Suppression of ferroelectricity by low uniaxial mechanical stresses in crystals with several structural phase transitions

S. N. Kallaev, V. V. Gladkiĭ, V. A. Kirikov, E. S. Ivanova, and L. A. Shuvalov

A. V. Shubnikov Institute of Crystallography of the Academy of Sciences of the USSR; Institute of Physics of the Dagestan Affiliate of the Academy of Sciences of the USSR

(Submitted 11 June 1990)
Zh. Eksp. Teor. Fiz. **98**, 1804–1813 (November 1990)

The suppression of ferroelectricity by a low uniaxial mechanical stress was investigated with a tetrachlorozincate-tetramethylammonium crystal as the example. The ferroelectric properties and the phase transitions were recorded by different methods based on measurements of the dielectric constant, the polarization, and the macroscopic quadrupole moment of the crystal. It was found that the spontaneous polarization P_s and the temperature range in which it exists at first decrease and then vanish as the crystal is compressed by stresses σ_{zz} and σ_{yy} and that the effect is absent for $\sigma_{xx} \neq 0$ (the **x** axis $\|\mathbf{P}_s$). In a multidomain crystal the width of the ferroelectric domains remains practically unchanged as P_s decreases. The $\sigma_{zz}-T$ and $\sigma_{yy}-T$ phase diagrams were constructed. Measurements showed that the effect is connected with the proximity of the state of the crystal to the critical point in the phase diagrams with $(\sigma_{zz})_{\rm cr} \approx 25$ kgf/cm^2 and $(\sigma_{yy})_{\rm cr} \approx 30$ kgf/cm^2. Some additional experimental data are presented and the possibility of observing a stronger effect and its modifications in other crystals is discussed.

INTRODUCTION

In Ref. 1 S. N. Kallaev reported observation of the suppression of ferroelectricity by a low uniaxial mechanical compressional stress σ, perpendicular to the direction of spontaneous polarization, in a tetrachlorozincate-tetramethylammonium crystal $\{N(CH_3)_4\}_2ZnCl_4$ (TMA-$ZnCl_4$). The effect is reversible: when σ is applied the spontaneous polarization P_s and the temperature range in which it exists rapidly diminish and vanish at some critical value $\sigma_{\rm cr}$ and when σ is removed the initial values are restored.

The rate of decrease of P_s as the stress σ is increased is high. The coefficient $D = \Delta P_s/\sigma \sim 10^{-6}$ ESU, which is close to the maximum values of the piezoelectric coefficients d of many ferroelectrics.[2] In this case, however, P_s vanishes under pressure not because of the standard piezoelectric effect but rather, as data from preliminary investigations in Ref. 1 show, because the state of the crystal is close to the critical point on the σ–T phase diagram.

We recently observed an analogous effect in polar phases of TMA-$CoCl_4$ and thiourea, $SC(NH_2)_2$, crystals which are intermediate with respect to temperature, and which, like TMA-$ZnCl_4$, have a sequence of several phase transitions.

The vanishing of one of the phases (or the appearance of a new phase) brought about by a weak external perturbation is apparently a characteristic feature of a large group of crystals whose lattice easily becomes unstable to different distortions, as a result of which many structural phase transitions occur. Examples of such crystals, for which, incidentally, "hydrostatic pressure p–temperature" phase diagrams illustrating the radical changes produced in the temperature sequence of the phases by the action of pressure p were obtained earlier, can be found in Refs. 3 and 4. It is important to note, however, that the critical values of the uniaxial stresses $\sigma_{\rm cr}$ at which the polar phase vanishes, as our data show, are 30 to 40 times lower than the critical values $p_{\rm cr}$ of the pressure. This difference between $\sigma_{\rm cr}$ and $p_{\rm cr}$ indicates that the effect is highly anisotropic.

In this paper the suppression of ferroelectricity by uniaxial mechanical stresses is investigated in detail, as is the anisotropy of the effect. New experimental proof of the fact that the spontaneous polarization vanishes as a result of a transition through the critical point on the "stress–temperature" phase diagrams is presented. The investigation is performed with TMA-$ZnCl_4$ crystals as an example.

