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^{166}Er Mössbauer spectroscopy study of magnetic ordering in a spinel-based potential spin-ice system: $CdEr_2S_4$

Anaëlle Legros,[1] D. H. Ryan,[1,a)] P. Dalmas de Réotier,[2] A. Yaouanc,[2] and C. Marin[2]
[1]*Physics Department and Centre for the Physics of Materials, McGill University, 3600 University Street, Montreal, Quebec H3A 2T8, Canada*
[2]*Institut Nanosciences et Cryogénie, SPSMS, CEA and Université Grenoble Alpes, F-38000 Grenoble, France*

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^{166}Er Mössbauer spectroscopy measurements of $CdEr_2S_4$ show a large hyperfine field (B_{hf}) of 727.6(8) T at 5 K and clear evidence for slow paramagnetic relaxation with an energy barrier to reversal of 114(3) K. This behaviour stands in strong contrast to that of the corresponding pyrochlores ($Er_2Sn_2O_7$ and $Er_2Ti_2O_7$) where no magnetic effects are seen down to 1.56 K. The clearly dynamic ^{166}Er Mössbauer spectra and the absence of a break in the susceptibility data suggest that there is no magnetic order above 1.8 K in $CdEr_2S_4$. *© 2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4906182]

I. INTRODUCTION

Geometrically frustrated materials often yield novel and complex phenomena such as spin ices where a highly degenerate magnetic ground state raises issues like the existence of a true ground state and the separation of magnetic poles. This exotic behaviour has already been seen and studied in systems with the pyrochlore crystal structure[1,2] (e.g., the rare earth stannates $R_2Sn_2O_7$ and titanates $R_2Ti_2O_7$), but questions remain concerning the generality of the spin ice concept.

Recently, the CdR_2S_4 and CdR_2Se_4 families were identified as geometrically frustrated systems based on a spinel structure ($Fd\bar{3}m$ space group)[3] and while they share the same basic structure as the pyrochlore systems (the magnetic ions form a network of corner-sharing tetrahedra) the coordination of the rare earth ions is quite different. The sixfold sulphur (or selenium) coordination around the R site in the spinels forms an almost perfect octahedron with S(Se)–R distances of ∼2.7 Å,[3] while the eightfold oxygen coordination in the pyrochlores includes two very short O–R bonds (∼2.2 Å (Ref. 4)). This substantial difference in coordination leads to differences in crystalline electric fields (CEF) and permits the impact of geometrical frustration to be studied in a quite different environment.

$CdEr_2Se_4$ has been identified as a spin ice[5] and the corresponding sulphide, $CdEr_2S_4$, exhibits the same "half-magnetisation" plateau in M(B) at 2 K as the selenide.[3,6] This may indicate that it too is a spin ice. Earlier ^{166}Er Mössbauer work was limited to a single spectrum at 4.2 K and showed $B_{hf} = 728(4)$ T, suggesting that a full Er moment was present and that the system was magnetically ordered at 4.2 K.[7]

We extend this work here by following the behaviour from 5 K to 60 K. We also compare the behaviour of the Er in the spinel $CdEr_2Se_4$, with that in the two pyrochlore systems $Er_2Sn_2O_7$ and $Er_2Ti_2O_7$.

II. EXPERIMENTAL METHODS

The polycrystalline $CdEr_2S_4$ spinel sample was prepared using a two step process in sealed quartz ampoules. The first step is a chemical vapor reaction between erbium and sulphur. High purity starting materials CdS (5*N*), erbium metal (5*N*), and sulphur (5*N*) were mixed together and sealed under vacuum. The temperature was raised gradually from 400 °C up to 900 °C to limit the pressure created by unreacted sulphur. The resulting mixture was then reground, pressed into pellets sealed under vacuum, and annealed for 2 weeks at 900 °C. The final material was checked by x-ray powder diffraction and was found to be single phased.

