Influence of uniaxial stress on ultrasonic wave propagation near the phase transition in a TGSe crystal

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Abstract. Changes in the velocity and attenuation coefficient of quasilongitudinal waves propagating in a TGSe crystal in the directions $z' = z - 4°$ and x, induced by uniaxial stress σ_x and σ_y, were measured in the temperature range of the ferroelectric phase transition. The uniaxial stress applied was found to shift the phase transition temperature by $\partial T_C / \partial \sigma_x = -0.074$ and $\partial T_C / \partial \sigma_y = -0.18$ K MPa^{-1}. Other effects appearing under the influence of external stress, such as a change in the jump of the wave velocity at the phase transition, increase in the attenuation coefficient and broadening of the phase transition range, are discussed on the basis of the phenomenological theory. The relaxation time of the order parameter fluctuations was determined. For stress exceeding 2 MPa an additional anomaly in the wave velocity and attenuation appeared, which was interpreted as a splitting of the phase transition. The nonlinear elastic effects at the phase transition, in the para- and ferroelectric phases, are also discussed.

1. Introduction

Triglycine selenate (TGSe), sulphate (TGS) and fluoroberylate (TGFB) make up a family of crystals whose physical properties have been studied for a few decades [1]. The crystals undergo a model second order phase transition of order–disorder type from the centrosymmetric paraelectric phase of $P2_1/m$ symmetry to the low-temperature ferroelectric phase of $P2_1$ symmetry. For TGSe, TGS and TGFB the temperatures of the phase transitions are 295, 322 and 343 K, respectively. Despite intensive studies the mechanisms leading to the appearance of spontaneous polarization in these crystals have not been fully recognized yet.

Relatively few authors have been concerned with investigation of elastic properties of these crystals by ultrasonic wave propagation. All the components of the elasticity tensor have been determined only at room temperature for TGS [2] and TGSe [3]. At the Curie temperature the coupling of the ultrasonic wave strain with spontaneous polarization causes a few per cent jumplike changes in the wave velocity and the appearance of maxima of sound attenuation.

The majority of authors studying the effect of mechanical stress on ferroelectric systems used hydrostatic pressure, as even when high it did not damage the crystal. Unfortunately, the use of hydrostatic pressure, which is a sum of uniaxial pressures acting along the main directions, prevents analysis of anisotropic properties of the crystals. The influence of uniaxial pressure on dielectric properties of pure and deuterated TGSe crystals is reported in [4]–[6], while the effect on elastic properties determined by Brillouin scattering in TGS crystals in [7] and in TGSe crystals in [8]. Although the ultrasonic method permits a more accurate

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determination of elastic properties than Brillouin scattering, it has not enjoyed much interest and only a study for a TGS crystal doped with L-α-alanine (LATGS) has been reported [9].

This paper reports results of a study on ultrasonic wave propagation velocity and attenuation along the x and $z' = z - 4°$ directions in a TGSe crystal subjected to uniaxial stress applied along the polar y axis and x direction, in the temperature range covering the phase transition.

2. Experimental procedure and results

TGSe crystals were grown in the paraelectric phase by slow evaporation of water solution, three times recrystallized, at a constant temperature of 305 K. Samples in the rectangular shape, size $7 \times 7 \times 5$ mm^3, were cut out from large optically homogeneous single crystals. The orientation of the axes was as follows: the y direction coincided with the ferroelectric b axis, the z direction with the c axis and the x direction was perpendicular to the two other axes. The accuracy of parallelism of the optically polished crystal surfaces was better than 10^{-4}, and the accuracy of the orientation of the edges was $\pm 0.5°$. The flatness of the surfaces, especially those parallel to the direction of the stress was checked by the method of Newton rings.

A piezoelectric transducer made of lithium niobate, attached to the sample surface with silicon grease, generated and received ultrasonic wave of 11 MHz frequency. The quasi-longitudinal waves propagated along the direction x and along the direction making an angle of $4°$ with the c axis in the bc plane ($z' = z - 4°$). For this second direction the deviation of the elastic displacement vector from that of the wave propagation, calculated on the basis of the data from [3], is zero so the wave is purely longitudinal. As reported in [10]–[12], the attenuation anomaly in the region of the phase transition becomes symmetric and the jumplike change of velocity is almost the same. The velocity and attenuation of the ultrasonic wave were measured by a MATEC system built of a generator/receiver (TB1000) and a digital oscilloscope (SR9010). The operation system was controlled by DSP 3.5 software ensuring the calculation of velocity and attenuation by the FFT procedure and fast deconvolution. The relative accuracy of velocity measurement was 3×10^{-6}, and attenuation 5×10^{-3}.

The samples were mounted in a special holder in which the velocity and attenuation coefficient of ultrasonic waves could be measured in the temperature range from 80 to 600 K, under uniaxial pressure up to 20 MPa and a constant electric field up to 200 kV m^{-1}. The uniaxial pressure was induced by pressing a carefully calibrated spring mounted outside the holder. In order to avoid the sample cracking as a result of possible inaccuracies of surface polishing, a thin metallized Mylar foil was placed between the sample and stainless steel pistons. The estimated error in stress determination was less than 3%.

As the preliminary measurements of the wave velocity and attenuation did not reveal any differences between heating and cooling, further measurements were performed only on monotonic cooling at the rate of 0.05 K min^{-1}, controlled by a temperature controller (UNIPAN 680). The stress was changed at 25 °C only in the paraelectric phase. Temperature was measured with an accuracy of ± 0.02 K by a copper–constantan thermocouple attached to the sample. To avoid the influence of the domain walls in the ferroelectric phase on the velocity and attenuation of elastic waves (such an effect was observed in a TGS crystal [13]), the samples studied were permanently polarized by an electric field of intensity 100 kV m^{-1}.