EXPERIMENTAL PROCEDURE

At atmospheric pressure the TMA-$ZnCl_4$ crystal has five structural phase transitions: $Pmcn(D_{2h}^{16}) \to$ incommensurate phase $\to P2_1cn(C_{2v}^9) \to P112_1/n(C_{2h}^5) \to P12_1/c1(C_{2v}^5) \to P2_12_12_1(D_2^4)$ at 20, 6.6, 3.3, -92, and -112 °C, respectively. The incommensurate phase is bordered on the temperature axis by the one C_{2v}^9 polar phase on the right and the C_{2h}^5 ferroelastic phase on the left. The spontaneous polarization is directed along the crystallographic axis a and the cell parameter along the c axis is five times larger than in the starting high-temperature phase D_{2h}^{16}. The polar phase vanishes under hydrostatic pressure $p \geqslant 1000$ bar.[3–5]

The investigations were performed on single crystals grown from solution. The samples were prepared in the form of rectangular bars with edges parallel to the $a(x)$, $b(y)$, and $c(z)$ axes; the dimensions of the bars were $2.5\times2.8\times4.7$ mm. The orientation of the samples was monitored on a Dron-2 x-ray diffractometer.

The ferroelectric properties of the crystal were recorded based on measurements of the anomalous parameters: the dielectric constant ε_{xx}, the polarization P_x in an electric field E_x, and the components of the macroscopic quadrupole moment q_{xz}. The measurements were performed in the temperature range of the polar phase for different values of the unaxial compressional stresses σ_{xx}, σ_{yy}, and σ_{zz} directed along three crystallographic axes. The dielectric constant ε_{xx} was measured at a frequency 1.6 kHz in a field $E_x = 10$ V/cm with the help of a standard capacitance bridge, and P_x was measured at a frequency of 50 Hz in a strong field $E_x \approx 1.5$ kV/cm. The spontaneous polarization P_s was calculated from the dielectric hysteresis loops of the dependence of P_x on E_x by the standard method.[2]

 0038-5646/90/111013-06$03.00

In any multidomain ferroelectric the displacement of the domain walls in an electric field makes an additional contribution to ε_{xx}. If the mobility of the walls is high, then the contribution to ε_{xx} is large and can significantly distort the form of the temperature anomalies in the dielectric constant ε_{xx} of a single-domain crystal. If, on the other hand, the mobility is low, then the additional contribution to ε_{xx} is small, but in this case even in a strong alternating electric field incomplete single-domain formation may occur and, as a consequence, the measured values of P_s can be too low.[2] In this connection the estimate of P_s was also monitored by dielectric hysteresis loops obtained by an electrometric method in a strong quasistatic field (with a period of ≈ 1 h), and when ε_{xx} was measured we used an additional polarizing constant electric field, exceeding the coercive field E_c which, according to the electrometric measurements, makes the crystal virtually a single-domain crystal.

It is especially important to take the precautions noted above in order to draw correct conclusions regarding the reasons for the gigantic changes observed in Ref. 1 in ε_{xx} and P_s when determining experimentally values of ε_{xx} and P_x which are close to the true values for a single-domain crystal, since they can decrease, generally speaking, not only because the ferroelectricity vanishes but also because of the anomalously large decrease in the mobility of domain walls in the field E_x (increase in the elastance) under uniaxial pressure.

