

Magnetic characterization of the sawtooth-lattice olivines ZnL_2S_4 ($L=Er, Tm, Yb$)

G. C. Lau,¹ B. G. Ueland,² R. S. Freitas,² M. L. Dahlberg,² P. Schiffer,² and R. J. Cava¹

¹Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

²Department of Physics and Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, USA

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We report the magnetic properties of the ZnL_2S_4 ($L=Er, Tm, Yb$) olivines, in which the magnetic lanthanide ions are in a potentially frustrated geometry consisting of sawtooth chains of corner-sharing triangles. Fits to the high-temperature magnetic susceptibility yielded Curie-Weiss temperatures of $\theta_W \approx -4, -13,$ and -75 K for the Er, Tm, and Yb compounds, respectively. None of the compounds displayed magnetic long-range order above $T=1.8$ K. The lack of ordering at temperatures near θ_W may be attributed to either the low dimensionality of the structure or the frustrating effect of the triangular geometry.

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I. INTRODUCTION

Geometrical magnetic frustration can occur in compounds where the magnetic lattice, typically composed of triangles or tetrahedra, suppresses the long-range ordering of spins and gives rise to many degenerate magnetic ground states. Magnetic atoms arranged in a corner-sharing tetrahedral motif are found in pyrochlore and spinel lattices, and studies have yielded many examples of physics associated with frustration in such structures.^{1,2} Examples of such frustration have been found in the transition metal sulfide spinels,³⁻⁵ with frustration of the structural degrees of freedom even leading to a ferroelectric state in $CdCr_2S_4$.⁶ The rare-earth spinels CdL_2Se_4 ($L=Dy, Ho$) and CdL_2S_4 ($L=Ho, Er, Tm, Yb$), also appear to be frustrated, showing no magnetic ordering down to $T=2$ K and only reaching partial saturation of the full expected moment up to applied fields of $H=9$ T.⁷ The work on these thio-spinels suggests that investigating the magnetic properties of sulfides in the olivine structure, a structure type closely related to the spinel structure, should be of interest from the viewpoint of magnetic frustration.

Considering only the B site, AB_2X_4 spinels can be built up by alternating two different types of layers: kagomé nets and triangular layers. However, in the AB_2X_4 olivines, only one type of layer exists: an incomplete kagomé net resulting in sawtooth chains of alternating triangles. These triangles are nearly equilateral, creating a possibly frustrating geometry. Figure 1 shows the magnetic lattice of an AB_2X_4 olivine with bond distances given for $ZnTm_2S_4$ as an example.⁸ Two crystallographically distinct sites exist for the L atoms, denoted as $M1$ and $M2$. The $M1$ sites sit along the shorter backbone segments of the chains. Each $M1$ site has four nearest-neighbor spins that form the sawtooth configuration. The partial kagomé net can be revealed by connecting the sawtooth chains with a column of missing L atoms. This kagomé net is slightly distorted, as the sawtooth chains are situated closer together than in the ideal kagomé framework. The distance labeled 7.33 Å would be closer to ~ 8 Å in the ideal case. Layers of isolated chains in the ab plane stack in an $ABAB$ sequence along the c direction. The sulfur atoms have not been shown, but they form edge-sharing octahedra around the L cations.

Transition metal oxide olivines have been well characterized.⁹⁻¹⁴ Both Mn_2SiO_4 and Mn_2GeO_4 were found to exhibit magnetic frustration with antiferromagnetic transition temperatures well below the Curie-Weiss temperature magnitude $|\theta_W|$. The frustration was found to be less pronounced in Fe_2SiO_4 , and nonexistent in Co_2SiO_4 . The inherent differences in the effects of crystal fields on lanthanide ions, and the potential for much stronger dipole-dipole interactions, suggests that the rare-earth olivines may exhibit unusual magnetic states.

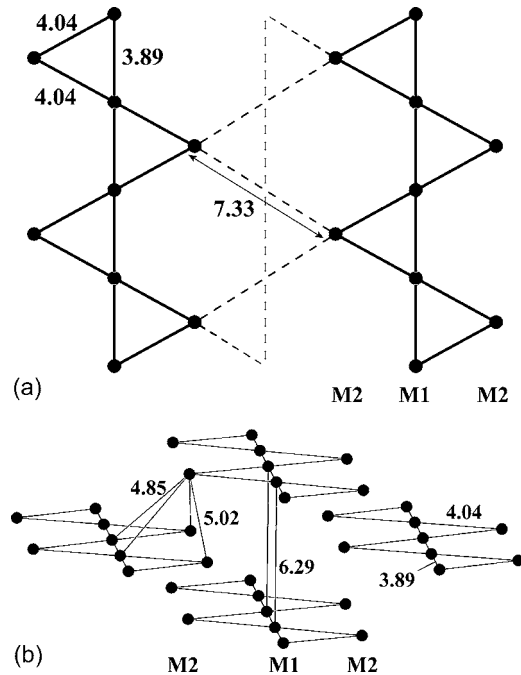


FIG. 1. The magnetic lattice of $ZnTm_2S_4$ with only Tm atoms shown. The $M1$ sites compose the backbone linear chain and connect to $M2$ sites to form alternating sawtooth isosceles triangles. The view from above of the ab plane (a) shows the isolated chains of solid black atoms connected by solid lines. Dashed lines illustrate the partial kagomé net by completing the slightly distorted lattice with a column of nonexistent atoms between the chains. Layers of these ab planes viewed from the side (b) show $ABAB$ stacking along the c axis. Distances are given in Å.

