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The pseudo-brookite spin-glass system studied by means of muon spin relaxation

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Zero-field muon spin relaxation (μ SR) experiments have been performed on the spin glass $\text{Fe}_{1.75}\text{Ti}_{1.25}\text{O}_5$. Above the spin-glass temperature of 44 K a distinct exponential μ SR rate (λ) is observed, while below T_g a square-root exponential decay occurs, indicating fast spin fluctuations. Near 8 K, a maximum in λ is indicative of transverse spin ordering. The low λ values and the sharp λ peak at T_g are very promising for the study of spin freezing models like the Vogel-Fulcher law or the power law.

The oxide spin glass Fe_2TiO_5 is an interesting case for experimental and theoretical studies due to the anisotropic magnetic properties.¹⁻⁶ The crystal structure of pseudo-brookite Fe_2TiO_5 , can be described by the space group D_{2h}^{17} , an orthorhombic structure in which the cations are located on the two crystallographic sites $8f$ and $4c$.⁷ The anisotropic spin-glass behavior is now attributed to a random distribution of the magnetic Fe^{3+} and nonmagnetic Ti^{4+} ions over the sublattices.⁸ The c -axis magnetic susceptibility exhibits a cusp at the spin-glass temperature at about 50 K (Refs. 1 and 9) while the perpendicular components indicate more or less paramagnetic behavior, down to 8 K, followed by a broad maximum around 6 K.⁶ This maximum of χ_t is supposed to be an indication of a crossover from a weak transverse order at $T < T_g$ to a stronger one at $T \ll T_g$.³ At still lower temperatures, $T < 1$ K, another unusual contribution to the magnetic susceptibility was reported due to "loose" spins which gives a Curie-Weiss term to χ .⁶

The spin freezing phenomena along the magnetic easy c axis of the pseudo-brookite Fe_2TiO_5 has been studied by magnetization, ac susceptibility, and neutron scattering experiments and analyzed with three different phenomenological laws.⁹⁻¹¹ In spin glasses a large spectrum of characteristic relaxation times can be observed. Neutron scattering yields information in the range from 10^{-12} to 10^{-8} s, which overlaps partially with the window seen with muon spin relaxation, 10^{-5} – 10^{-11} s. Magnetization and ac susceptibility measurements complete the range from 10^{-4} to 10^4 s. Since the muon stopping site in oxides is well established, muon spin relaxation (μ SR) is an excellent technique to study the spin-glass behavior of oxides.¹²⁻¹⁴

In this paper we report the μ SR experiments performed on single crystals of the spin glass $\text{Fe}_{1.75}\text{Ti}_{1.25}\text{O}_5$, a member of the Fe-Ti brookite series. The crystals were prepared from

the melt by a floating zone technique. The oxygen pressure (1 atm) during the melt process is crucial to obtain single phase material. To improve the oxygen stoichiometry, the crystals were annealed at $P_{\text{O}_2} \approx 0.05$ bar and 1300 °C for about 10 h, followed by rapidly cooling within 30 min to room temperature. The stoichiometric compound Fe_2TiO_5 , to which all previous spin-glass studies on Fe-Ti-brookite are referring, can easily form mixed crystals with an excess of titanium, $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{O}_5$ (Ref. 15) which implies the presence of Fe^{2+} ions in the crystal. During our attempts to grow stoichiometric Fe_2TiO_5 single crystals from the melt, we found that all crystals contained an amount of Fe^{2+} ions and that Fe^{2+} -free crystals were never obtained. In order to characterize the chemical composition of our specimens in a proper way we have chosen for our μ SR study a pseudo-brookite specimen with a known and relatively large excess of titanium $\text{Fe}_{1.75}\text{Ti}_{1.25}\text{O}_5$. Since ferrous ions show a uniaxial magnetic anisotropy¹⁶ one would expect strongly deviating properties for this compound. However, the rough features for the spin-glass behavior like the value of T_g , deduced from our μ SR measurements, are *not* very different from the data reported for Fe_2TiO_5 , which could imply that the effect of the Fe^{2+} ions is not so pronounced. We found another surprising behavior of the pseudo-brookite system for the electrical conductivity; with even a high concentration of Fe^{2+} up to 0.5 atoms per molecule we found a room-temperature resistivity of $10^3 \Omega \text{ cm}$ and activation energies ranging from 0.40 to 0.23 eV, which is in glaring contrast with the "metallic" conduction for ferroferrites.¹⁵

