# ON THE STRUCTURAL MECHANISM OF THE ELECTROOPTIC AND THERMOOPTIC EFFECTS IN FERROELECTRIC CRYSTALS OF THE TRIGLYCINE SULFATE TYPE

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## Abstract

## Full Text

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# ON THE STRUCTURAL MECHANISM OF THE ELECTROOPTIC AND THERMOOPTIC EFFECTS IN FERROELECTRIC CRYSTALS OF THE TRIGLYCINE SULFATE TYPE

*(Presented by Academician A. V. Shubnikov, 18 II 1966)*

It is known that the onset of spontaneous polarization in ferroelectric crystals of the TGS type is due to the displacement of the nitrogen atom from the plane of glycine along the $b$ axis ([1,2]). However, as recent investigations of the infrared spectra of these crystals ([3,4]) have shown, the $SO_4^{2-}$ ($SeO_4^{2-}$) ion plays by no means the least role in the occurrence of the phase transition in them. This symmetric, tetrahedral ion in the free state is, in a monoclinic crystal, in a distorted state; moreover, in the case of ferroelectric crystals of the TGS type, the distortion of its tetrahedral character occurs both in the ferroelectric and in the paraelectric phases, since both are monoclinic.

**Fig. 1.** Projection of the $SO_4^{2-}$ ion along the $c$ axis (after ([1])). The numbers indicate the values of the lengths of hydrogen bonds at room temperature. The oxygens of the $SO_4^{2-}$ ion are shaded.

The distortion of the $SO_4^{2-}$ ion is determined by the difference in the strengths of the hydrogen bonds connecting its oxygens with atoms of other groups of the crystal lattice. The shortest and, consequently, the strongest of these bonds is the hydrogen bond $O_I \cdots H—O_I$ of length 2.54 Å, connecting the oxygens of the $SO_4^{2-}$ ion and glycine I in a direction close to $a \sin\beta$ (Fig. 1). If there were no other bonds, the maximum electronic polarizability of the $SO_4^{2-}$ ion would

Fig. 2. Projection of the $CO_4^{2-}$ ion along the $b$ axis (schematic approximation). The letters $R$ and $H$ mark the position of the plane of the optical axes at room temperature and near the melting point, respectively.

Figure 2: Fig. 2. Projection of the $CO_4^{2-}$ ion along the $b$ axis (schematic approximation). The letters $R$ and $H$ mark the position of the plane of the optical axes at room temperature and near the melting point, respectively.

be observed precisely in this direction. However, because of the presence of other hydrogen bonds of the oxygens of the $SO_4^{2-}$ ion with $NH_3^+$ groups, the tetrahedron proves to be distorted most strongly not in the indicated direction, but in a certain other direction, determined by the resultant of all the hydrogen-bond forces acting on the ion in question.

As calculation shows, the determining contribution to the refraction of TGS crystals is made precisely by the $SO_4^{2-}$ ions. In considering the structure of TGS ($^1$), it is seen that along the $b$ axis there are two types of $SO_4^{2-}$ ions, but the second is a "twin" of the first rotated by 180°; therefore, for simplicity, the discussion presented here is limited to taking into account only one type of $SO_4^{2-}$ ions. In view of what has been said above, it is clear that the direction of maximum polarizability of crystals of the TGS type, and along with it the orientation

the refractive index $n_g$ and the plane of the optical axes differ from the direction of the bond $O_I \cdots H—O_I$ by some small angle (Fig. 2).

When the temperature changes in the paraelectric phase, because of the difference in the change of bond forces, the direction of the resultant, and hence also of the maximum distortion of the ion $SO_4^{2-}$, rotates about the $b$ axis. Consideration of the structure and allowance for the fact that, as the temperature rises, the distances between molecular groups increase and the hydrogen bonds weaken make it possible to establish the direction of rotation of the resultant (Fig. 2).

In light of the foregoing it is natural to assume that the change in the direction of maximum polarizability, i.e., the rotation of the indicatrix in TGS, is determined mainly by a change in the distortion of the tetrahedral ion $SO_4^{2-}$. Therefore the rotation of the indicatrix (see (5)) may serve as a measure of this distortion, together with the displacement of the $b$-component of the vibration $\nu_3$ in the infrared reflection spectrum (4). The smallest distortion of the tetrahedral ion $SO_4^{2-}$ occurs at high temperatures (near the melting point). The transition to the ferroelectric phase increases the distortion of the $SO_4$ ion owing to the growth of the polarization field caused by the ordering of the directions of displacement of the nitrogen atoms; moreover, this additional distortion is proportional to the square of the spontaneous polarization.

**Fig. 2.** Projection of the $CO_4^{2-}$ ion along the $b$ axis (schematic approximation).

The letters $R$ and $H$ mark the position of the plane of the optical axes at room temperature and near the melting point, respectively.

Upon isomorphous replacement of sulfur by selenium, the rigidity of the electron shell of the tetrahedral ion decreases (3). It may be assumed that, in a first approximation, the elasto-optic coefficient of the crystal is inversely proportional to the rigidity of the electron shell of the tetrahedral ion. Then one can calculate the ratio of the elasto-optic coefficients for TGS and TGSe and compare it with experiment. The theoretical ratio of the inverse rigidities (compliances) of the electron shells of the ions $SO_4^{2-}$ and $SeO_4^{2-}$, as shown in (3), is 0.92. The ratio of the shear elasto-optic coefficients in the paraelectric phase obtained from the data of work (5) proved to be 0.93. Such good agreement speaks in favor of the validity of the approach used.

