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DECAY OF THE COHERENT SPIN PRECESSION OF POLARIZED POSITIVE MUONS IN PARAMAGNETIC $MnCl_2$ SOLUTIONS*

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Slow depolarization of μ^+ in a transverse field has been used to measure relaxation effects in paramagnetic $MnCl_2$ solutions. T_2^{-1} data show nonlinear dependence on ion concentration. Consistent explanation is achieved by assuming that the muon replaces a proton, forming μHO, and applying relaxation mechanisms as developed for Mn^{2+} solutions from NMR and ESR studies. T_2 temperature dependence in a 3 M solution is compatible with concentration-dependent activation energy for rotational modes of the $Mn^{2+}(H_2O)_6$ complex.

It has been pointed out[1] that the study of depolarization phenomena of polarized positive muons, stopped in condensed-media targets, might reveal the muon as a very powerful experimental tool in investigating condensed-matter physics and some specific aspects of chemistry.

In two recent papers[2,3] we showed how muon depolarization studies indeed provide information about lattice structure and about muonium chemistry during and after the slowing down of the muons in liquid and solid targets.

With regard to aqueous solutions one can draw—from Refs. 2 and 3 as well as from arguments given by Hague et al.[4] in their analysis on a precision measurement of the magnetic moment of the muon in water—the conclusion that the muons, which have conserved their polarization during the slowing-down process, are most probably to be found in place of a proton in a water molecule (μHO). In aqueous solutions of paramagnetic ions, muon spin depolarization should consequently occur in direct analogy to the relaxation behavior of proton spins in proton NMR studies in the same solutions—that is, on a microsecond scale for sufficiently concentrated solutions.

A study of "slow" muon depolarization in transverse magnetic fields in $Fe(NO_3)_3$ solutions[5] with Fe^{3+} concentrations up to 3 M indeed did display the same T_2 concentration dependence as proton NMR measurements, and the ratio of proton and muon T_2 at the same concentration was proportional to the inverse ratio of the squared magnetic moments.

In this paper we present results on the "slow" muon spin relaxation in $MnCl_2$ solutions (with Mn^{2+} concentrations up to 5 M) and its temperature dependence in a 3 M solution. The results obtained deviate quite considerably from what one usually observes in proton NMR experiments.

The area of interest, of course, concerns the magnetic interactions of the muon, via its magnetic moment, with the medium in the "stopping target." These interactions lead to spin-flip transitions and/or to destruction of the phase relations among the polarized muon spins, thereby destroying the initial polarization. This depolarization can be detected by looking at the anisotropy of the electron distribution from muon decay ($\mu^+ \rightarrow e^+ + \nu + \bar{\nu}$) and its time dependence. If the stopping target is placed in a transverse magnetic field, the precession of muons leads to a decay-electron distribution in time detected by a counter in the plane of precession, which can be described by

$$N_2(t) = N_0\, e^{-t/\tau_\mu}\left[1 + \xi A e^{-t/T_2} \cos(\omega t + \phi)\right] + \text{bkg}, \tag{1}$$

where τ_μ, the mean muonium lifetime, is 2.20 μsec,

ω = Larmor precession frequency of the muons,

ξA = residual asymmetry as a result of "fast" depolarization ($\xi \leqslant 1$; see Ref. 3),

ϕ = phase of residual asymmetry,

bkg = background,

T_2 = transverse relaxation time of muon spin.

We are concerned only with T_2.

The experiment, performed at the 184-in. synchrocyclotron at the Lawrence Radiation Laboratory, Berkeley, used the same experimental setup as in Ref. 5. Measurements were made at 4.5 and 11 kG. The target was a 3-in. cube made of 5-mil Mylar or stainless steel, filled with the solution. The field inhomogeneity over the target volume was 5×10^{-6} (rms) of the center value and therefore too small to cause any artificial T_2. For each concentration or temperature, about 600 000 to 800 000 decay events were collected and edited in a rate-versus-elapsed-time histogram (0.5-nsec bins), which finally was used to fit Eq. (1) by a chi-squared minimization program.

Figure 1 shows T_2 data versus concentration from measurements in a transverse field of 11 kG at 295° K.

