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Ordered spin-ice state in the geometrically frustrated metallic ferromagnet $Sm_2Mo_2O_7$

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The recent discovery of spin ice is a spectacular example of the noncoplanar spin arrangements that can arise in the pyrochlore $A_2B_2O_7$ structure. We present magnetic and thermodynamic studies on the metallic ferromagnet pyrochlore $Sm_2Mo_2O_7$. Our studies, carried out on oriented crystals, suggest that the Sm spins have an ordered spin-ice ground state below about $T^* = 15$ K. The temperature and field evolution of the ordered spin-ice state are governed by an antiferromagnetic coupling between the Sm and Mo spins. We propose that as a consequence of a robust feature of this coupling, the tetrahedra aligned with the external field adopt a one-in, three-out spin structure as opposed to the three-in, one-out structure in dipolar spin ices, as the field exceeds a critical value.

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Geometrical frustration arises when the magnetic interactions on a lattice are incompatible with the underlying crystalline symmetry. Systems with magnetic ions on triangular or tetrahedral lattices can exhibit geometrical frustration, which is often relieved at sufficiently low temperatures by weak residual interactions, giving way to complex magnetic ground states.[1] One particularly important example of geometrical frustration arises in materials based on the pyrochlore structure ($A_2B_2O_7$), where A and B ions form networks of corner-linked tetrahedra displaced by half the unit cell dimension from each other. Among the several interesting results recently reported in these materials,[2] one of the most remarkable is the discovery of a spin-ice state in the insulating pyrochlores $Dy_2Ti_2O_7$ (DTO) and $Ho_2Ti_2O_7$ (HTO),[3–5] having a disordered ground state in which two spins on each tetrahedron point in and two spins point out, isomorphic to the proton ordering in water ice.[6]

The recent observation of the spin-ice state in the metallic ferromagnet pyrochlore $Nd_2Mo_2O_7$ (NMO) has opened up an entirely new avenue for future research in frustrated systems with itinerant degrees of freedom.[7–9] The spin chirality in NMO is believed to perturb the charge dynamics so strongly that unconventional transport properties emerge in the spin-ice state. The gigantic anomalous Hall component which appears in the spin-ice state in NMO, for example, cannot be described using any of the conventional theories of the anomalous Hall effect.[7,10] In addition to the spin-chirality mechanism, a two-component model has also recently been proposed to explain the anomalous Hall effect in these materials.[11] Despite these significant developments, the lack of similar systems that couple the itinerant and magnetic degrees of freedom on a frustrated lattice hampered further research in this field. In this Rapid Communication we have attempted to fill this void by presenting a second example of a spin-ice state in the metallic pyrochlore $Sm_2Mo_2O_7$ (SMO). We note that, very recently, $Pr_2Ir_2O_7$ has also been suggested as another possible metallic spin-ice pyrochlore.[12]

SMO is a metallic ferromagnet pyrochlore with a ferromagnetic temperature (T_C) of 80 K due to Mo spin ordering.[13] However, the ground state properties of the Sm spins in SMO remained unexplored, mainly for two reasons: (1) the large neutron absorption cross section of Sm, which precludes neutron scattering studies, and (2) the difficulties in growing large single crystals. Our investigations on oriented crystals of SMO show that the Sm spins in this compound have an ordered spin-ice ground state that develops below 15 K. The spin-ice state in SMO results from a robust antiferromagnetic (AF) coupling of Sm spins with a high degree of anisotropy along the [111] direction with Mo spins. Our observations suggest that the strength of AF f-d coupling between the rare-earth and Mo spins in SMO is much stronger than in NMO, which dramatically affects the evolution of the ordered spin-ice state under an applied magnetic field. We believe that the magnetic ground state for SMO is identical to the ordered spin structure that emerges in canonical spin-ice compounds when subjected to an external magnetic field, which should be contrasted with the more complicated ordered spin structures that develop in some other materials, including $Tb_2Sn_2O_7$ (Ref. 14) and $Ho_2Ru_2O_7$.[15]