Consideration of the influence of an external electric field $E_y$ on the deformation of the ion $SO_4^{2-}$ (or $SeO_4^{2-}$) in a single-domain TGS (or TGSe) crystal introduces nothing fundamentally new in comparison with taking into account the influence of the field of spontaneous polarization. The polarization field (both spontaneous and induced) affects the direction of maximum polarizability of TGS and TGSe mainly through the nitrogen atoms $N_{II}$ and $N_{III}$, changing their position relative to the ion $SO_4^{2-}$ ($SeO_4^{2-}$) (2). From the instability of the structure at the Curie point, in particular of the position of nitrogen relative to the plane of the glycine ion, it follows that here one may expect the greatest displacement of nitrogen under the action of even a not very large polarizing field $E_y$. It is precisely for this reason that the electro-optic coefficient $f_{s2}$ is maximal at the Curie point (6).

In a multidomain crystal the picture is complicated in no essential way by the presence of oppositely displaced nitrogen atoms in antipolarized domains. The moment of repolarization corresponds to the unstable, with respect to the field, state of the structure; consequently, here (as also at the Curie point) a maximum of the electro-optic coefficient should be observed.

If the spontaneous polarization is close to saturation (the structure is almost completely ordered), then the further change in the direction of maximum polarizability with decreasing temperature depends, as in the paraelectric phase, only on the redistribution of bond forces with temperature and follows, as experiment shows ($^5$), a law linear in the first approximation (at very low temperatures linearity, generally speaking, may be violated).

**Fig. 3.** Temperature dependence of the rotation of the optical indicatrix in TGS and TGSe crystals at high temperatures. The value $\varphi = 0$ corresponds to the position of the plane of the optical axes in both crystals at the Curie temperatures.

Interesting possibilities are opened up by measurements of the rotation of the optical indicatrix in the paraelectric phase at temperatures close to the melting point of the crystal (Fig. 3). In the paraelectric phase the crystal lattice of TGS

Fig. 3. Temperature dependence of the rotation of the optical indicatrix in TGS and TGSe crystals at high temperatures. The value $\varphi = 0$ corresponds to the position of the plane of the optical axes in both crystals at the Curie temperatures

Figure 3: Fig. 3. Temperature dependence of the rotation of the optical indicatrix in TGS and TGSe crystals at high temperatures. The value $\varphi = 0$ corresponds to the position of the plane of the optical axes in both crystals at the Curie temperatures

(or TGSe) may be regarded as a framework of heavy and rigid ions $SO_4^{2-}$ (or $SeO_4^{2-}$), joined by hydrogen bonds with light glycine groups "floating" inside it. The melting of the crystal will then be determined by the rupture of these bonds; but since their energies are different, the destruction of the bonds with increasing temperature occurs not simultaneously, but begins with the weakest (longest) bonds ($^7$). Then the "true" melting point will correspond to the rupture of the strongest bond $O_I \cdots H—O_I$. Since, as shown above, the rotation of the indicatrix is sensitive to the redistribution of bond forces, one may expect anomalous behavior of the temperature dependence of the rotation angle $\varphi(T)$ of the optical indicatrix not only at the Curie point, but also at the temperatures of bond rupture. We succeeded in observing these anomalies experimentally (Fig. 3).

Analyzing the curves given in Fig. 3 for TGS and TGSe, it is not difficult to see that above the Curie point for both crystals there are several characteristic temperatures $T_i$ (not counting the melting point) at which the dependences $\varphi(T)$ have breaks. These temperatures apparently should be attributed to the temperatures of rupture of the bonds $O_3 \cdots H—N_I$, $O_2 \cdots H—N_{II}$, $O_I \cdots H—N_{II}$, $O_I \cdots H—N_{III}$, i.e., of those bonds which have a component in the direction perpendicular to the *b* axis and can therefore most appreciably affect the rotation of the indicatrix.

The characteristic temperatures $T_i$ and the melting temperatures of TGS and TGSe crystals can be related to the rigidity of the electron shells of the central atoms of the $SO_4^{2-}$ and $SeO_4^{2-}$ ions in the same way as was done in (3) for the Curie points (Table 1). The table shows quite convincingly that the ratio of the corresponding characteristic temperatures (and melting temperatures) of these crystals is equal to the ratio of the rigidities of the electron shells of the central atoms of the $SO_4^{2-}$ and $SeO_4^{2-}$ ions.

**Table 1**

**Characteristic temperatures, °K**

| Crystal | $T_{melt}$ | $T_1$ | $T_2$ | $T_3$ | $T_4$ | $T_C$ |
|---|---|---|---|---|---|---|
| TGSe | 433 | 422 | 413 | 394 | 373 | 295 |
| TGS | 475 | 465 | 453 | 429 | 413 | 322 |
| Ratio | 0.913 | 0.908 | 0.912 | 0.918 | 0.902 | 0.917 |

| Crystal | $T_{\text{melt}}$ | $T_1$ | $T_2$ | $T_3$ | $T_4$ | $T_C$ |
|---|---|---|---|---|---|---|

The results obtained can also be extrapolated to other TGS-isomorphic crystals, in particular to triglycine fluoroberyllate (TGFB). For example, one may expect that the melting temperature of TGFB is about 230–235°C. We note only that high-temperature measurements on all crystals of the TGS group must be carried out in a neutral atmosphere or in oil, since in air these crystals show a strong tendency to decompose before reaching the melting point.

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*Note: Figure translations are in progress. See original paper for figures.*