INFLUENCE OF MICROSCOPIC POLARITY ON PARAMAGNETIC Cr³⁺ CLUSTERS IN TGS TYPE CRYSTALS

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EPR is used for determining coordination and the spin Hamiltonian parameters of the Cr^{3+} ion in the glycine crystals TGS, TGSe and TGFB. The influence of polarisation switching on the EPR spectrum of Cr^{3+} is determined both in temperature-rejuvenated and aged specimens. The molecular mechanism whereby by nearest neighbourhood of the Cr^{3+} ion changes on polarisation reversal is defined. A model of spontaneous polarisation fixing within a radius R about the Cr^{3+} ion is proposed, and the size of R is evaluated. According to the model proposed, the internal field E_b is related with volume charge on the boundaries of spheres, fixed by paramagnetic defect.

1. Introduction

Most papers on EPR studies of ferroelectrics define the symmetry and dynamics of individual molecular complexes from the viewpoint of the elucidation of details concerning the microscopic mechanism of spontaneous polarisation. From this viewpoint, the introduction of admixtures, or irradiation, is aimed at obtaining paramagnetic soundes (probes) within the lattice of the ferroelectric.

The Cr^{3+} ion is particularly well adapted to ferroelectric studies having recourse to its EPR spectrum. The latter, in fact, possesses a fine structure and its spectrum is relatively simple. TGS:Cr^{3+} simple crystals have been studied in 1966–1977 by us [1–3] as well as by others [4–6]. Also, we studied the complex ion Cr^{3+} in the isomorphous crystals TGSe and TGFB [7–9]. We published in 1974 [3] results on the influence of polarisation switching and neighbourhood on the EPR spectrum of Cr^{3+} in TGS, giving the mechanism according to which the nearest coordination neighbourhood of Cr^{3+} undergoes a change in the process of polarisation reversal.

Windsch et al., in papers published in 1975 and 1977, obtained similar results for the influence of temperature and polarisation reversal on the spectrum of Cr^{3+} in TGS; they draw attention to the important fact that the fine structure tensor D in TGS:Cr^{3+} can be expressed as a sum of the component D^{PE} in the paraelectric phase and the component

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ΔD proportional to the ferroelectric phase polarisation. Nishimura [6] had drawn attention to this indirectly in 1973, a clear illustration of the case when the entire axial deformation of the crystal field is due to the spontaneous polarisation P_s and vanishes above T_c is to be found in the TGFB:Cr^{3+}, studied by us [9].

The above results of EPR studies of Cr^{3+} in TGS, TGSe and TGFB crystals have been utilized by us in order to explain the molecular mechanism of polarisation reversal and ageing in this class of ferroelectrics.

2. Coordination of the Cr^{3+} ion in TGS, TGSe, TGFB, and the parameters of the spin Hamiltonian

The orthogonal system of reference for the study of the EPR spectrum anisotropy was chosen in conformity with the system of crystallographical axes a, b, c of Wood and Holden [10], with $X = a$, $Y = b$ and the Z-axis of the orthogonal system perpendicular to the a, b-plane.

Anisotropy studies of the EPR spectra of Cr^{3+} in TGS, TGSe and TGFB have shown the nearest coordination neighbourhood of the ion to consist of an octahedron of Gly II, Gly III and, respectively, two groups SO_4, SeO_4 or BeF_4. In TGS and TGSe, the octahedron undergoes distortion along the direction [111] in four distinct ways with equal probability; in combination with the distribution of the complexes in crystals having the symmetry C_2, this leads to eight magnetically though not spatially equivalent complexes of the Cr^{3+} ion which can be assigned to two types, I and II.
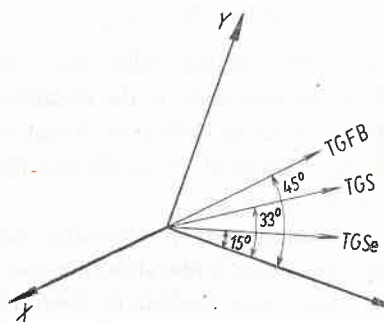

Fig. 1. The z-axis directions of the crystal field of type I Cr^{3+} complexes with respect to their coordination octahedron in TGS, TGSe and TGFB

The Cr^{3+} EPR spectrum easiest to interpret is that occurring in TGFB where, with respect to the smallness of the D-parameter ($D = 0.0620$ cm^{-1}), all spin-permitted lines are apparent in the X band. The coordination octahedron of Cr^{3+} in TGFB is distorted in two ways only, disposed in the crystal in accordance with C_2 thus leading to 4 complexes of the type I (following the classification exposed above). Type I complexes occur in all crystals of the TGS family; their Z-axis lies close to the ZY-plane of orthogonal coordinates.

Since, in these crystals, the crystal field gradient has the rhombic symmetry the deviation of the Z-axis from the direction [111] is completely determined by the non-axiality parameter $a = E/D$.

