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FAST TRACK COMMUNICATION

Absence of long-range magnetic ordering in the pyrochlore compound $\text{Er}_2\text{Sn}_2\text{O}_7$

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Abstract

The low temperature behaviour of powder $\text{Er}_2\text{Sn}_2\text{O}_7$ samples has been studied by magnetic susceptibility, heat capacity, and neutron scattering experiments. We report here the absence of magnetic ordering down to 100 mK. Anomalies in the heat capacity can be accounted for through an analysis of the crystal field spectrum observed by inelastic neutron scattering spectroscopy. These new measurements on $\text{Er}_2\text{Sn}_2\text{O}_7$ suggest a new lower bound for the frustration index of $f = |\Theta_{\text{CW}}|/T_{\text{N}} = 14/0.1 = 140$, placing this compound into a highly frustrated regime.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Frustration has been studied extensively for the last two decades yielding numerous novel and exotic magnetic ground states such as the spin ice and spin glass phases [1, 2]. Therefore it has become an important, although intricate concept in our understanding of the fundamental nature of magnetism. The search continues for new compounds which lack long-ranged ordered states at low temperatures as fundamental tests of the Nernst heat theorem. Nature tends to succumb to ordered states in the limit of zero kelvin, and while this has led to a number of intriguing ground states through energetic compromises, there are few examples of the ‘holy grails’ of modern condensed matter science such as Anderson’s elusive spin liquid phase [3].

One family of compounds that has captured the attention of the condensed matter community is the pyrochlore series [2]. The pyrochlores are denoted by the general

formula $\text{A}_2\text{B}_2\text{O}_7$ where A and B are trivalent rare earth metal and tetravalent transition metal ions respectively. They are described by the space group $Fd\bar{3}m$, constituting an interpenetrating network of corner-sharing tetrahedra shifted by $(1/2, 1/2, 1/2)$. Magnetic pyrochlores have provided scientists with a variety of unusual physical properties due to their frustrated corner-shared tetrahedral topology [4]. These properties range from exotic magnetic ground states, to interesting thermal properties, and even catalytic potential [2].

Many highly frustrated pyrochlores such as $\text{Pr}_2\text{Sn}_2\text{O}_7$ [5] and $\text{Tb}_2\text{Ti}_2\text{O}_7$ [6] are characterized by short-range ordering as T approaches 0 K in an attempt to comply with the third law of thermodynamics; yet previous studies have determined that certain frustrated pyrochlores are able to acquire long-range order through various mechanisms. For example, the well-studied magnetic pyrochlore $\text{Er}_2\text{Ti}_2\text{O}_7$ orders through an order through disorder mechanism at $T = 1.1$ K [8], although studies performed on the isostructural

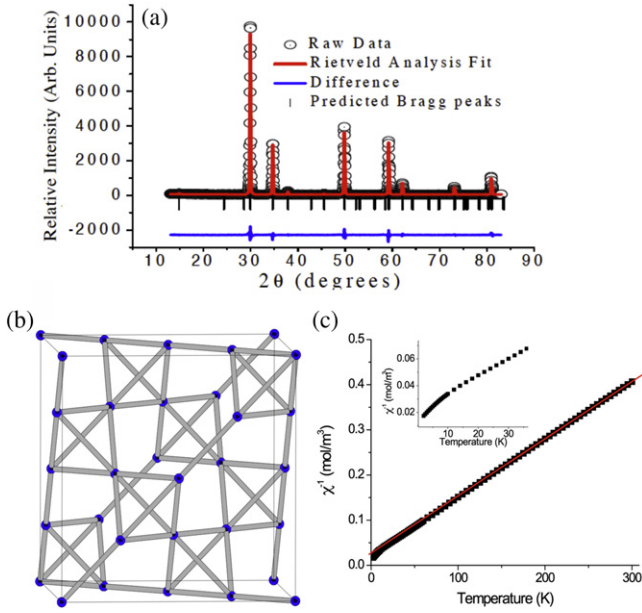


Figure 1. (a) Powder x-ray scattering of $\text{Er}_2\text{Sn}_2\text{O}_7$, with the indicated Rietveld refinement and residual. (b) The pyrochlore structure of $\text{Er}_2\text{Sn}_2\text{O}_7$. (c) The inverse of the DC susceptibility of $\text{Er}_2\text{Sn}_2\text{O}_7$, with lower temperatures emphasized in the inset.

compound $\text{Er}_2\text{Sn}_2\text{O}_7$ demonstrate no indication of long-range ordering down to $T = 0.13$ K [9, 10].

