

## ON THE ANISOTROPY OF THERMAL EXPANSION AND ELECTRICAL CONDUCTIVITY IN TRIGLYCINE SELENATE SINGLE CRYSTALS

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(Received 21 May 1990)

### ABSTRACT

Measurements of the thermal expansion of triglycine selenate (TGSe) crystals were carried out in the directions of five axes over a wide temperature range (123–323 K). The results show that the greatest expansion of the crystals lies approximately perpendicular to the direction of the axis  $a_{\text{HOP}}$ . The results of d.c. electrical conductivity ( $\sigma$ ) studies in the same five directions are also reported; the highest value of  $\sigma$  coincides with the direction of the greatest thermal expansion along which the lattice of the TGSe crystal is the least strongly bound.

### INTRODUCTION

Triglycine selenate  $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SeO}_4$  (TGSe) is a ferroelectric crystal possessing a structure isomorphous with that of triglycine sulphate  $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$  (TGS). The ferroelectric phase transition in TGSe is believed to be second order, as is that in TGS [1].

Preliminary X-ray and morphological studies of these crystals showed that its structure is monoclinic with space group  $P2_1$  in the ferroelectric phase, changing to  $P2_1/m$  above the Curie temperature [2,3]. The disappearance of the plane of symmetry ( $m$ ) is related to the emergence of spontaneous electric polarisation along the two-fold axis. The orientation of the symmetry axis is defined by the cleavage plane. The two-fold axis is

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parallel to the vector  $b$  of the unit cell, whereas the constants  $a$  and  $c$  are chosen according to convention.

Thermal expansion, as a thermodynamic property of crystals, results from an increasing amplitude of the thermal vibrations of the constituent atoms. In addition, investigation of the electrical conductivity of dielectric crystals is necessary not only for practical applications but also for the interpretation of various physical phenomena.

Studies concerning the thermal expansion and electrical conductivity of TGS crystals have been intensively reported [4–6]; however, fewer studies have been devoted to the investigation of TGSe crystals [7,8].

The present work aims at studying the anisotropy of the thermal expansion in TGSe single crystals, as well as the electrical conductivity, over a wide range of temperature.

## EXPERIMENTAL

### *Crystal growth*

Crystals of TGSe were prepared from a stoichiometric aqueous solution of aminoacetic acid ( $\text{NH}_2\text{CH}_2\text{COOH}$ ) and selenic acid ( $\text{H}_2\text{SeO}_4$ ) and then purified by three-fold recrystallisation from water. Single crystals of TGSe were obtained by slow evaporation. The crystals were grown above the Curie temperature (303 K). The samples were cut perpendicular to the ferroelectric axis,  $b$ .

### *Thermomechanical analysis (TMA)*

Thermomechanical analysis (TMA) was performed using a Heraeus TMA 500 dilatometer. The samples were prepared in the form of rectangular rods of dimension  $5 \times 5 \times 4$  mm. The temperature was monitored using a Ni, Cr–Ni thermocouple throughout the range extending from 123 to 323 K [9]. The heating rate was  $0.5 \text{ K min}^{-1}$ .

### *Electrical conductivity*

Samples used for electrical conductivity measurements were prepared in the form of rectangular plates about 1 mm thick. An area of about  $35 \text{ mm}^2$  was covered with graphite to act as electrodes. Each sample was held between two copper electrodes of a holder especially designed for this purpose. The temperature measurements were carried out using a pre-calibrated Cu-constantan thermocouple.

The electrical conductivity was measured as described previously [10]. In order to remove excess polarisation from the sample's surface, the crystal

was heated to a constant temperature, 323 K, while applying the required external electric field along the considered direction ( $E = 9 \text{ kV cm}^{-1}$ ).

Measurements of the temperature dependence of the steady state conductivity were performed in the single-domain state on cooling from 323 to 288 K with a cooling rate of about  $0.15 \text{ K min}^{-1}$ . The uncertainty in measuring  $\sigma$  was less than  $\pm 2\%$ .

