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## Effect of uniaxial pressure on the ferroelectric phase transition in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$

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**Abstract.** The effect of uniaxial pressure ( $X$ ) up to 1 kbar, applied along the three main directions, on the Curie temperature and the dielectric constant  $\epsilon_c$  of a  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  single crystal was investigated. The Curie temperature decreases with uniaxial pressure and the coefficient  $\gamma_i$  ( $\gamma_i \equiv \partial T_c / \partial (X_i)$ ) was determined as  $-6.5$ ,  $-7.0$  and  $-3.2$  K kbar<sup>-1</sup> for  $a$ -,  $b$ - and  $c$ -axis respectively. It has been found that uniaxial pressure applied along the  $c$ -axis strengthens the second order phase transition but applied along the directions perpendicular to the  $c$ -axis it may induce a tricritical point. The critical uniaxial pressure was estimated from the ratio  $C^+ / C^-$  against  $X$  to be about 2.4 kbar. A tentative description of the mechanism of changes in the phase transition order is given. The phenomenological relation describing  $\gamma_i$  is also discussed.

### 1. Introduction

Lead germanate (LGO)— $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ —undergoes a second order phase transition (PT) at  $\approx 450$  K from the paraelectric phase with a hexagonal space group  $P6$  to the ferroelectric phase with a trigonal space group  $P3$  [1]. From neutron diffraction studies [2–4] the structure of LGO was determined to consist of two layers arranged alternately along the  $c$ -axis in the Pb frame i.e. a layer of  $\text{GeO}_4$  tetrahedra and a layer of  $\text{Ge}_2\text{O}_7$  double tetrahedra. Polarization reversal may be described by the Pb atoms shift along the  $c$ -axis coupled with rotation plus a slight translation of  $\text{GeO}_4$  tetrahedra in the plane perpendicular to the  $c$ -axis. In this crystal structure the existence of an unstable or strongly agitated oxygen atom in the paraelectric phase has been observed. An unstable oxygen atom lying on the mirror plane perpendicular to the  $c$ -axis is related to reorientation of the  $\text{GeO}_4$  group [3]. The presence of an unstable oxygen atom in the paraelectric phase can be related to the possibility of tricritical point (TCP) induction in the LGO crystal. A similar situation occurred in the KDP crystal (with the unstable hydrogen atom) and in the SbSI crystal (with the unstable Sb atom) in which the hydrostatic pressure induced TCP was observed [5, 6].

The systems for which the line of the first order phase transition develops into that of the second order one, in the thermodynamical space of three independent fields, e.g. pressure ( $p$  or  $X$ ), temperature ( $T$ ) and electric field ( $E$ ), are known as showing the TCP [7]. The occurrence of TCP was established in a few ferroelectrics (for example see [8]). The most thoroughly studied crystals are the ferroelectrics with hydrogen bonds, such as KDP [5] and TGSe in which TCP is observed under relatively low hydrostatic pressures, and uniaxial pressure in the case of TGSe [8]. In the case of oxide ferroelectrics the TCP has been described only in  $\text{BaTiO}_3$  in which it is induced by a hydrostatic pressure of about 35 kbar [9].

This high-pressure range requires the use of non-standard measuring chambers for dielectric measurements which results in scarcely performed studies. According to the results of [8], TCP can be induced by uniaxial pressure lower by one order of magnitude than the necessary hydrostatic pressure.

Dielectric properties of LGO crystals under hydrostatic pressures up to 14 kbar were studied by a few authors. Kirk *et al* [10] reported the tendency of PT evaluation toward a first order transition with increasing pressure; however, they do not give any estimates of the necessary hydrostatic pressure which could induce the TCP. An other suggestion of TCP occurrence was made by Miller *et al* [11] who studied doped LGO crystals with barium replacing lead, in hydrostatic pressures to 8 kbar. High-pressure Raman scattering in LGO was performed by Soni and Jain [12] in pressures up to 50 kbar. They observed an anomalous behaviour of several phonons under a pressure of about 23 kbar. Moiseenko *et al* [13] reported a jump-like change in the hyper-Rayleigh light scattering at  $T_c = 438$  K in the LGO crystals slightly doped with lanthanum. Their results may suggest that PT in those crystal is the first order one. The referred examples suggest LGO or doped LGO as promising material for the model analysis of TCP within the group of oxide ferroelectric crystals.

