# *SPLITTING OF EPR LINES OF* $Cr^{3+}$ *IN* $ZnWO_4$ *BY AN EXTERNAL ELECTRIC FIELD*[1)]

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Submitted to JETP editor January 24, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 50, 1510–1518 (June, 1966)

Splitting of the EPR lines of $Cr^{3+}$ in $ZnWO_4$, induced by an external electric field, has been observed. An investigation is made of the angular dependence of the splitting (dependence of the splitting magnitude on the orientation of the external magnetic and electric fields relative to the crystallographic axes). A spin Hamiltonian describing the interaction between the system and external electric field is set up and corrections to the transition frequencies are found. The results of the theory describe satisfactorily the experimental angular dependences of the splitting. The corresponding spin-Hamiltonian constants are determined. A correlation effect is established for the first time between the angular dependence of the splitting and the angular dependence of the EPR line halfwidth in the absence of an external electric field. A qualitative interpretation of the phenomenon is presented.

## 1. INTRODUCTION

THE effect of splitting of EPR lines by an external electric field **E** was first observed in silicon doped with iron-group elements.[2] It was subsequently observed also in corundum.[3,4] Analogous effects were obtained in the optical range and for nuclear resonance (see, for example, [5]).

The observed phenomenon has uncovered new possibilities for the investigations of local centers (LC) in solids. Besides the additional quantitative information, this effect yields also new qualitative information on the structure of the LC. Thus, by virtue of the pseudovector nature of the magnetic field, ordinary EPR is not sensitive to differences between certain point groups of crystal symmetry (for example, isomorphic ones), whereas a procedure using an external electric field makes it possible to "resolve" these groups.

For the existence of an effect that is linear in the field **E** it is necessary that the position of the paramagnetic ion (atom) not be a symmetry center with respect to inversion. Favoring its observation is also the condition $J > 1/2$, where J is the quantum number of the square of the total angular momentum of the paramagnetic center. The external electric field leads to a linear shift (with respect to the field **E**) of the resonant magnetic field. For different non-equivalent positions of the ion in the crystal, this shift will, generally speaking, be different, as a result of which the effect can become manifest in the form of splitting of EPR lines.

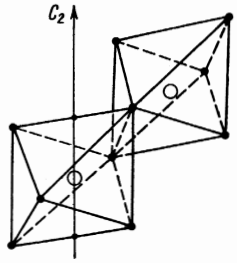


FIG. 1. Two nonequivalent positions of the $Zn^{2+}$ ion in the crystal lattice of $ZnWO_4$: ○ – zinc ions; ● – oxygen atoms; $C_2$ – twofold symmetry axis.

The ion $Cr^{3+}$ ($J = 3/2$) in zinc tungstate replaces the $Zn^{2+}$ ion,[6] the position of which is not a symmetry center with respect to inversion (point group $C_2$). In the $ZnWO_4$ crystal there are two nonequivalent positions of the $Zn^{2+}$ ion, differing in inversion with respect to the position occupied by the zinc ion (Fig. 1). By virtue of the foregoing we can expect a splitting of the EPR lines, linear in the field **E**, into two lines, each of which corresponds to a definite non-equivalent position of the $Cr^{3+}$ ion in $ZnWO_4$.

We have observed four EPR lines: two ($1/2 \rightarrow 3/2$ and $-1/2 \rightarrow -3/2$) correspond to transitions between sublevels of a Kramers doublet, and two ($-3/2 \rightarrow 1/2$) correspond to a transition between sublevels of different Kramers doublets. (The quantum numbers chosen to designate the levels will be correct in the region of extremely large

[1)] A preliminary report on the observed splitting was published in[1].

