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ELECTRON PARAMAGNETIC RESONANCE AND PARAMAGNETIC RELAXATION IN LIQUID AND SUPERCOOLED SOLUTIONS OF Ti^{+++} *SALTS*

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Electron paramagnetic resonance measurements in alcohol and glycerine solutions of the salts $TiCl_3 \cdot 6H_2O$ and $Ti_2(SO_4)_3 \cdot 4H_2O$ were carried out at frequencies 300 — 9460 Mc/sec and at temperatures of 300°, 200° and 77°K. Symmetric lines with ΔH dependent on the solvent and on the concentration of the solution were observed in supercooled solutions at a frequency $\nu = 300$ Mc/sec. Broad asymmetric lines due to the asymmetry of the g-factor were observed at a frequency of 9460 Mc/sec. The values of $g_{\|}$ and $g_{\perp}$ have been determined for supercooled glycerine and alcohol solutions. Narrow symmetric lines have been observed in dilute liquid solutions. Relaxation measurements in parallel fields were also carried out at frequencies of 300, 17, and 6 Mc/sec. The order of magnitude of the spin-lattice relaxation time, ρ_l, has been estimated, and it has been found that ρ_l depends both on the solvent and on the concentration of the solution.

1. INTRODUCTION

TRIVALENT titanium salts are among the paramagnetic compounds of elements of the iron group which have received very little study. This is related to the fact that the spin-lattice relaxation time has turned out to be very short in the majority of the Ti^{+++} salts that have been investigated. Therefore in the work of Bleaney et al.[1] electron paramagnetic resonance (e.p.r.) could be successfully observed in a single crystal of titanium cesium alum only at T = 4.2 — 2.5°K with $g_{\|} = 1.25$ and $g_{\perp} = 1.14 \pm 0.02$.

Bijl[2] has also investigated e.p.r. in powdered samples of the same alum at helium temperatures. The effective g-factor for the powders has turned out to depend on the temperature: $g_{eff} = 1.35$ at T = 6.33°K and $g_{eff} = 1.53$ at T = 7.88°K.

Wong[3] has made measurements of e.p.r. in a single crystal of $(TiAl)Cl_3 \cdot 6H_2O$ at liquid hydrogen and helium temperatures as a function of the concentration of Ti^{+++}. He has observed a symmetric line of width ~ 100 oe with an isotropic g-factor equal to 1.93 ± 0.02. It turned out that the line width does not depend strongly on the temperature and was ascribed by the author to the accidental inhomogeneities of the crystalline field. In the paper by Bowers and Owen[4] an investigation was made of e.p.r. in $KTi(C_2O_4)_2 \cdot 2H_2O$ at T = 90 — 20°K. Measurements have shown that $g_{\|} = 1.86$ and $g_{\perp} = 1.96$.

Finally, Jarrett[5] has, for the first time, found in $Ti[(CH_3CO)_2CH_3]_2$ at room temperature, paramagnetic resonance absorption which is due to the presence in this compound of a strong axial crystalline field. The values of $g_{\|} = 2$ and $g_{\perp} = 1.93$ were obtained.

It should also be pointed out that titanium cesium alum was the object of theoretical investigations[6,7] in which the mechanism of spin-lattice relaxation in magnetically diluted paramagnetic crystals was elucidated for the first time.

We have observed e.p.r. both in liquid glycerine and alcohol solutions of $TiCl_3 \cdot 6H_2O$, and also in the supercooled state at temperatures of 77 and 200°K. Investigation of e.p.r. in these solutions was carried out at 300 and 9460 Mc/sec.

In addition we have also carried out relaxation measurements (by the parallel field method) in supercooled solutions at 77°K. The method of carrying out these measurements has been described in an article by one of the present authors.[8] Finally, we have made an attempt to study by the e.p.r. method the pyridine complexes of Ti^{+++}, and also samples of silicate and borate glasses containing titanium compounds.

