

METHODS OF DETERMINING SPONTANEOUS POLARIZATION NEAR THE PHASE TRANSITION POINT OF TGSe CRYSTALS

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The efficacy of the three basic methods of determining P_s (from the hysteresis loop, from the pyroelectric current curves and from the polarization reversal current curves) was examined. The effect of the polarization conditions on the pyroelectric phenomenon in TGSe crystals was considered, and the applicability of Devonshire's theory to these crystals was checked.

1. Introduction

Spontaneous polarization is one of the more important properties of ferroelectric substances, and its variation with temperature is a vital bit of knowledge both from the theoretical and practical points of view. The changes of P_s near the phase transition point are particularly interesting from the theoretical aspect. This requires an accurate determination of the P_s value near the Curie point. The most commonly used Sawyer-Tower [1] oscillographic technique, however, does not enable accurate determinations of the spontaneous polarization to be made in the vicinity of the Curie point.

The author has made an attempt to assess the usability of two other known methods for this purpose, namely,

1) that based on measurements of the change in pyroelectric current during uniform heating of the crystal, and

2) that based on determinations of charge from the current of polarization reversal of the crystal by Merz's method [2].

The ferroelectric substance chosen for these investigations was triglycine selenate (TGSe), the ferroelectric properties of which were discovered by Matthias, Miller and Remeika [3]. Up to now, triglycine selenate is the least investigated substance among the three known triglycines (TGS, TGSe and TGFB). Thus, the research on the temperature variations of spontaneous polarization on TGSe crystals also provided new data, yet unknown in the literature, on the influence of a constant electric field on the temperature variations of this

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material's pyroelectric current, crystal polarization and domain coupling. Moreover, the conformity between the obtained dependence $P_s(T)$ with the thermodynamic theory of Devonshire [4] was checked.

2. Experimental technique

a) Preparation of the samples

The triglycine selenate crystals were obtained from aqueous solutions of aminoacetic acid and selenic acid [5]. The bred crystal was cleaved into plane-parallelepiped plates, utilizing the property of the crystal, whose cleavage plane (010) is perpendicular to the ferroelectric axis b . Only those platelets were selected for examination which were cleaved on both sides along planes parallel to the cleavage plane. This ensured perpendicularity between the active surfaces and the ferroelectric axis, and renders any precision polishing of the surfaces unnecessary. The thicknesses of the examined samples ranged from 0.1 to 0.2 cm, whereas the areas from 0.3 to 1 cm². After applying the electrodes (silver paste) the samples were annealed several tens of hours at a temperature about 50°C and placed in a tightly sealed and dehumidified holder. The holder was placed in a thermostat enabling variation and stabilization of the sample's temperature. Sample temperature was measured with an accuracy of up to 0.05°C by means of a thermocouple.

b) Determination of spontaneous polarization by the oscillographic technique

In determining the spontaneous polarization by the oscillographic technique use was made of the well-known arrangement based on the Sawyer-Tower method [1]. The electric hysteresis loops received on the oscillograph were photographed in the temperature range from 0 to 24°C, and from the obtained photographs the values of spontaneous polarization and coercive field strength were determined.

c) Determination of P_s from pyroelectric current measurements

The pyroelectric effect in crystals is usually examined by the static compensation method [6, 7, 8 and elsewhere], or by the dynamical method of Chynoweth [9, 10].

In this work a static non-compensating method was used. It consists in recording or measuring the pyroelectric current with a simultaneous measurement of time and sample temperature. Merits of this method over the dynamical method were pointed out by the authors of Ref. [11]. It allows the sample to be maintained in an almost shorted state throughout the measurement and makes it possible to determine the absolute pyroelectric coefficient μ .

Heating of the sample was done in a continuous manner with a constant rate of temperature rise. The temperature *versus* time changes of pyroelectric current obtained in this way may be used for determining P_s only when the data concern samples in the monopolar state ("single domain"). This state of the samples was obtained by polarizing it along a direction concurring with its natural polar axis. The polarization process was conducted when

the sample was being cooled from $T > T_c$ down to 0°C . After being polarized, the sample was shorted for several minutes and then included into the measuring circuit and heated.