The Z-axis directions of the crystal field acting on Cr^{3+} in complexes of type I with respect to the orthogonal system XYZ in TGS, TGSe and TGFB are shown in Fig. 1, whereas Table I gives the parameters of the spin Hamiltonian.

TABLE I

	g	D cm^{-1}	E cm^{-1}	$a = E/D$
$(NH_2CH_2COOH)_3H_2SeO_4:Cr^{3+}$ (TGSe)	1.985	0.634	0.132	0.208
$(NH_2CH_2COOH)_3H_2SO_4:Cr^{3+}$ (TGS)	1.987	0.435	0.061	0.140
$(NH_2CH_2COOH)_3H_2BeF_4:Cr^{3+}$ (TGFB)	$g_\parallel = 1.9805$ $g_\perp = 1.9815$	0.0620	0.012	0.196

In TGS and TGSe, there occur (not shown in Fig. 1) complexes of the type II with Z-axis lying on a cone about the X-axis, with an aperture of $\alpha \approx 30°$ for TFS and $\alpha \approx 60°$ for TGSe:Cr^{3+} [1, 7].

3. The spin Hamiltonian parameters of Cr^{3+} in the phase transition region

In the phase transition region of the crystals under consideration, the position and fine structure splitting of the EPR lines of Cr^{3+} undergo a modification. Figs 2a, b, c show D vs. temperature for TGS:Cr^{3+}, TGSe:Cr^{3+} and TGFB:Cr^{3+}. The splitting $\Delta D = D'_A - D_A$ increases with decreasing temperature and is proportional to the spontaneous polarisation P_s at the temperature considered.

At arbitrary temperature, the parameter D_t of the crystal field on Cr^{3+} in TGS and TGSe is given by the expression [7]:

$$D_t = D_0 \pm S\Delta D, \tag{1}$$

with: $\Delta D = D'_A - D_A$ at low temperatures, for which $S = 1$, D_0 — the EPR fine structure parameter at $T = T_c$, and S — the ordering parameter to which, in TGS crystal, the spontaneous polarisation P_s is proportional.

The crystal field gradient on Cr^{3+} consists of a distortional term, independent of $P_s(D_0$ at $T = T_c)$, and a term proportional to the spontaneous polarisation P_s of the ferroelectric. Fig. 2c shows D vs. temperature for TGFB:Cr^{3+}; one notes that above T_c the crystal field on Cr^{3+} possesses the cubic symmetry ($D_0 = 0$, no fine structure of the EPR spectrum), whereas in the ferroelectric phase D_t obeys the relation:
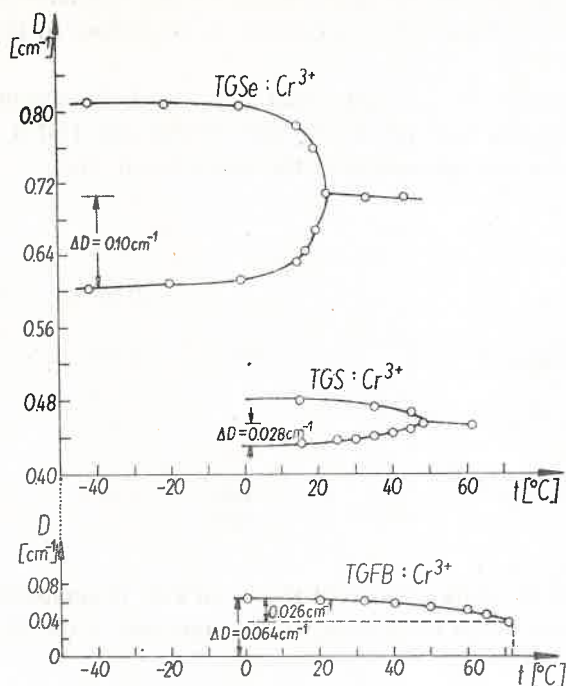
$$D_t = \pm S\Delta D, \tag{2}$$

Fig. 2 a, b, c. Parameter D vs temperature, for $TGSe:Cr^{3+}$, $TGS:Cr^{3+}$ and $TGFB:Cr^{3+}$

representing a particular case of Eq. (2). Consequently, in the case of $TGFB:Cr^{3+}$, the magnitude of the crystal field gradient is defined completely by the influence of spontaneous polarisation on the paramagnetic cluster of the Cr^{3+} ion.

4. The dielectric properties of Cr^{3+}-admixtured TGS, TGSe and TGFB crystals, and their EPR spectrum

The ion Cr^{3+}, inserted into TGS crystal, affects the shape and parameters of the dielectric hysteresis loop [11, 12]. The change in shape of the loop depends on the domain structure and dynamics (ageing) of the specimen. Measurements of P_s in "aged" and "rejuvenated" crystals of the $TGS:Cr^{3+}$ group show that admixtures of Cu^{2+} and Cr^{3+} considerably lower P_s compared to crystals free of those ions. The concentration of Cr^{3+} ions in $TGS:Cr^{3+}$, determined polarographically, amounted to $0.5 \times 10^{-3}\%$.

