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Abstract. Isobaric studies of the influence of uniaxial pressure on the transitions of pure TGSe crystals for the three directions x, y, z (a^*, b, c) are reported. The critical exponents, β, δ and γ, from dielectric constant and hysteresis loop measurements, as well as the coefficients ξ and ζ of the fourth and sixth powers of P in the free-energy expansion under uniaxial pressure were determined. It has been found that uniaxial pressure applied along the a^*-axis keeps the transition near a tricritical point for $0 < X < 200$ bar, but that when it is applied along the b- and c-axes it strengthens the second-order phase transition behaviour. The tricritical behaviour of TGSe crystals is discussed and a possible driving mechanism for the change in order of the phase transition is proposed.

1. Introduction

Thermodynamic systems in which a line of first-order transitions goes over into a line of second-order transitions were first studied by Landau [1]. The changeover, as shown by Griffiths [2], is characterized by the junction of three critical lines—hence the name: the tricritical point (TCP). At the TCP, critical phenomena are different from those at an ordinary critical point. The character of the tricritical nature is described by Landau's phenomenological theory, in which the basic assumption is that the free energy can be expanded in powers [3] of the order parameter—in the case of ferroelectrics, the spontaneous polarization P—as

$$G = G_0 + (1/2)\chi^{-1}P^2 + (1/4)\xi P^4 + (1/6)\zeta P^6 + \cdots \tag{1}$$

where χ^{-1}, ξ and ζ are the second-order, fourth-order and sixth-order terms, respectively. If ζ is positive, the order of a given phase transition (PT) is described by the sign of ξ. This transition is first order (I) for $\xi < 0$, and second order (II) for $\xi > 0$. A TCP is realized at $\xi = 0$. In this case the tricritical exponents for the spontaneous polarization, the critical isotherm, the inverse dielectric constant, and the specific heat are given by $P \propto (\Delta T)^\beta$, $\beta = 1/4$; $E \propto P^\delta$, $\delta = 5$; $\varepsilon^{-1} \propto (\Delta T)^\gamma$, $\gamma = 1$; $\Delta C_p \propto (\Delta T)^{-\alpha}$, $\alpha = 1/2$, instead of by $\beta = 1/2$, $\delta = 3$, $\gamma = 1$ and $\alpha = 0$, which are the usual critical exponents for second-order PT [4] ($\Delta T = T_c - T$).

Ferroelectrics are uniquely suited for experimental study of the TCP because the three independent fields: the pressure (p, X), temperature (T) and electric field (E) are easily accessible.

Hydrostatic pressure- (p-) induced TCP have been observed for KDP, BaTiO$_3$, PbTiO$_3$ and other ferroelectric crystals, as summarized in reviews by Srinivasan *et al* [5] and Gesi [6]. Uniaxial pressure (X) induces a change† from a first-order to a second-order PT for RbCaF$_3$ [7], KMnF$_3$ [8], and SrTiO$_3$ [9]. The review by Müller [10] summarizes the application of uniaxial stress in studies of a variety of multicritical points and suggested the possibility of their observation in SrTiO$_3$ and KMnF$_3$. There are known ferroelectric materials where isomorphic or isotopic substitution can also induce a tricritical behaviour. The reported examples of such ferroelectrics are: KNbO$_3$–KTaO$_3$ [11], PbTiO$_3$–PbZrO$_3$ [12], and PbTiO$_3$–CaTiO$_3$ [13] solid solutions.

Ferroelectric TGSe is a very interesting material in which isotope- and hydrostatic pressure-induced tricritical behaviour has been observed. We briefly summarize below some information about the crystal and the search for its TCP.

Triglicyne selenate, (NH$_2$CH$_2$COOH)$_3$H$_2$SeO$_4$, known as TGSe, is a well known ferroelectric material which belongs to the triglicyne sulphate family [14]. This salt undergoes a PT at $T_c \sim 22$ °C. The space group of the low-temperature phase is $P2_1$, and that of the high-temperature phase is $P2_1/m$. The main features of the PT in TGSe are similar to those established for other members of the family and, up to the present, it has been generally considered as a second-order [14] or continuous PT. Very recently [15] we indicated that the ferroelectric–paraelectric transition in TGSe may be treated as first order and very close to a TCP at atmospheric pressure.
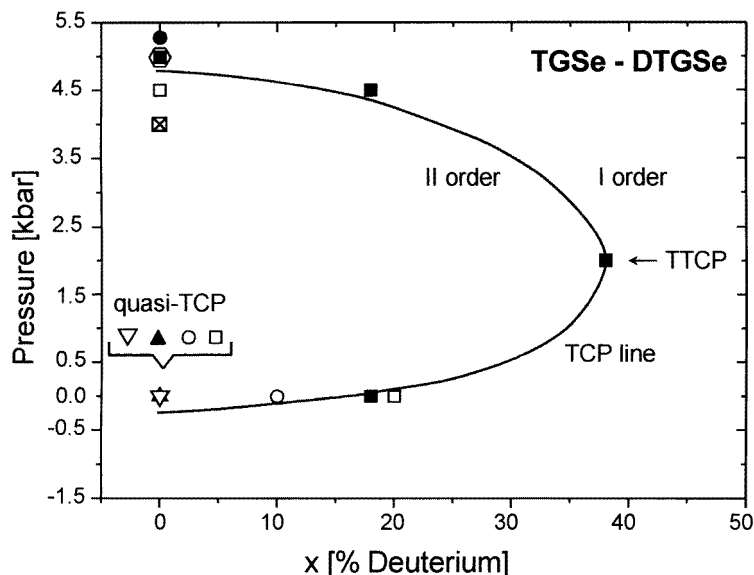

Figure 1. A schematic plot of the tricritical line in the hydrostatic pressure and deuterium content space for TGSe crystals. TTCP—tetracritical point; for other information see table 1.

