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Geometrical magnetic frustration in rare-earth chalcogenide spinels

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We have characterized the magnetic and structural properties of the $\mathrm{Cd}Ln_2\mathrm{Se}_4$ (Ln=Dy, Ho), and $\mathrm{Cd}Ln_2\mathrm{S}_4$ (Ln=Ho, Er, Tm, Yb), spinels. We observe all compounds to be normal spinels, possessing a geometrically frustrated sublattice of lanthanide atoms with no observable structural disorder. Fits to the high-temperature magnetic susceptibilities indicate these materials to have effective antiferromagnetic interactions, with Curie-Weiss temperatures $\Theta_W \sim -10$ K, except $\mathrm{CdYb_2S_4}$ for which $\Theta_W \sim -40$ K. The absence of magnetic long-range order or glassiness above $T=1.8$ K strongly suggests that these materials are a different venue in which to study the effects of strong geometrical frustration, potentially as rich in interesting physical phenomena as that of the pyrochlore oxides.

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INTRODUCTION

The geometry of the lanthanide ion sublattice in the pyrochlore structure is an array of corner sharing tetrahedra based on *kagomé* planes that connect via triangular layers. This arrangement of spins can show geometric frustration, such that no long-range magnetic ordering occurs, even at low temperatures.[1,2] The magnetic behavior of the $Ln_2\mathrm{Ti_2O_7}$ pyrochlores is widely studied, and, despite weak coupling between structural and magnetic degrees of freedom, the rare-earth pyrochlores exhibit a particularly rich range of magnetic behavior due to a balance between dipole interactions, single ion anisotropy, and exchange couplings.[3–9] Many of these materials possess strong crystal fields causing highly anisotropic spin states. In $\mathrm{Dy_2Ti_2O_7}$ and $\mathrm{Ho_2Ti_2O_7}$ the spins' directionality and effective ferromagnetic interactions produce Ising-like spins leading to spin ice characteristics, where the orientations of the spins are analogous to the H positions in ice.[10–24] Exotic low-temperature behavior has also been seen in $\mathrm{Gd_2Ti_2O_7}$,[25] $\mathrm{Yb_2Ti_2O_7}$,[26] and $\mathrm{Tb_2Ti_2O_7}$,[7–9,27,28] among others in this class of materials.

The octahedral cation sublattice in spinels is identical in geometry to the lanthanide cation sublattice in pyrochlores. Transition-metal spinel compounds such as $\mathrm{ZnCr_2O_4}$,[29] and $\mathrm{CdFe_2O_4}$,[30] are also widely studied in the context of geometric frustration. However, in contrast with the lanthanide pyrochlores, transition-metal spinels possess strong couplings between the spin and lattice degrees of freedom, often leading to rich phenomena where magnetic ordering and structural transitions couple.[31,32] Here we report magnetic and structural characterizations of $\mathrm{Cd}Ln_2\mathrm{Se}_4$ (Ln=Dy, Ho) and $\mathrm{Cd}Ln_2\mathrm{S}_4$ (Ln=Ho, Er, Tm, Yb) spinels, known as insulators with band gaps of 2 eV or more.[33,34] Due to the presence of nonmagnetic atoms on the A sites and an absence of disorder in the distribution of the ions, these compounds have magnetic sublattices analogous to the pyrochlores. Previous work exists on many of these compounds,[33–48] and the findings here expand on what has been reported. In addition, the properties reported in the literature are in disagreement, and no prior investigations into their potential to show different low-temperature properties associated with the presence of strong geometrical frustration exist. The differences in lanthanide-anion coordination and site symmetry between the pyrochlores and spinels intuitively suggest that the magnetic behavior of the lanthanides in the spinels differs from that found in the equivalent pyrochlores. The potential exists, however, for as rich a manifold of interesting magnetic behavior in the sub-K temperature regime.

