First-Order Transition in the Spin Dynamics of Geometrically Frustrated $Yb_2Ti_2O_7$

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Using neutron diffraction, ^{170}Yb Mössbauer and muon spin relaxation spectroscopies, we have examined the pyrochlore $Yb_2Ti_2O_7$, where the Yb^{3+} $S' = 1/2$ ground state has planar anisotropy. Below $\sim$0.24 K, the temperature of the known specific-heat λ transition, there is no long range magnetic order. We show that the transition corresponds to a first-order change in the fluctuation rate of the Yb^{3+} spins. Above the transition temperature, the rate, in the GHz range, follows a thermal excitation law, whereas below, the rate, in the MHz range, is temperature independent, indicative of a quantum fluctuation regime.

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Geometrically derived magnetic frustration arises when the spatial arrangement of the spins is such that it prevents the simultaneous minimization of all interaction energies [1–4]. In the crystallographically ordered pyrochlore structure compounds $R_2Ti_2O_7$, the rare earth ions (R) form a sublattice of corner sharing tetrahedra and a number of these compounds have been observed to exhibit frustration related behavior [5–12]. The low temperature magnetic behavior associated with a particular rare earth depends on the properties of the crystal field ground state and on the origin (exchange/dipole), size, and sign of the interionic interactions. For example, the recently identified spin-ice configuration [6,10,11] has been linked with an Ising-like anisotropy and a net ferromagnetic interaction. Most of the published work on the pyrochlores have concerned rare earth ions with Ising-like characteristics [6–12] and there has also been some interest in the properties of weakly anisotropic Gd^{3+} [5]. Less attention has been paid to the case, considered here, where the ion has planar anisotropy.

To date, in systems where geometrical frustration may be present, two different low temperature magnetic ground states have been considered. First, under the influence of the frustration the system does not experience a magnetic phase transition and remains in a collective paramagnetic state with the spin fluctuations persisting as $T \rightarrow 0$ [3,4,6–11,13]. Second, a long range ordered state is reached through a phase transition which may be first order [5,14,15]. Our results for $Yb_2Ti_2O_7$, obtained using neutron diffraction, ^{170}Yb Mössbauer spectroscopy, and muon spin relaxation (μSR), evidence a novel scenario: there is a first-order transition which does not correspond to a transition from a paramagnetic state to a (long or short range) magnetically ordered state. The transition chiefly concerns the time domain, and involves an abrupt slowing down of the dynamics of short range correlated spins; below the transition temperature, these spins continue to fluctuate at a temperature independent rate.

We have established the background magnetic characteristics for $Yb_2Ti_2O_7$ in a separate study [16,17]. The Yb^{3+} ion crystal field ground state is a very well isolated Kramers doublet with a planar anisotropy, $g_\perp/g_z \simeq 2.5$, where g_z and $g_\perp$ are, respectively, the spectroscopic factors along and perpendicular to a local [111] axis. The net interionic interaction is ferromagnetic (the paramagnetic Curie-Weiss temperature is 0.75 K) and it is dominated by exchange [the dipole-dipole interaction is relatively small due to the modest value, $1.15\mu_B$ (see below) of the Yb^{3+} moment]. Specific-heat measurements [18] (Fig. 1, top, inset) have evidenced a sharp peak (λ transition) at $\sim$0.2 K with an associated magnetic entropy of $\sim 0.18R \ln 2$, and a broad peak centered near 2 K. The total magnetic entropy was estimated to be $0.97R \ln 2$ [18], suggesting there may be a small amount of missing low temperature magnetic entropy.

Single phase, polycrystalline $Yb_2Ti_2O_7$ was prepared by heating the constituent oxides up to 1400 °C with four intermediate grindings. The neutron diffraction measurements were made down to 0.11 K on the G41 line (wavelength: 0.2427 nm) at the Laboratoire Léon Brillouin (Fig. 1) and to 0.065 K on the D1B line at the Institute Laue-Langevin. Figure 1 shows that the crystal structure does not change with temperature and that below 0.2 K there are no magnetic Bragg peaks, neither isolated nor superposed on the nuclear peaks. Had the moments of $1.15\mu_B$ (to be evidenced below) undergone long range ordering, the peaks would have easily been seen. We estimate that a magnetic Bragg peak would have remained