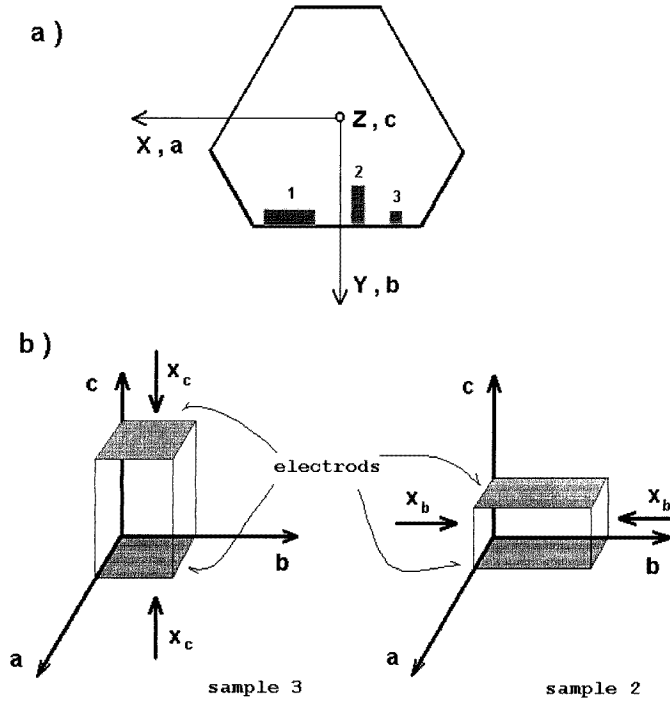
The studies reported in this paper were undertaken to check the effect of uniaxial pressure on the PT properties in LGO and verify the possibility of existence of a TCP in this crystal. Verification of the phenomenological relation and the sign of the electrostriction coefficient  $Q_{33}$  is also discussed.

## 2. Experimental details

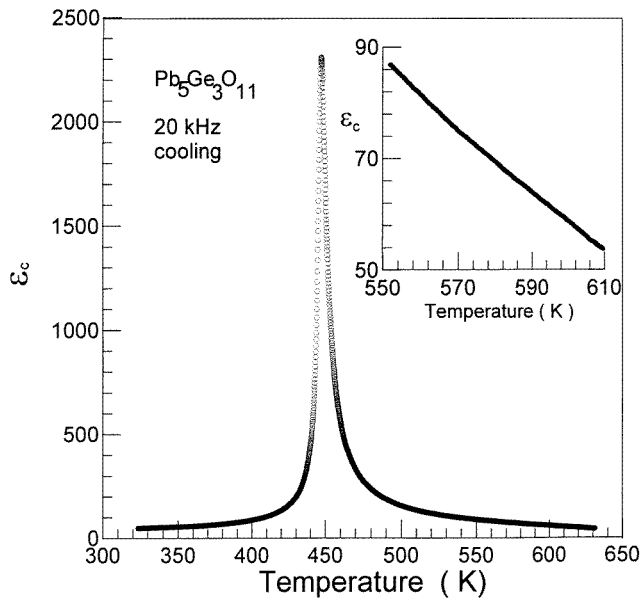
The single crystal of LGO was grown using the Czochralski technique by 'Monocrystal', Turnow, Czech Republic. It was pulled along the  $c$ -axis and was about 50 and 12 mm in length and diameter, respectively. The boule crystal was transparent dark yellow and showed a hexagonal cross section (see figure 1(a)). The Laue photographs were taken on a  $c$ -plate at room temperature to check the position of the  $c$ -axis. Several samples in the form of small parallelepipeds of approximately  $0.6 \times 0.5 \times 1.2$  mm<sup>3</sup> in size were prepared from the well oriented  $c$ -plate. The sample geometry is shown in figure 1(b). The silver paste electrodes were deposited always on the  $c$ -faces and fired for 0.25 h at 523 K. The Ag wires were attached to the electrodes and the samples were placed between mica plates under a piston inside the oven chamber. Uniaxial compression was applied to the bar samples with the use of a lever and a weight, within the range of 1 kbar. The accuracy of compression was estimated as  $\sim 10$  bar. Capacitance and loss factor were recorded under a constant pressure in subsequent cycles of heating and cooling. When reducing temperature after going from above the transition, no attempt was made to prevent ferroelectric twinning. The temperature was varied within the range 300–500 K, measured by a chromel–alumel thermocouple and read out by a digital microvoltmeter HP-34401-A. The Unipan temperature controller type 680 was used to maintain a constant rate of temperature change equal to  $0.4$  K min<sup>-1</sup>. The capacitance and loss factor were measured with a Tesla BM 595 capacitance meter. The measuring frequency was equal to 1, 2, 10 and 20 kHz. In addition, measurements at temperatures up to 650 K with no uniaxial pressure applied were performed. The data collection and processing were made by a PC unit.