EXPERIMENT

We synthesized $\mathrm{Cd}Ln_2\mathrm{S}_4$ (Ln=Ho, Er, Tm, Yb) spinels by firing CdS and $Ln_2\mathrm{S}_3$ ground together in an evacuated sealed quartz tube at 900 °C for 3–5 days. CdS was synthesized from CdO (99.998%) heated at 300 °C for 4 h under flowing argon bubbled through $\mathrm{CS_2}$ (99.9%). Stoichiometric amounts of Ho (99.9%), Er (99.9%), Tm (99.9%), and Yb (99.9%) metals were each reacted separately with S (precipitated purified) in sealed quartz tubes at 800 °C for 2 days to form $Ln_2\mathrm{S}_3$. $\mathrm{Cd}Ln_2\mathrm{Se}_4$ (Ln=Dy, Ho) was made by reacting the elements (Dy 99.9%) in evacuated sealed quartz tubes at 900 °C for 2 weeks.

We characterized the sample structures through x-ray powder-diffraction data using Cu$K\alpha$ radiation and a diffracted beam monochromater. Structural refinements were made using the Bruker AXS software package TOPAS 2.1© operated with a Pseudo-Voigt Thompson-Cox-Hastings (TCHZ) fitting profile. Refined parameters include zero corrections, sample displacement, scaling factors, cell dimensions, atomic positional coordinates, and thermal parameters (B_{eq}). We measured the dc magnetic susceptibility with a superconducting quantum interference device magnetometer (Quantum Design MPMS) on cooling over $T=290-2$ K in an applied field of $H=0.1$ T. We also performed measurements of ac magnetic susceptibility using the ACMS option for a Quantum Design Physical Property Measurement System (PPMS) cryostat. This instrument also gives dc magnetization measurements in fields up to 9 T using an extraction method. Curie-Weiss fits to the dc susceptibility data performed over $T=80-270$ K, with the exception of $\mathrm{CdYb_2S_4}$,

TABLE I. Structural parameters for $CdEr_2S_4$ at room temperature. Space group: Fd-$3m$ (#227); lattice constant $a=11.1178(4)$ Å. $\chi^2=1.23$; $R_{wp}=11.25$; $R_p=8.61$.

Atom	Position	x	y	z	Occ.	B_{eq}
Cd	8*b*	1/8	1/8	1/8	1	1.40(5)
Er	16*c*	1/2	1/2	1/2	1	1.14(4)
S	32*e*	0.2541(2)	0.2541(2)	0.2541(2)	1	1.50(6)

where fits were performed between $T=250-350$ K. The applied field dependence of the magnetization was measured at selected temperatures for all materials up to a field of 7 T.

RESULTS AND DISCUSSION

Structure refinement shows all samples to be normal spinels with lattice parameters similar to those found previously.[35,38,39] Contrary to one previous report,[41] we found no evidence for mixing of the cations among the two metal sites: refinements of the occupancies of the A and B sites did not result in statistically better fits compared to the ordered normal spinel structure. Table I lists the atomic positions for $CdEr_2S_4$ as an example. Table II lists the measured lattice parameters (a), atomic positions x (where $x=y=z$) for S or Se, and selected bond distances and angles for all of the samples studied.

Despite an analogous magnetic sublattice geometry, the local bonding Ln-X polyhedra surrounding the lanthanides in the spinel are drastically different from those in the pyrochlore structure. Figure 1 compares the local bonding environment of Er in $CdEr_2S_4$, determined in our structure refinement, with the Er in the reported crystal structure of $Er_2Ti_2O_7$ (Ref. 49) (which is equivalent to that found in all of the frustrated pyrochlores with only slight differences in bond lengths). The sixfold sulfur coordination around Er in $CdEr_2S_4$ forms an almost ideal octahedron, with a slight trigonal distortion from the normal 90° bond angles. The Er—S bond distance is equivalent for all six sulfurs. This presents a stark contrast to the eightfold oxygen coordination for Er in $Er_2Ti_2O_7$, where two very short Er—O bonds are found. Figure 1 shows that the short bonds in the pyrochlore point toward (and away from) the center of the lanthanide ion tetrahedra: this crystal field directs the Ising magnetic moments into the "in" and "out" configuration that is necessary for the display of spin ice behavior. The substantial difference in crystal fields between lanthanide spinels and pyrochlores suggests that their magnetic behavior will be quite different despite their analogous magnetic sublattice geometries. The longer Ln-Ln distance in the tetrahedral magnetic lattice in the spinel suggests weaker magnetic coupling than in the corresponding pyrochlore, but the values of θ_W are comparable and even sometimes larger, as described below.