This paper details the study of $\text{Er}_2\text{Sn}_2\text{O}_7$ by means of magnetic susceptibility, neutron scattering and heat capacity measurements. We have evidence that the Er^{3+} moments show no signs of long-range order down to $T = 100$ mK. Given that the local crystal field environments are similar for the titanate and stannate compounds, this raises interesting questions about the mechanism for ordering in $\text{Er}_2\text{Ti}_2\text{O}_7$, and also for the true ground state of $\text{Er}_2\text{Sn}_2\text{O}_7$.

2. Experiment

Polycrystalline samples of $\text{Er}_2\text{Sn}_2\text{O}_7$ were synthesized by a standard solid state reaction using stoichiometric amounts of analytical grade Er_2O_3 and SnO_2 . The oxides were mixed together, pelleted and fired at 1643 K for 24 h in air. The diffraction patterns were recorded by an x-ray powder diffractometer with $\text{Cu K}\alpha_1$ radiation (1.54059 \AA). The DC magnetic susceptibility measurements were made using a superconducting interference device (SQUID) magnetometer at the NHMFL in Tallahassee, Florida. The specific heat measurements were performed down to 0.35 K using a relaxation technique. The neutron scattering measurements were completed at NIST CHRNS using the disc chopper spectrometer (DCS) with a neutron beam of wavelengths of 1.8, 4.8, 7.0 and 9.0 \AA and a standard orange cryostat. A dilution refrigerator was used to obtain temperatures below 1.5 K.

3. Results

An x-ray diffraction pattern was taken of our compound; Rietveld analysis did not indicate any impurities present in

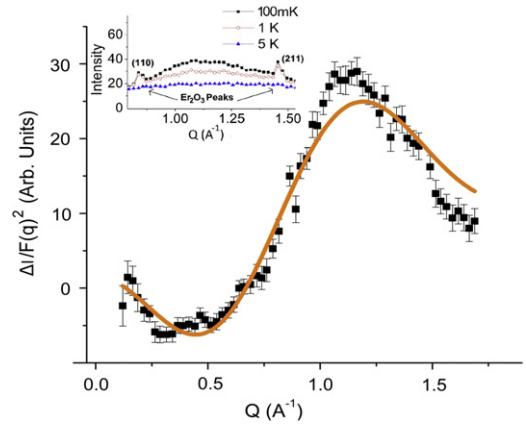


Figure 2. Magnetic diffuse scattering at 100 mK in $\text{Er}_2\text{Sn}_2\text{O}_7$. The fit is to a nearest neighbour correlation model described in the text. The error bars represent $\pm 1\sigma$. The inset shows the development of magnetic diffuse scattering as a function of temperature and the small magnetic Bragg peaks index on the Er_2O_3 impurity.

the sample, as shown in figure 1. The atomic coordinates and thermal parameters of our sample agree with other sources [9]. Also shown in figure 1 is the magnetic susceptibility of $\text{Er}_2\text{Sn}_2\text{O}_7$ tested over a temperature range of 2–300 K. The inset shows the DC susceptibility at low temperatures. The susceptibility can be fitted to a Curie–Weiss law above 30 K yielding $\Theta_{\text{CW}} = -14$ K which falls close to other reported values [9]. No sharp features can be seen down to 2 K which implies no signs of long-range ordering.

Neutron scattering experiments were performed on polycrystalline $\text{Er}_2\text{Sn}_2\text{O}_7$ at temperatures of 100 mK, 1 K, 5 K and 60 K. Diffuse scattering was observed between 0.7 and 1.7 \AA^{-1} starting at 5 K. The intensity of the diffuse scattering became more prominent with reducing temperature, as can be seen in figure 2. No observable collective modes or spin wave excitations can be seen; only the diffuse elastic scattering, indicative of short-range dynamic correlations between Er^{3+} spins even down to 100 mK. This would give $\text{Er}_2\text{Sn}_2\text{O}_7$ a remarkably high frustration factor of $f = 14/0.1 = 140$. An attempt to model the diffuse scattering was made by extracting the magnetic form factor and using a model to fit nearest neighbour and next nearest neighbour correlations. A reasonable fit to our powder 100 mK data is shown in figure 2; the inset is an energy cut of the diffuse scattering. A small impurity of Er_2O_3 was found which was not detected in our x-ray data. Er_2O_3 orders at 3.4 K, and we were able to see the (110) and (211) peaks overtop our diffuse scattering [11]. Our final fit to the data was made by subtracting out the impurity peaks and using the following empirical function for isotropic exchange:

$$S(Q) = \sum \langle S_i S_j \rangle \sin((Qd_i)/Qd_j) \quad (1)$$

where S_i is the spin at site i and d_i are the Er nearest neighbour (n.n.) and next nearest neighbour (n.n.n.) distances for the first two terms in the expression. Our fit implies weak antiferromagnetic n.n. interactions (first coefficient is negative) and ferromagnetic n.n.n. interactions (second coefficient is positive).

