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Magnetic ground-state of strongly frustrated pyrochlore anti-ferromagnet $Er_2Sn_2O_7$

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ABSTRACT

The experimental results of bulk magnetic susceptibility, isothermal magnetization and magnetic specific heat of the frustrated anti-ferromagnetic pyrochlore $Er_2Sn_2O_7$ are simulated and analyzed using appropriate crystal-field (CF) and molecular field tensors at Er-sites in the mean-field approach, which are found to be anisotropic along and normal to the local ⟨111⟩ axis of the frustrated tetrahedral spin-structure. Er-spins are constrained to lie in the local [111] easy-plane in the anti-ferromagnetic phase. Isothermal magnetization can be described by angle-averaged magnetization of the polycrystalline sample, expressed in terms of anisotropic *g*-tensors and exchange tensors. Temperature-dependent characteristic exchange splitting of the single-ion ground doublet describes the magnetic specific heat satisfactorily. The smaller exchange-splitting may cause rapid fluctuations of Er-spin moments in $Er_2Sn_2O_7$ and hence long-range ordering of Er-spins is not exhibited by $Er_2Sn_2O_7$ down to 100 mK, unlike in $Er_2Ti_2O_7$.

1. Introduction

Frustration of spin–spin interactions on the pyrochlore lattice structure has captured imagination of the condensed matter community for the last two decades due to novel and exotic magnetic ground-states, e.g., spin-ice, spin-liquid and spin-glass phases [1,2] found in these spin-structures. In the pyrochlore compounds, $R_2M_2O_7$ (R^{3+} = rare-earth, M^{4+} = transition or non-transition metals), R- and M-spins individually reside on an infinite network of corner-sharing tetrahedral. Strong spin frustration is, therefore, inherent in these systems due to combination of such topological structure and nearest-neighbor (n.n.) anti-ferromagnetic (AFM) Heisenberg exchange interactions, and induces a large degree of spin-degeneracy into the ground-state. As a consequence, the magnetic system remains in the paramagnetic phase with no long-range order (LRO) observed down to $T=0$ K. However it was found that mere existence of local AFM spin frustration is neither a necessity, nor a sufficient condition for magnetic frustration, and real materials often enter into a long-range ordered state promoted by few other weaker intrinsic perturbations in the spin-Hamiltonian, mainly coming from the directional anisotropies of single-ion crystal-field (CF) interactions at the R-site and exchange interactions, dipolar and further n.n. exchange interactions, as well as thermal and/or quantum fluctuations ('order-by-disorder' mechanism).

The role of local CF anisotropy is notably significant: strong axial (along the local ⟨111⟩ axis of tetrahedral) CF anisotropy favors a disordered 'spin-ice' state in the presence of the effective ferromagnetic coupling in $R_2Ti_2O_7$ and $R_2Sn_2O_7$ (R = Ho, Dy) [1], while a strong easy-plane ([111] plane) anisotropy leads to a Néel state in $Er_2Ti_2O_7$ [3], and conventional long-range order in $Gd_2M_2O_7$ where M = Ti, Sn, Zr, Hf. In this context, the Gd-based pyrochlores demand special attention on their own merits, as they exhibit very intriguing and contrasting behaviors. $Gd_2Ti_2O_7$ displays two successive phase transitions at $T_{c1}=1.02$ K and $T_{c2}=0.74$ K to multi-*k* structures. Specific heat $C_v(T)$ of $Gd_2Ti_2O_7$ shows an unconventional T^2 dependence below T_{c2}, where the dynamic Gd-spins align collinearly within the [111] plane but very weakly [4,5]. On the other hand, $Gd_2Sn_2O_7$ corresponds to the Palmer and Chalker (PC) ground-state with $k=(0, 0, 0)$ spin structure which exhibits a long-range ordered phase transition at $T_c \sim 1$ K, below which gapped magnetic excitation spectrum in $C_v \sim \exp(-\Delta/T)$ behavior is observed [6,7]. It was, therefore, surmised that the differences between the spin structures and spin dynamics in the low-temperature ordered phases of Gd-pyrochlores may be characterized by anisotropic exchange tensors along and normal to the n.n. bond separation and appreciable single-ion planar anisotropies [8].

