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Spin-Lattice Relaxation and Temperature Dependence of Electron-Paramagnetic-Resonance Linewidth of $\mathrm{Mn(Mg)SO_4 \cdot 4H_2O}$†

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We have measured the spin-lattice relaxation time of $\mathrm{Mn^{++}}$ in $\mathrm{Mn(Mg)SO_4 \cdot 4H_2O}$ (Mn:Mg=1) as a function of temperature between 1.9 and 4.2°K using the method of steady-state saturation at 9.3 Gc/sec. These measurements have been made to pursue a suggestion of Al'tshuler that the thermal modulation of the magnetic-dipole interaction dominates the spin-lattice relaxation process for S-state ions with large spin. We have found that T_1 increases with decreasing temperature from 4.2 to 2.5°K, below which T_1 becomes constant. This result supports Al'tshuler's suggestion and further suggests that cross relaxation becomes dominant below 2.5°K. We have also observed a linewidth whose temperature dependence gives qualitative agreement with a recent theory of Richards.

I. INTRODUCTION

THE S-state ions in the iron group occupy a unique place with regard to spin-lattice relaxation. As they have zero orbital angular momentum, we expect that relaxation via the spin-orbit interaction[1,2] will be small, and the spin-lattice relaxation time T_1 will be independent of magnetic concentration if this is the predominant mechanism. However, in highly concentrated salts we expect that cross relaxation[3] will play a large role in the behavior of the saturation of the paramagnetic resonance. Then the apparent relaxation behavior will be temperature-independent, and strongly concentration-dependent.

Before the discovery of cross relaxation, Al'tshuler[4] proposed that the observed concentration dependence of the room-temperature relaxation time for $\mathrm{Mn(SO_4) \cdot 4H_2O}$ might result from the thermal modulation of the magnetic-dipole interaction. The $\mathrm{Mn^{++}}$ ion has a spin of $\frac{5}{2}$ and consequently a very large magnetic moment. As the magnetic moment appears to the fourth power in the transition probabilities for both first- and second-order processes, the relaxation rate determined by the magnetic-dipole interaction is 625 times that of an ion with spin $\frac{1}{2}$.

To investigate this suggestion, we have measured the spin-lattice relaxation time of $\mathrm{Mn^{++}}$ in $\mathrm{Mn(Mg)SO_4 \cdot 4H_2O}$ between 1.9 and 4.2°K, using the method of steady-state saturation. If the saturation is governed by cross relaxation, the relaxation rate should be independent of the temperature. If the relaxation is governed by the thermal modulation of the magnetic-dipole interaction, T_1 should be strongly temperature-dependent.

One of the first microwave observations of paramagnetic resonance was made on $\mathrm{MnSO_4 \cdot 4H_2O}$ by Cummerow and Halliday.[5] The substance displays a resonance line which is more Lorentzian than Gaussian in shape and far narrower at the half-power points than is predicted by the theory of dipolar broadening.[6] This narrowing is attributed to the exchange interaction between closely spaced $\mathrm{Mn^{++}}$ ions.[7,8] Goldsborough *et al.*[9] have measured the commonly observed broadening of the exchange-narrowed resonance line in diphenylpicrylhydrazyl (DPPH) as temperature is lowered, and their observations contradict a recent theory of Richards.[10]

In the process of studying the steady-state saturation of the $\mathrm{Mn(Mg)SO_4 \cdot 4H_2O}$, we have also studied the temperature dependence of the exchange narrowing, finding qualitative agreement with Richard's theory.[10]

II. EXPERIMENTAL METHOD

If a two-level spin system undergoes magnetic resonance, the microwave power absorbed at the peak of the resonance line is given by

$$P_a = N_0 h\nu V/(1+2VT_1). \tag{1}$$

Here, N_0 is the difference in population between the two states in the absence of the resonant radiation, ν is the microwave frequency, V is the probability per unit time for transitions induced by the microwave radiation, and T_1 is the spin-lattice relaxation time.

While many relaxation processes are responsible for the behavior of multilevel spin systems, Lloyd and Pake[11] have shown that an equation of the same form as Eq. (1) still applies. However, T_1 is due to a multi-

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plicity of processes, and describes the behavior of the EPR saturation rather than the exponential decay of the magnetization.

The Mn^{++} (spin $\frac{5}{2}$) shows a splitting into six nearly equally spaced states in the presence of a magnetic field, there being negligible zero-field splitting for an S-state ion. Therefore, we see only a single resonance line containing contributions from all of the magnetic-dipole transitions, and the saturation of the resonance line involves saturation of all the transitions. The spectrum of $Mn(Mg)SO_4 \cdot 4H_2O$ is shown in Fig. 1.