From the results thus obtained, the values of the pyroelectric coefficient and spontaneous polarization were calculated from the known formula

$$j_p = \frac{dP_s}{dT} \frac{dT}{dt}$$

where $\frac{dP_s}{dT} = \mu$ is the pyroelectric coefficient and $\frac{dT}{dt} = v$ is the rate of the temperature changes.

This method, when a highly sensitive self-recording unit is used for registering the pyroelectric current, provides a means of obtaining a picture of domain decay near the Curie point (the Barkhausen effect).

d) Determination of P_s from polarization reversal currents

The determination of spontaneous polarization by this method consists in graphically integrating the time responses of the current associated with total reversal of sample polarization. The current was photographically recorded with the use of a mirror galvanometer,

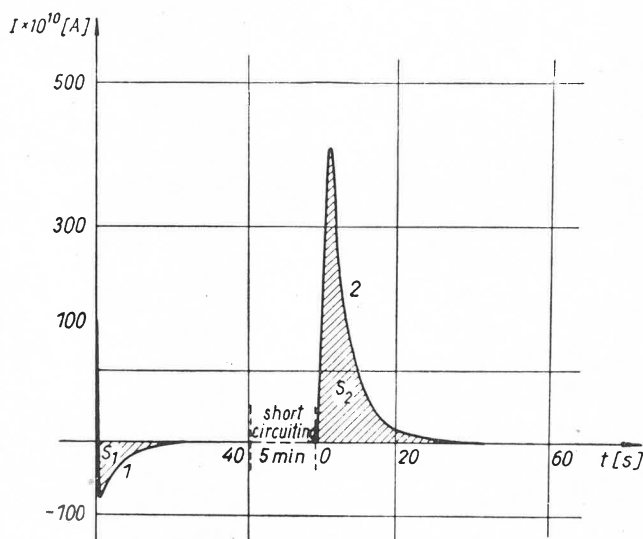


Fig. 1. Time changes of charging current (curve 1) and polarization reversal current (curve 2)

thus receiving ready graphs of the charging current and polarization reversal current (Fig. 1). If the sample was previously polarized completely along the polar axis and then shorted for a few minutes, then the area S_1 corresponds to the current associated with capacitor charging. On the other hand, the area S_2 corresponds to the charge $Q = \int I dt$ linked with the process of polarization reversal and charging of the capacitor which the sample with

its deposited electrodes and its leads make. The difference area ($S_2 - S_1$) corresponds to the charge (ΔQ) associated with the polarization reversal itself, that is,

$$\frac{\Delta Q}{S} = 2P_s$$

S is the active area of the sample, and P_s is spontaneous polarization.

The whole of such an experimental cycle must be conducted under constant sample temperature and with application of an electric field strength greater than the value of the coercive field.

3. Experimental results

The results of investigations presented below concern one sample alone, what enables elimination of discrepancies stemming from individual properties of different samples when comparing results obtained by different methods.

Figure 2 shows the temperature variations of the hysteresis loop. The values of spontaneous polarization and coercive field determined from the curves are presented in Fig. 3. The obtained P_s values agree with literature data acquired with the use of this method [12, 13, 14, 15].

The temperature dependence of the coercive field strength has a character similar to the same dependence in TGS [16], but does not conform with the curve given for TGSe by the authors of paper [15].

Figure 4 depicts the dependence of the pyroelectric coefficient (μ) upon sample temperature. Mean values of the coefficient μ were calculated from the responses of the pyroelectric current density at three different sample heating rates (0.2 deg/min; 0.4 deg/min; and 1 deg/min). The value of the weak pyroelectric current above the Curie point seen in the figure depends on the field strength used for polarizing the sample. The latter is shown in Fig. 5. It is seen that the plot of pyroelectric current density may serve as a means of determining P_s only when an appropriate electric field strength is used for polarizing the sample. Values of P_s determined from pyroelectric current density plots taken when an unpolarized sample is heated (curve 1) or when an incompletely polarized sample is heated (curve 2) will be underestimated owing to the presence of antiparallel domains. On the other hand, polarization with excessively high field strength lead to an error due to the increased participation of free carriers introduced into the crystal under the effect of the strong polarizing field.