## 3. Results and discussion

The temperature dependence of the dielectric constant along the  $c$ -axis ( $\epsilon_c$ ) of LGO crystals at zero uniaxial pressure is shown in figure 2. The maximum value of  $\epsilon_c$  at the Curie temperature



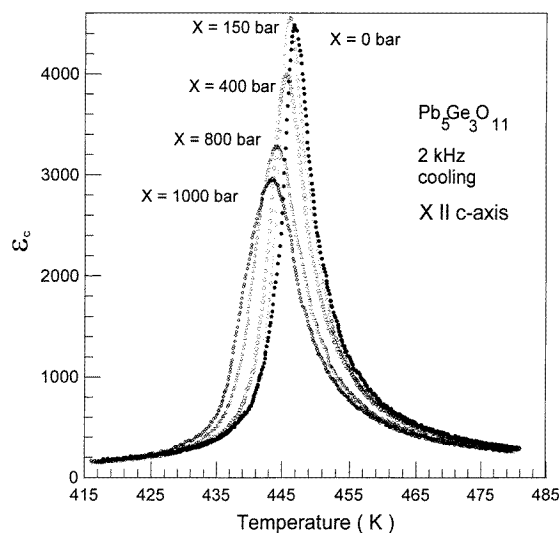
**Figure 1.** LGO crystal habit of boule pulled along  $Z \parallel c$ -axis showing the sample orientation (a) and sample geometry for dielectric constant measurement under uniaxial pressure along  $b$ -axis and  $c$ -axis (b).



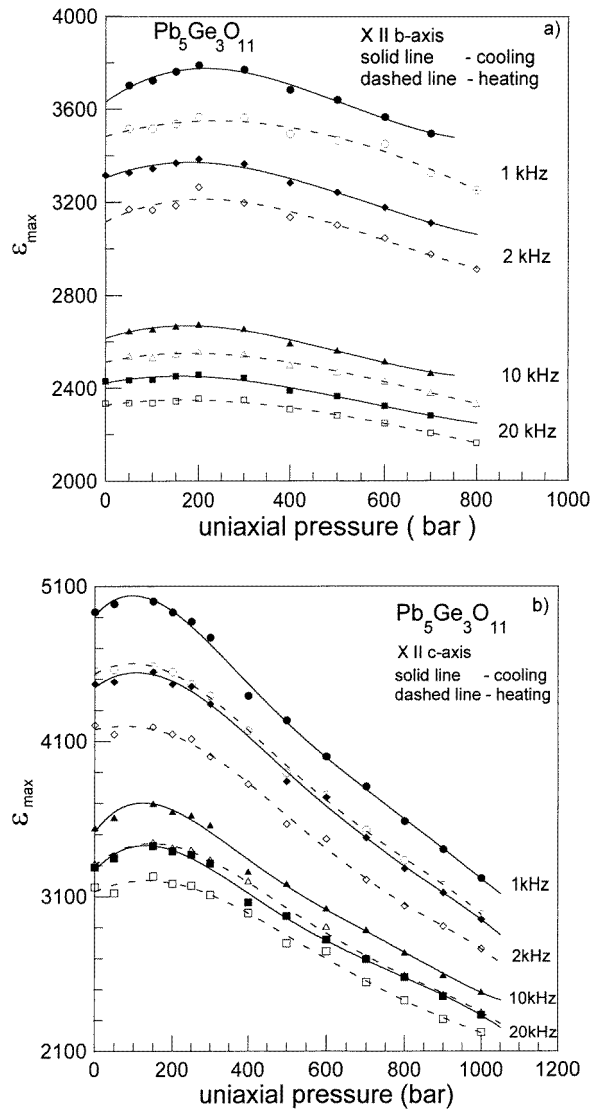
**Figure 2.** Temperature dependence of the dielectric constant  $\epsilon_c$  of the  $Pb_5Ge_3O_{11}$  single crystal. The inset shows the enlarged version in the high-temperature PT range (temperature range 550–610 K). Frequency: 20 kHz.

equal to  $\approx 5000$  for 1 kHz decreases to  $\approx 2500$  for 20 kHz (see also figure 4). The room temperature value of  $\epsilon_c$  is equal to about 40. Both the maximum and room temperature values of  $\epsilon_c$  change slightly depending on thermal and mechanical treatment of samples. The transition temperature  $T_c$ , determined as the temperature at which the dielectric constant reaches its maximum, does not depend on the measuring frequency. The reciprocal of the dielectric constant  $\epsilon_c$  satisfies the Curie–Weiss law. The Curie–Weiss temperature is about  $2.5^\circ\text{C}$  lower than  $T_c$  which remains in good agreement with earlier results for LGO crystal [14, 15]. The Curie–Weiss constant  $C^+$  in the paraelectric phase, determined at  $f = 2$  kHz, is  $C^+ = 1.15 \times 10^4$  K and  $C^+ = 1.19 \times 10^4$  K for cooling and heating respectively. These values are in quite a good agreement with that reported by Iwasaki *et al* [14] and Namamatsu *et al* [15]. The ratio of the slopes of  $\epsilon^{-1}$  against T below and above the transition ( $1/C^-/1/C^+ = C^+/C^-$ ) is calculated to be (at 2 kHz) 2.4 for cooling. Such values indicate that the paraelectric–ferroelectric PT is of second order which is in agreement with earlier results [1]. Moreover, we did not see any anomaly in the dielectric constant behaviour for all performed frequencies at the temperatures 570–590 K (see inset in figure 2). Our results confirm the supposition [16] that the transformation at 570 K is sample dependent despite the result reported by other authors [1] as a ‘high-temperature’ PT. This problem needs more detailed studies which will be the subject of a separate paper. Therefore, in our discussion of the uniaxial pressure influence we shall focus on the 450 K phase transition only.