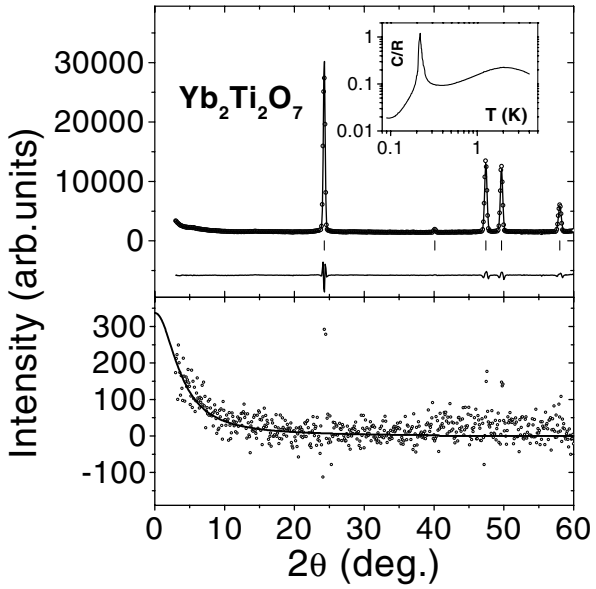

FIG. 1. Neutron diffraction measurements for $Yb_2Ti_2O_7$. Top: measured (points) and calculated (solid line) for the paramagnetic state at 7 K; the ticks indicate the positions of the nuclear Bragg peaks, and the difference between the measurement and the Rietveld refinement is also shown. Bottom: the points correspond to the difference between the measured values at 0.11 K (below the specific-heat λ transition) and at 7 K. No magnetic Bragg peaks are visible. The upturn observed below $2\theta \sim 15°$ and the fitted solid line are discussed in the text. The inset in the top panel shows the specific-heat data taken from Ref. [18].

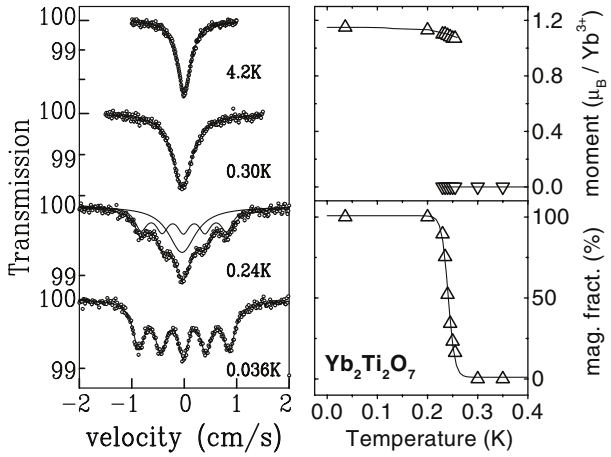

FIG. 2. Left panel: ^{170}Yb Mössbauer absorption in $Yb_2Ti_2O_7$ above, within, and below the first order transition occurring near 0.24 K. The γ-ray energy is $E_\gamma = 84$ keV, and the ground and excited nuclear spin states are $I_g = 0$ and $I_{ex} = 2$, respectively (1 cm/s corresponds to 680 MHz). Right panel: thermal variation of the size of the Yb^{3+} magnetic moment obtained from the hyperfine field (top) and relative weight of the static magnetic fraction (bottom). The lines are eye guides.

visible if the correlation length had exceeded 2 to 3 nm, so this provides an upper bound for the correlation length. An additional low angle contribution appears in the difference spectra below ~2 K (Fig. 1, bottom). Its intensity initially grows as the temperature decreases but there is no significant change when crossing the temperature of the specific-heat λ transition. If we interpret this additional contribution in terms of short range ferromagnetic correlations, then by using a model of noninteracting spherical clusters each having a uniform magnetisation (solid line in Fig. 1, bottom) [19], we obtain a sphere diameter of ~1.5(2) nm. It is possible that not all of the additional signal seen for $2\theta < 15°$ is of magnetic origin [20]. We consider our estimate of the magnetic correlation length below the specific-heat λ transition to correspond to an upper limit. The absence of long range order contradicts previous suppositions [5,18].

