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PARAMAGNETIC RELAXATION IN MANGANESE SALT SOLUTIONS

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Paramagnetic absorption in parallel fields was measured for aqueous manganese salt solutions at concentrations of 0.25 N and higher. It is shown that the thermodynamic theory of paramagnetic relaxation and the Brons-Van Vleck formula are valid for aqueous manganese salt solutions. The spin-lattice relaxation time equals 10^{-8} sec and depends on the nature of the anion and on the concentration of the Mn^{++} ions in the solutions. Its temperature dependence can be described by the Al'tshuler-Valiev theory. The internal field constants have been determined.

THE fast development of paramagnetic resonance and paramagnetic relaxation methods in recent years is connected with the great importance of the obtainable results for certain branches of physics and chemistry. These methods are of particular interest in the study of the structure of solids and liquids. The principal parameters of paramagnetic relaxation are: the spin-lattice relaxation time ρ_L, the spin-spin relaxation time ρ_S, and the constant b/c, which characterizes the internal field in a paramagnet.

In the present investigation, we measured the paramagnetic absorption in parallel and perpendicular fields for aqueous solutions of certain manganese salts at concentrations from 0.25 mole/liter and above.

The measurements were by the Q-meter method, previously described by one of the authors.[1] It was shown in that reference that the spin-lattice relaxation times in liquid solutions of electrolytes and the constant b/c can be determined with the Q-meter from measurements of χ'' at two frequencies assuming the Casimir and du Pré equation, corrected for spin-spin absorption after Shaposhnikov,[2,3] is correct.

The correction was determined by measuring the absorption in zero field as obtained from experiments in perpendicular fields; it was assumed here that the spin-spin absorption becomes negligibly small at fields ≥ 1500 oe.

We shall first treat here in greater detail the applicability of the formula

$$\chi'' = \chi_0 F \rho_L \nu / (1 + \rho_L^2 \nu^2), \qquad F = H^2 / (b/c + H^2) \quad (1)$$

to the description of the spin-lattice relaxation in liquid solutions of electrolytes. If the values ρ_L and b/c, obtained from measurements of $\chi''(H)$ at two frequencies, coincide with the values of ρ_L and b/c obtained at two other frequencies, this obviously will serve as evidence of applicability of (1) in the given frequency range to a description of relaxation processes in liquid electrolyte solutions. Frequencies of 12, 21, 32, and 42 Mcs were used in the measurements.

To calculate ρ_L we used all possible combinations of frequencies, with the exception of the combination $\nu = 32$ and $\nu = 42$ Mcs, which were too close to each other. From the values of ρ_L thus obtained the average was taken. The deviation of the individually computed value of ρ_L from the average amounted to approximately ±6%. The calculated values of $10^8 \rho_L$ (sec) for a 1 N solution of $MnSO_4$ at 22° C are given in Table I. The constant b/c, which characterizes the internal magnetic field in the paramagnet, was determined from the experimental curves and from the obtained val-

TABLE I

H, oe / $\nu_1 - \nu_2$	1200	1600	2000	2400	2800	3200	3600
12—21	0.9	1.3	1.45	1.6	1.78	1.85	1.94
12—32	1.28	1.47	1.5	1.7	1.77	1.86	1.97
12—42	1.11	1.24	1.45	1.61	1.75	1.8	1.88
21—42	1.25	1.4	1.47	1.63	1.75	1.8	1.86
21—32	1.38	1.52	1.6	1.71	1.8	1.9	2
average $10^8 \rho_L$	1.18±0.14	1.39±0.11	1.48±0.04	1.65±0.04	1.77±0.02	1.84±0.03	1.93±0.05

ues of ρ_L.[1] The deviation of individual calculated values of b/c from the average amounted to ~ ±10%. Table II lists the values of b/c for a 3.2 N solution of $MnSO_4$ at 22° C.

TABLE II

ν, Mcs	H_1	H_2	$(b/c)\cdot 10^{-6}$
42	2400	3200	2.165
	2800	3600	2.26
32	2400	3200	2.865
	2800	3600	2.56
21	2400	3200	2.43
	2800	3600	2.74
12	2400	3200	2.49
	2800	3600	2.355
		Average:	2.48±0.18

Figure 1 shows, by way of an example, an experimental curve of $\chi''(H)$ for a 3.2 N solution of $MnSO_4$ at 300° K for 12, 21, 32 and 42 Mcs (solid curves); the values of $\chi''(H)$, represented by the circles at 32 and 42 Mcs, were calculated from the values of ρ_L and b/c determined experimentally at 12 and 21 Mcs. It is seen from Fig. 1 that the experimental values of $\chi''(H)$ coincide with the computed ones.

