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Electron spin resonance study of the single-ion anisotropy in the pyrochlore antiferromagnet $\text{Gd}_2\text{Sn}_2\text{O}_7$

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Abstract

Single-ion anisotropy is of importance for the magnetic ordering of the frustrated pyrochlore antiferromagnets $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Sn}_2\text{O}_7$. The anisotropy parameters for $\text{Gd}_2\text{Sn}_2\text{O}_7$ were measured using the electron spin resonance technique. The anisotropy was found to be of the easy plane type, with the main constant $D = 140$ mK. This value is 35% smaller than the value of the corresponding anisotropy constant of the related compound $\text{Gd}_2\text{Ti}_2\text{O}_7$.

1. Introduction

Rare earth pyrochlore magnets $\text{R}_2\text{M}_2\text{O}_7$ (R—rare earth ion, M—transition metal) have recently attracted a lot of attention due to the specific geometry of the exchange bonds. Rare earth ions in a pyrochlore structure form a network of corner-sharing tetrahedra. The nearest neighbour antiferromagnetic (AF) exchange interaction is strongly frustrated in this lattice (see, e.g., [1]) and the classical ground state of this system should remain macroscopically degenerate down to $T = 0$.

Selection of a unique ground state in real magnets should occur due to other interactions like further neighbour exchange interactions, dipole interactions, single-ion anisotropy or due to the lifting of the degeneracy by fluctuations. Single-ion anisotropy is known to have a strong effect on the formation of the ground state: strong axial anisotropy favours an unusual spin-ice state in $\text{Dy}_2\text{Ti}_2\text{O}_7$ [2] while in the case of a strong easy plane anisotropy in $\text{Er}_2\text{Ti}_2\text{O}_7$ a Néel state is formed by the quantum order-by-disorder mechanism [3].

Gd-based pyrochlore magnets $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Sn}_2\text{O}_7$ were considered to be real examples of AF Heisenberg pyrochlores. Both compounds demonstrate a magnetic ordering at a temperature near 1 K, but their spin structures are quite different. In the case of $\text{Gd}_2\text{Ti}_2\text{O}_7$,

two successive transitions are observed at 1.02 and 0.74 K [4]. The low temperature magnetic structure is a complicated non-collinear multiple- k structure [5]. In the case of $\text{Gd}_2\text{Sn}_2\text{O}_7$, a unique phase transition is observed [4] and the magnetic structure is non-collinear with $k = 0$ [6].

Up to now, single-ion anisotropy effects were not considered for these compounds since the Gd^{3+} ion is an S-state ion with $L = 0$ [7]. However, a considerable anisotropy was found in $\text{Gd}_2\text{Ti}_2\text{O}_7$ [8]. A crystal field splitting of the ionic levels occurs because of a strong spin-orbit coupling among 4f electrons, which breaks the simple LS -scheme of the energy levels and leads to the admixture of the $L \neq 0$ states into the ground state of the Gd^{3+} ion. The main anisotropy constant B_2^0 was found to be equal to 74 mK in $\text{Gd}_2\text{Ti}_2\text{O}_7$, which makes the overall crystal field splitting $3B_2^0S^2 \simeq 2.7$ K comparable with the exchange energy $JS^2 \simeq 3.7$ K. Thus, it is important to determine the values of the single-ion anisotropy constants in $\text{Gd}_2\text{Sn}_2\text{O}_7$ as well. A difference in single-ion anisotropy could be important for understanding the above-mentioned difference of the magnetic ground states of $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Sn}_2\text{O}_7$.

To study single-ion effects, we used the non-magnetic isostructural compound $\text{Y}_2\text{Sn}_2\text{O}_7$ with a small amount (nominally 0.5%) of gadolinium substituting for yttrium. This enables us to determine the single-ion anisotropy parameters since magnetic ions are in the same surroundings [9–11] as in the concentrated magnet. We found the presence of a single-ion anisotropy, evidenced by the obvious splitting of the electron spin resonance (ESR) absorption spectrum, and we determined the values of the main anisotropy constants.

2. Experimental details and samples

Polycrystalline samples of $(\text{Y}_{0.995}\text{Gd}_{0.005})_2\text{Sn}_2\text{O}_7$ were prepared by heating a stoichiometric mixture of Y_2O_3 (99.99%), Gd_2O_3 (99.999%) and SnO_2 (99.9%) in air. The samples were heated between 1400 and 1450 °C for several hours with intermediate regrindings. The x-ray diffraction pattern obtained at room temperature with a Bruker D8 diffractometer corresponds to the pure phase with a small amount (<1%) of SnO_2 . A magnetic susceptibility curve was measured with a field of 80 Oe in the temperature range 20–250 K. The sample magnetization corresponds to the Curie law with the effective moment of 7.9 μ_B per Gd^{3+} ion, assuming the nominal Gd concentration of 0.5%.