Selected ^{170}Yb Mössbauer absorption spectra are shown in the left panel of Fig. 2. At 0.036 K, a five-line spectrum is observed, indicating that there is a "static" hyperfine field (H_{hf}) which we find amounts to 115 T. In the present case, "static" means the fluctuation frequency of the field is less than the lowest measurable ^{170}Yb value of ~15 MHz. Knowing that for Yb^{3+} the hyperfine field is proportional to the 4f shell magnetic moment, we find that each of the Yb^{3+} carries a magnetic moment of $1.15\mu_B$. Since there is no long range order, the hyperfine field is associated with the short range correlated Yb^{3+} moments.

In the absence of a significant quadrupole hyperfine interaction, we cannot obtain the local direction of the Yb^{3+} magnetic moment by directly measuring the angle it makes with the principal axis of the electric field gradient (a [111] direction). Instead, we make use of the fact that, for an anisotropic Kramers doublet, the size of the spontaneous magnetic moment is linked to the angle θ it makes with the local symmetry axis (a [111] axis) through the relation, $M_{Yb} = \frac{1}{2} g_\perp \mu_B / (\cos\theta \sqrt{r^2 + \tan^2\theta})$, where r is the anisotropy ratio $g_\perp / g_z$ [21]. Using the measured moment and the known g values, we find $\theta = 44(5)°$. Thus each moment does not lie perpendicular to its local [111] axis as would be expected if the orientation were governed only by the crystal field anisotropy. The uniform tilting of each moment away from its local [111] axis is probably related to the combined influence of the crystal field anisotropy and the (presumably anisotropic) exchange interaction with the noncollinear neighboring moments.

When the temperature is increased to 0.23 K, an additional single line subspectrum appears. It is linked with the fraction of the Yb^{3+} whose moments fluctuate "rapidly" so that the magnetic hyperfine splitting is "motionally narrowed." The two subspectra (see Fig. 2, left panel at 0.24 K) are both present up to 0.26 K, evidencing the coexistence of regions with "static" and "rapidly fluctuating" moments. The right panel in Fig. 2 shows that, as the temperature increases, there is a progressive decrease in the relative weight of the static hyperfine field subspectrum. These features clearly evidence a first order transition, taking place at slightly different temperatures in the different parts of the sample.

The single line (sub)spectrum progressively narrows as the temperature increases. Since magnetic correlations are still present above 0.24 K, we attribute this change to the progressive increase in ν_M, the fluctuation rate of $\vec{H}_{\rm hf}$. The relation between the dynamic line broadening, $\Delta\Gamma_R$, and ν_M is written $\Delta\Gamma_R = (\mu_I H_{\rm hf})^2/\nu_M$, where μ_I is the ^{170}Yb nuclear moment [22]. As shown in Fig. 4 below, when the temperature is lowered from $\sim$1 K to just above 0.24 K, the rate decreases from $\sim$15 to $\sim$2 GHz. This decrease is linked to the slowing down of the spin fluctuations which accompanies the development of the short range correlations. Below 0.24 K, ν_M drops to a value which is less than the lowest measurable ^{170}Yb Mössbauer value.

The μSR study [23] was carried out at the ISIS facility (some additional measurements were also made at the PSI facility) over the range 300–0.04 K, mostly in a longitudinal field of 2 mT so as to decouple the small contribution of the nuclear spins to the measured depolarization. Figure 3 shows typical results for the time dependence of the asymmetry which is written $aP_z^{\rm exp}(t) = a_z P_z(t) + a_{\rm bg}$, where the first term on the right-hand side originates from the sample and the second is a temperature independent constant background contribution linked with the muons stopping in the silver sample holder and in the cryostat ($a_{\rm bg} \simeq 0.065$ for ISIS and close to 0 for PSI).

From 300 to 0.275 K, $P_z(t)$ is well represented by an exponential relaxation function (solid lines at 4.3 and 0.275 K in Fig. 3a): $P_z(t) = \exp(-\lambda_z t)$, where λ_z is the muon spin-lattice relaxation rate. From 100 to $\sim$4 K, λ_z is small ($\sim$0.1 MHz) and, in keeping with the paramagnetic nature of the Yb^{3+}, it shows little thermal dependence. As the temperature is lowered below $\sim$1 K, λ_z increases progressively to reach 0.52(3) MHz at 0.275 K. The origin of this increase is the same as that for the dynamic broadening $\Delta\Gamma_R$ of the Mössbauer spectra, i.e., the slowing down of the electronic spin fluctuations.