## RESULTS AND DISCUSSION

All measurements were carried out along five arbitrary directions, i.e. along the ferroelectric axis,  $b$ , and in four directions in the plane perpendic-

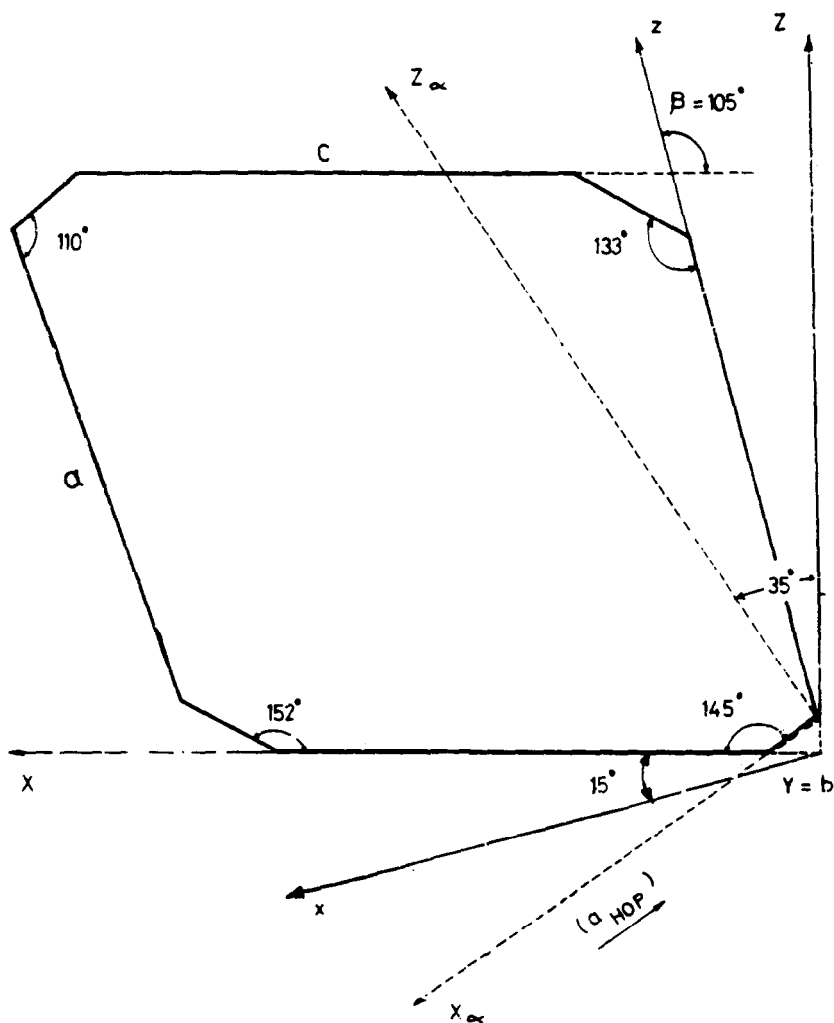


Fig. 1. Contour of TGSe crystal in the (010) plane with coordinate systems:  $x, y, z$ , konstantinova;  $X, Y, Z$ , applied in EPR work [11];  $X_\alpha, Y_\alpha, Z_\alpha$ , principal axes of tensor  $\alpha$  [4].

ular to it, namely the  $x$ ,  $z$ ,  $X_\alpha$  and  $Z_\alpha$  axes [4]. The axes of the two systems of reference are shown in Fig. 1.

### *Thermal expansion anisotropy*

The thermomechanical analysis (TMA) was performed throughout the temperature range 123–323 K for TGSe single crystals. It showed an interesting dependence of the linear thermal expansion coefficient on the measuring direction. The relative changes in dimension ( $\Delta L/L_0$ ) of the crystal in the chosen directions are shown in Fig. 2a and b.

