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Paramagnetic fluctuations in MnO

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Abstract. A shift in the muon spin-relaxation rate in MnO is observed around 540 K, i.e. about 4.5 times T_N. This result confirms earlier observations using spin-polarized electron diffraction of a significant change in the paramagnetic spin system taking place at this temperature. This change might be caused by the transition from a state with correlated magnetic clusters to independently fluctuating spins. Furthermore, we have confirmed previous findings that at low temperature, the implanted muons are situated at sites close to manganese ions and that, as the temperature is increased, they diffuse and are trapped at manganese vacancies. In addition, we have observed that the muons are detrapped and start to diffuse again at temperatures above 800 K.

1. Introduction

MnO crystallizes in the sodium chloride structure with the cubic cell axis $a \sim 4.43$ Å. It orders antiferromagnetically at about 118 K to a structure with a magnetic propagation vector $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$. The moments lie in the [1 1 1] planes and the transition is accompanied by a rhombohedral distortion. For a discussion of the structure, see Shaked *et al* [1].

Hermsmeier *et al* [2,3] have performed a spin-polarized photoelectron diffraction (SPPD) study of MnO. They considered the ^{5}S:^{7}S intensity ratios for the Mn 3s and Mn 3p multiplets and found an abrupt change in the temperature region 530 ± 20 K. They interpreted this change as indicating a new kind of short-range-order transition occurring at a temperature T_{SR}.

Mellergård *et al* [4] used reverse Monte Carlo powder (RMCPOW) fits to powder neutron diffraction data to study both structural and magnetic properties of MnO. These authors looked for an effect in their data around 530 K but none was observed. Only smooth gradual changes in the fitted values of the angles between neighbouring atoms were found for the temperature range between T_N and 1100 K. Furthermore, a constant value of the manganese-ion moment ($\mu_{\mathrm{Mn}} = 5.65\ \mu_B$, i.e. an effective $S = 2.37$) could be used to fit the data for all temperatures.

Muon spin relaxation, μSR [5, 6], is a very sensitive tool for the study of magnetic fluctuations. In the longitudinal-field (LF) and zero-field (ZF) techniques, the muons enter the sample with their polarization parallel to the beam direction, chosen as the z-direction. When the muons decay, they emit a positron preferentially in the direction of their spin. The polarization of the muons is measured as the difference between the numbers of positrons detected in the forward and backward detectors, i.e.

$$a(t) = a_0 G(t)_z = \frac{N(t)_F - \alpha N(t)_B}{N(t)_F + \alpha N(t)_B} \tag{1}$$

where a_0 is the initial polarization (asymmetry) and $G(t)_z$ is the depolarization function containing the experimental information. $N(t)_F$ and $N(t)_B$ are the numbers of positrons

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detected in the forward and backward detectors and α is a factor correcting for differences in detector efficiency, geometry, etc.

In a paramagnetic material, the muons are mainly depolarized by the magnetic moments which create a field B at the muon site. This relaxation function is exponential:

$$G_z(t) = \mathrm{e}^{-\lambda t} \tag{2}$$

with

$$\lambda = \gamma_\mu^2 \langle B^2 \rangle \tau_c \tag{3}$$

where τ_c is the correlation time for the fluctuations and $\langle B^2 \rangle$ is the average of the square of the deviation from the mean magnetic field at the muon site. $\gamma_\mu/(2\pi) = 135.5$ MHz T^{-1} is the muon gyromagnetic ratio.

Another independent source of depolarization may be the presence of nuclear dipoles. In ZF, random nuclear moments create fields that lead to the Gaussian Kubo–Toyabe depolarization function

$$G(t)_z = \frac{1}{3} + \frac{2}{3}(1 - \sigma^2 t^2)\mathrm{e}^{-(1/2)\sigma^2 t^2}. \tag{4}$$

At short times, the Kubo–Toyabe function is, to a good approximation, a Gaussian, $\mathrm{e}^{-\sigma^2 t^2}$. This function is observed if the muons remain immobile during the time of observation which is approximately 10–20 μs (the muon decay time is 2.2 μs). At higher temperatures, the muons may diffuse and equation (4) is gradually transformed towards a weak exponential depolarization.

A characteristic feature of the static depolarization from nuclear moments is that it can be decoupled by applying weak longitudinal fields (2–10 mT) while fields an order of magnitude higher are needed to influence the exponential depolarization of equation (2).

Several μSR studies have been carried out on MnO, e.g. Hayano *et al* [7], Uemura *et al* [8], Uemura *et al* [9], and a comparison with results for NiO and CoO and a discussion of the muon site can be found in Nishiyama *et al* [10]. To our knowledge, however, no work has previously been done in the paramagnetic region above about 400 K.

