Some features of the electric properties of the incommensurate phase of a ferroelectric

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It is shown that when a bounded ferroelectric crystal undergoes a transition into an incommensurate phase its macroscopic quadrupole moment is as typical a distinguishing characteristic of the electric structure of the phase as is the dipole moment in a ferroelectric phase transition. In the temperature range where an incommensurate phase exists in an ammonium fluoroberyllate crystal, spontaneous components of the quadrupole moment and the linear dependences of these components on the conjugate external action (the uniaxial mechanical stress) were observed and measured. The measurement data were used to determine the direction of the structure modulation of the incommensurate phase of the crystal, and to reveal certain thermodynamic nonpolar–incommensurate–polar phase transition features that follow from the phenomenological theory.

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INTRODUCTION

In some crystals there exists in a definite temperature interval a phase having a superstructure whose period is not an integer multiple of that of the main structure (incommensurate phase). In ferroelectrics such a phase occurs as a rule at a temperature intermediate between the nonpolar and polar commensurate phases, and according to the predictions of thermodynamic theory it should have a spatially modulated polarization.[1]

Phase transitions into the incommensurate phase of a semiconductor are accompanied by anomalies of various thermodynamic quantities—the dielectric constant, the coefficients of thermal expansion, the heat capacity, and others. These anomalies, however, are usually weakly pronounced and are not characteristic features of these transitions, i.e., their form cannot be used to identify unequivocally the phase into which the transition leads. We have recently observed[2] that in the incommensurate phase of a ferroelectric, in contrast to the ordinary commensurate phases, there appears an anomalously large spontaneous macroscopic quadrupole moment that corresponds to a spatially modulated polarization. In this paper we investigate in detail the electric properties due to the changes of the various components of the quadrupole moment in response to external action in the region of the nonpolar—incommensurate—polar phase transitions, using as an example the ammonium fluoroberyllate (AFB) crystal $(NH_4)_2BeF_4$.

1. INCOMMENSURATE PHASE OF FERROELECTRIC

The sequence of nonpolar—incommensurate—polar phase transitions can be described on the basis of the Landau theory. The thermodynamic potential is expressed as a function of the components of the order parameter that determines the distortion of the symmetry of the polar phase relative to the nonpolar one, with account taken of the Lifshitz gauge invariant.[1] In AFB crystals these phase transitions take place at temperatures $T_i = 181$ K and $T_C = 175$ K. The high temperature phase is polar (C_{2v}^{17}) with double the period of the translation along the X_1 axis and with spontaneous polarization along X_2.[3] According to neutron-scattering data,[4] the phase of intermediate temperature is the incommensurate one.

We present some of the results, which will be needed later, of the phenomenological analysis[1] of the phase transitions in the AFB crystal. The density of the thermodynamic potential is given by

$$\psi_0=\frac{\alpha}{2}(\eta^2+\xi^2)+\frac{\beta_1}{4}(\eta^2+\xi^2)^2+\frac{\beta_2}{4}[(\eta^2-\xi^2]^2-2(\eta\xi)^2]+2b\eta\xi P_2$$
$$+\gamma\left(\frac{\partial\eta}{\partial x_1}\xi-\frac{\partial\xi}{\partial x_1}\eta\right)+\frac{\delta}{2}\left[\left(\frac{\partial\eta}{\partial x_1}\right)^2+\left(\frac{\partial\xi}{\partial x_1}\right)^2\right], \qquad (1)$$

where η and ξ are the components of the order parameter, P_2 is the component of the polarization vector along the X_2 axis, and only the coefficient $\alpha = \alpha\ (T-\Theta)$ depends on the temperature T. In the initial polar phase $\eta=\xi=0$. In the polar phase there appear the spontaneous quantities η and ξ, which are homogeneous over the volume, while in the incommensurate phase there appear the spontaneous inhomogeneous quantities η_0 and ξ_0. Near the temperature T_i of the transition from the incommensurate into the polar phase, their equilibrium values are

$$\eta_0=\rho_0\cos(2\pi x_1/L+\varphi),\quad \xi_0=\rho_0\sin(2\pi x_1/L+\varphi). \qquad (2)$$

Here

$$\rho_0^2=\alpha_0(T_i-T)/\beta_1,\quad L=2\pi\delta/|\gamma|,\quad T_i=\Theta+\gamma^2/\alpha_0\delta,$$

φ is an arbitrary quantity.

