First Order Transition in the Spin Dynamics of Geometrically Frustrated Yb$_2$Ti$_2$O$_7$.

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Using neutron diffraction, $^{170}$Yb Mössbauer and $\mu$SR spectroscopies, we have examined the pyrochlore Yb$_2$Ti$_2$O$_7$ where the Yb$^{3+}$ $S' = 1/2$ ground state has planar anisotropy. Below ~ 0.24 K, the temperature of the known specific heat $\lambda$-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 minimisation of all interaction energies $\square$. In the crystallographically ordered pyrochlore structure compounds R$_2$Ti$_2$O$_7$, the rare earth ions (R) form a sub-lattice of corner sharing tetrahedra and a number of these compounds have been shown to exhibit frustration related behaviour $\square$. The low temperature magnetic behaviour 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 inter-ionic interactions. For example, the recently identified spin-ice configuration $\square$ has been linked with an Ising-like anisotropy and a net ferromagnetic interaction. Most of the published work on the pyrochlores has concerned rare earth ions with Ising-like characteristics $\square$ and there has also been some interest in the properties of weakly anisotropic Gd$^{3+}$ $\square$. 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 $T \to 0$ $\square$. Second, a long range ordered state is reached through a phase transition which may be first order $\square$. Our results for Yb$_2$Ti$_2$O$_7$, obtained using neutron diffraction, $^{170}$Yb Mössbauer spectroscopy and muon spin relaxation ($\mu$SR), 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$_2$Ti$_2$O$_7$ in a separate study $\square$. 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 $g_\perp$ and $g_z$ are respectively the spectroscopic factors along and perpendicular to a local [111] axis. The net inter-ionic 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 $\square$ (Fig. 1, top, inset) have evidenced a sharp peak ($\lambda$ transition) at ~ 0.2 K with an associated magnetic entropy of $\sim 0.18 R \ln 2$, and a broad peak centered near 2 K. The total magnetic entropy was estimated to be 0.97 $R \ln 2$ $\square$ suggesting there may be a small amount of missing low temperature magnetic entropy.

Single phase, polycrystalline Yb$_2$Ti$_2$O$_7$ 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. Fig. 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 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 $\sim 2$ K (Fig. 1, bottom). Its intensity initially grows as the temperature decreases but there is no significant change on crossing the temperature of the specific heat $\lambda$-transition. If we interpret this additional contribution in terms of short range ferromagnetic correlations, then using a model of non-interacting spherical clusters each having a uniform magnetisation (solid line on Fig. 1, bottom) [15] we obtain a sphere diameter of $\sim 1.5(2)$ nm. It is possible that not all of the additional signal seen for $2\theta < 15^\circ$ is of magnetic origin [20]. We consider our estimate of the magnetic correlation length below the specific heat $\lambda$-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 on the left panel of Fig. 2. At 0.036 K, a five line spectrum is observed indicating there is a “static” hyperfine field ($H_{\text{hf}}$) 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 $\sim 15$ MHz. Knowing that for Yb$^{3+}$ the hyperfine field is proportional to the 4f shell magnetic moment, we obtain that each of the Yb$^{3+}$ carries a magnetic moment of 1.15 $\mu_B$. As 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 property that for an anisotropic Kramers doublet, the size of the spontaneous magnetic moment is linked to the angle $\theta$ it makes with the local symmetry axis (a [111] axis) through the relation: $M_{\text{Yb}} = \frac{1}{2}g_{\perp}\mu_B/(\cos\theta\sqrt{r^2 + \tan^2 \theta})$ where $r$ is the anisotropy ratio $g_{\perp}/g_{\parallel}$ [21]. Using the measured moment and the known $g$ values, we find $\theta = 44(5)^\circ$. 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 of the (presumably anisotropic) exchange interaction with the non-collinear neighbouring moments.

When the temperature is increased to 0.23 K, an additional single line sub-spectrum appears. It is linked with the fraction of the Yb$^{3+}$ whose moments fluctuate “rapidly” so that the magnetic hyperfine splitting is “motionaly narrowed”. The two sub-spectra (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. Fig. 2, right panel, shows that as the temperature increases, there is a progressive decrease

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**FIG. 1.** Neutron diffraction measurements for Yb$_2$Ti$_2$O$_7$. 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 $\lambda$-transition) and at 7 K. No magnetic Bragg peaks are visible. The upturn observed below $2\theta \sim 15^\circ$ and the fitted solid line are discussed in the text. The inset in the top part shows the specific heat data taken from ref. [13].