**Table I.** Functions of the field components and the operator functions corresponding to the irreducible representations $\Gamma_1$ and $\Gamma_2$ of group $C_2$.

| Field components | | Operator functions | | Field components | | Operator functions | |
|---|---|---|---|---|---|---|---|
| $\Gamma_1$ | $\Gamma_2$ | $\Gamma_1$ | $\Gamma_2$ | $\Gamma_1$ | $\Gamma_2$ | $\Gamma_1$ | $\Gamma_2$ |
| $E_y$ | $E_x$ | $\hat{J}_y$ | $\hat{J}_z$ | $H_yE_y$ | $H_yE_x$ | $\{\hat{J}_z\hat{J}_x\}^*$ | $\{\hat{J}_y\hat{J}_z\}$ |
| $H_xE_x$ | $E_z$ | $\hat{J}_x^2-\hat{J}_y^2$ | $\hat{J}_x$ | $H_zE_x$ | $H_yE_z$ | $\hat{J}^2$ | |
| $H_xE_z$ | $H_xE_y$ | $3\hat{J}_z^2-\hat{J}^2$ | $\{\hat{J}_x\hat{J}_y\}$ | $H_zE_z$ | $H_zE_y$ | | |

* $\{\hat{J}_i\,\hat{J}_j\}=\hat{J}_i\,\hat{J}_j+\hat{J}_j\,\hat{J}_i$.

magnetic fields.) In an external electric field, each of the four lines splits into two.

We consider below the theory of this phenomenon, and present the experimental results and their interpretation.

## 2. THEORY

The spin Hamiltonian of the system considered by us can be represented in the form

$$\hat{W}=\hat{W}_0+\hat{W}_E, \tag{1}$$

where $\hat{W}_0$ is the spin Hamiltonian in the absence of an external electric field **E** and $\hat{W}_E$ is an addition that takes into account the interaction with the field **E**. The expression for $\hat{W}_0$ is [6]

$$\hat{W}_0=\beta\sum_{j=1}^{3}g_iH_i\hat{J}_i+D\,[\hat{J}_z^2-{}^1/_3J\,(J+1)]$$
$$+E\,(\hat{J}_x^2-\hat{J}_y^2),$$

where $J={}^3/_2$, D = 25.47 kMHz, E = −2.42 kMHz, $g_1$ = 1.958, $g_2$ = 1.963, $g_3$ = 1.968, and $\beta$ is the Bohr magneton. The choice of the coordinate axes and their designation coincide with those assumed in [6]. In particular, we align the y axis with the twofold symmetry axis.

To obtain the operator $\hat{W}_E$, we use the method of invariants.[7] We take into consideration terms that are linear in the field **E**, including terms proportional to products of the $E_iH_j$ (i, j = 1, 2, 3; x → 1, y → 2, z → 3).

In Table I are written out the functions of the field components and the operator functions, which transform as the bases of the transformations $\Gamma_1$ and $\Gamma_2$. The characters of the irreducible representations of group $C_2$ are given below:

| | $E$ | $C_2$ |
|---|---|---|
| $\Gamma_1$ | 1 | 1 |
| $\Gamma_2$ | 1 | −1 |

We have excluded the operator functions containing products of the type $\hat{J}_i\hat{J}_j\hat{J}_k$, since the terms corresponding to them are usually much smaller than the terms proportional to the first power of $\hat{J}_i$.[8]

Combining the operator-functions with the functions of the field components, with allowance for the limitations imposed by symmetry under time reversal,[7] and carrying out several transformations, we obtain

$$\hat{W}_E=\hat{W}_1+\hat{W}_2, \tag{2}$$

where

$$\hat{W}_1=(\alpha_1\hat{J}^2+\alpha_2\hat{J}_x^2+\alpha_3\hat{J}_z^2+\alpha_4\{\hat{J}_x\hat{J}_z\})\,E_y$$
$$+(\alpha_5E_x+\alpha_8E_z)\{\hat{J}_y\hat{J}_z\}+(\alpha_7E_x+\alpha_6E_z)\{\hat{J}_y\hat{J}_x\}, \tag{3}$$

$$\hat{W}_2=E_y\,[\beta_2\hat{J}_yH_y+\hat{J}_x\,(\beta_7H_x+\beta_8H_z)+\hat{J}_z\,(\beta_{11}H_x+\beta_{12}H_z)]$$
$$+E_x\,[\hat{J}_y\,(\beta_1H_x+\beta_4H_z)+H_y\,(\hat{J}_x\beta_6+\hat{J}_z\beta_{10})]$$
$$+E_z\,[\hat{J}_y\,(\beta_3H_z+\beta_5H_x)+H_y\,(\beta_9\hat{J}_x+\beta_{13}\hat{J}_z)]. \tag{4}$$

The term $\hat{W}_1$ contains terms which are linear in **E**, while $\hat{W}_2$ contains terms linear in the products of the type $E_iH_j$.

