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MEASUREMENT OF SPIN-LATTICE RELAXATION TIME IN Mn^{++} SALT SOLUTIONS

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A Q-meter was used to measure the spin-lattice relaxation time and internal field parameters in certain Mn^{++} salt solutions. The spin-lattice relaxation time of $MnCl_2 \cdot 4H_2O$ in glycerin and water-glycerin solutions is satisfactorily described by the Casimir-Du Pré theory when allowance is made for spin-spin absorption, and is also in good agreement with the Brons-Van Vleck formula. The spin-lattice relaxation time is only slightly dependent on the paramagnetic salt concentration and on the viscosity of the solution.

1. APPARATUS AND METHOD OF MEASUREMENT

RELAXATION processes in paramagnetic substances can be investigated by measuring either the high-frequency susceptibility χ' or the absorption component χ'' .^{1,2} In the present work measurements of χ'' are obtained based on variations in the Q of the coil of the tuned oscillatory circuit. The relation between ΔQ and its cause χ'' is given by³⁻⁵

$$\Delta Q = -4\pi\eta\chi''Q^2. \quad (1)$$

Here Q is the figure of merit and η is the "filling" factor of the coil when occupied by the paramagnet. Equation (1) can be written more conveniently as^{3,4}

$$\Delta E = -4\pi\eta\chi''EQ, \quad (2)$$

where E is the voltage generated in the tuned circuit and ΔE is the variation of this voltage associated with χ'' .

Apparatus which measures Q can be used in two different ways to determine the spin-lattice relaxation time ρ_L in a paramagnetic: 1) by using measurements of χ'' (in absolute units according to (2) or in comparable relative units)

over a broad range of frequencies ν to construct $\chi''(\nu)$ curves for a given constant magnetic field H; 2) from measurements of χ'' at two frequencies using the equation of Casimir and Du Pré:¹

$$\chi'' = \chi_0 F \rho_L \nu / (1 + \rho_L^2 \nu^2), \quad F = H^2 / (b/c + H^2). \quad (3)$$

Here b/c is a constant which characterizes the internal magnetic field of the paramagnetic.

The basis of the two-frequency method of determining ρ_L is as follows. Writing (3) for a given constant magnetic field H_1 and using two values of the frequency ν , we obtain from (2) and (3)*

$$\rho_{H_1} = \sqrt{(k-1)/(\nu_2^2 - k\nu_1^2)}, \quad k = \Delta E_{\nu_1} E_{\nu_2} Q_{\nu_2} \nu_2 / \Delta E_{\nu_2} E_{\nu_1} Q_{\nu_1} \nu_1. \quad (4)$$

Here all quantities that determine ρ_{H_1} can be measured. The equation contains neither η nor the absolute value of χ'' , while only the first power of Q appears; the relaxation time is consequently measured more accurately.

It has been verified experimentally that a Q-meter can be used to determine spin-lattice relaxation times from measurements at two frequencies

*Yu. Ya. Shamonin was the first to point out that a commercial type KV-1 Q-meter could be used for oscilloscopic observation of paramagnetic resonance absorption curves.

No. of experiment	H, Oe	1200	1600	2000	2400	2800	3200	3600
1	$\rho_L \cdot 10^8$	1.1	1.45	1.7	2.1	2.45	2.7	3.1
2	$\rho_L \cdot 10^8$	1.4	1.7	1.95	2.3	2.7	2.9	3.15
3	$\rho_L \cdot 10^8$	1.4	1.65	1.85	2.15	2.5	2.75	3.05

according to (4). A Type KV-1 Q-meter fed from lead storage batteries was used to measure Q at several frequencies when a given paramagnet was within the coil. The coil and specimen of $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were placed in a static magnetic field which could be directed at will either parallel (H_{\parallel}) or perpendicular (H_{\perp}) to the coil axis. ΔE was measured in the fields H_{\parallel} and H_{\perp} at the same frequencies, a PPTV-1 potentiometer being used. Experiments with $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ at frequencies of 1, 1.5, 2 and 3 Mcs were repeated several times. ρ_L was calculated from the values of Q and ΔE in the field H_{\parallel} for each of the two frequencies; five values of ρ_L obtained in this way were averaged. The maximum deviation of ρ_L from its mean value was 3% and the results agreed to within 4% with Gorter's data.¹

Another manganese salt, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, was used in similar experiments at 3.5, 5.25, 7 and 10 Mcs. In this case the relaxation times agree almost as well as Kozyrev's results for paramagnetic absorption⁶ (5% deviation from the mean) and not quite so well with Gorter's results¹ for the dispersion of susceptibility. The values obtained for ρ_L were used to calculate b/c; good agreement was obtained with other writers^{1,7,8} for both of the salts. These experiments on $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ prove that it is possible to determine spin-lattice relaxation times in paramagnetic salts from (4), by means of the Q-meter, to within ~ 5%.

