Macroscopic Anisotropy and Symmetry Breaking in the Pyrochlore Antiferromagnet Gd$_2$Ti$_2$O$_7$

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In the Heisenberg antiferromagnet Gd$_2$Ti$_2$O$_7$, the exchange interactions are geometrically frustrated by the pyrochlore lattice structure. This ESR study reveals a strong temperature dependent anisotropy with respect to a [111] body diagonal below a temperature $T_A = 80$ K, despite the spin only nature of the Gd$^{3+}$ ion. Anisotropy and symmetry breaking can nevertheless appear through the superexchange interaction. The presence of short range planar correlation restricted to specific Kagomé planes is sufficient to explain the two ESR modes studied in this work.

In antiferromagnets with competing interactions, no single spin-configuration realizes a local energy minimum for all exchange bonds: exchange interactions are “frustrated”. Among all the possible sources of frustration, the most common one has a geometrical origin. On a number of lattices (Kagomé [1], fcc, pyrochlore [2]), magnetic ions are located at the vertices of equilateral triangles: the product of exchange interaction on any closed path being negative, these structures are naturally frustrated. In the two-dimensional (2D) Kagomé lattice, equilateral triangles are connected only through their vertices leaving a number of spin-degree of freedom unconstrained. Similarly, in the pyrochlore lattice, spins are at the vertices of tetrahedra with equilateral triangular faces. This lattice offers little additional constraints since all the tetrahedra are connected in the three-dimensional (3D) structure through their corners. This confers a very high degree of degeneracy to the ground state (GS) manifold: for classical spins, one or more families of continuous rotations leave the energy of any classical ground state unchanged. As a consequence, smaller anisotropic interactions select a particular GS through a mechanism which is specific to the material considered. For example, a variety of ground states have been identified [2, 3] in the pyrochlore family R$_2$Ti$_2$O$_7$ where the rare earth ions R are antiferromagnetically coupled. The crystal field anisotropy on the rare earth ion R$^{3+}$ plays an important role in the GS selection except for Gd$_2$Ti$_2$O$_7$, where the single-ion anisotropy of the spin-only $S = 7/2$ ion Gd$^{3+}$ (4$f^7$) is weak: Gd$_2$Ti$_2$O$_7$ is the only nearly-isotropic Heisenberg pyrochlore antiferromagnet. Frustration depresses its 3D ordering transition which has been observed in specific heat measurements [3, 4] at a temperature $T_c = 0.97$ K considerably smaller than the Curie-Weiss temperature $\theta_{CW} = -9.9$ K.

In this Letter, an electron spin resonance (ESR) study of the pyrochlore antiferromagnet Gd$_2$Ti$_2$O$_7$ is presented. Below a temperature $T_A \approx 80$ K much larger than $\theta_{CW}$, two strongly temperature dependent and anisotropic resonance lines are observed. They identify a macroscopic anisotropy with respect to a specific [111] body diagonal. These ESR modes are consistent with non-collinear spin correlations in the Kagomé planes perpendicular to this [111] axis below $T_A$. This local order also agrees with the ordered state observed below $T_c$ by neutron scattering [3]. We propose an exchange-driven symmetry breaking mechanism involving the Hund term on the oxygen ion. This ion is in the center of Gd$^{3+}$ tetrahedra and is common to all the dominant superexchange paths between Gd$^{3+}$ ions. The resulting superexchange bonds connecting the (111) Kagomé planes are weakened compared to the exchange between the spins within these planes. Other anisotropic forces (Dzyaloshinskii-Moriya [6] exchange and dipolar) control the magnitude of the anisotropy and the final selection of the ground state.

The single crystals of Gd$_2$Ti$_2$O$_7$ were grown by slow cooling from a molten flux [3]. Crystals appeared as brown, well shaped octahedra with ca. 1 mm edge. Gd$_2$Ti$_2$O$_7$ is an insulator which crystallizes in the cubic, face centered space group $Fd\bar{3}m$ with a lattice constant $a_0 = 10.184$ Å at room temperature. In the (111) planes, perpendicular to the cube diagonal, the Gd spins are arranged in a 2D Kagomé lattice (see inset of figure [1]). Only the Gd$^{3+}$ ions possess a magnetic moment $\mu \approx 7.9\mu_B$, close to the free-ion value (7.94$\mu_B$). The measured dc-magnetic susceptibility in a field of $B_{ext} = 0.1$ T has a Curie-Weiss $\chi = -\frac{C}{T-\theta_{CW}}$ behavior typical of antiferromagnetic interactions with the same $\theta_{CW} = -9.9$ K previously reported by Raju and coworkers [3]. The ESR measurements were performed at different frequencies and temperatures using a home built multi-frequency high-field ESR spectrometer. Different frequencies were investigated (54 GHz – 115 GHz) using back-wave oscillators and Gunn diode sources, guided to the sample with oversized waveguides in a transmission probe. The spectra were recorded as a function of magnetic field at a fixed frequency. In this study, we have measured (a) the temperature dependence of the ESR spectrum, (b) its orientation dependence with respect to the crystal axes...
and (c) its evolution with frequency and magnetic field.