To check on the correctness of our expressions, we have used also the perturbation-matrix method.[9] In that case the operator $\hat{W}_E$ was obtained in matrix form.

The expression for $\hat{W}_1$ and $\hat{W}_2$ is best written in the following compact form, which reflects explicitly the tensor character of the spin-Hamiltonian coefficients:

$$\hat{W}_E=\sum_i\sum_{j\leqslant k}\alpha_{ijk}E_i\,(\hat{J}_i\hat{J}_k+\hat{J}_k\hat{J}_j)+\sum_{ijk}\beta_{ijk}E_iH_j\hat{J}_k,$$

where the new parameters $\alpha$ and $\beta$ are connected with the old ones as follows:

$\alpha_{222}=\alpha_1/2$, $\alpha_{211}=(\alpha_1+\alpha_2)/2$, $\alpha_{233}=(\alpha_1+\alpha_3)/2$, $\alpha_{213}=\alpha_4$, $\alpha_{123}=\alpha_5$, $\alpha_{112}=\alpha_7$, $\alpha_{323}=\alpha_8$, $\alpha_{312}=\alpha_6$, $\beta_{112}=\beta_1$, $\beta_{121}=\beta_6$, $\beta_{123}=\beta_{10}$, $\beta_{132}=\beta_4$, $\beta_{211}=\beta_7$, $\beta_{213}=\beta_{11}$, $\beta_{222}=\beta_2$, $\beta_{231}=\beta_8$, $\beta_{233}=\beta_{12}$, $\beta_{312}=\beta_5$, $\beta_{321}=\beta_9$, $\beta_{323}=\beta_{13}$, $\beta_{332}=\beta_3$;

the remaining coefficients $\alpha_{ijk}$ and $\beta_{ijk}$ vanish.

To determine the eigenvalues of the operator $\hat{W}$, we assume that the problem of finding the ei-

genvalues of the operator $\hat{W}_0$ has been solved, and regard the operator $\hat{W}_E$ as a perturbation.

The correct zeroth-approximation wave function can be represented in the following general form:

$$\varphi_p = a_p\chi_{-3/2} + b_p\chi_{-1/2} + c_p\chi_{1/2} + d_p\chi_{3/2}, \quad (5)$$

where the index p takes on values 1, 2, 3, and 4, characterizing the energy levels of the zeroth approximation, while $\chi_\nu$ is the set of spin functions ($J = {}^3/_2$). The coefficients a, b, c, and d are functions of the parameters D, E, and $g_i$ and of the components of the magnetic-field intensity vector.

Using (2)–(5), we obtain the following expression for the correction to the frequency in first order of perturbation theory:

$$\begin{aligned} h\nu_{pq}^{E} &= E_y[\alpha_2 A_{pq}^{(1)} + \alpha_3 A_{pq}^{(2)} + \alpha_4 A_{pq}^{(3)} \\ &+ A_{pq}^{(6)}(\beta_{11}H_x + \beta_{12}H_z) + A_{pq}^{(7)}(\beta_7 H_x + \beta_8 H_z) \\ &+ \beta_2 H_y A_{pq}^{(8)}] + E_x[\alpha_5 A_{pq}^{(4)} + \alpha_7 A_{pq}^{(5)} \\ &+ H_y(\beta_{10}A_{pq}^{(6)} + \beta_6 A_{pq}^{(7)}) + A_{pq}^{(8)}(\beta_1 H_x + \beta_4 H_z)] \\ &+ E_z[\alpha_8 A_{pq}^{(4)} + \alpha_6 A_{pq}^{(5)} + H_y(\beta_{13}A_{pq}^{(6)} + \beta_9 A_{pq}^{(7)}) \\ &+ A_{pq}^{(8)}(\beta_5 H_x + \beta_3 H_z)], \end{aligned} \quad (6)$$