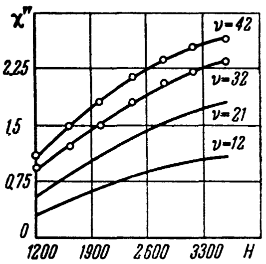

FIG. 1

The results obtained thus testify to the applicability of Eq. (1) for the spin-lattice relaxation in aqueous solutions of electrolytes at the given frequency range. The experimental values of ρ_L for aqueous solutions of $Mn(NO_3)_2$, $MnSO_4$, and $MnCl_2$ at concentrations ranging from 0.25 N upward are on the order of 10^{-8} sec, which is almost one order of magnitude less than the ρ_L of the corresponding solid substances.[2] Experiment has shown that the dependence of ρ_L on the intensity of the constant field H is described by the Brons-Van Vleck equation

$$\rho_L = \rho_0 \frac{b/c + H^2}{b/c + pH^2}; \qquad (2)$$

where ρ_0 is the spin-lattice relaxation time for H = 0 and p is a constant (p < 1).

Figure 2 shows a comparison of the experimental values of $\rho_L(H)$ for 2 N solutions of nitrate, sulfate, and chloride of manganese (circles) and the values calculated by the Brons-Van Vleck formula (solid curves). It is seen from this figure that ρ_L depends substantially on the type of anion.

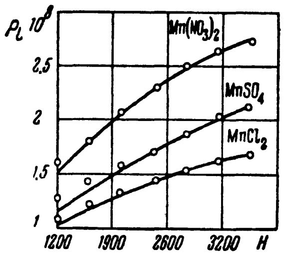

FIG. 2

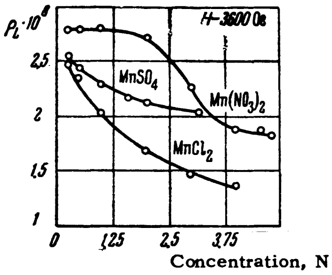

FIG. 3

The dependence of ρ_L on the type of anion and on the concentration (N) of the Mn^{++} ions in aqueous solutions of $Mn(NO_3)_2$, $MnSO_4$, and $MnCl_2$ is shown in Fig. 3. It is found that the spin-lattice relaxation times increase with dilution. The greatest increase in ρ_L with changing concentration is observed in manganese chloride.

The difference in ρ_L between solutions of different salts becomes equalized at small concentrations. At concentrations from 1.5 N to 2 N and lower the value of ρ_L of manganese nitrate remains constant, within the limits of experimental error; ρ_L remains likewise almost constant as the concentration increases from 4 N upward.

An attempt can be made to explain the observed dependence of ρ_L on the concentration, as well as the individual behavior of the curves for all three solutions, by arguing as follows.

In solid crystals the Mn^{++} ion makes up, together with its nearest diamagnetic surrounding, a paramagnetic complex MnX_6, where X is a water molecule or some other diamagnetic particle. Judging from the chemical formulas, one can assume that in solid hydrated sulfate and chloride of manganese the nearest surrounding includes also anions in addition to the water molecules, whereas in the case of manganese nitrate the nearest surrounding consists of six water molecules. One can assume further that in sufficiently concentrated solutions the structure of the corresponding hydrated crystal is retained, i.e., the nearest surrounding of the ion includes anions along with the water molecules and, in addition, entire molecular aggregates may be retained. This conclusion has been obtained by several authors[4-6] on the basis of results of x-ray diffraction investigations, a study of the Raman spectra, etc.

As the dilution increases, the groups break up, the anions become "washed out" with water, and as a result in strongly diluted solutions the paramagnetic ions will be surrounded by water molecules only.

According to the Al'tshuler-Valiev theory,[7] we shall assume that the relaxation time is determined above all by the interaction within the complex, formed by the paramagnetic ion together with its closest surrounding. The Brownian motion of the molecules in the liquid disturbs the natural oscillations of the complex and this changes the electric field in which the paramagnetic particle is located.