Above 80 K, the ESR spectrum at the frequency of 54 GHz consists of a single line centered at $B_r \approx 2$ T, close to the expected resonance field ($1.93$ T) for a $g$-factor of 2 (as expected for the spin-only Gd$^{3+}$). As the temperature is lowered, two resonance lines appear below $T_A \approx 80$ K. Their splitting is strongly anisotropic and temperature dependent, and becomes comparable to the spin-exchange frequencies ($4$ T $\equiv 5.4$ K) at low temperature. This is represented in figure 1b which shows the ESR spectra at 54 GHz for different temperatures, with the magnetic field applied parallel to a specific body diagonal of the crystal ($[111] \equiv \hat{n}$ axis, perpendicular to Kagomé planes), such that the angle $\theta = \angle(\hat{B}, \hat{n}) = 0$. Fitting the spectra below 80 K with two Lorentzian lines (1) and (2), the position of the resonance fields can be plotted as a function of temperature. Line (2) is strongly temperature dependent as clearly seen in figure 1b. Its resonance field shifts towards higher values as the temperature is decreased, the shift being very large ($\sim 4$ T) at low temperature (4.2 K). As the line shifts, a broadening is also observed. While the width of line (1) also increases when lowering the temperature, the line shift is much weaker: its resonance field moves towards lower values, the change being of the order of 0.3 T at 4.2 K.

On the other hand, when the magnetic field is applied perpendicular to the body diagonal $\hat{n}$ (i.e., $\theta = 90^\circ$), at the same frequency 54 GHz, the position of the observed signal also shifts to higher fields with decreasing temperature, but the shift is smaller, $\sim 1$ T at 4.2 K. An analysis of the temperature dependence of the resonance fields below 80 K is presented in figure 2 for (i) both orientations $\theta = 0$ and $\theta = 90^\circ$ at 54 GHz, and (ii) for $\theta = 0$ at 73 GHz. The solid lines are fits to the phenomenological expression $B_r(T) = B_0 + D \exp(-\frac{T}{\theta_{\text{CW}}})$, where $B_0$ is the resonance field at high temperature and $D$ a parameter), consistent with an activated behavior with an activation energy $k_B \theta_{\text{CW}}$. From the fits, the obtained values of $T_0$ are $10.1 \pm 0.5$ K ($10.8 \pm 2.1$ K) at 54 GHz for $\theta = 0$ ($\theta = 90^\circ$), and $8.5 \pm 0.5$ K at 73 GHz for $\theta = 0$. These values are comparable to the Curie-Weiss temperature, $\theta_{\text{CW}} \approx -10$ K.

Although there is no long range order at the temperatures studied in this work, the large temperature dependence of the position of line (2) reveals the presence of an internal field at the frequencies probed in the experiment. Roughly speaking, this local field adds or subtracts to the external field and produces the observed shifts. The presence of local fields signals the growth of short range correlations as the temperature is lowered. Since local fields fluctuations on timescales faster than the precession period average to zero, the observed frequency shifts decrease with increasing temperature on a scale characteristic of the short range spin dynamics. A
dependence of the resonance fields on the orientation of a complete rotation. This is further evidenced by the inset of figure 3, where and establishes the macroscopic nature of the anisotropy. and $D$ have a uniaxial character, with an angular dependence for the resonance field $B_\parallel$ and the body diagonal $n$ increases until it reaches a minimum at the [111] direction of the crystal, the resonance position decreases as the magnetic field is rotated away from the [111] direction. Hence, the anisotropy has its minimum at $\theta = 90^\circ$ with respect to the [111] direction. As the magnetic field is rotated away from the [111] direction of the crystal, the resonance position decreases until it reaches a minimum at $\theta = 90^\circ$ and recovers its $\theta = 0^\circ$ value as the field is rotated towards $180^\circ$ with respect to the [111] direction. Hence, the anisotropy has a uniaxial character, with an angular dependence for the resonance field $B_\parallel(\theta) = B_0^\parallel + D \cos^2 \theta$ (with $B_0^\parallel = 2.5$ T and $D = 3.6$ T). This minimum in the resonance field $B_\parallel$ occurs when the magnetic field is in the (111) Kagomé plane $\perp \hat{n}$. This singles out a unique anisotropy axis and establishes the macroscopic nature of the anisotropy. This is further evidenced by the inset of figure 3, where a complete rotation $\phi$ in that plane is presented. The dependence of the resonance fields on the orientation of the magnetic field is weaker, $\Delta B_{r,\text{max}} \sim 0.7$ T, and may be attributed to dipolar and/or demagnetization effects.

