Single-ion anisotropy in the gadolinium pyrochlores studied by an electron paramagnetic resonance

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The electron paramagnetic resonance is used to measure the single-ion anisotropy of Gd3+ ions in the pyrochlore structure of (Y1−xGd)x2Ti2O7. A rather strong easy-plane type anisotropy is found. The anisotropy constant D is comparable to the exchange integral J in the prototype Gd2Ti2O7, D ≈ 0.75J, and exceeds the dipolar energy scale. Physical implications of an easy-plane anisotropy for a pyrochlore antiferromagnet are considered. We calculate the magnetization curves at T = 0 and discuss phase transitions in magnetic field.

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Pyrochlore antiferromagnets have been actively studied in the past due to their unusual properties. The magnetic ions in these compounds form a network of corner-sharing tetrahedra, which is prone to a high degree of geometric frustration. The ground state of a classical Heisenberg antiferromagnet on a pyrochlore lattice is macroscopically degenerate and remains disordered. Since weaker residual interactions are always present in real magnetic materials, an important question is about a separation of energy scales. The corresponding knowledge helps to clarify how the macroscopic entropy freezes as T → 0 and what type of magnetically ordered, spinliquid, or glassy state is eventually stabilized.

Gadolinium pyrochlores Gd2Ti2O7 and Gd2Sn2O7 are considered to be the best realizations of the Heisenberg model on a pyrochlore lattice, since Gd3+ is, nominally, in a 5S7/2 state with completely frozen orbital degrees of freedom. Both compounds order at temperatures of about 1 K while Gd2Ti2O7 exhibits also multiple phases in magnetic field. This has been attributed to weaker dipolar interactions between the S = 7/2 gadolinium spins though no unambiguous explanation neither of the phase diagram of Gd2Ti2O7 nor of the neutron-diffraction measurements has been presented.

Single-ion effects have so far been neglected for the two gadolinium pyrochlores. However, strong spin-orbit coupling of the 4f electrons breaks the LS-scheme of the energy levels of the Gd3+ ion and mixes the 5S7/2 and 5P7/2 states. Since the ground-state multiplet contains an admixture of the L ≠ 0 states, it can be split by the crystal field. Crystal-field splitting of the order of 0.8 K was observed for Gd3+ ions in yttrium-gallium garnet. The amplitude of such a splitting is comparable to the exchange coupling and the dipolar energy in the prototype Gd3Ga5O12. Thus, an accurate study of the single-ion anisotropy in the Gd-based pyrochlores is necessary to understand the magnetic properties of these materials.

To study properties of isolated Gd3+ ions we have prepared single-crystals of non-magnetic Y2Ti2O7 diluted with a small amount (nominally 0.5%) of Gd. The crystals were grown by traveling solvent floating zone technique. After growth the oriented single-crystals were annealed in an oxygen atmosphere. The absence of parasitic phases has been verified by powder X-ray diffraction. The magnetization of the reference sample of nominally pure Y2Ti2O7 corresponds to no more than 0.06% of S = 1/2 impurities per yttrium. The lattice parameters and geometry of the oxygen surrounding of the rare-earth site are very close for Y2Ti2O7 and Gd2Ti2O7. Hence, single-ion parameters for Gd3+ ions in (Y0.995Gd0.005)2Ti2O7 and Gd2Ti2O7 are also expected to be very close. An electric field gradient at the Gd site in Gd2Sn2O7 determined from the quadrupolar Mössbauer spectra is 30% smaller than that of Gd2Ti2O7, which should lead to the corresponding decrease of the single-ion anisotropy.

Electron paramagnetic resonance (EPR) is a conventional tool to probe small crystal-field splitting of the energy levels of magnetic ions. The zero-field splitting of the multiplet leads to an easily detected change of the resonant absorption frequencies. We have used a set of home-made spectrometers with transmission type cavity for the high-frequency (20–115 GHz) measurements, and a commercial Bruker EPR spectrometer for the high-precision X-band (9.36 GHz) and Q-band (34.0 GHz) measurements.

The local surrounding of the rare-earth site in the pyrochlore structure corresponds to a trigonal point symmetry D3d (5m). A general form of the single-site Hamiltonian is, then,

$$\hat{H} = B_3^0 \hat{O}_3^0 + B_4^0 \hat{O}_4^0 + B_3^1 \hat{O}_3^1 + B_6^0 \hat{O}_6^0 + B_3^3 \hat{O}_3^3 + B_6^4 \hat{O}_6^4 - g\mu_B \mathbf{H} \cdot \mathbf{S},$$

where the Stevens operators $\hat{O}^j$ are functions of the components of the total angular momentum $\mathbf{S} = 7/2$, with $\hat{z} \parallel (111)$ and $\hat{x} \parallel (11\bar{2})$. The lowest-order
anisotropy term $B_0^i \hat{O}_i^2$ can be rewritten up to an additive constant as $DS^2$ with $D = 3B_0^i$.