where

$$A_{pq} = A_p - A_q,$$

$$\begin{aligned} A_t^{(1)} &= |b_t|^2 + |c_t|^2 + {}^1/_2\sqrt{3}(a_t^* c_t + b_t^* d_t + \text{c.c.}), \\ A_t^{(2)} &= 2(|a_t|^2 + |d_t|^2), \quad A_t^{(3)} = \sqrt{3}(c_t^* d_t + a_t^* b_t + \text{c.c.}), \\ A_t^{(4)} &= i\sqrt{3}(b_t^* a_t + c_t^* d_t - \text{c.c.}), \\ A_t^{(5)} &= i\sqrt{3}(a_t^* c_t + b_t^* d_t - \text{c.c.}), \\ A_t^{(6)} &= {}^1/_2(|c_t|^2 + 3|d_t|^2 - |b_t|^2 - 3|a_t|^2), \\ A_t^{(7)} &= b_t^* c_t + {}^1/_2\sqrt{3}(a_t^* b_t + c_t^* d_t) + \text{c.c.}, \\ A_t^{(8)} &= i[b_t^* c_t + {}^1/_2\sqrt{3}(a_t^* b_t + c_t^* d_t) - \text{c.c.}]; \end{aligned}$$

$i = \sqrt{-1}$; c.c.—complex conjugate; h—Planck's constant.

In the absence of an external electric **E**, the connection between the klystron frequency $\nu$ and the resonant value of the magnetic field $H_0$ is determined by the following expression:

$$\nu = \nu_{pq}^{0}(H_0),$$

where $\nu_{pq}^{0}(H_0)$ is the theoretical expression for the frequency of the transition between the levels p and q, obtained as a result of diagonalization of the operator $\hat{W}_0$.

In the presence of an electric field we have

$$\nu = \nu_{pq}^{0}(H_0 + \Delta H_{1,2}) \pm \nu_{pq}^{E}(H_0 + \Delta H_{1,2}),$$

where $\Delta H$ is the displacement of the resonant value of the magnetic field. The indices 1 and 2, and also the signs + and −, correspond to two nonequivalent positions of the ions.

For small values of $\Delta H$ ($H_0 \gg \Delta H$), we obtain the sought expressions for the splitting of the EPR line:

$$|\Delta H_1 - \Delta H_2| = \left| 2\nu_{pq}^{E}(H_0) \Big/ \frac{\partial \nu_{pq}^{0}(H_0)}{\partial H_0} \right|. \quad (7)$$

In many cases of practical interest, formula (7) can be greatly simplified. Thus, for sufficiently small magnetic fields ($g\beta H \ll D$), we can choose as the zeroth-approximation Hamiltonian the operator $D[\hat{J}_Z^2 - ({}^1/_3)J(J+1)]$, and the remaining terms in $\hat{W}$, including the operator $\hat{W}_E$, can be regarded as a perturbation. In this case the corrections to the energy levels can be obtained by the method of perturbation theory in the presence of degeneracy.[10]

Accurate to second-order terms of the theory, we obtain for the splitting of the lines corresponding to the transitions between the sublevels of the Kramers doublets

$$\begin{aligned} |\Delta H_1 - \Delta H_2|_{-1/2 \to -3/2} &= \frac{[1 + 3\sin^2\theta]^{1/2}}{[1 + 3\sin^2\theta(1 - 2ED^{-1}\cos 2\varphi)]^2} \\ &\times l\{(E_x B^{(1)} + E_z B^{(2)})\sin 2\theta \sin\varphi \\ &+ (E_x B^{(3)} + E_z B^{(4)})\sin^2\theta \sin^2\varphi + \\ &+ E_y[B^{(5)}\sin 2\theta\cos\varphi + B^{(6)}\cos^2\theta \\ &+ \sin^2\theta(B^{(7)}\cos^2\varphi + B^{(8)}\sin^2\varphi)]\}, \end{aligned} \quad (8)$$

where $\theta$ and $\varphi$ are the polar and azimuthal angles of the vector **H**,

$$\begin{aligned} B^{(1)} &= {}^1/_2(\beta_{10} + 4\beta_4 - k\alpha_5), \quad B^{(2)} = {}^1/_2(\beta_{13} + 4\beta_3 - k\alpha_8), \\ B^{(3)} &= 2(\beta_6 + \beta_1 - k\alpha_7), \quad B^{(4)} = 2(\beta_5 + \beta_9 - k\alpha_6), \\ B^{(5)} &= {}^1/_2(\beta_{11} + 4\beta_8 - k\alpha_4), \quad B^{(6)} = \beta_{12}, \\ B^{(7)} &= 4\beta_7 - k\alpha_2, \quad B^{(8)} = 4\beta_2 + k\alpha_2, \\ l &= 2h\nu/g^2\beta^2, \quad k = 3g\beta/D, \quad g = (g_x + g_y + g_z)/3; \end{aligned}$$