Figures 2 and 3 show the magnetic susceptibilities of $CdLn_2X_4$ spinels as inverse susceptibility vs temperature plots. The high-temperature portion of each data set fits the Curie-Weiss law $[1/\chi=(1/C)(T-\theta_W)$, where C is the Curie constant], yielding the θ_W intercepts and effective moments shown in Table III. The experimental magnetic moments are consistent with the expected values for Ln^{3+} ions. Our negative θ_W values are generally similar to those previously reported, among which there is considerable variation. It is notable that the θ_W values are negative for the Ho and Dy spinels (-7 to -8 K) and much larger than those for the analogous spin ice pyrochlores.[23] This is possibly due to the influence of the substantially different crystal fields. Our Er spinel data is in contrast with a previous report, where the susceptibility of $CdEr_2S_4$ shows a turn over below 10 K.[35] $CdYb_2S_4$ has a much larger θ_W than the other spinels, and shows deviations from the Curie-Weiss fit below 150 K. This behavior results from the influence of low-lying crystal-field levels that become populated at lower temperatures.[35,43] The unusually large θ_W of $CdYb_2S_4$ obtained from the susceptibility above 150 K is therefore not solely a measure of the spin-spin interaction because the system is not in the crystal-field ground state at high temperatures. The analysis of $\chi(T)$ in terms of exchange and crystal-field effects for the specific case of $CdYb_2S_4$ is reported previously.[43]

Given the antiferromagnetic interactions implied by the negative values of θ_W, one might expect the onset of ordering

TABLE II. Structural parameters for $CdLn_2X_4$ at room temperature. Space group: Fd-$3m$ (#227).

Compound	Lattice constant, a (Å)	S or Se position (x)	Cd-X distance (Å)	Ln-X distance (Å)	X-Ln-X bond angle (deg)	χ^2	R_{wp} (%)
$CdDy_2Se_4$	11.6467(9)	0.2549(1)	2.620(3)	2.856(2)	87.70(7)	1.19	14.94
$CdHo_2Se_4$	11.6273(5)	0.2554(1)	2.625(2)	2.846(1)	87.46(6)	1.29	14.31
$CdHo_2S_4$	11.1582(3)	0.2544(2)	2.501(3)	2.741(2)	87.92(8)	1.25	13.29
$CdEr_2S_4$	11.1178(4)	0.2541(2)	2.486(3)	2.735(2)	88.07(8)	1.23	11.25
$CdTm_2S_4$	11.0900(4)	0.2555(2)	2.507(3)	2.713(2)	87.38(8)	1.19	12.24
$CdYb_2S_4$	11.0562(3)	0.2579(2)	2.545(3)	2.679(2)	86.20(9)	1.36	14.60

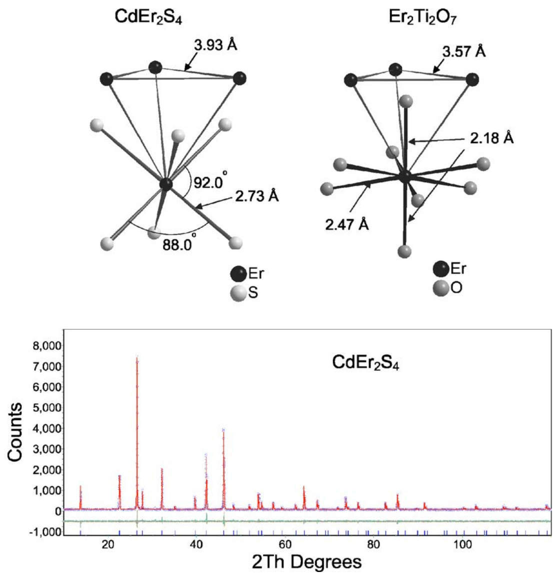

FIG. 1. (Color online) Upper portion: comparison of the Er-S coordination polyhedron in $CdEr_2S_4$ and the Er-O coordination polyhedron in $Er_2Ti_2O_7$ (Ref. 49). Also shown are the lanthanide tetrahedra, illustrating the differences in the orientations of the Er-*X* crystal fields with respect to the magnetic lattice geometry. Lower portion: Observed and calculated powder x-ray-diffraction pattern at ambient temperature for $CdEr_2S_4$. Lower line, difference between observed and calculated intensities.