The ESR study was performed at frequencies of 18–100 GHz using a set of home-made transmission-type ESR spectrometers equipped with a He-cooled cryomagnet. The ESR absorption spectra were recorded as field dependences of the transmitted microwave signal.

3. Experimental results and discussion

Electron spin resonance study is a sensitive method for the determination of the spin Hamiltonian constants (see, e.g., [12]). The microwave absorption power per spin is

$$P_{\text{abs}} = \frac{\pi g^2 \mu_B^2 \omega}{2\hbar} \sum_{E_j > E_i} \frac{e^{-E_i/T} - e^{-E_j/T}}{Z} | \langle i | (\hat{S} \cdot \mathbf{h}) | j \rangle |^2 \delta(\omega - \omega_{ji}), \quad (1)$$

where \mathbf{h} is the microwave field of the frequency ω , E_i , E_j are the energies of the corresponding spin states, $\omega_{ji} = (E_j - E_i)/\hbar$ and $Z = \sum \exp\{-E_n/T\}$.

The microwave field is polarized perpendicular to the external magnetic field in our experiments. Thus, only dipolar transitions with $\Delta S_H = \pm 1$ are observed (S_H is the spin projection onto the magnetic field direction). In the absence of single-ion anisotropy, a single resonance line should be observed at the resonance frequency $\omega = g\mu_B H/\hbar$. The presence

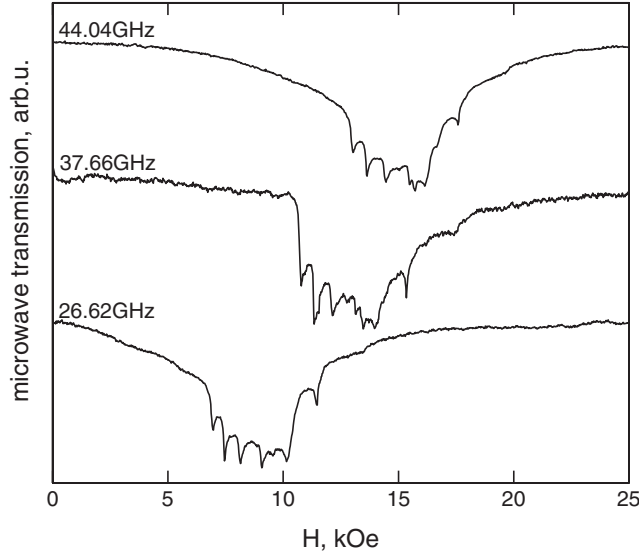


Figure 1. ESR absorption spectra obtained for $(\text{Y}_{0.995}\text{Gd}_{0.005})_2\text{Sn}_2\text{O}_7$ at 4.5 K with different frequencies.

of a single-ion anisotropy results in a multi-component absorption spectrum. The amplitudes and the signs of the spin Hamiltonian parameters may be determined from the positions and the relative intensities of these components.

ESR absorption spectra measured at different microwave frequencies and at different temperatures are shown in figures 1 and 2. The absorption spectrum is clearly multi-component, which indicates the presence of crystal field splitting of the single-ion energy levels.

For powder samples the absorption is averaged over all possible orientations of the crystallographic axes. The point symmetry of the Gd ion surroundings is D_{3d} , and the main term in the anisotropy energy is the second-order axial term with the anisotropy axis along the $\langle 111 \rangle$ direction. Measurements on the single crystals of the pyrochlore titanate have shown that this term is the most important [8]. As a first step of the present analysis, we will consider a simplified model restricted to this term only:

$$\mathcal{H} = g\mu_B \mathbf{H} \cdot \hat{\mathbf{S}} + DS_z^2. \quad (2)$$

Treating the anisotropy term in the first order of perturbation theory, for the magnetic field applied at the angle θ with respect to the anisotropy axis z , we obtain for the energies, up to a constant term,

$$E(m) = (g\mu_B H)m + \frac{D}{2}(3\cos^2\theta - 1)m^2, \quad (3)$$

where m is the spin projection on the direction of the magnetic field. The resonance field corresponding to the $|m\rangle \leftrightarrow |m+1\rangle$ dipolar transition is

$$H_m(\theta) = H_0 - \frac{D}{2g\mu_B}(3\cos^2\theta - 1)(2m+1), \quad (4)$$

where $H_0 = \hbar\omega/(g\mu_B)$ is a free spin resonance field. When averaging over the orientation, grains with the anisotropy axis perpendicular to the field direction enter with higher weight.

