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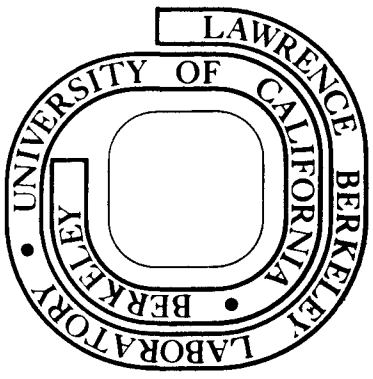

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DISCLAIMER

NEGATIVE MUON SPIN ROTATION AT OXYGEN SITE IN PARAMAGNETIC MnO*

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ABSTRACT

Negative muon spin rotation (μ^-SR) at the oxygen site in paramagnetic MnO has been observed at room temperature. A paramagnetic shift of 1.16 ± 0.21 % was observed, approximately one-third the shift observed for the ^{17}O NMR in MnO. The muon spin relaxation time extrapolated to zero external field was determined to be $1.5 \pm {}^{0.8}_{0.4}$ μsec. Possible mechanisms for explaining these observations are presented.

The negative muon (μ^-) is a new probe in the study of solid state physics.[1] If μ^- is bound to a spinless nucleus, the muon-nucleus system (the ground-state muonic atom) is a pure magnetic probe because its spin is one-half. The bound-muon spin is polarized up to about 17 %, which causes an asymmetric angular distribution of electrons decaying from the muons, and thus the muon spin rotation (μSR) in the presence of magnetic field can be detected from a time distribution of decay electrons. In this Letter we report observation of the negative muon spin rotation (μ^-SR) at the oxygen site in paramagnetic MnO. The oxygen atom in this magnetic oxide plays an important role in the superexchange interaction which gives rise to antiferromagnetic ordering of Mn^{2+} d-electrons below T_N = 116 K.[2] To study local fields at oxygen sites in such an oxide, however, conventional NMR methos is hardly applicable, not only because of the quite low natural abundance of ^{17}O (0.04 %) but also because of a large quadrupole broadening at non-cubic site, while the μ^-SR method is promising and powerful. Since μ^-O has a lifetime of 1.8 μsec, which is much longer than the lifetimes (100-200 nsec) of μ^- trapped by heavier elements, the muon signal from oxygen can be selectively separated. Furthermore, the μ^-SR method may reveal new phenomena, since the μ^-O probe behaves as a nitrogen-like impurity but with rather broader magnetization distribution as compared with the nitrogen nucleus.

Thus far, no μ^-SR experiments have been reported on magnetic oxides. We started our measurements with paramagnetic MnO, since it is the exceptional case where the ^{17}O NMR has been observed.[3] Goals of our work are a) to determine the paramagnetic shift (Δ) of muons at oxygen sites and the muon relaxation time (T_2), and b) to compare these with the ^{17}O NMR data.

The experimental set-up and the procedure of measurements were the same

as those reported before.[1,4] Negative muons from the 184" Cyclotron at LBL were stopped at rate of 10^3 sec^{-1} in a target of single crystal MnO (3 cm × 4 cm × 5 gr/cm^2; made by Nakazumi Crystal Co.). An external magnetic field (6.830 and 1.1061 kOe) was applied on the target perpendicularly to the beam direction. An (100) axis of MnO was parallel to the field. Temperature was $\sim$ 300 K at which the MnO was in paramagnetic phase.

The time spectrum of decay electrons from muons, as shown in Fig. 1(a), involves two decay components with lifetimes of 232 ± 3 nsec and 1.84 ± 0.02 μsec, which are in good agreement with the known lifetimes[5] of μ^-Mn and μ^-O, respectively. Since the muon spin associated with the Mn nucleus is expected to be depolarized rapidly enough, we have subtracted the short-lived component and analyzed the long-lived component only, which gives information on muons at oxygen sites in MnO.