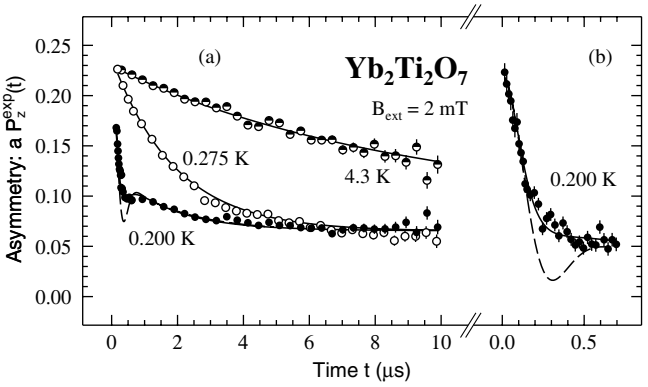

FIG. 3. (a) μSR spectra recorded at ISIS in a longitudinal field of 2 mT. A marked change occurs on crossing the temperature ($\sim$0.24 K) of the specific-heat λ transition. (b) Short time part of the PSI data at 0.200 K confirming that there are no short time oscillations. The slight difference visible between the ISIS and PSI data at 0.200 K is linked with the first-order nature of the transition and the different thermal and magnetic field histories of the two experiments. The dashed and solid line fits are described in the text.

As the temperature is lowered below 0.275 K, $P_z(t)$ first becomes moderately nonexponential and then towards 0.2 K it abruptly becomes strongly nonexponential (Fig. 3a). Below 0.2 K, $P_z(t)$ is independent of temperature and there are no spontaneous oscillations, in accordance with the neutron result that there is no long range order. The spectrum of Fig. 3b which extends to shorter times, clearly confirms this result. The shape of $P_z(t)$ below 0.2 K is reminiscent of a dynamic Kubo-Toyabe (KT) decay [24] associated with a slowly fluctuating ensemble of moments, the decrease of $P_z(t)$ beyond $\sim$1 μs indicating that fluctuations are still present. The KT decay provides an approximate account of the shape of $P_z(t)$ but there is a noticeable misfit below 0.5 μs (dashed lines in Fig. 3). A similar misfit was also observed for $Y_2Mo_2O_7$ near 0.03 μs at 2.5 K [13]. A better fit is provided by the Gaussian broadened Gaussian (GBG) model [25], where the single Gaussian distribution of the KT model is replaced by a collection of distributions (solid lines at 0.200 K in Fig. 3). From the fit of Fig. 3a, the mean value of the GBG distribution is $\Delta_{\rm LT}/\gamma_\mu \simeq 5.7$ mT, the ratio of the width of the collection of distributions to the mean value is $\simeq$0.38, and the electronic fluctuation rate ν_μ is $\simeq$1 MHz. All are independent of temperature below 0.2 K.

To obtain an estimate of the effective value of the spin fluctuation rate, ν_μ, at temperatures above 0.24 K, we insert the experimental values for λ_z (obtained in 2 mT) into the expression $\lambda_z = 2\Delta_{\rm HT}^2/\nu_\mu$. The value for ν_μ then depends on the value of $\Delta_{\rm HT}$, the Yb^{3+}—muon spin coupling above 0.24 K. With the choice $\Delta_{\rm HT}/\gamma_\mu = 31.8$ mT, the ν_μ obtained from the muon measurements scale remarkably well with the ν_M obtained from the Mössbauer measurements (Fig. 4). Their common thermal dependence is well fitted (solid line in Fig. 4) by the thermal excitation law $\nu = \nu_0 \exp[-E_{\rm bh}/(k_B T)]$, with $\nu_0 = 17$ GHz and mean barrier height $E_{\rm bh} = 0.5$ K. The associated drop in ν_μ at 0.24 K amounts to a factor of 10^3. Choosing a different value for $\Delta_{\rm HT}/\gamma_\mu$ would lead to different rates above 0.24 K and to a different size for the drop. For example, with $\Delta_{\rm HT}/\gamma_\mu = 5.7$ mT (the value we obtained for $\Delta_{\rm LT}/\gamma_\mu$ below 0.24 K), the drop is $\simeq 10^2$ (this is also the minimum size of the drop allowed by the Mössbauer results), and with $\Delta_{\rm HT}/\gamma_\mu = 85.6$ mT, obtained by scaling from $Tb_2Ti_2O_7$ [8], it is $\simeq 10^4$. Combining the Mössbauer and the muon results thus indicates that the spin fluctuation rate undergoes a first-order change by a factor of 10^2 to 10^4. We mention that, between 2 and 0.275 K, we find that λ_z does not have the usual Lorentzian dependence on the applied longitudinal field. This anomalous behavior will be discussed in a separate publication.