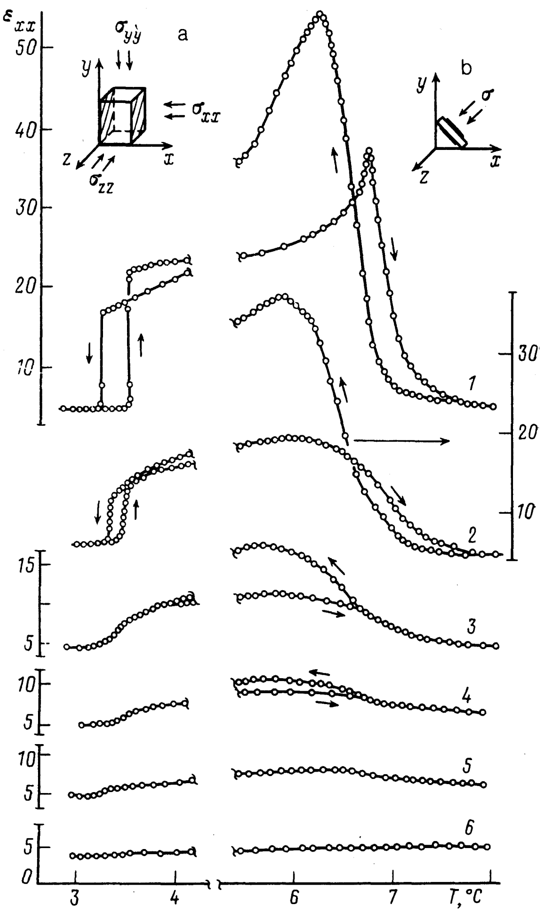

FIG. 1. The temperature dependence of the dielectric constant ε_{xx} of the crystal TMA-$ZnCl_4$ in the region of the polar phase for different uniaxial compressive stresses σ_{zz}:σ_{zz} = 0 (1), 10 (2), 20 (3), 28 (4), 36 (5), and 45 (6) kgf/cm^2. The orientation of the samples of the crystal and the direction of compression σ are shown in the insets; the faces that are coated with the electrodes are hatched (a) or thicker (b).

To investigate the suppression of the spontaneous polarization P_s by the stresses σ_{yy} and σ_{zz} we employed a geometry of the experiment in which the electrodes covered sample faces that are perpendicular to the faces through which the stress was transmitted (Fig. 1, inset a). A different geometry of the experiment was also used to check the possible effect of nonuniform strains on the observed phenomenon; such strains can develop in this case in the layers near the electrodes when the sample is compressed (edge effects), resulting in the destruction of the structure of the layers and, possibly, reducing the measured values of P_x and ε_{xx}. In this case a $3\times3\times1$ mm plate was used. The large faces, which made an angle of 45° with the x and y (or z) axes, were coated with silver electrodes, and the uniaxial pressure σ was transmitted through the same faces (Fig. 1, inset b). In this case the components $\sigma_{xx} = \sigma/2$ and $\sigma_{yy} = \sigma/2$ (or $\sigma_{zz} = \sigma/2$) acted simultaneously on the sample and the spontaneous polarization $P = 2^{-1/2}P_s$ was measured, and there were virtually no nonuniform strains in the layers near the electrodes. The data on the effect of σ_{yy} and σ_{zz} on P_s (the component σ_{xx} is inactive, see below) which were obtained on such plates were in satisfactory quantitative agreement with the data for bars, i.e., the edge effects which can be produced by the nonuniform strains when the bars are employed, have virtually no effect on the measurements.

The macroscopic quadrupole moment q_{ij} can give information about the change in the parameters of the domain structure accompanying compression of a multidomain crystal. The 180-degree domain structure makes the main contribution, proportional to P_s and to the width L of the domain, to one of the components of the tensor q_{ij}.[6] For TMA-$ZnCl_4$ this anomalous component is

$$q_{xz} = {}^1/_2 P_s L, \tag{1}$$

where $\mathbf{x} \| \mathbf{P}_s$ and the normal to the domain walls is oriented along the z axis.

The quadrupole moment q_{xz} can be estimated experimentally from data on the bound electric charge[7] arising on the four edges, parallel to the y axis, of a rectangular crystal sample. The density τ of the charge on the edges is equal to

$$\tau = 2q_{xz}. \tag{2}$$

From Eqs. (1) and (2) we obtain the following simple equation for the width of the domains:

$$L = \tau/P_s, \tag{3}$$

i.e., the change in L accompanying a change in the external conditions can be judged from measurements of P_s and τ. Of course, this estimate gives the average value of L over the volume of the crystal.

All electric characteristics were measured in a nitrogen cryostat. Silver paste was used to deposit electrodes on the samples: to measure ε_{xx} and P_x the electrodes were deposited on the faces of the sample perpendicular to the x axis and to measure the charge τ they were deposited on the edges parallel to the y axis.

RESULTS AND DISCUSSION

The electric properties of the crystal were measured on several samples having different spontaneous polarization

P_s and dieletric constant ε_{xx}. The values of P_s and ε_{xx}, obtained (in the absence of uniaxial pressures) by different authors (see, for example, Refs. 5 and 8), differ by approximately a factor of two. This spread in the values of P_s and ε_{xx} is apparently characteristic for all crystals in this group.

The main results of the measurements are as follows.

1. Anomalously large values of ε_{xx} and P_s are observed when the crystal is compressed by uniaxial stresses σ_{zz} and σ_{yy}. The stress σ_{xx} ($x \| P_s$) results only in a small reduction of ε_{xx} and P_s; this reduction is apparently connected with the usual piezoelectric effect. The piezoelectric coefficient $d_{111} = \Delta P_s/\sigma_{xx}$ is equal to $3\cdot 10^{-8}$ ESU.

