Muon diffusion and electronic magnetism in Y\textsubscript{2}TiO\textsubscript{7}

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We report a \(\mu\)SR study in a \(Y_2\text{Ti}_2\text{O}_7\) single crystal. We observe slow local field fluctuations at low temperature which become faster as the temperature is increased. Our analysis suggests that muon diffusion is present in this system and becomes small below 40 K and therefore incoherent. A surprisingly strong electronic magnetic signal is observed with features typical for muons thermally diffusing towards magnetic traps below \(\approx 100\) K and released from them above this temperature. We attribute the traps to \(T_i^{3+}\) defects in the diluted limit. Our observations are highly relevant to the persistent spin dynamics debate on \(R_2\text{Ti}_2\text{O}_7\) pyrochlores and their crystal quality.

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The rare-earth titanates and stanates series of compounds, \(R_2\text{M}_2\text{O}_7\) (\(R\) is a rare-earth ion and \(M\) is Ti or Sn), which crystallize in the pyrochlore crystal structure (space group \(Fd\overline{3}m\)), are prone to strong geometrical frustration.\textsuperscript{1} Their study has revealed a wealth of exotic magnetic properties. These include (i) the spin-ice ground state of \(\text{Ho}_2\text{Ti}_2\text{O}_7\) and \(\text{Dy}_2\text{Ti}_2\text{O}_7\),\textsuperscript{2–4} (ii) the ground state reached by \(\text{Yb}_2\text{Ti}_2\text{O}_7\) after a sharp transition in the spin dynamics fingerprinted by a pronounced peak in the specific heat,\textsuperscript{5} (iii) the unconventional dynamical ground state of \(\text{Tb}_2\text{Sn}_2\text{O}_7\) for which magnetic Bragg reflections are observed by neutron diffraction,\textsuperscript{6} while no spontaneous magnetic field is measured by the zero field (ZF) muon spin relaxation (\(\mu\)SR) technique,\textsuperscript{7} (iv) the persistent spin dynamics (PSD) detected in the ordered states of \(\text{Gd}_2\text{Sn}_2\text{O}_7\), \(\text{Gd}_2\text{Ti}_2\text{O}_7\) and \(\text{Er}_2\text{Ti}_2\text{O}_7\),\textsuperscript{8–12} and the non-ordered PSD state of \(\text{Tb}_2\text{Ti}_2\text{O}_7\).\textsuperscript{13–15}

The first report of PSD was for \(\text{SrCr}_8\text{Ga}_4\text{O}_{19}\) using \(\mu\)SR.\textsuperscript{15} It was found that this kagome compound does not exhibit magnetic Bragg reflections down to 50 mK. Although mostly observed by \(\mu\)SR, PSD has been also proposed by other techniques, e.g., in \(\text{Gd}_2\text{Sn}_2\text{O}_7\) using \(^{155}\text{Gd}\) Mössbauer spectroscopy.\textsuperscript{8} Both \(\mu\)SR and the neutron spin echo have observed PSD in \(\text{Tb}_2\text{Sn}_2\text{O}_7\)\textsuperscript{7–10} as well as \(\text{Dy}_2\text{Ti}_2\text{O}_7\).\textsuperscript{4} \textsuperscript{17} \textsuperscript{18} However, the existence and nature of PSD is still under debate.\textsuperscript{9–11} Recently, it was suggested that PSD does not exist for \(\text{Dy}_2\text{Ti}_2\text{O}_7\) and that the observed relaxation results from coherent muon diffusion.\textsuperscript{20} In that work it was proposed to perform \(\mu\)SR measurements in \(Y_2\text{Ti}_2\text{O}_7\) to investigate the possibility of coherent muon diffusion in a compound where frustrated magnetism does not play any role as no 4f-magnetism should be present. In this letter we report ZF and Longitudinal Field (LF) \(\mu\)SR measurements on \(Y_2\text{Ti}_2\text{O}_7\). We show that there is no detectable neutral muonium formation, and that the positive-muon hopping rate at low temperature is much smaller than what was proposed for \(\text{Dy}_2\text{Ti}_2\text{O}_7\).\textsuperscript{20} Also, we have observed a relatively strong muon spin relaxation which we attribute to a small density of \(T_i^{3+}\) magnetic defects. Note that this system has already been studied by Dunsiger using \(\mu\)SR.\textsuperscript{21} Nevertheless, that study was less extensive than the one reported here and did not consider the possibility of coherent diffusion at low temperature. When a comparison is possible, our data and that from Dunsiger are similar.