Experimental observations of several unconventional properties of many pyrochlore magnetic materials have been published world-wide, which have given birth to urge for theoretical analysis

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and justifications of these properties vis-à-vis frustration of spins. Er-based pyrochlore $Er_2Sn_2O_7$ is one such material of immense interest which was studied by means of magnetic susceptibility and isothermal magnetization [9], neutron scattering, and specific heat measurements [10]. Er^{3+}-spins in $Er_2Sn_2O_7$ show no signs of long-range order down to $T=100$ mK, although it has appreciable AFM spin–spin interactions reflected through the negative Curie – Weiss temperature $\theta_{CW}=-14$ K [9,10]. To compare $Er_2Sn_2O_7$ with its isomorphous compound $Er_2Ti_2O_7$, we noted that the latter compound is an $\langle XY \rangle$ anti-ferromagnet having $\theta_{CW}=-22$ K which orders in the [111] plane by order-through-disorder mechanism at $T_N=1.173$ K [3]. The frustration index which measures the degree of spin-frustration (or degree of disability of order) is defined by $f=|\theta_{CW}|/T_N$ [1] and is found to be 18.7 for $Er_2Ti_2O_7$. To the first approximation, if we assume that both these Er-compounds are fashioned by similar crystal-field (disregarding their slightly different lattice constants, $a_0=10.352$ Å and 10.087 Å for $Er_2Sn_2O_7$ and $Er_2Ti_2O_7$ [11], respectively) and isotropic exchange interactions (despite their different strength of θ_{CW}), f would be the same for $Er_2Sn_2O_7$ which implies that the Er-stannate should also exhibit long-ranged ordering at any finite temperature $T \leq 1$ K. However, in contrast to this prediction, the lack of LRO in the Er-stannate definitely points that order-by-disorder mechanism, which splits the degenerate ground-state manifold and stabilizes a particular ordering wave-vector in $Er_2Ti_2O_7$ [12], is either absent or quiescent due to different local crystalline environments (hence different local CF anisotropies along $\langle 111 \rangle$ axis and its normal direction) and slight change in the internal molecular field tensors (due to different n.n. bond separations $r_{n.n.}=a_0/\sqrt{8}$) along and perpendicular to the n.n. bond separation.

In the present work, we, therefore, address ourselves to explore the effect of anisotropies in the part of CF and internal molecular fields at the site of magnetic Er-ions lying onto the tetrahedral lattice network in $Er_2Sn_2O_7$ on the observed physical properties, e.g., magnetic susceptibility, magnetization [9], and magnetic specific heat [10] and to find out the possible origin of lack of LRO in $Er_2Sn_2O_7$. To this end, we proceed as follows. In Section 2, we construct a Hamiltonian within the frame work of a CF theory appropriate to the $4f^{11}$ electronic configuration of Er^{3+}-ion and a mean-field approximation by adopting dipolar and exchange interactions among Er^{3+}-ions situated on the tetrahedral sub-lattice. An exact relation between the bulk and single-ion susceptibility was used to simulate the experimental susceptibility of $Er_2Sn_2O_7$. In Section 3, we analyze our calculated results, and finally in Section 4, further discussion of the above analyses followed by conclusions is given.

2. Theoretical outline

The R-ions in the pyrochlore lattice are located within a trigonally (D_{3d}) distorted scalenohedra formed by eight O^{2-} anions, of which six equally spaced O^{2-} (48f) lie on an equatorial plane and two O^{2-} (8b) are normal (i.e., along $\langle 111 \rangle$ direction) to this plane [11]. The magnetic properties of the central R-ion are, therefore, influenced by a D_{3d} crystal-field which causes the local magnetic susceptibility to be different along the local $\langle 111 \rangle$ axis and in the perpendicular plane, thereby producing a single-ion CF magnetic anisotropy at the R-site. Further, the directions of the local symmetry axes for four R-ions occupying the vertices of a particular tetrahedron are nonequivalent and are different from the crystallographic axis as well as from the n.n. bond directions. As a result, the measured (bulk) susceptibility differs from the above local (site) susceptibility at the R-site. To derive a relation between the bulk and local single-ion susceptibilities, taking into account the long-range dipolar and anisotropic exchange interactions among R-ions in appropriate manner, we construct the total Hamiltonian of a single R-ion in crystalline lattice within the frame work of the CF theory in combination with a mean-field approximation shown as follows [13]:

$$H_t(i)=H_{FI}(i)+H_{CF}(i)+H_Z+\vec{\mu}(i)\cdot\vec{H}_{int}(i) \qquad (1)$$

where H_{FI} and H_{CF} are, respectively, free-ion and D_{3d} CF contributions. $H_Z=-g_J\mu_B\vec{H}_{eff}\cdot\vec{J}$ represents the Zeeman coupling between the 4f R-ion and the effective magnetic field $\vec{H}_{eff}$ (external field corrected for demagnetization effects). $\vec{H}_{int}$ is the local internal magnetic field (in the absence of the external field) at the R-site appearing due to exchange and magnetic dipole–dipole interactions. The spin – spin exchange tensor is defined by three principal independent components which couple the n.n. spins along ($\lambda_{\parallel}$) and normal ($\lambda_{\perp x}$, $\lambda_{\perp,y}$) to the bond direction [13].