Mechanical stress, varied from zero to that causing destruction of the crystal was applied at 300 K, so in the paraelectric phase of the TGSe crystals, both along the x direction and the ferroelectric axis. Although when the stress was applied in the direction perpendicular to the cleavage plane the samples were destroyed when the stress reached 13–15 MPa, when the
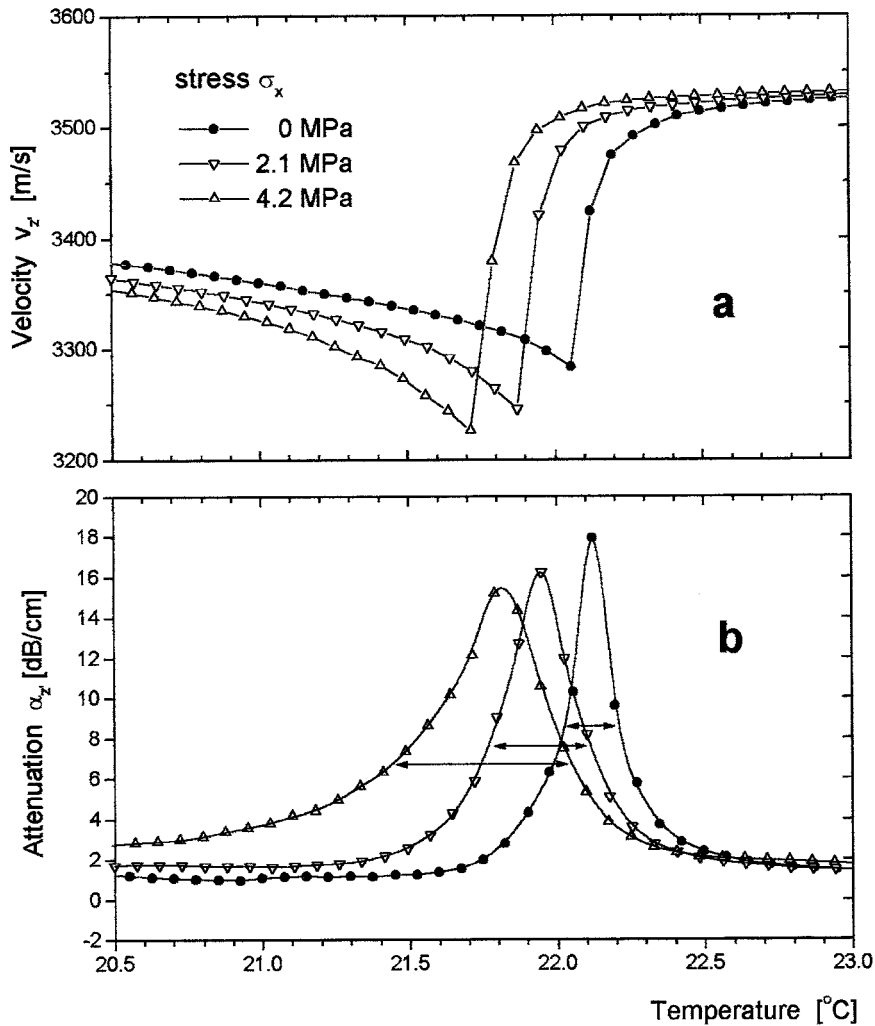
Figure 1. Temperature dependences of the velocity (a) and attenuation (b) of the longitudinal wave propagating along the $z' = z - 4°$ direction under uniaxial stress σ_x.

stress was applied in the x direction the crystal was damaged already at a few MPa. Figures 1 and 2 present the temperature dependences of the velocity and attenuation coefficient of waves propagating along both the $z' = z - 4°$ and x directions for a few chosen values of the applied stress.

As evident from figures 1 and 2, the phase transition temperature decreases with the stress applied in both directions. Moreover, with increasing stress σ_y the jumplike change in the sound velocity decreases, whereas increasing σ_x causes its increase. The stress applied in both directions causes an increase of the width of the phase transition, understood as the range of temperatures of the anomalous changes of the velocity and attenuation. It can be well approximated by the 'full width at half maximum' of the curve $(\alpha - \alpha_0)$ against $(T - T_C)$. Another interesting effect is the split of the phase transition appearing as a result of application of stress higher than 2 MPa along the ferroelectric axis. The uniaxial stress applied in both directions caused small changes in the wave velocity in the entire temperature range studied.
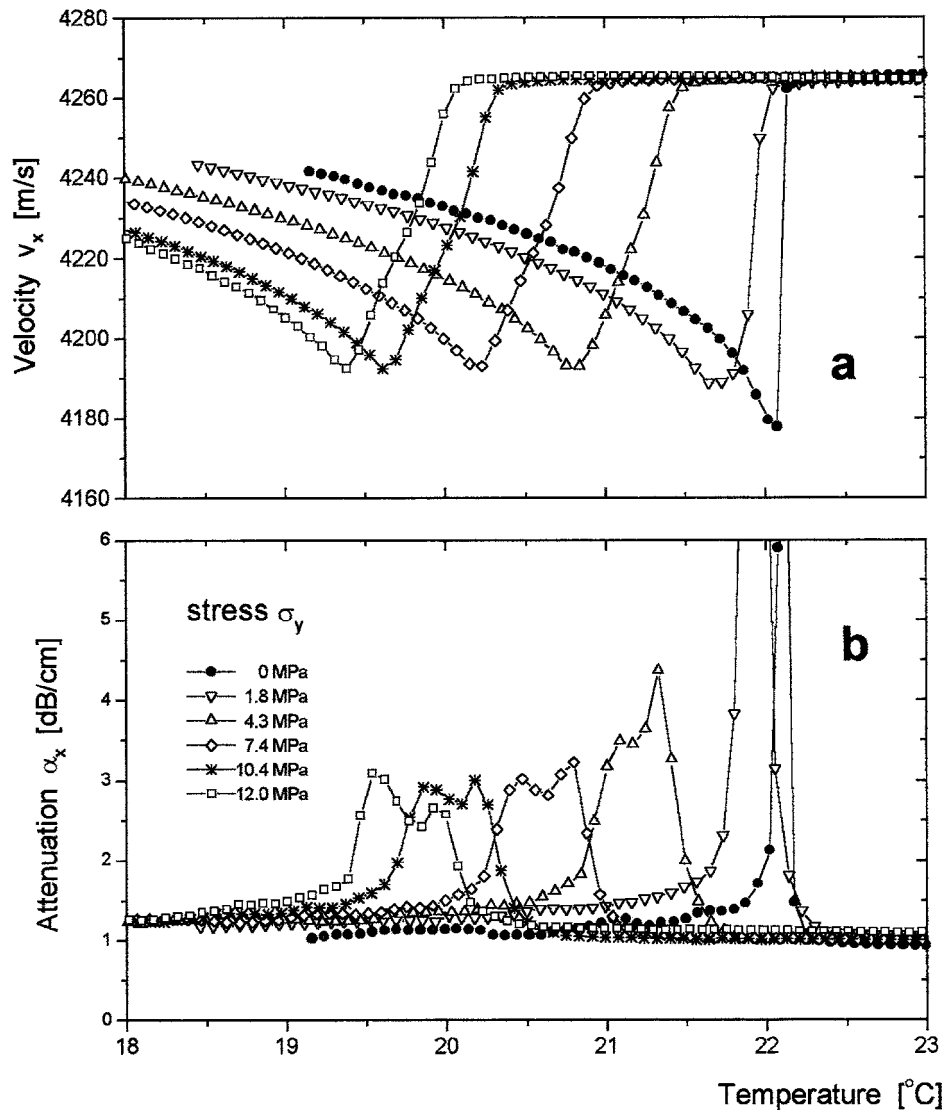
Figure 2. Temperature dependences of the velocity (a) and attenuation (b) of the quasilongitudinal wave propagating in the direction x under uniaxial stress σ_y.