Susceptibility measurements were made using a Quantum Design Physical Properties Measurement System. The source for the ^{166}Er Mössbauer measurements was prepared by neutron irradiation of $Ho_{0.4}Y_{0.6}H_2$ to produce ∼9 GBq of the ^{166}Ho parent isotope ($T_{1/2} = 26.9$ h). Both the source and sample were mounted vertically in a helium flow cryostat and a high-purity germanium detector was used to isolate the 80.56 keV gamma. The spectrometer was operated in sine-mode and calibrated using a laser interferometer. Spectra were fitted using a full solution to the nuclear Hamiltonian[8] and a standard Blume-Tjon spin-flip model[9] was used to fit the dynamic spectra.

III. RESULTS AND DISCUSSION

We observed no frequency dependence (10 Hz–10 kHz) to the susceptibility between 1.8 K and 300 K, and the entire range could be fitted to a conventional Curie-Weiss form with an effective moment (p_{eff}) of 9.51(1) μ_B consistent with the 9.59 μ_B expected for Er^{3+}. Figure 1 shows no evidence of the previously reported flattening of $1/\chi(T)$ below 10 K.[6] Fitting the low-temperature range (1.8 K–50 K) gives a Curie-Weiss temperature (θ_{CW}) of −0.4(1) K, much closer to zero than the −6.9(2) K reported by Lau *et al.*,[3] but consistent with the −1.3(6) K reported for $CdEr_2Se_4$.[5] No sign of magnetic ordering was detected.

[a)] Author to whom correspondence should be addressed. Electronic mail: dhryan@physics.mcgill.ca.

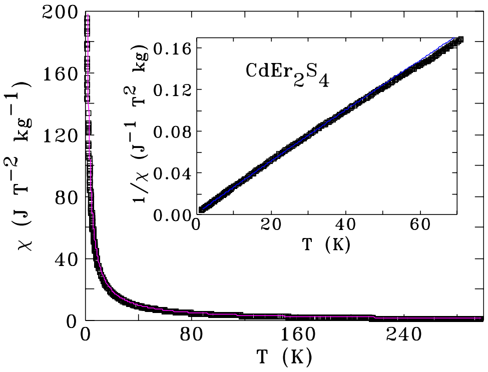

FIG. 1. AC susceptibility for CdEr$_2$S$_4$ in a drive field of 1 mT at frequencies of 10 Hz, 100 Hz, 1 kHz, and 10 kHz (no frequency dependence was apparent, so no distinction is made in the plot). The inset shows $1/\chi$(T). In both cases, the solid line is a Curie-Weiss fit as described in the text.

At 5 K, we observe a well-split five-line ^{166}Er Mössbauer spectrum (Figure 2) with $B_{hf} = 727.6(8)$ T ($\sim$95% of the free-ion value of 770 T (Ref. 10)) and a quadrupole interaction of 15.8(2) mm/s. These values are consistent with the previous report[7] and imply a fully stretched $J = \frac{15}{2}$ ground state for the Er^{3+} ion. We note that the electric field gradient observed by ^{166}Er Mössbauer spectroscopy is dominated by a 4*f* contribution, and as we were unable to obtain a fully paramagnetic spectrum of CdEr$_2$S$_4$ due to the persistence of slow paramagnetic relaxation (vide infra), we cannot comment on the orientation of the erbium moments here.

Closer inspection of the spectrum at 5 K reveals that the five absorption lines do not have the equal intensities expected for the $m_I = 2 \rightarrow m_I = 0$ ^{166}Er transition, and that the central line (just left of 0 mm/s in Figure 2) is slightly deeper. This deviation from equality becomes more apparent on warming and the evolution of the spectral shape clearly reflects the impact of slow paramagnetic relaxation of the erbium moments. The relaxation rate at 5 K fits as 11(7) MHz, at the edge of the ^{166}Er Mössbauer window, but it increases rapidly above 20 K and CdEr$_2$S$_4$ is almost paramagnetic by 50 K (the upper temperature limit of our measurements is set by the rapidly falling recoil-free fraction or *f*–factor).