The components of the polarization vector P take, accurate to second order of smallness in η and ξ, the form

$$P_1=0,\quad P_2=-2b\eta\xi/\varkappa,\quad P_3=0. \qquad (3)$$

as a result, not only η and ξ, but also the component P_2 are spatially modulated in the incommensurate phase of the crystal. Near T_i we have according to (2) and (3)

$$P_1=0,\quad P_2=-\frac{b}{\varkappa}\rho_0^2\sin\left(\frac{4\pi}{L}x_1+\varphi\right),\quad P_3=0. \qquad (4)$$

On going away from T_i and approaching the tempera-

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ture T_C of the phase transition into the polar phase, the modulation period L increases, and higher harmonics appear in the solution (2) and (4), i.e., the components of P take the form

$$P_1=0,\quad P_2=\sum_{n=0}^{\infty}p_n\sin\left[2(2n+1)\frac{2\pi}{L}x_1+\varphi\right],\quad P_3=0 \tag{5}$$

and the superstructure of the crystal becomes more and more reminiscent of the domain structure of the ferroelectric phase.

It is important that in the incommensurate phase the spontaneous polarization is zero but, as will be shown below, the spontaneous macroscopic quadrupole moment of the crystal sample can be different from zero.

2. MACROSCOPIC QUADRUPOLE MOMENT OF INCOMMENSURATE PHASE OF A FERROELECTRIC

The macroscopic quadrupole moment, described by a second-rank symmetrical tensor, can serve as a characteristic of the distribution of the electric charge in the crystal. The crystal symmetry imposes certain limitations on the form of the matrix of this tensor. If the symmetry is lowered as a result of the structural phase transition, then new components of the quadrupole moment, corresponding to the point group of the asymmetrical phase, can be observed.^{5}

According to Ref. 6, the symmetry of a bounded crystal sample and of its macroscopic properties can be lower than the symmetry of the crystal regarded as an infinite medium. In other words, a sample oriented in definite fashion relative to the crystallographic coordinate system can have besides the allowed tensor property components, also some that are forbidden by the point group of the crystal. In particular, in contrast to the point group, the symmetry group of the system need not include those symmetry axes and planes which are screw axes and glancing-reflection planes in the space group. Using this rule, it is easy to verify that out of all the elements of space group D_{2h}^{18} that characterizes the symmetry of the high-temperature and incommensurate phases, there remain for the AFB crystal only a rotary symmetry axis parallel to the X_3 axis, the plane of specular reflection perpendicular to it, and the inversion center, while the symmetry group C_{2h} of the sample will be a subgroup of the crystal point group D_{2h}. As a result, the sample should have, besides the diagonal tensor components q_{ij} that are allowed by the point group, also a nonzero off-diagonal component $q_{12}=q_{21}$, which is forbidden by the point group.

We shall show now that in the incommensurate phase the spontaneous component q_{12} of the AFB crystal can have an increment q_{12}^0 connected with the appearance of spatially modulated polarization in this component (see Sec. 1). We assume for simplicity that the sample spans an integer number of supercells with period L, i.e., an integer number of modulated-polarization periods. Assuming for the density q_{ij} of the quadrupole moment of the homogeneous sample the usual expression

$$q_{ij}=\frac{1}{2v}\int\rho x_i x_j\,dv=\frac{1}{2v}\int(P_i x_j+P_j x_i)\,dv \tag{6}$$

