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HYPERFINE STRUCTURE OF THE EPR LINES OF THE V^{50} *AND* V^{51} *ISOTOPES*

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The isotropic and anisotropic hyperfine structure of the EPR lines in liquid and supercooled solutions of VOF_2 and $VOCl_2$ compounds in concentrated hydrofluoric and hydrochloric acids, due to the V^{50} and V^{51} isotopes, is studied at a frequency $\nu = 9320$ Mc/s and at temperatures 295 and 77°K. The isotropic and anisotropic hyperfine structure constants (2) and (4) are determined and the results are qualitatively compared with the theory.

In 1952 two groups of workers [1,2] first investigated, almost simultaneously, the isotropic hyperfine structure (hfs) of the electron paramagnetic resonance (EPR) of the isotope V^{50}, and found its spin to be $I = 6$. Their results were analyzed in greater detail somewhat later [3].

The measurements were made in the centimeter radio band using magnetically dilute single crystals $V(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $K_4V(CN)_6 \cdot 3H_2O$, enriched to 23 and 20 per cent V^{50}, respectively. In these cases the ion $V^{2+}(3d^3)$ is in a state $^4F_{3/2}$ and has an effective electron spin $S = 3/2$.

The spectra obtained against the background of strong hfs lines of V^{51} ($I = 7/2$) disclosed some weak hyperfine components of V^{50}. The intensity ratio of the V^{50} and V^{51} lines was approximately 1 : 5, almost coinciding with the calculated value.

As a net result there was also obtained the ratio of the isotropic nuclear g factors[1] $g^{50}/g^{51} = 0.3792 \pm 0.0008$, which is equivalent to the ratio of the hfs constants. The absolute value of the splitting of the hfs components of V^{50} was estimated in one particular case for the lines corresponding to the nuclear spin projections $m_I = +1$ and $m_I = +2$, and is equal to 35 Oe.

In the present study we investigated the isotropic and anisotropic hfs of the EPR lines of the ion V^{4+} in liquid and supercooled solutions. The measurements were made with a type RÉ 13-01 double modulation radio spectroscope at $\nu = 9320$ Mc/s in VOF_2 and $VOCl_2$ compounds enriched to 26 per cent V^{50}. The desire to obtain the spectrum of this isotope with best resolution has caused us to employ as solvents 20 per cent hydrogen fluoride (paraffinized capillaries were used) and 30 per cent hydrochloric acid.

The EPR spectrum obtained at room temperature from the hydrochloric solution of VOF_2 is shown in Fig. 1. The spectrum consists of superimposed isotropic hfs of the isotopes V^{50} and V^{51}, and is described by an isotropic spin Hamiltonian

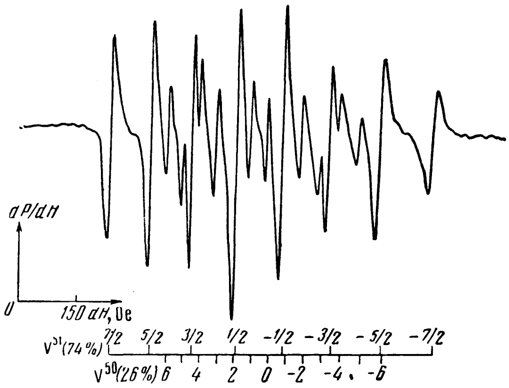

FIG. 1. Hfs of the EPR lines of the VO^{2+} ion in hydrofluoric acid (concentration ~ 0.05 mole/liter relative to $VOCl_2$) due to the nuclei V^{50} and V^{51}; T = 295°K.

$$\mathcal{H} = g\beta H_0 S_z + A\,(I_x S_x + I_y S_y + I_z S_z) \qquad (1)$$

with

$$S = 1/2, \quad I^{51} = 7/2, \quad I^{50} = 6, \quad A^{51} = 116 \pm 3\text{Oe},$$
$$A^{50} = 44 \pm 3\text{Oe}, \quad g = 1{,}968 \pm 0{,}002. \qquad (2)$$

As can be seen from Fig. 1, the widths δH (interval over the field between the minimum and maximum of the first derivative of the absorption curve) of the well resolved hfs lines from V^{50} with nuclear spin projection $m_I = 0, +1, +3$, and $+6$ are narrower than the widths of the narrowest

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[1] The superscripts 50 and 51 denote everywhere that the parameter in question pertains to V^{50} or V^{51} respectively.

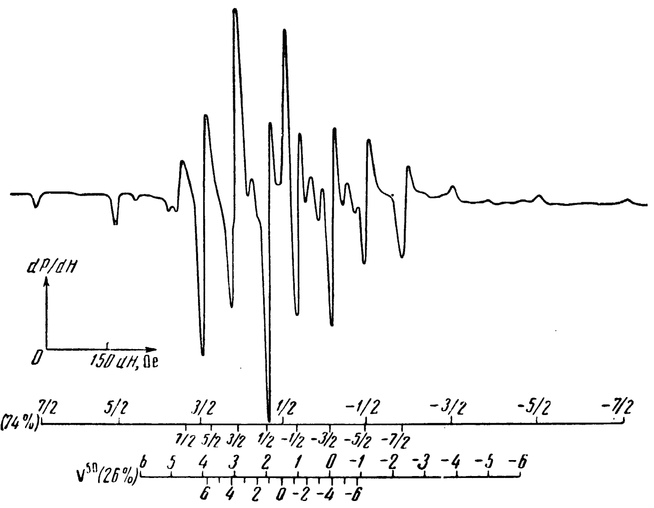

FIG. 2. Hfs of the EPR lines of the VO^{2+} ion in hydrochloric acid (concentration ~ 0.02 mole/liter relative to VOF_2), due to the nuclei V^{50} and V^{51}; T = 77°K.

lines with $m_I = \pm 1/2$ for the isotope V^{51} [4,5].