The model, used by Bernheim et al.[6] and Bloembergen and Morgan,[7] is that the paramagnetic Mn^{2+} ions are surrounded by six water molecules forming a hydration sphere. Protons (or muons) in this hydration sphere are subject to two magnetic interactions: dipole-dipole interaction between paramagnetic ion and proton (or muon), and a scalar coupling or spin-exchange interaction caused by the nonvanishing wave function of the ion at the site of the proton (or muon) in the hydration sphere. These interactions lead to the following expressions for the transverse relaxation time T_2.[6, 7]

$$\frac{1}{T_2} = \frac{4}{60}\,\frac{1}{r^6}\,S(S+1)\,\gamma^2_{p(\mu)}\,\gamma^2_{ion}\,h^2\left[7\tau_c + 13\tau_c\left(1+\omega^2_s\tau^2_c\right)^{-1}\right]p$$

$$+\ \frac{1}{3}\,S(S+1)\,A^2_{p(\mu)}\,h^{-2}\left[\tau_e + \tau_e\left(1+\omega^2_s\tau^2_e\right)^{-1}\right]p. \qquad (2)$$

The first part on the right-hand side of Eq. (2) is due to the dipole-dipole interactions, and the second part is caused by the spin-exchange interactions. The symbols are defined as follows: S = ion spin (5/2); r = internuclear distance between ion and proton (muon); γ_p or γ_μ and γ_{ion} = the respective gyromagnetic ratios; $A_\mu = 3.18\ A_p$, the coupling constant for exchange interaction; ω_s = Larmor precession frequency of the ion, p = the probability of finding a proton (or a muon) in the hydration sphere; and τ_c and τ_e are the respective correlation times.

Bloembergen and Morgan[7] were able to describe proton-relaxation dependence upon magnetic field strength and temperature in $MnCl_2$ solutions very well by adopting Eq. (2) and reasonable values for the correlation times and their temperature dependence. NMR measurements were, however, done only in solutions of relatively low concentration.[8]

The upper dashed curve in Fig. 1(a) corresponds to the dipole-dipole relaxation mechanism, the lower one to the spin-exchange mechanism. The solid line represents their combined result from use of Eq. (2) according to Ref. 7. As can be seen, the measured T_2 data seem to follow Eq. (2) only at concentrations less than 0.1 M, whereas in the region 0.5 to 0.2 M, T_2 becomes nearly independent of ion concentration and finally starts again to be dependent on concentration at about 3 M. A reasonable approach toward understanding these deviations from Eq. (2) is to assume that some of the correlation times become concentration-dependent at higher concentrations due to intermolecular interactions of Mn^{2+} complexes. In particular, spin-spin interactions among Mn^{2+} ions might lead to concentration-dependent correlation times. ESR measurements indeed show a concentration-dependent line width in concentrated Mn^{2+} solutions.[9, 10]

Hinckley and Morgan[10] have measured ESR line widths in $Mn(ClO_4)_2$ solutions and their temperature dependence in Mn^{2+} concentrations between 1.1 and 3.2 M. The total ESR line width in a certain transition is the sum of two contributions: the Bloembergen electron spin relaxation mechanism due to intramolecular interactions which leads to correlation time τ_s[7] and the contribution due to spin-spin interactions among Mn^{2+} ions. Results presented in Ref. 10 correspond to the ESR transitions $m_s = +1/2 \rightarrow m_s = -1/2$. From their results we calculate a relaxation time for the intermolecular process, and write the usual approximation[11]

$$\tau_s^* \equiv \{T_{1(e)} \approx T_{2(e)} \approx T_{2(e)}(\tfrac{1}{2} \rightarrow -\tfrac{1}{2})\}, \tag{3}$$

where τ_s^* is now used as an additional effective correlation time in the proton (muon) -ion interactions. In Fig. 1(b) we show τ_s^* versus ion concentration at 295° K as obtained from Ref. 10. The data can be approximated by

$$\tau_s^* = \frac{1.24 \times 10^{-9}}{N^2} + 1.27 \times 10^{-11} \text{ sec}, \tag{4}$$

with N = ion concentration in moles/liter. The temperature dependence of τ_s^* can also be obtained from Ref. 10. For a 3 M solution, one finds

$$\frac{1}{\tau_s^*} = 1.76 \times 10^7 \,[710 - 2.8\times 10^3 \exp(-\frac{1.26\times 10^3}{RT})]. \qquad (5)$$

The total correlation time τ_e for the spin-exchange interaction is now given by

$$\frac{1}{\tau_e} = \frac{1}{\tau_s} + \frac{1}{\tau_s^*} + \frac{1}{\tau_h}, \qquad (6)$$

where τ_s is the usual electron spin relaxation time and τ_h is the mean time for the muon to remain in the hydration sphere. The total correlation time τ_c for the dipole-dipole interaction is given by

$$\frac{1}{\tau_c} = \frac{1}{\tau_r} + \frac{1}{\tau_h} + \frac{1}{\tau_s} + \frac{1}{\tau_s^*}, \qquad (7)$$

where τ_r is the rotational correlation time. At room temperature $\tau_s \approx 3\times 10^{-9}$, $\tau_h \approx 2\times 10^{-8}$, $\tau_r \approx 3\times 10^{-11}$ sec.[7]