(here ρ is the density of the electric charge) and assuming that in the incommensurate phase the polarization components are determined by formulas (5), we obtain after integrating in (6) over the sample volume

$$q_{12}{}^0=\frac{1}{8\pi}\sum_{n=0}^{\infty}\frac{p_n}{2n+1}L\cos\varphi,\quad q_{13}{}^0=q_{23}{}^0=0. \tag{7}$$

Near the temperature T_i, where the solutions (4) are valid, expression (7) with account taken of the temperature dependence of ρ_0^2, takes the form

$$q_{12}{}^0=\frac{b\alpha_0}{8\pi\varkappa\beta_i}(T_i-T)L\cos\varphi,\quad q_{13}{}^0=q_{23}{}^0=0. \tag{8}$$

It is seen from (7) and (8) that in a bounded crystal there can appear a tensor component q_{12}^0 corresponding to the spatially modulated polarization. The value of q_{12}^0 depends on the phase φ in the sine and cosine functions of (2), (4), and (5), i.e., on the values of the components η_0 and ξ_0 on the crystal boundaries. The absolute value of q_{12}^0 is maximal at $\varphi=n\pi$ $(n=0,1,\dots)$ when $\xi_0=0$ on the boundaries.

The thermodynamic potential of a crystal sample whose density is given by (1) does not depend on φ, therefore φ can generally speaking assume arbitrary values, and the component q_{12}^0 can be arbitrary in the interval determined by $\cos\varphi$ in formulas (7) and (8). It follows therefore that the sample can contain macroscopic regions with different values of φ, and hence with different q_{12}^0. Such regions can be formed because the values of φ and q_{12}^0 become fixed at different crystal-lattice imperfections.

If the crystal in the incommensurate phase actually consists of regions with different values of q_{12}^0, then one can expect the external action conjugate to q_{12} to strive to cause φ in all such regions to take on the same value, corresponding to the minimum of the crystal energy. It is also possible that a state with φ constant in the entire sample volume will be preserved long enough also after the external action is stopped. Then q_{12} as a function of this action, as for example the dependence of the polarization on the electric field in the ferroelectric phase, should exhibit hysteresis.

The action conjugate to q_{ij} can be either the gradient of the inhomogeneous electric field E, since the expression for the field energy includes the term

$$W=\int q_{ij}\nabla_i E_j\,dv,$$

or else a uniform mechanical stress σ_{ij} that alters not only the corresponding strain components, but also the corresponding components of the tensor q_{ij}. An isolated crystal sample of any symmetry group should then be subject to the relation

$$\nabla_i E_j=g_{ijkl}\sigma_{kl},$$

which describes the piezoelectric effect connected with the change of the quadrupole moment. In particular, for the component q_{12} the conjugate components should be $\nabla_1 E_2$ and σ_{12}.

In addition to the electric properties listed above, one can expect anomalous temperature dependences of the quantities $dq_{ij}/d(\nabla_i E_j)$ and $dq_{ij}/d\sigma_{ij}$ in the region of the transition into the incommensurate phase. These quantities, just as the dielectric constant in the transition to the polar phase, should characterize the "pliability" of the crystal with respect to external actions that produce in it the same electric charge-density redistribution which sets in spontaneously in the phase transition.

We note one more possible distinguishing feature of the quadrupole moment of the ferroelectric sample in the incommensurate phase. According to formula (6),

$$q\sim|\bar{P}|L\sim\frac{e}{a}\left(\frac{L}{a}\right),$$

where $|\bar{P}|$ is the absolute value of the averaged (over the sample) amplitude of the modulated polarization, e is the electron charge, and a is the unit-cell parameter. In a commensurate phase of the crystal it can be assumed that $L\sim a$, and therefore $q\sim e/a\sim 10^{-2}$ cgs esu. In the incommensurate phase the modulation period $L>a$, and q can increase by a factor equal to the ratio L/a. Thus, that component q_{ij} which should appear spontaneously in the incommensurate phase, can be anomalously larger than any quadrupole-moment component of the commensurate phase.