This effect is explained as a result of the third order nonlinear elasticity. All the effects will be discussed in the next section.

3. Discussion

3.1. Shift of the phase transition temperature

As expected, according to Pippard–Janovec theory, the application of uniaxial stress σ_x and σ_y resulted in a decrease of the phase transition temperature. The obtained values were: $\gamma_1 = \partial T_C / \partial \sigma_x = -0.074$ K MPa^{-1} and $\gamma_2 = \partial T_C / \partial \sigma_y = -0.18$ K MPa^{-1}. In our case the

Table 1. Changes in the phase transition temperature in TGSe and TGS crystals under the influence of uniaxial stress, determined by the following methods: D—dielectric; B—Brillouin scattering, U—ultrasonic wave propagation, E—thermal expansion.

Crystal	$\gamma_1 = \partial T_C/\partial \sigma_x$	$\gamma_2 = \partial T_C/\partial \sigma_y$	$\gamma_3 = \partial T_C/\partial \sigma_z$	Method
TGSe	−0.166	−0.094	+0.30	D [4]
	−0.159	−0.087	+0.283	D [6]
	—	−0.15	—	B [8]
	−0.074	−0.18	—	U [this work]
TGS	−0.067	−0,091	+0.19	D [14]
	−0.072	−0.12	+0.23	D [15]
	−0.036	−0.067	+0.11	E [16]
LATGS	−0.045			U [9]

influence of σ_y on the phase transition temperature is greater than the changes reported in [6], where the applied stress was very high—up to 50 MPa, but consistent with the results of [8]. Moreover, our value of γ_1 is lower than that obtained in [6]. Table 1 illustrates the influence of uniaxial stress applied in different directions on T_C, determined by different methods, for TGSe and TGS crystals.

Crystals of triglycine sulphate and triglycine selenate are structurally similar and thus it can be expected that anisotropy of their physical properties will be alike. For the TGS crystal, according to [15] $\gamma_1:\gamma_2:\gamma_3 \approx -1:-1.8:3.2$, whereas the corresponding anisotropy for the TGS crystal on the basis of the data from [4, 6] is $\gamma_1:\gamma_2:\gamma_3 \approx -1.8:-1:3.2$. Our result is $\gamma_1:\gamma_2:\gamma_3 \approx -1.8:-1:x$ (unfortunately the effect of σ_z was not studied).

3.2. Thermodynamical theory of elastic anomalies at the second order phase transition

In order to describe changes of velocity and attenuation of the ultrasonic wave taking place at the second order phase transition under external stress, after Landau and Devonshire [17], the general Gibbs potential can be expanded into a Taylor series with respect to spontaneous polarization (P_2) as an order parameter, mechanical deformation of the ultrasonic wave (η^U) and the crystal deformation caused by external stress (η^S):

$$\Phi(T, P_2, \eta^U, \eta^S) = \Phi_0(T) + \tfrac{1}{2}\alpha P_2^2 + \tfrac{1}{4}\beta P_2^4 + \xi^U P_2^2 \eta^U + \xi^S P_2^2 \eta^S + \zeta^S P_2^4 \eta^S + \tfrac{1}{2}c^0 \eta^{U2} \quad (1)$$

where $\Phi_0(T)$ is the background lattice free energy density. It is assumed (as usual) that only the coefficient α depends on temperature $\alpha = \alpha_0(T - T_C)$. The coefficients ξ and ζ are the components of the fourth and sixth order electrostriction tensor. The last term is the elastic energy of an ultrasonic wave.

The minimization of free energy with respect to polarization ($\partial\Phi/\partial P_2 = 0$) gives, for zero electric field, the following expression:

$$P_2^2 = -\frac{\alpha + 2\xi^U \eta^U + 2\xi^S \eta^S}{\beta + 4\zeta^S \eta^S}. \quad (2)$$

At the phase transition temperature $T = T_C$, spontaneous polarization is zero and thus:

$$\alpha_0(T_C^S - T_C^0) + 2\xi^U \eta^U + 2\xi^S \eta^S = 0 \quad (3)$$

where T_C^0 and T_C^S are the phase transition temperatures in the absence and in the presence of external stress respectively. Taking into regard the fact that the ultrasonic wave strain is small

relative to that induced by external stress, and resorting to the Hook's law, the change in the phase transition temperature caused by external stress is described by:

$$T_C^S - T_C^0 = -\frac{2\Xi^S \sigma_i^S}{\alpha_0} \tag{4}$$

where Ξ^S is the tensor of electrostriction whose components are related to the corresponding ones of the susceptibility tensor through the relation:

$$\Xi_{2i}^S = \xi_{2k}^S S_{ki}^S \tag{5}$$

where $i = 1, 2$ (the uniaxial stress applied in our experiment) and $k = 1, 2, 3, 5$ according to the monoclinic symmetry of TGSe crystals.