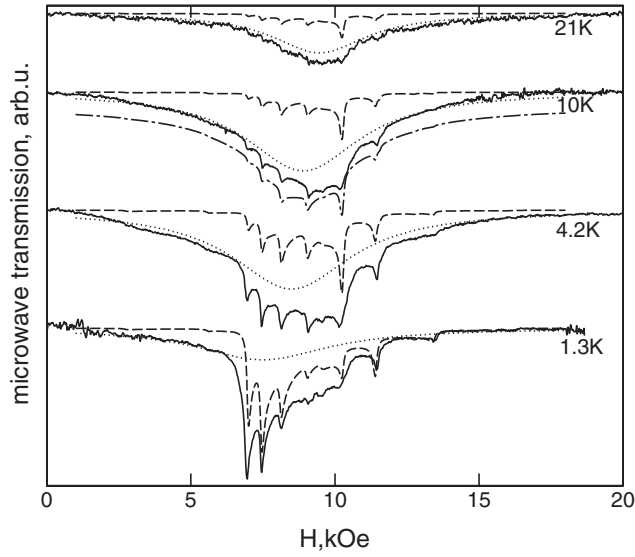


Figure 2. ESR absorption spectra obtained for $(Y_{0.995}Gd_{0.005})_2Sn_2O_7$ with $f = 26.62$ GHz at different temperatures (solid lines); calculated ESR absorption spectra (dashed lines); additional broad absorption signal (dotted lines); at 10 K, sum of the calculated ESR absorption and of an additional broad absorption line (dash-dotted line, shifted for clarity).

For the case of a narrow resonance line, this averaging yields

$$I_m(H) \propto \frac{1}{\sqrt{\frac{H_0 - H}{\Delta H_m} + 1}}, \quad (5)$$

where $\Delta H_m = D(2m + 1)/(2g\mu_B)$, $m \neq -1/2$. The magnetic fields at which the resonance absorption is observed are limited by the values $H_0 - 2\Delta H_m$ and $H_0 + \Delta H_m$, corresponding to grains with $\theta = 0$ and $\pi/2$, respectively. Thus, the averaged ESR absorption line corresponding to a given $|m\rangle \leftrightarrow |m + 1\rangle$ transition should demonstrate sharp edges both on the left and on the right of the paramagnetic resonance position. At the end corresponding to grains with $\theta = 0$ it should have a step-like edge, while at the other end ($\theta = \pi/2$ grains) it should demonstrate a sharp increase of absorption corresponding to the square root divergency in (5). Whether this increase in absorption is to the left or to the right from the free spin resonance position H_0 depends, for a given m , on the sign of the D constant only.

We have studied the ESR absorption at different temperatures (see figure 2). At low temperatures, the contributions to the absorption arising from the states with a large negative m ($-7/2$ and $-5/2$) dominate. In figure 2 one can clearly see that an intense absorption at low temperatures occurs on the left edge of the ESR spectra, while on the right edge there are several step-like features of smaller amplitude. This distribution of the intensities corresponds to a positive sign for the D constant, i.e. to an easy plane anisotropy.

The above considerations suggest a way to identify the ESR absorption spectrum features corresponding to $\theta = 0, \pi/2$. Intense slightly asymmetric peaks observed on the left of the paramagnetic resonance position at low temperatures and peaks of similar shape that become more intense on heating correspond to $\theta = \pi/2$. Step-like changes of the absorption observed on the left and on the right of the paramagnetic resonance position, and intense features observed at low temperatures on the right of the paramagnetic resonance position correspond to grains with $\theta = 0$.

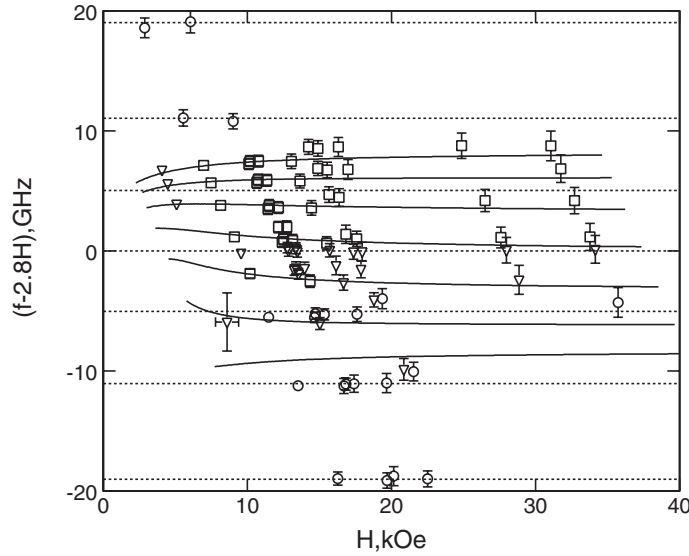


Figure 3. Frequency–field dependences for the different lines of the observed ESR absorption spectra (symbols) and calculated dependences (lines). A linear quantity $f = g\mu_B H$, with $g = 2.0$, has been subtracted. $\theta = 0$ features (circles); $\theta = \pi/2$ features (squares); features of the ESR absorption which were hard to identify (triangles); calculated frequency–field dependences for $\theta = \pi/2$ (solid lines); calculated frequency–field dependences for $\theta = 0$ (dashed lines).