In Fig. 2(a) we again present our data from Fig. 1(a); however, the concentration (p) dependence is now divided out. If the correlation times were concentration-independent, $1/T_2p$ would be constant. If we insert the total correlation times τ_e and τ_c [Eqs. (6) and (7)] into the general expression Eq. (2) with the other parameters taken from Ref. 6, we get the solid line in Fig. 2(a), which fits our data excellently. The dashed lines in Fig. 2(a) represent spin-exchange and dipole-dipole contributions separately.

If we use, however, Eq. (2) together with Eqs. (5)-(7) and the temperature dependence for τ_r and τ_h from Ref. 7, we obtain the dotted curve in Fig. 2(b) for 11 kG, which—as is clearly evident—does not adequately describe the measured T_2-versus-temperature data in a 3 M solution.

By assuming that Eq. (6) correctly described the temperature dependence of τ_s^* and not considering an abnormal τ_h behavior, we are forced to adopt parameters different from the ones in Ref. 7 in the expression

$$\tau_r = \tau_r^0 \exp(V_r/RT), \qquad (8)$$

where V_r is the activation energy of the rotational motion of the Mn^{2+} complex. Using V_r = 8.5 kcal/mole-liter and $\tau_r^0 = 1.73 \times 10^{-17}$ sec, we obtain for $1/T_2p$ versus temperature the lower solid curve at 11 kG and the upper one at 4.5 kG external field strength.[12]

The large value for the activation energy at 3 M concentration as compared with V_r = 4.5 kcal/mole-liter at low concentrations seems to be reasonable in view of the strongly increased viscosity of a 3 M $MnCl_2$ solution [η(3 M) ≈ 3.2 centipoises]. It would be of great interest to establish some firm experimental relationships here with respect to the dynamics of this liquid.[12]

We now discuss some questionable assumptions in our analysis.

1) The results of Ref. 10 for ESR line width were obtained in an external field of 3 kG. In our analysis we neglected possible field dependence of the ESR line widths and assumed the same values in fields of 4.5 and 11 kG. This is justified only if the relevant correlation time τ obeys the inequality $\tau\omega_s$ (11 kG) < 1 or $\tau < 5 \times 10^{-12}$ sec.

2) The results of Ref. 10 were obtained in $Mn(ClO_4)_2$ solutions, whereas we used $MnCl_2$ solutions.

3) Although we had to change V_r and τ_r^0 in order to fit the temperature dependence of a 3 M solution, we had to assume that τ_r remains relatively independent of concentration at 295°K in order to obtain the fit in Fig. 2(a).

4) In view of the quality of the fit, as shown in Fig. 2(a), τ_h has been assumed to be concentration-independent. This assumption needs, of course, further justification. In particular, a concentration-dependent activation energy for

chemical exchange might reduce the value of V_r to less than 8.5 kcal/mole-liter.

5) The whole analysis was performed on the basic assumption that $Mn(H_2O)_6^{2+}$ formation continues almost unchanged up to the strongest concentrations.

These assumptions emphasize how further use of muon-depolarization studies might also contribute to our knowledge about structure and dynamics of fluids. In order to accomplish this program in Mn^{2+} solutions, measurements of relaxation times have to be performed in transverse as well as in longitudinal fields, as a function of varying field strengths, as a function of temperature in various concentrations, and finally in solution with different anions.

The elegance and "simplicity" of the described method of using muons instead of protons in NMR measurement is of course realized only in situations in which the muon polarization is destroyed on a microsecond or faster scale. These are just the situations where muon techniques will compete successfully with proton NMR techniques, because—since no high-frequency techniques are necessary—the problems concerned with line width, signal amplitudes, dielectric effects, and sample size will be absent. Further, it is advantageous to study relaxation phenomena without interference from strong external high-frequency fields.