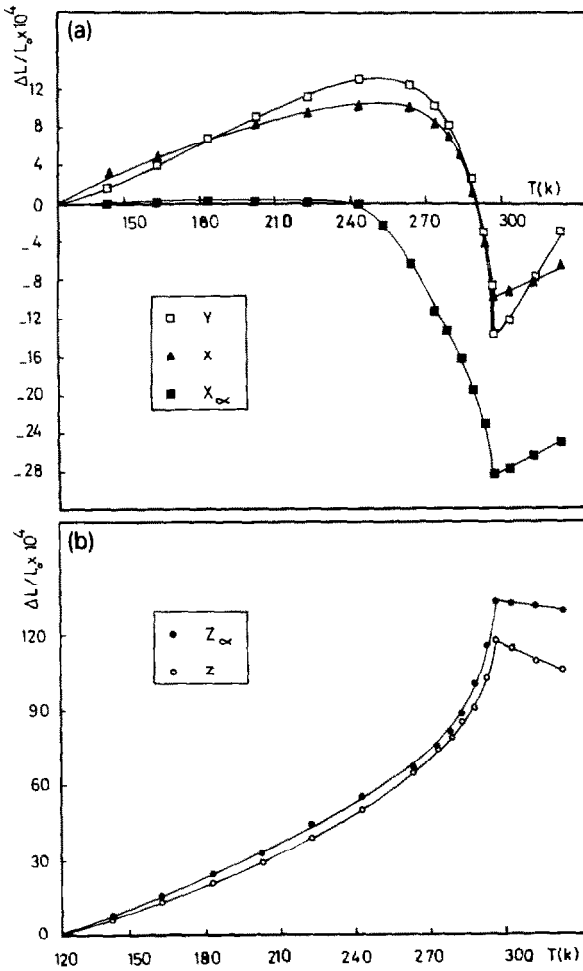


Fig. 2. (a) The temperature dependence of the relative change of the length,  $\Delta L/L_0$ , measured along the Y,  $x$  and  $X_\alpha$  axes for TGSe crystals; (b) the temperature dependence of the relative change of the length,  $\Delta L/L_0$ , measured along the  $z$  and  $Z_\alpha$  axes for TGSe crystals.

TABLE 1

The values of thermal expansion coefficient obtained for the chosen directions in the ferro- and paraelectric phases, and the measured values of  $\Delta L/L_0$  very close to the transition temperature,  $T_c$

Directions	Thermal expansion coeff. ( $\alpha$ ) $\times 10^{-5}$			$\Delta L/L_0$ $\times 10^{-4}$
	$123 < T < 243$	$243 < T < T_c$	$T > T_c$	
$Y$	+1.33	-12.0	+2.66	-14
$x$	+0.90	-10.6	+1.06	-10
$X_\alpha$	+0.10	-7.1	+1.33	-28
$z$	+4.50	+30	-5.00	+117
$Z_\alpha$	+5.00	+35	-2.00	+135

In all directions, there was an inflection in the change of length vs. temperature relationship observed near the phase transition temperature,  $T_c$ . As shown in Fig. 2a, it is obvious that  $(\Delta L/L_0)$  increases along the  $Y$ ,  $x$  and  $X_\alpha$  axes with temperature increase up to 243 K, at which point the sign of the thermal expansion coefficient changes. Starting from that temperature, a contraction in  $(\Delta L/L_0)$  was observed up to the distinct transition point  $T_c$  (296 K). In the paraelectric phase, there is an increase in  $(\Delta L/L_0)$  with temperature.

On the other hand, along the other two directions, the  $z$  and  $Z_\alpha$  axes (Fig. 2b), a positive overall expansion occurs. This positive expansion is relatively weak at low temperatures, and is then followed by a sharp increase as one approaches the transition temperature,  $T_c$ . Above  $T_c$  (in the paraelectric phase), there is a contraction in  $(\Delta L/L_0)$  with temperature increase.

Table 1 presents the values of the thermal expansion coefficient obtained for the chosen directions in the ferro- and paraelectric phases and the measured values of  $(\Delta L/L_0)$  very close to the transition temperature,  $T_c$ .

From Fig. 2a and b, it can be seen that from about 243 K the expansion in the  $Y$  and  $Z$  directions is related, and occurs in an opposite direction up to the paraelectric phase: an increase in dimension in the  $Y$  direction leads to a decrease in the  $Z$  direction. This is in agreement with the previously reported data [4]. On transition from the para- to the ferroelectric phase, the change in the position of Glycine I, and the deviation of the  $\text{NH}_3$  group with decreasing temperature, causes an increase in the dimension along the ferroelectric axis ( $Y$  axis) of the crystal [4]. Hence there is a negative expansion coefficient in the  $Y$  direction and a positive value is observed in the  $Z$  direction below the transition temperature,  $T_c$  (Fig. 2a and b). The large expansion coefficient along the  $z$  and  $Z_\alpha$  axes near  $T_c$  is related to the flipping of Glycine I [4].