The effects of hydrostatic pressure and deuterium substitution on the PT of TGSe have been investigated by many authors. The main results are collected together in table 1 and illustrated by figure 1. We may notice that for pure TGSe crystal, a TCP is realized at

† We are not concerned here with ferroelastic crystals, for which several examples of a TCP or Lifshitz TCP (LTCP) are known and have been studied both experimentally and theoretically.

Table 1. The tricritical point induced by hydrostatic pressure and deuteration in TGSe crystals (after various authors). (ΔT—thermal hysteresis.)

Point (figure 1)	Parameter discussed	TCP coordination	References	Remarks
Open square	ε_{max}, ΔT $T_c - T$, C^+/C^-	1 bar—0% 4.5 kbar—0% 1 bar—20%	[16]	Determination of the TCP not accurate
Open circle	$T_c - T$, ε_{max}, ΔT	1 bar—10%	[17]	Quantities studied tend to zero
Full circle	ΔT, ξ	5.28 kbar—0%	[18]	Clear thermal hysteresis in ε
Full triangle	β	1 bar—0%	[19]	$\beta = 1/4$ at 295 K
Crossed square	α	<4 kbar—0%	[20]	Not conclusive results
Hexagon	$T_c - T$, ΔT, ξ, ζ	5 kbar—0%	[21]	Nonlinear behaviour of ξ versus p
Full square	ξ, ζ	5 kbar—0% 1 bar—18% 4.5 kbar—18% 2.3 kbar—38%	[22]	Determination of the tetracritical point
Inverted open triangle	α, β, γ, δ ΔT, C^+/C^-	1 bar—0%	[15]	Quasi-tricritical behaviour

around 5 kbar, and nearly tricritical behaviour of this crystal appears at atmospheric pressure. Extrapolation of the tricritical line in figure 1 gives a second TCP for pure TGSe crystal at a hypothetical negative hydrostatic pressure of around 0.3 kbar. Uncertainties in the TCP coordinates are a consequence of the changes in quality of the samples, the methods of their preparation, and inaccuracies of the method used to characterize the tricritical state. Also, in contrast to the case for TGS, a moderate amount of deuteration (see figure 1) induces a clear discontinuity at the PT accompanied by sizable thermal hysteresis. Simultaneous effects of deuteration and hydrostatic pressure on the PT in TGSe give rise to two TCP which coalescence at a pressure of 2.3 kbar and at a deuterium concentration of 38%, as has been established by Takeuchi and Tatsuzaki [22]. The coalescence point is considered to be a tetracritical point (TTCP), detected for the first time in a ferroelectric system. Okada and Suzuki [24] gave a topological discussion of the tetracritical point in TGSe. However, until now no accurate experiments allowing determination of critical indices at that point have been performed. As a consequence of addition of SO_4 to pure TGSe crystal, the hydrostatic pressure at which the TCP may be induced increases. For the solid solution $TGS_{0.1}TGSe_{0.9}$, a TCP may be observed [25] at a hydrostatic pressure $\sim$11 kbar. A TCP may also be observed [26] for TGFB crystals at a slightly higher hydrostatic pressure, i.e. around 11.5 kbar. In both cases the critical hydrostatic pressure has been established by extrapolation of ξ versus p to $\xi = 0$. However, no detailed study of the TCP has been performed for these two above-mentioned crystals until now. It is worth noting that for TGS and DTGS no evidence of a TCP was found in the nondestructive hydrostatic pressure range [27, 28]. Our

recent [29] careful examination has also shown that for nondestructive uniaxial pressure, a TCP cannot be induced in TGS or in DTGS crystals with different degrees of deuteration. Results of recent studies on irradiated TGSe [30] and DTGSe [31] crystals indicate that the character of the phase transition in these crystals tends to be a second-order one. Similar suggestions have been made by Hamed [32] in his recent work on the effect of a small uniaxial pressure applied to 90%-deuterated TGSe crystal along the Z_α-axis. An updated short review of the studies on the effect of uniaxial pressure on TGS-type crystals is given in our paper [29] devoted to DTGS crystals.

The nature of the PT in TGSe crystals and the mechanism for changes in its character have not yet been identified. However, an analysis of the effects of γ-irradiation as well as of deuteration suggests the important role of hydrogen bonds in this process. It is expected that the application of uniaxial pressure, which is an anisotropic parameter as compared with hydrostatic pressure, will permit the analysis of the effects of pressure on individual hydrogen bonds, which may allow their identification, and possibly determination of the role of hydrogen bonds in inducing TCP in TGS-type crystals. The possibility of inducing a TCP in TGSe by the application of uniaxial pressure is also indicated by the small hypothetical negative hydrostatic pressure at which the TCP may be expected (figure 1).

The studies reported in this paper were undertaken to check the effect of uniaxial pressure on the PT properties in TGSe, to verify the presence of a TCP in these crystals, and to give a tentative microscopic description of the change in the PT character in TGS-type crystals.

2. Experimental procedure

Single crystals of TGSe were grown by the dynamical method, systematically lowering the temperature of its aqueous solution. All of the crystals were colourless and of high optical quality. The *b*-axis of the single crystal was determined by the cleavage plane (010). The coordination system used is xyz (or a^*bc) (see Stankowska *et al* [33]). The a^*-axis ($a^* \perp b, c$) and *c*-axes were determined through the morphology of the crystals. The samples were small parallelepipeds, approximately $2 \times 5 \times 5$ mm in size. Gold-leaf electrodes were attached to each *b*-face.