2. When the crystal is compressed by the stresses σ_{zz} and σ_{yy} the values of ε_{xx} and P_s and their temperature hysteresis as well as the temperature range of the polar phase decrease. Figures 1 and 2 show the temperature dependences of ε_{xx} and P_s for different values of the stresses σ_{zz}, obtained when the temperature is both decreased and increased. One can see that in the region of the points of the phase transitions the temperature hystereses of ε_{xx} and P_s completely vanish for $\sigma_{zz} \geqslant 20$ kgf/cm^2, and the hysteresis of ε_{xx} at the center of the polar phase vanishes only at $\sigma_{zz} \geqslant 30$ kgf/cm^2.

3. The character of the change brought about in the hysteresis loop by the "active" stresses σ_{zz} and σ_{yy}—the decreases in the amplitude of the change in the polarization P_x and the coercive field E_c (Fig. 2, inset)—indicates that when the crystal is compressed it is the spontaneous polarization P_s that decreases, not the mobility of the domain walls in an electric field E_x and their contribution to P_x. In the opposite case the stresses σ_{zz} and σ_{yy} should increase E_c. Data from control measurements of the dependence of P_x on E_x in a slowly varying (quasistatic) field confirm this conclusion: as σ_{zz} and σ_{yy} increase the hysteresis loops $P_x(E_x)$ change just like the loop in Fig. 2, obtained in a 50 Hz alternating field. The values of P_s calculated from the loops, measured in alternating and quasistatic regimes, are the same to within 10%.

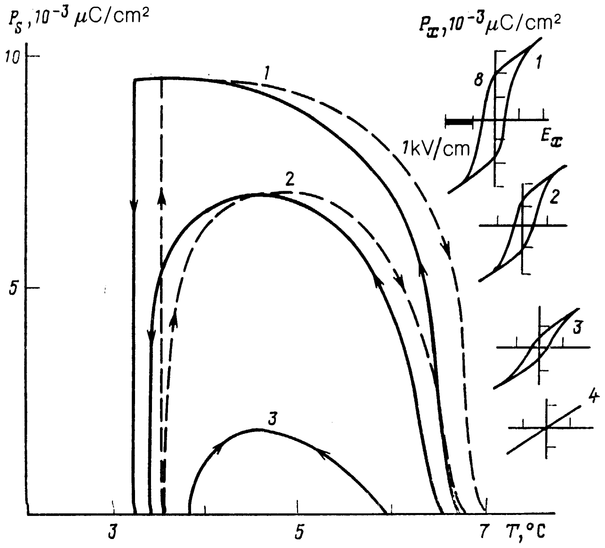

FIG. 2. The temperature dependence of the spontaneous polarization P_s of the TMA-ZnCl$_4$ crystal for different uniaxial compressive stresses σ_{zz}. Dielectric hysteresis loops $P_x(E_x)$ are shown in the insets at $T = 5$ °C: $\sigma_{zz} = 1$ (1), 10 (2), 20 (3), and 28 (4) kgf/cm^2.

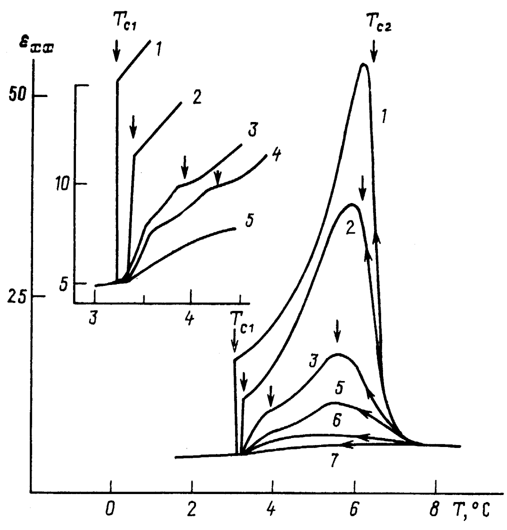

FIG. 3. The temperature dependence ε_{xx} obtained while cooling the TMA-ZnCl$_4$ crystal: $\sigma_{zz} = 0$ (1), 10 (2), 20 (3), 24 (4), 28 (5), 35 (6), and 45 (7) kgf/cm^2. The arrows mark the temperatures of the structural transitions out of the polar phase into phases in which $P_s = 0$.