To characterize the crystal field scheme, we analysed the inelastic neutron scattering data and specific heat data both shown in figure 4. Integrating the specific heat over temperature shows that the crystal field ground state is a Kramer's doublet. The specific heat data can be fitted to a multiple level Schottky anomaly which agrees with our crystal field scheme. There is an anomalous rise in the specific heat at 0.35 K. This could be due to a split in the lowest lying crystal field doublet, or the proximity to an ordering phase transition at lower temperatures. There are some reports that $\text{Er}_2\text{Sn}_2\text{O}_7$ orders at temperatures less than 100 mK [7], but there are no neutron scattering measurements published to date to resolve this issue.

4. Discussion

$\text{Er}_2\text{Ti}_2\text{O}_7$ is a well-studied system which has a clear magnetic ordering through at $T_N = 1.173$ K with a $k = (0, 0, 0)$ wavevector. $\text{Er}_2\text{Sn}_2\text{O}_7$, by contrast, has not been studied to the same extent as $\text{Er}_2\text{Ti}_2\text{O}_7$, owing to the difficulty in obtaining single crystals, and the interest in comparisons to other well known titanates as model magnets. This recent work has shown that the crystal field structure has only varied slightly in the stannate compound compared to the titanate—the inelastic neutron scattering spectra of crystal field levels are shifted by 1.0 meV for the two samples [8]. However, the properties of the two compounds are dramatically different—the titanate orders at 1.173 K as an *XY* antiferromagnet with strong planar correlations, whereas the stannate does not order down to 100 mK with a fundamentally different diffuse scattering profile.

This begs the question as to why the two materials, with similar crystal field schemes and magnetic interactions, can be so different with respect to their magnetic properties. The Er^{3+} ion in common with both materials has a $4f^{11}$ electronic configuration with a $^4I_{15/2}$ single-ion ground state ($L = 6, S = 3/2$). The same $\langle 111 \rangle$ *XY* anisotropy should be present for both systems, although the spin interactions are larger in the titanate with a smaller lattice constant than the stannate. This is reflected in the different size of the Curie–Weiss constant of -22 K for $\text{Er}_2\text{Ti}_2\text{O}_7$ compared to -14 K for $\text{Er}_2\text{Sn}_2\text{O}_7$. One outstanding issue in the crystal field scheme calculated for the titanate is the large deviation of the moment in the ground state of $3.0 \mu_B$ compared to the theoretical moment of $9.59 \mu_B$ expected from the single-ion case. Poole *et al* have recently shown that this is largely due to quantum fluctuations which play an important role in the low temperature properties of this material [12]. This 'order by disorder' mechanism splits the degenerate ground state manifold and lowers the free energy of a particular ordering wavevector. A similar calculation would have to be made in the case of the stannate to determine the nature of the ground state.

One explanation for the lack of long-ranged order in the stannate down to 100 mK could be due to the weaker net spin interactions, which results in a lower Curie–Weiss temperature of -14 K. Using the titanate as a model, the frustration index is $f = |\Theta_{\text{CW}}|/T_N = 22 \text{ K}/1.173 \text{ K} = 18.7$. Assuming that a similar crystal field scheme is present, shifted

by slightly different local environments in the case of the stannate, the frustration index should be similar, resulting in a predicted ordering temperature of $|\Theta_{\text{CW}}|/f = 14 \text{ K}/18.7 = 0.74$ K. Since this work notes the lack of long-ranged order in the stannate, this implies that there is a qualitatively different mechanism in place, since the frustration index is $14/0.1 = 140$, or roughly an order of magnitude more. It is difficult to reconcile the same mechanism for the stannate case with that of the titanate. We note in passing that the 'order by disorder' mechanism fails to capture the spin excitation spectrum detailed by Champion *et al* [8]. The inclusion of an anisotropic term in the Hamiltonian, such as through the Dzyaloshinskii–Moriya interaction, could be insightful towards understanding the excitations.