at temperatures $\sim|\theta_W|$. The onset of such ordering is not seen in any of the samples studied, although, as shown in Fig. 3, $CdTm_2S_4$ does display a decreasing slope in $M(T)$ at the lowest temperatures, possibly due to the dominance of Van Vleck susceptibility at those low temperatures.[35,44] There is no frequency dependence in the ac susceptibility or differences between the field-cooled and zero-field-cooled magnetization in any of the samples (data not shown). The absence of these signatures of glass-type freezing excludes the possibility of a spin-glass state above $T=1.8$ K. The suppression of any sort of freezing or ordering down to temperatures well below $|\theta_W|$ confirms that the magnetism in these materials should be considered to be geometrically frustrated, as might have been guessed from their structure and the negative values of θ_W.

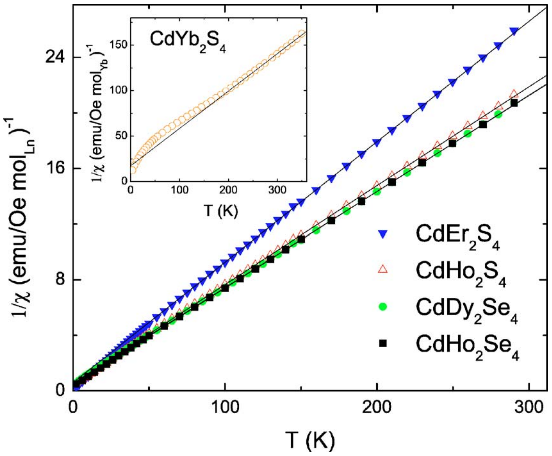

FIG. 2. (Color online) Magnetic susceptibilities measured in an applied field of 1 kOe, plotted as inverse susceptibility vs temperature, for $CdLn_2X_4$ spinels. Lines shown are the fits to the high-temperature data. Inset: the data for $CdYb_2S_4$.

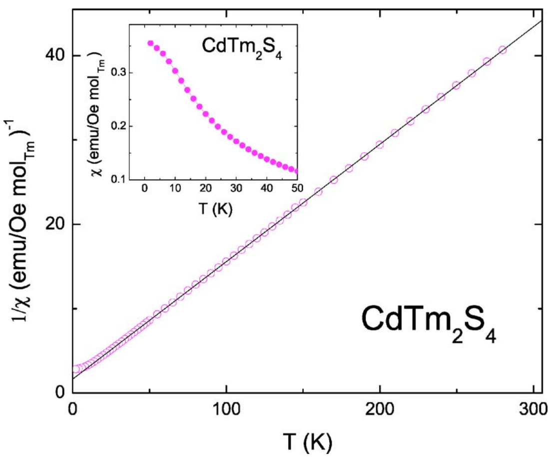

FIG. 3. (Color online) Magnetic susceptibility measured in an applied field of 1 kOe, plotted as inverse susceptibility vs temperature for $CdTm_2S_4$ spinel. Line shown is the fit to the high-temperature data. Inset: detail of linear susceptibility vs temperature in the low-temperature region for $CdTm_2S_4$.

We have also studied the field dependence of the magnetization, since there have been suggestions of interesting field-induced states in geometrically frustrated materials and demonstration of field induced states in single crystals of the spin ice materials.[17] Data taken on our materials at $T=2$ K up to a field of $H=9$ T demonstrate that none display such behavior. They do not, however, approach the expected full saturated moment for the free ions. This indicates that the crystal-field levels restrict the available spin states, as, for example, is the case for the frustrated spin ice compounds. In particular, $CdEr_2S_4$ shows a dramatic half magnetization plateau that is clearly developed at $T=2$ K (Figs. 4 and 5), reminiscent of what is seen in the spin ice compounds, $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$.[17,23,24] A half magnetization plateau is also seen in $Er_2Ti_2O_7$,[23] which has been described as a realization of the frustrated (111) *XY* pyrochlore lattice antiferromagnet.[3] Our results suggest that the same may be true for $CdEr_2S_4$, but a detailed study of the crystal-field levels is necessary to confirm this possibility.