In the supercooled hydrochloric solution $VOCl_2$ at liquid-nitrogen temperature there is observed a complicated EPR spectrum (Fig. 2) consisting of four partially overlapping isotropic hyperfine structures of V^{51} and V^{50}. It is represented for the case of axial symmetry by a spin Hamiltonian

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y) \qquad (3)$$

with values

$$S = {}^1/_2, \qquad I^{51} = {}^7/_2, \qquad I^{50} = 6;$$

$$A_{\parallel}^{51} = 202 \pm 10\,\text{Oe}, \qquad A_{\perp}^{51} = 76 \pm 5\,\text{Oe};$$

$$A_{\parallel}^{50} = 78 \pm 5\,\text{Oe}, \qquad A_{\perp}^{50} = 31 \pm 5\,\text{Oe};$$

$$g_{\parallel} = 1.93 \pm 0{,}01, \qquad g_{\perp} = 2.00 \pm 0.01. \qquad (4)$$

Comparing the values of the anisotropic constants $A_{\parallel}$ and $A_{\perp}$, which we obtained experimentally from this spectrum, with the averaged isotropic hyperfine structure constant $A = (A_{\parallel} + 2A_{\perp})/3$ determined above (observed in liquid solutions of paramagnets which have a ground state ^2D and low viscosity) we find that the constants $A_{\parallel}$ and $A_{\perp}$ for the isotopes V^{50} and V^{51} are both positive.

As is well known, the orbital levels of the ion V^{4+} are similar to the levels of Ti^{3+}, and these ions have a ground state ^2D. In our vanadyl solutions the magnetic ion V^{4+} is in an octahedral field produced by five molecules of the solvent and an oxygen atom with strong axial component along the bond axis $(V = O)^{2+}$. The cubic field of the octahedron splits the fivefold orbital level of the $3d^1$ electron into an upper doublet and a lower triplet. The field of the axial symmetry causes in turn a splitting of the orbital triplet into a lower singlet and an upper doublet.

The relaxation mechanism of the EPR lines in supercooled acid solutions, i.e., glasses containing $(V = O)^{2+}$, can be interpreted on the basis of the theory proposed by Van Vleck for titanium cesium alum [6]. In this case the spin lattice relaxation time is $T_1 \sim \Delta^6$ where Δ is the splitting of the lower orbital triplet.

According to Rogers [7] and Kivelson [8], each hfs line corresponding to the transition $-1/2, m_I \longleftrightarrow 1/2, m_I$ has a Lorentz shape with width

$$\delta H = a_1 + a_2 m_I + a_3 m_I^2,$$

where

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

$$a_2 = -\tfrac{7}{15} b\, (\Delta g \beta H \hbar^{-1})\, \tau_c, \qquad a_3 = (b^2/10)\, \tau_c$$

are coefficients which determine the width of each hfs line and are connected with the anisotropic parameters of the spin Hamiltonian $\Delta g = g_{\parallel} - g_{\perp}$ and $b = (2/3)(A_{\parallel} + A_{\perp})\hbar$ (they are determined from experiments in supercooled solutions); τ_c is the characteristic time of the correlation function of the rotational Brownian motion.

From an analysis of these formulas, as well as from experiment (as noted above), it follows that for solutions which are in the liquid state the value of δH for the hyperfine components of the isotope V^{50} are smaller than the values of δH for the isotope V^{51}. We can therefore conclude in liquid solutions of VO^{2+} the form of the hfs lines is described by the McConnell relaxation mechanism [9].

As was to be expected, the ratios of the isotropic and anisotropic hfs constants of the isotope V^{50} and V^{51}, calculated with allowance for the spins, turn out to be, within the limits of experimental error, equal to the ratio of the corresponding nuclear moments, i.e.,

$$\frac{A^{50} I^{50}}{A^{51} I^{51}} \approx \frac{A_{\parallel}^{50} I^{50}}{A_{\parallel}^{51} I^{51}} \approx \frac{A_{\perp}^{50} I^{50}}{A_{\perp}^{51} I^{51}} \approx \frac{\mu^{50}}{\mu^{51}} = \frac{3.3413}{5.139} \approx 0.65$$

(the values of μ without the diamagnetic correction were taken from [10]).

In conclusion we note that on going from the liquid to the supercooled state the local electric fields of the ion V^{4+} do not change, since $g_{av} = 1/3(g_{\parallel} + 2g_{\perp}) \approx 1.97 \pm 0.01$ agrees well with $g = 1.968 \pm 0.0002$, determined from a solution in the liquid state.

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