The values of spontaneous polarization, which is depicted as a function of temperature by curve 2 of Fig. 8, were determined from the chosen current responses obtained when the sample was polarized with a field of strength $E = 3$ kV/cm.

An interesting case is the picture of changes in pyroelectric current recorded with the use of a recorder of high voltage sensitivity (Fig. 6). The recorded jumps are probably caused by the jump-wise liberation of volume charge during the evanescence of the domains. The height of these jumps depends on the value of the field strength in which the sample

was polarized. An almost identical picture of the jumps was obtained after each repetition of the recording (for the given sample).

Figure 7 presents the dependence of sample polarization on the strength of the field reversing polarization. It was determined by the method described in subsection 2d. Each

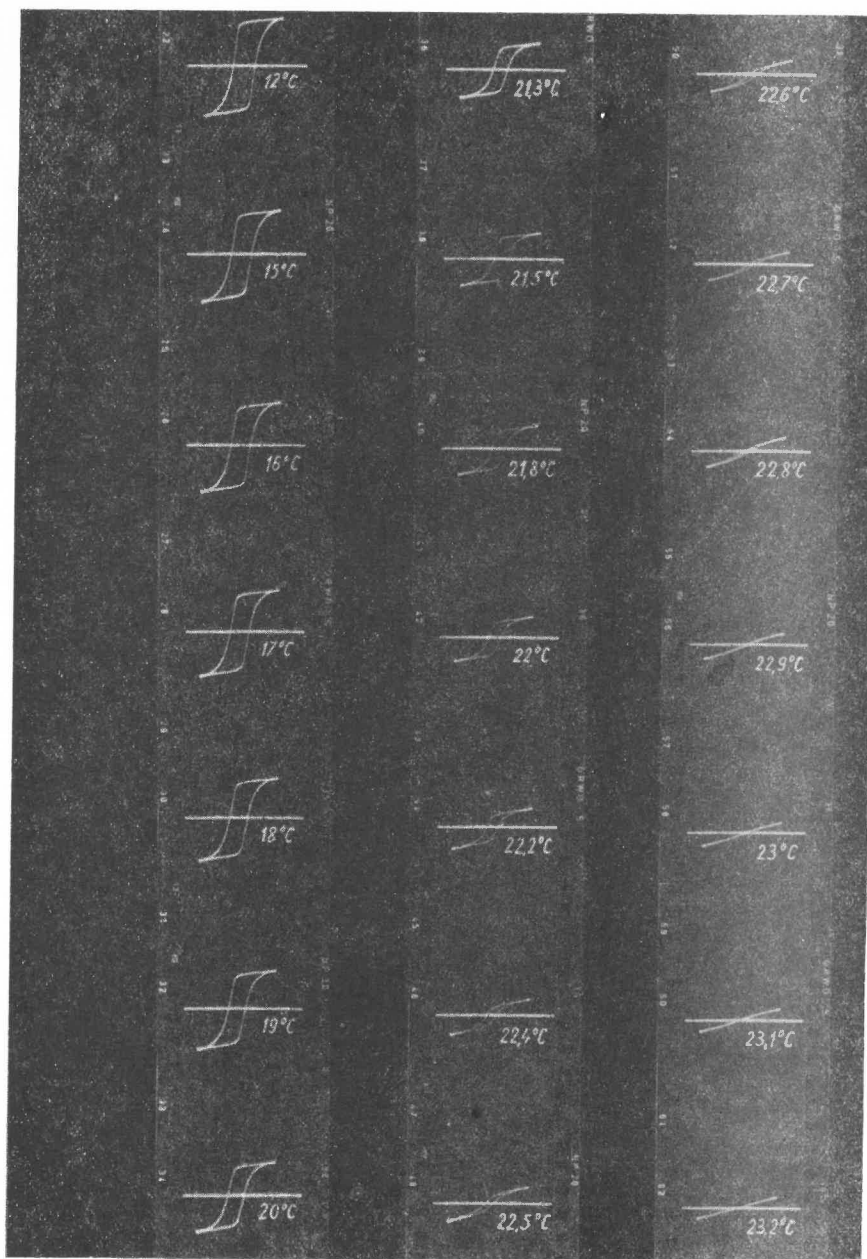


Fig. 2. Changes of the hysteresis loop of a heated TGSe crystal

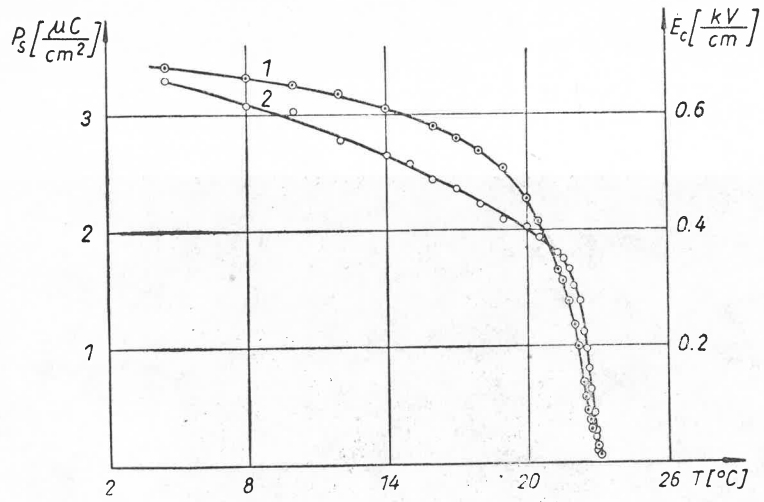


Fig. 3. Temperature dependence of spontaneous polarization (curve 1) and coercive field (curve 2)

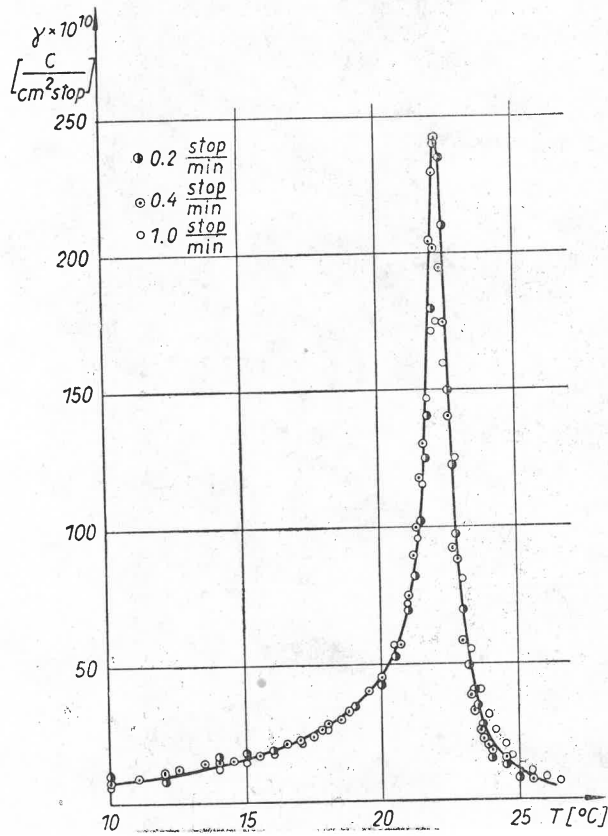


Fig. 4. Pyroelectric coefficient versus temperature for sample polarized with field of strength $E = 5 \text{ kV}/\text{cm}$