2. MEASUREMENTS ON GLYCERIN SOLUTIONS OF Mn^{++} SALTS

We also performed experiments to determine the possibility of applying the foregoing method to measure spin-lattice relaxation times and b/c in liquid solutions of paramagnetic salts.

Paramagnetic relaxation in liquid solutions of manganese salts was discovered by Zavoiskii in 1944.^{2*} The literature contains no further information on work of this type, although the study of paramagnetic relaxation times in electrolytic solutions is of considerable interest both for the theory of relaxation processes and for investigations

*A similar attempt by Teunisson and Gorter⁹ in 1940 was unsuccessful.

of the structure and molecular properties of solutions. We have therefore attempted to apply the procedure developed for solids to such solutions as well.

The investigation of paramagnetic absorption in electrolytic solutions is rendered difficult by large electric losses which exceed paramagnetic absorption by several orders of magnitude. We may expect, however, that the accuracy of χ'' (and thus of ρ_L) will be independent of electric losses in the Q-meter method, where ΔQ means the change of the coil figure of merit as a result of paramagnetic absorption alone and Q is taken when the electrolyte is within the coil.

Glycerin solutions of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were used in these experiments at 12, 21.5, 32 and 43 Mcs. Just as in the case of solid manganese salts the comparison method at selected frequencies was used to determine the Q of a coil around the solution contained in a cylindrical glass ampule. The dependence of ΔE on H_{\parallel} and H_{\perp} was also obtained. The $\Delta E(H_{\perp})$ curve was required in order to determine absorption at $H = 0$ and thus compute the loss resulting from the spin-spin interaction.^{1,10} Ampules of different lengths and diameters were used accompanied, of course, by different changes of Q resulting from electric losses.

The table gives the spin-lattice relaxation times calculated from (4) in three experiments on a glycerin solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (3.9 mole/liter). In the first two experiments, conducted under identical conditions, an ampule of 7 mm diameter and 4 mm length was used; at 43 Mcs, Q was reduced from 217 to 210 when the ampule was inserted into the coil. In the third experiment an ampule of 10 mm diameter and 19 mm length was used; Q dropped from 217 to 154 at 43 Mcs.

The large (~ 10%) spread of ρ_L in low fields H resulted from the smallness of the observed effect in such fields. Measurements and calculations for all solutions were performed in the same order as for the solid salts.

The values obtained for ΔE can be checked somewhat roughly by using the formula $\chi''_{\perp}(0) \Delta H / \chi_0 = \text{const}$, where ΔH is the half-width of the $\chi''(H_{\perp})$ curve and $\chi''_{\perp}(0)$ is the absorption factor for $H_{\perp} = 0$. This equation has frequently been tested on solid paramagnets.¹¹ For our measure-

ments on glycerin solutions it is accurate to within $\sim 10\%$.

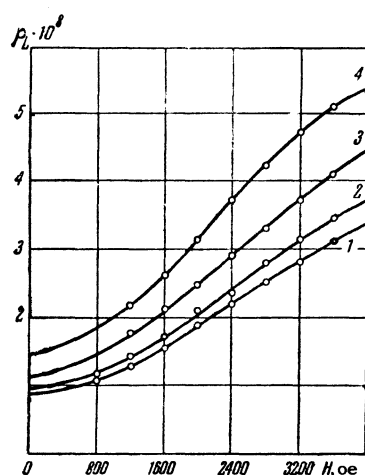
The example described above indicates that it is possible to use the procedure in question for measurements of spin-lattice relaxation times in liquid solutions of paramagnets with an accuracy of $\sim 5\%$.

Glycerin solutions of $MnCl_2 \cdot 4H_2O$ were investigated at concentrations of 3.9, 1.8, 0.9, 0.45 and 0.225 mole/liter. The relaxation times ρ_L were used to determine b/c for all concentrations by means of the formula

$$b/c = (H_2^2 - AH_1^2) / (A - 1),$$

$$A = \Delta E_{H_1} H_2^2 \rho_{LH_2} (1 + \rho_{LH_1}^2 \nu^2) / \Delta E_{H_2} H_1^2 \rho_{LH_1} (1 + \rho_{LH_2}^2 \nu^2),$$

which is easily obtained from the spin-lattice relaxation theory.¹ The spread in the values of b/c was 7–10%.