$$\begin{aligned} |\Delta H_1 - \Delta H_2|_{1/2 \to 3/2} &= \frac{l}{3\cos^2\theta}[\sin\theta\sin\varphi(B^{(9)}E_x + B^{(10)}E_z) \\ &+ E_y(B^{(11)}\sin\theta\cos\varphi + B^{(6)}\cos\theta)], \end{aligned} \quad (9)$$

where

$$B^{(9)} = \beta_{10} + {}^1/_3 k\alpha_5, \quad B^{(10)} = \beta_{13} + {}^1/_3 k\alpha_8,$$

$$B^{(11)} = \beta_{11} + {}^1/_3 k\alpha_4.$$

We note that for the transition ${}^1/_2 \to {}^3/_2$ the value of the magnetic field H increases sharply as $\theta \to 90°$, and the limiting transition to $\theta = 90°$ in formula (9) is meaningless.

One must bear in mind one more circumstance when using formulas (8) and (9). At field orientations **E** ∥ y and **H** ∥ z ($\theta = 0°$), the splitting is determined by the parameter B (6), which is equal to the constant $\beta_{12}$. If furthermore this splitting is different from zero (as was the case in our experiment), we can assume that $\beta_{12} \neq 0$ and determine its value from the obtained splitting. Actually, however, as shown by an analysis with the aid of

the more accurate formula (7), the constant B (6) includes terms of higher order of perturbation theory, containing the parameter $\alpha$. It is just these terms which determine the splitting observed at $\theta = 0°$ and $\mathbf{E} \parallel y$. This remark does not pertain, however, to the description of the angular dependence of such a splitting, for in this case the nature of the parameter B (6) is immaterial.

For transitions between sublevels of different Kramers doublets, $g\beta H \sim D$ when working in the 3-cm band, so that the approximation considered above is not valid.

## 3. EXPERIMENTAL PROCEDURE, RESULTS, AND DISCUSSION

In our experiments we used $ZnWO_4$ single crystals grown from the melt by the Czochralski method. The chromium impurity was introduced into the melt during the course of crystal production. In addition to the chromium impurity, the crystal contained ten times more lithium than chromium. All the experiments were carried out with samples containing 0.1% chromium in the charge.

The orientation of the $ZnWO_4$ samples was facilitated by the fact that the $ZnWO_4$ crystal cleaved easily along the (010) plane, that is, the b axis of the crystal was perpendicular to the cleavage plane, and the a and c axes were in that plane. It is also known[6] that the magnetic y axis is parallel to the crystallographic b axis of the crystal, while the x and z axes also lie in the cleavage plane, but do not coincide with the crystallographic a and c axes. We have obtained the x and z axes from the symmetry of the angular dependences of the EPR spectra.

In experiments with electric fields, the external electric field E was applied in succession along each of the axes x, y, and z. For investigations at orientation $\mathbf{E} \parallel y$, the samples were cleaved into plates 0.5 mm thick and 2 × 4 mm in area. For investigations at other orientations of the external electric field ($\mathbf{E} \parallel x$ or $\mathbf{E} \parallel z$), the samples were cut with a diamond saw. Preliminary orientation of the crystal prior to cutting was on the basis of the angular dependences of the EPR spectrum, using a special resonator.

The influence of the external electric field on the EPR spectra was investigated with a 3-cm superheterodyne spectrometer at room temperature.[2)] To produce the electric field in the sample, the usual method was used: metallic electrodes (silver films) were deposited on opposite sides of the sample, which was cut in the form of a plate. The sample was pressed against the bottom or the sidewall of a $H_{101}$ cavity through one of the electrodes, and a thin wire with teflon insulation (MGTF wire) was soldered to the other electrode and was led out of the resonator through an opening 1 mm in diameter in line with the sample. To prevent electric breakdown in the air, the sample was potted in Picein. This simple procedure made it possible to carry out investigations in electric fields up to 300 kV/cm. A high-voltage rectifier with controlled output voltage was used (maximum 15 kV) to obtain the high voltage.