Hysteresis loops were observed by means of a simple Sawyer–Tower circuit with phase compensation at a frequency of 30 Hz in a digital high-resolution (4000 points per loop) oscilloscope (Nicolet-310). The oscilloscope allowed automatic data storage and access to a computer (an IBM PC) for further data analysis. The capacitance (C) and loss factor (D) were measured for several frequencies between 1 kHz and 1 MHz by a precision LCR-meter (Hewlett–Packard model HP-4284 A). From these data, both the real and the imaginary parts of the dielectric constant could be obtained. The temperature was measured by means of a chromel–alumel thermocouple attached directly to the sample, and read out from a digital microvoltmeter (Keithley-DMM 196). The sample holder was inserted in a thick metal tube and immersed in an oil bath. The temperature of the bath was controlled by a temperature controller (Haake model F-3). For cooling below room temperature (RT) a simple flow system with Haake cooler was used. During isobaric measurement of P_s and C the sample was slowly cooled or heated at a rate 1 °C h^{-1} or less (in the vicinity of the PT, $\sim$0.5 °C h^{-1}). A known force was applied to the sample through a lower piston connected to a lever. The compressive stress was generated by tightening a spring/screw system. The pressure was monitored by the use of a bridge including two linear variable differential transformers (LVDT) (Schaevitz 400 HR). The system was calibrated and its accuracy was around $\sim$10 bar. To produce uniform pressure we followed the method used by Imai [34], i.e. sheets of soft thick paper were inserted between the contact face of the

piston and the crystal under investigation. To avoid producing defects or early cracking of the sample studied, the pressure was increased slowly. We found that depending on the condition and crystalline perfection of the sample used, we could avoid cracking for uniaxial pressure growing up to $\sim$0.5 kbar.

3. Results

3.1. The dielectric constant

The temperature dependence of the dielectric constant ε of TGSe crystals at zero uniaxial pressure was discussed in detail in our recent paper [15]. Very small thermal hysteresis (ΔT), of about $\Delta T \sim 0.045$ °C, was observed for the sample prepared for studies with the uniaxial pressure (X) applied along the b-axis, at $X = 0$. Furthermore, the ratio of the slopes of $\varepsilon^{-1}(T)$ versus T below and above the transition, $(1/C^-)/(1/C^+) \sim 4.5$, is close to the value of 4 corresponding to TCP behaviour, and considerably higher than the value of 2 pertaining to the standard critical point for a second-order PT. The calculated value of the Curie constant is $C_0 = 4050$ K, which is in good agreement with previous data [14]. The exponent γ corresponding to $\varepsilon^{-1}(\Delta T)$ was calculated from the best fit to be $\gamma \sim 0.98 \pm 0.04$, close to the theoretically predicted value: $\gamma = 1$. The samples prepared for studies with uniaxial pressure X applied along the a^*- and c-axes ($X = 0$) show a behaviour more or less the same as that with a pressure $X = 0$ applied along the b-axis.

The uniaxial pressure applied along the a^*-, b- and c-axes causes, in general, a decrease in the ε-value, and an upward shift of T_c when applied along the c-axis and a downward shift when applied along the a^*- and b-axes. We take the temperature of the peak of the dielectric constant as T_c. The very small thermal hysteresis (ΔT) at zero pressure and its negligible change with increasing pressure, as well as the lack of discontinuity in the PT observed with increasing pressure, justify this choice of T_c. The uniaxial pressure dependence of ΔT does not give any conclusive information on the change of the order of the PT in TGSe in the uniaxial pressure range studied and for the three directions considered. Another indicator of the PT order change may be the ratio C^+/C^-, as mentioned earlier. The experimental problems encountered when determining the ratio C^+/C^- as a function of X prevented us from drawing exact quantitative conclusions; we could only signal the tendency of the changes in C^+/C^-. The difficulties come from the smearing of the temperature dependence of ε with increasing a pressure applied along the c-axis, and from the double-peak behaviour of ε when $X \parallel b$- and a^*-axes. However, for a low pressure (i.e. $X < 100$ bar) the ratio C^+/C^- decreases from 4.5 to around 3 when pressure is applied along the b- and c-axes. For $X \parallel a^*$ the behaviour of C^+/C^- is much less significant. Hence we conclude that uniaxial pressure applied along the b- and c-axes strengthens the second-order PT behaviour, and so there is movement away from the TCP, but for the a^*-direction no conclusive information may be drawn from the ratio C^+/C^- alone.

The Curie constant is observed to be almost independent of the uniaxial pressure within the experimental error for $X \parallel a^*$-, b-, c-axes in the pressure range studied. We should note that C_0 for TGSe is independent [21] of hydrostatic pressure up to 6 kbar. Moreover Imai [34] established that for TGS crystals C_0 is not dependent on uniaxial pressure up to 0.6 kbar.
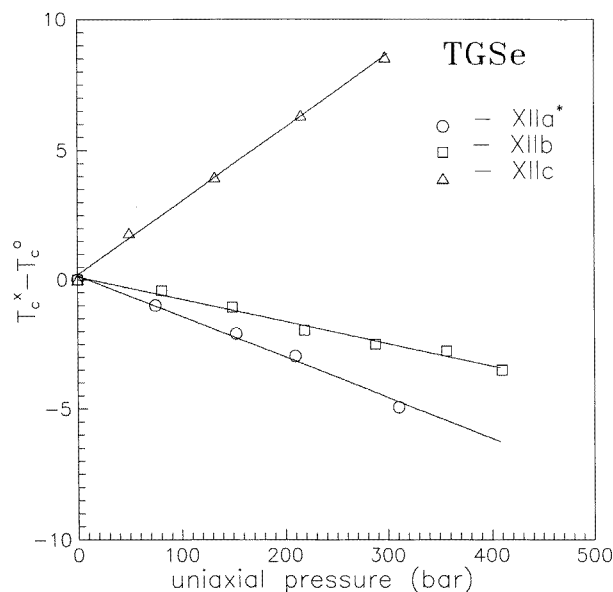
The shift of the Curie temperature under uniaxial pressure is shown in figure 2. It can be seen that the dependence of T_c on uniaxial pressure is linear for the three axes studied. The rate of increase of the transition temperature can be expressed by the following equation:

$$T_c^X = T_c^0 + \gamma_i X_i \qquad (i = a^*, b, c) \tag{2}$$

Table 2. Some ferroelectric and pressure parameters for TGSe and DTGSe crystals (if the results are not our own, references are given in parentheses).