McClarty *et al* take this point of view in their recent work on the ordering mechanism in $\text{Er}_2\text{Ti}_2\text{O}_7$ by considering terms within the Hamiltonian that are anisotropic [13]. Their work shows explicitly that isotropic exchange interactions are not sufficient enough to explain the ordering in the titanate. There must be an inherent anisotropy to the interactions (in fact, a very particular six-fold anisotropy due to the ψ_2 states) for this to occur. Ultimately, though, McClarty *et al* conclude that neither scenario adequately explains the neutron scattering results on $\text{Er}_2\text{Ti}_2\text{O}_7$. This leaves the 'order by disorder' mechanism questionable for the titanate, and not a viable scenario for the stannate.

It is worth emphasizing that significant differences between the stannates and titanates have been observed before among many members of the rare earth series. In the case of $\text{Gd}_2\text{Sn}_2\text{O}_7$, Wills *et al* have completed a comprehensive study of the differences between the magnetic ordering between this compound and $\text{Gd}_2\text{Ti}_2\text{O}_7$ [14]. It was found that the differences between the structures in the ordered phases is due to difference in sign of the third nearest neighbour super-exchange interaction among the Gd spins. The differences in the low temperature ground state of $\text{Er}_2\text{Sn}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$ might have a similar origin.

The inelastic spectrum of $\text{Er}_2\text{Sn}_2\text{O}_7$ suggests that significant low-energy spin fluctuations exist at 100 mK which have a clear dispersion away from the expected single-ion doublet (figure 3). Qualitatively, these data appear similar to the low temperature inelastic scattering spectrum of $\text{Tb}_2\text{Ti}_2\text{O}_7$, where a spin liquid state has been postulated for the zero field phase [15]. While single crystals do not yet exist for $\text{Er}_2\text{Sn}_2\text{O}_7$, it is imperative to investigate these features in more detail, and at lower temperatures, to reconcile the issues brought forward in this work. It has been recently shown by Ruff *et al* that $\text{Er}_2\text{Ti}_2\text{O}_7$ has a quantum phase transition in small applied fields ($H = 1.5$ T) where the transition temperature appears to approach zero Kelvin [16, 17]. The slight change in internal fields in the stannate compound could explain why there is a lack of order in this compound—it may be naturally tuned to a quantum phase transition. This is reminiscent of the related pyrochlore compounds $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Sn}_2\text{O}_7$. $\text{Tb}_2\text{Sn}_2\text{O}_7$ appears to order at low temperatures, but $\text{Tb}_2\text{Ti}_2\text{O}_7$ is a spin liquid in the limit of zero Kelvin. One approach taken to describe this system is that the delicate liquid state is disturbed by

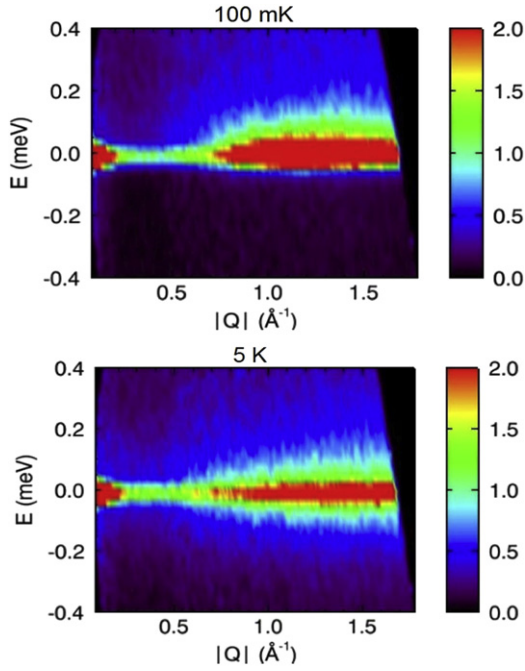


Figure 3. Inelastic neutron scattering profile of $\text{Er}_2\text{Sn}_2\text{O}_7$ at (a) 5 K and (b) 100 mK. Note the presence of significant spin fluctuations even at the lowest temperature recorded, and no new magnetic Bragg peaks are distinguishable.