Polycrystalline \(Y_2\text{Ti}_2\text{O}_7\) was prepared by a solid state reaction. Starting materials of \(\text{Y}_2\text{O}_3\) and \(\text{TiO}_2\) with 99.99\% purity were mixed and ground. They were then heat treated at 900-1150°C in air for more than 100h with several intermediate grindings. The resulting powder was hydrostatically pressed in the form of rods (8 mm in diameter and 60 mm in length). The rods were subsequently sintered at 1150°C during 15h. The crystal growth was done using an optical floating zone furnace with four 1000W halogen lamps as a heat source. The growing conditions were: growth rate of 10 mm/h, feeding and seeding rods were rotated at about 20 rpm in opposite directions (to have homogeneity of the liquid), growth done in 4 bar pressure of an argon and oxygen mixture (50:50). The crystal was post-annealed at 1150°C in argon for 15h in order to remove possible over stoichiometric oxygen. Phase purity of the grown crystal was checked with conventional powder x-ray diffractometer and the obtained lattice parameter \(a=10.099\)Å is in good agreement with the literature.\textsuperscript{22} The crystal was then aligned using an X-ray Laue camera, and magnetization measurements were performed down to 1.9 K (see Fig. 1).

The \(\mu\)SR measurements were carried out on the General Purpose Spectrometer (GPS) at the Swiss Muon Source facility of the Paul Scherrer Institut (Switzerland). Most of the measurements were done in the LF geometry for which the initial muon spin and the external magnetic field \(B_{\text{ext}}\) are parallel.\textsuperscript{23, 24} We define
the $Z$ axis to be parallel to the initial muon spin direction, with the positron detectors centered along this axis. With this geometry the measured asymmetry (i.e. $\mu$SR signal) is written as $a_0P_Z(t)$, where $a_0$ is the initial asymmetry (a characteristic of the spectrometer and the geometry of the sample), and $P_Z(t)$ is the longitudinal muon polarization function which contains information on the local magnetic fields in sample. In addition, three measurements were done with the Transverse Field (TF) geometry where $B_{ext}$ is perpendicular to $Z$.

It is important to know if there is muonium formation in $Y_2Ti_2O_7$, as this entity is known to diffuse coherently at low temperature in some systems. Typical ZF and LF (50 mT) spectra measured at different temperatures are shown in Fig. 2. The initial asymmetry is temperature and field independent with a value $a_0 \approx 0.25$ typical for the GPS. This is a strong indication that there is no muonium formation in the whole temperature range. As expected for the absence of muonium, no re-polarization (a recovery of the missing asymmetry) by the LF is observed. The absence of muonium is further supported by the TF and ZF signals at 2.4 K (Fig. 3), where the initial asymmetry is found to be the same for the two spectra and the only frequency observed in TF is that of the applied field. This is further supported by Fourier Transform of the TF signal shown in the inset of Fig. 3. If an appreciable vacuum-muonium fraction was present, we would expect to observe an oscillation at a frequency $\approx 103\gamma_B B_{ext}/(2\pi) = 9.8$ MHz ($\gamma_B = 851.615$ Mrad s$^{-1}$ T$^{-1}$) in the Fourier spectrum, and/or a reduction of the initial asymmetry due to the fast muonium precession. Therefore, we find no evidence of neutral muonium states in $Y_2Ti_2O_7$. The reason for the muonium absence in the pyrochlore oxides is not understood, and it is certainly a subject of much interest.