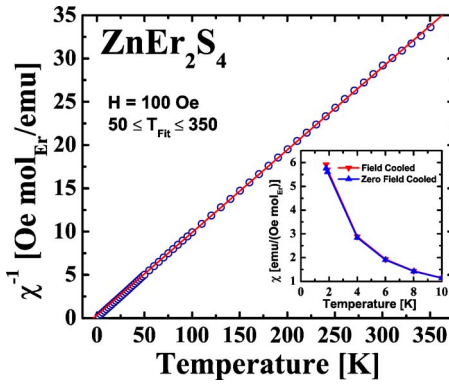


FIG. 2. (Color online) The inverse dc magnetic susceptibility versus temperature of ZnEr_2S_4 as measured in an applied field of $H=100$ Oe. The solid line was obtained through a fit to the high temperature points. Inset: Field-cooled and zero-field-cooled susceptibility plotted versus temperature for ZnEr_2S_4 .

The ZnL_2S_4 ($L=\text{Er}, \text{Tm}, \text{Yb}$) system represents a good candidate for the study of lanthanide olivines because the rare-earth atoms fully occupy the frustrating lattice sites with no cation mixing.⁸ The synthesis and structure of these compounds is described in earlier papers^{8,14} but, to our knowledge, thorough studies of their magnetic properties do not exist. Here we report the magnetic susceptibility $\chi(T)$ and magnetization $M(H)$ of ZnEr_2S_4 , ZnTm_2S_4 , and ZnYb_2S_4 over a temperature range of $T=350$ – 1.8 K and in magnetic fields up to $H=9$ T.

II. EXPERIMENTAL

Polycrystalline samples of ZnL_2S_4 ($L=\text{Er}, \text{Tm}, \text{Yb}$) were synthesized as previously reported.¹⁴ Stoichiometric amounts of Er (99.9%), Tm (99.9%), and Yb (99.9%) metals were each reacted separately with S (precipitated purified) in sealed evacuated quartz tubes at 800°C for 2 days to form $L_2\text{S}_3$. $L_2\text{S}_3$ was fired with ZnS (99.99%) in a one to one molar ratio in a sealed evacuated quartz tube at 1000°C for 3–5 days with intermittent shaking of the tube to form the olivine product. ZnEr_2S_4 formed in the same manner, but required a heating temperature of 1200°C . Sample purity was confirmed through x-ray powder diffraction using $\text{CuK}\alpha$ radiation and a diffracted beam monochromator.

We measured the dc magnetic susceptibility with a SQUID magnetometer (Quantum Design MPMS) on cooling over $T=350$ – 1.8 K in an applied field of $H=0.01$ T. The ACMS option for a Quantum Design PPMS cryostat was employed for dc magnetization measurements as a function of field using an extraction technique. Curie-Weiss fits to the dc susceptibility data were performed over $T=50$ – 350 K.

III. RESULTS AND DISCUSSION

Figures 2–4 show the magnetic susceptibilities of ZnEr_2S_4 , ZnTm_2S_4 , and ZnYb_2S_4 , respectively, as $\chi^{-1}(T)$. The high-temperature portion of each data set fits the Curie-Weiss law [$\chi^{-1}(T)=(T-\theta_W)/C$, where C is the Curie constant], yielding the θ_W values and effective moments shown

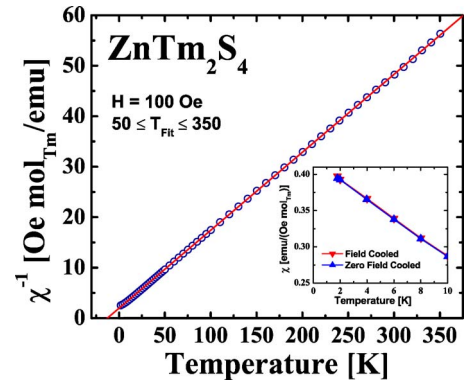


FIG. 3. (Color online) The inverse dc magnetic susceptibility versus temperature of ZnTm_2S_4 as measured in an applied field of $H=100$ Oe. The solid line was obtained through a fit to the high temperature points. Inset: Field-cooled and zero-field-cooled susceptibility plotted versus temperature for ZnTm_2S_4 .

