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Intrinsic spin-disordered ground state of the Ising garnet $Ho_3Ga_5O_{12}$

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Motivated by predictions of a spin-ice state on the Ising garnet lattice, we have completed neutron-scattering experiments on single crystals of $Ho_3Ga_5O_{12}$. Our results show that although the Ho^{3+} spins have Ising-type character with an easy-axis anisotropy, the low-temperature ground state has coexisting long-range- and short-range-ordered spins and is therefore not an ice state. Inelastic neutron-scattering measurements reveal the presence of low-lying crystal-field states that develop a softening at the onset of short-range magnetic ordering. We suggest that the specific tuning of the exchange and dipolar interactions, along with the accessibility of these low-lying excitations, conspire to drive the system to a disordered state.

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Residual entropy states in condensed-matter systems have been the target of many recent experimental and theoretical studies. The new physics displayed in these materials, including Kasteleyn phases,[1] the possibility of "dynamic" ground states,[2] and magnetic monopoles in spin ices,[3] has provided insight into a variety of new and interdisciplinary problems. Despite this surge in interest, there have been relatively few relevant systems to study that retain a significant amount of spin disorder as the temperature approaches 0 K. Out of the so-called spin-ice candidates, only two materials have been verified to have truly disordered ground states: $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$,[4] which are due to the delicate balance of magnetic exchange, dipolar interactions, and crystal-field schemes that are needed to preserve this relatively fragile state of matter.

Outside of the pyrochlores, there are relatively few examples of spin-ice physics. The singular exception in the literature is the "Kagomé" ice state, which is obtained through applying a field along the [111] direction in the known pyrochlores and is not a true example of two-dimensional (2D) spin-ice physics.[5] There have been several key theoretical studies which search for spin-ice physics in 2D Kagomé systems and other three-dimensional (3D) systems such as the "hyper-Kagomé" garnets but little progress has been made. However, in the pioneering work of Yoshioka *et al.*,[6] a spin-icelike state is predicted for the cubic garnet system for certain ratios of the dipolar interaction compared to the magnetic exchange.

One good candidate for such a state is the Ising garnet system $Ho_3Ga_5O_{12}$ (HGO). An early specific-heat study of HGO shows a Schottky anomaly at around 3 K and no evidence of magnetic ordering down to 0.35 K. The residual entropy at low temperatures was not calculated, presumably due to the large nuclear Schottky term.[7] In this Rapid Communication, we present recent neutron-scattering data on HGO. Although we find that HGO is not a spin ice, we report here the existence of a different disordered ground state of coexisting long-range-ordered (LRO) and short-range-ordered (SRO) spins and make comparisons to the Heisenberg system $Gd_3Ga_5O_{12}$ (GGG). We suggest that the specific tuning of the exchange and dipolar interactions, along with the accessibility to low-lying crystal-field excitations, conspire to drive the system to a disordered state.

Single crystals of $Ho_3Ga_5O_{12}$ were grown by the traveling-solvent floating-zone (TSFZ) technique. The magnetic-susceptibility measurements were made with a dc superconducting quantum interference device (SQUID) magnetometer with applied magnetic field $\mu_0 H = 1.0$ T along the [111] direction. Neutron-scattering measurements were completed at NIST using the disk chopper spectrometer (DCS) with a wavelength of 4.8 Å. The crystal (mass of 5 g) was aligned in the plane perpendicular to the [111] direction and with a vertical magnetic field applied along the [111] direction. A dilution fridge was used which had a base temperature of 0.05 K.

Figure 1(a) shows the positions of the magnetic Ho ions in the garnet structure, which can be visualized as a three-dimensional network of corner-shared triangular plaquettes along the cubic [111] direction [Fig. 1(b)]. The high-temperature susceptibility of $Ho_3Ga_5O_{12}$ [Fig. 1(c)] reveals an effective moment of $\mu_{\text{eff}} = 10.55(3)$ μ_B and a Curie Weiss temperature of −9.5(2) K, which would suggest that there are dominant antiferromagnetic interactions between the moments. However, this analysis does not take into account the presence of low-lying crystal-field states (in $Ho_3Ga_5O_{12}$, it is known that the ground state is a doublet, with another doublet at 6 K above the ground state[8]) or long-ranged dipolar interactions. The effective Curie Weiss temperature is likely to be smaller than −9.5 K since it is obscured by crystal-field effects.