The low temperature magnetic properties of $Yb_2Ti_2O_7$ are therefore unusual. In the short range correlated region

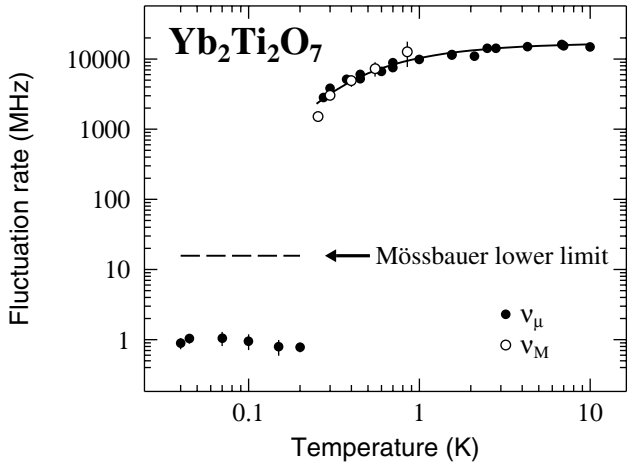

FIG. 4. Estimate of the Yb^{3+} fluctuation rates as obtained from ^{170}Yb Mössbauer (ν_M) and μSR (ν_μ) measurements. The first-order change in the fluctuation rate takes place at the specific-heat λ transition. Below $\sim$0.24 K, the fluctuation rate is independent of temperature and has dropped below the lowest value which is measurable with the Mössbauer method (dashed line). The solid line follows a thermal excitation law as described in the text.

from $\sim$2 to $\sim$0.24 K, the spin fluctuation rates follow a thermal excitation law. This crystallographically ordered compound thus possesses barriers against spin reorientation. When crossing the temperature of the specific-heat λ peak [18], no long range order appears, but there is a first-order drop, of 2 to 4 orders of magnitude, in the fluctuation rates of the correlated moments. As $T \rightarrow 0$, the fluctuations persist at a temperature independent rate of $\simeq$1 MHz, and they take place between directions which make an angle of $\sim$44° relative to the local anisotropy axis (a [111] direction). The fluctuations of the moments thus conserve this angle and hence involve spin flips or spin spirals around a [111] axis.

Above 0.24 K, we speculate that the spin fluctuations could link more random directions. The first-order drop in the fluctuation rate would then be associated with a change in the nature of the fluctuations such that, below 0.24 K, the system explores a subset of the states that are explored at higher temperatures. The described transition, first order without the appearance of any long range correlations and with a change of dynamics, shows properties which parallel aspects of the general gas-liquid transition or of the specific water-ice transition. To our knowledge, such a transition has not previously been observed in a magnetic system.

When exotic low temperature properties have previously been observed in the rare earth pyrochlores, they have related to ions with Ising character (Tb^{3+}, Dy^{3+}, Ho^{3+}). The present results show that further novel behavior is evidenced when the rare earth has a planar anisotropy. Although $Yb_2Ti_2O_7$ does not correspond to the spin-ice scenario (in addition to the planar anisotropy, there is, at most, only a small missing entropy), it shares with the spin-ice state the characteristic of short range correlated moments which continue to fluctuate between specific directions as $T \rightarrow 0$. Here, however, the low temperature state is reached through a novel route: a first-order dynamical transition which can be viewed as a change from a thermally excited regime to a low temperature quantum (or tunneling) regime.

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