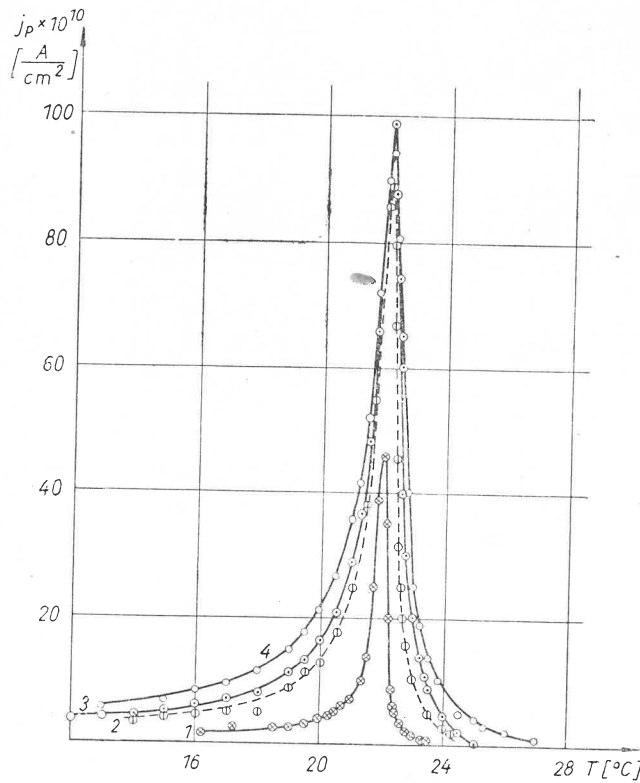


Fig. 5. Temperature changes of pyroelectric current density for unpolarized sample (curve 1), and sample polarized with field of strength: 1 kV/cm (curve 2); 3 kV/cm (curve 3) and 5 kV/cm (curve 4)

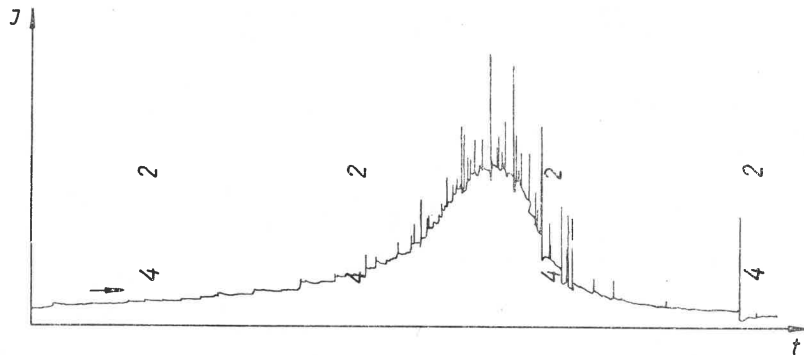


Fig. 6. Changes of pyroelectric current for sample polarized with field of strength 5 kV/cm

curve corresponds to the temperature given in the figure. The values of polarization in the saturated state are maximum values at the given temperature. This figure shows that for polarization of a simple at temperatures higher than $+2^{\circ}\text{C}$ a field of strength not less than 3 kV/cm must be used. Changes of P_s values with temperature received at this least field

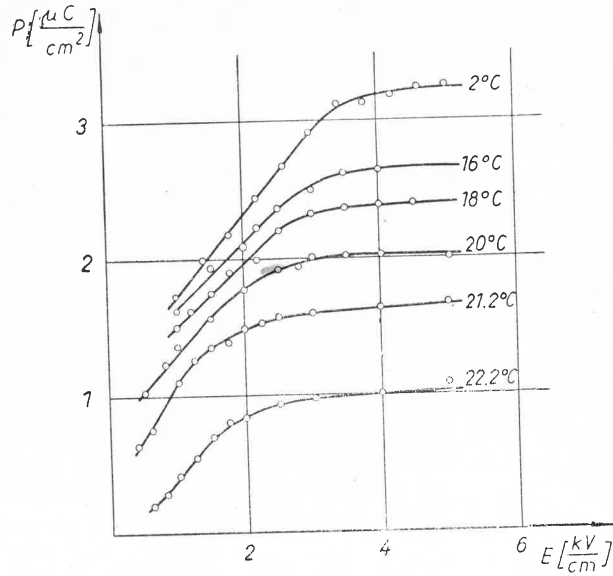


Fig. 7. Dependence of polarization on strength of polarization reversal field (for temperatures given in the figure)