4. The temperature limits of the polar phase, where P_s vanishes, are marked by the anomalies in ε_{xx}. In Figs. 3 and 4, where the temperature dependences of ε_{xx}, measured with decreasing temperature, are presented, these limits are marked by arrows. One can see that at $\sigma_{zz} \neq 0$ inflection points appear on the temperature dependences ε_{xx} at the point T_{c1} of the low-temperature transition from the polar phase (Fig. 3), and the maxima of ε_{xx} lie close to the points T_{c2} of the high-temperature transition from the polar phase into the incommensurate phase.

5. Oscillations of the domain walls make the dominant contribution to ε_{xx}. This contribution also causes the maximum of ε_{xx} to not coincide with the point of the phase transition T_{c2}. For this reason a constant electric field E_x, which causes single-domain formation in the crystal, introduces significant changes in the temperature dependence of ε_{xx}: the values of ε_{xx} in the region of the polar phase decrease; temperature hysteresis, which is absent for some $\sigma_{zz} \neq 0$ and $E_x = 0$, appears again at the point of the phase transition T_{c1} (Fig. 4a); and, the temperature of the maximum of ε_{xx} falls exactly on the point of the phase transition T_{c2} (Fig. 4b).

6. The stress σ_{zz} (compression along the z axis—the direction of the structural modulation of the crystal) suppresses ferroelectricity more effectively. Figure 5 shows the temperature dependences of P_s for the stresses σ_{zz} and σ_{yy}, measured with the crystal being cooled, while Fig. 6 shows the dependences of P_s and ε_{xx} on σ_{zz}, σ_{yy}, and σ_{xx} at a constant temperature and approximately at the center of the polar phase. All dependences were obtained for the same sample of the crystal. We note that the value of P_s for this sample is almost two times lower than for the sample used for the measurements shown in Figs. 1–4.

7. The measurements of the anomalous component of the macroscopic quadrupole moment $\tau = 2q_{xz}$ of the crystal under the action of the stress σ_{yy} are shown in Fig. 5 (dot-dashed lines). One can see that first, within the polar phase the changes in P_s and τ with the temperature and pressure σ_{yy} are virtually identical and, second, outside the polar

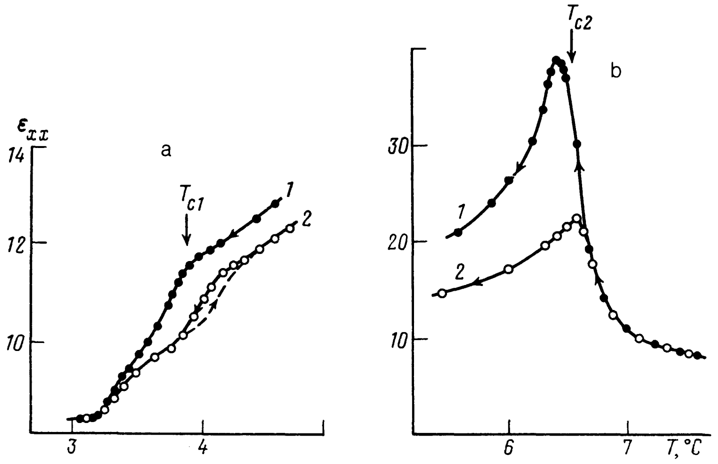

FIG. 4. The temperature dependence of ε_{xx} of a TMA-$ZnCl_4$ crystal, polarized with a constant electric field E_x, near the low-temperature (a) and high-temperature (b) structural transitions out of the polar phase: $E_x = 0$ (1) and 0.5 (2) kV/cm; $\sigma_{zz} = 15$ kgf/cm^2 (a) and $\sigma_{zz} = 0$ (b). The arrows mark the temperatures of the structural transitions out of the polar phase into phases in which $P_s = 0$.