We turn now to discussing the ZF and LF data in Fig. 2 where we observe a surprisingly high relaxation rate. A priori, electronic magnetism should not be present in $Y_2Ti_2O_7$ since both $Y^{3+}$ and Ti$^{3+}$ ions are non-magnetic. Therefore, only nuclear magnetic mo-
In general, we note that the ternary pyrochlore compounds are of the general formula $A_2B_2O_7$. The $B$ element can be a transition metal with a variable oxidation state. This gives the possibility of substitution on the $B$ site (see Ref. [26] and references therein). The structure also tolerates vacancies at the $A$ and $O$ sites to a certain extent. Around the $A$ and $B$ cations one finds 8- and 6-fold coordination polyhedron of oxygen, respectively. Focusing on $Y_2Ti_2O_7$, in terms of the oxidation states we have $Y^{3+}Ti^{2+}O_7^{2−}$. $Ti^{4+}$ is diamagnetic since it is in a $d^0$ configuration. Depending on its coordination the $Ti^{4+}$ ionic radius is 74.4 or 88 pm, which is smaller than the $Y^{3+}$ ionic radius of 104 or 115.9 pm. Now we consider a magnetic configuration for at least one of the three involved elements. The obvious candidate is $Ti^{3+}$ which has about the same ionic radius as $Ti^{4+}$. This ion is known to be rather unstable and it has been suggested to locate it in the $A$ site. In this case we can write $(Y_{2−x}Ti_{x})Ti_2O_7$, where we have neglected the substitution of $Y^{3+}$ in the $B$. This does not change our conclusions since $Y^{3+}$ is non-magnetic. $Ti^{3+}$ has an electronic configuration $d^3$ and therefore, as a free ion, carries one Bohr magneton. Another possibility, which is less likely though cannot be ruled out, is $O$ vacancies in the structure. Such defects will also introduce two $Ti^{3+}$ magnetic moments for each vacancy. Note that both types of defects will produce essentially the same effect on the implanted muons and cannot be distinguished in our measurements.

We now consider qualitatively the ZF and 50 mT LF spectra of Fig. 2. In ZF and low temperatures we observe a signal with a fast and a slow relaxing components. As the temperature is increased, the relaxation rate of the fast component decreases slightly and then increases until this component disappears above 150 K. The relaxation of the slow component decreases continuously with temperature. In the LF measurements the overall relaxation rate start increasing as the temperature is increased, peaks at 100 K, and then it decreases to a small value above 150 K. Referring to the original work of Borghini et al. and the latter works reviewed in Ref. 25, the temperature dependence of the spectra is typical for a muon trapping/detrapping effect. At low temperature the overall relaxation is small because a big fraction of muons are implanted “far” from $Ti^{3+}$ magnetic defects. As the temperature is increased, the relaxation increases because muons diffuse towards magnetic defects and become trapped. At even higher temperatures, trapping/detrapping become faster leading to a decrease of the relaxation rate due to the fast fluctuating magnetic field sensed by the muons. The 50 mT field is sufficient to quench the relaxation except around 100 K, where a $B_{ext} = 200$ mT was needed to suppress the relaxation at this temperature. This is consistent with muons diffusing and accumulating near magnetic defects at this temperature, i.e. the trapping rate is higher than the detrapping rate.

We base our analysis on a multi-state model and, for simplicity, we restrict ourselves to a two-state model. In this model the muon can be diffusing in the undisturbed regions or trapped near a magnetic impurity. The relaxation rate from muons in the trapped state is expected to be higher since they are closer to magnetic defects and therefore experience stronger magnetic fields. Also, muons in undisturbed regions can diffuse and reach trapping sites (at a given trapping rate), while trapped muons can escape traps if the temperature is high enough (at a given detrapping rate). The muon polarization function for such a two-state model can be approximated by the sum of two relaxing signals.

$$P_z(t) = f \exp(-\lambda_1 t) + (1 - f) \exp(-\lambda_2 t), \quad (1)$$

where $\lambda_1$ and $\lambda_2$ are the relaxation rates of the two components and $f$ is the contribution of the first component to the full signal. At the limit of zero trapping/detrapping rates, $\lambda_1$ and $\lambda_2$ represent the relaxation rate of muons in traps and undisturbed regions, respectively, while $f$ is the fraction of muons in traps. Eq. (1) provides a good qualitative description of the ZF data at all temperatures as shown by the solid lines in the top panel of Fig. 2. The temperature dependence of the three parameters in ZF is shown in Fig. 5. We find $f \approx 0.20$ and temperature independent below 40 K, indicating that the muon trapping and detrapping rates are constant below 40 K. Furthermore, the fact that for these temperatures the signal can be decoupled by small applied fields, is evidence that most of the muons cannot diffuse to reach a high field trapping site during the experimental time window (8.5 µs). Therefore, we conclude that below 40 K the trapping and detrapping rates must be small. At higher temperatures $f$ increases due to the enhanced muon trapping caused by a faster diffusion in the undisturbed regions, and then goes to zero at 135 K indicating that muons trap and detrapping so fast.
that they experience fast fluctuating magnetic fields (motional narrowing) and relax following a single exponential behaviour. We want to point out that fitting the data with a temperature independent \( f \) does not produce satisfactory fits; and fitting with a power-exponential function produces very bad results for temperatures above 70 K. Also, an implementation of the two-state model as presented in Ref. 31 can not account for the observed temperature dependence of \( f \); probably because of the assumption that the relaxation rate within each region (state) is exponential in the whole temperature range.