FOOTNOTES AND REFERENCES

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1. I. V. Ivanter and I. G. Smilga, Sov. Phys.-JETP 28, 796 (1969).
2. A. Schenck and K. M. Crowe, Phys. Rev. Lett. 26, 57 (1971).
3. J. H. Brewer, K. M. Crowe, R. F. Johnson, A. Schenck, and R. W. Williams, Phys. Rev. Lett. 27, 297 (1971).
4. J. F. Hague, J. E. Rothberg, A. Schenck, D. L. Williams, R. W. Williams, K. K. Young, and K. M. Crowe, Phys. Rev. Lett. 25, 628 (1970) and a more detailed account to be published.
5. A. Schenck, Phys. Lett. 32A, 19 (1970).
6. R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, J. Chem. Phys. 30, 950 (1959).
7. N. Bloembergen and L. O. Morgan, J. Chem. Phys. 34, 842 (1961).
8. See, for instance, N. J. Poulis and W. P. A. Hass, in Landolt-Bornstein, *Zahlenwerte und Funktionen*, Vol. II, Part 9 (Magnetic Properties I) (Springer-Verlag, Berlin, 1962).
9. M. A. Garstens and S. H. Liebson, J. Chem. Phys. 20, 1647 (1951).
10. C. C. Hinckley and L. O. Morgan, J. Chem. Phys. 44, 898 (1966).
11. A. W. Nolle and L. O. Morgan, J. Chem. Phys. 36, 378 (1962).
12. B. B. Garrett and L. Morgan, J. Chem. Phys. 44, 890 (1966).

FIGURE CAPTIONS

Fig. 1(a). T_2 data versus Mn^{2+} concentration.

The dashed lines represent the spin-exchange and dipole-dipole terms of Eq. (2), following Ref. 7. The solid line is the combined result. (b) Plot of τ_s^* versus Mn^{2+} concentration at 295°K as obtained from Ref. 10. The solid line represents the interpolation used in Eq. (4).

Fig. 2(a). Plot of $1/T_{2p}$ versus Mn^{2+} concentration. The solid curve is obtained by combining NMR and ESR results in Eq. (2). The dashed curves show separately the contributions from spin-exchange and dipole-dipole interactions. (b) Plot of $1/T_{2p}$ versus temperature. The dotted curve represents Eq. (2) combined with Eq. (5) and the temperature dependence of τ_h and τ_r from Ref. 7 at 11 kG. Solid curves represent the result of our analysis (see text) at 4.5 and 11 kG respectively. The dashed curves represent the spin-exchange and dipole-dipole contributions of our analysis separately to 11 kG.

