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Authors
Schenck, A.
Williams, D.L.
Brewer, J.H.
et al.

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DECAY OF THE COHERENT SPIN PRECESSION OF POLARIZED POSITIVE MUONS IN PARAMAGNETIC MnCl₂ SOLUTIONS

A. Schenck† and D. L. Williams
Department of Physics, University of Washington
Seattle, Washington 98105

and

J. H. Brewer, K. M. Crowe, and R. F. Johnson
Lawrence Radiation Laboratory, University of California
Berkeley, California 94720

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Slow depolarization of μ⁺ in a transverse field has been used to measure relaxation effects in paramagnetic MnCl₂ solutions. $T_2^{-1}$ data show nonlinear dependence on ion concentration. Consistent explanation is achieved by assuming that the muon replaces a proton, forming μH₂O, and applying relaxation mechanisms as developed for Mn²⁺ 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 Mn²⁺ (H₂O)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 papers²,³ 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. 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 (H₂O). 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(NO₃)₃ solutions with Fe³⁺ 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 MnCl₂ solutions (with Mn²⁺ 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

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

where \( \tau \), the mean muonium lifetime, is 2.20 \( \mu \)sec,

\( \omega \) = Larmor precession frequency of the muons,

\( \xi A \) = residual asymmetry as a result of "fast" depolarization

(\( \xi \leq 1; \) see Ref. 3),

\( \phi \) = phase of residual asymmetry,

\( \text{bkg} \) = 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 set-up 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 \( 5 \times 10^{-6} \) (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 $T_2$.

$$\frac{1}{T_2} = \frac{4}{60} \frac{1}{r^6} S(S + 1) \gamma_p^2 \gamma_{\text{ion}}^2 h^2 [7 \tau_c + 13 \tau_c (1 + \omega_s^2 \tau_e^2)^{-1}] p$$

$$+ \frac{1}{3} S(S + 1) A_{\mu}^2 \gamma_{\text{ion}}^2 h^{-2} \left[ \tau_e + \tau_e (1 + \omega_s^2 \tau_e^2)^{-1} \right] p.$$  \hspace{1cm} (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: $S = \text{ion spin (5/2)}$; $r = \text{internuclear distance between ion and proton (muon)}$; $\gamma_p$ or $\gamma_{\mu}$ and $\gamma_{\text{ion}} = \text{the respective gyromagnetic ratios}$; $A_{\mu} = 3.18 A_p$, the coupling constant for exchange interaction; $\omega_s = \text{Larmor precession frequency of the ion}$, $p = \text{the probability of finding a proton (or a muon) in the hydration sphere}$; and $\tau_c$ and $\tau_e$ are the respective correlation times.

Bloembergen and Morgan 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.

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 $\tau_s^7$ and the contribution due to spin-spin interactions among Mn$^{2+}$ ions. Results presented in Ref. 10 correspond to the ESR transitions $m_s = \pm 1/2 \rightarrow m_s = -1/2$. From their results we calculate a relaxation time for the intermolecular process, and write the usual approximation 11

$$\tau_s^* = \{T_1(e) \approx T_2(e) \approx T_2(e) \left( \frac{1}{2} \rightarrow - \frac{1}{2} \right) \},$$

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

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

with $N =$ ion concentration in moles/liter. The temperature dependence of $\tau_s^*$ can also be obtained from Ref. 10. For a 3 M solution, one finds
\[
\frac{1}{\tau_s} = 1.76 \times 10^7 [710 - 2.8 \times 10^3 \exp(-\frac{1.26 \times 10^3}{R T})].
\] (5)

The total correlation time \( \tau_e \) for the spin-exchange interaction is now given by

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

where \( \tau_s \) is the usual electron spin relaxation time and \( \tau_h \) is the mean time for the muon to remain in the hydration sphere. The total correlation time \( \tau_c \) for the dipole-dipole interaction is given by

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

where \( \tau_r \) is the rotational correlation time. At room temperature \( \tau_s \approx 3 \times 10^{-9}, \tau_h \approx 2 \times 10^{-8}, \tau_r \approx 3 \times 10^{-11} \text{ sec.} \)

In Fig. 2(a) we again present our data from Fig. 1(a); however, the concentration \( \rho \) dependence is now divided out. If the correlation times were concentration-independent, \( 1/T_2^p \) would be constant. If we insert the total correlation times \( \tau_e \) and \( \tau_c \) [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 \( \tau_r \) and \( \tau_h \) 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 \( \tau_s^* \) and not considering an abnormal \( \tau_h \) behavior, we are forced to
adopt parameters different from the ones in Ref. 7 in the expression

\[ \tau_r = \tau_r^0 \exp \left( \frac{V_r}{RT} \right), \]

where \( V_r \) is the activation energy of the rotational motion of the Mn\textsuperscript{2+} complex. Using \( V_r = 8.5 \text{ kcal/mole-liter} \) and \( \tau_r^0 = 1.73 \times 10^{-17} \text{ sec} \), we obtain for \( 1/T_2 \) 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 \( V_r = 4.5 \text{ kcal/mole-liter} \) at low concentrations seems to be reasonable in view of the strongly increased viscosity of a 3 M MnCl\textsubscript{2} solution \( \{\eta(3 \text{ M}) \approx 3.2 \text{ centipoises}\} \). 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 \( \tau \) obeys the inequality

\[ \tau \omega_s (11 \text{ kG}) < 1 \text{ or } \tau < 5 \times 10^{-12} \text{ sec}. \]

2) The results of Ref. 10 were obtained in Mn(ClO\textsubscript{4})\textsubscript{2} solutions, whereas we used MnCl\textsubscript{2} solutions.

3) Although we had to change \( V_r \) and \( \tau_r^0 \) in order to fit the temperature dependence of a 3 M solution, we had to assume that \( \tau_r \) remains relatively independent of concentration at 295\textdegree 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), \( \tau_h \) 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$_2$O)$_6^{2+}$ 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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†Present address: I. Physikalisches Institut, Universität Heidelberg, Heidelberg, Germany.

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 $\tau_s^*$ versus Mn$^{2+}$ concentration at 295$^\circ$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 $\tau_h$ and $\tau_r$ 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.
Fig. 1
Fig. 2
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