The single crystal of SMO was grown using the optical floating-zone method in a purified Ar atmosphere. The lattice parameter of 10.420 Å for the grown crystal is in good agreement with the value reported earlier.[16] The successful growth of cm^3-size crystals of SMO is achieved by overcoming specific difficulties, including the decomposition of the pyrochlore phase at low temperatures,[16] the highly volatile nature of MoO_2, and the dependency of the oxidation state of Mo on small variations in the growth atmosphere. The magnetization measurements were done with a Quantum Design superconducting quantum interference device magnetometer. The specific heat (C) was measured using a standard relaxation technique on a Quantum Design physical properties measurement system. The lattice contribution (C_{latt}) to the C of SMO is approximated by the specific heat of the nonmagnetic analog $La_2Zr_2O_7$ after molar mass correction.

The temperature dependence of the magnetization $M(T)$ of SMO under several magnetic fields applied parallel to the [111] direction is shown in Fig. 1. The steplike increase in $M(T)$ below 80 K marks the onset of ferromagnetic (FM) ordering in the Mo sublattice. Below T_C, the magnetization

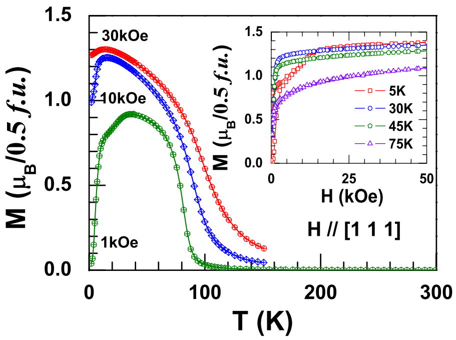

FIG. 1. (Color online) Temperature and magnetic field (inset) dependence of magnetization under several applied fields along [111] in a $Sm_2Mo_2O_7$ crystal.

exhibits two prominent features: a broad maximum centered around 35 K, observed only at low fields, followed by a sharp drop near 15 K. We argue that the low-temperature features in $M(T)$ of SMO arise from AF correlations developing between the Sm and Mo spins. The AF coupling between the Sm and Mo spins can be inferred from the $M(H)$ isotherms plotted in Fig. 1. The magnitude of the $T=5$ K magnetization is dramatically suppressed compared to the $T=30$ K value for a field applied along the [111] direction. This likely arises from the tendency of Sm spins to align antiferromagnetically to the ferromagnetically ordered Mo spins.

In the pyrochlore SMO, the trigonal symmetry (D_{3d}) of the crystalline electric field (CEF) splits the $^6H_{5/2}$ ground state in a free Sm^{3+} ion into three Kramers doublets. From Raman scattering and specific heat studies, we estimated that the excited CEF levels in the analogous titanate ($Sm_2Ti_2O_7$) are located well above the ground state doublet near $T=90$ and 175 K.[17] As the anionic arrangement around Sm is similar in both the compounds, we expect the Kramers doublet ground state of Sm in SMO to be an anisotropic well-isolated doublet.

The anisotropic magnetic behavior is evident from Fig. 2 where $M(H)$ isotherms are shown for magnetic fields along the [100], [110], and [111] axes at $T=2$ and 25 K. While the magnetization behavior is nearly isotropic at 25 K, highly anisotropic behaviors emerge at 2 K with easy- and hard-axis behaviors along [100] and [110], respectively, and a spin-flip transition in the [111] magnetization at $H_C \sim 15$ kOe. Since the FM state due to Mo spin ordering is nearly isotropic, as evidenced by the 25 K magnetization and the temperature variation of $M(T)$ above $T^*=15$ K along the [100] and [111] directions [inset, Fig. 2(d)], the huge anisotropy is likely due to the CEF-induced single-ion properties of the Sm spins ordering below T^*. While one would expect a small reduction in the [100] magnetization below T^*, there is no sign of such a reduction in Fig. 2. We attribute this to the fact that the Sm moment is much smaller than the Mo moment so that the reduction may be masked by an increasing magnetization in the ferromagnetically aligned Mo sublattice with decreasing temperature. In the pyrochlore structure, due to a severe trigonal distortion along the local [111] axes, the axial component of the CEF tends to confine the

