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Uniform Pressure Effect on Low-Temperature EPR Spectrum of V^{2+} Ion in Zinc Fluosilicate

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In honour of Prof. Dr. Dr. h.c. P. GÖRLICH's 70th birthday

A diamagnetic crystal of trigonal zinc fluosilicate with small amounts of divalent vanadium impurity ions has been used to investigate the effect of high uniform pressure on EPR spectra.

EPR measurements were carried out in the pressure range up to 12 kbar on a 4 mm spectrometer using the crystal-resonator technique at 4.2 K. The optically homogeneous crystals of zinc fluosilicate, $ZnSiF_6 \cdot 6H_2O$, from which crystal-resonators were made, contain about 1% V^{2+} ions. The mixture of transformer oil with kerosine used as pressure-transfer medium enables one to get uniform high hydrostatic pressure at low temperatures (1).

The accuracy of pressure measurements in the range of 1 to 12 kbar is 3%. Measurement errors in the values of the parameters D and A do not exceed 1%, the g-factor was measured with accuracy up to ± 0.005.

The V^{2+} ion spectrum in $ZnSiF_6 \cdot 6H_2O$ is described by the spin Hamiltonian with S = 3/2 and I = 7/2 (2):

$$\mathcal{H}_S = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + \\ + A I_z S_z + B(I_x S_x + I_y S_y) \quad , \tag{1}$$

where $g_{\parallel} = g_{\perp} = 1.98 \pm 0.005$, $A = B = (85.2 \pm 0.8)\times 10^{-4}$ cm^{-1} and $D = (810 \pm 5)\times 10^{-4}$ cm^{-1} at zero pressure.

Measurements showed that the parameter D of axial zero-field splitting strongly and nonlinearly depends on the applied pressure (Fig. 1). The hyperfine interaction constant A is also pressure dependent. Contrary to the parameter D the hyper-

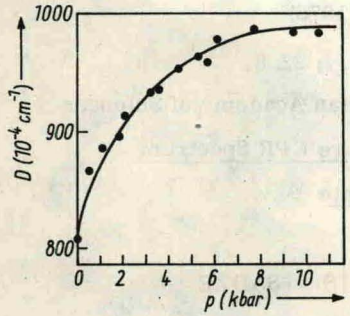

Fig. 1

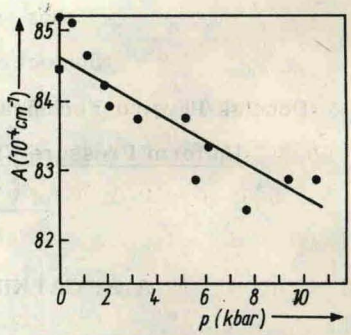

Fig. 2

Fig. 1. Pressure dependence of the parameter D of zero-field splitting of the V^{2+} ion in $ZnSiF_6 \cdot 6H_2O$

Fig. 2. Pressure dependence of the hyperfine interaction constant A of the V^{2+} ion in $ZnSiF_6 \cdot 6H_2O$. The point ■ is taken from reference (2)

fine interaction constant decreases with increasing pressure (Fig. 2). The behaviour of the g-factor and the D(p) and A(p) dependences can be described at least qualitatively using the simple crystal field theory.

The spin Hamiltonian (1) contains $g_{\parallel}$ and $g_{\perp}$ which deviate from the free spin value because of the combined effect of spin-orbit interaction and crystal field of predominantly octahedral symmetry with trigonal distortion. Their values are given in reference (3) to

$$g_{\parallel} = g_S - \frac{8\lambda}{\Delta_0} ; \qquad g_{\perp} = g_S - \frac{8\lambda}{\Delta_1} , \tag{2}$$

where $g_S = 2.0023$; λ is the constant of spin-orbit interaction, Δ_0 and Δ_1 are the distances between the ground orbital singlet, Γ_2, and the singlet and doublet, respectively, in which the first excited orbital level Γ_5 of octahedral symmetry is split by the trigonal distortion.

The g-factor constancy in the range of pressures used shows that spin-orbit interaction and the trigonal crystal field component do not change within an accuracy of first-order perturbation theory. The expression (3)

$$D = \frac{4\lambda^2(\Delta_o - \Delta_1)}{\Delta_o \Delta_1} \qquad (3)$$

is valid for the zero-field splitting parameter D in the second order of perturbation theory. The notation is the same as in equation (2).

If both Δ_o and Δ_1 do not essentially change then the change of D must be the result of a change in the difference, $\Delta_o - \Delta_1$, which is equal to the splitting of the Γ_5 triplet by the trigonal distortion. This assumption and the experimental results permit to evaluate the change of g-tensor components described by equation (2).

Increasing the pressure from 0 to 12 kbar leads to a change of D by 180x x10^{-4} cm^{-1} with $\lambda \approx 45$ cm^{-1} (for a crystal) and $\Delta_o \approx \Delta_1 \approx 12000$ cm^{-1}, then the g-tensor components should change by 0.0005, that is within the experimental error.

The change of hyperfine interaction can be evaluated by means of the change of D in the framework of the model used. The hyperfine field H^{hf}, acting on a nucleus is estimated by the numerical expression (4) (in G)

$$H^{hf} = 1.25 \times 10^5 \left\langle \frac{1}{r^3} \right\rangle \Delta g_L . \qquad (4)$$

The value $\left\langle \frac{1}{r^3} \right\rangle$ is expressed in atomic units. The shift $\Delta g = -8\lambda/\Delta_o$ is written as Δg_L to outline that the shift of the g-factor has orbital nature and is not connected with the admixture of other spin substates to the ground state. This condition is fulfilled in the case of V^{2+} in octahedral surroundings, as the ground state of the ion is a singlet one.

From equation (4) using formulas (2) and (3) one can evaluate the change of the orbital hyperfine field (in G):

$$\delta H^{hf} = 1.25 \times 10^5 \frac{4}{3\lambda} \delta D \left\langle \frac{1}{r^3} \right\rangle . \qquad (5)$$

For the V^{2+} ion $\left\langle \frac{1}{r^3} \right\rangle = 2.75$ at. units. Using the experimentally obtained change of D one finds $|\delta H^{hf}| \approx 190$ G. At p = 0 $\Delta g_L = -0.02$ and $H^{hf} = -6.88$ kG. With increasing pressure $|\Delta g_L|$ decreases and consequently $|H^{hf}|$ decreases, too,

which results in a decrease of the hyperfine structure constant.

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