SOVIET PHYSICS

JETP

A translation of the Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki.

Vol. 15, No. 5, pp. 791-991 (Russ. orig. Vol. 42, No. 5, pp. 1145-1429, May 1962) November 1962

ELECTRON PARAMAGNETIC RESONANCE IN DILUTE VANADYL CHLORIDE SOLUTIONS

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Submitted to JETP editor November 9, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) **42**, 1145-1148 (May, 1962)

The EPR hyperfine line half-width δH of the VO^{2+} ion in liquid solutions was studied at 9320 Mc as a function of the temperature and viscosity of the solvent. It is shown that although the variation of δH with the nuclear spin projection m_I can be accounted for by the McConnell relaxation mechanism, the temperature dependence of δH indicates that some other mechanism is dominant.

WE have previously [1] reported measurements of electron paramagnetic resonance in highly concentrated solutions of vanadyl chloride ($VOCl_2$) at 9320 Mc. It is important to investigate EPR in dilute solutions of the same salt as a check on McConnell's relaxation mechanism. [2,3] Rogers and Pake [4] have recently shown that Kivelson's formulas [3] are a good description of the way in which line widths in the hyperfine structure of EPR for a dilute $VOCl_2$ solution depend on the Larmor frequency ω_0. The theoretically predicted dependence of these widths on the temperature and viscosity of the solution was not checked experimentally. In the present work we have studied mainly the temperature dependence of EPR line shape for dilute solutions of $VOCl_2$ in different solvents at temperatures ranging from ~ 20° to ~ 80°C. A standard microwave spectrometer (RÉ-1301) was used at 9320 Mc.

In aqueous $VOCl_2$ solutions at room temperature resolution of hyperfine peaks begins at the concentration $c(VOCl_2) \approx 1$ mole/liter. At $c \approx 0.1$ mole/liter complete resolution of the hyperfine structure begins; the widths of individual peaks decrease somewhat with dilution down to $c \approx 0.02$ mole/liter, but are unaffected by further dilution. All the experimental data reported below were therefore obtained at 0.02 mole/liter. The VO^{2+} spectrum for low concentrations is characterized by asymmetry of each hyperfine peak and by a dependence of the peak width on the nuclear spin projection m_I. [1,4]

The evident asymmetry of individual hyperfine peaks for aqueous solutions of vanadyl chloride was first noted by Rogers and Pake. [4] This asymmetry can have two causes. First, it can result from the incomplete averaging of the anisotropy parameters of the spin Hamiltonian due to the Brownian motion of the liquid; second, it can result from appreciable electric conductivity of the solution. It has been shown in [5] that in conducting media the effective coefficient of paramagnetic absorption is a linear combination of χ'' and χ' when the penetration depth of the microwave field is much less than the thickness of the specimen. The nature of the asymmetry was not conclusively determined in [4].

We have measured EPR in an aqueous solution containing 0.02 mole/liter of $VOCl_2$ in glass capillary tubes of different diameters. With decreasing diameter the asymmetry of individual hyperfine lines became weaker and finally disappeared. It follows that the asymmetry is caused by the electric conductivity of the solution and not by incomplete averaging of the parameters. The same conclusion resulted from a study of line shapes for

Solvent	Acetone		Water		Methanol		Ethanol		Propanol	
t, °C	22	80	22	73	22	78	22	65	22	68
a_1	13.7	12.8	16.1	13.4	17.1	13.2	24.7	16.4	22.6	13.1
a_2	—0.16	0	—1.29	—0.57	—1.29	—0.65	—2.2	—1.6	—2.0	—0.3
a_3	+0.22	0	0.43	0.21	0.44	0.21	1.4	0.9	1.6	0.26
a_2/a_3			—3,00	—2.71	—2,93	—3,10	—1.57	—1.77	—1.25	—1,15

VOCl$_2$ in different solvents. Decreased electric conductivity is accompanied by increasing line symmetry for a given capillary diameter. All measurements discussed below were obtained under the conditions when the hyperfine line shapes were symmetrical.