phase, when $P_s = 0$, τ is also different from zero and decreases slowly away from the phase-transition points T_{c1} and T_{c2}. The first fact indicates that compression of a polydomain crystal by the stress σ_{yy} changes only P_s, while the width of the domains L remains practically constant. An estimate using the formula (3) gives $L = (16 \pm 2) \cdot 10^{-4}$ cm, which agrees with the direct observations[9] under an electron microscope in the absence of pressure, where $L = (5\text{–}20) \cdot 10^{-4}$ cm. The second fact could be a consequence of the fact that spatially modulated polarization exists on both sides of the polar phase on the temperature scale; this is what makes the anomalously high contribution to q_{xz} (see Ref. 7), i.e., the phases which adjoin the polar phase at $\sigma_{yy} \neq 0$ are incommensurate. In addition, whereas for $T > T_{c2}$ the incommensurate superstructure also exists in the absence of pressure, as proved by the direct method of neutron scattering,[10] for $T_3 < T < T_{c1}$ (T_3 is the point of the transition into the ferroelastic phase) an incommensurate superstructure apparently results only from compression of the crystal. The last conclusion is consistent with the assumption, made in Ref. 5, that hydrostatic pressure induces in TMA-$ZnCl_4$ a second incommensurate phase. It must be added that the decrease in the spontaneous quantity q_{xz} upon compression of the crystal can be regarded as another indication of the fact that under uniaxial pressures it is P_s that decreases and not the mobility of the domain walls in the field E_x. Otherwise the decrease observed in P_x as σ_{yy} increases would not be accompanied by a decrease in q_{xz}.

8. The σ_{zz}–T and σ_{yy}–T diagrams were constructed from measurements of ε_{xx} and P_s for the TMA-$ZnCl_4$ crystal (Fig. 7). One can see that uniaxial pressures, just like the hydrostatic pressure p in Ref. 5, at first induce a new phase II′, which wedges in between the polar phase III and the ferroelastic phase IV, and then eliminate the polar phase III. The phase III vanishes at a critical stress $(\sigma_{yy})_{cr} \approx 30$ kgf/cm^2 or $(\sigma_{zz})_{cr} \approx 25$ kgf/cm^2.

Figure 7 shows only the part of the diagram with lines of phase transitions occurring as the temperature decreases. On the complete diagram, which also includes phase transitions occurring as the temperature increases, there appear additional lines displaced from those shown in the figure by the amount of temperature hysteresis (see Figs. 1 and 2). The temperature hystereses vanish approximately for $\sigma \geqslant 20$ kgf/cm^2 and every two lines corresponding to an increase and decrease of the temperature of the crystal merge into one line.

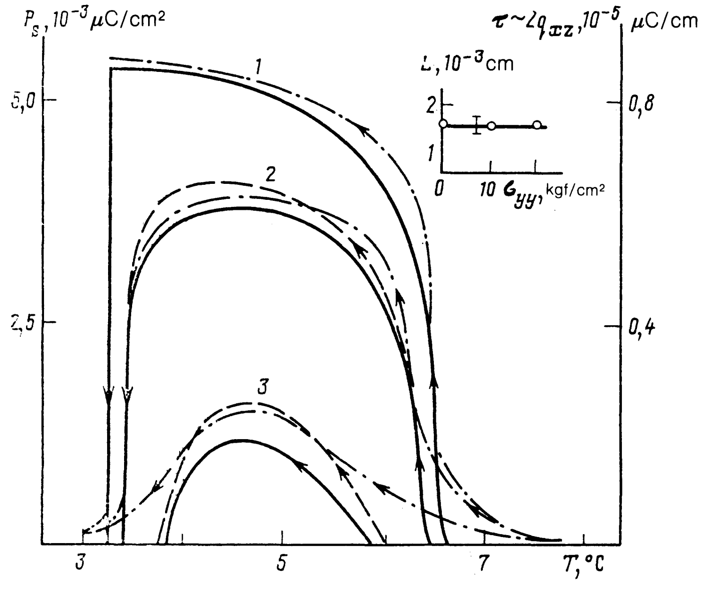

FIG. 5. The temperature dependences of the spontaneous polarization P_s with different stresses σ_{zz} (solid lines), σ_{yy} (dashed lines), and the temperature dependence of the macroscopic quadrupole moment $\tau = 2q_{xz}$ for different values of σ_{yy} (dot-dashed lines) for a TMA-$ZnCl_4$ crystal: $\sigma = 0$ (1), 10 (2), and 20 (3) kgf/cm^2. The dependence of the width of the domains L on σ_{yy} at $T = 5$ °C is shown in the inset.