In the absence of the single-ion anisotropy Hamiltonian $H$ contains only the Zeeman term. In this case the frequencies of all allowed transitions are equal and only a single resonance absorption line should be observed at a field determined by $\hbar \omega = g\mu_B H$. The measured EPR absorption spectra, see Figs. 1 and 2, contain multiple components demonstrating the presence of a non-negligible anisotropy. The analysis of the EPR spectra is complicated by the existence of nine inequivalent magnetic ion positions. At high frequencies and $\mathbf{H} \parallel [111]$ it is possible to separate seven absorption components, which correspond to the spins with anisotropy axis parallel to the field direction. They include absorption component with the largest value of the resonance field and are almost equidistant (see Fig. 2). This indicates that the second order axial term $(DS^2)$ is the most important one, its magnitude estimated from the total splitting of the spectra is $|D| \sim 0.25$K. In order to refine the values of the anisotropy constants, we have modeled numerically the EPR absorption for different directions of magnetic field and different microwave frequencies trying to obtain best correspondence of the observed and modeled resonance fields values (see, e.g., Fig. 1). To determine the sign of the main anisotropy constant (resonance-field position determine only relative signs of the anisotropy constants), we have studied the temperature dependence of the intensity of different components at high microwave frequency. This analysis yielded that the main anisotropy term is of the easy-plane type and the spin Hamiltonian parameters are $g = 1.987$, $B_2^0 = (74.3 \pm 0.3) \times 10^{-3}$K, $B_1^0 = (5.7 \pm 0.9) \times 10^{-3}$K, $B_3^0 = (1.8 \pm 0.2) \times 10^{-3}$K. The determination of the 6-th order anisotropy parameters has been impossible due to a presence of small (0.5° or less) misorientation of the sample. We were able to estimate only the upper bounds: $|B_6^0| < 10^{-9}$K, $|B_4^0| < 2 \times 10^{-9}$K, $|B_3^0| < 10^{-6}$K.

The measured value of the $B_0^0$ coefficient indicates that the single-ion anisotropy is the second largest interaction in the effective spin Hamiltonian of Gd$_2$Ti$_2$O$_7$. Indeed, the nearest-neighbor exchange integral is estimated from the Curie-Weiss temperature $\theta_{CW} = -9.5$ K as $J S^2 \approx 3.7$ K, whereas $DS^2 \approx 2.73$ K. The dipolar constant $E_{dd} = (g\mu_B S)^2/(a \sqrt{2}/4)^3$ for the interaction between adjacent magnetic ions for above values of the $g$-factor and lattice parameter amounts to only $E_{dd} \approx 0.65$ K. In the following, we discuss several properties of magnetic pyrochlore materials, which might be affected by a strong single-ion anisotropy of the easy-plane type.

The first question to be addressed theoretically is whether a significant single-ion anisotropy modifies the value of the exchange constant obtained from $\theta_{CW}$. Standard high-temperature expansion of the susceptibility tensor includes in general a contribution from the single-ion term $D \sum_i (\mathbf{n}_i \cdot \mathbf{S}_i)^2$:

$$\chi^{\alpha\beta} = \frac{g^2 \mu_B^2 S(S+1)}{3T} \left\{ \delta^{\alpha\beta} - \frac{S(S+1)}{3T} \sum_j J_{ij} \right\} - \frac{2D}{3T}(S - \frac{1}{2})(S + \frac{1}{2})(\langle n_\alpha n_\beta \rangle - \frac{1}{3} \delta^{\alpha\beta}) \right\} \right) \right)$$

(2)

In the case of a pyrochlore lattice the averaging in Eq. (2) has to be done over four inequivalent directions of the local anisotropy axis $n_i$ corresponding to the principal cube diagonals. Using the identity $\frac{1}{4} \sum_{i=1}^4 n_i^\alpha n_i^\beta = \frac{1}{6} \delta^{\alpha\beta}$ we find that the single-ion contribution vanishes in the second-order of the $1/T$ expansion. Therefore, the Curie-
Weiss constant is not affected by the single-ion term and is given by the same expression as in a pure Heisenberg case: \(\theta_{C,W} = zJS(S+1)/3\), where \(z = 6\) is the number of nearest-neighbor magnetic atoms.