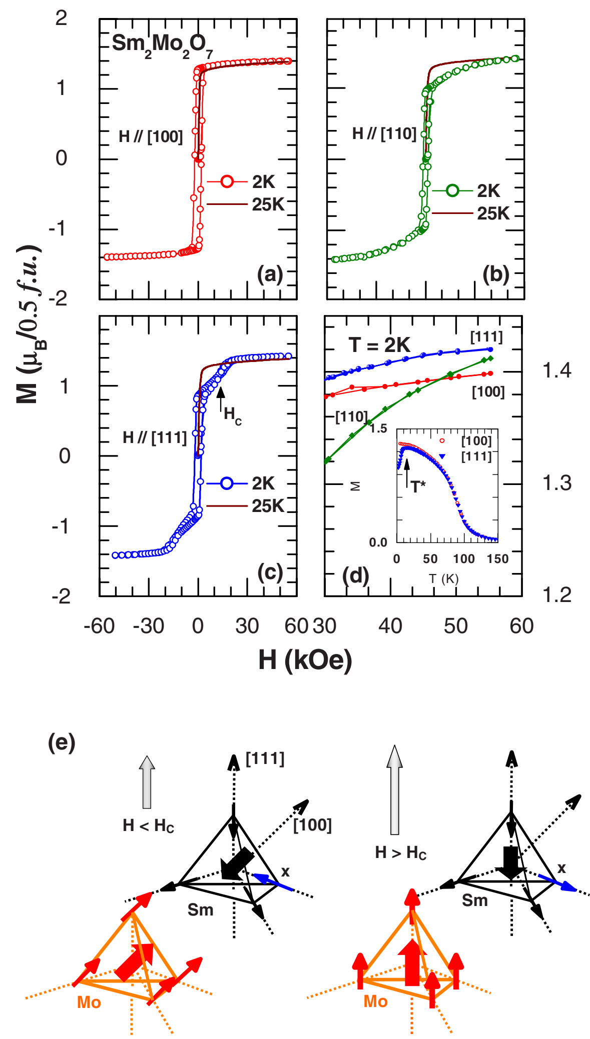

FIG. 2. (Color online) Isothermal magnetization in a single crystal of $Sm_2Mo_2O_7$ at $T=2$ and 25 K. Applied field along (a) [100], (b) [110], and (c) [111] crystallographic directions. (d) The expanded view shows the magnetization along the three axes close to saturation. The inset in (d) shows the temperature dependence of magnetization under a 10 kOe field applied along the [100] and [111] axes. (e) Schematics of the proposed mechanism for the spin-flip transition under a [111] field in $Sm_2Mo_2O_7$. The spin configuration on the Sm tetrahedron changes from the two-in, two-out to the one-in, three-out state (via flipping of the spin at site labeled x) as the applied field (H) exceeds a critical value H_C. The *resultant* magnetic moment per Mo (Sm) tetrahedron is indicated by the thick arrow at the center of each tetrahedron.

spins either along the local [111] axes of an elementary tetrahedron (Ising anisotropy) or in planes perpendicular to the [111] directions (planar anisotropy). The Dy (Nd) spins in DTO (NMO), for example, are Ising-like.[7,8]

We note that the nature of magnetic anisotropy in SMO below T^* (Fig. 2) bears a striking similarity to that of the dipolar spin ices DTO (Ref. 18) and HTO,[19] and the spin-ice ground state of the Ising FM model on the pyrochlore lattice due to Harris *et al.*[20] This suggests that the Sm spins in the pyrochlore SMO are Ising-like, having a spin-ice-like ground state. However, the temperature below which SMO shows spin-ice-like behavior is much higher than the corresponding