So far in description of the changes in elastic wave velocity at a second order ferroelectric transition only the coupling term $P^2\eta$ [18] has been used, while we have added the term $P^4\eta$. Differentiation of equation (1) with respect to the elastic wave strain leads to the expression:

$$\frac{\partial \Phi}{\partial \eta^U} = \xi^U P_2^2 + c^0 \eta^U. \tag{6}$$

Substituting (2) into this equation and differentiating it again with respect to the ultrasonic wave strain, we obtain the equation describing the change in the quasi-longitudinal wave velocity at the ferroelectric second order phase transition:

$$\frac{\partial^2 \Phi}{\partial \eta^{U^2}} = \operatorname{Re} c = \rho v^2 = c^0 - \frac{2\xi^{U^2}}{\beta + 4Z^S \sigma_i^S} \tag{7}$$

where Z^S is the sixth order tensor of electrostriction whose components are related to the corresponding components of the elastic susceptibility tensor, similarly as in equation (5), through the relation:

$$Z_{22i}^S = \zeta_{22k}^S S_{ki}^S. \tag{8}$$

It is evident that the jumplike change in the ultrasonic wave velocity can increase or decrease under the effect of external stress, depending on the sign of the appropriate component of the sixth order electrostriction tensor.

The effect of uniaxial stress on the jumplike change in the ultrasonic wave velocity measured for the two above-mentioned directions is illustrated in figure 3. The dependences are nonlinear and the increase in Δv_x for σ_y greater than 4 MPa is due to nonlinear elasticity in the paraelectric phase. The relative changes of the coefficient β appearing in the free energy expansion, calculated for small stress (up to 2 MPa) are: $1/\beta \partial(\Delta\beta)/\partial\sigma_x = -0.061$ and $1/\beta \partial(\Delta\beta)/\partial\sigma_y = 0.097$ MPa^{-1}. In [6] these changes are presented as linear up to 30 MPa, and their values are: -0.013 and 0.10 MPa^{-1} respectively.

3.3. Anomalous changes in velocity and attenuation of elastic wave related to fluctuations of the order parameter

Anomalous increase in the ultrasonic wave attenuation in the ferroelectric phase is explained in the terms of the Landau–Khalatnikov relaxation theory [19]. In the centrosymmetric paraelectric phase, there is no linear coupling between the order parameter and elastic wave strain and the anomaly in the ultrasonic wave attenuation is interpreted as due to the interaction between the ultrasonic wave and thermal fluctuations of the order parameter [20, 21]. This interaction also affects the temperature dependence of velocity above T_C and is responsible for its high-temperature tail. Figure 4 presents the influence of the interaction of the elastic
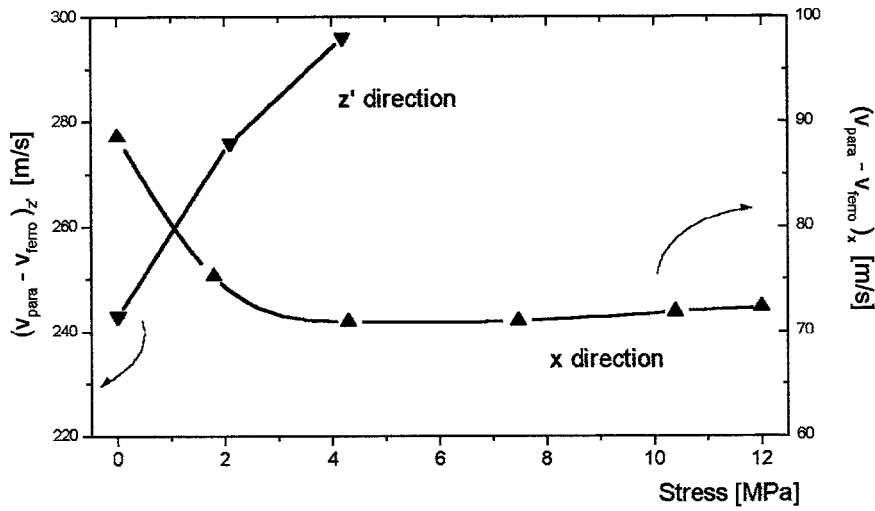
Figure 3. The effect of uniaxial stress on the jump-wise change in the ultrasonic wave velocity.

wave strain and the order parameter fluctuations on the ultrasonic wave propagation velocity and its attenuation for the two directions of propagation at zero external stress.

The effective relaxation time of a given order parameter can be estimated from changes in ultrasonic wave attenuation, according to the relation [22]:

$$\Delta\alpha = \alpha(\omega) - \alpha_0 = \frac{1}{2}\frac{v_\infty^2 - v_0^2}{v_0^3}\frac{\omega^2\tau_{eff}}{1+\omega^2\tau_{eff}^2} \tag{9}$$

where α_0 is the background attenuation in the paraelectric phase which is not related to the fluctuation mechanism and v_∞ and v_0 are the wave velocities above and below the phase transition point. The temperature dependence of the relaxation time calculated from equation (9) is shown in figure 5, in the semilogarithmic scale for the z' and x directions and for uniaxial stress equal to zero and 4 MPa.

In the vicinity of the phase transition, in the range $0.1 < T - T_C < 1$ K, the relaxation time changes as the power law $\tau_{eff} = A(T - T_C)^{-\kappa}$ while at higher temperatures, $T - T_C > 1$ K, its temperature dependence is logarithmic in character. The exponent κ takes a value of 1.05 and 1.25, for the x and z' directions, respectively, and increases up to 2.2 and 1.8, when the stress of 4 MPa is applied. These temperature and stress dependences of the relaxation time cannot be explained by the monodispersive mechanism implied by the mean field theory, and, on the other hand, the stress does not change the value of the proportionality coefficient A, which is: 1.4×10^{-11} and 5.3×10^{-11} s^{-1} for the directions x and z' respectively. For the sake of comparison, in the TGS crystal in the direction y, this coefficient is 1.0×10^{-11} s^{-1} [23].