The unusual ordering wave-vector \((\frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2})\) in Gd₂Ti₂O₇ is probably determined by a delicate balance between the long-range dipolar interaction and several weak next-neighbor exchanges. The full analysis of the role of the single-ion anisotropy for such models lies beyond the scope of present study. We will discuss instead properties of a simplified classical spin model on a pyrochlore lattice, which takes into account only the nearest-neighbor exchange interaction and a staggered single-ion term:

\[
\hat{H} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + D \sum_i (\mathbf{n}_i \cdot \mathbf{S}_i)^2 - \mathbf{H} \cdot \sum_i \mathbf{S}_i .
\]  

(3)

Transformation to classical spins of unit length \(|\mathbf{S}_i| = 1\) amounts to the following redefinition of the physical parameters: \(J \rightarrow JS^2\), \(D \rightarrow DS^2\), \(H \rightarrow g\mu_B HS\). The minimum of the Heisenberg interaction in zero field is attained for states with zero total spin on every tetrahedron: \(\mathbf{S}_{\text{tet}} = \sum_i \mathbf{S}_i = 0\). The key observation for the anisotropic model \((3)\) is that the \(\mathbf{S}_{\text{tet}} = 0\) constraint is compatible with local spins being oriented perpendicular to their local hard axes: the exchange and the anisotropy terms can be simultaneously minimized. In particular, for one tetrahedron there is one free continuous parameter (angle), which describes the possible ground states. The remaining degeneracy of the lattice model is infinite but not extensive: the number of continuous degrees of freedom per tetrahedron and \(O(L^3)\) variables for the lattice problem.

To complement the above zero-field consideration we now discuss the magnetization process of the model \((3)\). The total spin operator does not commute with the Hamiltonian in the presence of anisotropic interactions. Consequently, the magnetization plateaus, e.g., the 1/2-plateau, do not appear on the magnetization curves of the gadolinium pyrochlores and \(M(H)\) approaches the saturation value at high fields only asymptotically. Besides, the staggered (within one unit cell) single ion anisotropy might also smear phase transitions in finite magnetic fields for ‘nonsymmetric’ field orientations.

Returning back to the Hamiltonian \((3)\) the minimum of the Heisenberg and the Zeeman interactions is given by the states obeying \(\mathbf{S}_{\text{tet}} = \mathbf{H}/2J\). Simple extension of the zero-field consideration suggests that in weak magnetic fields spins remain in their respective local easy-planes. It is again possible to simultaneously minimize the local single-ion anisotropy terms and to satisfy the magnetization constraint. The magnetization curve is initially a straight line: \(M(H) = H/8J\). The remaining degeneracy corresponds to one continuous degree of freedom per tetrahedron and \(O(L^3)\) variables for the lattice

The full analysis of the role of the single-ion anisotropy constant and is determined purely by geometry. It can be calculated analytically for fields applied along the easy-planes of a pyrochlore lattice:

\[
H_c^{[001]} = 8J\sqrt{2}/3 , \quad H_c^{[111]} = 8J(3 + \sqrt{2})/7 , \quad H_c^{[110]} = 4J(1 + 1/\sqrt{3}) .
\]

(4)

The fields \(H_c^{[001]}\) and \(H_c^{[111]}\) give, respectively, the maximal and the minimal value for \(H_c(\theta, \phi)\). The magnetization process at \(T = 0\) for the above two orientations found by standard numerical minimization of the classical energy of a single spin tetrahedron is presented in Fig. 6. For \(\mathbf{H} \parallel [001]\) the magnetization curve exhibits a kink at \(H_c\) and, then, the behavior of \(M(H)\) becomes nonlinear with full saturation \(M = 1\) reached only asymptotically. A nondegenerate spin structure above \(H_c\) preserves the \(C_3\) rotational symmetry about the field direction, which is broken at \(H < H_c\). Thus, \(H_c\) describes a robust phase transition for this field orientation. The zero-temperature magnetization curve for arbitrary field orientation resembles the behavior for \(\mathbf{H} \parallel [001]\). The main difference is an absence of a spin-rotational symmetry about the field direction, which may lead to a smearing of the phase transition at \(H = H_c\). The other two field orientations, which have stable phase transitions at \(H = H_c\) are those for the field along the [110] and the [111] axes. In the latter case the magnetization curve exhibits two kinks: at \(H_{c1} \approx H_c \approx 5.045J\) and at a second critical field \(H_{c2} > H_{\text{sat}}\), see the right panel in Fig. 6. Above \(H_{c2}\) the spin structure preserves the \(C_{3v}\) symme-
transverse magnetization per one spin of the classical easy-plane pyrochlore antiferromagnet at $T = 0$ for $D = 0.75J$ and various field orientations.

In conclusion, the measured local anisotropy of Gd$^{3+}$ ions strongly affects magnetic properties of Gd-based pyrochlores. Though, the toy model is apparently not sufficient to explain the ordered structure seen by neutrons, the quite anisotropic phase diagram in magnetic fields is compatible with our experimental and theoretical findings. In particular, we have demonstrated that depending on an applied field orientation in a cubic crystal there are possible either one or two transitions in magnetic field. The Mössbauer measurements also agree with our ESR results pointing at ordered moments oriented perpendicular to local trigonal axes. The presented theory of the magnetization process is relevant for $\text{Er}_2\text{Ti}_2\text{O}_7$, which is a $D/J \rightarrow \infty$ realization of the model.

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