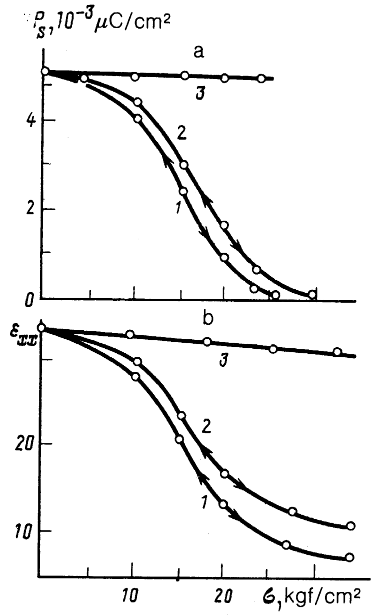

FIG. 6. The spontaneous polarization P_s (a) and the dielectric constant ε_{xx} (b) versus the uniaxial stresses σ_{zz} (1), σ_{yy} (2), and σ_{xx} (3) for a TMA-$ZnCl_4$ crystal at $T = 5$ °C.

Preliminary measurements showed that in a TMA-$CoCl_4$ crystal the polar phase III also vanishes at the lower value $\sigma_{zz} \approx 15$ kgf/cm^2. We note that the indication in Ref. 1 of another (fourth) phase boundary (between the phases II and III), which could indicate a second additional phase induced by the pressure σ_{zz}, is incorrect.

The phenomenological description of the set of successive structural phase transitions, occurring through incommensurate phases, in crystals of the group TMA-MeX_4 is given in Refs. 11 and 12. Invariant terms in the series expansion in powers of the two-component transition parameter η, ξ (in Ref. 11 up to tenth order inclusively), which are isotropic and anisotropic in the (η, ξ) space, are taken into account in the free energy. The temperature sequence, the number of transitions, and the temperature intervals of different phases depend strongly on the values of the coefficients in the free energy. By choosing different values of the coefficients, which are functions of the hydrostatic pressure p, of the composition of the crystal x, and of the temperature T, it is possible to construct complicated phase diagrams[11,12]

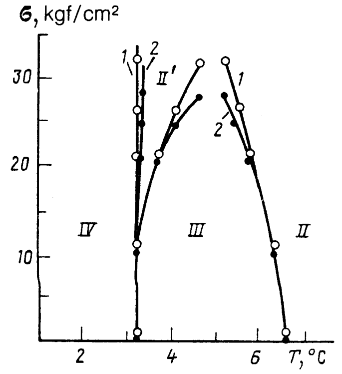

FIG. 7. The σ–T phase diagrams of a TMA-$ZnCl_4$ crystal: $\sigma = \sigma_{yy}$ (1) and $\sigma = \sigma_{zz}$ (2).

similar to the experimental p, T, and x diagrams in Refs. 3 and 4 for TMA-MeX_4 crystals.

The uniaxial stresses σ_{xx}, σ_{yy}, and σ_{zz} do not change the symmetry of the crystal, i.e., they are invariant under symmetry transformations of the starting phase D_{2h}^{16} for TMA-$ZnCl_4$. For this reason, the coefficients in the free energy can depend on any of these uniaxial stresses, just as on the hydrostatic pressure $p = \sigma_{xx} + \sigma_{yy} + \sigma_{zz}$, and the σ, T, and x phase diagrams must be similar to the p, T, and x diagram. This can be verified by comparing the diagram in Fig. 7 with the data from Refs. 3 and 4.

For values of σ_{yy} and σ_{zz} close to the critical values $(\sigma_{yy})_{cr}$ and $(\sigma_{zz})_{cr}$ the dielectric properties of the crystal do not have distinct temperature anomalies which could be reliably identified with phase-transition points, and for this reason the diagrams in Fig. 7 were not extended. The same problem also occurs when the p–T diagrams for crystals of the group TMA-MeX_4 near the critical points are determined from the dielectric measurements.[4] For TMA-$ZnCl_4$ crystals the most probable are two variants of σ–T diagrams. In the first variant, the two lines bounding the polar phase III converge and terminate at one point. The region II′ in Fig. 7 is then the incommensurate phase II. In the second variant two lines merge at a point into one line, the transition through which (from phase II′ into II) is accompanied by a jump-like change in the period of the incommensurate superstructure (triple point). We note that such a phase transition, accompanied by a change in the period of the superstructure, is realized in deuterated TMA-$ZnCl_4$ crystals, where no polar phase is observed when external pressure is not applied.[3,4]

CONCLUSIONS

Measurements of different dielectric properties of TMA-$ZnCl_4$ and some other crystals in the region of structural transitions into the polar phase show that the uniaxial compressive stresses σ_{zz} and σ_{yy} reduce the spontaneous polarization and the temperature range of spontaneous polarization and then they completely eliminate the polar phase. When the stress σ_{xx}, directed along the spontaneous polarization, is applied the effect does not occur. The boundaries of the polar phase on the σ_{zz}–T and σ_{yy}–T diagrams are determined from the points at which the spontaneous polarization vanishes and from the anomalies of the dielectric constant ε_{xx}. Thus the effective suppression of ferroelectricity by uniaxial stresses is a consequence of the proximity of the state of the crystal to critical points in the σ–T phase diagrams.

