kycia, Phys. Rev. Lett. **99**, 097201 (2007).

[16] A. S. Wills, M. E. Zhitomirsky, B. Canals, J. P. Sanchez, P. Bonville, P. Dalmas de Réotier, and A. Yaouanc, J. Phys.: Condens. Matter **18**, L37 (2006).

[17] P. Bonville, J. A. Hodges, M. Ocio, J. P. Sanchez, P. Vulliet, S. Sosin, and D. Braithwaite, J. Phys.: Condens. Matter **15**, 7777 (2003).

[18] O. A. Petrenko, M. R. Lees, G. Balakrishnan, and D. M. Paul, Phys. Rev. B **70**, 012402 (2004).

[19] A. P. Ramirez, B. S. Shastry, A. Hayashi, J. J. Krajewski, D. A. Huse, and R. J. Cava, Phys. Rev. Lett. **89**, 067202 (2002).

[20] E. Bertin, P. Bonville, J.-P. Bouchaud, J. A. Hodges, J. P. Sanchez, and P. Vulliet, Eur. Phys. J. B **27**, 347 (2002).

[21] J. D. M. Champion, A. S. Wills, T. Fennell, S. T. Bramwell, J. S. Gardner, and M. A. Green, Phys. Rev. B **64**, 140407(R) (2001).

[22] J. R. Stewart, G. Ehlers, A. S. Wills, S. T. Bramwell, and J. S. Gardner, J. Phys.: Condens. Matter **16**, L321 (2004).

[23] P. Dalmas de Réotier, P. C. M. Gubbens, and A. Yaouanc, J. Phys.: Condens. Matter **16**, S4687 (2004).

[24] A. Yaouanc, P. Dalmas de Réotier, V. Glazkov, C. Marin, P. Bonville, J. A. Hodges, P. C. M. Gubbens, S. Sakarya, and C. Baines, Phys. Rev. Lett. **95**, 047203 (2005).

[25] J. S. Gardner, G. Ehlers, S. T. Bramwell, and B. D. Gaulin, J. Phys.: Condens. Matter **16**, S643 (2004).

[26] Adrian Del Maestro and Michel J. P. Gingras, Phys. Rev. B **76**, 064418 (2007).

[27] J. Rodriguez-Carvajal, Physica B (Amsterdam) **192**, 55 (1993).

[28] O. A. Petrenko, M. R. Lees, G. Balakrishnan, and D. McK. Paul, Phys. Rev. B **70**, 012402 (2004).

[29] P. Schiffer, A. P. Ramirez, D. A. Huse, and A. J. Valentino, Phys. Rev. Lett. **73**, 2500 (1994).

[30] S. R. Dunsiger, J. S. Gardner, J. A. Chakhalian, A. L. Cornelius, M. Jaime, R. F. Kiefl, R. Movshovich, W. A. MacFarlane, R. I. Miller, J. E. Sonier, and B. D. Gaulin, Phys. Rev. Lett. **85**, 3504 (2000).

[31] Taras Yavors'kii, Matthew Enjalran, and Michel J. P. Gingras, Phys. Rev. Lett. **97**, 267203 (2006).