Crystal	ξ (10^{11} J m^5 C^{-4})	γ_h (K kbar^{-1})	γ_1 (K kbar^{-1})	γ_2 (K kbar^{-1})	γ_3 (K kbar^{-1})
TGSe	0.5	3.7	−15.9	−8.7	28.3
		[14]	−16.6	−9.4	30
			[33]	[33]	[33]
40% DTGSe	—	—	—	—	19
					[32]
90%	−0.05	3.6^a	—	—	35
	[44]	[23]			[32]

^{a} In the pressure range 0–2 kbar, $\gamma_h \approx 5$ K kbar^{-1}.

Figure 2. The shift of the Curie point ($T_c^X - T_c^0$) as a function of uniaxial pressure applied parallel to the principal directions, a^*, b and c, of the TGSe crystal.

where T_c^X and T_c^0 are the transition temperatures under uniaxial pressure X and atmospheric pressure respectively ($T_c^0 \sim 22$ °C). The coefficients $\gamma_i \equiv \partial T_c / \partial X_i$ were obtained from the best fit to the experimental isobaric points, and they are collected together in table 2. The values of γ_i are in good agreement with the ones obtained previously by Stankowska *et al* [33] for the low-uniaxial pressure range (see table 2).

3.2. Spontaneous polarization

Typical hysteresis loops were observed for all of the samples under uniaxial pressure applied parallel to the a^*-, b- and c-axes. Measurements were performed in the temperature range from 10 to 35 °C depending on the shift of the phase transition with uniaxial pressure (see figure 2). The spontaneous polarization was determined from the residual polarization

which, except for when T is very close to T_c, was nearly equal to the polarization value extrapolated linearly to zero external electric field ($E = 0$).

In order to check whether or not a TCP is approached with uniaxial pressure applied to one of the specified axes of TGSe crystals, an attempt was made to evaluate the coefficients ξ and ζ in the free-energy expansion given earlier, as equation (1). The stability condition $\partial G/\partial P = 0$ for zero external electric field ($E = 0$) gives the following equation (terms of order higher than the sixth are neglected):

$$\chi^{-1} + \xi P^2 + \zeta P^4 = 0 \tag{3}$$

where P is the spontaneous polarization P_s in the ferroelectric phase, χ is the dielectric susceptibility in the paraelectric phase given by $\chi = C_0/(T - T_0)$, where T_0 is the Curie–Weiss temperature which depends on uniaxial pressure as described by equation (2) (in the case of a second-order PT, $T_c = T_0$), and C_0 is the Curie constant, independent of uniaxial pressure as mentioned in section 3.1.
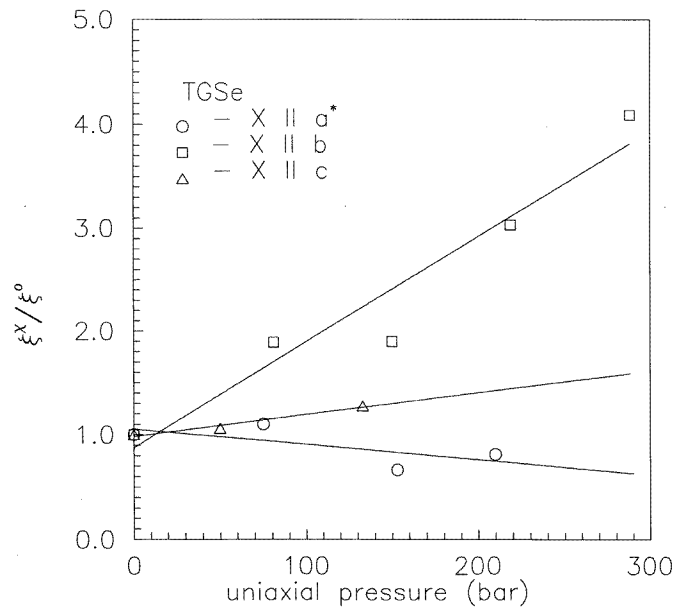

Figure 3. The normalized coefficient ξ^X of P_s^4 in the free-energy expansion as a function of uniaxial pressure applied in the a^*-, b- and c-directions for TGSe crystal. The lines represent the fit to the experimental points of the linear equation.

The coefficients ξ and ζ were calculated by the least-squares method to obtain the best fit of the experimental values of P_s at each uniaxial pressure applied along the a^*-, b- and c-axes to equation (3). In these calculations C_0 was taken equal to 4050 K. The values obtained for zero uniaxial pressure: $\xi^0 = (0.5 \pm 0.3) \times 10^{11}$ J m^5 C^{-4} and $\zeta^0 = (8 \pm 3) \times 10^{14}$ J m^9 C^{-6}, which contained considerable uncertainties, were used for plotting the normalized ξ- and ζ-coefficients as a functions of the uniaxial pressure (see figure 3). It is worth noting that the absolute values of ξ^0 and ζ^0 are in good agreement with published results (see [14]). Changes of ζ with uniaxial pressure are very small in the cases of the a^*- and c-axis directions so it may be treated as constant, in the pressure range studied. Only in the case of the b-axis is a small decrease with increasing uniaxial