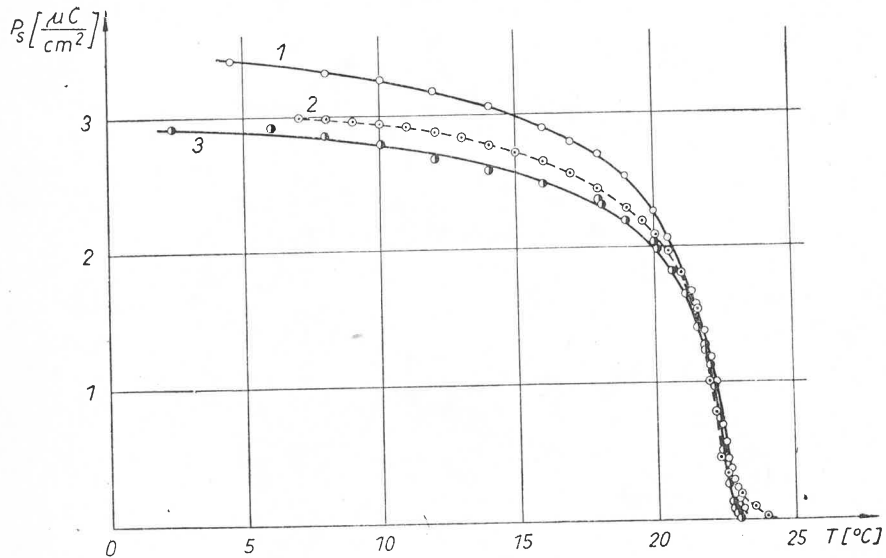


Fig. 8. Dependence of spontaneous polarization on temperature determined from: electric hysteresis loop (curve 1), pyroelectric current plots (curve 2), polarization reversal current plots (curve 3)

strength are presented by curve 3 of Fig. 8. For the sake of comparison, this figure also includes the values of spontaneous polarization determined from the oscillographic hysteresis loops (curve 1) and from plots of the pyroelectric coefficient (curve 2).

3. Discussion

a) The temperature variations of spontaneous polarization shows in Fig. 8, obtained by all of the methods described here, are similar, and in a narrow range of temperatures above 20°C even overlap within experimental error limits. At temperatures below 20°C the discrepancy between the P_s values obtained by each of the methods is about 10 per cent. They are due the converse consequences of the action of the constant and variable electric fields. A constant electric field causes volume charges to become accumulated in the regions at the electrodes and at domain boundaries (the ageing process). They partly compensate the total polarization of the crystal and, thus, the obtained values of P_s are somewhat lower than when a variable field acts on the sample. For a variable field removes the layer of volume charge from the near-electrode regions and domain boundaries, and hinders the formation of antiparallel polarization (sample regeneration). From the study as a whole it follows that the most exact method of determining spontaneous polarization is that of polarization reversal. It also allows accurate determination of the temperature at which P_s completely vanishes. For this is the temperature at which the difference between the polarization reversal current and the sample charging current disappears; then area S_2 equals area S_1 in Fig. 1. Polarization induced by the constant field, and the related appearance of an induced ferroelectric phase above the Curie point, leaves the P_s value unaffected, because a reversal of the field repolarizing the sample (with respect to the direction of the field charging the sample) does not change the value of induced polarization. Moreover, the measured areas S_1 and S_2 are large at the Curie point. This, hence, is quite the opposite situation as in the oscillographic method, in which the hysteresis loop (being the basis for P_s determination) decreases and vanishes when approaching the Curie point.

There is a possibility in the polarization reversal method to accurately stabilize temperature at each measurement. This is unachievable in all of the methods based on the pyroelectric effect. The values of spontaneous polarization determined from the temperature *versus* time responses of the pyroelectric coefficient are, in addition, affected by an error stemming on the one hand from the relatively slow decay of free charges appearing in the near-electrode regions, especially when the electric conductivity of the crystal is low. On the other hand, the free charges of these layers uncompensated above the Curie point are a source of local fields which gives rise to the existence of a certain polarization remanence, at least in the near-electrode regions [17, 18]. These effects perturb the picture of P_s changes in the vicinity of the Curie point. In the polarization reversal method these effects play but an insignificant role when the field strength is appropriately selected. In truth, in this case also the application of a relatively strong field causes the formation of free charge layers, but it is the difference of charges determined *via* graphical integration of the curves of the polarization reversal and sample charging currents which is taken as a measure of P_s . This eliminates the influence of this effect on the determined values of P_s .

b) It follows from the thermodynamic theory that the relation $P_s(T)$ is expressed by the formula

$$P_s^2 = a(\Theta - T) - b(\Theta - T)^2 + \dots$$

where Θ is the Curie-Weiss temperature (for TGSe $\Theta = T_c$), T is the temperature of the measurement, and a and b are coefficients associated with the factors appearing in the expansion into a series of the free energy as a function of polarization.