Were we to adhere to the assumption that, in TGS, each Cr^{3+} ion immobilizes glycine and SO_4 groups in its nearest coordination neighbourhood only, the circumstance that the bonding by a Cr^{3+} ion of (on the average) 1 elementary cell per 1.6×10^4 cells of TGS lowers P_s by $0.4 \, \mu C/cm^2$ compared to admixture-free TGS would be incomprehensible. In our opinion, the reason is that the "effective radius" of distortion of P_s by the admixture ions is much larger than the metal-ligand radius of the first coordination sphere.

The spontaneous polarisation of TGS crystals without admixtures can be described by the relation:

$$P_s = 2\mu N S_1, \tag{3}$$

where 2μ is the dipole moment of the elementary cell, N — the number of TGS cells, and $S = (N_+ - N_-)/(N_+ + N_-)$ the ferroelectric order parameter. On the other hand, P_s in TGS with admixtures is well described by the relation:

$$P_{s,d} = 2\mu(N-n)S_2, \tag{4}$$

where n is the number of cells "blocked" by the admixture. The parameters $S_{1,2}$, at a given temperature, can be determined from the ratio $S = P_s/P_0$, where P_0 is the saturation value of P_s (at 0 K, or in low temperatures when P_s is practically temperature-independent). The values of S, determined in this way for admixture-free TGS and that determined by EPR from Eq. (1), are identical. Hence, in TGS:Cr^{3+} containing $0.5 \times 10^{-3}\%$ weight of the admixture, the latter does not modify the ferroelectric ordering parameter S. Moreover, the crystal field gradient related with ferroelectricity is proportional to S.

The fact that the parameters S_1 and S_2 are equal enables us to express P_s, for admixtured TGS, in the following form:

$$P_{s,d}(T) = P_s(T)\left[1 - \frac{n}{N}\right], \tag{5}$$

with: P_s the spontaneous polarisation of pure TGS n — the number of cells "blocked" by a Cr^{3+} ion, and N — the number of cells per Cr^{3+} ion.

The values measured for $P_{s,d}$ and P_s jointly with Eq. (5) lead to $n = 2400$ out of the 1.6×10^4 elementary cells per each Cr^{3+} ion. Hence, we calculated the radius of the sphere of n cells blocked by a Cr^{3+} ion as equal to $R \approx 73$ Å. Our evaluation was carried out for the $P_s(Cr^{3+})$ and P_{s0} values of TGS crystals rejuvenated by annealing at 100°C for many hrs. A similar evaluation for well aged TGS:Cr^{3+} led to $R \approx 90$ Å, pointing to an increase of the region of "clamped" spontaneous polarisation as the result of ageing in TGS:Cr^{3+}.

At first, so large a radius of interaction of the admixture ion might seem exaggerated. However, it should be noted that the fine structure parameter D of the EPR spectrum is related with the atomic environment of the paramagnetic ion the source of the crystal field acting on the ion as follows [13]:

$$D = K\left(\frac{\lambda}{\varDelta}\right)^2 \vartheta \tag{6}$$

with K — a dimensionless constant, λ — the spin-orbit coupling constant, ϑ — the parameter of the trigonal field, and $\varDelta$ — that of the cubic field.

The parameters ϑ and $\varDelta$ are expressed by way of sums A_n^m, the calculation of which would involve the knowledge of the coordinates R_i, $\varTheta_i$, φ_i of the atoms with respect to

the centre of the admixture ion. After Ref. [14] we have:

$$\Delta \equiv 10Dq = 10\left\{3\sqrt{2}\,A_4^3 - \frac{4}{27}\left[A_4^0 - \frac{A_4^3}{20\sqrt{2}}\right]\right\}\frac{2}{105}\langle r^4\rangle,$$

$$\vartheta = \frac{6}{7}A_2^0\langle r^2\rangle + \frac{160}{63}\left[A_4^0 - \frac{A_4^3}{20\sqrt{2}}\right]\langle r^4\rangle,$$

$$A_2^0 = \sum_i \frac{e_i(3\cos^2\Theta_i - 1)}{4R_i^3},$$

$$A_4^0 = \sum_i \frac{e_i(35\cos^4\Theta_i - 30\cos^2\Theta_i + 3)}{64R_i^5},$$

$$A_4^3 = \sum_i \frac{70e_i\sin^3\Theta_i\cos\Theta_i}{16R_i^5}, \qquad (7)$$

where $\langle r^2\rangle$, and $\langle r^4\rangle$ are mean values of the distance of the d-electron of the ion from the nucleus, and e_i is the charge on the ion i.

