Change in the symmetry and magnitude of the crystal field in a paramagnetic crystal under the influence of hydrostatic pressure

S. N. Lukin and G. A. Tsintsadze

Donets Physico-technical Institute, Ukrainian Academy of Sciences

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We have studied the effect of high hydrostatic pressure on the spectrum of electron paramagnetic resonance of the Co^{2+} ion implanted in the crystal lattice of trigonal zinc fluorosilicate. The measurements were made with microwave spectrometers in the wavelength ranges 3 cm and 4 mm at a temperature of 4.2 K and pressures up to 12 kbar with the crystal-cavity method. A strong dependence of the components of the *g* and *A* tensors on applied pressure was observed. With increasing pressure the anisotropy of the spectrum decreases and at a definite value in the extrapolation portion it should become cubic. The results are interpreted in terms of crystal field theory.

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INTRODUCTION

The principal factors determining the properties of paramagnetic crystals are the magnitude and symmetry of the crystal field. These characteristics, however, are completely determined by the nature of the crystal and the location of ions in it and therefore they have been uncontrollable. Application of high pressures, especially at low temperatures, has made it possible to influence qualitatively not only the magnitude of the components of the crystal field but also its symmetry. Study of EPR spectra permits the nature of this influence to be determined.

In the present work we have studied the effect of high pressure on the EPR spectrum of the Co^{2+} ion in the lattice of trigonal zinc fluorosilicate.

For an ion with configuration $3d^7$ the orbital triplet Γ_4 is the lowest in the octahedral field; this triplet is split as the result of the spin-orbit interaction and, if the octahedron is distorted, then also as the result of presence in the crystal field potential of terms of lower symmetry. The strong coupling of the triplet through the spin-orbit interaction with the lattice leads to the highest spin-lattice relaxation rate in the iron group. Therefore a necessary condition for investigation of the EPR spectra of the Co^{2+} ion in octahedral environments is the use of low temperatures (20 K and lower). In most hydrated salts the splittings due to the low-symmetry components of the crystal field are comparable in magnitude with the splittings due to spin-orbit coupling. The problem of splitting in a static model of point charges has been studied in detail by Abragam and Pryce.[1]

FEATURES OF THE MEASUREMENT TECHNIQUE

To study the influence of high pressure on the EPR spectrum of Co^{2+} ions we used optically homogeneous crystals of zinc fluorosilicate $ZnSiF_6 \cdot 6H_2O$ grown by the temperature reduction method. The samples contained 0.5% Co^{2+} ions. The measurements were made in microwave spectrometers in the wavelength ranges 3 cm and 4 mm with use of the crystal-cavity technique.

The crystal cavity is a cylindrical sample calculated in the appropriate way as a resonator completely filled with dielectric in the TE_{11n} or TE_{01n} mode. In contrast to oxide crystals, where the crystal cavity is covered with a layer of fired silver, in the case of the fluorosilicates the sample was placed in a cylindrical yoke of electrolytic copper. As experiments showed, the presence of the yoke (wall thickness less than 0.03 mm) did not affect the results of the measurements.

Among the advantages of the crystal-cavity technique in comparison with other methods are an increase in the filling factor, a decrease in the nonuniformity in the resonator volume, practically complete exclusion of penetration of the medium transmitting the pressure into the microwave resonator and, as a consequence, a substantial increase in sensitivity of the EPR spectrometer as a whole.

It should be specially noted that the crystal-cavity technique permits investigation of the effect of high pressure on the EPR spectra of ions at low temperatures (77–4.2 K).

As the medium transmitting the pressure we used a mixture of transformer oil and kerosene, which enabled us to obtain a highly hydrostatic pressure at low temperatures (T = 4.2 K) and pressures[2] up to 10–14 kbar.

The pressure in the vessel at room temperature was determined from the resistance of a manganin probe calibrated from the secondary standard at the All-Union Research Institute of Physico-technical and Electronic Measurements. At a temperature of 4.2 K, the pressure was determined from a plot of the pressure as a function of the initial pressure at 300 K.

To determine all the necessary constants of the EPR spectrum in one geometry of crystal-cavity location relative to the superconducting solenoid, the sample was prepared of two parts of a cylinder, one of which contained the crystal axis C_3 along the directrix, and the other in the basal plane of the cylinder. This geometry permits, without rotation of the magnetic field, observation in a single experiment of the spectrum both in the parallel and perpendicular orientations and monitoring of the magnitude of the trace of the g tensor. The accuracy in determination of the g factors was 1% or better. The hyperfine-structure constants A and B were measured with accuracies of 2 and 5%, respectively.

EXPERIMENTAL RESULTS AND DISCUSSION

The spectrum of the Co^{2+} ion in the trigonal crystal field of zinc fluorosilicate is described by the axially symmetric spin Hamiltonian[3]:

$$\mathscr{H}_S=\beta[g_{\parallel}H_zS_z+g_{\perp}(H_xS_x+H_yS_y)]+AS_zI_z+B(S_xI_x+S_yI_y) \qquad (1)$$

where S = 1/2 and I = 7/2. In the present work we studied the dependence of $g_{\parallel}$, $g_{\perp}$, A, and B on the applied high pressure. In Fig. 1 we have shown the dependence of the g factors on pressure. As can be seen from the graph, $(\partial g_{\parallel}/\partial P)_T = -5.70 \times 10^{-2}$ kbar^{-1}, and $(\partial g_{\perp}/\partial P)_T = +2.85 \times 10^{-2}$ kbar^{-1}.