Figure 2 shows the elastic neutron-scattering profile for samples oriented with the defining scattering plane $(H, -H, 0)$-$(K, K, -2K)$, perpendicular to [111] direction, and with the applied magnetic field along [111] axis. Figures 2(a)–2(c) show data in a zero field at $T = 4$, 0.6, and 0.05 K, respectively. Figure 2(d) shows data at $T = 0.05$ K with an applied magnetic field $\mu_0 H = 2$ T. At 4 K, nuclear Bragg peaks allowed by the $Ia\,\bar{3}d$ garnet structure are observed. At temperatures below 0.6 K, the data show pronounced mag-

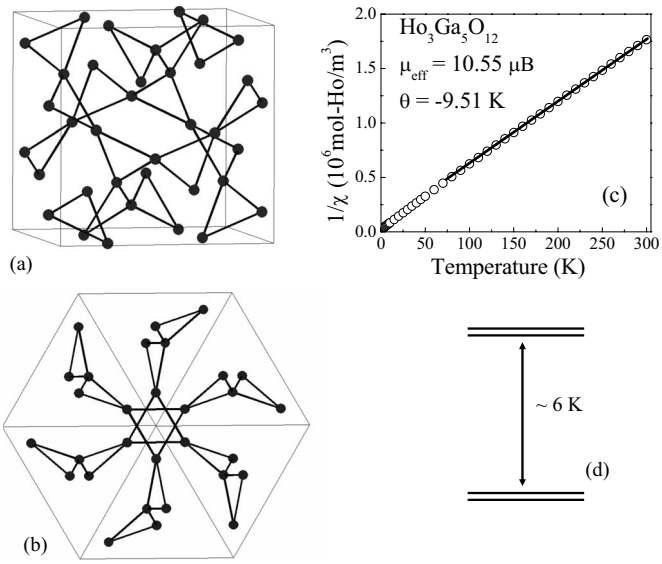

FIG. 1. (a) Positions of the magnetic Ho ions in the garnet structure; (b) the projection of the garnet structure along the [111] direction; (c) the inverse of the dc magnetic susceptibility for $Ho_3Ga_5O_{12}$; and (d) the low-temperature crystal-field scheme, with two doublets separated by 6 K.

netic diffuse scattering at antiferromagnetic zone centers, such as $(1,0,-1)$ and $(3,-3,0)$ which are forbidden by symmetry in the crystal structure [Fig. 2(b)]. This scattering results from strong short-ranged spin-spin correlations that are antiferromagnetic in nature. By 0.05 K, this diffuse scattering coexists with strong magnetic Bragg peaks [Fig. 2(c)]. As shown in Fig. 2(d), a modest field of 2 T quenches the diffuse scattering leaving only the Bragg peaks, indicative of a LRO structure.

Figure 3(a) shows the Q-dependent scattering near the $(3,-3,0)$ position at different temperatures. There is weak diffuse scattering at $T=0.6$ K; the intensity of which increases with decreasing temperature. At $T=0.3$ K, on top of the diffuse scattering, a sharper commensurate elastic peak abruptly appears. This peak becomes stronger in intensity and sharper in Q with decreasing temperature. In order to elucidate the low-temperature magnetic phase diagram of $Ho_3Ga_5O_{12}$, a parametric study of the $(3,-3,0)$ peak is carried out. Figure 3(c) shows the temperature dependence of the integrated intensity of the $(3,-3,0)$ peak and the diffuse scattering beneath this feature. The integrated diffuse scattering intensity slowly increases from $T=0.6$ K and almost saturates below $T=0.3$ K. On the other hand, the integrated Bragg-peak intensity of $(3,-3,0)$ rises immediately at $T=0.3$ K and saturates below $T=0.2$ K. With $\mu_0 H=2$ T, the spectra just show a sharp Bragg peak at $T=0.05$ K, as shown in Fig. 2(b). Accordingly, the low-temperature magnetic phase of $Ho_3Ga_5O_{12}$ can be described as: (i) a short-ranged antiferromagnetic-correlated spin system below 0.6 K and (ii) a coexistence of a short-ranged and long-ranged antiferromagnetic states below 0.3 K. These states appear to be independent since the intensity of the SRO elastic feature does not decrease as the LRO appears; (iii) in 2 T, the ordered structure persists but the diffuse scattering from the SRO state is suppressed.