3. PROCEDURE FOR MEASURING QUADRUPOLE EFFECTS

The electric field corresponding to the macroscopic quadrupole moment q_{ij} is essentially inhomogeneous, and its distribution in space does not depend on the shape and orientation of the crystal. If the sample is homogeneous with a density $q_{ij}=\text{const}$ over its entire volume, and is a right parallelepiped whose edges are parallel to the coordinate axes, then it can be shown[7] that the field corresponding to q_{ij} is equivalent to the field or ordinary electric double layers on the faces of the samples and of the charges on its edges. The density P_i^{sur} of the dipole moment of a double layer on a face perpendicular to the X_i axis is determined by the diagonal component of the tensor q_{ij}, $|P_i^{\text{sur}}|=|q_{ii}|$, and the density of the linear charges τ_i on the edges parallel to the X_i axis is determined by the off-diagonal component, $|\tau_i|=2|q_{jk}|$ $(i\neq j\neq k)$. The directions of P_i^{sur} on opposite faces are opposite, as are the signs of the charges on neighboring edges.

The symmetrical arrangement of the equivalent charges and of the electric double layers on the sample surface makes it possible to separate electric signals due to different components of the tensor q_{ij}. By measuring the charges on the edges we can track only the variation of a definite off-diagonal component, while the potential difference between the points of intersecting faces gives an idea of the variation of the diagonal components. In fact, the potential at the center of a face perpendicular to the X_i axis is equal to the sum of the potentials from the electric double layers on all the faces of the sample[7]:

$$\Phi_i=\sum_{j=1,2,3}|P_j^{\text{sur}}|\Omega_j=\sum_{j=1,2,3}|q_{jj}|\Omega_j,$$

where Ω_j is the solid angle at which the faces perpendicular to the X_j axis are seen from the potential-measurement point. If the sample is a cube (Fig. 1, left) then the potential difference between the centers of any two faces takes the simple form

$$v_{i,j}=\Phi_i-\Phi_j=A(q_{ii}-q_{jj}),\ A\approx 3\pi. \tag{9}$$

For a sample cut at an angle 45° to the axes X_i and X_j (Fig. 1, right) the potential difference is

$$V_{i,j}=\Phi_i'-\Phi_j'=A(q_{ii}'-q_{jj}')=-2Aq_{ij}, \tag{10}$$

where the prime denotes that the corresponding quantity pertains to the new coordinate system X_1', X_2', X_3'.

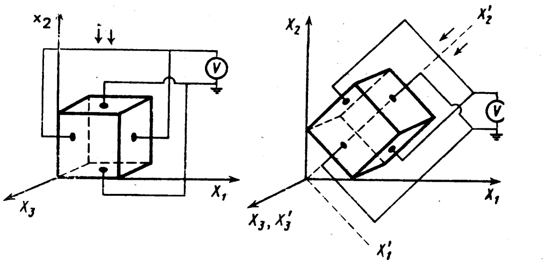

FIG. 1. Shape and orientation of crystal samples, and configuration of the electrodes used to measure the macroscopic quadrupole effects. The arrows show the compression direction.

It is seen from (10) that $V_{i,j}$ for a 45° sample, just as the charge on the edges of the right sample, is connected only with one off-diagonal component q_{ij}. It is easy to show that for rectangular samples with edges of different size the formula (10) will include also other components, but the dependence of V_{ij} on the off-diagonal component q_{ij} is, naturally, preserved.

The examples considered above show that, by choosing different shapes and orientations of the samples, it is possible in principle to identify those tensor components q_{ij} which vary anomalously during the phase transition.

To investigate quadrupole effects in AFB crystals we used samples having the shape and orientation shown in Fig. 1. The samples measured 3×3×5 mm. The external action was uniaxial compression[1)] with stress components σ_{ij} having the same indices as the measured components q_{ij}. The pressure was transmitted by steel pistons placed flush against two sample faces perpendicular to the long edge. The electrode under the piston covered the entire surface of the face. The electric signals were measured between two pairs of electrodes (see Fig. 1). The two electrodes of each pair were located on opposite faces, and were at the same potential by virtue of the symmetry of the quadrupole moment. This arrangement of the electrodes eliminates the influence that can be exerted on measurement of the electric field by the dipole moment that can be induced in the sample upon compression by the strain gradient produced when the sample is accidentally skewed.[8] The electric signals were measured by an electrometric method.