The change in sign of the expansion coefficient along the  $Y$  axis which takes place in the ferroelectric phase at about 243 K, confirms that the large difference between coefficients for the  $Y$  and  $z$  axes is due to a superposi-

tion of the effects of normal, positive expansion and those originating in the chain structure [4].

In the lower temperature region, the expansion coefficient in the  $Y$  direction is positive, because the changes in dimensions due to deviation of  $\text{NH}_3$  cease to predominate over normal positive expansions. From Fig. 2a and b, it seems that the  $z_\alpha$  axis has the highest expansion.

### Electrical conductivity anisotropy

Figure 3 shows the electrical conductivity ( $\log \sigma$ ) as a function of  $1/T$  for TGSe crystals along chosen directions. It can be seen that the exponential law,  $\sigma = \sigma_0 \exp(-W/kT)$ , is obeyed and the activation energy ( $W$ ) changes at the phase transition temperature  $T_c$ ;  $\sigma_0$  is the conductivity at high temperature. From our steady state electrical conductivity measurements for TGSe crystals, it can be stated that the activation energy of electrical transport changes at the Curie point and that the activation energy in the

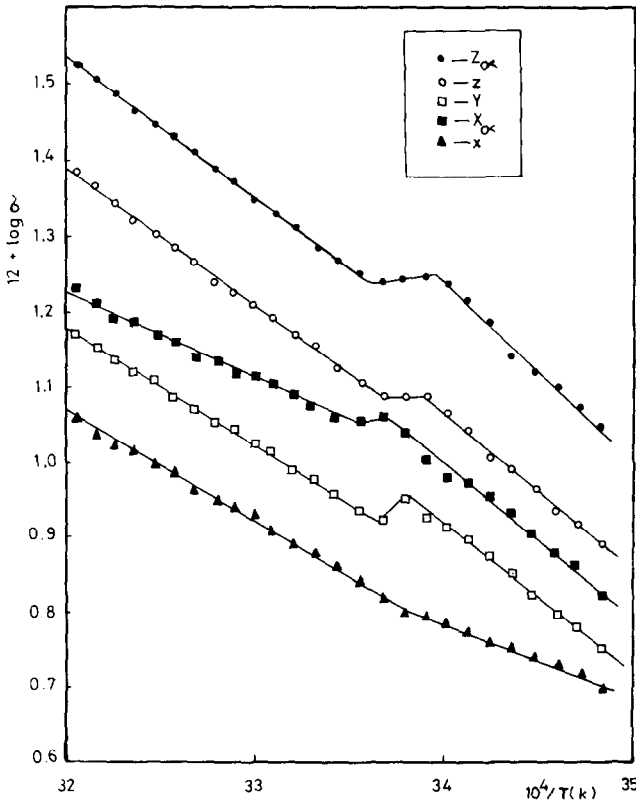


Fig. 3. Temperature dependence of electrical conductivity of TGSe crystals measured along the  $Y$ ,  $x$ ,  $X_\alpha$ ,  $z$  and  $Z_\alpha$  axes ( $E = 9 \text{ kV cm}^{-1}$ ).

ferroelectric phase is higher than that in the paraelectric phase. It is also observed that the conductivity is characterised by a peak at the transition temperature,  $T_c$ .

The greatest conductivity value was found to occur along the  $Z_\alpha$  axis which is tilted by as little as 35 degrees of arc from the direction normal to the crystallographic  $a$  axis in which the thermal dilativity tensor attains its greatest value.

The lowest electrical conductivity values in the para- and ferroelectric phases were observed in the direction of the  $x$  axis. The activation energies in the ferro- and paraelectric phases were found to change only slightly within the studied directions.

## CONCLUSION

From the study of the anisotropy of thermal expansion in TGSe crystals, it is concluded that the TGSe crystal lattice is least strongly bound along the  $Z_\alpha$  axis.

The electrical conductivity measurements shed more light on the anisotropic behaviour of these crystals. However more studies are needed to explore fully the role of electrical ordering in these crystals.

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