As shown in Fig. 3(b), at $T=0.05$ K, the diffuse scattering around $(3,-3,0)$ is broader in Q space than the instrumental resolution and the peak shape can be fit to a resolution-convoluted Lorentzian form. The total magnetic spectra at $(3,-3,0)$ then can be fit to

$$S(Q) = A\ \exp[-(Q-Q_0)^2/2c^2] + B\frac{\Gamma_{SRO}}{\pi(\Gamma_{SRO}^2+Q^2)}, \quad (1)$$

where the first term represents the Bragg peak and the second term represents the component from the diffuse scattering (A and B are proportionality coefficients $c=\Gamma_{LRO}/\sqrt{2\ln 2}$ where Γ_{LRO} is the half width in the first term and Γ_{SRO} is the half width of the diffuse scattering in the second term). In Fig. 3(b), the fit of Eq. (1) to the experimental data is shown as the red line, with the diffuse scattering contribution as the blue line. The correlation lengths for the LRO and SRO then could be estimated as $\xi_{LRO}=1/(\Gamma_{LRO})$ and $\xi_{SRO}=1/(\Gamma_{SRO})$. As shown in Fig. 3(d), ξ_{LRO} increases with decreasing temperature. At $T=0.05$ K, $\xi_{LRO}\sim 100$ Å. On the other hand, ξ_{SRO} retains almost the same value below $T=0.3$ K of 6 Å. The nearest-neighbor Ho^{3+} spins in $Ho_3Ga_5O_{12}$ are separated by the distance $(\sqrt{6}/8)a=3.8$ Å (the lattice constant at low temperature was found to be $a=12.4$ Å). Therefore, the LRO in the sample covers almost 25 nearest neighbors and the SRO extends over only $1\sim 2$ nearest neighbors.

Comparing the magnetic phase diagram of $Ho_3Ga_5O_{12}$ to that of another well-studied garnet $Gd_3Ga_5O_{12}$, we note that both samples of GGG and HGO show a partially ordered ground state, with long-range ordering setting in a 140 mK for GGG and at 300 mK for HGO (the previous results of Petrenko *et al.*[9] indicate a partially ordered state at low temperatures, with the coexistence of Bragg peaks and diffuse scattering at $T=140$ mK). The original interpretation of this state was a mixture of a spin-liquid state and a set of ordered domains that nucleated around impurities.[9] A similar scenario may be present in HGO, however, we could detect very little Ho-Ga site disorder through neutron-scattering and x-ray measurements. Also, the magnetic structure between the two samples must be very different since different Bragg peaks are observed (GGG is incommensurate, while HGO appears to be commensurate with the lattice). Furthermore, a recent theoretical study of GGG suggests that the incommensurate order is *intrinsic* to the sample—taking into account next-nearest-neighbor exchange and dipolar terms, the ground state can be explicitly determined *without* invoking impurities as a source.[10]

It is important at this point to clarify the difference in the local magnetic symmetry of the two garnet sublattices. In GGG, for $^8S_{7/2}Gd^{3+}$ ions, $J=S(L=0)$. The anisotropy for the spins is weak and the system can be treated as a classical Heisenberg model. On the other hand, in $Ho_3Ga_5O_{12}$, for $^5I_8Ho^{3+}$ ions, $J=L+S(L\neq 0)$. The anisotropy for the spins from the crystal fields should be stronger than that of GGG and the spin system should be treated as an Ising spin system with a ground-state doublet (with an easy axis along the z direction for every Ho site). The theoretical study of Yoshioka *et al.*[6] of the frustrated Ising model on the garnet lattice shows that (1) with only the nearest-neighbor interac-

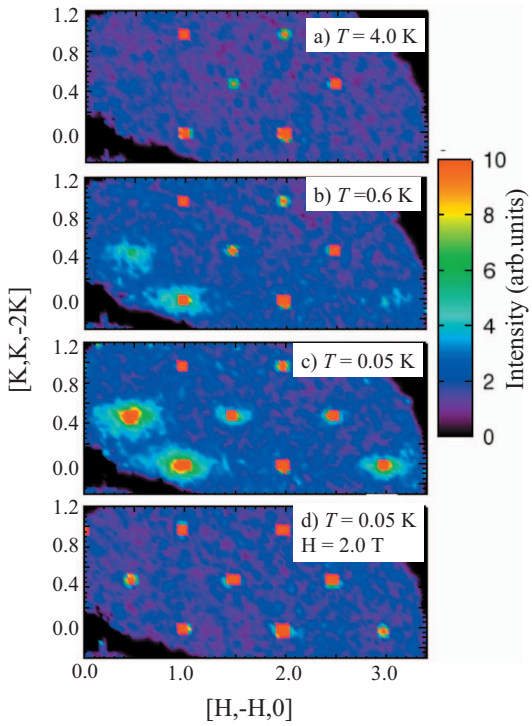

FIG. 2. (Color) Elastic neutron scattering (-0.02 meV$<\hbar\omega<0.02$ meV) within the scattering plane perpendicular to the [111] direction of $Ho_3Ga_5O_{12}$ at (a) T=4 K and μ_0H=0 T, (b) T =0.6 T and μ_0H=0 T, (c) T=0.05 K and μ_0H=0 T, and (d) T =0.05 K and μ_0H=2 T.