The time spectrum of the long-lived component will be expressed by

$$N(t) = N_0\, e^{-t/\tau}\, [1 + A\, e^{-t/T_2} \cos(2\pi f+\phi)], \qquad (1)$$

where τ = 1.84 ± 0.02 μsec, A is the asymmetry, T_2 is the relaxation time, and f is the Larmor frequency. Fig. 1(b) shows χ^2-fits for this long-lived component at H = 6.830 kOe as a function of f. The χ^2's have a sharp minimum at f = 93.57 ± 0.19 MHz. The χ^2-fits for a carbon target under the same condition, as shown also in Fig. 1(b), gave a minimum at f_0(carbon) = 92.52 ± 0.04 MHz. After a small correction for the difference of the muon g-factors between oxygen and carbon,[6] we have a paramagnetic shift Δ of μ^-O in MnO,

$$\Delta \equiv \frac{\delta H}{H} = 1.16 \pm 0.21\ \%. \qquad (2)$$

The value of Δ determined at H = 1.1061 kOe [0.9 ± 0.8 %] involves larger

error but in agreement with the above value (2).

The relaxation time T_2 has also been determined by χ^2-fits. Results are $0.7 \pm {}^{0.7}_{0.3}$ μsec at H = 6.830 kOe and $1.3 \pm {}^{0.7}_{0.3}$ μsec at H = 1.1061 kOe. By extrapolating these two values to zero external field, like the case of the ^{17}O NMR,[3] we obtain

$$T_2 = 1.5 \pm {}^{0.8}_{0.4} \text{ μsec} \quad (\text{at } H = 0). \tag{3}$$

The asymmetry A obtained from the best fits is around 3 %.

We have carefully examined possible effects of long-lived background from muons stopped in the surrounding counters, since its lifetime is around 1.8 μsec. From measurements on various other targets we have estimated that the long-lived background in the present case is less than one-third the μ^-O signal and it has the frequency f_0(carbon) with amplitude less than 1.5 %. After various careful analyses we have finally found that the experimental value (2) is free from the effect of this background.

The present results are summarized and compared with the NMR data in Table 1. The paramagnetic shift for μ^-O is approximately one-third the shift observed for the ^{17}O NMR. It is interesting to compare g^2T_2 for μ^-O and ^{17}O, since the relaxation rate is proportional to g^2. As shown in column 5 of Table 1, g^2T_2 for μ^-O turns out to be one order of magnitude larger than g^2T_2 for ^{17}O.

The paramagnetic shift is expressed as[3]

$$\Delta = -(6\langle S_z\rangle/H)(H_{hf}/S) + 3\chi H_{hf}/S, \tag{4}$$

where $\langle S_z\rangle$ is the thermal average of the six enighboring Mn^{2+} spins (S = 5/2) in the presence of an external field H, χ is the atomic susceptibility, and

H_{hf} is the local hyperfine field at the oxygen site exerted from one neighboring Mn^{2+} spin,

$$H_{hf} = f_s \frac{8\pi}{3} \mu_B |\psi_{2s}(0)|^2. \tag{5}$$

Here f_s is the effective fractional occupancy by unpaired spins of 2s orbitals at the oxygen site.[2,3] The relaxation rate at high-temperature limit which is subject to the exchange narrowing is written as

$$\frac{1}{g^2 T_2} = 4\sqrt{\frac{\pi}{2}} \frac{S+1}{S} \frac{(\mu_N H_{hf}/\hbar)^2}{\omega_e}, \tag{6}$$

where ω_e, the exchange frequency, is related to the exchange integral J as follows[7]

$$\omega_e = \sqrt{2S(S+1)/3}\, J/\hbar. \tag{7}$$

Assuming χ and ω_e be constant, we would expect a "Korringa-type" relation,

$$\Delta^2 g^2 T_2 = \text{const.}, \tag{8}$$

which is consistent with the experimental observations (see column 6 of Table 1). Thus, this simple-minded consideration would indicate that $H_{hf}(\mu^- O)$ is one-third of $H_{hf}(^{17}O)$.

For further interpretation of the experimental results, however, a more detailed analysis has to be done. First of all we should recognize that the $\mu^- O$ probe behaves like a dilute N^{3-} impurity at the oxygen site in MnO. The only difference between $\mu^- O$ and N^{3-} lies in the spatial distribution of the probe: the N nucleus has a sharp cut-off radius with R = 2 fm while $\mu^- O$ has a broad exponential-type distribution with a Bohr radius of $\sim$ 30 fm.

However, since the latter is still 200 times smaller than the electron Bohr radius, we ignore possible hyperfine anomaly[8] in the following discussions.