The critical values σ_{cr} are small compared with the critical hydrostatic pressure p_{cr} and, apparently, they are all the smaller the lower the value of p_{cr}. Thus, for example, for TMA-$ZnCl_4$, and TMA-$CoCl_4$ these values are respectively, $p_{cr} \approx 1000$ kgf/cm^2 (Ref. 5), $(\sigma_{zz})_{cr} \approx 25$ kgf/cm^2 and $p_{cr} \approx 500$ kgf/cm^2 (Ref. 5), $(\sigma_{zz})_{cr} \approx 15$ kgf/cm^2.

It is obvious that since $p_{cr} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})_{cr}$ is much greater than $(\sigma_{yy})_{cr}$ and $(\sigma_{zz})_{cr}$, the result of the simultaneous action of three components of the tensor σ_{ij} on the crystal is not an additive quantity, i.e., the suppression of ferroelectricity by mechanical stresses is significantly nonlinear. It is possible that the decisive factor for the manifestation of the effect is the fact that the polar and incommensurate phases, whose free energies are close,[11,12] adjoin one another and even low stresses σ result in a substantial displacement of their phase boundaries.

Existing data on the p–T diagrams for crystals with several phase transitions (see, for example, Refs. 3 and 4) suggest that, first of all, σ_{cr} can be even lower [for example, in TMA-$CuBr_4$, where $p_{cr} \approx 200$ kgf/cm^2 (Ref. 4)], and, second, there should exist a more complicated effect, when the uniaxial stress σ at first induces a ferroelectric phase and then suppresses it [for example, in TMA-$FeCl_4$ and TMA-$MnCl_4$ (Ref. 4)].

In the future it would be interesting to investigate the effect of uniaxial pressures on other physical properties of crystals and, primarily, their spectral and structural characteristics. This will make it possible to give a more definite answer to the questions of how the structure of the crystal changes under compression in different directions, which structural elements are responsible for the observed suppression of ferroelectricity, and what is the form of the phase diagrams at pressures close to the critical values.

We are grateful to Sh. Savada and I. I. Polovinko for providing the crystals used for the investigations and S. A. Minyukov and A. P. Levanyuk for a discussion of the results of this work.

[1] S. N. Kallaev, Pis'ma Zh. Eksp. Teor. Fiz. **50**, 98 (1989) [JETP Lett. **50**, 113 (1989)].
[2] M. Lines and A. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Clarendon Press, Oxford, 1977.
[3] J. D. Axe, M. Iizumi, and G. Shirane in *Incommensurate Phases in Dielectrics. 2. Materials*, edited by R. Blinc and A. P. Levanyuk, North-Holland, Amsterdam (1986), pp. 1–48.
[4] K. Gesi, Ferroelectrics **66**, 269 (1986).
[5] H. Shimizu *et al.*, J. Phys. Soc. Jpn. **49**, 223 (1980).
[6] V. V. Gladkii *et al.*, Ferroelectrics Lett. **2**, 177 (1984).
[7] V. V. Gladkii, Phase Transitions, Sec. A **6**, 273 (1986).
[8] B. A. Strukov and E. P. Kurulenko, Vestn. MGU. Ser. Fiz., astron. **29**, 58 (1988).
[9] R. Le Bihan *et al.*, Ferroelectrics Lett. **9**, 151 (1989).
[10] K. Gesi and M. Iizumi, J. Phys. Soc. Jpn. Lett. **48**, 337 (1980).
[11] H. Mashiyama, J. Phys. Soc. Jpn. **49**, 2270 (1980).
[12] D. G. Sannikov, Zh. Eksp. Teor. Fiz. **96**, 2198 (1989) [Sov. Phys. JETP **69**, 1244 (1989)].

Translated by M. E. Alferieff