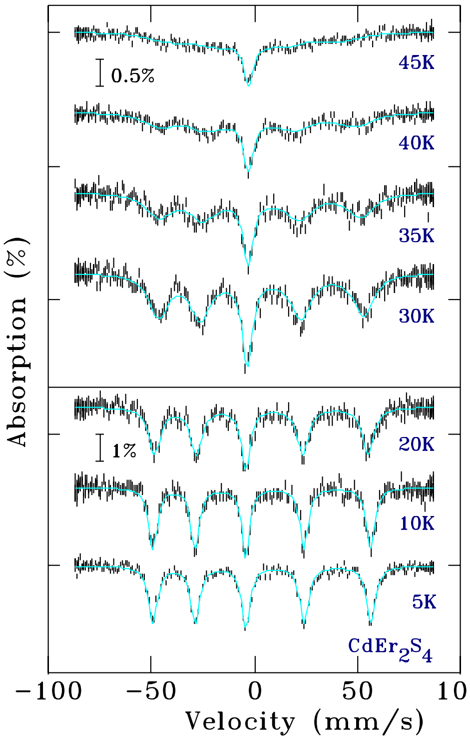

FIG. 2. ^{166}Er Mössbauer spectra of CdEr$_2$S$_4$ showing a well-split pentet at 5 K and the clear onset of dynamics above 20 K. The solid lines are fits described in the text.

Fitting the spectra with a simple ± spin-flip model[9] reproduces the spectra in Figure 2 and the behaviour of the derived relaxation rate shown in Figure 3 suggests a simple activated process, i.e.,

$$f \propto \exp(-\Delta/T),$$

where Δ is the energy barrier to spin reversal. The spectra taken above 20 K are most sensitive to the impacts of the relaxation and a fit using the activation model over the range of 30 K–45 K (inset of Figure 3) gives an energy barrier of 114(3) K. This likely corresponds to the energy of one of the CEF levels. Heat capacity measurements on the corresponding selenide (CdEr$_2$Se$_4$) placed the first excited CEF level at 47 K,[5] but this would be a poor match to our relaxation barrier for the sulphide. A full comparison will require both ^{166}Er Mössbauer measurements and heat capacity data for the selenide and sulphide, respectively. While confirmation that a CEF level is involved in the relaxation behaviour requires a full determination of the CEF level scheme by inelastic neutron scattering measurements.

The dynamic behaviour observed in the CdEr$_2$S$_4$ spectra stands in stark contrast to the behaviour of the erbium pyrochlores, Er$_2$Sn$_2$O$_7$ and Er$_2$Ti$_2$O$_7$, where we found neither magnetic splitting nor any evidence of line broadening down to 1.56 K (see Figure 4). While this may not be immediately surprising for Er$_2$Sn$_2$O$_7$ which does not order above 100 mK,[11,12] Er$_2$Ti$_2$O$_7$ orders at 1.2 K (Ref. 13) and many Er compounds exhibit relaxation effects well above T$_N$. Furthermore, the first CEF level for Er$_2$Ti$_2$O$_7$ lies at $\sim$70 K,[13,14] and that for Er$_2$Sn$_2$O$_7$ is at 59 K.[12] Both are somewhat higher than the 47 K estimated for CdEr$_2$Se$_4$, but all of them are below our estimate

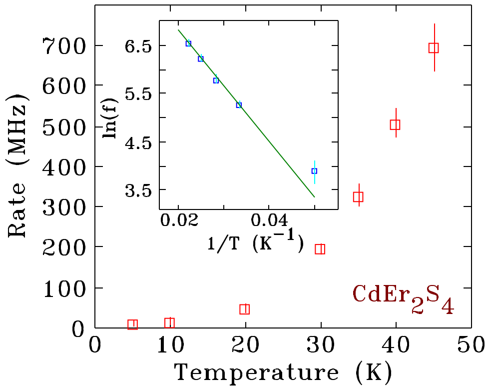

FIG. 3. Temperature dependence of the relaxation rate in CdEr$_2$S$_4$ (see text for details). Inset shows ln(*f*) vs. 1/T with the fit used to obtain the energy barrier to spin reversal. The point at 20 K ($1/T = 0.05$ K^{-1}) is shown but was not included in the fit.