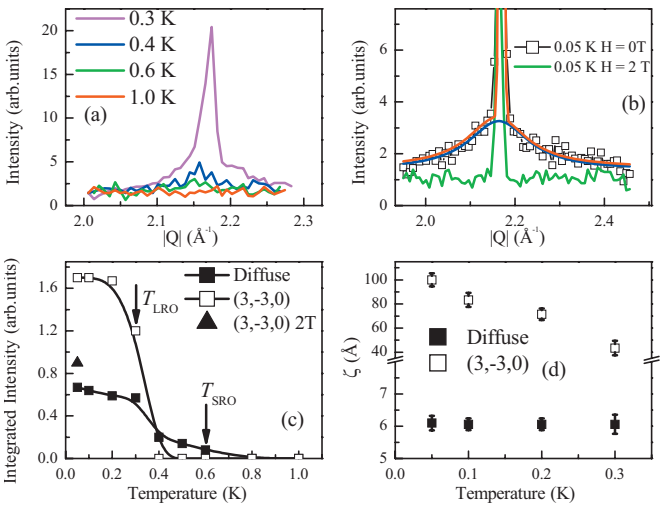

FIG. 3. (Color) (a) The diffuse scattering and Bragg peak at $(3,-3,0)$ at different temperatures; (b) the diffuse scattering and Bragg peak at $(3,-3,0)$ at T=0.05 K with μ_0H=0 T (the open squares) and μ_0H=2 T (the green line). The red line is the result of fit to the full scattering cross section described in the text, the blue line shows the contribution from diffuse scattering; (c) the integrated intensity of the diffuse scattering and Bragg peak at $(3,-3,0)$ as a function of temperature; and (d) the calculated correlation lengths for the diffuse scattering and long-range magnetic ordering for the Bragg peak $(3,-3,0)$.

tion, the system exhibits spin-ice behavior without phase transitions and (2) when the long-range dipolar interaction is taken into account, the system could show a partially ordered phase. According to their model, this unusual ground state has fluctuating spins which coexist in addition to the ordered spins. In $Ho_3Ga_5O_{12}$, the dipolar interaction energy scale is significant: $D_{nn}=\mu_0/4\pi(\mu_B^2/r_{nn})^3\sim 1$ K (taking the Ho^{3+} magnetic moment as 10.6 μ_B and the nearest-neighbor distance is r_{nn}=3.8 Å). This value is comparable to the exchange interactions, indicating that both exchange and dipolar interactions are important in this system. Therefore, such a state is plausible; although we emphasize here that long-ranged interactions, when included on finite-sized lattices, are notorious for generating erroneous ground states.[10] A full calculation of the Ising garnet is needed using a method such as Ewald sums for the identification of the true ground state.

Although the ground state of HGO is disordered, with coexisting regions of ordered and disordered spins, with an applied field along the [111] direction, a long-range-ordered state appears. We also notice that the intensity of $(3,-3,0)$ peak actually decreases in 2 T [Fig. 3(c)]. Since the SRO intensity is completely suppressed with an applied field of 2 T, this suggests that there is not a simple transfer of scattering from the SRO diffuse feature to the LRO Bragg peaks. It is likely that there is a spin reorientation involved with the