Calculations of the terms A_n^m for Cr^{3+} in $MgAl_2O_3$ and $Zn(Al_2O_3)$ show that the series A_4^0 ($\Delta \sim A_4^0$) converges within a radius of $R = 8$ Å whereas, in order to achieve convergence of the series A_2^0 ($\vartheta \sim A_2^0$), summation has to be performed for $R = 35 \div 40$ Å, where the differences in value for several spheres more do not exceed 10% of A_2^0. The trigonal distortion of the nearest surroundings of the complex can be thought to be the result of an interaction reaching far beyond the first coordination sphere.

Studies by other authors [15, 16] appear to confirm our evaluations. Work by Krajewski [15] on the thermal diffusivity coefficients of TGS crystals, pure and admixtured with Cu^{2+} and Cr^{3+} ions, has permitted the calculation of the regions perturbed by the admixture. The edge of the cube perturbed by a Cr^{3+} ion, at a Cr^{3+} concentration of 0.5×10^3% weight, is equal aftei Ref. [15] to $d = 100$ Å, in good agreement with the evaluation proposed by us. Kornfeld and Lemanov [17], studying quadrupole effects in the EPR spectrum, have shown that the perturbation caused by Ag^+ and K^+ in the lattice of NaCl admixtured with Ag^+, or K^+, amounts to 8.9 Å and, respectively, 16.7 Å.

5. EPR study of polarisation reversal in TGS, TGSe and TGFB:Cr^{3+}

The EPR spectra of Cr^{3+} in TGS, TGSe and TGFB were studied in their dependence on the state of polarisation of the crystals using a JEOL 3BX spectrometer and Saver-Tower circuit which permitted the simultaneous observation od the EPR spectra and hysteresis loops. The crystal in the resonance cavity was rotated about the X-axis of orthogonal coordinates, as shown in Fig. 3. In this way, it was possible to carry out observations of the EPR lines for complexes of the types $I_{A'}$ and $I_{B'}$, along the principal z-axis directions of their crystal field. An accurate investigation of the positions, splitting and intensities of the EPR lines AA' and BB' as functions of the state of ageing and polarisation of TGS and TGSe crystals showed that [18]:

1. The principal x, y and z-directions of the crystal field of the paramagnetic complexes do not change their orientation in space (within the accuracy of experiment) in the para-electric phase, or on applying a static electric field E;

2. In $TGS:Cr^{3+}$ and $TGSe:Cr^{3+}$, rejuvenated by annealing at 100°C during 24 hrs, the dielectric hysteresis loop is symmetric and the EPR line intensities fulfil, respectively, the equalities: $A = B$, $A' = B'$;
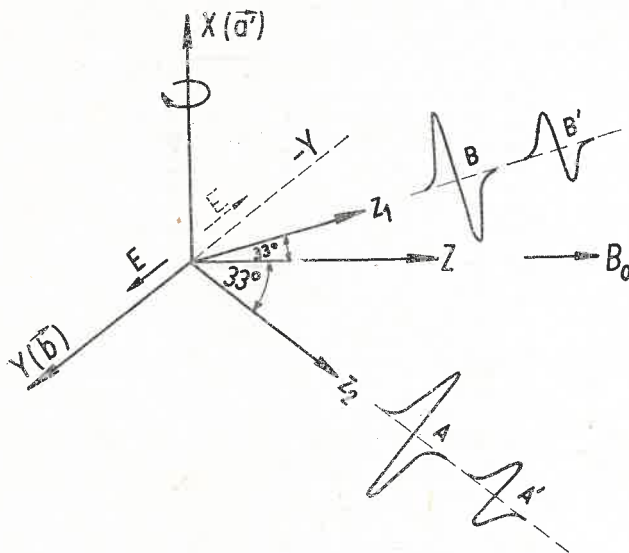

Fig. 3. Crystal orientation applied when studying the influence of polarisation reversal on the line intensities of complexes A, A' and B, B' (type I)

3. On polarizing the TGS crystal with a field $E_{\pm}^{+}$, the EPR lines B, A' practically vanish whereas the lines A, B' double their intensities. The macroscopic hysteresis loop shifts by a value of E_b with respect to the origin of coordinates P_s;

4. The inverse i.e. a vanishing of the intensity of the lines A, B' and a doubling of that of B, A' is obtained in a field $E_{\pm}^{-}$ (the sign of E being a matter of convention) provided the specimen was subjected to "rejuvenation" previous to application of the field;

5. Polarisation reversal in a crystal polarized with a field $E_{\pm}^{+}$ (see, 3°), if unaccompanied by rejuvenation, shifts the loop by $-E_b$ and causes the following changes in the EPR spectrum: $A' \to A$, $B \to B'$.

Those transitions Stankowski named as vertical [23].