TABLE III. Weiss constants and magnetic moments determined from the Curie-Weiss fits of high temperature portions of the magnetic susceptibilities.

Compound	θ_W (K)	p expt.	p calc. $(g[J(J+1)]^{1/2})$
$CdDy_2Se_4$	-7.6 ± 0.2	10.760 ± 0.007	10.63
$CdHo_2Se_4$	-7.0 ± 0.2	10.740 ± 0.006	10.6
$CdHo_2S_4$	-7.6 ± 0.2	10.600 ± 0.005	10.6
$CdEr_2S_4$	-6.9 ± 0.2	9.600 ± 0.005	9.59
$CdTm_2S_4$	-11.8 ± 0.2	7.58 ± 0.01	7.57
$CdYb_2S_4$	-42 ± 2	4.41 ± 0.04	4.54

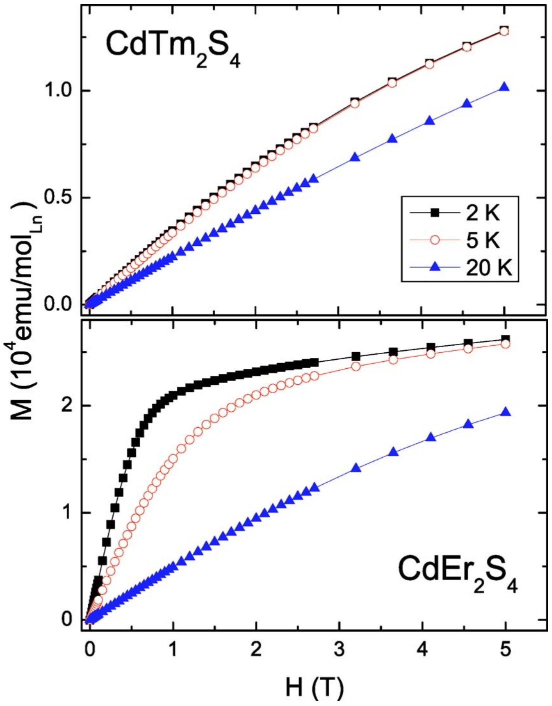

FIG. 4. (Color online) Magnetization vs applied field for two spinels, $CdTm_2S_4$ and $CdEr_2S_4$, measured to fields of 5 T at three representative temperatures.

CONCLUSION

In summary, we have investigated the possibility of geometrical frustration in the rare-earth chalcogenide spinels. While our results do not indicate ordering of any sort, it is the absence of such behavior down to temperatures well below the scale expected from θ_W which indicates the importance of frustration to the magnetic behavior of these unique compounds. These materials present the opportunity for uncovering physics as rich and complex as that observed in the frustrated oxide spinels and pyrochlores. Future studies to pursue such phenomena will probe at lower temperatures and in single-crystal samples.

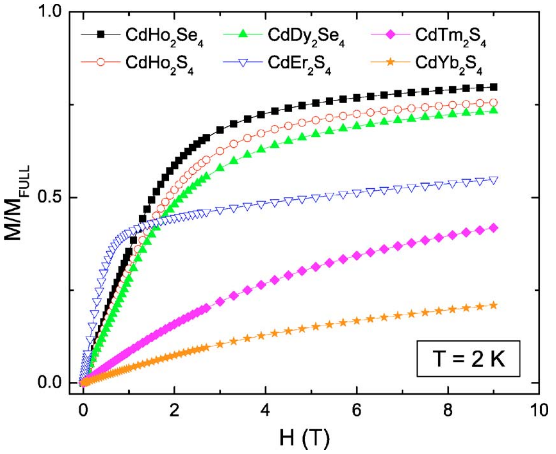

FIG. 5. (Color online) Variation of the normalized magnetization with applied field for all spinels studied at 2 K up to applied fields of 9 T. The measured magnetization has been normalized by the value expected based on the effective number of Bohr magnetons determined in the high-temperature susceptibility measurements.

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