in Table I. The experimentally determined moments are consistent with the expected values for the free L^{3+} ions. Unlike the transition metal olivines, none of our rare-earth olivines show signs of long-range magnetic order above $T=1.8$ K. Curie-Weiss temperatures determined for the frustrated rare-earth oxide pyrochlores depend significantly on the degree of spin exchange, dipolar interactions, and the effect of the crystal field surrounding the lanthanide ions.^{15–18} The same statement should apply for lanthanide olivines, thus the θ_W values determined here from fits to the high-temperature data are used simply as an initial probe for the general interaction strength of magnetic spins. ZnYb_2S_4 has an artificially larger $|\theta_W|$ than the other two due to deviations from the Curie-Weiss fit below 150 K. This behavior has been seen in other Yb containing compounds and is normally attributed to low-lying crystal field levels becoming depopulated at low temperatures.^{19–23}

The susceptibilities of these lanthanide olivines are similar to their spinel counterparts.⁷ As with the CdL_2S_4 ($L=\text{Er}, \text{Tm}, \text{Yb}$) spinels, the negative values of θ_W in the olivines suggests antiferromagnetic spin-spin interactions. We observe no ordering transitions down to $T=1.8$ K, although

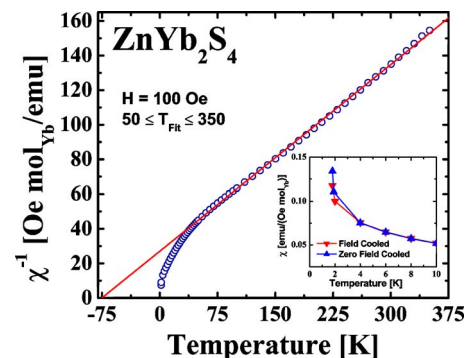


FIG. 4. (Color online) The inverse dc magnetic susceptibility versus temperature of ZnYb_2S_4 as measured in an applied field of $H=100$ Oe. The solid line was obtained through a fit to the high temperature points. Inset: Field-cooled and zero-field-cooled susceptibility plotted versus temperature for ZnYb_2S_4 .

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

Compound	θ_W (K)	p Exptl.	p Calc. $(g[J(J+1)]^{1/2})$
ZnEr ₂ S ₄	-3.6 ± 0.3	9.15 ± 0.01	9.59
ZnTm ₂ S ₄	-12.8 ± 0.2	7.19 ± 0.01	7.57
ZnYb ₂ S ₄	-75.2 ± 0.9	4.72 ± 0.01	4.54

Fig. 3 shows that $\chi^{-1}(T)$ of ZnTm₂S₄ displays a decreasing slope in $M(T)$ at the lowest temperatures, similar to what is observed in CdTm₂S₄.⁷ The insets in Figs. 2–4 illustrate that there is minimal difference between the field-cooled and zero-field-cooled magnetization. The lack of a bifurcation between the two measurements appears to exclude the possibility of a spin glass state or other frozen short-range ordered state in these materials above $T=1.8$ K. We believe the absence of long-range order down to temperatures below $|\theta_W|$ is likely due to the frustration of antiferromagnetic interactions between L spins on a triangular lattice. However, given the one-dimensional (1D) nature of the isolated sawtooth chains in olivines, we cannot rule out that the ordering temperature may also be suppressed by the reduction in spatial dimensionality.

The field-dependent magnetizations at $T=2$ K of the three L olivines are shown in Fig. 5. These measurements were used to probe for unusual field induced states as, for example, have been seen in the transition metal silicate olivines.²⁴ While the low T , high H data taken on our materials do not illustrate any magnetic transitions, the three samples also did not achieve their full saturated values. The ZnEr₂S₄ data in particular show saturation below the expected value for free Er ions, similar to what is seen in CdEr₂S₄.⁷ This incomplete saturation may be a result of single-ion anisotropy in these randomly oriented polycrystalline samples.²⁵

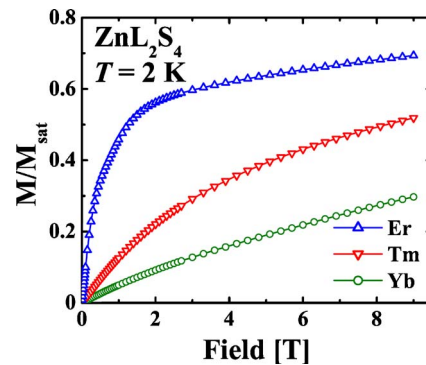


FIG. 5. (Color online) The normalized magnetizations versus applied field for the three olivines studied at $T=2$ K up to applied fields of $H=9$ T. The magnetizations have been normalized by the values expected for fully saturated free L^{3+} ions ($M=gJ$).

In summary, we report the magnetic properties of three lanthanide sulfide olivines, ZnL₂S₄ ($L=Er, Tm, Yb$). The absence of an observed transition down to temperatures well below $|\theta_W|$ suggests that either low dimensionality or geometrical frustration in the sawtooth triangular chains of these compounds suppresses long-range magnetic order. Furthermore, our magnetization data may indicate the presence of single-ion anisotropy in ZnEr₂S₄. The sawtooth lattice is well known as a frustrating geometry,^{26–28} but data on these lanthanide olivine sulfides at lower temperatures and on single crystals would be necessary to reveal any unexpected ground state properties in analogy to geometrically frustrated oxides.

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