In our case one can assume, for the solution of manganese nitrate, that at high concentrations (starting approximately with 4 or 5 N), entire particle aggregates exist, which begin to break up upon dilution, causing ρ_L to increase, and after these groups have entirely disappeared further dilution should no longer influence the spin-lattice relaxation time.

In the case of manganese sulfate and chloride solutions, the region of strong dilution, when the Mn^{++} ion is surrounded only by six water molecules and where ρ_L should remain constant, lies apparently below 0.25 N and was not investigated here. At a concentration of approximately 0.5 N and above, apparently, the anion begins to penetrate into the first surrounding sphere of the Mn^{++} ion; at concentrations greater than 3.5 N for the sulfate and greater than 5 N for the chloride of manganese, this penetration is essentially complete. At the same time, at these concentrations the influence of the ions becomes most strongly pronounced, and as a result of this the ρ_L of the sulfate and chloride of manganese exhibit the greatest difference from each other in strongly concentrated solutions.

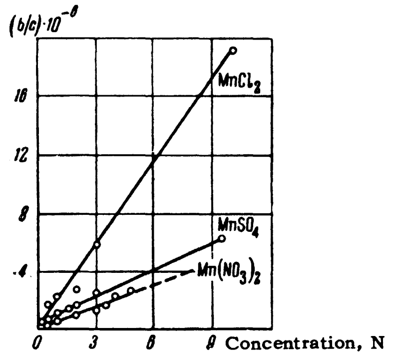

FIG. 4

Figure 4 shows the dependence of the constant of the internal field b/c on the type of the anion and on the concentration N of the solutions of nitrate, sulfate, and chloride of manganese. It is found that b/c varies approximately linearly with concentration, and the values of b/c for the solid salts (6.2×10^6 for $MnSO_4 \cdot 4H_2O$ and 19.3×10^6 for $MnCl_2 \cdot 4H_2O$) fit well on the corresponding straight lines. The linear dependence of b/c on N is typical for each salt, i.e., the dependence on the type of anion becomes manifest. This is an additional confirmation of the correctness of the model used to explain the dependence on the concentration and on the type of anion. In fact, the increase in b/c with increasing concentration can be explained by assuming that the structure of the solution approaches the structure of the solid.

Preliminary measurements of the magnetic absorption in parallel fields for alcohol solutions of $MnCl_2$ at concentrations from 0.25 N to 1.7 N have shown that the ρ_L of alcohol solutions differs very little from those of aqueous solutions within the same concentration range.

To explain the dependence of ρ_L on the temperature, measurements were made with a 2 N solution of $Mn(NO_3)_2$ at −2, +22, and +58° C. A value of 2 N was chosen for the concentration because further dilution from this value leaves ρ_L almost unchanged and it can be assumed that the Al'tshuler-Valiev mechanism holds in this range of concentration, i.e., ρ_L is determined essentially by the natural oscillations of the paramagnetic complex $Mn(H_2O)_6$, perturbed by the Brownian motion of the molecules of the liquid.

Measurements made at these temperatures have shown that, in agreement with the theory, the curve $\rho_L(T)$ passes through a maximum; the maximum occurs at $t \approx 20°C$ ($\rho_L = 2.7 \times 10^{-8}$ sec at $H = 3600$ oe); at −2 and +58° C, ρ_L decreases to 2.05 and 2.4×10^{-8} sec respectively.

These measurements were performed several times. The difference in the values of ρ_L at different temperatures lies outside the limits of experimental errors.

Such a temperature dependence of the spin-lattice relaxation time is confirmed by measurements of the line widths in solutions of Mn^{++}.[8,9]

However, the minimum line width $\Delta H \approx 1/\rho_L + 1/\rho_S$ is observed not at ~ 20° C but at ~ 80° C. This is understandable, for according to Bloembergen, Purcell, and Pound,[10] the contribution of magnetic dipole-dipole interactions to ΔH should decrease monotonically with increasing temperature. A clarification of the temperature dependence of ρ_L in solutions of paramagnetic salts requires further experimental study.