3.4. Width of the phase transition

As follows from figures 1 and 2, with increasing stress the width of the phase transition, as defined in section 2, increases. Figure 6 shows the phase transition width defined as the range of temperatures in which the wave attenuation decreases by half. Under zero stress the transition width, for the wave propagating along the x direction, is 0.06 K and then it rapidly increases with increasing stress, reaching 0.46 K, and in the range of the stress where the transition splits
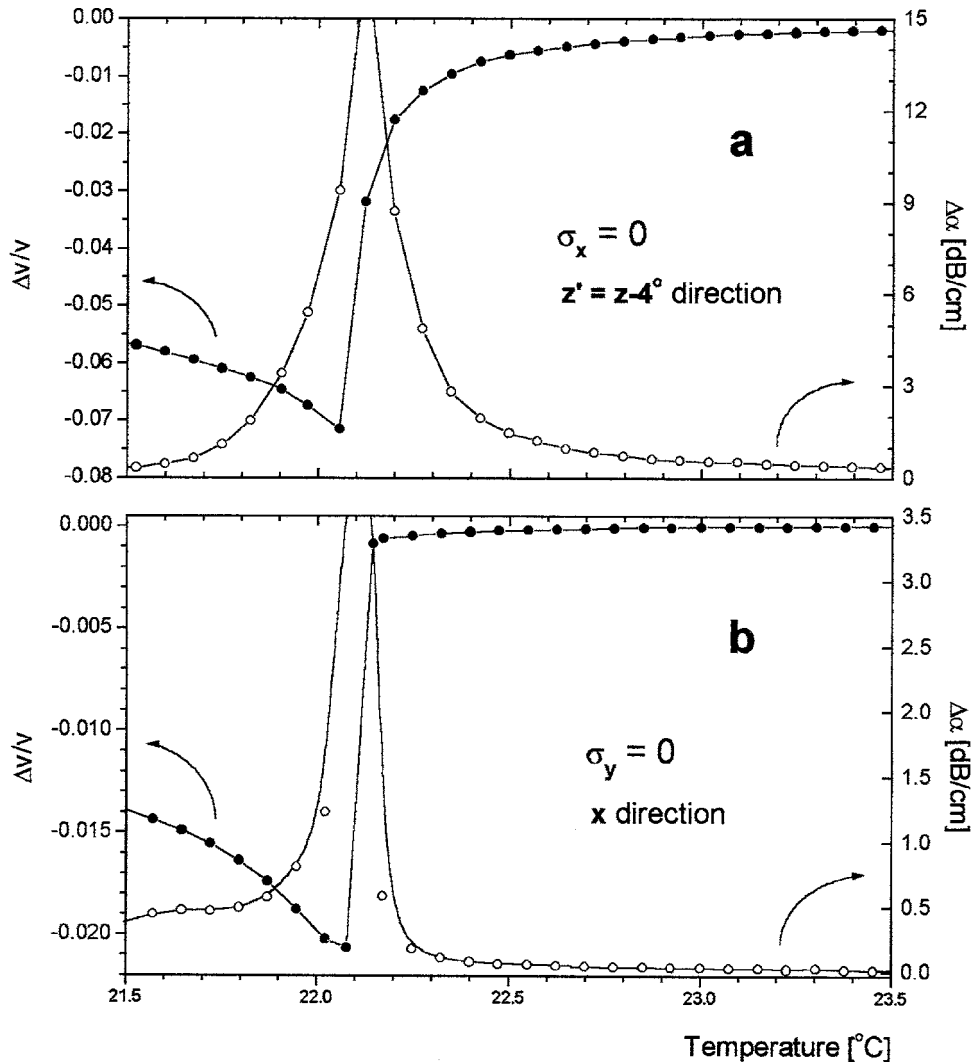
Figure 4. Changes in the velocity and attenuation of the ultrasonic wave in the paraelectric phase, caused by the interaction of the wave with the order parameter fluctuations: (a) for the z' direction, (b) for the x direction.

the width remains almost unchanged. Also for the wave propagating along the z' direction, the width of the phase transition increases from 0.17 K for zero stress to 0.50 K for $\sigma_x = 4.2$ MPa.

Since TGSe crystal is centrosymmetric in the paraelectric phase, the coupling between the strain and polarization is linearly square below T_C, so the external stress can affect the phase transition temperature, the jumplike change of the wave velocity at the phase transition but cannot broaden the phase transition. Such a broadening was observed when the crystal was subjected to a strong electric field [12]. The coupling between the polarization and electric field is bilinear, taking into regard the experimental results expected for the relation between the strain and polarization. This would require the appearance of a piezoelectric effect at the phase transition and the coupling term would be of the form: $hP\eta$, where h is the piezoelectric coefficient. It is also hardly probable that a small external stress could change the crystal
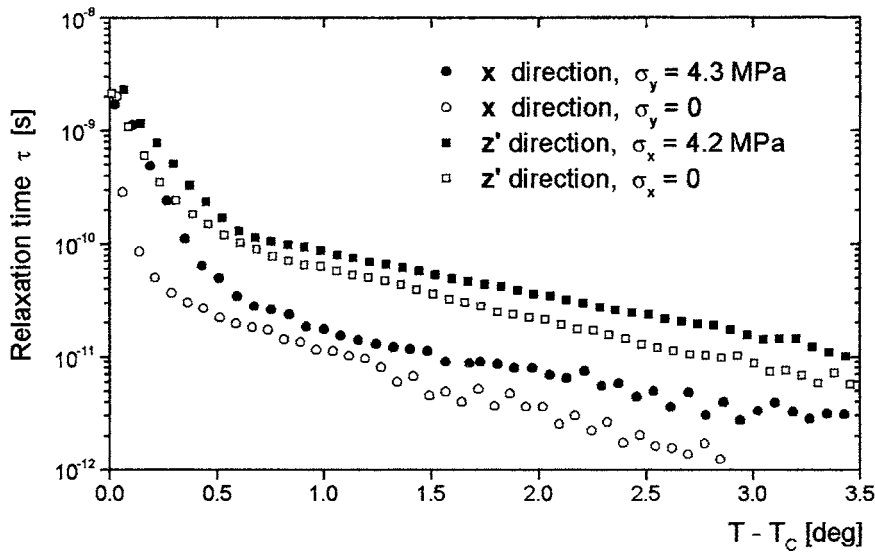
Figure 5. The effective relaxation time of order parameter fluctuations for $T > T_C$. Open symbols—zero stress, full symbols—$\sigma = 4$ MPa.
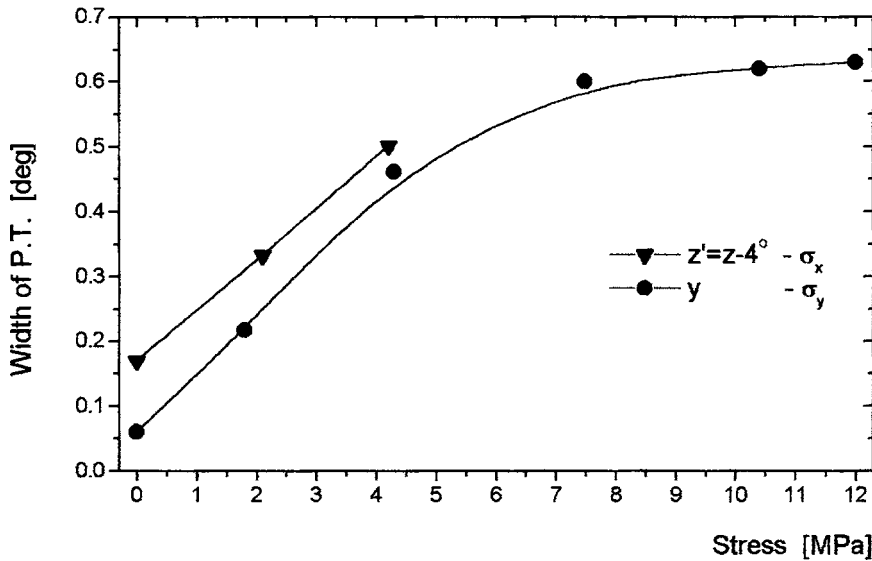