Curve 1— $C=3.9$ mole/liter; $b/c=2.5 \times 10^6$ oe^2 ; $\rho_0=0.88 \times 10^{-8}$ sec; $p=0.147$ Curve 2— $C=1.8$ mole/liter; $b/c=2.4 \times 10^6$ oe^2 ; $\rho_0=0.95 \times 10^{-8}$ sec; $p=0.15$ Curve 3— $C=0.9$ mole/liter; $b/c=2.27 \times 10^6$ oe^2 ; $\rho_0=1.14 \times 10^{-8}$ sec; $p=0.155$ Curve 4— $C=0.45$ mole/liter; $b/c=2.1 \times 10^6$ oe^2 ; $\rho_0=1.5 \times 10^{-8}$ sec; $p=0.17$

The figure compares the experimental values of $\rho(H)$ (points on the curve) with the theoretical (continuous) curves of $\rho_L(H)$ plotted according to the Brons-Van Vleck equation for all of the investigated concentrations:

$$\rho_L = \rho_0 \frac{b/c + H^2}{b/c + pH^2},$$

where ρ_0 is the spin-lattice relaxation time for $H=0$ and p is a constant. The experimental value of ρ_L for concentration $c=0.225$ mole/liter does not differ within the limit of error from that for $c=0.45$ mole/liter.

An analysis of the experimental values of ρ_L given in the figure shows that the theory of Casi-

mir and Du Pré correctly describes paramagnetic relaxation in glycerin solutions of manganese and that the Brons-Van Vleck equation can be used for such solutions.

The results obtained with solutions of $MnCl_2 \cdot 4H_2O$ indicate that it is possible to investigate the dependence of ρ_L and b/c on the composition of the solvent (water-glycerin mixture) and on the amount of diamagnetic salt that is added. The first of such experiments determines the dependence of ρ_L and b/c on the viscosity of the solutions; the second experiment determines the dependence of the same quantities on magnetic dilution with approximately invariant electrical interactions in the solutions. These experiments were performed with a 2 mole/liter concentration of $MnCl_2 \cdot 4H_2O$ and the following percentages of water by weight in the solvent: 0.6, 5.5, 10.6, 20.6, 40.6, 55.6, 70.6, 85.6 and 100%. The viscosity measured by a Höppler viscometer at 20°C varied monotonically from 3950 centipoise for a glycerin solution to 1.95 centipoise for an aqueous solution. When the viscosity is reduced by a factor of 2000 the relaxation time decreases by a factor of only about 3. For example, when $H=3600$, ρ_L decreases from 4.4×10^{-8} to 1.4×10^{-8} sec. b/c , which for a solution of $MnCl_2 \cdot 4H_2O$ in water equals 1.8×10^6 oe^2 , increases to 5×10^6 oe^2 as glycerin is added. $b/c=5 \times 10^6$ oe^2 corresponds to the presence of equal numbers of moles of glycerin and $MnCl_2 \cdot 4H_2O$ in the solution. With further increase of the glycerin content b/c decreases to 2.5×10^6 oe^2 (for a pure glycerin solution). This dependence of b/c on the composition of the solvent can be attributed to the presence of mixed water-glycerin solvate envelopes around manganese ions which decrease the electric field symmetry at the ions.

To study the dependence of ρ_L on magnetic dilution without changing the electrical conditions, experiments were performed on a solution of $MnCl_2 \cdot 4H_2O$ at a concentration of 0.45 mole/liter with the addition of 1.35 mole/liter of $CaCl_2 \cdot 4H_2O$. The relaxation times ρ_L are in good agreement with the Brons-Van Vleck formula for $\rho_0=1.4 \times 10^{-8}$ sec, $p=0.236$ and $b/c=2.35$ oe^2 .

A more detailed description of the experiments on $MnCl_2 \cdot 4H_2O$ in water-glycerin solutions, and also when a diamagnetic salt is added, will be published elsewhere together with a discussion of the results.

In conclusion I take this opportunity to thank B. M. Kozyrev for directing and assisting with this work, and V. I. Avvakumov for participating in a discussion of the results.

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