Experimental data make it possible to calculate the spin-spin relaxation time ρ_S. This is calculated from experimental data by the formula

$$\rho_S = [(1 + \rho_L^2 \nu^2)^2 - \sqrt{(1 + \rho_L^2 \nu^2)^2 - 4k^2 F^2 \nu^2 \rho_L^2}\,] / 2kF\rho_L \nu^2, \tag{3}$$

where

$$k = \chi''_{\perp}(0) / \chi''_{\parallel}(H),$$

and ρ_L was taken to be the spin-spin relaxation time for H = 3600 oe. This formula was obtained under the assumption that the Casimir and du Pré equation holds for fields ≥ 2,000 oe and the equation

$$\chi''(H_\perp = 0)/\chi_0 = \rho_S\nu/(1+\rho_S^2\nu^2) \tag{4}$$

is valid. This equation is derived in Shaposhnikov's general theory of paramagnetic relaxation.[3] Rivkind[11] has verified Eq. (4) experimentally and demonstrated its correctness. The sign of the root in (3) is determined from the experimental frequency dependence of $\chi(\nu)$. The values of ρ_S calculated with Eq. (3) are plotted in Fig. 5 as functions of the concentration N of the magnetic ions for solutions of $MnCl_2$.

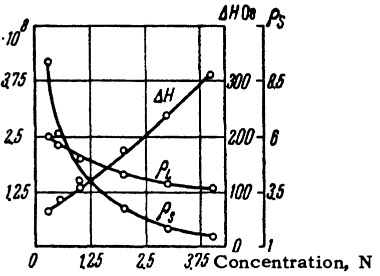

FIG. 5

The paramagnetic-resonance absorption line widths in perpendicular fields and the spin-spin and spin-lattice relaxation times are determined essentially by the same interactions. The line width ΔH and the relaxation times ρ_L and ρ_S are frequently[12] connected by the approximate relation

$$\Delta H \approx 1/\rho_S \mp 1/\rho_L. \tag{5}$$

We calculated ΔH by using the value of ρ_L at H = 0, the latter being obtained with the aid of the Brons-Van Vleck equation from the experimental value of $\rho_L(H)$. Figure 5 shows a comparison of the values of ΔH calculated with the foregoing formula (continuous line) and those obtained by measuring χ'' in perpendicular fields[11] [circles on the ΔH(N) curve] for aqueous solutions of $MnCl_2$.

Analogous calculations of ΔH were carried out also for solutions of manganese sulfate and nitrate. For low concentrations (≤ 1 N) the agreement between the calculated and the experimental values of ΔH is just as good as for solutions of manganese chloride. At high concentrations the discrepancy in the calculated values of ΔH reaches in some cases up to ~ 30%. This is not surprising, for actually the connection between ΔH and the relaxation time is much more complicated than that given by (5).

It is seen from the above that a study of the spin-lattice relaxation in liquid solutions of electrolytes also offers great possibilities for the investigation of the structure of these solutions.

In conclusion, we take this occasion to thank B. M. Kozyrev for guidance and continuous aid in this work and B. K. Silant'eva for participating in the experiments.

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[1] P. G. Tishkov, JETP **36**, 1337 (1959), Soviet Phys. JETP **9**, 949 (1959).

[2] C. J. Gorter, Paramagnetic Relaxation, Elsevier, N.Y., 1948.

[3] I. G. Shaposhnikov, Doctoral Dissertation, Phys. Inst. Acad. Sci., 1949.

[4] O. Ya. Samoĭlov, Структура водных растворов электролитов и гидратация ионов (Structure of Aqueous Solutions of Electrolytes and Hydration of Ions), Acad. Sci. Press, 1957.

[5] J. Beck, Phys. Z. **40**, 474 (1939).

[6] J. P. Mathieu and M. Lounsbury, Compt. rend. **229**, 1315 (1949).

[7] S. A. Al'tshuler and K. A. Valiev, JETP **35**, 947 (1959), Soviet Phys. JETP **8**, 661 (1959).

[8] B. M. Kozyrev, Doctoral Dissertation, Phys. Inst. Acad. Sci., 1957.

[9] B. M. Kozyrev, Izv. Akad. Nauk SSSR, Ser. Fiz. **21**, 828 (1957), Columbia Tech. Transl. p. 828.

[10] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

[11] A. I. Rivkind, Dissertation, Ural University, 1952.

[12] S. A. Al'tshuler and B. M. Kozyrev, Usp. Fiz. Nauk **63**, 533 (1957).

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