The temperature dependence of the dielectric constant  $\epsilon_c$  at various uniaxial pressures applied along the  $c$ -axis is shown in figure 3. Within the low-pressure range i.e. up to 200 bar the maximum value of  $\epsilon_c$  at  $T_c$  slightly increases with the uniaxial pressure applied and reveals a broad maximum at about 120 bar (see figure 4(b)) for all frequencies applied. In the higher-pressure range the maximum value of the dielectric constant at  $T_c$  decreases sharply with increasing pressure. For the pressure applied perpendicularly to the  $c$ -axis (that is along the  $a$ - or  $b$ -axes) the broad maximum is shifted to slightly higher pressures i.e. 160 bar and the



**Figure 3.** Temperature dependence of the dielectric constant  $\epsilon_c$  of the  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  single crystal at various uniaxial pressures applied along the  $c$ -axis. Frequency: 2 kHz (every fifth collected point is shown).



**Figure 4.** The maximal value of the dielectric constant  $\epsilon_c$  as a function of uniaxial pressure applied along the  $b$ -axis (a) and  $c$ -axis (b) of the  $Pb_5Ge_3O_{11}$  single crystal. Frequency: 1, 2, 10, 20 kHz.

decrease of  $\epsilon_{max}$  with increasing pressure is much reduced (see figure 4(a)). The rate of change of  $\epsilon_{max}$  with uniaxial pressure applied perpendicularly to the  $c$ -axis is several times lower than the corresponding rate of change for the pressure applied along the  $c$ -axis (see figures 4(a) and 4(b)). It should be noticed that the decrease of  $\epsilon$  values with increasing pressure (both hydrostatic and uniaxial) is commonly observed for ferroelectric crystals [1, 17]. The anisotropic differences in the rate change of  $\epsilon_{max}$  caused by uniaxial pressure applied along a particular axis of ferroelectric crystals, to our knowledge, have not been discussed yet in the literature. In our opinion such behaviour (see the discussion below) may be precursory information on the order of PT change. However, an extensive collection of data is necessary to establish an empirical rule.

As mentioned, the pressure applied and changed from the ambient up to 100–150 bar caused an increase in the maximum value of the dielectric constant. This phenomenon may be connected to the internal structure of the sample, that is to the presence of defects or domain walls. Indeed, the LGO crystals are known as having very small size domains which appear as small hexagons [18, 19]. The network of the domain walls may be affected not only by electric field but also by applied stress. Very recently Liu *et al* [20], from high-resolution dilatometry measurement of SrTiO<sub>3</sub>, concluded that the uniaxial stress and the biaxial stress have forced the crystal into an aligned domain structure or into a single domain. It seems that in the LGO crystal under a low axial pressure (below  $\approx 150$  bar) the domain walls are released. Their participation in the PT process leads to the dielectric constant peak increase. A similar behaviour of  $\varepsilon_{max}$  against  $X$  was observed for double metal oxides with perovskite structure and the value of this pressure was close to 100 bar [21].

The uniaxial pressure dependence of the Curie–Weiss constant and the ratio of  $C^+/C^-$  are shown in figure 5. The Curie constant is independent of the uniaxial pressure within the experimental uncertainties in the pressure range studied. A small jump-like change in the Curie–Weiss constant was noted under a very small uniaxial pressure whose sign depends on whether the pressure is applied in parallel or perpendicular to the  $c$ -axis (figure 5(a)). More spectacular is the ratio of  $C^+/C^-$  dependence on the uniaxial pressure (figure 5(b)). For pressure applied in the direction parallel to the  $c$ -axis, the ratio of  $C^+/C^-$  slightly decreases with increasing pressure, while for pressure applied along the  $a$ - or  $b$ -axes, the  $C^+/C^-$  ratio distinctly increases with increasing pressure. The above behaviour have been observed for the heating and cooling runs. To explain such a behaviour we present below a description of the possible nature of the changes observed in the ratio  $C^+/C^-$  and the value of  $C^+$ , based on free energy expansion. A general expression for the free energy in terms of uniaxial pressure or stress  $X$  and polarization  $P$  can be written in the following way (for simplicity we eliminate suffixes and summation signs) [22, 23]:

$$A(X, P) = A_0 + (1/2)s^P X^2 - bXP + qXP^2 + (1/2)\alpha P^2 + (1/4)\xi P^4 + (1/6)\zeta P^6 + \dots \quad (1)$$

where the first three terms correspond to the elastic ( $s^P$ ), piezoelectric ( $b$ ) and electrostatic ( $q$ ) contribution to the free energy. In our experiment the Curie–Weiss law was valid also for  $X \neq 0$  and thus for LGO we have:

$$\varepsilon^X = C^X / (T - T_0^X). \quad (2)$$

It was observed that  $T_0^X$  obtained from fitting for each characteristic  $\varepsilon^{-1}(X, T)$  analysed was about 2.5 °C lower than  $T_c^X$  within an accuracy of  $\pm 0.6$  °C; however, no regular tendency related to  $X$  behaviour was noticed. In the vicinity of the transition temperature  $T_c^X$  the dielectric constant becomes very large and susceptibility  $\kappa$  can be approximated by:

$$\varepsilon \cong \kappa \cong 1/\chi \quad (3a)$$

and effectively under the uniaxial pressure:

$$\varepsilon^X \cong \kappa^X \cong 1/\chi^X. \quad (3b)$$

The second derivative of  $A(X, P)$  obtained from equation (1) with respect to the order parameter  $P = P_3 = P_s$  (the spontaneous polarization  $P_s$  is equal to polarization  $P_3$  along the  $c$ -axis) gives the expression for the calculation of the reciprocal susceptibility  $\chi$ . Having determined the difference  $\Delta\chi^X = \chi^X - \chi$  on the basis of the  $\chi$  values calculated for the two cases i.e. for  $X = 0$  and  $X \neq 0$ , and making use of the relations (2) and (3) it is possible to describe the changes in the in Curie–Weiss constant induced by the uniaxial pressure. Detailed quantitative calculation is omitted because the uniaxial pressure and temperature dependence are not known yet for all the coefficients in equation (1). Hereafter, we are able to discuss only

a rough estimate which gives us an insight into the possible nature of the Curie–Weiss constant changes. Taking into account the non-zero value elements of piezoelectric moduli  $d_{ijk}$  and elastic stiffness  $c_{nm}$  known for the LGO crystal [24] and following the procedure introduced above (terms of order higher than 2 have been neglected), we receive the main contributions to the  $\Delta\chi^X$  described by:

$$\Delta\chi^{Xc} \propto d_{33}^2 c_{33} \quad (4a)$$

$$\Delta\chi^{Xb} \propto d_{31}^2 c_{13}. \quad (4b)$$

It can be deduced from equation (4) that in both cases changes in  $\Delta\chi^X$  will be overwhelmed by particular piezoelectric moduli and their temperature dependences. The temperature dependence of  $d_{33}$  is not known and thus we cannot discuss its influence. The  $d_{31}$  coefficient shows a nonlinear temperature dependence with a rapid increase when temperature approaches the transition point and vanishes above it [24]. From relations (2), (3) and (4b)) it follows that this anomalous behaviour of  $d_{31}$  may explain the observed  $C^+/C^-$  behaviour and a slower rate of change of  $\varepsilon_{max}$  caused by the uniaxial pressure applied along the  $b$ -axis.

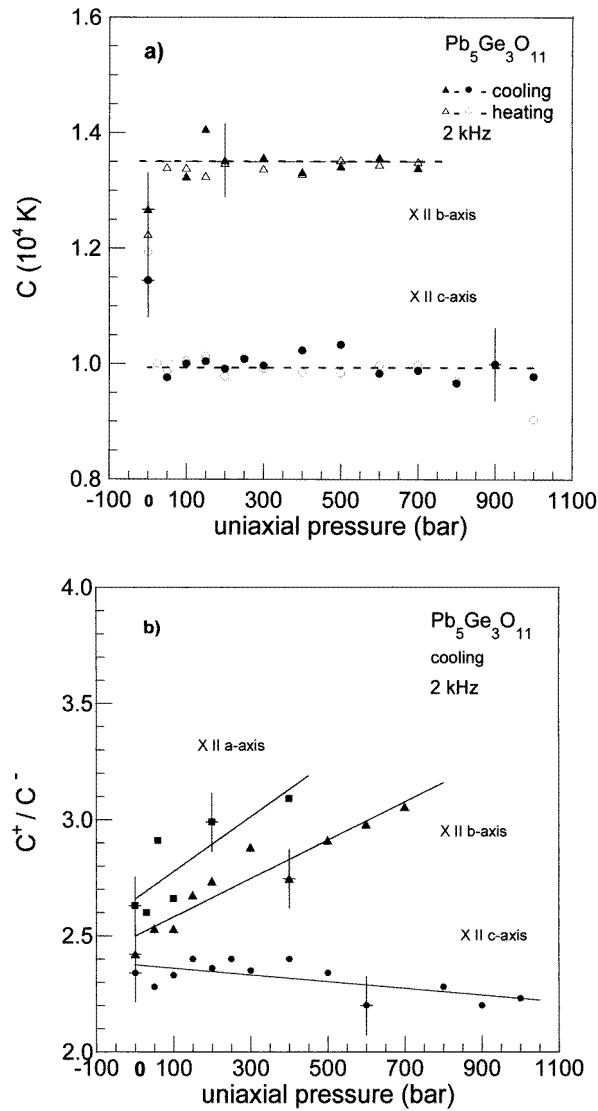
Within the paraelectric phase the LGO crystal remains piezoelectric with  $d_{33} = d_{31} = 0$  and non-zero  $d_{22}$  and  $d_{11}$  coefficients only. Therefore under the influence of uniaxial pressure  $\Delta\chi^{Xb}$  gives a non-zero contribution to reciprocal susceptibility described by:

$$\Delta\chi^{Xb} \propto d_{22}^2 c_{11}. \quad (5)$$

The piezoelectric modulus  $d_{22}$  shows a very slight but linear dependence on temperature in the paraelectric phase [24]. Its contribution manifested by the primary (in the case of  $X \parallel b$ -axis) and secondary ( $X \parallel c$ -axis) piezoelectric effect may explain a small jump of  $C^+$  observed (see figure 5(a)) when pressure is applied to the crystal.

It is well known from the Landau theory of phase transitions that when the phase transition is of second order then the ratio  $C^+/C^-$  should be equal to 2 and while the crystal approaches a tricritical point this ratio reaches 4 [22, 23]. A comparison of this theoretical expectation and our result presented in figure 5(b) indicates the possibility of the TCP appearance in the LGO crystal. The uniaxial pressure applied along the  $c$ -axis leads to a slight decrease of the  $C^+/C^-$  ratio from 2.4 towards 2. Such behaviour may be interpreted as the strengthening of the second order character of the phase transition investigated. When the uniaxial pressure was applied along the  $a$ - or  $b$ -axis, the  $C^+/C^-$  value increased above 3. This means that a value expected for TCP to occur might be reached at a high enough pressure. The data received for the sample configuration when pressure  $X$  was parallel to the  $b$ -axis were used for determination of the critical uniaxial pressure at which the observation of TCP would be possible. The estimated value of this pressure was  $p_b^* = (2.4 \pm 0.5)$  kbar. Temperature and pressure coordinates of TCP for LGO are given in table 1. For comparison, the respective experimental data of oxide ( $BaTiO_3$ ) and hydrogen-bond (TGSe, KDP) ferroelectrics are also shown. For TGSe crystal it was experimentally established [8] that the critical uniaxial pressure and the critical hydrostatic pressure inducing TCP differ by one order of magnitude (see table 1). This proportion suggests that one can expect for LGO a critical hydrostatic pressure  $p_h^*$  at about 24 kbar. A correlation may be noticed between the estimated  $p_h^*$  and hydrostatic pressure ( $\approx 23$  kbar) at which the break-in pressure dependence in certain phonon modes was observed by Soni and Jain [12]. However, in [12] no details are given which would suggest that the Raman studies in this range of pressures should be repeated to clear the implications for TCP appearance. The estimated critical value of the hydrostatic pressure  $p_h^*$  inducing the TCP for LGO is 24 kbar and is by 10 kbar lower than the corresponding value measured for  $BaTiO_3$ . It should be mentioned that the values of  $p_h^*$  for oxide ferroelectrics are much higher (a few times) than those for TGSe [8] and KDP [5] crystals, representing the group of ferroelectrics with hydrogen bonds.





**Figure 5.** The Curie–Weiss constant (a) and the ratio of Curie constant above and below  $T_c$  ( $C^+/C^-$ ) (b) as a function of uniaxial pressure applied along the  $a$ -axis,  $b$ -axis and  $c$ -axis of the  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  single crystal. Frequency: 2 kHz. Error bars are equal for each points, dotted line is a guide for the eyes only.

The shifts of the phase transition temperature  $T_c^X$  caused by uniaxial pressure acting along the  $a$ -,  $b$ - and  $c$ -axes obtained from  $\varepsilon(X, T)$  recorded for decreasing temperature (i.e. on cooling) are shown in figure 6. This dependence is linear and the rate of decrease in the transition temperature can be expressed by the following equation:

$$T_c^X = T_c^0 + \gamma_i X_i \quad (i = a, b, c) \quad (6)$$

where  $T_c^X$  and  $T_c^0$  are the transition temperatures at uniaxial pressure  $X_i$  and atmospheric pressure, respectively ( $T_c^0 \approx 450 \text{ K}$ ). The coefficients  $\gamma_i \approx \partial T_c / \partial X_i$  were obtained from the best fit to the experimental isobaric points and they are collected in table 2.

**Table 1.** Phase transition temperature and estimated TCP coordinates for hydrostatic and uniaxial pressure for LGO compared with experimental values for several ferroelectric crystals.

Crystal	$T_c$ (K)	$P^*$ (kbar)		$T^*$ (K)		Ref.
		Hydrostatic	Uniaxial	Hydrostatic	Uniaxial	
LGO	450	$\sim 24^a$ $\sim 23^e$	$\sim 2.4^b$	63 <sup>c</sup>	433 <sup>d</sup>	
BaTiO <sub>3</sub>	403	34	—	291	—	[9]
		35	—	233	—	[9]
TGSe	295	$\sim 5$	0.6 <sup>f</sup>	313	285.5	[8]
KDP	122	$\sim 2$	—	113	—	[5]

<sup>a</sup> Estimated from uniaxial pressure data.

