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Piezoelectricity and flexoelectricity in crystalline dielectrics

A. K. Tagantsev
A. F. Ioffe Physico-Technical Institute, Academy of Sciences of the USSR,
194021 Leningrad, Union of Soviet Socialist Republics

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Piezoelectricity in pyroelectrics and the linear response of polarization to a strain gradient (flexoelectricity) are discussed in the framework of the unified approach. It was pointed out by Born and Huang and by Martin, that there was a difference between the piezoelectric response for the cases of a sound wave and of a uniform strain in a finite crystal, and that only the "proper" parts of piezoelectric constants coincided for these cases. It is shown in this paper that there is no such difference if an accurate definition of piezoelectricity is applied. The theory of flexoelectricity in solid crystalline dielectrics is developed. It is shown that the general properties of flexoelectric response strongly differ from those of piezoelectric response: (1) there is an appreciable surface contribution to the flexoelectric response and (2) the bulk flexoelectric responses for the case of a propagating sound wave and for that of a static uniform strain gradient are considerably different. It is proposed to use flexoelectric effect as a method of crystal surface investigation.

I. INTRODUCTION

It is commonly believed that piezoelectricity is a bulk effect.[1] But there are some papers[2-5] in which this point is argued. The debate on this matter continued until recently.[2-7] Nowadays the bulk nature of piezoelectricity seems to be settled.

The first purpose of this paper is to consider a property of piezoelectricity that is closely related to its bulk nature. It has been pointed out by Born and Huang[1] and Martin[8] that there is a difference between the piezoelectric response for the case of a sound wave and for that of a uniform strain in a finite crystal. Occurring only in ferroelectrics[8] or pyroelectrics[1] this difference is given by the following terms:[9]

$$p_j^0\epsilon_{ij}-p_i^0\epsilon_{jj}\ , \tag{1}$$

where ϵ_{ij} is the unsymmetrized macroscopic strain and p^0 is the spontaneous polarization. Thus in accordance with Ref. 8 only the "proper" part of the piezoelectric response [without terms (1)] is the same for those cases. We show in this paper, that there are no such terms in the piezoelectric response if we follow strictly an accurate definition of piezoelectricity.[10] Also we show that the vanishing of terms (1) is related to the bulk nature of piezoelectricity and moreover, that the bulk nature of piezoelectricity "requires" this vanishing.

The other purpose of this paper is to consider flexoelectricity in solid crystalline dielectrics. In accordance with the definition given by Indenbom, Loginov, and Osipov,[11] flexoelectricity in such substances is the linear response of the dielectric polarization to a macroscopic strain gradient. This phenomenon was first predicted by Mashkevich and Tolpygo.[12,13] A phenomenological description was proposed by Kogan.[14] He took into account the term

$$f_{ijkl}P_i\frac{\partial\epsilon_{jk}}{\partial x_l} \tag{2}$$

in the thermodynamic potential expansion. In (2) **P** is the dielectric polarization. The properties of the tensor $\underline{f}$ symmetry have been investigated.[11]

Although flexoelectricity can take place in crystals of any symmetry, centrosymmetric crystals are of special interest, as there is no piezoelectricity in them. In such substances the effect is of importance for the description of the interaction of the elastic deformation with free carriers, because the contribution of the flexoelectric effect to this interaction and that of the deformation potential are of the same order of magnitude.[13,14]

It is commonly believed that the general properties of flexoelectricity and those of piezoelectricity are alike.[11-14] It is assumed that (a) flexoelectricity is a bulk effect, i.e., the surface contribution is small in comparison with the bulk one as d/L, where d is the thickness of the disturbed surface layer and L is the specimen dimension; (b) the flexoelectric response is equal for the cases of a static nonuniform strain and a propagating sound wave. We shall show in this paper that none of these assumptions is right: (a) there is an appreciable surface contribution to flexoelectricity; (b) the same crystal bulk effect is different for the static and dynamic cases.

Also we propose an improved phenomenological description of bulk flexoelectricity.

II. PIEZOELECTRICITY IN PYROELECTRICS

In this section we consider piezoelectricity for the case of a uniform strain in a finite crystal and show that in contradiction to Born and Huang[1] and Martin[8] there are no terms alike [Eq. (1)] in the piezoelectric response of a crystal of any symmetry, if an accurate definition of piezoelectricity is applied.

The change of the finite crystal polarization, induced by a uniform strain ϵ_{ij}, is given by[8]

$$P_i=P_j^0\epsilon_{ij}-P_i^0\epsilon_{jj}+e_{ijk}\epsilon_{jk}\ , \tag{3}$$

where

$$\mathbf{P}^0 = V^{-1} \int \mathbf{x}\rho(\mathbf{x}) d^3x \ . \tag{4}$$

$\rho(\mathbf{x})$ and V are the charge density and the volume of the crystal in the absence of strain and e_{ijk} is the "proper"[8] piezoelectric constant. For the longitudinal effect, $i=k$, e_{ijk} coincides with the expression for the piezoelectric constant, which may be derived by the method of the long waves.[1,8]