**FIG. 2.** Left panel: $^{170}$Yb Mössbauer absorption in Yb$_2$Ti$_2$O$_7$ above, within, and below the first order transition occurring near 0.24 K. The $\gamma$-ray energy is $E_\gamma = 84$ keV, and the ground and excited nuclear spin states are $I_e = 0$ 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.
in the relative weight of the “static” hyperfine field sub-spectrum. 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)pectrum progressively narrows as the temperature increases. As magnetic correlations are still present above 0.24 K, we attribute this change to the progressive increase in \( \nu_M \), the fluctuation rate of \( H_M \). The relation between the dynamic line broadening, \( \Delta \Gamma_R \), and \( \nu_M \), is written \( \Delta \Gamma_R = (\mu_1 H_M)^2/\nu_M \) where \( \mu_1 \) is the \( ^{170} \text{Yb} \) nuclear moment. As shown on Fig. 4 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, \( \nu_M \) drops to a value which is less than the lowest measurable \( ^{170} \text{Yb} \) Mössbauer value.

The \( \mu \text{SR} \) study was carried out at the ISIS facility (some additional measurements were also made at the PSI facility) over the range 300 to 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 depolarisation. Fig. 3 shows typical results for the time dependence of the asymmetry which is written \( a_{P\text{exp}}(t) = a_z P_z(t) + a_{bg} \) 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 \( a_{bg} \simeq 0.065 \) for ISIS and close to 0 for PSI.

FIG. 3. Panel a: \( \mu \text{SR} \) spectra recorded at ISIS in a longitudinal field of 2 mT. A marked change occurs on crossing the temperature \((\sim 0.24 \text{K})\) of the specific heat \( \lambda \) transition. Panel b: short time part of the PSI data at 0.200 K confirming 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.

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 on Fig. 3): \( P_z(t) = \exp(-\lambda_z t) \) where \( \lambda_z \) is the muon spin-lattice relaxation rate. From 100 to \( \sim 4 \) K, \( \lambda_z \) is small \((\sim 0.1 \text{ MHz})\) and in keeping with the paramagnetic nature of the \( ^{170} \text{Yb}^{3+} \), it shows little thermal dependence. As the temperature is lowered below \( \sim 1 \) K, \( \lambda_z \) 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.

As the temperature is lowered below 0.275 K, \( P_z(t) \) first becomes moderately non-exponential and then towards 0.2 K it abruptly becomes strongly non-exponential (Fig. 3b). 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 associated with a slowly fluctuating ensemble of moments, the decrease of \( P_z(t) \) beyond \( \sim 1 \mu \text{s} \) 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 \( \mu \text{s} \) (dashed lines on Fig. 3). A similar misfit was also observed for \( ^{31} \text{Mo}_2 \text{O}_7 \) near 0.03 \( \mu \text{s} \) at 2.5 K. A better fit is provided by the Gaussian Broadened Gaussian (GBG) model, where the single Gaussian distribution of the KT model is replaced by a collection of distributions (solid lines at 0.200 K on Fig. 3). From the fit of Fig. 3a, the mean value of the GBG distribution is \( \lambda_{\text{HT}}/\gamma_{\mu} \simeq 5.7 \text{ mT} \), the ratio of the width of the collection of distributions to the mean value is \( \simeq 0.38 \) and the electronic fluctuation rate \( \nu_{\mu} \) is \( \simeq 1 \text{ MHz} \). All are independent of temperature below 0.2 K.

To obtain an estimate of the effective value of the spin fluctuation rate, \( \nu_{\mu} \), at temperatures above 0.24 K, we insert the experimental values for \( \lambda_z \) (obtained in 2 mT) into the expression \( \lambda_z = 2\Delta \Gamma_{\text{HT}}/\nu_{\mu} \). The value for \( \nu_{\mu} \) then depends on the value of \( \Delta \Gamma_{\text{HT}} \), the \( ^{170} \text{Yb}^{3+} \) - muon spin coupling above 0.24 K. With the choice \( \Delta \Gamma_{\text{HT}}/\gamma_{\mu} = 31.8 \text{ mT} \), the \( \nu_{\mu} \) obtained from the muon measurements scale remarkably well with the \( \nu_M \) obtained from the Mössbauer measurements (Fig. 4). Their common thermal dependence is well fitted (solid line on Fig. 4) by the thermal excitation law \( \nu = \nu_0 \exp[-E_{\text{bh}}/(k_B T)] \), with \( \nu_0 = 17 \text{ GHz} \) and mean barrier height \( E_{\text{bh}} = 0.5 \text{ K} \). The associated drop in \( \nu_{\mu} \) at 0.24 K amounts to a factor of \( 10^{3} \). Choosing a different value for \( \Delta \Gamma_{\text{HT}}/\gamma_{\mu} \) would lead to different rates above 0.24 K and to a different size for the drop. For example, with \( \Delta \Gamma_{\text{HT}}/\gamma_{\mu} = 5.7 \text{ mT} \) (the value we obtained for \( \Delta \Gamma_{\text{HT}}/\gamma_{\mu} \) below 0.24 K), the drop is \( \approx 10^2 \) (this is also the minimum size of the drop allowed by the Mössbauer results) and with \( \Delta \Gamma_{\text{HT}}/\gamma_{\mu} = 85.6 \text{ mT} \), obtained by scaling from \( ^{31} \text{Ti}_2 \text{O}_7 \), it is \( \approx 10^4 \). 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 $\lambda_{\perp}$ does not have the usual Lorentzian dependence on the applied longitudinal field. This anomalous behaviour will be discussed in a separate publication.