According to [4] the width of hyperfine lines is given by

$$\delta H = a_1 + a_2 m_I + a_3 m_I^2, \qquad (1)$$

where

$$a_1 = \tau_c \left\{ \tfrac{7}{45} (\Delta g \beta H \hbar^{-1})^2 + \tfrac{1}{4} I(I+1) b^2 \right\} + K,$$

$$a_2 = -7\tau_c b \beta H \Delta g / 15\hbar, \quad a_3 = \tau_c b^2/10;$$

$$\Delta g = g_{\parallel} - g_{\perp}, \quad g = (g_{\parallel} + 2g_{\perp})/3, \quad b = \tfrac{2}{3}(A - B)/\hbar. \qquad (2)$$

Here H is the external constant magnetic field; $g_{\parallel}$ and $g_{\perp}$ are the components of the anisotropy g tensor; A and B are the hyperfine interaction constants; τ_C is the characteristic time of the correlation function of rotational Brownian motion $\exp(-|\tau|/\tau_C)$; m_I is the projection of the nuclear spin. Thus a_1, a_2, and a_3 are coefficients determining the width of each hyperfine line and are associated with the anisotropy parameters Δg and b of the spin Hamiltonian of VO^{2+}. In addition, a_1 takes into account the contribution K to the half-width δH from other relaxation mechanisms that are insensitive to the nuclear spin orientation. The mechanism suggested by Al'tshuler and Valiev [6] is the most probable cause of this line broadening.

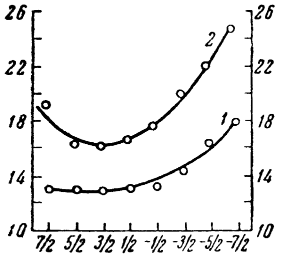

FIG. 1. Hyperfine half-widths δ H (denoted by circles) for VO^{2+} in methanol for different nuclear spin projections m_I at 1 – t = 78°C and 2 – t = 22°C.

Figures 1 and 2 show typical relations between the hyperfine half-widths δH and m_I. The half-width δH was measured between the minimum and maximum of the first derivative of the absorption curve.

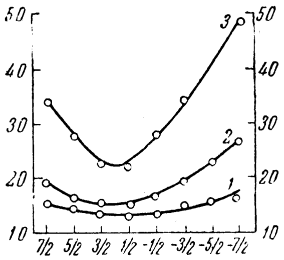

FIG. 2. Values of δH for solutions of vanadyl chloride in 1 – acetone, 2 – water, 3 – isopropanol. (t = 22°C).

Increasing temperature and the associated reduction of viscosity lead to the single result that the dependence of δH on m_I is weakened. These and similar experimental data were used to determine the coefficients a_1, a_2, and a_3 in the table.

According to [2-4], we can expect a reduction of the coefficients a_2 and a_3 with increasing temperature (or with reduced viscosity) because of a shortened correlation time τ_C. It also follows from these investigations that the ratio a_2/a_3 is independent of both the temperature and viscosity when the condition $\omega_0^2 \tau_C^2 \ll 1$ is satisfied. This condition holds true for all our solutions. The table shows that these conclusions are confirmed experimentally within the limits of accuracy.

It is also noteworthy that the temperature dependence of a_1 is considerably weaker than that of either a_2 or a_3. This proves the dominant role of K, i.e., of a relaxation mechanism different from the McConnell mechanism, in a_1, and therefore in the portion of the hyperfine half-width that is independent of nuclear spin orientation.

A similar result was obtained in [5] from measurements of nuclear relaxation times associated with electron paramagnetic relaxation in VO^{2+} solutions. In principle these indirect measurements cannot, of course, reveal differences in hyperfine line widths. Nevertheless, the observed relations enable us to determine the dominant mechanism of electron paramagnetic relaxation; according to our data this was not the McConnell mechanism.

We note that the dependence of a_1, a_2, and a_3 on the particular solvent cannot be interpreted only through the differences in viscosity. This is obvious for the Al'tshuler-Valiev mechanism. For the McConnell mechanism also, in addition to the difference in viscosity the local electric fields acting on the magnetic ion are important since they determine Δg and b.

It must be mentioned in conclusion that in some $VOCl_2$ solutions (in glycerin at 22°C, in propanol at 0°C etc.) when the viscosity is too high to permit complete averaging of the anisotropy parameters of the spin Hamiltonian, i.e., when

$$\frac{\Delta g \beta H}{\hbar} \tau_c \gg 1 \quad \text{and} \quad b\tau_c \gg 1,$$

a double hyperfine structure is observed, similar to that found in glasses.[7]

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Translated by I. Emin
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