In order to investigate further the nature of this local order, we studied the orientation dependence of the ESR modes of our single crystal. A plot of the resonant fields versus the angle $\theta$ between the applied magnetic field and the body diagonal $\hat{n}$ is shown in figure 3 at fixed frequency (54 GHz) and for two different temperatures, 150 K and 4.5 K. The single resonance observed at 150 K is independent of the orientation of the field. At 150 K, the single resonance observed is independent of the orientation of the field.

parallel can be drawn with ESR experiments on low dimensional magnets where the change in resonance field as the temperature is lowered are interpreted in terms of short range order effects [8].

The main experimental findings may be summarized as follows: below $T_A$, a macroscopic anisotropy appears with respect to a broken symmetry axis $\hat{n}$ lying along a specific body diagonal of the crystal. This macroscopic character has been checked through dc-torque measurements [10]. This anisotropy develops gradually as the temperature is lowered. This is illustrated in figure 3, where the difference between the resonance fields of line (2) for $\theta = 0^\circ$ and $\theta = 90^\circ$ is plotted versus the temperature. Anisotropies of local origin, such as g-factor and
single-ion, are usually unaffected by spin-correlations and thus temperature independent. Below the ordering temperature at \( T_o = 0.97 \) K, the structure of the ordered state has been identified in a neutron scattering experiment [1] with an isotope enriched \(^{160}\)Gd\(_2\)Ti\(_2\)O\(_7\) sample: within the Kagomé plane, spins are ordered in a chiral \( 120^\circ \) structure (the same as the \( 'y = 0' \) spin structure observed in ordered Kagomé antiferromagnets [11]), while the structure for the spins in between the planes has not been definitively established. This structure is fully consistent with the anisotropic local order observed here at higher temperatures. Mössbauer experiments also conclude in a planar structure for the spins in the Kagomé planes below \( T_o \) [12].

We now consider the microscopic forces which could give rise to this macroscopic anisotropy with respect to a specific body diagonal. Let us first consider the main super-exchange interaction between neighboring Gd\(^{3+}\) ions. Two oxygen ions bridge the vertices of the tetrahedral Gd\(^{3+}\) pyramid. The shortest bridge goes through the oxygen located in the center of the tetrahedron, which bridges all four Gd\(^{3+}\) ions at the tetrahedron vertices. We focus on this shortest bridge. If only the strong ligand electric fields are considered, the four oxygen orbitals are identical \( sp^3 \) mixtures pointing toward the tetrahedron vertices. In a \( T_d \) symmetry, the Hund term on the oxygen splits the four \( sp^3 \) orbitals into a singlet and a triplet [13]. This energy splitting will reduce the super-exchange coupling between the Gd\(^{3+}\) ion coupled to this singlet \( sp^3 \) oxygen orbital with respect to all other three Gd\(^{3+}\) ions. If all singlet \( sp^3 \) oxygen orbitals belonging to different tetrahedra “lock” along the same [111] body diagonal, the system has chosen the appropriate broken symmetry axis. This form of “orbital ordering” would naturally occur at a much higher temperature (\( T_A \approx 80 \) K) than the typical exchange coupling measured by the Curie-Weiss temperature, \( \theta_{cw} \approx -10 \) K. This mechanism by itself does not provide a spin-anisotropy. However, the Dzyaloshinskii-Moryia exchange interactions [14] will provide in this circumstance a macroscopic coupling \( D_{ij}\) \( \vec{n} \cdot \vec{S}_i \times \vec{S}_j \) for the spins \( \vec{S}_i \) and \( \vec{S}_j \) in the Kagomé plane. For a pure Kagomé lattice, this term is known [14] to give rise to the same chiral order as observed by neutron scattering [14]. Dipolar interactions [15] could also favor such a state, once the spins are restricted to the Kagomé planes. In order to experimentally validate this scenario, the knowledge of the magnetic structure for the different magnetic phases in a magnetic field [15] would be decisive.

Whether this exchange mechanism plays a significant role in other pyrochlore magnets with large single-ion anisotropies is also open. For example, in the Tb\(_2\)Ti\(_2\)O\(_7\) pyrochlore, the crystal field splitting of the Tb\(^{3+}\) ion is estimated to be in the 15 − 20 K range [14] which is far less than the temperature (50 K) where short range order sets in [17]. In such circumstances, an exchange-driven anisotropy could be important.

In conclusion, this ESR study has revealed an unexpectedly large magnetic anisotropy for a pyrochlore magnet with spin-only Gd\(^{3+}\) ions. Its possible exchange driven nature stresses the importance of the subtleties of the microscopic coupling between the rare earth ions in these frustrated magnets where a large degree of degeneracy is present.

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