From the theory developed specially for the Co^{2+} ion,[1] it follows that Sp g = 13. In the case of Co^{2+} in an axial field we have Sp g = $g_{\parallel} + 2g_{\perp}$.

Analysis of the plot shows that the trace of the g tensor is a constant quantity over the entire pressure region. This circumstance leads to the conclusion that on application of hydrostatic pressure to the crystal no low-symmetry components of the crystal field of rhombic or lower symmetry arise.

It is clear that this record change in g factor with pressure, in comparison with other ions, is due first of all to the fact that a crystal field which changes both in magnitude and in symmetry is acting directly on the orbital contribution to the magnetic moment, and through the term λ(LS) also on the spin contribution.

A high degree of anisotropy arises on deviation of the local symmetry of the crystal field from cubic. Together with the action of spin-orbit coupling, the trigonal component leads to formation of a series of Kramers doublets, in the lowest of which EPR is observed.

From the measured values of $g_{\parallel}$ and $g_{\perp}$ we can find[4] the values

$$a=(g_{\parallel}-4.33)/16.396, \qquad (2)$$

$$a=(4.33-g_{\perp})/8.197. \qquad (3)$$

The plot constructed of the anisotropy coefficient a (the trigonality parameter) is shown in Fig. 2. In the extrapolation portion near 21 kbar we have a → 0, i.e., the symmetry of the crystal field at the Co^{2+} ion should go over to strictly cubic.

In plots of the dependence on pressure of both the g-factor components and particularly the trigonality parameter, the existence of two straight portions with different slopes is noteworthy. If we assume that in the pressure region 4–5 kbar the crystal lattice of zinc fluorosilicate changes its compressibility (a phase transition of the second kind), then this behavior of the parameters of the spin Hamiltonian can be plausibly explained.

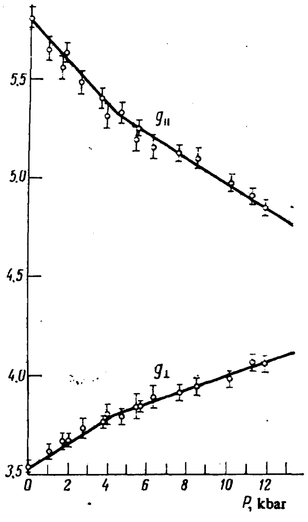

FIG. 1. Dependence of g factors of the Co^{2+} ion in $ZnSiF_6 \cdot 6H_2O$ on pressure.

However, the absence of any data on the dependence of the elastic properties of the crystal on pressure permits us to suggest also another possible mechanism. Variations in the magnitude and symmetry of the crystal field can affect to a different degree the orbital and spin components of the magnetic moment. In the region of low pressures the decreasing orbital contribution to the magnetic moment is responsible for the change in the g factors. In the region of higher pressures the first mechanism becomes ineffective (orbital saturation) and only the change in the spin contribution leads to a change in the g factors.

Thus, the change in the g-factor components leads to the conslusion that there is a change in the symmetry and magnitude of the crystal field under the influence of hydrostatic pressure. Here we must emphasize particularly that, over the entire region of existence of the EPR spectrum of the Co^{2+} ion in zinc fluorosilicate (from 30 K down), none of the parameters of the spin Hamiltonian depends on temperature, i.e., all changes must be assigned to the pure crystal field effect.

To explain the behavior of the hyperfine-structure constants (see Fig. 3) it is necessary to introduce into the discussion the pseudonuclear Zeeman effect (paramagnetic screening) according to which the nucleus is an effective field $H_Z(1 + \sigma)$, where[5]

$$\sigma=-5.84\left\langle\frac{1}{r^3}\right\rangle\frac{\Delta g_L}{\lambda}. \qquad (4)$$

The quantity $\langle r^{-3}\rangle$ is expressed in atomic units, and λ in cm^{-1}.

The correction for paramagnetic screening is small for the singlet ground state (~1%), but for ions which have excited states separated from the ground state by an energy of the order of several hundred cm^{-1} as in the case of Co^{2+}, this correction is substantial. Thus, we can state that the hyperfine interaction of Co^{2+} ions on application of high pressure changes as the result of the change in the orbital contribution to the effective field acting on the nucleus.

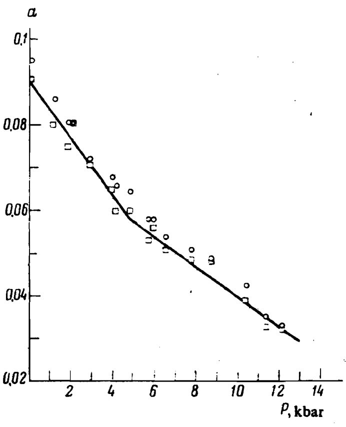

FIG. 2

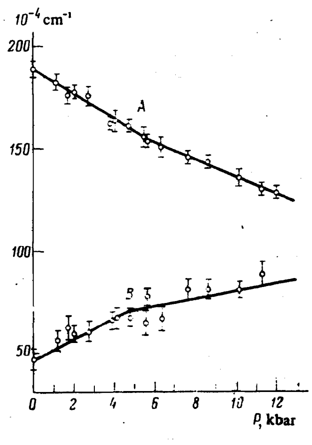

FIG. 3

FIG. 2. Dependence of the trigonality parameter a on pressure: ○—from Eq. (2), □—from Eq. (3).

FIG. 3. Dependence of the hyperfine-interaction constants of the Co^{2+} ion in $ZnSiF_6 \cdot 6H_2O$ on pressure.

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