The details of steady-state saturation experiments may be found elsewhere.[12–15]

III. RESULTS

A. Line Shape

Our experiment was performed on a single crystal of $Mn(Mg)SO_4 \cdot 4H_2O$ with equal members of Mn^{++} and Mg^{++} ions. While it would have been preferable to enhance the exchange interaction by eliminating the nonparamagnetic ion Mg^{++}, single crystals of $MnSO_4 \cdot 4H_2O$ proved too brittle for the experiment; we would have obtained the spectrum of a powder rather than a single crystal. For this reason, Fig. 2, which gives us the degree of exchange narrowing of the resonance line, shows less narrowing than we would have obtained from an ideal crystal of $MnSO_4 \cdot 4H_2O$. The shape analysis of the type shown in Fig. 2 was first used by Weidner and Whitmer.[16] It is explained as follows: The equation of the Lorentz-type resonance line is

$$f_L = \{1 + [2(H - H_0)/\Delta H]^2\}^{-1}. \qquad (2)$$

The normalized shape function f is given in terms of H_0, the resonant magnetic field strength, the variable magnetic field H, and the full linewidth at the half-power points. If we plot $2(H - H_0)/\Delta H$ versus $(f^{-1} - 1)$, we get the solid straight line shown in Fig. 2. The Gauss-type resonance line is given by

$$f_G = \exp\{\log 2[2(H - H_0)/\Delta H]^2\}, \qquad (3)$$

and by plotting the same quantities as above for the Gaussian curve, the solid curved line in Fig. 2 is obtained.

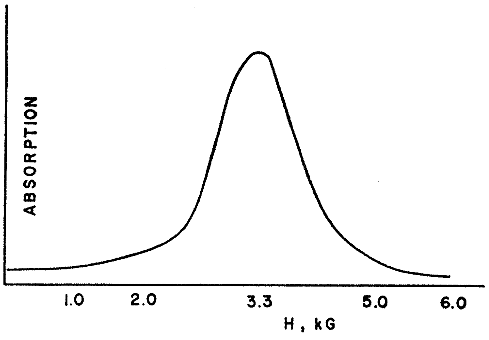

Fig. 1. The EPR spectrum on $Mn(Mg)SO_4 \cdot 4H_2O$ (Mn:Mg = 1) at 9.3 Gc/sec and 1.60°K.

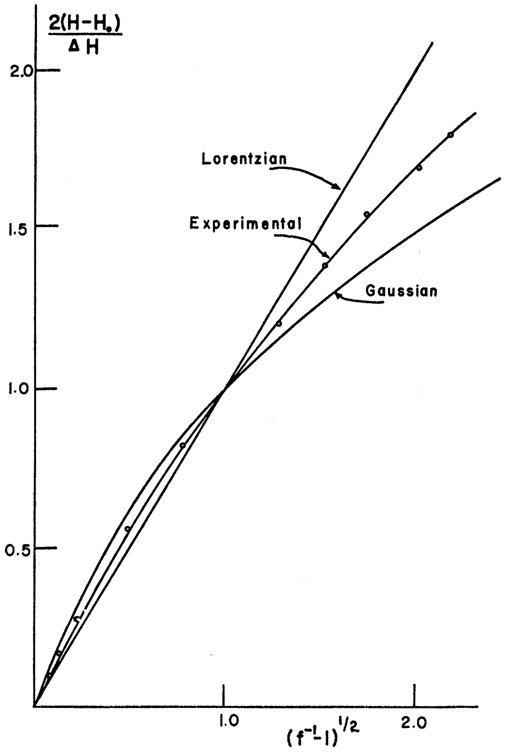

Fig. 2. Shape analysis of $Mn(Mg)SO_4 \cdot 4H_2O$ (Mn:Mg = 1) resonance at 1.66°K and 9.3 Gc/sec.

The experimental points in Fig. 2 show that the resonance line of $Mn(Mg)SO_4 \cdot 4H_2O$ with equal numbers of Mn^{++} and Mg^{++} ions has considerable exchange narrowing, and one expects that $MnSO_4 \cdot 4H_2O$ would have yielded a resonance line more closely approximating the Lorentzian shape.

Figure 3 gives the dependence on temperature of the product of the area of the absorption curve, the linewidth, and coth $\hbar\omega/2kT$. Richards' theory predicts that this product should decrease as the temperature is lowered.[10] Our data agree with this prediction, but indicate the possibility of a relative minimum near 2°K. The theoretical relationship is given as[17]

$$(\text{Area})\Delta H(\coth \hbar\omega/2kT) \approx (2/\gamma)\langle\Delta\omega\rangle^2/\omega_e. \qquad (4)$$

Richards' obtains the above-mentioned temperature dependence by showing that $\langle\Delta\omega\rangle^2$ decreases and ω_e increases as temperature is increased. As the shape