2. Experimental procedure

Two single-crystal samples were examined on the EMU beamline at ISIS at the Rutherford Appleton Laboratory, one with a (1 0 0) surface measuring $13 \times 12 \times 2$ mm^3 and a second one with a (1 1 1) surface measuring $10 \times 10 \times 2$ mm^3. The flat faces were aligned perpendicular to the beam direction. Both samples were examined in a closed-cycle refrigerator (CCR) between 120 and 380 K. The (1 0 0) crystal was also examined in a oven from 290 to 1000 K. The samples were found to give the same result but the statistical errors of the smaller (1 1 1) sample became much larger and we only present the (1 0 0) data. The samples were mounted on a silver plate in the CCR and attached with titanium foil in the oven. Both these backing materials give undamped background signals. The measurements were made at zero field for all temperatures and with an applied longitudinal field at selected temperature points.

The ISIS muon source is pulsed with a muon pulse time width of 80 ns with the pulses separated by 20 ms. Therefore, it has a very low background and samples with low relaxation rates can be studied. One limitation is that the width of the pulse makes it difficult to reliably study muon signals with $\lambda > 5\ \mu\mathrm{s}^{-1}$.

3. Results and discussion

The μSR signal was fitted with two components at all temperatures, i.e. the *sum* of one background component with no damping and one sample component. The sample component was initially described by an exponential function. When a longitudinal (along the beam direction) field of 0.010 T was applied, the depolarization rate decreased. No further effect was observed when increasing the field to 0.050 T. We therefore conclude that there is a contribution to the depolarization rate from nuclear magnetic dipoles. The much larger electronic magnetic dipoles are unaffected by fields of this small amplitude. Furthermore, these data showed that the muons are static in the material up to a temperature of 723 K. The sample component of the data was therefore fitted with the function

$$a(t) = a_0 \mathrm{e}^{-\lambda t} \mathrm{e}^{-\sigma^2 t^2} \tag{5}$$

where λ is the depolarization caused by the electronic magnetic dipoles of the manganese, and the Gaussian depolarization with rate σ is caused by the manganese nuclear magnetic dipoles. The oxygen nuclei do not carry magnetic moments. The separation of the two contributions to the depolarization is valid since they are of different origins.

Longitudinal-field experiments at 723 K and 423 K were employed to deduce the Gaussian contribution, which we find to be $\sigma = 0.05(1)\ \mathrm{s}^{-1}$. Above 750 K this contribution gradually vanished and at 1000 K, the data were best fitted with an almost pure exponential function, the Gaussian contribution being only $\sigma = 0.005(10)\ \mu\mathrm{s}^{-1}$. The exponential depolarization rate λ obtained from equation (2) as a function of temperature is displayed in figure 2.

The initial asymmetry of the sample signal as a function of temperature is shown in figure 1. It is clear from figure 1 that the asymmetry increases as a function of temperature as a *smooth, continuous function*. We have also included the asymmetry data of Hayano *et al* [7] in the plot, normalized to our own data. We see that the temperature dependence is the same for the two samples. A temperature-dependent fraction of the muons is thus depolarized too rapidly to be observed at the ISIS facility. This missing fraction remains unexplained. There is no trace of a rapidly decaying signal in the raw data. One explanation could be the formation

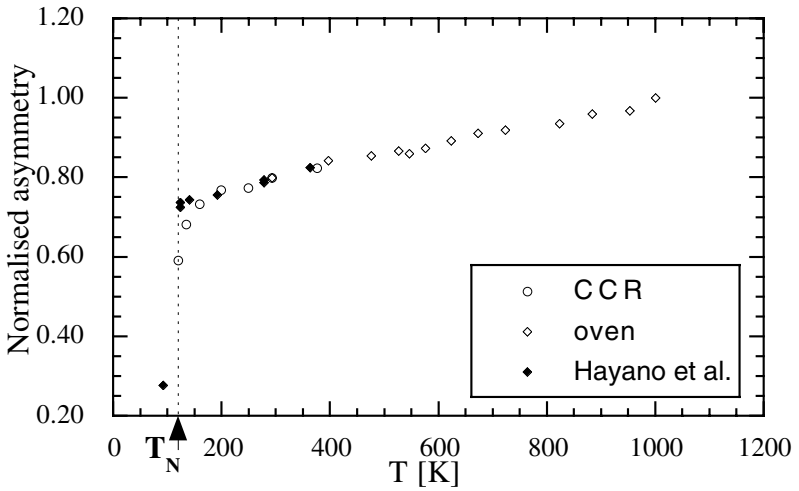

Figure 1. The asymmetry of the μSR signal from the (1 0 0) sample normalized to 1 at 1000 K. The data obtained in the CCR have been normalized to the oven data in the overlap region. We include the data of Hayano *et al* [7] for comparison.

of muonium which sometimes occurs in insulators. MnO is known to be a good insulator with a linear dependence of the logarithm of its resistivity as a function of the inverse of the temperature [11]. It is possible that the decrease of the resistivity as the temperature increases reduces the likelihood of muonium formation, and thus leads to a larger observed μSR signal.