2. RESULTS OF MEASUREMENTS

1. $\nu = 300$ Mc/sec. As is well known, the majority of the investigated compounds of Ti^{+++} possess a strongly anisotropic g-factor. This

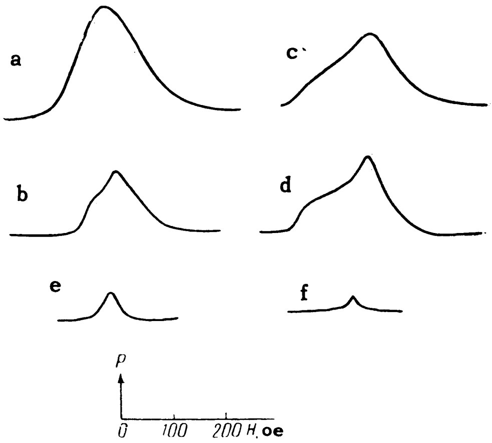
Table I

Concentration of solution, mole/liter	ΔH, oe			Concentration of solution, mole/liter	ΔH, oe		
	77 °K	200 °K	295 °K		77° K	200° K	295° K
Glycerine solution of $TiCl_3 \cdot 6H_2O$				Alcohol solution of $TiCl_3 \cdot 6H_2O$			
2	54	60	—	1	63	—	—
1	32	35	—	0,5	35	—	20
0.5	17	18	—	0,25	27	—	10
0,25	14	17	10	0,1	17	—	10
0,1	13	16	10	0,05	16	—	10
0,01	13	16	10	0,01	16	—	10

leads to the result that when e.p.r. is measured in polycrystalline samples in the microwave frequency range the form of the resonance line is primarily determined by the anisotropy of the g-factor. Therefore, we have carried out investigations of the concentration and the temperature dependence of the line at $\nu = 300$ Mc/sec.

Table I shows the dependence of the line width ΔH on the concentration of Ti^{+++} in different solvents at three different temperatures (the line width ΔH has been measured between the points on the absorption curve corresponding to half of the maximum intensity). The value of the g-factor is everywhere equal to 1.9 ± 0.1.

As can be seen from the table, ΔH in supercooled solutions falls off rapidly as the concentration is diminished and tends to a constant value independent of the concentration. It should be noted that in 2 mole/liter glycerine and in 1 mole/liter alcohol supercooled solutions there exists at 77°K zero-field absorption $\chi''(H = 0)$. The intensity of this zero-field absorption falls off rapidly both as the frequency ν is increased and as the concentration is diminished.



E.p.r. lines for solutions of $TiCl_3 \cdot 6H_2O$ at a frequency of 9460 Mc/sec. The supercooled state (77°K) of the solution in glycerine of concentration: a) 2 mole/liter, b) 0.05 mole/liter; in alcohol: c) 1 mole/liter, d) 0.05 mole/liter. The liquid state of the solution (295°K) in glycerine: e) 0.25 mole/liter; in alcohol: f) 0.25 mole/liter

The line width is greater in supercooled alcohol solutions than in glycerine solutions. In going over from the supercooled state to the liquid state the intensity of the e.p.r. line diminishes strongly. At the same time for low concentrations the line width becomes somewhat narrower.

2. $\underline{\nu = 9460 \text{ Mc/sec}}$. In supercooled alcohol and glycerine solutions of $TiCl_3 \cdot 6H_2O$ there is observed at 77°K a wide asymmetric e.p.r. line with an unresolved second absorption maximum (cf. diagram, a, b, c, d). As the concentration of the magnetic ion is decreased the asymmetry of the line increases, although the line width diminishes slightly at the same time. The values of $g_{\parallel}$ and $g_{\perp}$ determined from the experimental e.p.r. curves (at $\nu = 9460$ Mc/sec) are shown in Table II.

Table II

$g_{\parallel}$	$g_{\perp}$	g_{eff}
77 °K		290 °K
Glycerine solution of $TiCl_3 \cdot 6H_2O$		
1.99	1.93	1.95
Alcohol solution of $TiCl_3 \cdot 6H_2O$		
2.00	1.90	1.94

As can be seen from this table, the anisotropy of the g-factor in supercooled alcohol solutions is greater than in glycerine solutions. As the temperature is increased the line widths and the asymmetry of the curves in supercooled solutions diminish, and when the liquid state is reached symmetric and fairly narrow lines are observed (cf. diagrams e and f).

At the same time it should be noted that in liquid alcohol solutions a line with ΔH = 10 oe is observed for 0.25 mole/liter at T = 295°K both at 9460 Mc/sec, and at 300 Mc/sec, while in a glycerine solution at the same temperature and concentration the line width depends on the frequency: ΔH = 50 oe at $\nu = 9460$ Mc/sec and ΔH = 10 oe at $\nu = 300$ Mc/sec. As the temperature is increased above room temperature (~400°K) the frequency dependence disappears, and the line width decreases and becomes equal to ΔH = 10 oe. Finally, in pyridine complexes fairly broad lines are observed, whose asymmetry is considerably greater than in alcohol supercooled solutions. We have not succeeded in observing e.p.r. in silicate and borate glasses containing titanium compounds.