At low values of P_s and coefficient b the second term can be neglected for some ferroelectric substances [19, 20] and we then get a linear relation $P_s^2(T)$. For TGS such a linear dependence was found in a 10 degree range below the Curie point [20]. Figure 9 demonstrates

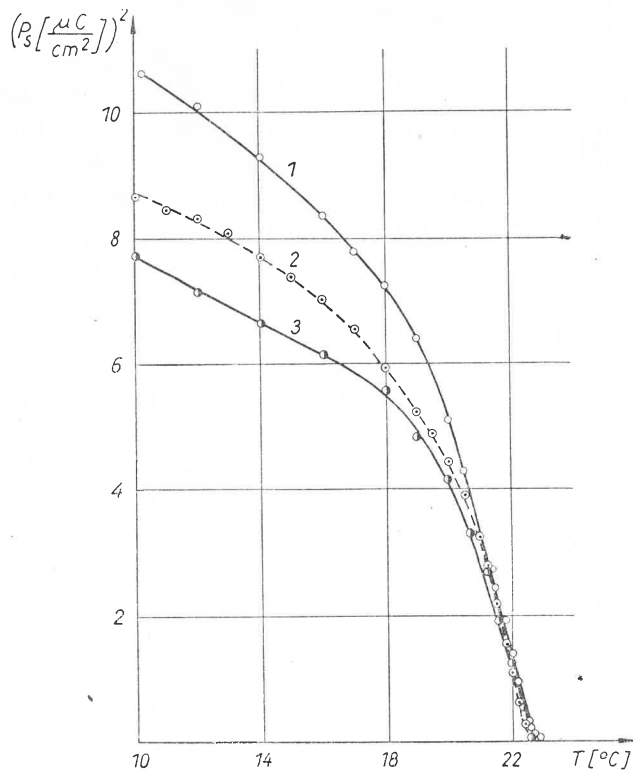


Fig. 9. Temperature dependence of square of spontaneous polarization (curve 1 concerns data determined from the hysteresis loop, curve 2 from the pyroelectric effect, and curve 3 from the polarization reversal)

that a linear $P_s^2(T)$ dependence appears only in a two to three degree range below T_c . The same range of linear dependence for TGSe was obtained by the authors of Ref. [22], who determined P_s values from pyroelectric current investigated by the static compensation technique. It was ascertained that in this temperature range the Curie-Weiss law also applies. The narrower range of the linear $P_s^2(T)$ dependence for TGSe compared with TGS becomes quite understandable when we compare the rate of P_s changes near the Curie point in both crystals [14, 21] and take into account the assumption of small P_s when neglecting the second term in the formula for P_s^2 . The much faster rise in P_s values for TGSe than for TGS (when decreasing temperature going through T_c) causes that already at temperatures lower than T_c by 2 to 3 degrees account must be taken of the second term of the sum in the formula for P_s^2 for TGSe, what leads to the non-linearity of the dependence.

The temperature variations of the pyroelectric coefficient presented in Fig. 4 agree with the results obtained by the authors of Refs [22, 23] for wholly unipolar samples (polarized during the cooling process by an applied electric field) and do not exhibit any anomalies before reaching the Curie point. Gavrilova and collaborators observed anomalies of the pyroelectric current at temperatures 1-2 and 11 degrees above T_c for samples unpolarized or polarized oppositely to the natural direction of polarization. These anomalies are probably due to incomplete mono-domain structure or partial reversal of polarization of the weaker coupled, domains in their own electric field generated by the depolarizing charge accumulated on the electrodes (in the compensation method the sample remains in the unshorted state). Such anomalies observed in KH_2PO_4 crystals are explained by the author of Ref. [24] as being due to incomplete single-domain structure of the sample.

From the data in Fig. 6 the conclusion may be reached that the process of domain evanescence begins long before the Curie point. Its maximum intensity is near T_c , where in the large strongly coupled domains vanish only at temperatures higher than the Curie temperature. During this process a volume charge is liberated which is a source of rudimentary pyroelectric current. The figure exhibits larger and increasingly rarer current jumps beyond the Curie point. Since the quantity of accumulated charge in the near-electrode layers and on the boundaries of the large domains increases with increasing strength of the field polarizing the sample [25], an increase in the rudimentary pyroelectric current is observed when this field's strength increases (Fig. 5).