1. $|\psi_{2s}(0)|^2$: Using recent Hartree-Fock calculation[9] for Na^+, Ne, F^-, O^+, O, O^-, N^+, N and N^-, we estimated $|\psi_{2s}(0)|^2_{O^{2-}} = 44 \times 10^{24}$ cm^{-3} and $|\psi_{2s}(0)|^2_{N^{3-}} = 26 \times 10^{24}$ cm^{-3}, and thus, $|\psi_{2s}(0)|^2_{N^{3-}}/|\psi_{2s}(0)|^2_{O^{2-}} = 0.6$, which is certainly a part of the origin of the observed reduction in H_{hf}.

2. f_s: The excess negative charge of μ^-O compared to ^{17}O will push out 2p and 2s electrons farther from the oxygen site, which will increase the local metal-oxygen covalency (2p-3d and 2s-3d mixtures). Since f_s is related to the covalency parameter λ_s and the overlap S_s between 2s and 3d through the expression of $f_s = (S_s + \lambda_s)^2$,[3] it is expected that $f_s(\mu^-O) > f_s(^{17}O)$. This sets a lower limit 0.6 on $H_{hf}(\mu^-O)/H_{hf}(^{17}O)$, which cannot account for the observed reduction in Δ. This conclusion might be altered, if the 1s electron polarization plays a significant role in H_{hf}, but the following point seems to be more important.

3. $\langle S_z \rangle$ and ω_e: So far we have neglected possible difference in $\langle S_z \rangle$ and ω_e between μ^-O and ^{17}O. However, since the presence of μ^-O increases the local covalency and thus enhances the local superexchange interaction, $\langle S_z \rangle$ and ω_e in Eqs. (4) and (6) should now be read as the local average $\langle S_z \rangle$ (which can be named local susceptibility) and local exchange frequency. If the enhanced superexchange interaction causes an increase of the local Weiss temperature Θ ($\Theta \propto J/k$), and Θ is still related to χ by

$$\chi \propto 1/(T+\Theta), \qquad (9)$$

the local χ would be smaller than the bulk susceptibility. Considering that $H_{hf}(\mu^-O) > 0.6\ H_{hf}(^{17}O)$, we would obtain $\Theta_{local} > 2000$ K in order to account

for $\Delta(\mu^-O)$, while Θ_{bulk} = 610 K. Obviously the observed relaxation time would require that the local exchange frequency should increase in accordance with the relation

$$\omega_e \propto \Theta. \tag{10}$$

If such a situation is real, the temperature dependence of $\Delta(\mu^-O)$ will be different from that of χ_{bulk}, but this point is open to further experimental studies.

At this stage it is already clear that the μ^-O probe offers a unique opportunity for investigating various phenomena that are not accessible by any conventional means, even in cases where ^{17}O NMR data are available. The μ^-SR method will be applied to other magnetic oxides particularly where the ^{17}O NMR becomes exceedingly difficult because of quadrupole interactions.

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TABLE 1

Summary of the paramagnetic shift Δ and relaxation time T_2 observed at room temperature by different methods for paramagnetic MnO. The relaxation times have been obtained from extrapolation of experimental data to zero external magnetic field.

Probe	g-Factor (μ_N)	Δ (%)	T_2 (μsec)	g^2T_2 ($10^2\mu$sec)	$\Delta^2g^2T_2$ ($10^{-2}\mu$sec)	Ref.
μ^-O	17.76[a)]	1.16 ± 0.21	$1.5 \pm {}^{0.8}_{0.4}$	$4.7 \pm {}^{2.5}_{1.3}$	$6.4 \pm {}^{3.7}_{1.8}$	present
^{17}O	-0.7575	3.21 ± 0.02	74 ± 26	0.42 ± 0.15	4.4 ± 1.6	3

a) $g(\mu^-O)$ measured in nonmagnetic substance (Ref. 6).

FIGURE CAPTIONS

FIG. 1 (a) Time spectrum of decay electrons from the muons stopped in a MnO target. The long-lived component comes from μ^-O and the short-lived one from μ^-Mn.

(b) The χ^2 versus the Larmor frequency for the μ^-O component in paramagnetic MnO at room temperature and at H = 6.830 kOe (upper) and for a carbon target under the same experimental conditions (lower), showing a paramagnetic shift of 1.16 ± 0.21 % after the correction for the g-factor difference between μ^-O and μ^-C.