pressure observed. Comparable changes of ξ and ζ with the uniaxial pressure applied along the *b*-axis are shown in figure 4.
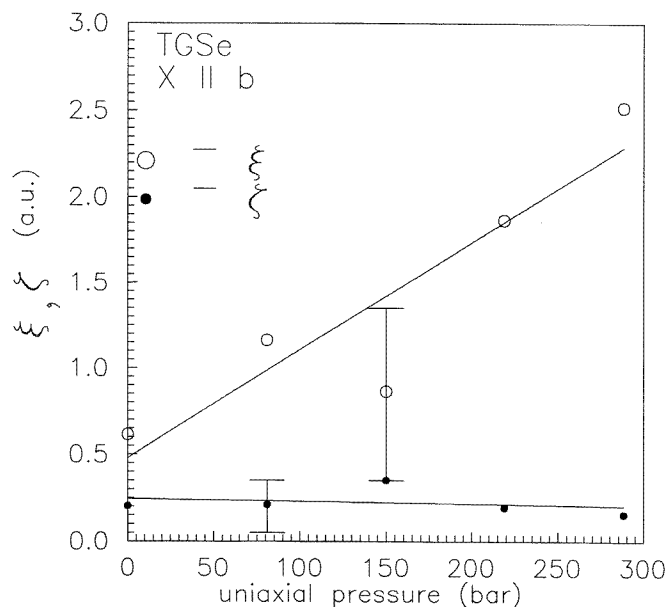

Figure 4. The coefficients ξ and ζ in the free-energy expansion as functions of the uniaxial pressure applied in the *b*-directions of TGSe crystals.

For all three cases the ξ-coefficient shows pressure dependence, which in the case of the a^*-axis may lead to ξ^X being equal to zero, i.e. the TCP may be induced by the uniaxial pressure. In the case of the *b*-axis and the *c*-axis, ξ^X increases with pressure, which means that there is movement away from the TCP, i.e. the second-order PT behaviour is strengthening. The changes in the ξ_i^X-coefficient with uniaxial pressure may be described (as is seen in figure 3) by a simple linear equation of the type

$$\xi_i^X = \xi_i^0 + A_i X_i \qquad (i = a^*, b, c) \tag{4}$$

where the A_i are constants. In the case of the a^*-axis the above relation allows calculation of a critical uniaxial pressure for which the TCP may be achieved. The critical pressure is established to be equal to $X_{TCP} \approx 600 \pm 100$ bar. Because of the mechanical damage of the sample we were not able to get closer to the TCP. To provide further evidence regarding tricritical or quasi-tricritical behaviour, we made an attempt to find a uniaxial pressure dependence of the critical indices β and δ (see section 1). From log–log plots of P_s as a function of $\Delta T = T_c - T$ for several values of the uniaxial pressure applied along the a^*-, *b*- and *c*-axes, the values of the β-exponent were estimated, and their pressure dependence for the three directions is shown in figure 5. For zero pressure the value of β was in the range 0.26–0.30, i.e. close to the tricritical value $\beta = 1/4$. As seen from figure 5, the dependence of β on uniaxial pressure confirms our conclusion about the tricriticality drawn from the analysis of the ξ_i^X-behaviour.

For zero pressure the value of δ, the other exponent which can be calculated from our measurements (see section 1), was estimated to be $\delta = 4.4 \pm 0.6$. Because of the small rounding effect in $P_s(T)$ for different uniaxial pressures, and due to some difficulties
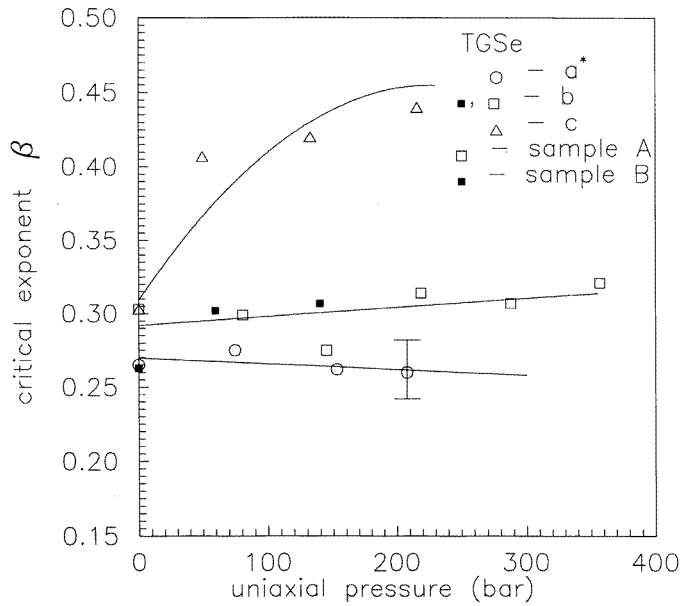
Figure 5. The critical exponent β as a function of the uniaxial pressure applied in the a^*-, b- and c-directions of TGSe crystal.

preventing a very accurate determination of temperature close or equal to the actual transition temperature, the errors in the pressure dependence of the exponent δ were high. This means that the information obtained about tricriticality is not so significant as in the previous case. However, for the low-pressure range (<80 bar) where the error in establishing the δ-value from log–log plots of P versus E at temperatures very close or equal to the respective actual transition temperatures was the smallest, we observed a tendency (not enough points for a quantitative relation) of the δ-values to change in the same way as that implied by estimates of the β-exponent. The above difficulties prevented us from checking Widom's equality $\beta(\delta - 1) \approx \gamma$ for the case of uniaxial pressure, but it is worth noting that at zero pressure the exponents obtained satisfy this equality very well.

