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N. S. GARIF' YANOV

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Abstract

Full Text

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N. S. GARIF' YANOV

ON THE HYPERFINE STRUCTURE OF THE E.P.R. LINE IN AQUEOUS SOLUTIONS OF V^{2+} SALTS

(Presented by Academician A. E. Arbuzov, 19 I 1961)

In liquid solutions of salts of paramagnetic ions of elements of the iron group, the hyperfine structure (h.f.s.) of electron paramagnetic resonance (e.p.r.) lines under conditions of strong fields has been investigated only for Mn^{2+}, VO^{2+}, and Cu^{2+} ([1–8]). Data on the h.f.s. in liquid solutions for other paramagnetic ions of this group have not been obtained either because of the large width of the e.p.r. lines (Co^{2+}, V^{3+}), or because of the small magnetic moments of the nuclei.

Our investigations of e.p.r. of violet solutions of VCl_2 salts were carried out at a frequency of 9598 MHz in the temperature range 295–400° K. Water, alcohols, and glycerol were used as solvents. The solution under study was sealed into a glass barometric tube with a special heating device, which was then placed in the beam of magnetic lines of force of a rectangular H_{103} resonator. The method of these measurements is described in work ([9]). In aqueous solutions of VCl_2 within the concentration range 0.5–0.05 mole/l at room temperature, a single e.p.r. line is observed with width $\Delta H = 800$ oersted and with spectroscopic splitting factor $g = 1.96 \pm 0.01$. The width of this line is determined by the unresolved h.f.s.

Fig. 1. H.f.s. spectrum of the e.p.r. lines of a 0.05 mole/l VCl_2 solution in water; $\nu = 9598$ MHz, $T = 400°K$

When the temperature of the solution was raised to 400° K, it was possible to detect 8 peaks of an almost isotropic h.f.s., corresponding to the nuclear spin $I = 7/2$ of V^{51}. The form of the h.f.s. spectra at 400°K within the concentration range 0.5–0.05 mole/l practically does not change. As is seen from Fig. 1, the h.f.s. spectrum is not resolved completely.

It should be noted that when VCl_2 solutions are heated, strong oxidation does not occur, since upon repeated increase or decrease of temperature the corresponding intensity of the e.p.r. lines is practically preserved.

Graphical analysis of the spectra showed that the width ΔH of the h.f.s. component of the absorption lines of VCl_2, 0.05 mole/l in water at $T = 400$°K, is ~ 100 oersted. For room temperature the width of the unresolved h.f.s. components must be ~ 300 oersted. The position of the 8 resonance lines of the h.f.s. may be described by the expression

$$H^* = H_0' - Am - \frac{A}{2H_0}\left[I(I+1) - m^2\right] - \frac{A^2 m}{2H_0}(2M-1); \qquad (1)$$

Here H^* is the resonance value of the static magnetic field H, A is the hyperfine-splitting constant, m and M are the magnetic quantum numbers of the nucleus and of the electron shell of the ion under study, respectively, $H_0 = \frac{h\nu}{g\beta}$; good agreement with experiment was obtained for the values $A = 96$ Oe and $g = 1.965 \pm 0.002$. Equation (1) follows from the general theory of the structure of paramagnetic-resonance lines under the assumption that fine splittings of the lines, due to the action of local electric fields, are absent or very small in comparison with the hyperfine splitting.

In some solid solutions of salts of V^{2+}, which has the ground state $^4F_{3/2}$, the fine-splitting constant is greater than or comparable with the constant A. In these solid solutions the g-factor is isotropic.

In aqueous solutions of 0.05 mole/liter VCl_2, the width ΔH of the components of the h.f.s. lines of e.p.r. is almost an order of magnitude greater than ΔH of the h.f.s. components in aqueous solutions of Mn^{2+} and VO^{2+} of corresponding concentration. It is therefore necessary to suppose that, in violet aqueous solutions of VCl_2 salts, the width of the h.f.s. components is determined mainly by fine splittings. This assumption also explains the absence of a concentration dependence of the width ΔH of the h.f.s. component of the e.p.r. lines in VCl_2 solutions. We believe that the electric field at the V^{2+} ion in violet aqueous VCl_2 solutions has essentially cubic symmetry with a small admixture of fields of axial symmetry, produced by a somewhat distorted water octahedron as a result of the Jahn-Teller effect. These electric fields are not completely averaged by motion. In addition, a small admixture of fields of lower symmetry, due to the action of particles of the second coordination sphere, is also superposed on the V^{2+} ion. As the temperature of the solution is raised, this low-symmetry

crystalline field at the V^{2+} ion is averaged by motion, and the e.p.r. line narrows.

In alcoholic and glycerol solutions of VCl_2 in the interval $T = 295\text{–}400^\circ K$, the e.p.r. line could not be detected. Such a large width of these lines in the indicated organic solvents is explained by the presence of a strong axial component of the crystalline field, which is due to the ionic molecules ([9], [10]).

In these organic solvents, in the supercooled state, it was possible to detect an e.p.r. line with $\Delta H = 1000$ Oe ([11], [12]).

Finally, it should be noted that the constant A in aqueous VCl_2 solutions has the same magnitude as in solid solutions of V^{2+} salts ([3]), and is 22 Oe smaller than A in aqueous $VOCl_2$ solutions ([14]).

In conclusion, the author expresses his gratitude to B. M. Kozyrev for discussion of the results and to N. F. Usacheva for assistance in the experiment.

Physico-Technical Institute
of the Kazan Branch of the Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.