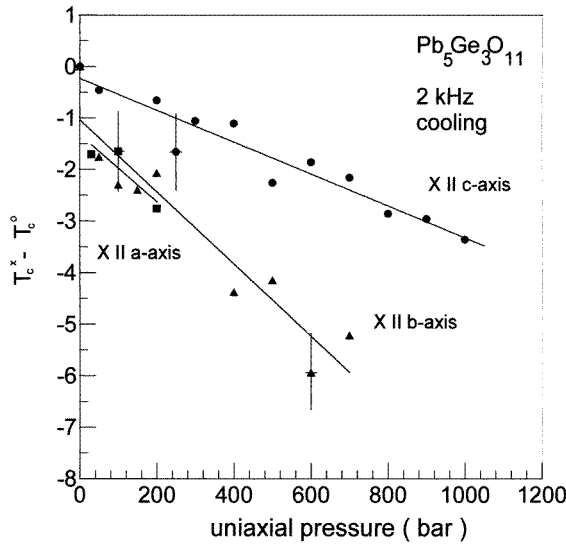
<sup>b</sup> Perpendicular to the  $c$ -axis ( $X \parallel b$ -axis), estimated from relation  $C^+/C^-$  against  $X$ .

<sup>c</sup> Calculated using  $\gamma_h = -15.5$  K kbar<sup>-1</sup>.

<sup>d</sup> Calculated using  $\gamma_b = -7.0$  K kbar<sup>-1</sup>.

<sup>e</sup> The break-in pressure dependence of some phonon modes observed by Soni and Jain [12]

<sup>f</sup>  $X \parallel a^*$ -axis.

**Figure 6.** Shift of the Curie point ( $T_c^X - T_c^0$ ) as a function of uniaxial pressure applied in parallel to the principal directions  $a$ ,  $b$  and  $c$  measured for decreasing temperature for the  $Pb_5Ge_3O_{11}$  single crystal. Frequency: 2 kHz; error bars are equal for each points.

The same coefficients measured for increasing temperature (i.e. on heating) are consistent with the values obtained on cooling, within the limits of the experimental uncertainties ( $\Delta\gamma_i \approx 0.3$  K kbar<sup>-1</sup>). This table contains also the corresponding  $\gamma_i$  and  $\gamma_h$  as well as electrostriction coefficients  $Q_{ki}$  for oxide ferroelectrics: BaTiO<sub>3</sub> and SrTiO<sub>3</sub>. The values of  $\gamma_i$  for the three oxide ferroelectrics are of the same order. The hydrostatic pressure coefficient  $\gamma_h$  can be calculated as a sum of the three main uniaxial pressure coefficients  $\gamma_i$  measured that is  $\gamma_h = \Sigma\gamma_i = (-16.7 \pm 0.9)$  K kbar<sup>-1</sup>. The values collected in table 2 show a very good agreement between  $\gamma_h$  measured directly [10, 27] and calculated as a sum of  $\gamma_i$ . A significant difference between  $\gamma_h$  calculated by us and the value reported by Gesi and Ozawa [26] requires some explanation. The reported relation between  $T_c$  and  $p$  shows a non-linear dependence

**Table 2.** Pressure and electrostriction parameters for oxide ferroelectric crystals (respective references are given in parentheses).

Crystal	$\gamma_h$	$\gamma_a$	$\gamma_b$	$\gamma_c$	$Q_{k1}$	$Q_{k3}$
	(K kbar <sup>-1</sup> )				(m <sup>4</sup> C <sup>-2</sup> )	
LGO	-6.7 <sup>a</sup> [26]	-5.8 <sup>b</sup>	-6.7	-2.8		
	-14.5 [27]	-6.5 <sup>c</sup>	-7.0	-3.2		
	-15.5 [10]	-5.8 <sup>d</sup>	—	3.6	0.246	-0.200 [28]
	-16.7 <sup>e</sup>	-3.4 <sup>f</sup>	—	-3.6	0.141	0.203 [14]
SrTiO <sub>3</sub>	≤-16 [29]	6.4 <sup>g</sup> [25]	—	—	-0.05 [1]	—
BaTiO <sub>3</sub>	-5.2 [30]	—	—	-9.5 <sup>h</sup>	—	0.04 [1]

<sup>a</sup> For pressure below 1.5 kbar; the relation obtained by the authors is nonlinear, but the average value up to 8 kbar is equal to -13.9 K kbar<sup>-1</sup>.

<sup>b</sup> On heating.

<sup>c</sup> On cooling.

<sup>d</sup> Calculated using  $Q_{ki}$  from [28].

<sup>e</sup> Calculated  $\gamma_h = \Sigma \gamma_i$ ,  $\gamma_i$  – experimental data on cooling.