The free-ion and CF components are written as [14,15]

$$H_{FI}+H_{CF}=\left[\sum_{i=1}^{3}E^ie_i+\zeta_{so}\vec{L}\cdot\vec{S}+\alpha L(L+1)+\beta G(G_2)+\gamma G(R_7)\right] + \sum U_{kq}B_{kq}\ (k=2,\ 4,\ 6;\ q=0,\ \pm 3,\ \pm 6) \qquad (2)$$

The symbols bear their usual meanings. B_{kq} is the even-parity CF parameter (CFP) [15]. Because of the electrostatic, spin–orbit and configuration interactions, the free-ion terms of Er^{3+} are mixed and form intermediately-coupled (IC) states. The energy matrix of H_t is formed with 330 $|LSJ\rangle$ basis states with the principal LS percentages derived from the 16 different low-lying Russell–Saunders terms, e.g., ^4S, ^4D, ^4F, ^4G, ^4I, ^2P, $^2D^{(1)}$, $^2D^{(2)}$,$^2F^{(1)}$, $^2F^{(2)}$, $^2G^{(1)}$, $^2G^{(2)}$, $^2H^{(1)}$, $^2H^{(2)}$,^2I, ^2K, corresponding to the $4f^{11}$ electronic configuration of Er^{3+}-ion [16]. We diagonalized the Hamiltonian (2) by treating all the terms on equal footing following the standard procedure and found that 16-fold degenerate ground-multiplet $^4I_{15/2}$ of Er^{3+}-ion splits into 8 Kramers doublets in the D_{3d} symmetry. The energy values and wave-functions are then used to evaluate single-ion susceptibilities χ_j^s($j=\parallel,\perp$to the local $\langle 111 \rangle$ quantization axis of the crystal-field) using Van Vleck's expression. χ_j^s is next used to *renormalize* the effective site susceptibilities χ_j and simulate bulk susceptibility $\overline{\chi}$ of $Er_2Sn_2O_7$ as functions of CFP's B_{kq}, and exchange interactions $\lambda_{\parallel}$ and $\lambda_{\perp}$ (for simplicity, we assume $\lambda_{\perp x}=\lambda_{\perp,y}=\lambda_{\perp}$):

$$\chi_{\parallel}=\frac{\chi_{\parallel}^s}{\Delta}[1+(3\lambda_{\parallel}-\lambda_{\perp}+2q-p)\chi_{\perp}^s], \qquad (3)$$

$$\chi_{\perp}=\frac{\chi_{\perp}^s}{\Delta}[1+(2\lambda_{\perp}+p-q)\chi_{\parallel}^s], \qquad (4)$$

where the symbols are defined in Refs. [8,13]. The bulk susceptibility equals $\overline{\chi}=(N_a/3)(\chi_{\parallel}+2\chi_{\perp})$, where N_a is Avogadro number. The demagnetizing factor was taken to be $N=0.99\pm 0.03$ for polycrystalline $Er_2Sn_2O_7$ [17].

3. Results and analysis

3.1. DC magnetic susceptibility

The temperature dependence of the dc magnetic susceptibility $\overline{\chi}$ of polycrystalline samples of $Er_2Sn_2O_7$ was measured by Matsuhira et al. [9] and Sarte et al. [10] in the temperature range 1.8–300 K, as shown in Fig. 1. All these measurements agree qualitatively and obeys a CW law above ~20 K with the values of $\theta_{CW}\sim-14$ K and $\mu_{eff}=9.55\ \mu_B$/Er. The estimated μ_{eff} obtained from the high-temperature zone agrees with the free-ion value of 9.59 μ_B/Er for the ground-multiplet $^4I_{15/2}$ of Er^{3+}-ion. No sharp features were observed in $\overline{\chi}$ down to 0.2 K [9] which can be identified as a signature of long-range ordering of Er-spins. Only below 20 K,