6. The molecular mechanism of polarisation reversal in crystals of the $TGS:Cr^{3+}$ group, and the model of the internal field E_b

On the basis of our evaluations (Section 4) of the effective radius $R \approx 73$ Å of inter-action of the paramagnetic ion Cr^{3+} with its ferroelectric environment, we established a model providing an explanation of the decrease in P_s in admixtured $TGS:Cr^{3+}$ crystals

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and of the behaviour of the EPR spectrum in the process of polarisation reversal (see, Section 5, 1°—5°). Thus, in a two-domain rejuvenated TGS:Cr^{3+} crystal, the disposition of the Cr^{3+} complexes can be represented as shown in Fig. 4. Bold-face type arrows denote the dipole moment of a complex. To the paramagnetic complex (Cr^{3+} ion + nearest coordination surroundings) we assign a dipole moment in the z-axis direction of the D-tensor as done by Fujimoto for VO^{2+} complexes in DGTS [19]. It is now clear why, in the paraelectric phase of TGS:Cr^{3+}, we have to deal with complexes A and B only,
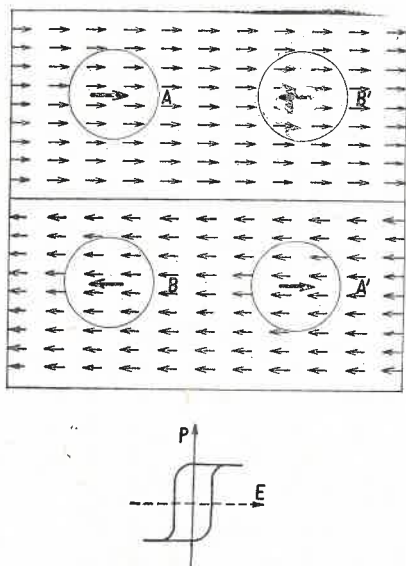

Fig. 4. Disposition of the dipole moment of complexes A, A' and B, B' in a two-domain rejuvenated TGS:Cr^{3+} crystal

whereas in the ferroelectric phase we have complexes A, B and A', B' as a result of the difference in energy of the dipole moment in the directions parallel and antiparallel to the direction of P_s (Fig. 4).

The change in dipole moment $\pm \Delta \mu$ of the complex due to the emergence of spontaneous polarisation P_s in the crystal below T_c is easy to evaluate. By (6), we can write $D_{A'}$ and D_A as follows:

$$D'_A = K \left(\frac{\lambda}{\Delta_2} \right)^2 \vartheta_2, \tag{8}$$

$$D_A = K \left(\frac{\lambda}{\Delta_1} \right)^2 \vartheta_1.$$

Hence

$$\frac{D_{A'}}{D_A} = \left(\frac{\Delta_1}{\Delta_2} \right)^2 \frac{\vartheta_2}{\vartheta_1}. \tag{9}$$

Since the direction of trigonal distortion is conserved for the complexes A and A', we can assume that:

$$\frac{\vartheta_2}{\varDelta_2} = \frac{\vartheta_1}{\varDelta_1} = \text{const.} \tag{10}$$

Eq. (9), in conjunction with the condition (10), leads to:

$$\frac{D_A}{D_{A'}} = \frac{\varDelta_1}{\varDelta_2}. \tag{11}$$

On insertion of the experimental values of $D_{A'}$ and D_A we obtain: $\varDelta_1/\varDelta_2 = 1.11.$ at room temperature.

On the assumption that the cubic component of the crystal field is due primarily to ligands of the first coordination sphere one can evaluate the change $\varDelta r$ in radius of that sphere on transition of the complex from the state A to A' from the expression:

$$\frac{\varDelta_1}{\varDelta_2} = \left(\frac{r_1}{r_2}\right)^5. \tag{12}$$

On taking as r_1 the distance from the plane of the coordination octahedron of Cr^{3+} to the oxygen number 4 after HOP [24] of the SO_4 group ($r_1 \approx 1.91$ Å from X-ray studies), Eq. (12) leads to $\varDelta r = r_1 - r_2 \approx 0.04$ Å (the change in length of the bond in SO_4 being of the order of 0.01 Å [21] on transition from 57°C to 19°C). A change in length of the metal-ligand by $\varDelta r \approx 0.04$ Å involves a change in dipole moment of the complex by $\pm 0.19\,D$.

By [19], the intensity ratio of the lines A and A' is given by the expression:

$$\frac{A'}{A} = e^{\frac{-\varDelta U}{KT}}, \tag{13}$$

where $\varDelta U$ is the difference in energy of the complex in the states A' and A, amounting to:

$$\varDelta U = 2\varDelta\mu E \cos\alpha, \tag{14}$$

with E denoting the molecular field originating in the system of dipoles of the ferroelectric.