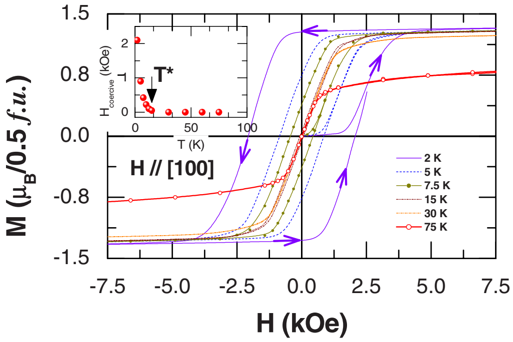

FIG. 3. (Color online) Magnetic hysteresis loops in the [100] oriented crystal of $Sm_2Mo_2O_7$ at several temperatures between 2 (outermost loop) and 75 K. Inset shows a sharp increase in the coercive field, determined from the main figure panel, in the ordered spin-ice state below T^*.

temperature in dipolar spin ices. This is because the effective FM force between the Sm spins results from their AF coupling with the ordered Mo spins. Further, the two-in, two-out configurations on each Sm tetrahedron in SMO are expected to be identical in the presence of the uniform internal magnetic field of the Mo sublattice, akin to the ordered two-in, two-out configuration realized in dipolar spin ices under externally applied magnetic fields.[21]

Spin ices under magnetic fields (i.e., in their ordered spin-ice state) show remarkable irreversibility in magnetization behavior. Hysteresis loops in DTO are found to be reversible above 0.65 K but highly irreversible at lower temperatures with coercivity of 2 kOe.[22,23] The ordered spin-ice state in SMO exhibits a similar irreversibility (Fig. 3) with the coercive field rising sharply to a value of 2.5 kOe below $T^*=15$ K (inset, Fig. 3).

Figure 4 (inset) shows the temperature variations of C/T and C_{mag}/T in SMO. The anomaly at $T_C=78$ K arises from the FM ordering of the Mo spins. A broad Schottky anomaly is found at lower temperatures as the system enters an ordered spin-ice state, similar to what is observed in NMO. We argue that the two-in, two-out ordering in these compounds is essentially a noncooperative phenomenon that occurs over a broad temperature range. This is reflected in the neutron scattering studies where the intensity of the magnetic Bragg peaks in NMO due to Nd^{3+} moments ordering in a two-in, two-out arrangement began to grow slowly near 40 K and continue to grow monotonically down to at least 8 K.[7]

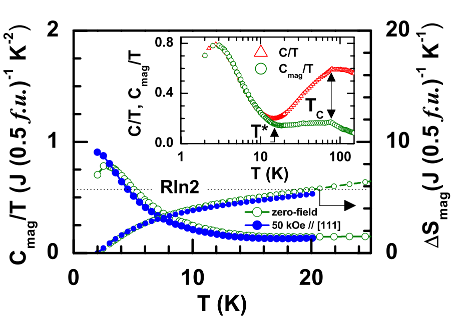

FIG. 4. (Color online) Specific heat (C), magnetic specific heat (C_{mag}), and change in magnetic entropy (ΔS_{mag}) in $Sm_2Mo_2O_7$.

The change in magnetic entropy in SMO in the $[2,T]$ K range, $\Delta S_{mag}(T)$ (Fig. 4), obtained by integrating C_{mag}/T, reaches 87% of $R\ln 2$ at T^*. Since, in the temperature range $T<T^*$ the C_{mag} is mainly due to the Sm spins,[24] we recover nearly the full $R\ln 2$ entropy associated with the Kramers doublet ground state, even though the entropy below 2 K $[0.67\ \mathrm{J}\ (\frac{1}{2}\ \mathrm{f.u.})^{-1}\ \mathrm{K}^{-1}$ based on linear extrapolation to zero$]$ is not included in our analysis. In dipolar spin ices, where the two-in, two-out ground state is highly degenerate, the spin entropy in zero field saturates to a value that is nearly 30% short of $R\ln 2$, consistent with the "missing entropy" predicted for water ice.[5] The absence of missing entropy in SMO, as also in dipolar spin ices under applied fields,[25] is consistent with an ordered two-in, two-out ground state for SMO. The increase in ΔS_{mag} above $R\ln 2$ at higher temperatures is presumably due to additional contributions to C_{mag}, including excited CEF levels of Sm and the Mo spins below T_C.