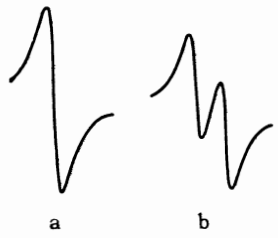


FIG. 2. EPR line shapes recorded with the automatic plotter for one of the orientations of E and H: a – E = 0; b – E = 200 kV/cm.

The splitting of the EPR lines of $Cr^{3+}$ in $ZnWO_4$, in an electric field 250 kV/cm, is of the order of the half-width of the corresponding line or smaller. A typical picture of the splitting is shown in Fig. 2b. To calculate the correct splitting in such cases it is necessary to take into account the EPR line shape and the degree of overlap of the split components.[11] According to our estimates, the EPR lines, corresponding to different transitions of the EPR spectrum of $Cr^{3+}$ and $ZnWO_4$ are close to Lorentzian in shape. Figure 3 shows the splitting of two EPR lines of the $Cr^{3+}$ ion in $ZnWO_4$ vs. the electric field **E**, calculated with allowance for the corrections for the overlap of the component.[11] The experimental points fit a straight line quite well, thus indicating that we are dealing with an effect linear in the electric field. Similar plots were obtained also for other transitions at different orientations of **H** and **E**.

We have observed a strong angular dependence of the splitting of the EPR lines, that is, a depend-

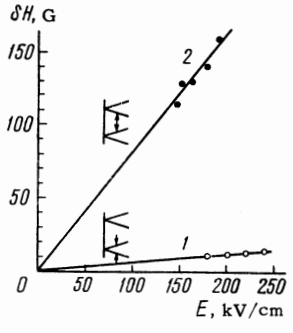


FIG. 3. EPR line splitting vs. external electric field for $\mathbf{H} \parallel z$ and $\mathbf{E} \parallel y$: 1 – for the transition $-3/2 \rightarrow -1/2$; 2 – for the transition $-3/2 \rightarrow +1/2$.

[2)] A detailed description of the EPR spectrometer constructed by us will be published elsewhere.

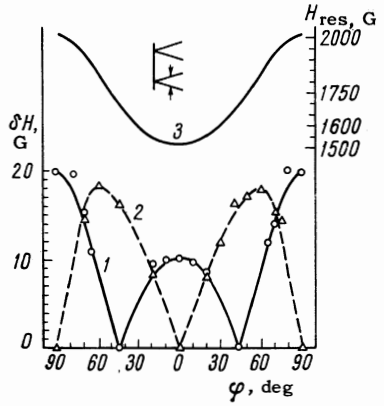


FIG. 4. Angular dependence of the splitting of the EPR line of the transition $-3/2 \rightarrow -1/2$ as H is rotated in the xy plane: curve 1 – E || y (E = 250 kV/cm); solid curve – theory, o – experiment; curve 2 – E || z (E = 225 kV/cm), dashed curve – theory, △ – experiment; curve 3 – angular dependence of the position of the same EPR line, drawn through the experimental points; δH – magnitude of splitting, $H_{res}$ – values of resonant field.

ence of the splitting on the orientation of the external electric and magnetic fields. To obtain the corresponding curves, the electric field was applied along one of the coordinate axes, and the orientation of the magnetic field was varied in planes perpendicular to the coordinate axes. For all the curves investigated by us, some of which are shown in Fig. 4 and Fig. 5 (curve 2) and Fig. 6 (curve 2), the agreement between the theoretical plots based on formulas (8) and (9) and the experimental values of the splitting can be regarded as good. The discrepancies amount to 5–10%, that is, they lie within the limits of the experimental error.

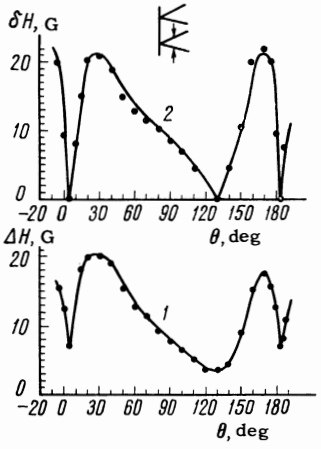


FIG. 5. Angular dependence of the half-width (1) and of the splitting (2) of the EPR line (transition $-3/2 \rightarrow -1/2$) upon rotation of H in the xz plane. Curve 1(E = 0) is drawn through the experimental point; curve 2(E || y, E = 180 kV/cm) – theory, points – experiment.