<sup>f</sup> Calculated using  $Q_{ki}$  from [14].

<sup>g</sup> Stress-induced ferroelectric transition.

<sup>h</sup> Calculated from the data for hydrostatic and two-dimensional pressure [31].

giving a small value of  $\gamma_h = -6.7$  K kbar<sup>-1</sup> at low pressure [26]. However, no such behaviour was observed in other hydrostatic pressure studies [10, 27]. After all, Kirk *et al* [10] suggest that this discrepancy is probably related to the sample treatment.

According to the phenomenological theory [32] the coefficient  $\gamma_i$  can be also calculated from the relation:

$$\partial T_c / \partial X_i = -2C \varepsilon_0 Q_{ki} \quad (7)$$

where  $Q_{ki}$  is the electrostriction coefficient,  $C$  the Curie–Weiss constant and  $\varepsilon_0$  the permittivity of free space. Using our data of  $C$  and the value of  $Q_{ki}$  taken from the literature [14, 28] we calculated  $\gamma_i$  for LGO single crystals. The results are collected in table 2. Quite a good agreement with the experimental value can be noted. Our experimental results indicate that the sign of  $Q_{33}$  should be positive in agreement with the data in [14], not negative because only then can the proper sign of  $\gamma_c$  can be obtained from the calculations based on relation (7).

According to the empirical relationship between the mechanism of the ferroelectric PT and the pressure coefficient given by Samara [33] negative coefficients are related to the displacive type or hydrogen-tunnelling type phase transitions. Both uniaxial and hydrostatic pressure cause a decrease in  $T_c$ , which means that the coefficients  $\gamma_h$  and  $\gamma_i$  are negative. Therefore, as there are no H-bonds in LGO, our experiments confirm the displacive type of PT in LGO in accord to the structural investigations [2–4]. The anisotropic effect of pressure applied in the direction perpendicular to the  $c$ -axis is manifested as an increase in  $\gamma_i$  ( $\gamma_a \approx \gamma_b \approx 2\gamma_c$ ) and as the possibility of inducing TCP. We would like to bound its origin to a microscopic mechanism, pointing out the probable pressure interaction with LGO crystal lattice dynamics. Despite the lack of structural data for LGO under hydrostatic or uniaxial pressure, it can be presumed that pressure, in the range considered, introduces ordering of torsional motions of the germanate groups with no direct changes in the bond lengths. It is known that much higher pressure (than used in our experiment) is demanded to affect the bond lengths in crystals [34]. Similarly, one can expect that when the pressure is applied perpendicularly to the  $c$ -axis it creates more favourable conditions for Pb atoms to translate along the  $c$ -axis, whose movement is related to the generation of a dipole moment in an elementary cell. In contrast, the pressure applied along the  $c$ -axis prevents a correlated translation of Pb atoms along it. It can be supposed that the

uniaxial pressure applied in the direction perpendicular to the  $c$ -axis i.e. in a layer of  $GeO_4$  is more effective in synchronizing  $GeO_4$  group vibrations with simultaneous action on Pb atoms. From this symmetry point of view the applied pressure close to the critical conditions  $p^*$  and  $T^*$  may cause a jump-like ordering leading to a discontinuous change in some parameters such as  $\varepsilon$  and  $P_s$ . Further studies are planned to verify the above expectations.

#### 4. Conclusions

Our experiment shows a linear change of  $T_c$  with uniaxial pressure applied along the  $a$ -,  $b$ - and  $c$ -axes up to 1 kbar. The negative values of  $\gamma_i$  indicate the displacive character of PT in the LGO single crystal in accord with Samara's empirical rules. A good correlation between the  $\gamma_i$  values measured and calculated on the basis of the phenomenological relation was obtained. It was concluded that the sign of electrostriction coefficient  $Q_{33}$  should be positive.

The behaviour of  $\varepsilon_c$  and the ratio of  $C^+/C^-$  with uniaxial pressure indicates that:

- uniaxial pressure applied along the  $c$ -axis strengthens the second order PT behaviour,
- uniaxial pressure applied perpendicularly to the  $c$ -axis (i.e.  $X \parallel b$ -axis or  $X \parallel a$ -axis) may induce TCP at a critical uniaxial pressure estimated to be equal to  $\approx 24$  kbar.

The critical hydrostatic pressure estimated for LGO to be equal to  $\approx 24$  kbar is lower than that reported for other oxide ferroelectrics which we hope give impetus for further pressure studies of  $Pb_5Ge_3O_{11}$ .

In the tentative description, we show that the mechanism of changes in the character of PT in LGO crystals is connected to the anomalous behaviour of piezoelectric modulus  $d_{31}$  and can microscopically be related to the ordering of torsional motion of  $GeO_4$  groups in the (001) plane. The results of our studies support the general thesis about the essential role of the unstable atom in the paraelectric phase in TCP induction.

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