Let us estimate the possible maximum order of magnitude of the electric quadrupole effects. Using the estimates given in Sec. 1 for the quadrupole moment as well as Eq. (9) or (10), we obtain for the ordinary commensurate phase of the crystal $V_c \sim 3\pi q \sim 60$ V, and for the incommensurate phase with $L/a \sim 50$, the same value as in AFB,[4] $V_{in} \sim V_c L/a \sim 3000$ V. The estimates are, of course, approximate, since the sample crystals were assumed to be homogeneous with respect to the density of the quadrupole moment. In fact, the measured electric signals can receive contributions also from other effects connected with the inhomogeneous state of the sample as a result of the presence of boundaries, with defects, and with change of the sample shape upon compression.

4. MEASUREMENT RESULTS

In the investigation of AFB we measured the electric effects of crystals that were mechanically free as well as those deformed by a uniaxial compression stress σ in the region of both phase transitions. The measurements were made on samples with different orientations, so that a picture could be formed of the changes of all the components of the quadrupole-moment tensor, i.e., on the anisotropy of the quadrupole effects in the crystal.

The measurements disclosed the following:

1. In the commensurate phase of mechanically free crystals ($\sigma = 0$) there exist spontaneous potential differences $V_{1,2}^0 \sim q_{12}^0$ and $V_{1,3}^0 \sim q_{13}^0$, which increases when the crystal is cooled and reach anomalously high values (Fig. 2). The plots of $V_{1,2}^0$ and $V_{1,3}^0$ against temperature are similar when the crystal is heated and cooled. No spontaneous potential differences corresponding to other components q_{ij} were observed.

2. The dependences of $V_{1,2}$ on the stress σ_{12} and of $V_{1,3}$ on σ_{13} are linear in the commensurate nonpolar and polar phases, and are nonlinear in the commensurate phase, where they look like hysteresis loops. The residual $V_{1,2}^{res}$ and $V_{1,3}^{res}$ determined by measuring the hysteresis loops as the stress is decreased from the maximum value to zero determine exactly the temperature region in which the incommensurate phase exists (Fig. 3). The residual signals are weaker than the spontaneous ones measured in the absence of the stresses σ. No analogous nonlinear dependences of $V_{2,3} \sim q_{23}$ on σ_{23} were observed, and $V_{2,3}(\sigma_{23})$ is linear in the entire temperature region.

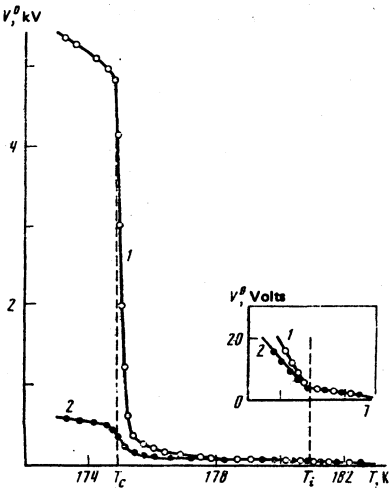

FIG. 2. Spontaneous potential differences V_0 proportional to the components q_{12}^0 and q_{13}^0 of the quadrupole moment of a mechanically free crystal of ammonium fluoroberyllate. 1) $V^0 = V_{1,2}^0(q_{12})$, 2) $V_{1,3}^0(q_{13})$.