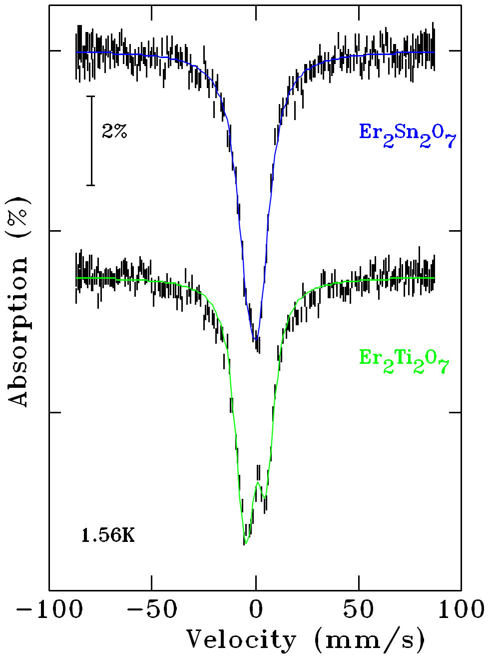

FIG. 4. ^{166}Er Mössbauer spectra of $Er_2Sn_2O_7$ (top) and $Er_2Ti_2O_7$ (bottom) at 1.56 K showing purely paramagnetic patterns with quadrupole splittings (eQV_{zz}) of −14(1) mm/s and +24.5(4) mm/s, respectively. There is no static or dynamic magnetic contribution in either spectrum.

of ~110 K for the reversal barrier in $CdEr_2S_4$. However, the ratios of 70/1.56 and 59/1.56 between the first excited CEF levels and the lowest experimental temperatures for the two pyrochlores are somewhat larger than the 114/5 used for $CdEr_2S_4$. This comparison would naively lead us to expect more rapid relaxation at the base temperature of our measurements in the spinel than in the two pyrochlores, which is just opposite to our observation. While a quantitative interpretation would require the knowledge of the CEF levels and wavefunctions in the spinel, one can already infer that the relaxation mechanisms in the pyrochlores and sulphide proceed by a quite different path. The difference in the paths may reflect the different local anisotropies: while $Er_2Ti_2O_7$[13,14] and $Er_2Sn_2O_7$[15] have local planar anisotropy, $CdEr_2S_4$ is expected to have the same axial anisotropy as $CdEr_2Se_4$.[5]

The absence of a magnetic transition down to 1.8 K, the small value for the Curie-Weiss temperature, magnetisation behaviour similar to that of $CdEr_2Se_4$, and the very slow relaxation found at low temperature for the Er^{3+} ions, suggesting the absence of low-lying CEF excited levels, make $CdEr_2S_4$ a candidate for a new spin ice system. We expect a confirmation of this result from a full magnetic characterisation of $CdEr_2S_4$ which is underway and a comparison with a ^{166}Er Mössbauer study of the established spin-ice $CdEr_2Se_4$.

IV. CONCLUSIONS

$CdEr_2S_4$ does not order above 1.8 K but rather exhibits slow magnetic relaxation with an energy barrier of 114(3) K. By contrast, the corresponding pyrochlores $Er_2Sn_2O_7$ and $Er_2Ti_2O_7$ are found strongly dynamic down to 1.56 K, despite having roughly comparable gaps to the first CEF level. This is strong evidence that the relaxation mechanisms in the spinel and pyrochlore systems are quite different. Given the similarities between the magnetic properties of $CdEr_2S_4$ and $CdEr_2Se_4$, an established spin-ice, our results are consistent with a spin ice state for $CdEr_2S_4$.

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