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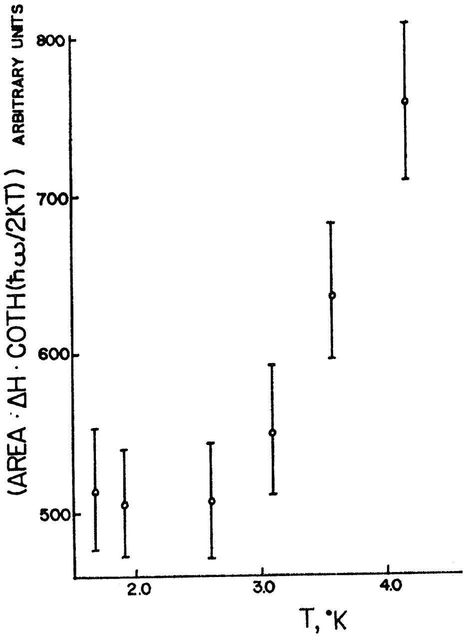

FIG. 3. The full linewidth at the half-power points as a function of temperature variation of linewidth for Mn(Mg)$SO_4 \cdot 4H_2O$ (Mn:Mg=1) at 9.3 Gc/sec.

analysis in Fig. 2 is the same for all temperatures at which we have taken data, we have been unable to detect a variation of $\langle\Delta\omega\rangle^2$ with temperature, and attribute the temperature dependence solely to ω_e.

Our agreement with Richards' theory corrects a previously reported disagreement which was based on a misinterpretation of the theory.[18]

B. Spin-Lattice Relaxation

For the purpose of obtaining the relaxation time T_1, we have made use of a saturation curve of the type used by Bolger *et al.*[15] This curve, appearing in Fig. 4, is essentially a plot of Eq. (1) in the form

$$V/P_a = (1/N_0 h\nu) + 2VT_1/N_0 h\nu. \tag{5}$$

Representation in terms of the coordinates in Fig. 4 can be accomplished by the method shown in Turoff's thesis.[19]

Thus we obtain a curve whose slope is proportional to T_1. In Fig. 4, we see the bending of the saturation curve which has been observed many times before.[15,19,20] The cause of this bending has been conjectured to arise from crystal heating,[15] "exchange pockets," or other rapidly relaxing irregularities in the spin system.[21] The time T_1 is obtained from the slope at low power levels.

In Fig. 5 we show our results for the temperature dependence of the relaxation rate T_1^{-1} between 1.9 and 4.2°K. It is clear that this is a transition region between temperature-dependent and temperature-independent regions. While it is easy to see the increase of the relaxation rate with temperature above 2.5°K, we do not have sufficient points to determine whether the dominant process is direct or indirect.

We believe that the temperature-independent relaxation mechanism which is dominant below 2.5°K is cross relaxation, and that the temperature-dependent mechansim dominant above 2.5°*K* is the thermal modulation of the magnetic-dipole interaction. The reasons for this latter conclusion are as follows:

The temperature-dependent mechanisms of which we are aware are (1) thermal-modulation of the magnetic-dipole interaction, (2) thermal modulation of the spin-orbit coupling, and (3) thermal modulation of the exchange interaction.

It is highly unlikely that the temperature-dependent mechansim is (2). The Mn^{++} ion is an *S*-state ion for which Al'tshuler[4] calculated a relaxation time of the order of magnitude of $T_1 \approx 10^2 - 10^3$ sec. Furthermore, the spin-orbit coupling mechanism would not give rise to the experimental observation of a room-temperature concentration dependence also reported by Al'tshuler.

It is similarly unlikely that the relaxation is dominated by the exchange interaction. The isotropic exchange interaction operator $J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2$ has only diagonal matrix elements and cannot, therefore, directly affect the spin-lattice relaxation.[4] Anisotropic exchange interactions[22,23] depend on the angle between the direction of the spin and the vector from one spin to

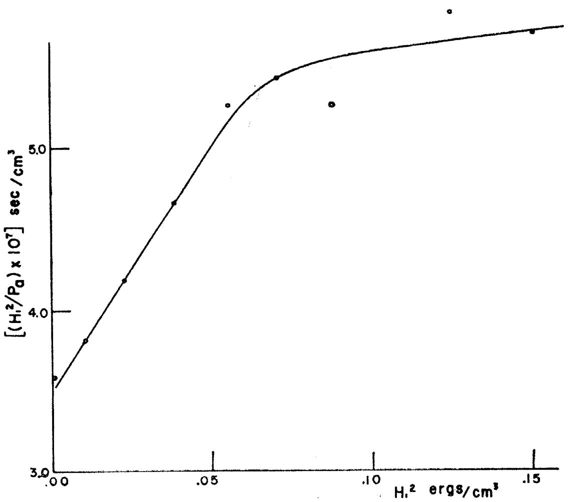

FIG. 4. Saturation curve at 2.60°K and 9.3 Gc/sec for Mn(Mg)$SO_4 \cdot 4H_2O$ (Mn:Mg=1).