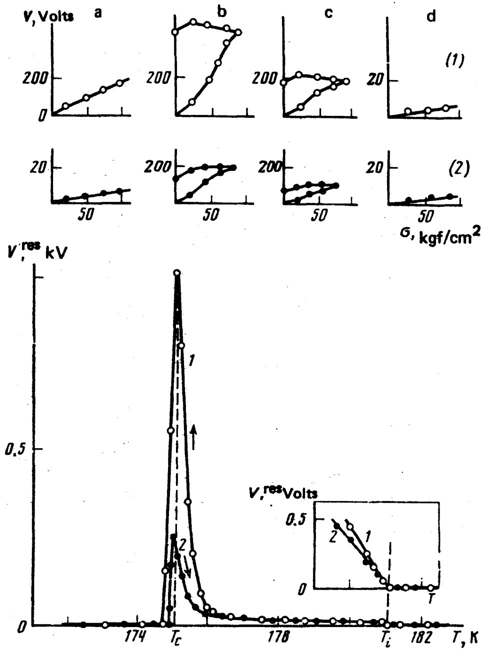

FIG. 3. Dependences of the potential differences $V=-V_{1,2} \sim -q_{12}$ on the shear stress $\sigma=\sigma_{12}$ (1), $V=-V_{1,3}\sim q_{13}$ on $\sigma=\sigma_{13}$ (2), and of the residual $V_{res}=-V_{1,2}^{res}$ (curve 1) and $V_{1,3}^{res}$ (curve 2) on the temperature for the ammonium fluoroberyllate crystal: a) $T=174.1$, b) 175.3, c) 176.2, d) 182.8 K.

It is remarkable that the hysteretic functions $V_{i,j}(\sigma_{ij})$, in contrast to spontaneous signals, can be observed only when the crystal temperature changes, before it becomes stabilized, is effected in a strictly defined direction: the $V_{1,2}(\sigma_{12})$ dependence appears only after cooling, and $V_{1,3}(\sigma_{13})$ only after heating. When the temperature varies in the opposite direction, regardless of the crystal phase prior to the measurements, no hysteresis loop is observed.

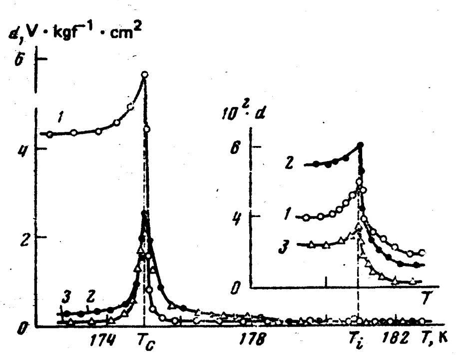

FIG. 4. Pliability coefficients d of ammonium fluoroberyllate crystal: 1) $d=V_{1,2}/\sigma_{12} \sim q_{12}/\sigma_{12}$, 2) $d=-V_{1,3}/\sigma_{13} \sim -q_{13}/\sigma_{13}$, 3) $d=-V_{2,3}/\sigma_{23} \sim q_{23}/\sigma_{23}$.

3. The "pliability" coefficients $V_{1,2}/\sigma_{12}$, $V_{1,3}/\sigma_{13}$, and $V_{2,3}/\sigma_{23}$, in contrast to the dielectric constant[1] have well pronounced λ anomalies in both phase transitions (Fig. 4).

4. The potential difference $v_{i,j}$ due to the change of the diagonal components q_{ij} also has temperature anomalies. The residual $v_{i,j}$, however, are smaller by approximately two orders of magnitude, and the corresponding pliability coefficients are smaller by about one order than the corresponding values that characterize the change of the off-diagonal components q_{12} and q_{13} (Figs. 5 and 6). A hysteresis in $v_{i,j}$ (σ_{ij}) was observed only when the crystal was cooled to a specific temperature.