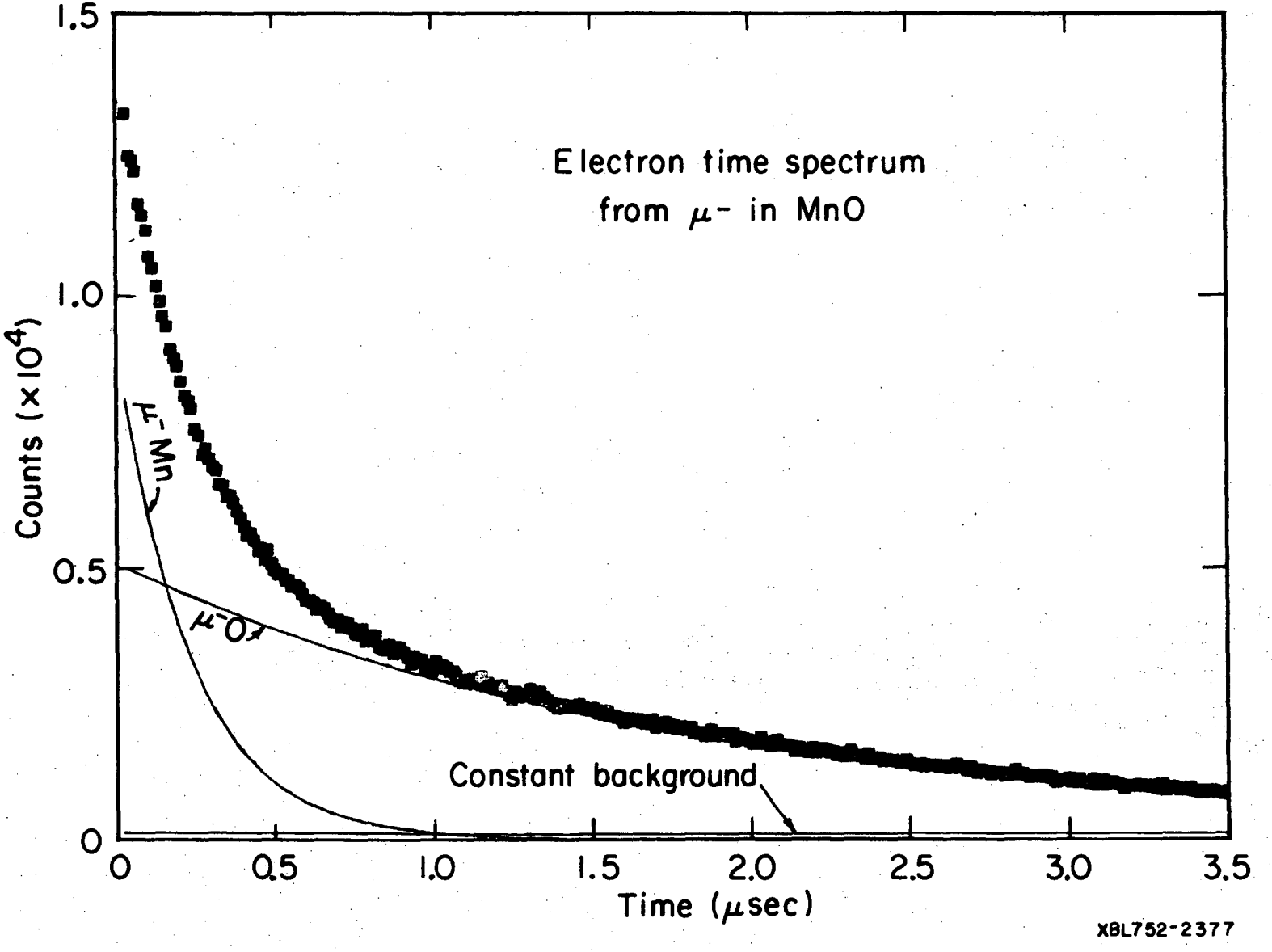
Electron time spectrum
from μ- in MnO
Counts (x10⁴)
1.5
1.0
0.5
0
μ⁻Mn
μ⁻O
Constant background
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Time (μsec)
XBL752-2377