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another. If this vector is an axis of symmetry of the ions and their surroundings, the anisotropic exchange can be written in a form similar in appearance to the magnetic-dipole interaction,

$$V_{12}=D_{12}(r_{12})\,(\mathbf{S}_1\cdot\mathbf{S}_2-3(\mathbf{S}_1\cdot\mathbf{r}_{12})(\mathbf{S}_2\cdot\mathbf{r}_{12})/r_{12}^2). \quad (6)$$

While this interaction has off-diagonal matrix elements and can induce transitions, its physical origin indicates that it cannot be strong for a system of S-state ions. It arises from an indirect effect on the spin-orbit coupling of the crystalline electric field. For S-state ions $\lambda\mathbf{L}\cdot\mathbf{S}$ is very small. Thus, we should be able to ignore relaxation by thermal modulation of the anisotropic exchange for the same reason that we can ignore relaxation by thermal modulation of the spin-orbit coupling.

However, the most cogent reason for regarding the magnetic-dipole mechanism as the dominant relaxation mechansim is the appropriate agreement between the magnitudes of experimentally observed relaxation times and those calculated from the formulas derived by Al'tshuler[4] for the transition probabilities induced by the magnetic-dipole interaction between nearest neighbors. The transition probability when one ion undergoes a transition and the other does not (single transition) is given by

$$A_1=\frac{4\pi^3}{3h^4}\frac{(g\beta)^3}{v\rho^5}\left[\frac{(g^2\beta^2)}{r_0^3}\right]^2\frac{\exp(g\beta H/kT)}{\exp(g\beta H/kT)-1}\times S(2S+1)(S+1)^2H^3 \quad (7)$$

for direct processes, where v is the velocity of sound, r_0 is the distance between nearest paramagnetic ions, ρ is the density of the crystal, and other terms retain their customary meanings. The transition probability when both ions undergo magnetic-dipole transitions (double transitions) is given for direct processes by

$$A_2=\frac{16\pi^3}{3h^4}\frac{(2g\beta)^3}{\rho v^5}\left[\frac{g^2\beta^2}{r_0^3}\right]\frac{\exp(2g\beta H/kT)}{\exp(2g\beta H/kT)-1}\times(2S+1)^2(S+1)^2H^3. \quad (8)$$

Comparing (2) and (3), we see that $A_2/A_1\approx 128$ for $S=\frac{5}{2}$ and $T=4$°K.

Thus if $\rho=2$ g/cm^3, $S=\frac{5}{2}$, $v_0=2\times10^5$ cm/sec, $r_0^3=2\times10^{-22}$ cm^3 [all reasonable assumptions for $Mn(Mg)\cdot SO_4\cdot 4H_2O$ when Mn/Mg=1], $H=3200$ Oe and $T=4$°K, $T_1\approx(2A_2)^{-1}\approx 2.5\times10^{-3}$ sec. Our measured value of T_1 is 2.5×10^{-5} sec. In view of the uncertainties of the above quantities, and the high powers to which they are raised in (8), this can be considered satisfactory agreement.

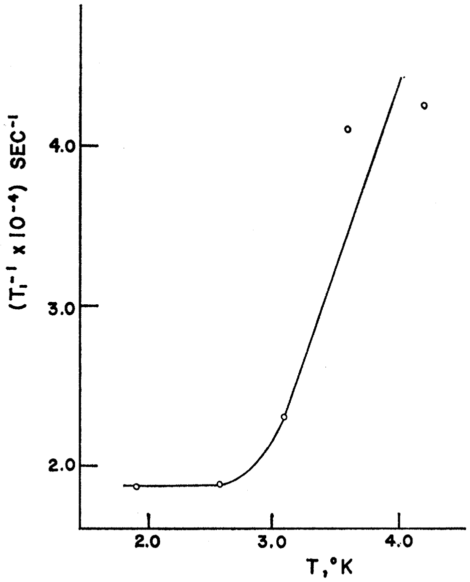

FIG. 5. The temperature dependence of T_1^{-1} for $Mn(Mg)SO_4\cdot 4H_2O$ between 1.9 and 4.2°K at 9.3 Gc/sec.

The indirect process, for which the probabilities are also given by Al'tshuler, gives $T_1\approx 4\times10^3$ sec under the same conditions.

IV. CONCLUSIONS

On the basis of the above considerations, we believe that the spin-lattice relaxation of $Mn(Mg)SO_4\cdot 4H_2O$ (Mn:Mg=1) is governed by the thermal modulation of the magnetic-dipole interaction down to 2.5°K below which cross relaxation becomes dominant.

From our measurements of linewidth as a function of temperature as represented in Fig. 2, and from our inability to detect any variation of the second moment with temperature, we conclude that the temperature dependence of the linewidth results form the temperature variation of ω_e.

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