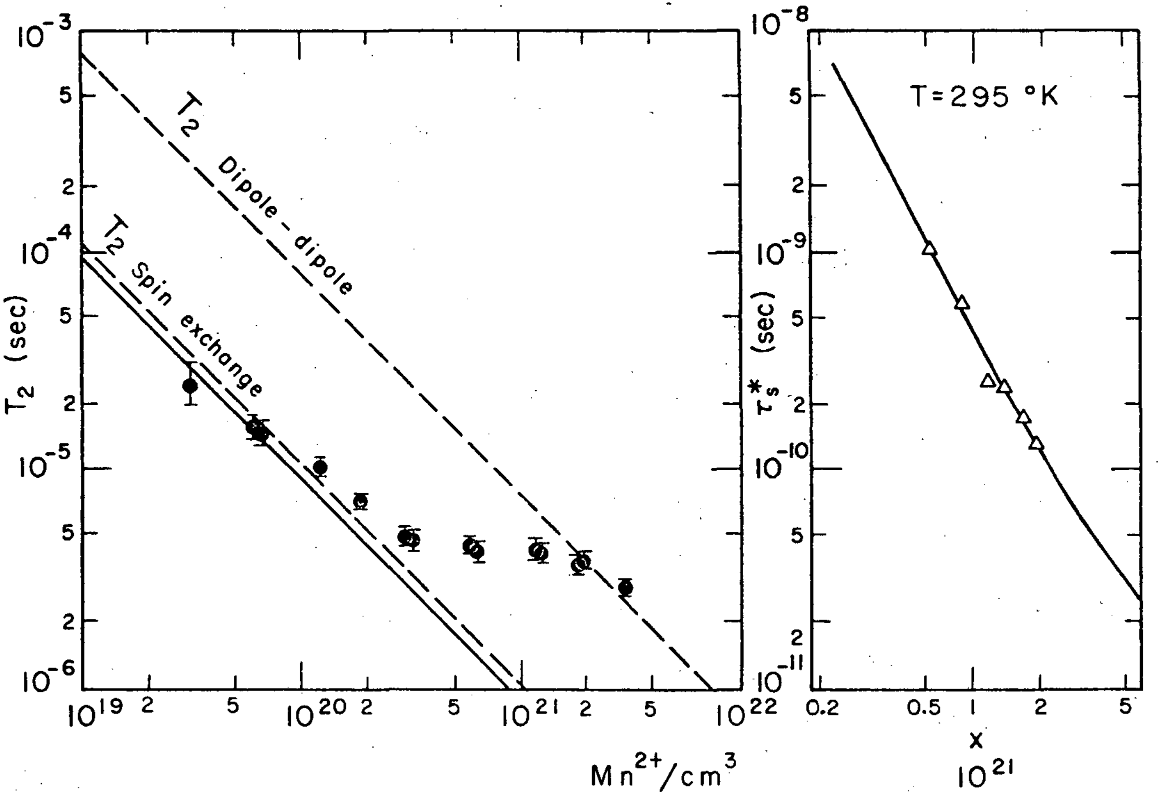

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Fig. 1

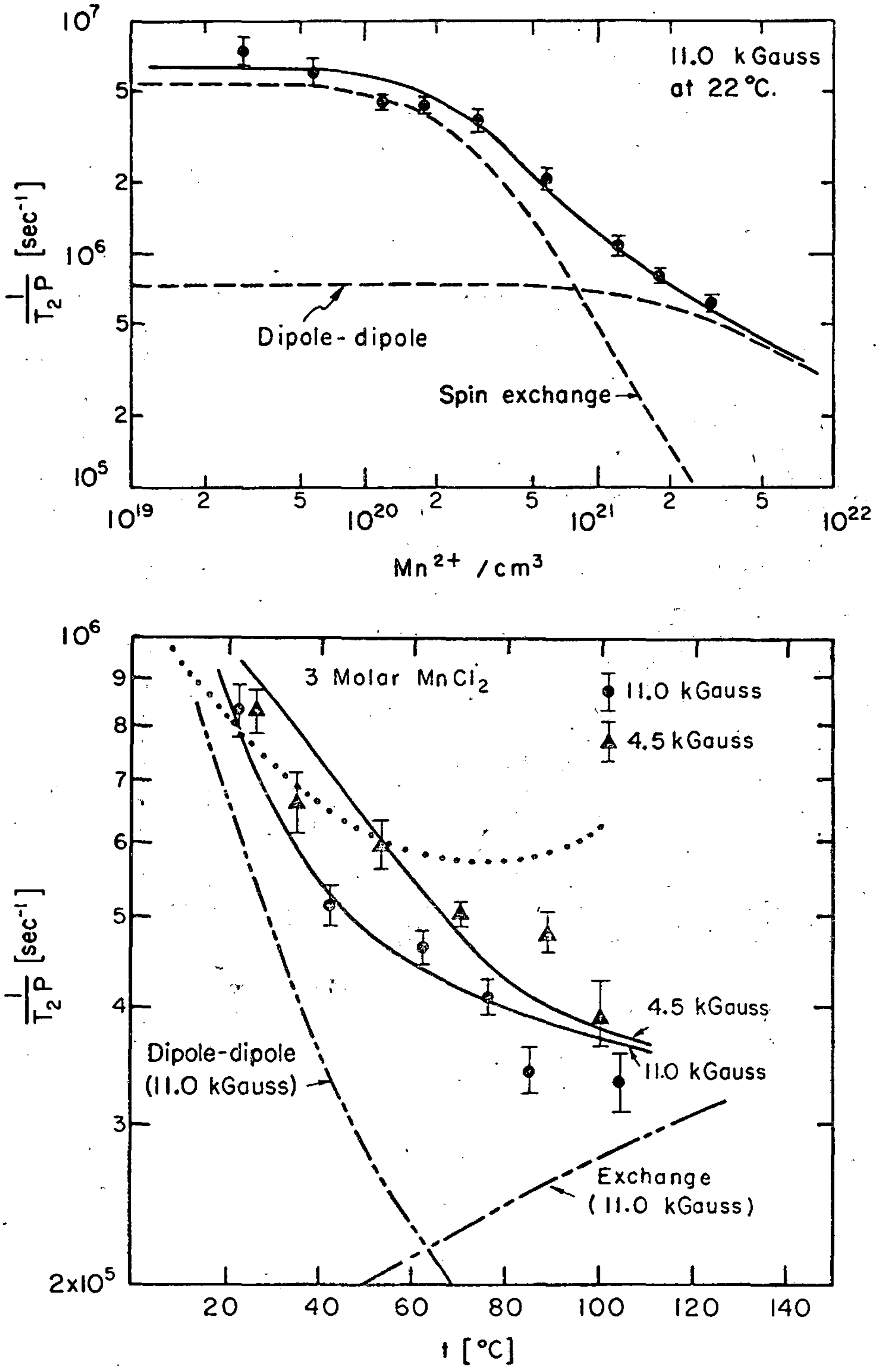

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Fig. 2

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