For the observed part of the muon signal, there are time effects. Uemura *et al* [8] performed μSR Knight shift measurements on MnO. They found that the Knight shift evolved in time, i.e. that different Knight shifts were obtained for the first μs as compared to that found for the second μs and so forth. It was concluded in their study that the muon is first trapped in some interstitial site such as the $(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})$ position. It then migrates to a manganese vacancy with a probability that is temperature dependent, with an approximate activation energy $E_a/k_B = 800$ K. Above $T \approx 300$ K this process is very rapid compared to the muon lifetime. It is known [12] that there is an oxygen surplus of 0.1–1% in MnO single crystals. If we calculate the Gaussian depolarization rate for a point-like muon at such a manganese vacancy, neglecting possible electric quadrupolar effects, we find $\sigma = 0.081\ \mu s^{-1}$, which is compatible with the experimental value of $0.05(1)\ \mu s^{-1}$ obtained as stated above. Thus, the main fraction of the muons rapidly diffuses to manganese vacancies where they are trapped and where the depolarization rate is slow enough for the signal to be observed under the experimental conditions of this study. The reduction of the Gaussian depolarization rate σ above 750 K indicates motional narrowing and that the muons are detrapped from the manganese vacancies at these temperatures. We cannot draw any conclusions from our data about the site of the muons that are rapidly depolarized, but that still contributed to the Knight shift in the measurements performed by Uemura *et al* [8], other than that they must be situated close to manganese ions. Possible muon sites are discussed by Nishiyama *et al* [10] on the basis of the observed muon precession frequency in the ordered state. Usually in oxides, muons are trapped close to oxygen, but our experimental data for the depolarization rate, both from nuclear and from electronic moments, contradict such a site attribution for this material.

The depolarization rate λ as a function of temperature is displayed in figure 2. The depolarization rate is constant at high temperatures at $\sim 0.055\ \mu s^{-1}$. When the temperature

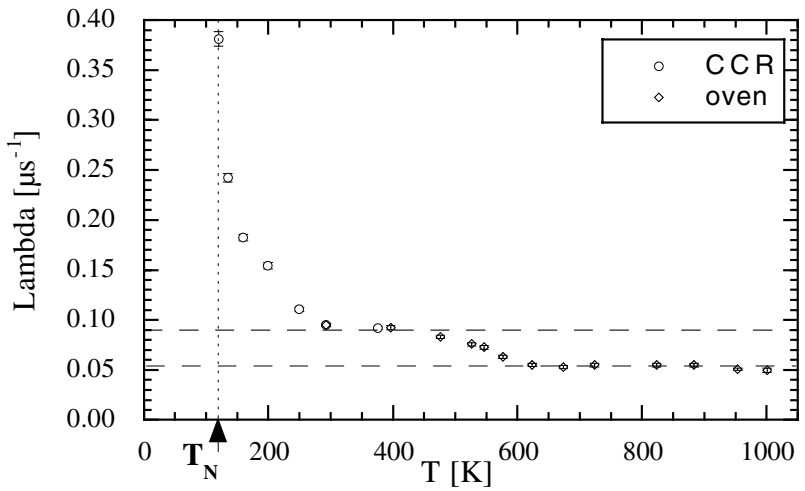

Figure 2. The exponential depolarization rate λ obtained from fits to equation (5). A constant value of $\sigma = 0.05\ \mu s^{-1}$ was used below 750 K, above which temperature the Gaussian contribution was gradually decreased as described in the text.

is decreased, the rate increases from between 600 K and 475 K and reaches a new value of $\sim 0.090\ \mu s^{-1}$. Finally, the depolarization rate λ increases as the antiferromagnetic ordering temperature is approached. This increase is due to the slowing down of magnetic fluctuations towards the ordering temperature and is normal. The same effect is observed for a large number of materials; see for example Karlsson [13] and Dalmas de Réotier and Yaouanc [14]. There is no reason to believe that this change in depolarization rate close to T_N is only due to a gradual change of the proportion of the population of different muon sites as proposed by Uemura *et al* [8]. The jump in the depolarization rate around 540 K, on the other hand, is quite unusual. This is precisely the temperature interval in which Hermsmeier *et al* [2,3] observed a change in the ^{5}S:^{7}S intensity ratio in their SPPD data.