5. DISCUSSION OF RESULTS

The measurement results confirm in the main the assumptions concerning the character of the change of the macroscopic quadrupole moment in the incommensurate phase of a ferroelectric. Indeed, clearly pronounced electromechanical effects are observed in AFB crystals and are due to the appearance of the following in the incommensurate phase of a spontaneous component q^0_{12} of the quadrupole moment: the spontaneous potential difference $V^0_{1,2}$, a hysteresis dependence of $V_{1,2}$ on the comparision stress σ_{12} and a λ anomaly of the complicance coefficient $V_{1,2}/\sigma_{12}$ at the phase-transition temperatures. The phase transition from the nonpolar into the incommensurate phase is of second order, and near this transition the spontaneous component q^0_{12} depends, in accord with (8), linearly on the temperature (Figs. 2 and 3). The phase transition from the incommensurate into the polar phase is of first order: the residual and spontaneous values of q_{12} change jumpwise at the transition point (Fig. 3). The very appearance of the spontaneous component q^0_{12} indicates the direction of the structural modulation in the incommensurate phase of AFB, which agrees with the direction previously determined from neutron-scattering data.[4]

The observed effects due to the anomalous change of the component q_{12} and their temperature dependences do not contradict the phenomenological theory.[1] In AFB crystals, however, there are also observed effects whose existence does not follow from an analysis of the potential (1) and should be connected with other components of the tensor q_0. Let us examine their possible causes.

The potential difference $V_{1,3} \sim q_{13}$ and the nonlinear $V_{1,3}$ (σ_{13}) dependences indicate that in the incommensurate phase of AFB there should be a second polarization component P_3, modulated in magnitude in the same manner as P_2, along the X_1 axis. This situation is possible if the high-temperature phase of the crystal has a symmetry group for which

$$P_3 \sim (\eta^2 - \xi^2) \sim \rho_0^2 \cos(4\pi x_1/L + \varphi)$$

differs in phase by $\pi/2$ from

$$P_2 \sim \rho_0^2 \sin(4\pi x_1/L + \varphi).$$

Then the spatially modulated polarization should constitute a helix twisted along the X_1 axis, just as, for example in the case considered in Ref. 9. The helix is compressed in the direction of the X_3 axis, since $V_{1,3}(q_{13}) < V_{1,2}(q_{12})$ (Figs. 2 and 3), and consequently $q^0_{13} < q^0_{12}$ and $|\overline{P}_3| < |\overline{P}_2|$. It seems possible on the basis of these data that the AFB crystals have another space group, which is the result of a weak distortion of the D^{18}_{2h} group determined from x-ray analysis data.

The temperature anomalies of the pliability coefficients in the region of the phase transitions (Fig. 4) remind us of the anomalies of the dielectric constant ε in the transition to the polar phase. The difference is that near the polar phase the only anomalous components of the tensor ε are those connected with the polarization components that arise spontaneously in the polar phase, while near the incommensurate phase all three pliability coefficients q_{12}/σ_{12}, q_{13}/σ_{13} and q_{23}/σ_{23} are anomalous, and only the first two are connected with the components q^0_{12} and q^0_{13} that arise spontaneously in the incommensurate phase. The reason for the temperature anomaly of the third coefficient is apparently that in a real sample, consisting of regions with different phases φ of the polarization modulated along the X_1 axis, the components P_2 and P_3 can be unequal in magnitude (and sign) also along the axes X_2 and X_3. The stress σ_{23} conjugate to q_{23} induces the same periodic distribution of P_2 and P_3 along X_3 and X_1 that appears spontaneously along X_1, with a phase φ corresponding to the minimum of the energy

$$W \sim \int q_{23}\sigma_{23}\,dv.$$

Near the transition into the incommensurate phase, the crystal is particularly pliable to the ordering action of σ_{23} and as a result, as is usual in such cases, a λ anomaly of the coefficient q_{23}/σ_{23} takes place.

Weaker anomalies of the potential difference $v_{i,j}$ the corresponds to the change of the diagonal components

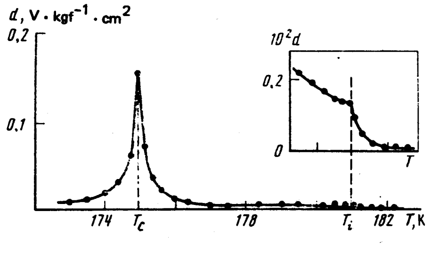

FIG. 5. Pliability coefficient $d = v_{1,2}/\sigma_{22}$ of ammonium fluoroberyllate crystal.