Figure 6. The phase transition width as a function of stress.

symmetry and eliminate the centre of inversion. However, in the paraelectric phase close to T_C, there are fluctuations of polarization so in these regions the piezoelectric phenomenon could appear. The external uniaxial stress can change the value of a local piezoeffect and thus affect the temperature dependences of the ultrasonic wave velocity and attenuation. As a consequence, the range of temperatures in which there is the jumplike change in the wave velocity and anomalous change in the wave attenuation increases, and simultaneously the maximum attenuation at the phase transition decreases.
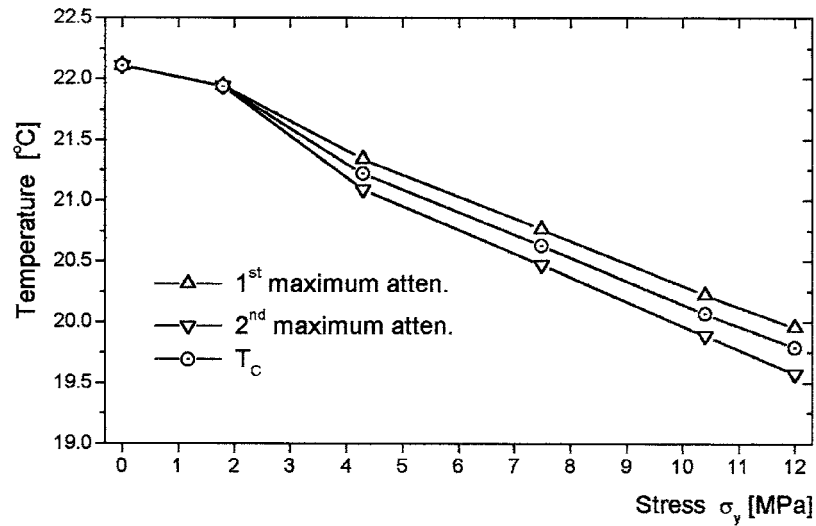
Figure 7. The phase transition temperature and temperatures of the two attenuation maxima versus applied stress.

3.5. Splitting of the phase transition

For the stress σ_y higher than 2 MPa, the phase transition was observed to split—see figure 2. The splitting is particularly well seen for the attenuation coefficient. The anomaly in attenuation is related to the time of spontaneous polarization relaxation [24] and for stress up to 2 MPa, its maximum value decreases. The effect is similar to a decrease in the maximum value of dielectric constant under the influence of stress [6]. However, for stress higher than 2 MPa the appearance of an additional maximum of attenuation was observed below T_C, whose value increased with increasing stress and which was shifted towards lower temperatures. At the same time the value of the first maximum decreased and was shifted towards higher temperatures relative to T_C. The temperature changes in the position of the two maxima are shown in figure 7. At the temperatures of the attenuation maxima anomalous changes in the wave velocity were also observed, manifested as inflection points in its temperature dependence.

The splitting of the phase transition in TGSe crystals occurs only under the influence of the stress σ_y. The stress applied in the other directions causes only a shift in the phase transition temperature and an insignificant (of the order of 10^{-3}) change in the wave velocity caused by nonlinear elastic properties of the crystal. The splitting is difficult to explain within the phenomenological theory assuming that spontaneous polarization is a single-component order parameter. However, if we assume that free energy in the ordered phase is related to the two-component order parameter, it can be described by the following expression [25]:

$$\Phi = \alpha(q_1^2 + q_2^2) + \beta_1 q_1^2 q_2^2 + \beta_2(q_1^2 - q_2^2)^2 + \delta_1 q_1 q_2 x_1$$
$$+ \delta_2(q_1^2 - q_2^2)x_2 + K_1 x_1^2 + K_2 x_2^2 - x_1 X_1 - x_2 X_2 \qquad (10)$$

where q_1, q_2 are the components of the microscopic order parameter and x_1, x_2 are macroscopic variables related to external fields X_1, X_2. The splitting of the phase transition will appear when the effective potential depending only on the parameters η_1 and η_2 is used. This effective potential can be obtained by minimizing potential (10) with respect to x_1 and x_2: $\partial\Phi/\partial x_1 = 0$ and $\partial\Phi/\partial x_2 = 0$:

$$\Phi^* = \alpha_1 q_1^2 + \alpha_2 q_2^2 + \beta_1' q_1^2 q_2^2 + \beta_2'(q_1^2 - q_2^2) - X_2^2/4K_2 \qquad (11)$$

in which for $X_1 = 0$, the following notation has been introduced:

$$\alpha_1 = \alpha + x_2\delta_2/2K_2 \qquad \alpha_2 = \alpha - x_2\delta_2/2K_2$$
$$\beta_1' = \beta_1 - \delta_1^2/4K_1 \qquad \beta_2' = \beta_2 - \delta_2^2/4K_2. \qquad (12)$$

The effective potential Φ^* contains two square invariants $a_1q_1^2$ and $a_2q_2^2$, which implies that with decreasing temperature and under the influence of an external field X_2, at first a phase type $(q_1, 0)$ or $(0, q_2)$ may appear, followed by a phase type (q_1, q_2). This indirect influence of an external field on the order parameter can lead to the splitting of the phase transition into two close lying transitions [26].