With regard to (13) and (14), we easily obtain the following expression for the molecular field E:

$$E = \frac{KT}{2\varDelta\mu \cos\alpha} \ln \frac{A'}{A}. \tag{15}$$

We studied the behaviour of the intensity ratio A'/A in the process of rejuvenation and ageing of TGS:Cr^{3+} crystal [3]. Fig. 5 shows the evolution in time of the changes in A'/A permitting, with (15), the determination of the molecular field E as 2×10^7 V/cm.

The rearrangement of the nearest coordination surroundings of the Cr^{3+} ion consists in the following. For complete compensation of its positive electric charge, the Cr^{3+} ion

coordinated to glycines II and III requires bonding to the SO_4^{2-} group, as a result of which the Cr^{3+} complex in TGS has the following structure (Fig. 6):

$$Cr(NH_2CH_2COO)_2H_2SO_4 \cdot HSO_4^-$$

$$Cr(NH_2CH_2COO)_2HSO_4^- \cdot H_2SO_4$$
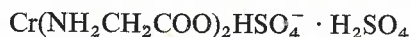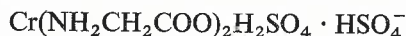
From Fig. 6 one notes that the presence or lack of a proton on the left or right side of the octahedron leads to a favouring of the distortion z_1 or z_2. As a result of the reversal
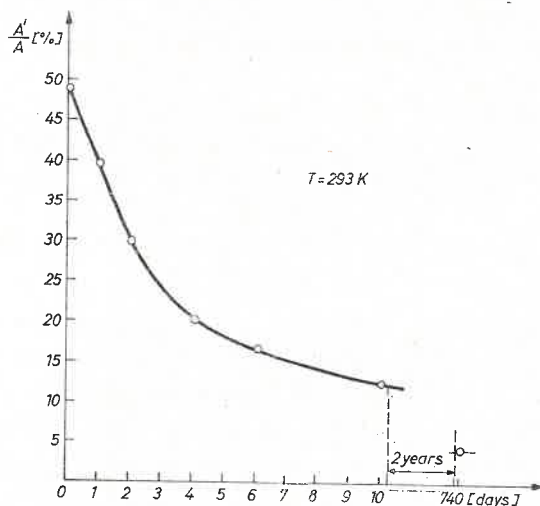

Fig. 5. Time-evolution of the intensity ratio A/A'

of P_s (the reversal of glycine I) we are able to distinguish the direction z_1 or z_2. Hence, polarisation of the TGS crystal in one direction causes a shift of the proton in the long hydrogen Gly I–SO$_4$ bond.

A similar effect has been discovered by Du Varney [20] in irradiated KDP. The EPR lines of KDP could be assigned to four doublets $2A + 2B$, of equal intensity. Polarisation of the E_c crystal with an external field $E \geqslant E_c$ led to a transfer of spin density to two octahedra ($2A$). The transfer of spin density between octahedra A and B is, according to Ref. [20], due to a displacement of the proton along the bond OH...O from "upper" to "lower" oxygenes of PO_4^- groups depending on the sense of the external electric field. The circumstance that the spin density mechanism in hydrogen-bonded ferroelectrics, like those of the types of TGS and KDP, are similar, points to an essential role of proton jumps in the mechanism of polarisation reversal.

The Cr^{3+} ion complexes in TGS and TGSe exhibit a rhombic distortion of their crystal field, as well as a dipole moment μ_0, already in the paraelectric phase. In the ferroelectric phase, as a result of further distortion, the dipole moment of the complex amounts to $\mu_0 \pm \Delta\mu$. The disposition of such a moment within a ferroelectric leads to four distinct energy states A, A' and B, B' of the complex, as is shown in the model (Fig. 4).
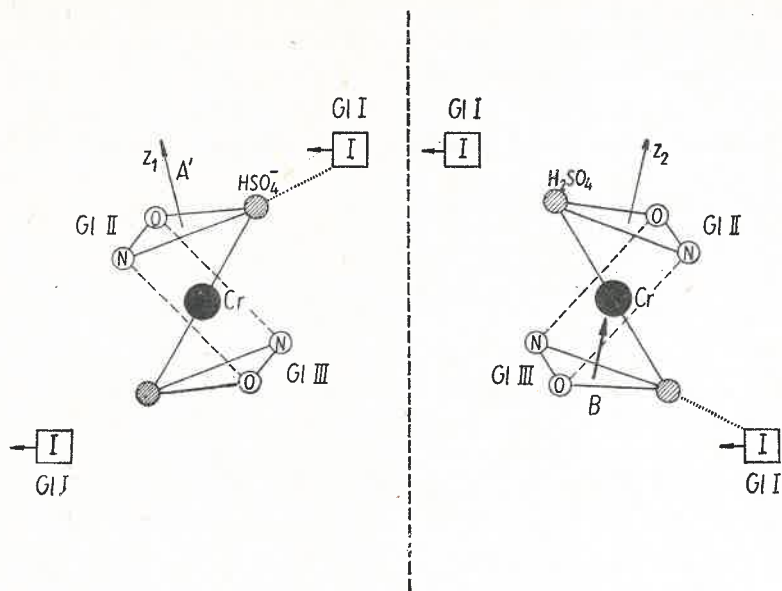
Fig. 6. Structure of Cr³⁺ complexes in TGS, TGSe and TGFB, and model of the mechanism "triggering" the changes in the direction of distortion
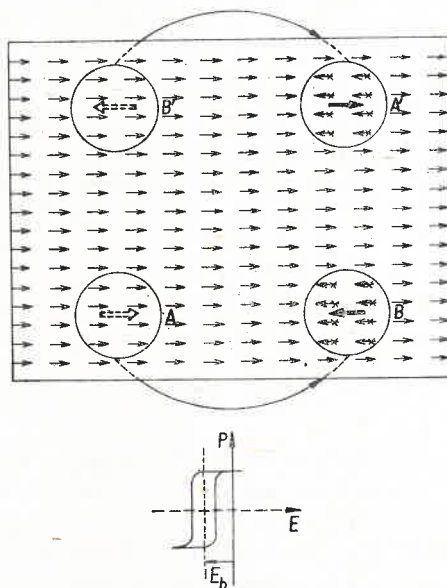