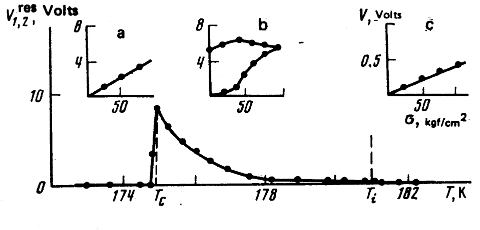

FIG. 6. Residual potential difference $v^{res}_{1,2}$ and dependences of $v_{1,2}$ on σ_{22} for an ammonium fluorberyllate crystal: a) $T = 174.2$, b) 175.2, c) 181.2 K.

of the vector q_{ij} [see (9)] are effects of higher order (Figs. 5 and 6). In fact, if we take into account mixed invariants up to fourth orders in η and ξ in the thermodynamic potential (1), then it can be shown that the component

$$P_1 \sim \eta\xi(\eta^2-\xi^2) = \rho_0^4 \sin 2(4\pi x_1/L+\varphi)$$

is no longer equal to zero, and in accordance with (6) and (9) there should appear in the incommensurate phase of AFB a spontaneous component $q_{11}^0 \sim |\overline{P}_1| L \approx \rho_0^4 L$ and the electrical effects associated with it, which are much smaller than the effects determined by the component q_{12}^0.

We note that the spontaneous potential differences $V_{1,2}^0 \sim q_{12}^0$ and $V_{1,3}^0 \sim q_{13}^0$ of mechanically free samples have no anomalies on going from the incommensurate into the polar phase, and they remain just as large in the polar phase as in the incommensurate phase (Fig. 2). This singularity is apparently connected with the fact that the macroscopic electrical structure on the sample in the absence of external actions remains practically unchanged in this phase transition and the superstructure of the incommensurate phase goes over smoothly into a ferroelectric domain structure (see Sec. 1). We emphasize, however, that the ability of these two structures to change when a mechanical stress is applied is greatly different, as follows from Fig. 3.

What is unexpected in the behavior of the crystals in the incommensurate phase is the appearance of hysteresis in the components q_{ij} due to the mechanical stresses σ_{ij} only when the crystal temperature changes in a definite direction. Hysteresis is observed for some components only after the crystal is heated to a given temperature, and for others only when it is cooled (see Sec. 4). The presently available theoretical and experimental data are still insufficient to identify the cause of this peculiarity of the rearrangement of the electric structure of the incommensurate phase under the influence of the mechanical stresses.

Anomalies of the components of the tensor of the macroscopic quadrupole moment, similar to those cited above, were observed by us recently also in the region of incommensurate phases of the ferroelectrics potassium selenate, rubidium trihydroselenite, and ammonium Rochelle salt.

CONCLUSION

The results of the paper show that the macroscopic quadrupole moment of a crystal sample is a characteristic quantity that changes anomalously in a phase transition into an incommensurate phase that borders on a nonpolar and polar phase. Measurement of the electric effects due to the change of the quadrupole moment can be used as a method for registering such incommensurate phases. It cannot only determine, from the character of the anisotropy of the effects, the direction and singularity of the modulation of the structure, but can also track the temperature evolution of the phase and its thermodynamic properties.

In contrast to the recently proposed methods of generating the second harmonic of light[10,11] and of nuclear quadrupole resonance[12] which register the local lowering of the crystal lattice symmetry in the incommensurate phase, the method of investigating the quadrupole moment reflects the specific features of the macroscopic electric properties of such phases, which are connected with the appearance of spatially modulated polarization in the crystal.

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[1)] No influence of the gradient of an external inhomogeneous electric field on the quadrupole mement of the AFB crystals could be observed, apparently because of the "rigidity" of the crystal to this action.

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