The μ SR experiments were performed at the stopped muon channel of the "Clinton P. Anderson Meson Physics Facility, (LAMPF)." In this experiment a beam of polarized muons hits the sample under study, the μ^+ polarization being preserved during the slowing down and thermaliza-

tion. The μ^+ decay produces now a positron and two neutrinos ($\mu^+ \rightarrow e^+ + \nu_\mu + \bar{\nu}_e$), and from conservation laws it follows that the positron is emitted preferentially in the muon spin direction. The decay positron is detected in a given solid angle with respect to the initial beam direction. By counting the number of positrons as function of time elapsed after a muon stops in the sample, a time histogram is made describing the muon relaxation. For a detailed description of the technique see also Refs. 17 and 18. This time histogram can be analyzed with the equation

$$N(t) = N_0 \exp(-t/\tau_\mu) \{1 + A_s G(t) [\cos(\omega_\mu t + \theta)]\}, \quad (1)$$

an exponential decay with the characteristic life time of the muon ($\tau_\mu = 2.2 \mu\text{s}$) modulated by the Larmor frequencies determined by the local fields and further suppressed by the depolarization $G(t)$. The important experimental parameters are the asymmetry A_s , the Larmor frequencies ω_μ , and the depolarization rate. The rate was determined as function of temperature with zero external field in a standard longitudinal arrangement.¹⁹

μSR studies on other iron oxides^{20,21} have demonstrated that at temperatures around and just below RT, the muon forms a muon oxygen complex $(\mu\text{O})^-$. Below about 100 K, the muon is localized near an oxygen ion. Between 100 and 400 K, the muon diffuses locally in the environment of the oxygen ion. Especially when localized below 100 K, the muon spin probes the internal magnetism of the target through dipole-dipole and superhyperfine interactions.^{20,21} For the pseudo-brookite system it is expected that the muon will behave similar as in other oxides, which makes μSR a suitable probe of the spin-glass behavior of this system.

The most relevant data we obtained with our μSR experiments are the asymmetry (A_s) as a function of temperature, depicted in Fig. 1, and the muon spin relaxation rate (λ), shown in Fig. 2. As can be seen from the A_s reduction to about 1/3 and the cusp in λ , T_g can readily be determined to be $44 \pm 0.5 \text{ K}$, about 6 K lower than reported for Fe_2TiO_5 .⁹ The small reduction in T_g can be explained by the higher concentration of nonmagnetic Ti^{4+} ions and the simultaneous decrease of Fe^{3+} and increase of Fe^{2+} concentration.

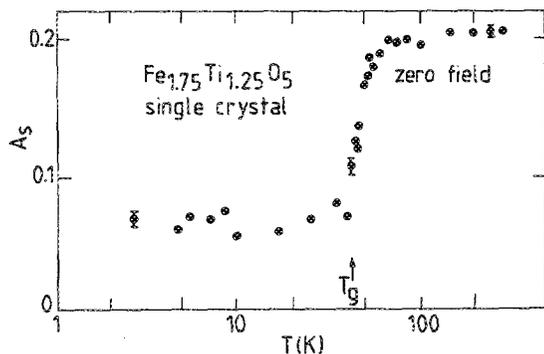


FIG. 1. Temperature dependence of the asymmetry of the zero-field μSR signal observed for $\text{Fe}_{1.75}\text{Ti}_{1.25}\text{O}_5$. At the spin-glass temperature ($T_g \approx 44 \text{ K}$) A_s drops sharply to the 1/3 value due to fast increasing internal fields.

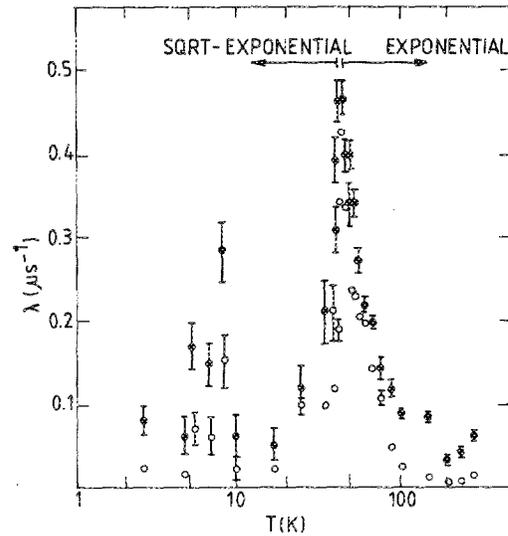


FIG. 2. Temperature dependence of the muon spin relaxation rate (λ) of the zero-field μSR signal observed for $\text{Fe}_{1.75}\text{Ti}_{1.25}\text{O}_5$. Open circles represent data fit with an exponential depolarization function, and the solid circles a fit with a square root exponential function. A χ^2 selection indicates an abrupt change in the depolarization function at the peak in rate at T_g .