Fig. 7. Disposition of the dipole moments of complexes A, A' and B, B' in a single-domain TGS:Cr³⁺ crystal polarized with a field $E_{\pm}$ immediately after rejuvenation

In the case of TGFB, upwards of T_c the Cr^{3+} complexes are situated in a cubic crystal field, whereas below T_c rhombic distortion sets in with a moment $\pm \Delta \mu$, proportional to P_s, and the spectrum shows but complexes A and B in the direction z_1 and z_2.

As far as the radius R of interaction between the admixture ion and ferroelectric environment extends, the spontaneous polarisation P_s is clamped as a result of interaction
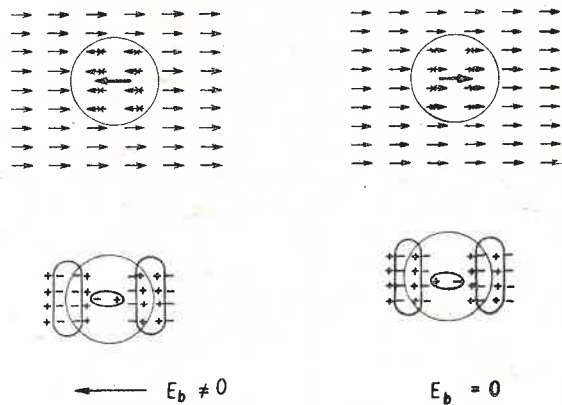

Fig. 8. The emergence of uncompensated charge on the surface of the sphere R, the clamped dipole moments within the sphere being directed oppositely to the polarisation within the domain
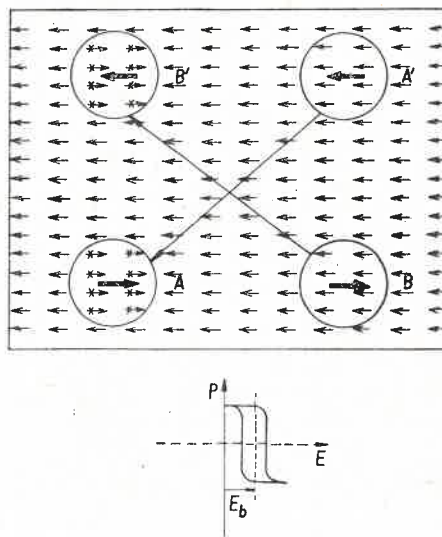

Fig. 9. Disposition of the dipole moments of complexes A, A' and B, B' in the single-domain crystal of Fig. 7 subsequent to polarisation reversal with a field $E_=$ (without rejuvenation)

between the dipole moment of the paramagnetic cluster, which was determined by us on $10\,D$ [23], and its ferroelectric environment [18]. Monodomainization of the two-domain crystal by means of a field $E_=$ (see model, Fig. 4) leads to the following rearrangement of the ferroelectric (Fig. 7). Due to polarisation clamping within the sphere of radius R

by a complex in the state B or A', an uncompensated charge arises on the surface of the sphere to which an internal displacement field E_b is proportional (Fig. 8). The application of a field $E_=$ of opposite sign without previous rejuvenation of the crystal shown in Fig. 7 causes the ferroelectric crystal to undergo a rearrangement (Fig. 9) with the emergence of a field $-E_b$. The spectral situation, corresponding to the disposition of complexes in their energy states A, B, A' and B', is in fact observed in experiment (Figs. 7 and 9).