Also we have not succeeded in observing resonance absorption in aqueous solutions of $TiCl_3 \cdot 6H_2O$ and $Ti_2(SO_4)_3 \cdot 4H_2O$.

3. Relaxation measurements in parallel fields. At a frequency of 300 Mc/sec one can observe the absorption $\chi''_s(H)$ due to spin-spin relaxation in a 2-molar glycerine solution of $TiCl_3 \cdot 6H_2O$ at 77°K. As the concentration of the solution is decreased by only a factor of two the intensity of this absorption practically falls to zero. Such a rapid decrease in the intensity of $\chi''_s(H)$ can be explained by the disappearance of the "zero-field absorption" $\chi''(H = 0)$. At a frequency of 17 Mc/sec at 77°K the form of the relaxation depends on the concentration of the solution: from 2 to 1.5 mole/liter inclusive the absorption $\chi''_l(H)$ due to spin-lattice relaxation is observed, while from 1.5 to 0.1 mole/liter the absorption $\chi''_s(H)$ due to spin-spin relaxation is observed.

At a frequency of 6 Mc/sec in these supercooled solutions, the absorption $\chi''_l(H)$ is observed over the greater range from 2 to 0.05 mole/liter, while $\chi''_s(H)$ occurs in solutions of concentrations from 0.5 to 0.1 mole/liter. Thus, the domain of spin-spin relaxation depends on the concentration of the magnetic ions: the lower the concentration the lower the frequencies at which the absorption $\chi''_s(H)$ is observed.

Moreover, the shape of the curves $\chi''_l(H)$ and $\chi''_s(H)$ also depends on the concentration: the lower the concentration of the magnetic ions, the lower the values of H at which $\chi''_s(H)$ and $\chi''_l(H)$ cease to depend on the intensity of the constant magnetic field. For those concentrations of the supercooled solutions of $TiCl_3 \cdot 6H_2O$ which we have investigated, the curves of $\chi''_s(H)$ are described by Shaposhnikov's theory, while the curves of $\chi''_l(H)$ are described by the theory of Casimir and Du Pre.[10]

Finally, it should be noted that the curves of $\chi''_s(H)$ for alcohol solutions at 77°K are observed at higher frequencies than in glycerine solutions of corresponding concentrations at the same temperature.

3. DISCUSSION OF RESULTS

At a frequency of 300 Mc/sec the e.p.r. line in concentrated glycerine and alcohol solutions has at 77°K a Gaussian shape and, as has already been noted, its width ΔH depends on the concentration. Therefore the ΔH of the e.p.r. curves in these solutions is due to dipole-dipole magnetic interactions. This assumption is also supported by the very weak dependence of ΔH on T in the temperature range 200 – 77°K.

In dilute solutions the width ΔH which does not depend on the concentration is due to the anisotropy of the g-factor and to the contribution of the magnetic moments of the protons from molecules of the immediate surroundings. Moreover, the insignificant increase in ΔH of dilute supercooled solutions as the temperature is raised from 77 to 200°K indicates that spin-lattice relaxation makes a contribution to ΔH in accordance with the relation

$$\Delta H \sim 1/\rho_s + 1/\rho_l.$$

A decrease in the line width in the transition from a supercooled solution to the liquid state is due to the influence of motion. In liquid alcohol and glycerine solutions the intensity of the e.p.r. line is very low in spite of the narrowness of the absorption curves. This can be explained by the presence in liquid solutions of two types of Ti^{+++} ions: Ti^{+++} ions whose crystalline electric field has a high symmetry, and ions in which the crystalline field has a sufficiently strong component of low symmetry that is not averaged out by motion. Therefore e.p.r. in liquid solutions is due only to Ti^{+++} ions of the latter type. In aqueous solutions of Ti^{+++} salts only electric fields of the first type are present.

At a frequency of 9460 Mc/sec the shape of the e.p.r. curves in the supercooled state is typical of ions with a strongly anisotropic g-factor.[11]

As can be seen from the figure, in concentrated glycerine solutions in the supercooled state the line is more symmetric than in alcohol and in dilute glycerine solutions. This is explained by the fact that in a 2-molar glycerine solution the width due to the magnetic dipole-dipole interactions dominates over the width associated with the anisotropy of the g-factor.