The splitting of the magnetic phase transition was observed in a $KMnF_3$ crystal [27]. In this case there was no external field but its role was played by a distortion of the crystal lattice appearing during the structural phase transition. A strong electric field splits the transition from the incommensurate to the commensurate phase in the $(NH_4)_2BeF_4$ crystal [28]. Moreover, the splitting of the phase transition under the effect of uniaxial mechanical stress was found in NH_4HSeO_4 crystals [29] and $(NH_4)_2ZnCl_4$ [30].

However, in all the above examples the order parameter describing the phase transition is a two-component one. In order to explain the splitting in TGSe crystals, we also assume a two-component order parameter. The elastic wave propagating in the crystal does not interact with spontaneous polarization, which is a macroscopic order parameter but with dipole moments of molecular groups building the crystal lattice. In the TGS family crystals spontaneous polarization appears along the direction y as a result of ordering of mainly glycine I zwitterions [31]. In the paraelectric phase glycine I is planar and lies in the (010) plane. NMR studies of deuterated TGS [32] proved that below T_C glycine I becomes non-planar and the temperature dependences of the directions of its C–N and C–C bonds in the carboxyl group are different. Moreover, the jumps of the NH_3^+ group, moving in a double potential well, become ordered. These molecular and orientational changes responsible for the appearance and increase of macroscopic spontaneous polarization with decreasing temperature may be the two components of the microscopic order parameter we have been looking for. The mechanical stress acting along the twofold axis can alter the conditions of motion of the NH_3^+ group and thus induce a deformation of the bonds in glycine I, leading to the splitting of the phase transition. However, the question about the crystal symmetry in the intermediate phase is still open. Finally it should be noted that in the KDP crystal, which is a classical ferroelectric with spontaneous polarization being a single-component macroscopic order parameter, the new orthorhombic metastable phase was observed to be induced below 121 K by the stress $\sigma_6 > 16$ MPa [33].

3.6. Nonlinear elastic effects

In substances subjected to external stress, the velocity of ultrasonic wave propagation can be expressed through the components of the second and third order elasticity tensors [34]. Because of experimental difficulties, and a large number of independent components of the sixth rank tensor of nonlinear elasticity, the objects of studies were mainly isotropic materials or crystals of high—cubic or hexagonal—symmetry. Investigation of nonlinear elasticity is particularly important in the regions of the phase transitions, both in ferroelastic and ferroelectric crystals [35, 36], and requires taking into regard the interaction of the elastic wave deformation with fluctuations of the order parameter and defected crystal structure.

In contrast to the method of generation of the second harmonics of the elastic wave in which the adiabatic third order elastic moduli are determined: $c_{ijklmn}^S = (\partial c_{ijkl}^S / \partial u_{mn})_S$, the dependence of the wave velocity on external stress allows a determination of the mixed moduli
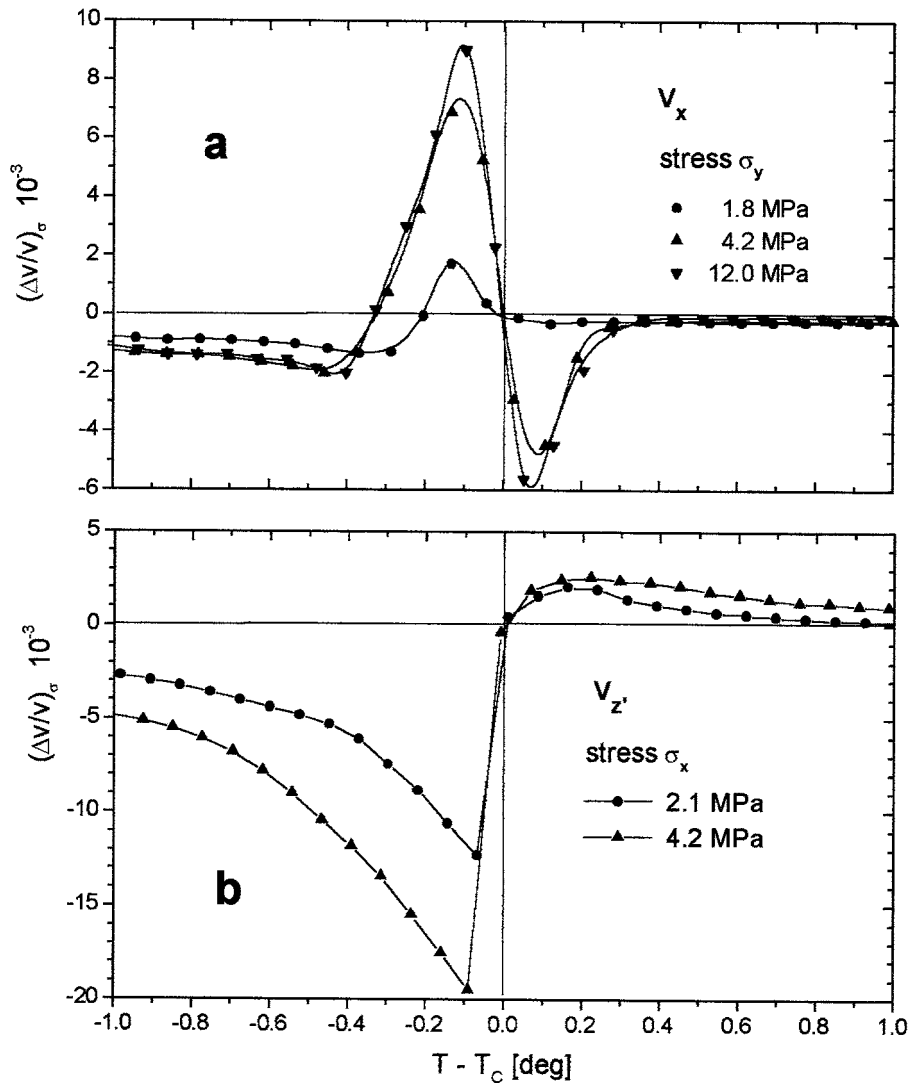
Figure 8. External stress induced relative changes in the ultrasonic wave velocity: (a) v_x wave, stress σ_y; (b) v_z wave, stress σ_x.