Under an applied field of 50 kOe along the [111] direction, the Schottky peak shifts to slightly lower temperatures. This small negative shift suggests that, even at 50 kOe, the Zeeman splitting in SMO is determined mainly by the AF f-d exchange. In NMO the internal field changes sign from negative to positive when the external field exceeds 30 kOe.[26] This suggests that the AF f-d coupling in SMO is much stronger than in NMO, which explains why the low-temperature peak in our specific heat studies and similar studies reported in Ref. 27 on polycrystalline samples up to 130 kOe shifts monotonically to lower temperatures. Finally, we note that the low-temperature integrated entropy in SMO changes only very slightly between $H=0$ and 50 kOe (Fig. 4), consistent with the proposal that the $H=0$ ground state of SMO is an ordered spin-ice state.

We shall now briefly discuss the saturation magnetization in SMO along the three field directions. In SMO, the expected saturation moment in the high-field limit along the three field directions is given by[28] $\sigma_{100}=[\mu_{Mo}+(1/\sqrt{3})\mu_{Sm}]$, $\sigma_{111}=[\mu_{Mo}+(1/2)\mu_{Sm}]$, and $\sigma_{110}=[\mu_{Mo}+(1/\sqrt{6})\mu_{Sm}]$, where μ_{Mo} and μ_{Sm} are the ordered Mo and Sm moments, respectively. In Fig. 2(d), $M(H)$ in SMO along the three field directions is shown on an enlarged scale. While M_H along [100] saturates at $1.4\mu_B/(\frac{1}{2}\mathrm{f.u.})$, the magnetization along [110] continues to increase with increasing field, exceeding the $1.4\mu_B/(\frac{1}{2}\mathrm{f.u.})$ value above 50 kOe, contrary to expectations. This argues that the saturation value attained along [100] does not reflect the complete saturation magnetization. These results can be understood if we suppose that the AF f-d exchange forces the magnetization vectors on the two sublattices to remain antiparallel up to the highest fields. In this framework, μ_{Mo} and μ_{Sm} are calculated to be $1.54\mu B$ and $0.25\mu_B$, respectively, slightly smaller than the free ion moments ($2\mu B$ and $0.7\mu_B$). Similarly reduced values for rare-earth and Mo moments were previously reported for $Nd_2Mo_2O_7$ (Ref. 29) and $(Tb_{1-x}La_x)_2Mo_2O_7$.[30]

The spin-flip transition in the [111] magnetization of SMO can be understood in terms of a reorientation of the Mo spins from the [100] direction to the [111] direction above a critical field of $H_C=15$ kOe. The robust f-d coupling produces a direction reversal of one of the Sm spins in the basal plane, leading to a one-in, three-out spin-ordered state. This is illustrated schematically in Fig. 2(e). It should be compared to the spin-flip transition under a [111] field in dipolar spin ices, where the spin arrangement on the tetrahedra aligned with the external field changes from the two-in, two-out to the three-in, one-out state at the spin-flip transition, when the weak dipolar forces are overwhelmed by the increasing Zeeman energy.

To summarize, using bulk measurements on oriented crystals we argue that the Sm spins in the metallic ferromagnet pyrochlore SMO have an ordered spin-ice ground state. The ordered spin ice in SMO is nondipolar in origin, but rather develops as a result of AF coupling of the Sm spins with ferromagnetically ordered Mo spins. This coupling is shown to be exceptionally robust. As a consequence of the robust feature of this coupling, the spin-flip transition in SMO under a [111] field is interpreted as a change in spin arrangement from the two-in, two-out to the one-in, three-out state, as opposed to the three-in, one-out state in dipolar spin ices. Because of the large effective FM interactions between the Sm ions, SMO offers an opportunity to investigate spin-ice dynamics at much higher temperatures than the dipolar systems. Furthermore, we propose SMO, with its spin-ice-like ground state that shows a distinct spin-flip transition under a [111] field, as an excellent candidate for testing the validity of the spin chirality mechanism of the anomalous Hall effect.

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