The frequency dependence of ΔH in liquid glycerine solutions at room temperature referred to previously is explained by the fact that, owing to the high value of the viscosity, the frequency of rotation of the "magnetic complex" formed with the immediate surroundings is lower than the Larmor precession frequency. Therefore, at this frequency the line width is due to the anisotropy of the g-factor.

As the temperature is raised the average frequency of rotation of the "magnetic complex" increases, and the g-factor takes on the averaged effective value $g_{\text{eff}} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$. In this case the e.p.r. line is described by the following spin-Hamiltonian:

$$\mathcal{H} = \sum_{i=1}^{N} g\beta H S_{zi} + \Delta g\beta H \left(\cos^2\theta_i - \tfrac{1}{3}\right) S_{zi} + \tfrac{1}{2}\Delta g\beta H \sin\theta_i \cos\theta_i \cdot [S_{+i} + S_{-i}],$$

where $g = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$ and $\Delta g = g_{\parallel} - g_{\perp}$.

One of the present authors[12] has shown earlier that the constant b of the magnetic specific heat of the spin-system is related to the half width $\Delta H_{\parallel}$ of the $\chi_s''(H)$ curves by the expression

$$b = C(1 + \sqrt{2})\Delta H_{\parallel}, \quad (1)$$

where C is the Curie constant. It follows from the results of our relaxation measurements that as the supercooled solutions of Ti^{+++} are made more dilute the half width $\Delta H_{\parallel}$ of the $\chi_s''(H)$ curves decreases to a very small value. Therefore, according to relation (1) the constant b will also diminish. Such a decrease in the constant b is explained by the fact that for compounds of Ti^{+++} with $S = \frac{1}{2}$ the specific heat of the spin-system will be determined only by the value of the dipole-dipole magnetic interactions.[8]

The displacement of spin-spin relaxation into the low frequency region as the concentration is diminished indicates an increase in the spin-lattice relaxation time which could be explained by means of the heat reservoirs proposed by Bloembergen and Wang[13-15] if exchange interaction existed at the high concentrations utilized by us. However, this assumption is untenable since in concentrated solutions in parallel fields narrow relaxation curves $\chi_s''(H)$ are observed.[16]

The absence of exchange is also confirmed by the fact that as the solution is made more dilute the e.p.r. lines become narrower, while they should have a tendency to become more broad. It is therefore possible that the variation of ρ_l with concentration is related to the existence of cross-relaxation effects[17] in the concentrated supercooled solutions.

Relaxation measurements (at 77°K) have also enabled us to estimate the order of magnitude of ρ_l and the dependence of ρ_l on concentration and on solvent. It has turned out that for a 2 mole/liter glycerine solution the value is $\rho_l \sim 5 \times 10^{-8}$ sec and for 0.1 mole/liter the value is $\rho_l \sim 5 \times 10^{-7}$ sec. In alcohol solutions the value of ρ_l is smaller by approximately an order of magnitude than in glycerine solutions. This result is in good agreement with the estimated value of the splitting of the lowest orbital triplet Δ due to the axially symmetric field; an estimate of Δ for the supercooled glycerine and alcohol solutions may be obtained from a comparison of the theoretical and the experimental values of the g-factor.

Indeed, for a field possessing trigonal symmetry $g_{\parallel} = 2.0$, $g_{\perp} = 2(1 - 3\lambda/\Delta)$, where $\lambda = 154\ \text{cm}^{-1}$ is the spin-orbit coupling constant. From this by utilizing the data of Table II we obtain $\Delta \sim 15000\ \text{cm}^{-1}$ for glycerine solutions and $\Delta \sim 9000\ \text{cm}^{-1}$ for alcohol solutions. On the other hand, in accordance with reference 7 we have $\rho_l \sim \Delta^4$. Therefore, assuming that the other parameters determining ρ_l do not vary significantly when the solvent is replaced, we obtain

$$\rho_{l\,\text{glycerine}} / \rho_{l\,\text{alcohol}} \approx (\Delta_{\text{glycerine}} / \Delta_{\text{alcohol}})^4 \approx 7.8,$$

as is observed experimentally. The absence of e.p.r. in silicate and borate glasses indicates that in the glasses titanium has a valence of four, since the symmetry of the electric field in the glasses does not differ significantly from the electric field in the supercooled solutions.

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