(adiabatic–isothermal): $c^{TS}_{ijklmn} = (\partial c^{S}_{ijkl}/\partial u_{mn})_T$ [37]. Usually the difference between them does not exceed 10%. The TGSe crystal belongs to the monoclinic system (point group 2) and has 13 and 34 independent components of the second order and third order elasticity tensor, respectively. A determination of the values of all components of the nonlinear third order elasticity tensor requires many independent measurements and probably that is why there is only one paper in which almost all these components for TGS have been established [9].

The accurate values of nonlinear coefficients have to be calculated by the procedure developed by Brugger [38]; however, this is beyond the scope of our work. Nevertheless, the relative changes in the elastic wave velocity induced by external stress can be treated as a measure of nonlinear elastic susceptibility. They are shown in figure 8 as a function of the distance from the phase transition temperature in order to eliminate the stress-induced change
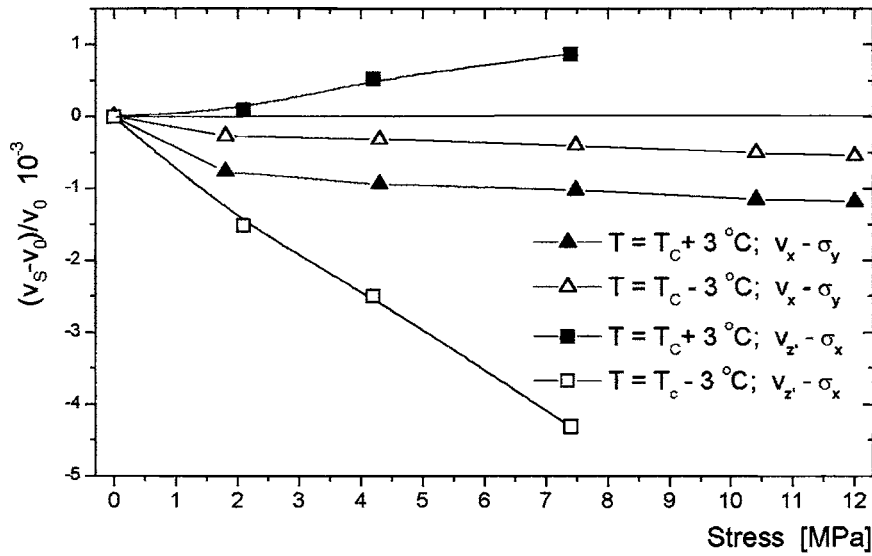
Figure 9. Nonlinear elastic effects above and below the phase transition.

of T_C. Three temperature-dependent regions can be distinguished: the paraelectric phase for $T > T_C + 0.3$ K, the phase transition vicinity and the ferroelectric phase $T < T_C - 0.4$ K. In the phase transition region the elastic wave velocity is the most susceptible to the effect of uniaxial stress and the changes reach: +1% for v_x and σ_y, and −2% for $v_{z'}$ and σ_x. The reason for such pronounced changes may be the interaction of the wave deformation with the fluctuations of the order parameter altered by the stress, described in sections 3.3 and 3.4. In the ferroelectric phase far from the phase transition, the changes in the velocity of the two waves studied are affected by the jumplike velocity change at T_C and the classical nonlinear elasticity of the crystal lattice. In the paraelectric phase, far from T_C, the influence of the phase transition phenomena is nonessential, the velocity changes do not depend on temperature and we can deal only with the nonlinearity of the crystal lattice. Figure 9 illustrates the changes of velocities as a function of uniaxial stress for temperatures far from the phase transition point $T = T_C \pm 3$ K. It is worth mentioning that in the ferroelectric phase stress of both kinds causes a decrease in the velocity, while in the paraelectric one the effects of the two kinds of stress are opposite, and for the wave propagating along the x direction and stress applied along the ferroelectric axis the changes are nonlinear.

The calculated values of the stress derivatives of the relative velocity changes in the linear part are (in 10^{-11} Pa^{-1}): $1/v_{z'}(\partial v_{z'}/\partial \sigma_x) = 12$ and -59, as well as $1/v_x(\partial v_x/\partial \sigma_y) = -2.7$ and -4.1, for $T = T_C + 3$ K and $T = T_C - 3$ K, respectively. The results are comparable with the data obtained for the NaCl crystal, when the stress applied is perpendicular to the direction of the wave propagation: -3.2×10^{-11} Pa^{-1} [39] and for the paraelectric phase of the KDP crystal (longitudinal wave): $2–3.5 \times 10^{-11}$ Pa^{-1} [40].

4. Summary

In the ferroelectric crystal of triglycine selenate (TGSe) the temperature dependences of the velocity and attenuation coefficient of a quasilongitudinal ultrasonic wave, propagating along the directions $z' = z - 4°$ and x in the (ac) plane were determined, and the effect of uniaxial

stress applied in the x and y directions on these quantities was measured. A jumplike change in the wave velocity and an anomalous increase in the attenuation coefficient at T_C, typical of second order phase transitions, were observed. The uniaxial stress applied resulted in a decrease in the phase transition temperature. The results are in disagreement with the literature data [4], in which the effects of uniaxial stress on dielectric properties were studied, but are close to the results obtained for the TGS crystal.

The external stress also causes a change in the value of the jump in the wave velocity at T_C, an increase in the attenuation coefficient (in paraelectric and ferroelectric phases) and a broadening of the phase transition range. These effects have been analysed in the terms of the modified phenomenological Landau theory. The anomalous changes in the velocity and attenuation of an elastic wave above the phase transition temperature are a result of the wave interaction with the fluctuations of the order parameter. The relaxation time of these fluctuations and its change due to the stress were found. The temperature dependence of this relaxation time is of complex character and does not comply with the power law following from the averaged field theory.

An interesting phenomenon was the split of the phase transition taking place under the effect of stress higher than 2 MPa applied along the ferroelectric axis. For interpretation of the effect we assumed that the elastic wave interacts with the internal order parameter which is composed of two components and the external stress changes their ratio. The change in the velocity of the elastic wave propagating in the crystal of a given symmetry and induced by uniaxial stress, can be described by the appropriate components of the elasticity tensors of the fourth rank (linear) and the sixth rank (nonlinear). The temperature course of the changes has been described in three temperature ranges: in the vicinity of the phase transition, in the paraelectric and ferroelectric phase far from T_C.

Acknowledgments

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