It is evident from Figs 3 (curve 2) and 7 that the values of the coercive field determined from the hysteresis loop ($f = 50$ Hz) are somewhat larger than the values obtained by reversing polarization with a constant electric field. This fact seems to be reasonable if the known dependence of coercive field on frequency of the polarizing field is considered.

The experimental data presented in Figs 2, 3, 5, 6 and 7 partly supplement the vacancies in the literature for the studied material (TGSe) which, owing to its high pyroelectric activity and ease of polarization reversal with a large current signal, may be utilized for practical purposes [26].

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REFERENCES

- [1] C. B. Sawyer, C. H. Tower, *Phys. Rev.*, **38**, 296 (1930).
- [2] W. J. Merz, *Phys. Rev.*, **95**, 690 (1954).
- [3] B. T. Matthias, C. E. Miller, J. P. Remeika, *Phys. Rev.*, **104**, 849 (1956).
- [4] A. F. Devonshire, *Phil. Mag. Suppl.*, **3**, 85 (1954).
- [5] R. Nitsche, *Helv. Phys. Acta*, **31**, 306 (1958).
- [6] W. Ackerman, *Amer. Phys.*, **46**, 217 (1915).
- [7] N. D. Gavrilova, *Kristallografiya*, **10**, 346 (1965).
- [8] V. A. Koptsik, N. D. Gavrilova, *Izv. Akad. Nauk SSSR ser. fiz.*, **29**, 1969 (1965).
- [9] A. G. Chynoweth, *J. Appl. Phys.*, **27**, 78 (1956).
- [10] T. Krajewski, J. Kilarska, *Acta Phys. Polon.*, **36**, 791 (1961).
- [11] V. Z. Borodin, L. M. Berberova, S. G. Gah *et al.*, *Izv. Akad. Nauk SSSR ser. fiz.*, **31**, 1818 (1967).
- [12] R. Pepinsky, Y. Okaya, F. Jona, *Bull. Amer. Phys. Soc.*, **2**, No 4, 220 (1957).

- [13] F. Jona, G. Shirane, *Phys. Rev.*, **117**, 139 (1960).
- [14] F. Jona, G. Shirane, *Ferroelectric Crystals*, Oxford-London-New-York-Paris 1962.
- [15] J. Stankowska, I. Jackowiak, *Fiz. Diel. Rad.*, **V/1**, 47, Poznań 1969 (in Polish).
- [16] S. Domanski, *Proc. Phys. Soc.*, **B72**, 306 (1958).
- [17] W. Kanzig, *Phys. Rev.*, **98**, 549 (1955).
- [18] A. G. Chynoweth, *Phys. Rev.*, **117**, 1235 (1960).
- [19] S. Triebwasser, *IBM J. Res. and Developm.*, **2**, 212 (1958).
- [20] G. A. Smolenskii, N. N. Krainik, *Segnetoelektriki i antisegetoelektriki*, Moscow 1968.
- [21] S. Hoshino, T. Mitsui, F. Jona, R. Pepinsky, *Phys. Rev.*, **107**, 1255 (1957).
- [22] N. D. Gavrilova, V. K. Koptsik, V. A. Novik, *Kristallografiya*, **13**, No 6, 1088 (1968).
- [23] N. D. Gavrilova, V. K. Novik, V. A. Koptsik, S. V. Ivanova, *Izv. Akad. Nauk SSSR, ser. fiz.*, **33**, No 2, 306 (1969).
- [24] V. V. Gladkii, I. S. Zheludov, E. V. Sidnenko, *Izv. Akad. Nauk SSSR, ser. fiz.* **33**, No 2, 300 (1969).
- [25] E. G. Fesenko, A. I. Dantsinger, V. Z. Borodin, A. V. Turik, *Polaryzatsiya piezokeramiki*, Izd. Rostovsk. Univers. 1968.
- [26] I. S. Rez, *Izv. Akad. Nauk SSSR, ser. fiz.*, **33**, No 2, 289 (1969).