The general expression for the μSR exponential depolarization rate is given as equation (2) above. We see that the reason for the change in the depolarization rate could be a change in the amplitude of the magnetic field fluctuations on the muon position, to a change in the correlation time or a combination of the two. The change in depolarization rate λ from about 0.055 to $0.090\ \mu s^{-1}$ would correspond to an increase of $\langle B^2 \rangle$ or τ_c by 40%. If the manganese-ion spin fluctuations are correlated, this would indeed give rise to a larger value of $\langle B^2 \rangle$.

In the high-temperature limit where magnetic moments are uncorrelated in a material, the depolarization rate has been derived by Moriya to be [7, 15, 16]

$$\lambda = n \frac{4}{\hbar^2} \left(\frac{\mu_0}{4\pi} \frac{\mu_N \mu_B \gamma_\mu g_J}{r^3} \right)^2 \frac{1}{3} S(S+1) \sqrt{\frac{\pi}{2}} \frac{1}{\omega_{ex}} \tag{6}$$

where n, the number of nearest neighbours, is 12 in our case. μ_0 is the vacuum permeability, μ_N is the nuclear magneton, γ_μ is the muon gyromagnetic ratio, g_J is the Landé factor, S is the spin and r is the distance between the muon and the magnetic moment. The characteristic exchange frequency $\omega_{ex} = 5.17 \times 10^{12}$ rad s^{-1} [17], as determined from infrared antiferromagnetic resonance at 1.5 K. The calculation of λ from equation (6) gives $\lambda = 0.10\ \mu s^{-1}$ for the manganese vacancy site. If we use the experimental value of $\mu_{Mn} = 5.65\ \mu_B$ instead of the $S = 5/2$ value of $5.92\ \mu_B$, the depolarization rate is reduced to 0.09. Extending the summation over the lattice, we find a value of $0.11\ \mu s^{-1}$. Our experimental value of $0.055\ \mu s^{-1}$ is close to the calculated value, given the approximations inherent in the theory. The assumption that the muon is located at a manganese vacancy is also supported by this result.

We need to compare our findings with those of other experimental techniques. Using neutron diffraction, a snapshot of the magnetic configuration is obtained during a probe correlation time that depends on the experimental conditions. The SLAD diffractometer [18] at the Studsvik Neutron Research Laboratory, Sweden, that was used by Mellergård *et al* [4] has an angular resolution of 0.6° in 2θ at 56° at a wavelength of 1.1 Å . This translates to a probe correlation time of $\sim 3 \times 10^{-12}$ s. The SPPD data of Hermsmeier *et al* [2,3], on the other hand, were obtained through photoemission with a timescale of 10^{-17}–10^{-16} s. The study by Mellergård *et al* did not reveal any abrupt change in the spin system in the temperature region where the SPPD study found a clear change in the data. From equation (6) we obtain the fluctuation time

$$\tau_c = \sqrt{\frac{\pi}{2}} \frac{1}{\omega_{ex}} = 2.4 \times 10^{-13}\ \text{s}$$

i.e. more than 12 times shorter than the neutron probe correlation time. The neutron powder diffraction study was therefore not sensitive to a possible change in the spin system in this temperature region, whilst this change could be detected by the SPPD study.

It would be of interest to study MnO in a neutron scattering set-up with a much smaller time window. Another technique that it might be possible to use is x-ray magnetic scattering; see Gibbs *et al* [19] and references therein. For this technique, the probe correlation time is

of the order of 10^{-15} s. Unfortunately, preliminary results show that such an experiment is very difficult to perform due to the low signal-to-noise ratio for scattering from MnO [20]. Finally, to our knowledge, there are no theoretical predictions that can explain this unusual, phase-transition-like behaviour in the paramagnetic regime.

4. Conclusions

We have observed that a clear change takes place in the spin dynamics of MnO at about 540 K, i.e. about 4.5 times T_N. This change could well be the result of the final break-up of magnetically correlated regions into independently fluctuating spins. Unfortunately, there is at present no theoretical understanding of the mechanism of such a transition. We have compared our data with those obtained using other methods without encountering any inconsistencies.

Previous findings have been confirmed showing that, as the temperature is increased, muons diffuse and are trapped at manganese vacancies with increasing likelihood. In addition, we have observed that the muons start to diffuse again at temperatures above 800 K.

Acknowledgments

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