the slightly different exchange constants and crystal field scheme—indeed, $\text{Tb}_2\text{Ti}_2\text{O}_7$ can be found to order in small applied magnetic fields [15]. It appears that $\text{Tb}_2\text{Sn}_2\text{O}_7$ has

behaviour qualitatively related to $\text{Tb}_2\text{Ti}_2\text{O}_7$ under applied fields [18]. A similar relationship may be occurring in $\text{Er}_2\text{Sn}_2\text{O}_7$ —it is a finely tuned spin liquid that orders under small perturbations (in this case, by changing the crystal field scheme slightly to the manifold present in $\text{Er}_2\text{Ti}_2\text{O}_7$). Further studies in applied fields of the stannates would be interesting to induce the ordering and discover the symmetry class of such a transition. Given that the stannate might be tuned to such a natural ground state, this implies that the liquid-like correlations noted in this paper are indicative of a spin liquid state similar to the titanate $\text{Tb}_2\text{Ti}_2\text{O}_7$. This would place $\text{Er}_2\text{Sn}_2\text{O}_7$ as a model quantum magnet among the stannate pyrochlores.

5. Conclusion

$\text{Er}_2\text{Sn}_2\text{O}_7$ has been studied through magnetic susceptibility, heat capacity and neutron scattering experiments. A viable crystal field scheme which is only slightly modified from $\text{Er}_2\text{Ti}_2\text{O}_7$ can adequately explain the bulk features of our data consisting of single-ion excitations with the f-electron manifold. A lack of long-ranged order has been observed down to 100 mK, placing the frustration index of $\text{Er}_2\text{Sn}_2\text{O}_7$ at $f = 140$, in contrast to $f = 18$ for the titanate. The ‘order by disorder’ mechanism suggested to play a role in the titanate has been discussed in the context our of results, and has been found to be inadequate in explaining why the titanate orders and the stannate fails to order.

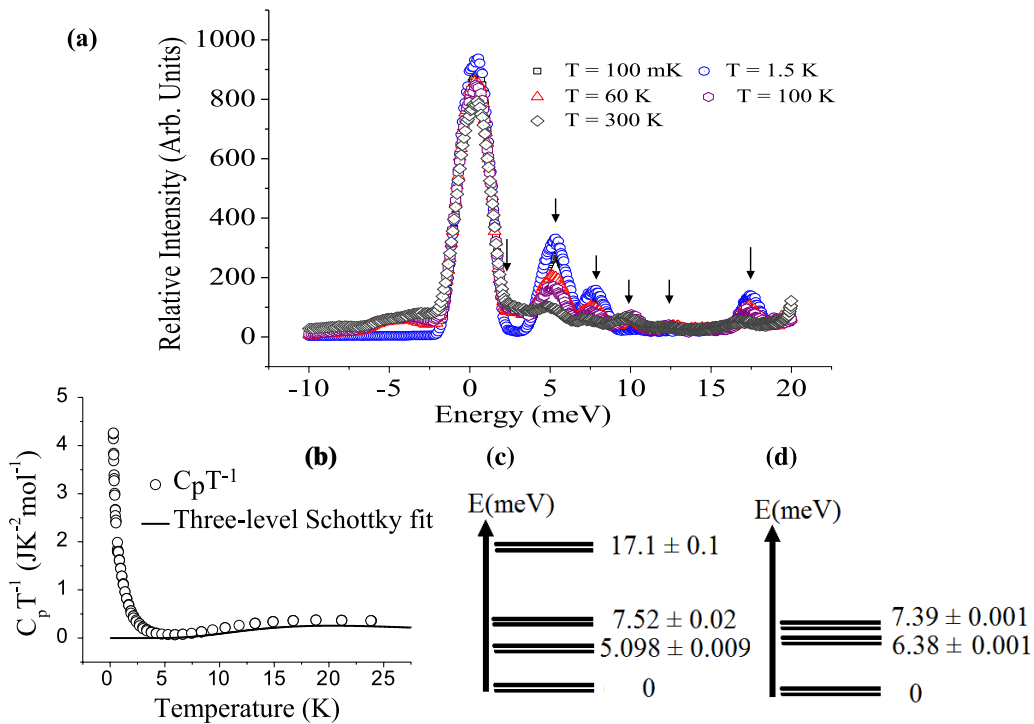


Figure 4. (a) Q -integrated scattering in $\text{Er}_2\text{Sn}_2\text{O}_7$ as a function of temperature. Crystal field transitions are noted. (b) Lattice-subtracted specific heat of $\text{Er}_2\text{Sn}_2\text{O}_7$ as a function of temperature. The line is a fit using the crystal field scheme shown in (c). The values obtained for the fit are directly from the crystal field excitations noted in (a). (d) The crystal field scheme of $\text{Er}_2\text{Ti}_2\text{O}_7$ from Champion *et al* [8].

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