Studies of the hysteresis loops allow us to ascertain whether the uniaxial pressure induces a change of P_s only through the upward or downward shift of the phase transition temperature, or whether other intrinsic pressure effects are important in these phenomena. In figure 6 we plot the normalized spontaneous polarization versus uniaxial pressure at a constant distance from the Curie point, equal to 4 K. In the direction of b and c, a decrease of P_s with increasing uniaxial pressure is observed; only in the a^*-direction may a small increase of P_s with increasing pressure be noticed. For temperatures below T_c, spontaneous polarization can be obtained from equation (3) in an explicit form by means of the equation

$$P_s^2 = (1/2)\zeta[(\xi^2 - 4\zeta\chi^{-1})^{1/2} - \xi]. \tag{5}$$

Since χ is independent of the uniaxial pressure while ζ is only slightly dependent on uniaxial pressure, the pressure dependence of P_s is, from equation (5), determined by the parameter ξ. According to this equation P_s either decreases with increasing ξ, or, alternatively, P_s increases with decreasing ξ. A comparison of the dependences shown in figures 3 and 6 supports the above conclusion, and the changes of P_s^X/P_s^0 as a function of uniaxial
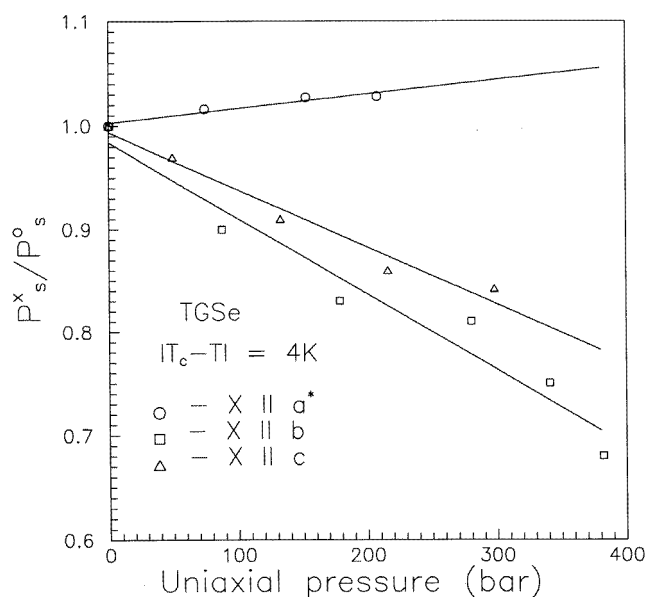
Figure 6. The changes in the normalized spontaneous polarization (P_s^X/P_s^0) induced by uniaxial pressure as a function of the uniaxial pressure applied in the a^*-, b- and c-directions for TGSe crystal.

pressure estimated using the ξ-value from figure 3 are in fair agreement with experimental data. Consequently, the uniaxial pressure dependence of the spontaneous polarization is mainly related to the uniaxial pressure dependence of ξ.

4. Discussion

The results presented in section 3 indicate that the uniaxial pressure applied along the a^*-axis moves the PT of TGSe in the direction towards a first-order transition. Thus, the effect of uniaxial pressure applied along the a^*-axis is similar to the changes caused by deuteration of the crystal. As illustrated in figure 1, a small percentage of deuterium in TGSe crystals is sufficient to produce a definite first-order PT. It is known that hydrostatic pressure induces the TCP both in pure and in deuterated TGSe crystals. Hydrostatic pressure will affect primarily the hydrogen-bonding system and secondarily the geometry of the constituent complex ions, as has been experimentally verified for KDP-type crystals [35]. No such detailed studies have been performed for TGS-type crystals. Moreover, no x-ray studies have been carried out for KDP- or TGS-type crystals under uniaxial pressure, but one can expect similar changes to those observed under hydrostatic pressure. It seems that the studies using uniaxial pressure up to 0.5 kbar, as in our case, do not cover a sufficient range of pressures to affect bonds other than hydrogen ones in TGSe or in other TGS-type crystals. The above indicates that the mechanism responsible for a change in PT character should involve certain changes in the lengths of the hydrogen bonds.

A comparison of the values of γ_i for TGS and DTGS crystals (see our paper [29]) shows large changes in the direction of the a^*- and c-axes and small ones along the b-axis. The results reported in this work, as well as the data of Stankowska *et al* [33], indicate
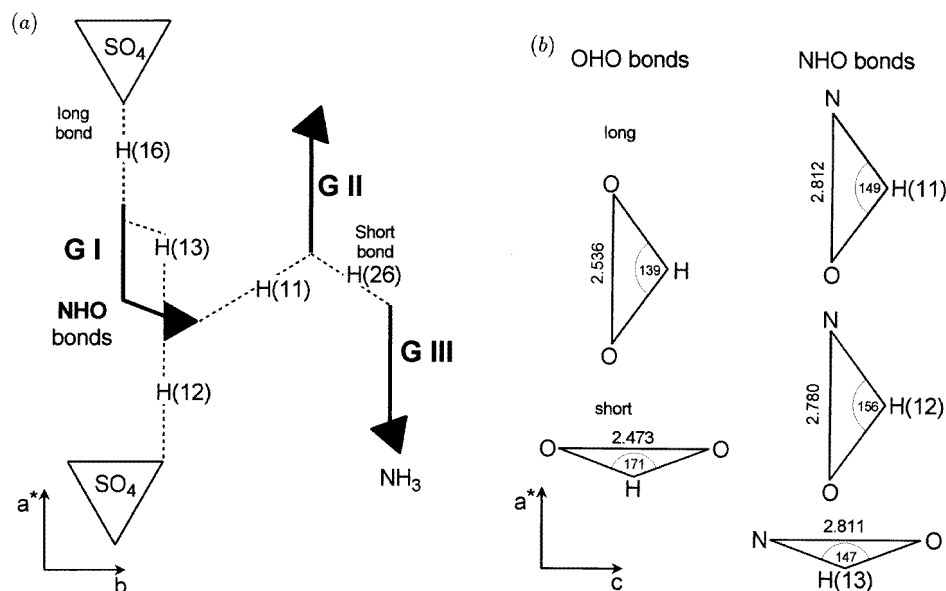
Figure 7. A schematic [001] projection of part of the elementary cell with an indication of the selected hydrogen-bond positions (a) and the geometry of the hydrogen bonds in the *ac*-plane (b) for TGS crystal (notation after Fletcher, Keve and Skapski [36] for the ferroelectric phase; lengths in Å and angles in degrees).