**Table II.** Experimentally obtained parameters of spin-Hamiltonian $\hat{W}_E$

| Parameters* | Value of the parameter, MHz-kV$^{-1}$cm |
|---|---|
| $\alpha_{211} - \alpha_{222}$ | 0.33±0.02 |
| $\alpha_{233} - \alpha_{222}$ | 0.18±0.02 |
| $\alpha_{213}$ | 0.60±0.03 |
| $\alpha_{123}$ | 0.38±0.04 |
| $\alpha_{312}$ | 0.41±0.04 |

*The parameters $\alpha_{112}$ and $\alpha_{323}$, and also all the parameters $\beta$, are equal to zero within the limits of experimental accuracy.

To determine the spin-Hamiltonian parameters directly, we used formula (7). Simultaneously (for control), corresponding estimates were made in accordance with the approximate formulas (8) and (9). The results of the calculations are listed in Table II. We note that the parameter $\alpha_1$ does not enter the formulas for the corrections to the transition frequencies (terms containing the parameter $\alpha_1$ lead to an identical shift of all four levels). By virtue of this, we cannot determine it from EPR experiments. As a result, Table II includes only the differences $\alpha_{211}-\alpha_{222}$ and $\alpha_{233}-\alpha_{222}$.

We have observed also a correlation effect between the angular dependence of the EPR line splitting in the external electric field and the angular dependence of the half-width of the corresponding EPR lines in the absence of an external electric field (see Fig. 5 and 6). Insofar as we know, there are no published reports of a correlation of this type, although indications pointing to the dependence of the half-width of the EPR line on the orientation of the magnetic field are contained in [12].

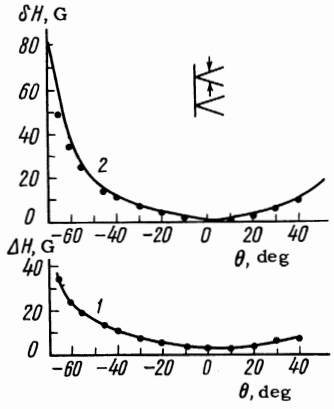


FIG. 6. Angular dependence of the half-width (1) and of the splitting (2) of the EPR line (transition $1/2 \rightarrow 3/2$) upon rotation of H in xz plane. Curve 1 (E = 0) is drawn through the experimental points; curve 2 (E || y, E = 200 kV/cm) – theory, points – experiment.

In our opinion, the noted correspondence between the two curves is connected with the presence of intracrystalline electric fields which are different in different regions of the crystal. These additional electric fields cause broadening of the EPR line, the position of which is determined by the Zeeman energy and the intracrystalline field (connected with the constants D and E), which are the same for all local centers of the same type.

The hypothesis advanced is confirmed by the correlation noted above. Indeed, for any orientation of the magnetic field in the xz plane, the splitting of the EPR line is due only to the y component of the electric field. By virtue of this, the angular dependence of the half width of the EPR line is similar to the angular dependence of the line splitting (the x and z components of the additional intracrystalline field do not manifest themselves). With change of the magnetic field in the xy and yz planes, splitting is completely missing only if the orientation of the electric field is respectively along the x and z axes. Therefore the angular dependence of the half-width of the line in these planes, generally speaking, does not duplicate the angular dependence of the splitting of the line when the external electric field orientation is along the y or z(x) axis. To explain the angular dependence of the line half width in this case it is necessary to have a superposition of two corresponding splitting curves.

One of the possible sources of the additional intercrystalline field may be the $Li^+$ ions which are added to the crystal to compensate the charge.

In conclusion we are grateful to M. F. Deĭgen and V. B. Shteĭnshleĭger for continuous interest in the work, V. A. Atsarkin for a discussion of the individual questions touched upon in the article, and L. I. Datsenko for help with the measurements.

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Translated by J. G. Adashko
181