FIG. 1(a)

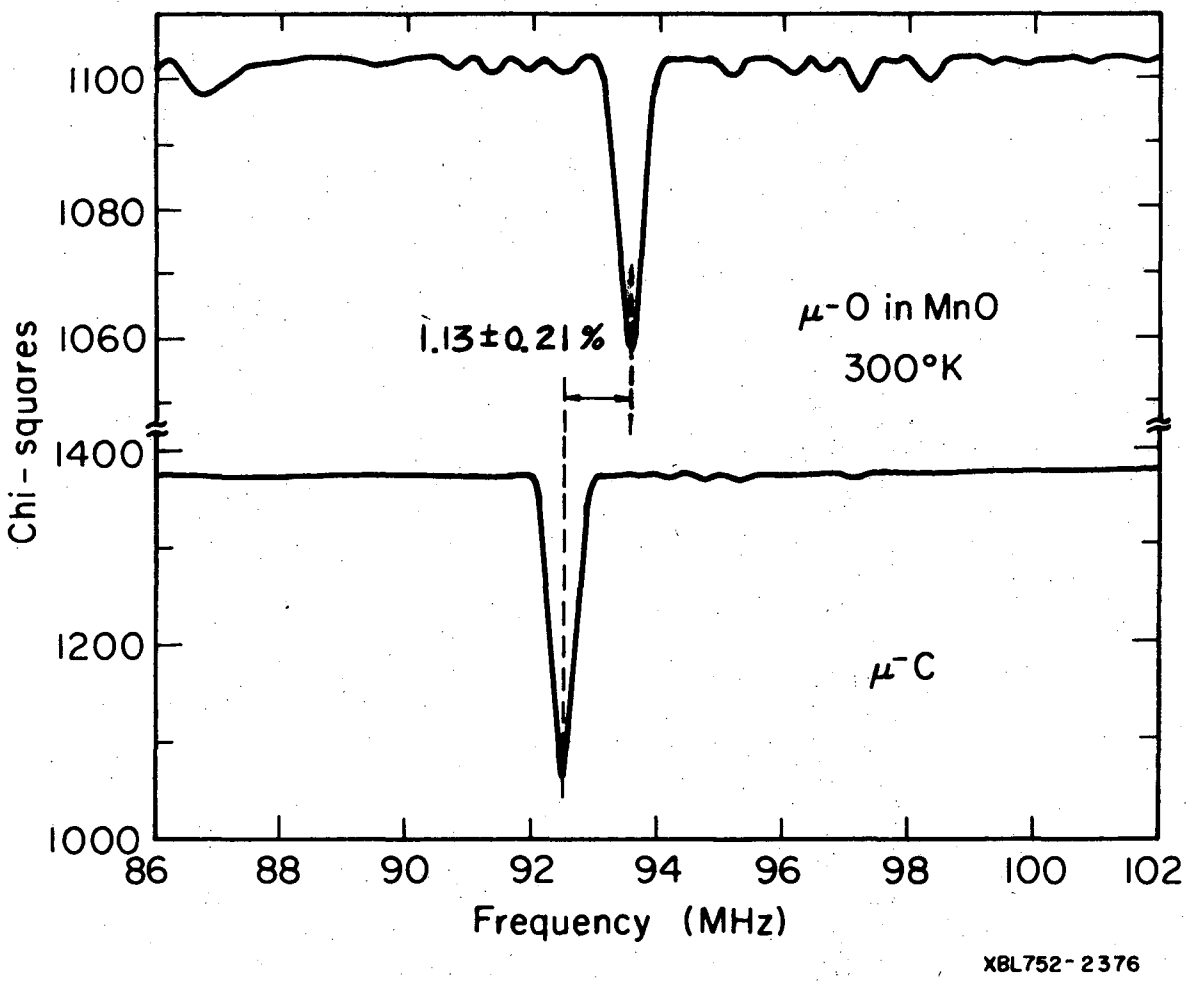
1100
1080
1060
1400
1200
1000
Chi-squares
1.13±0.21%
μ-O in MnO
300°K
μ-C
86
88
90
92
94
96
98
100
102
Frequency (MHz)
XBL752-2376

FIG. 1(b)

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