

phys. stat. sol. (b) 71, K205 (1975)

Subject classification: 19 and 13.4; 22.8

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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  $\pm 0.005$ .

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):

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

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

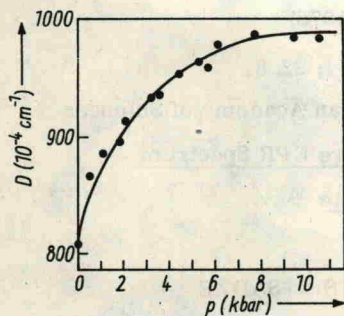


Fig. 1

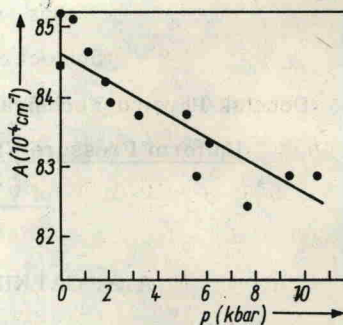


Fig. 2

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

$$g_{\parallel} = g_S - \frac{8\lambda}{\Delta_0}; \quad g_{\perp} = g_S - \frac{8\lambda}{\Delta_1}, \quad (2)$$

where  $g_S = 2.0023$ ;  $\lambda$  is the constant of spin-orbit interaction,  $\Delta_0$  and  $\Delta_1$  are the distances between the ground orbital singlet,  $\Gamma_2$ , and the singlet and doublet, respectively, in which the first excited orbital level  $\Gamma_5$  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)