7. Summary

1. The nearest coordination position of the ion Cr^{3+} in TGS, TGSe and TGFB consists of Gly II and Gly III as well as the respective two ions SO_4, SeO_4 and BeF_4.

2. In TGS and TGSe, the crystal field gradient on Cr^{3+} consists of a distortional term ($D_0 \neq 0$ at $T \geqslant T_c$) and a term ΔD, proportional to the spontaneous polarisation P_s (Fig. 2a, b)).

3. Upwards of T_c, Cr^{3+} in TGFB is situated in a crystal field of cubic symmetry ($D_0 = 0$) and the distortion of the crystal field below T_c is due to the spontaneous polarisation alone (Fig. 2c).

4. In TGFB:Cr^{3+}, contrary to TGS and TGSe:Cr^{3+}, no excited complexes A', B' arise on rejuvenation of the crystal.

5. From the decrease in P_s caused by the presence of Cr^{3+} ions at a given concentration, the radius R of the perturbation due to the Cr^{3+} cluster in the ferroelectric is evaluated ($R \approx 73$ Å). Most probably, this is the distance at which the trigonal component of the crystal field vanishes ($\vartheta \sim A_2^0$).

6. A model of spontaneous polarisation clamping within a radius equal to R about the admixture, in the process of polarisation reversal by a field $E_=$ in thermally rejuvenated TGS type crystals, is proposed (Fig. 7).

7. The energy of the complex in the crystal is determined by the orientation of its dipole moment and that of the polarisation within the sphere of radius R (Figs 4, 7, 9).

8. Reversal of the field $E_=$ unaccompanied by rejuvenation removes the clamping in some regions (complexes A', B) and causes clamping in others (A, B') (Fig. 9).

9. It is proposed that the ageing process in admixtured ferroelectrics of the TGS type consists in an increase in the radius R about the dipolar centre whereas rejuvenation consists in the "melting" of outer zones of the spheres (i.e. in a decrease of R) [18].

10. The internal field E_b is related with microscopic volume charge on the surfaces of the spheres clamped by the paramagnetic defect.

REFERENCES

[1] S. Waplak, J. Stankowski, *Acta Phys. Pol.* **36**, 171 (1969).
[2] J. Stankowski, S. Waplak, A. Dezor, B. Sczaniecki, *Phys. Status Solidi* **23**, K159 (1967).
[3] S. Waplak, V. A. Yurin, J. Stankowski, *Acta Phys. Pol.* **A46**, 175 (1974).
[4] S. Wartewig, W. Windsch, *Ann. Phys.* (Germany) **24**, 243 (1970).
[5] W. Windsch, G. Völkel, *Ferroelectrics* **9**, 187 (1975).
[6] K. Nishimura, T. Hashimoto, *J. Phys. Soc. Jap.* **35**, No 6 (1973).

[7] S. Waplak, T. Terlecka, M. Krupski, *Acta Phys. Pol.* **A50**, 71 (1976).

[8] J. Stankowski, S. Waplak, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **19**, No 4 (1971).

[9] J. Stankowski, S. Waplak, *J. Phys. C* **2**, 33 (1972).

[10] E. A. Wood, N. Holden, *Acta Crystallogr.* **10**, 145 (1957).

[11] J. Stankowski, *Acta Phys. Pol.* **31**, 527 (1967).

[12] J. Stankowska, *Acta Phys. Pol.* **A43**, 603 (1973).

[13] P. H. Meyer, H. J. Geristen, *Phys. Rev.* **100**, 742 (1955).

[14] V. B. Kravchenko, A. E. Levschin, E. N. Muravyev, *Spektroskopiya Kristallov*, Moscow 1970.

[15] T. Krajewski, M. A. Riad, J. Łoginov, *Fiz. Dielektr. Radiosp.* **8**, 111 (1976).

[16] T. Krajewski, M. A. Riad, *Acta Phys. Pol.* **A48**, 649 (1975).

[17] M. T. Kornfeld, V. V. Lemanov, *Zh. Eksp. Teor. Fiz.* **43**, 2021 (1962).

[18] S. Waplak, *Prace IF PAN*, Warszawa 1977 (in press).

[19] M. Fujimoto, L. A. Dressel, *Ferroelectrics* **8**, 611 (1974).

[20] R. C. Du Varney, R. P. Kohin, *Phys. Rev. Lett.* **20**, 259 (1968).

[21] K. Itoh, T. Mitsui, *Ferroelectrics* **5**, 235 (1973).

[22] V. A. Yurin, S. Waplak, J. Stankowski, M. A. Ankudinov, I. S. Zheludev, *Kristallografiya* **21**, 327 (1976).

[23] J. Stankowski, *Ferroelectrics* (in press as plenary lecture of IFM-4 at Leningrad).

[24] S. Hoshino, Y. Okaya, R. Pepinsky, *Phys. Rev.* **115**, 323 (1959).