To study the dynamic behavior at 2.4 K, we fit the LF data using the polarization function (see Fig. 3),

\[
P_Z(t) = f \ast p^{KT}(\Delta_1, \nu_1, B_{ext}, t) + (1 - f) p^{KT}(\Delta_2, \nu_2, B_{ext}, t),
\]

where \( p^{KT} \) is the analytical approximation of a Gaussian Kubo-Toyabe function proposed by Keren. 32 By construction, this equation assumes two independent muon fractions and therefore it represents the two-state model in the limit of zero trapping and detrapping rates. In each region (or state) the muons sense random fields from a Gaussian distribution of width \( \Delta_i \). This field can fluctuate at a rate \( \nu_i \) due to fluctuations of the magnetic defects or hopping of the muon from one site to another within the same region. In the fit, \( f \) was fixed to its ZF value (0.2) and \( B_{ext} \) to the applied LF. The fit is good and completely captures the decoupling of the signal, further supporting our assumption of small muon trapping and detrapping rates. The values of the fitted parameters are: \( \Delta_1 = 3.00(5) \) mT, \( \nu_1 = 2.4(2) \) \( \mu s^{-1} \), \( \Delta_2 = 0.318(5) \) mT and \( \nu_2 = 1.52(7) \) \( \mu s^{-1} \). \( \Delta_1 \), which correspond to the trapped state, is consistent with the dipolar field expected in a region of 8 Å around a 1\( \mu_B \) magnetic impurity (see discussion below); and \( \nu_2 \) imposes a maximum limit in the hopping rate of muons in the undisturbed regions. We want to note though that \( \nu_1 \) and \( \nu_2 \) are very similar and, in fact, the data can be fit with a common fluctuations rate with no significant effect on the quality of the fit. Since the contribution from the paramagnetic defects to \( \nu_1 \) and \( \nu_2 \) is the same, this indicates that the hopping rate in the undisturbed regions is probably much smaller than \( \nu_2 \).

One point that needs to be discussed is the relatively large \( f \) fraction found at low temperature. There are sixteen \( Y^{3+} \) ions per cubic unit cell of volume \( V_{cc} = a^3 \). Let us denote \( y \) the percentage of magnetic defects relative to the \( Y^{3+} \) population: \( y = x/2 \), i.e. there are \( 16y = 8x \) \( Ti^{3+} \) ions in \( V_{cc} \). Let us assume that a muon is trapped in a domain of relative weight \( f \) when implanted within a distance \( d \) from a defect, and also that the size and number of these domains are small enough such that they do not overlap. Therefore, the volume around a defect in which a muon is trapped is \( V_\mu = 8x(4\pi/3)d^3 \). Since \( f = V_\mu/V_{cc} \), we conclude that \( d = [(3/32\pi)(f/x)]^{1/3}a \). With \( f \approx 0.20 \) and \( y = 0.6\% \) (see caption of Fig. 1), we compute \( d = 0.79a = 8 \) Å which is a reasonable value.

This relatively long-range influence of a defect is due to the long range of both, the dipolar interaction and the nature of the elastic distortion field. 33, 34

In conclusion, we find that the muon hopping rate at 2.4 K, in both stopping regions, is smaller than \( \approx 2 \mu s^{-1} \). This value is far below that observed for coherent diffusion in metals as well as the \( \approx 10\mu s^{-1} \) proposed for coherent muon diffusion of positive-muons in Dy\( _2 \)Ti\( _2 \)O\( _7 \). 20 Therefore we find it unlikely that coherent muon diffusion is present in Y\( _2 \)Ti\( _2 \)O\( _7 \). Nevertheless, an appropriate theoretical microscopic calculation for the behaviour of positive-muons in this system is needed to completely rule out or confirm coherent muon diffusion. However, any theory should include the extended magnetic defects found by our measurements. In this regard, our observations add to the growing evidence that defects in pyrochlores are important to understand their magnetic properties. 13, 28, 39, 40, and in particular those of Dy\( _2 \)Ti\( _2 \)O\( _7 \). Finally, an analysis to extract trapping and detrapping rates in the whole temperature range would have to follow the lines of that in Ref. 31 but allowing for non-exponential relaxation rates and/or going beyond the two states model.

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