![Graph showing fluctuation rates](image)

**FIG. 4.** Estimate of the $\text{Yb}^{3+}$ fluctuation rates as obtained from $^{170}\text{Yb}$ Mössbauer ($\nu_M$) and $\mu$SR ($\nu_{\mu}$) measurements. The first order change in the fluctuation rate takes place at the specific heat $\lambda$ 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.

The low temperature magnetic properties of $\text{Yb}_2\text{Ti}_2\text{O}_7$ are therefore unusual. In the short range correlated region from $\sim 2$ K to $\sim 0.24$ K, the spin fluctuation rates follow a thermal excitation law. This crystallographically ordered compound thus possesses barriers against spin re-orientation. On crossing the temperature of the specific heat $\lambda$ 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.

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, evidences 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 (Th$^{3+}$, Dy$^{3+}$, Ho$^{3+}$). The present results show that further novel behaviour is evidenced when the rare earth has a planar anisotropy. Although $\text{Yb}_2\text{Ti}_2\text{O}_7$ 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 $T \to 0$. 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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[1] H.T. Diep, editor, Magnetic Systems with Competing Interactions, (World Scientific, Singapore, 1994).
[2] P. Schiffer, A.P. Ramirez, Comments Cond. Mat. Phys. 18, 21 (1996).
[3] R. Moessner, Canadian J. Phys. 79, 1283 (2001).
[4] J. Villain, Z. Physik 33, 31 (1979)
[5] N.P. Raju et al., Phys. Rev. B 59, 14 489 (1999).
[6] M.J. Harris et al., Phys. Rev. Lett. 79, 2554 (1997).
[7] M.J. Harris et al., J. Mag. Mag. Mat. 177-181, 757 (1998).
[8] J.S. Gardner et al., Phys. Rev. Lett. 82, 1012 (1999).
[9] M.J.P. Gingras et al., Phys. Rev. B 62, 6496 (2000).
[10] B.C. den Hertog, M.J.P. Gingras, Phys. Rev. Lett. 84, 3430 (2000).
[11] A.P. Ramirez et al., Nature 399, 333 (1999).
[12] S.T. Bramwell et al., Phys. Rev. Lett. 87 (2001) 047205.
[13] S.R. Dunsiger et al., Phys. Rev. B 54, 9019 (1996).
[14] S.T. Bramwell, M.J.P. Gingras, J.N. Reimers, J. Appl. Phys. 75, 5525 (1994).
[15] R.G. Melko et al., Phys. Rev. Lett. 87, 067203 (2001).
[16] J.A. Hodges et al., J. Phys.: Condens. Matter. 13, 9301 (2001)
[17] J.A. Hodges et al., Canadian J. Phys. 79, 1373 (2001).
[18] H.W.J. Blöte, R.F. Wielinga, W.J. Huiskamp, Physica 43, 549 (1969).
[19] A. Guinier, G. Fournet, Small Angle Scattering of X-Rays, (Wiley, New York, 1955).
[20] The additional signal may, in part, be due to superfluid helium coating the grains, C. Broholm, private communication.
[21] P. Bonville et al., Phys. Rev. B 18, 2196 (1978) (Appendix).
[22] S. Dattagupta, Hyperfine Interactions 11, 77 (1981).
[23] For a recent review, see P. Dalmas de Rétotier, A. Yeoauac, J. Phys.: Condens. Matter. 9, 9113 (1997).
[24] R.S. Hayano et al., Phys. Rev. B 20, 850 (1979).
[25] R.D. Noakes, J. Phys. Condens. Matter. 11, 1589 (1999)