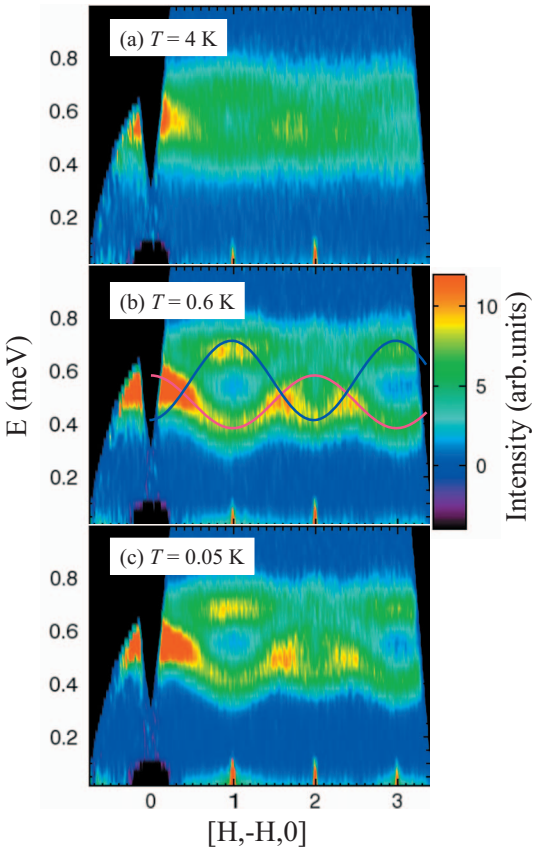

FIG. 4. (Color) Neutron scattering for 0 meV$<\hbar\omega<1.0$ meV within the $(H,-H,0)$-energy plane at (a) T=4, (b) 0.6, and (c) 0.05 K. The pink (the antiferromagnetic mode) and blue (the ferromagnetic mode) lines in (b) are the results of fit to the spin excitations described in the text.

concomitant long-ranged ordering. This could be an indication of a complicated magnetic-induced phase transition in HGO, which is similar to the state in GGG.[11,12] Further studies under magnetic fields are needed to determine the nature of this new ordered phase.

Figure 4 shows the inelastic neutron scattering within the $(H,-H,0)$-energy plane at different temperatures. At 4 K, the data show two bands around 0.5 and 0.7 meV with only weak dispersion from magnetic exchange. This is interpreted as being due to excitations between the ground-state doublet and the first-excited state doublet at 6 K ($\sim$0.6 meV). This is consistent with the specific-heat studies of HGO and another garnet $Ho_3Al_5O_{12}$, which both show a ground doublet state separated from the first-excited doublet state with an energy gap $\Delta = \sim 6$ K.[7,13] At 0.6 K, the spectrum is markedly different than that at 4 K. We observe sharp dispersive spin-wave excitations. These excitations appear to have minima in their dispersion near $(1,-1,0)$, $(2,-2,0)$, and $(3,-3,0)$ within the $(H,-H,0)$-energy plane. For the $Ia\,\bar{3}d$ space group, $(1,-1,0)$ and $(3,-3,0)$ are forbidden lattice Q-wave vectors and thus represent antiferromagnetic mode-softening points. By the converse argument, the $(2,-2,0)$ point indicates ferromagnetic mode softening. The excitations in Fig. 4(b) were fit to mixture of two modes and each mode is described by pair of simple linear spin-wave functions. Within this crude model, the ratio of the amplitudes of the modes suggests that the ratio of the ferromagnetic to antiferromagnetic J constants is roughly 3:2.

The appearance of a dispersion within the crystal-field excitations is indicative of strong correlations between the moments building at the onset of short-ranged ordering. The softening does not appear to change at the onset of long-ranged ordering nor is there any real change in the excitation spectrum [Fig. 4(c)]. This is reminiscent of the mode softening seen in other frustrated Ising-type systems that have short-range order, such as the pyrochlore $Tb_2Ti_2O_7$. In $Tb_2Ti_2O_7$, there is a mode softening at the Q-wave vector where there is a peak in the magnetic diffuse scattering.[2] It is noteworthy that some modulation of the crystal fields are already visible at 4 K, which indicates that the spin correlations already happen at higher temperatures than the SRO temperature. Although the physical origin of these features is unknown at this point, one idea put forward is that the excitation is a collective tumbling of spins over one tetrahedral.[2] In the case of HGO within the short-range-ordered phase, the positions of the diffuse scattering suggest that nearest-neighbor spins are antiferromagnetically coupled over nearest neighbors and it is at this Q where a mode softening occurs. The existence of a ferromagnetic mode is likely due to next-nearest-neighbor spins, as in the case of GGG.

In conclusion, we have found that HGO is not a spin ice but has a mixed ground state that is composed of coexisting LRO and SRO clusters. The existence of the low-lying modes provides a natural explanation for the dynamic nature of this system at low temperatures: virtual-crystal-field excitations ($\Delta = 6$ K for the first doublet) aided by the large value of exchange energy disrupts longed-ranged ordering until very low temperatures, where dipolar energy scales become significant ($D = 1$ K).[14] Further theoretical work is needed to take into account the long-range nature of the dipolar interaction to predict the nature of the ground state in HGO.

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