significant changes in the γ_i-coefficient in the (010) plane. In crystals of the TGS family we have a quite complicated three-dimensional (3-d) hydrogen-bonding network. Because the greatest effects of uniaxial pressure appear in the (010) plane we correlate them with changes in the hydrogen bonds lying close to this plane, neglecting in the first approximation the contribution of others. Inspection of the structure of TGS-type crystals shows that we are concerned with hydrogen bonds formed by nitrogen from the ammonium group of glycinium I (GlyI) and oxygen from the XO_4 (X = S, Se) (i.e. the bond N(1)–H(12) ... O(3)), and with two O–H ... O bonds. One is the so-called 'long' bond between the oxygen O(11) of GlyI and O(1) of the second XO_4 ion, and the other is the so-called 'short' bond between oxygens of GlyII and GlyIII, i.e. O(22)–H(26)–O(32) (in all cases the notation of Fletcher *et al* [36] is used). The infrared measurements of Baran [37] show also that the 'long' bond lies in the (010) plane and the 'short' one subtends an angle of 25° with this plane. A very much schematic projection of the above-mentioned bonds is shown in figure 7. One may note that the 'long' and NH(12)O bonds lie more or less parallel to the a^*-axis, but the 'short' bond lies parallel to the c-axis. The positions of the other two NHO bonds formed by the ammonium group of GlyI are also shown schematically in figure 7. The NH(12)O bond, the shortest and most 'linear' of the three in the ammonium group, is the stronger one. These 'long' bonds and NH(12)O bonds form a chain through the crystal lattice which is equivalent to the classical 1-d H-bond chain. From another point of view a 'long' bond may be regarded as a pseudo-0-d H bond. Also a 'short' bond may be treated as a pseudo-0-d H bond. Its role seems to be very important for two reasons: first, it is very short, and thus easy to order; and, second, it has a common oxygen (O(22)) with the NH(12)O bond. Ordering in a 'short' bond may work as the triggering mechanism for the orientation process taking place in the GlyI, through the influence on the proton H(11).

Application of uniaxial pressure to a particular axis affects simultaneously all NHO and OHO bonds. Pressure applied along the a^*-axis elongates the 'short' bond and shortens the 'long' and NH(12)O bonds, which may give rise to a slight downwards shift of T_c, moving the character of the PT in the direction of the PT of first-order character (see figures 3, 5). Uniaxial pressure applied along the c-axis elongates the 'long' and NH(12)O bonds and shortens the 'short' bond giving rise to an upwards shift of T_c, moving it in the direction of the PT of second-order character.
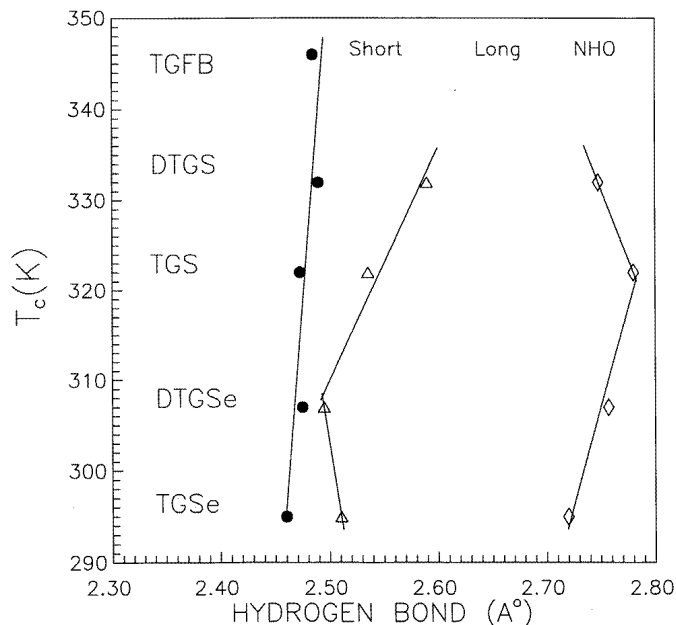

Figure 8. The relation between the transition point T_c and selected hydrogen-bond distances in TGS-type crystals.

Existing data in the literature [38] made it possible to examine the correlation between the transition temperature T_c and the above-mentioned three-H-bond distance in TGS-type crystals. The relation between T_c and R_{00} (in the ferroelectric phase and at temperatures close to RT, in the DTGS case only, data are for the paraelectric phase, i.e. $T = 65\ {}^\circ\text{C}$) is shown in figure 8. For TGFB we have OHF and NHF bonds and these are not shown in figure 8. For the 'short' bond a linear regression analysis gives the relation

$$T_c = 1493(R - 2.262) \tag{6}$$

where T_c is expressed in K and R in Å. The linear relation obtained is similar to those established for classical H-bond crystals [39, 40]. A linear relation appears to be the general rule for crystals with 0-d to 3-d H-bond networks [40]. In the case of 'long' and NH(12)O bonds step-like changes in slope are observed (see figure 8). Especially interesting shortening of the 'long' bond for the DTGSe crystal may be noted. When the 'long' bond becomes shorter, it will be more likely to affect the GlyI rearrangement. In our opinion this shortening of the 'long' bond may be directly related to the change of the character of the order in the case of DTGSe crystals.