The frequency–field diagram of the observed transitions is shown in figure 3. Note that the $\theta = 0$ components do not form equidistant lines. This indicates the presence of higher order contributions to the anisotropy energy. The general form of the spin Hamiltonian for the $S = 7/2$ Gd^{3+} ion in the surroundings of D_{3d} symmetry is

$$\mathcal{H} = g\mu_B \mathbf{H} \cdot \hat{\mathbf{S}} + B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^3 \hat{O}_4^3 + B_6^0 \hat{O}_6^0 + B_6^3 \hat{O}_6^3 + B_6^6 \hat{O}_6^6 \quad (6)$$

where the Stevens operators [12] \hat{O}_j^i are functions of the components of the total angular momentum $S = 7/2$, with $\mathbf{z} \parallel \langle 111 \rangle$ and $\mathbf{x} \parallel \langle 11\bar{2} \rangle$. In the notation of (2), $D = 3B_2^0$.

We will consider only the second- and fourth-order axial terms, and we will suppose $g = 2.0$ in the further analysis. The B_2^0 and B_4^0 constants can be found from the positions of the well-defined $\theta = 0$ components corresponding to the $|-7/2\rangle \leftrightarrow |-5/2\rangle$ and $|-5/2\rangle \leftrightarrow |-3/2\rangle$ transitions (two lowermost lines in figure 3). Deviations of these transition frequencies from the paramagnetic resonance position are 19.0 ± 0.3 and 11.2 ± 0.3 GHz respectively. This gives the following values for the spin Hamiltonian constants: $B_2^0 = (47 \pm 1)$ mK and $B_4^0 = (0.05 \pm 0.02)$ mK. The amplitude of the second-order anisotropy constant ($D = 3B_2^0 = 140$ mK) is 35% smaller than the corresponding value for $\text{Gd}_2\text{Ti}_2\text{O}_7$ ($D = 223$ mK). The frequency–field dependences for $\theta = 0, \pi/2$ calculated for these parameter values are shown in figure 3. Additionally, we have modelled the ESR absorption line using (1). The simulation was performed by exact numerical diagonalization of the Hamiltonian matrix combined with averaging over the orientations of the grain crystallographic axes. The results are presented in figure 2. The calculated frequency–field dependences are in good agreement with the observed ones. The simulated absorption spectra also demonstrate good agreement with the experimental data—they correctly reproduce the details of the line shape as well as the tendencies of the line shape change with temperature.

Note that the correspondence between the simulated and observed absorption spectra can be improved by adding a broad absorption line located near the paramagnetic resonance position (see figure 2). This additional contribution cannot be attributed to isolated Gd^{3+} spins in the crystal field. The intensity of this additional absorption component increases with increasing temperature at low temperatures: the integral intensity of this broad line at 4.2 K is twice as large as its integral intensity at 1.3 K. The ratio of the intensities of the suggested broad absorption line and of the crystal field split absorption is also temperature dependent: at 1.3 K most of the integral intensity is due to the crystal field split absorption lines, while at 20 K the broad absorption line dominates. A possible origin of this broad absorption line is the formation of antiferromagnetically coupled pairs of Gd ions. The ground state of a pair is a non-magnetic singlet; the total splitting between the $S = 0$ ground state and the highest energy state ($S = 7$) is about $2J S_{\text{Gd}}^2 \sim 7$ K. The dominating intensity of the broad line at 20 K suggests a high concentration of these pairs, which indicates a tendency toward formation of Gd clusters in the $\text{Y}_2\text{Sn}_2\text{O}_7$ matrix. However, the characteristic multi-component signal corresponding to the isolated $S = 7/2$ Gd^{3+} ions can be distinguished and analysed at low temperatures. The presence of exchange coupled pairs has also been observed, via ^{170}Yb Mössbauer spectroscopy, in $\text{Y}_2\text{Ti}_2\text{O}_7$ doped with Yb [13].

4. Conclusions

We report on the ESR in powder samples of $(\text{Y}_{0.995}\text{Gd}_{0.005})_2\text{Sn}_2\text{O}_7$. The observed splitting of the ESR absorption line allows us to determine the values of the single-ion anisotropy constant for the Gd ion. We find that the value of the main anisotropy constant is about 35% smaller than that of titanate $\text{Gd}_2\text{Ti}_2\text{O}_7$. Possibly this change of the anisotropy energy is responsible for the strong difference of the ordered state formed in $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Sn}_2\text{O}_7$ at low temperatures.

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