A distinct exponential λ behavior is observed above T_g (Fig. 2), while below T_g a square-root exponential decay is seen. The muon spin relaxation function $G(t)$ is analyzed with

$$G(t) = \exp(-\lambda t) \text{ for } T > T_g$$

and with

$$G(t) = \exp[-(\lambda T)^{1/2} t] \text{ for } T < T_g.$$

This indicates that below T_g fast fluctuation modes exist in a "frozen" state, which is consistent with what has been found for metallic spin glasses.²²⁻²⁴

Near 8 K a maximum in λ is observed which is also characteristic for a magnetic transition. This peak might be experimental evidence for the recently proposed transverse spin ordering at this temperature, as deduced from magnetic susceptibility measurements.^{3,4} To explain the origin of the transverse effect, the spin Hamiltonian needs at least an anisotropy term and in addition to its random nature, this term must have a short-range character. The presence of the localized magnetically anisotropic Fe^{2+} ions in the lattice might be connected with this effect.

Another remarkable aspect of our μSR results is that λ is rather low near T_g ($< 1 \mu\text{s}^{-1}$), probably due to the well defined $(\mu\text{O})^-$ state in the single crystal. For polycrystalline Fe-Ti sesquioxides¹³ values of about $2.5 \mu\text{s}^{-1}$ were reported at $T = 1.3 T_g$, whereas we observed for $\text{Fe}_{1.75}\text{Ti}_{1.25}\text{O}_5$ at $1.3 T_g$ a value of $0.22 \mu\text{s}^{-1}$. These low values of λ found in the present muon data makes a preliminary comparison possible between the spin freezing models. Taking λ proportional to τ_c (Refs. 13 and 22-24) the results above 50 K ($\approx 1.1 T_g$) are consistent with the Vogel-Fulcher (VF)

$$\tau_c = \tau_0 \exp[E_a/k(T - T_g)], \quad (2)$$

and with the standard power law²⁴

$$\tau_c = \tau_0 [T / (T - T_g)]^\epsilon. \quad (3)$$

The fitting with an Arrhenius law was not successful, and

resulted in unrealistic values for the activation energy. From the VF fit in the temperature range of 50–100 K, E_a/k was determined to be $20(\pm 5)$ K, which is of the order of magnitude of the temperature range expected for insulating spin glasses²⁵; however, this value deviates by a factor of 8 from the experimental value of 170 K for Fe_2TiO_5 (Ref. 9) determined with neutron and magnetic susceptibility experiments. In the range from $1.1 T_g$ down T_g , the experimental errors in the present data are too large for a useful comparison. Since rather low values of λ are found close to T_g , high statistical measurements between $1.1 T_g$ and T_g are planned to increase the accuracy of the data; this will make it possible to differentiate between the two models. In this particular temperature range the VF law is quite different from the power law.

From Fig. 2 it can be noted that the drastic changes in λ occur between T_g and $2T_g$, whereas for polycrystalline Fe-Ti sesquioxides¹³ such changes occurred over a larger range ($T_g < T < 3T_g$), and for metallic spin glasses^{22–24} over a smaller one ($T_g < T < 0.4 T_g$). Whether these different ranges have something to do with the competing magnetic interactions or with the atomic microstructure of the spin glasses is at the moment not yet clear.

Summarizing the definite conclusions which can be drawn from our initial μSR experiments on $\text{Fe}_{1.75}\text{Ti}_{4.25}\text{O}_5$, it can be stated that:

(i) The quick reduction of A_s to the 1/3 value within a few degrees at T_g points to rapid increase of internal fields with decreasing T , indicating a real phase transition.

(ii) The T dependence of λ reveals three characteristics in the spin-glass behavior of the pseudo-brookite system: (a) the transverse spin ordering, below 10 K; (b) the occurrence of fast spin fluctuations below T_g ; and (c) a well-defined drastic increase of λ above T_g when approaching T_g .

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