Deuteration generally increases the overall O ... O distance slightly, except perhaps in

very long bonds. The increase is often about 0.02 Å, but there is no simple correlation between the length and the isotope effect. There are known examples in which, upon deuteration, the O ... O bond length is decreased [41]. It looks like TGSe and DTGSe are examples exhibiting such a behaviour. According to a suggestion of Rundle [42] and to a more detailed theoretical treatment by Sinha and Wood [43], a zero isotope effect is to be expected for a short OHO bond with a single potential well, or a flattened potential well, effectively with a single minimum. For a large R_{00}, H/D atoms can move in the double-minimum potential. With decreasing R_{00} the potential curve reduces gradually to a single minimum. In other words, the possible locations for the protons within a given H bond change from two sites to a single site. The critical H-bond distance r_c at this point is estimated [40] to be about 2.40 to 2.45 Å. However, for $M_3H(SeO_4)_2$, which are 0-d H-bond crystals [40], r_c is estimated to be 2.495 Å. It is worth noting that R_{00} for the 'long' bond for DTGSe is equal to 2.495 Å at 24 °C. There is no doubt that the dipole moment of TGS-type crystals originates from the tilting of C–N of GlyI and a GlyI as a whole, from the (010) plane. Consequently, the ordering of the protons in the H bonds cannot account directly for P_s being parallel to (010) like in $PbHPO_4$, but it may play the main role in the driving mechanism of GlyI ordering. Single-site ordering of the 'long' and the NH(12)O H bonds forces most of the C–N atoms to move in a direction away from (010) mirror plane. So, at the PT the dipole moment may have a certain finite value that gives rise to a discontinuous change in P_s. For DTGSe, the values of R_{00} for the 'short' H-bond (R_{00}^S) and the 'long' H bond (R_{00}^L) are small (see figure 8) and nearly equal to the critical distance r_c. Cooperative ordering of the 'short' and 'long' H bonds can be easily produced at a large scale exactly at the PT temperature, so a discontinuous change in P_s is observed in DTGSe crystals.

For TGSe crystals R_{00}^L is only slightly larger than in DTGSe, and external perturbations such as hydrostatic or uniaxial pressure decreasing R_{00}^L can give rise to changes in the character of the phase transition. Hydrogen bonds change with hydrostatic pressure at a rate of approximately 0.0023 Å kbar^{-1}, as one may estimate from data for KDP crystal [35, 39]. 5 kbar—a hydrostatic pressure at which the TCP is observed for TGSe—would induce a change of R_{00}^L equal to ∼0.012 Å, a value which is in excellent agreement with the measured difference in R_{00}^L between TGSe and DTGSe crystals (see figure 8). For TGS and DTGSe such a difference in R_{00}^L is equal to ∼0.041 Å. The critical pressure inducing the TCP in TGS should be around 20 kbar. However, for such high pressure, deterioration or destruction of the TGS crystals was observed [27]. Uniaxial pressure applied along a^* keeps the transition near a tricritical point. Changes of several coefficients with uniaxial pressure indicate that the TCP might be induced at around 0.6 ± 0.1 kbar; however, direct studies are limited because of mechanical damage of the crystal. From another point of view it is common knowledge that the uniaxial pressure effect is equivalent to approximately a tenth of the hydrostatic pressure [45]; thus the critical uniaxial pressure estimated seems to be very reasonable. The above discussion and estimations clearly support the assertion that a major role is played by the 'long' H bond in the changing of the character of the PT in TGSe crystals.

γ-irradiation produces noticeable changes in the dielectric properties of the pure and deuterated TGSe crystal [30, 31], revealing that γ-irradiation can produce a change of the PT order from I to II. In γ-irradiated TGS-type crystals two kinds of radical are mainly produced, $\dot{C}H_2COO^-$ and $NH_3\dot{C}HCOO^-$. The first one localizes on GlyI, and its production is related to the breaking or elongation of NHO and 'long' H bonds. Such behaviour of the order of the PT in DTGSe for γ-irradiated crystals again supports our assertion of the crucial role played by the 'long' H bond in inducing a TCP in TGSe crystals.

Systematic measurement of hydrogen bonds in the TGX–DTGX system by neutron diffraction are still needed for a better quantitative description of the phenomenon discussed.

5. Conclusions

Our measurements show a linear change of T_c (for the three axes studied) with uniaxial pressure up to ∼0.5 kbar, i.e. the pressure at which TGSe crystals break. Large changes of γ_i observed in the *ac*-plane appear to be correlated with changes in the length of three main H bonds lying close to this plane.

(i) Uniaxial pressure ($0 < X < 200$ bar) applied along the a^*-axis can keep the PT close to the TCP in TGSe crystals.

(ii) Uniaxial pressure applied along the *b*- and *c*-axes strengthens the second-order PT behaviour.

(iii) A linear dependence on T_c of the 'short'-bond distance in TGS-type crystals confirms the role of this bond in triggering the ferroelectricity of TGSe crystals, as postulated earlier.

(iv) In our opinion a significant shortening of the 'long' bond in DTGSe relative to those in the other crystals of this group is responsible for the first-order character of the PT in this crystal.

(v) The results of our measurements, as well as those reported by other authors, allow us to conclude that the most important factor determining the proximity to a TCP for TGSe crystals is the shortening of the 'long' bond (R_{00}^L) in this crystal to a distance corresponding to a single potential minimum, i.e. to the critical H-bond distance at which the central barrier between two minima disappears.

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