Martin[8] assumed that $\mathbf{P}^0$ was the spontaneous polarization, so the first and the second terms in Eq. (3) did not vanish in ferroelectrics. Also he pointed out that those two terms resulted from the rotation and dilatation of the existing moment in a ferroelectric. On the contrary, we believe that a nonzero moment $\mathbf{P}^0$ can exist in a nonferroelectric as well. Indeed, in accordance with Eq. (4) $\mathbf{P}^0$ is the average dipole moment density of the whole crystal and depends on the crystal termination and its surface properties. Even though a crystal structure has inversion symmetry (e.g., the NaCl structure), a finite crystal may be terminated in an asymmetric manner [e.g., a (111) plane of Na ions on the side and a plane of Cl^- ions on the other side], so that the finite crystal can have a macroscopic dipole moment, proportional to the volume of the sample,[7] and $P^0 \neq 0$. All these facts indicate that there is no one-to-one correspondence between P^0 and ferroelectric spontaneous polarization. Then the question arises of how to interpret the first and the second terms in (3). One can answer this question with the help of an accurate definition of piezoelectricity. In accordance with Nye's textbook on the physics of crystals,[10] piezoelectricity is the appearance of a crystal dipole moment under the influence of a uniform strain, not a change in the moment which existed in the absence of strain. So if we want to investigate the genuine piezoelectric response, we must require that the dipole moment of the initial sample be zero. This means that $P^0=0$, and the first and the second terms in (3) vanish. We want to emphasize that this is the unique way to determine the piezoelectric coefficient in order for this quantity to be a bulk one. Otherwise, the piezoelectric response will contain terms [the first and the second in (3)] which are in fact of surface nature. Then one can say that the bulk nature of piezoelectricity "requires" the vanishing of the additional contributions to the piezoelectric constant of a finite crystal, compared with the one obtained with the help of the method of long waves.

In conclusion we want to discuss in detail the condition $P^0=0$. It is a natural condition for a free crystal in the air in the absence of an external electric field. Indeed, if we do not change pressure and temperature for a long time, the macroscopic electric field inside and outside the crystal vanishes. (This vanishing may be achieved with the help of free charges from the air, or with the help of the carriers of the crystal.) Therefore, all multipole moments of the sample must be equal to zero, and so is the dipole one. On the other hand, the requirement $P^0=0$ is in accordance with the quantitative definition of the piezoelectric constant as the polarization partial derivative with respect to strain in the absence of macroscopic electric field,[15] for if $P^0 \neq 0$, generally speaking, we have a nonzero depolarization field.

The condition $P^0=0$ in the absence of macroscopic electric field might not occur[16] if we use for the piezoelectric measurement a scheme with the sample between the plates of a shorted capacitor and if we determine the piezoelectric coefficient by measuring the current flow through the shorting wire, as one varies the stress on the sample. It is obvious that in this case the average electric field in the crystal may be zero whereas the depolarization field and P^0 of the sample are not zero. So, one may expect that in this case the contribution of the first two terms from Eq. (3) would reveal itself in the piezoelectric response. But it appears that if we use a common (and, in fact, the only one used in piezoelectric measurements) capacitor with plates stuck tight to the sides of the crystal (so they move together, as one varies the stress on the sample), the contribution in question does not reveal itself in the piezoelectric response.

To make the fact stated above easily understood one should take into consideration the following: (a) It is the change of the dipole moment average density of all charges of the capacitor (including the induced charges on the plates) that is measured in that scheme. (b) For such a capacitor we may treat the induced charges as surface charges of the sample and therefore take them into account in the integral (4). If we proceed in this way the quantity P^0 becomes equal to zero. As a result we see that the piezoelectric response measured in this way is expressed by Eq. (3) without the first two terms.

Therefore, we conclude (i) that there are no terms like (1) in the piezoelectric response, if an accurate definition of piezoelectricity[10] is applied, and (ii) that (what is more important) a common piezoelectric measurement is, in fact, in agreement with that definition, so the contribution of the terms in question does reveal itself if the course of the piezoelectric coefficient determination, if the ordinary scheme with a shorted capacitor (with plates stuck tight to the sides of the crystal) is used for a piezoelectric measurement.

III. FLEXOELECTRICITY: UNIFORM STRAIN GRADIENT IN A FINITE CRYSTAL

A general expression for the polarization response to a uniform strain gradient in a finite crystal may be derived with the help of the technique applied by Martin[8] to the problem of piezoelectricity. In this paper we restrict ourselves by the flexoelectricity consideration, using the rigid-ion model,[1] for this model is enough to reveal the main features of the phenomenon, whereas in the framework of such an approach the consideration itself becomes much simpler.

Consider a uniform strain gradient in a finite but macroscopic or bulk crystal, so

$$\epsilon_{ij}(\mathbf{x}) = \epsilon_{ij}(0) + \frac{\partial \epsilon_{ij}}{\partial x_k} x_k \ ,$$

$$\epsilon_{ij}(0) = V^{-1} \int_V \epsilon_{ij}(\mathbf{x}) d^3x \ ,$$

where x_i are the Cartesian coordinates of a point inside the crystal in the absence of strain. In the presence of such a strain a particle initially at $\mathbf{R}$ is moved to $\mathbf{R}'=\mathbf{R}+\mathbf{r}$, where

$$r_i=\epsilon_{ij}(0)R_j+\frac{1}{2}\frac{\partial\epsilon_{ij}}{\partial x_K}R_jR_k+u_i^{(1)}(\mathbf{R})+u_i^{(2)}(\mathbf{R}) \ . \tag{5}$$

In Eq. (5) $\mathbf{u}^{(1)}$ and $\mathbf{u}^{(2)}$ are the linear response of the internal strain to the macroscopic strain ϵ_{ij} and to its gradient $\partial\epsilon_{ij}/\partial x_k$. Far from the surface of the crystal $\mathbf{u}^{(1)}$ and $\mathbf{u}^{(2)}$ can be cast in the form

$$u_i^{(1)}(\mathbf{R})=u_{i,p}^{(1)}(\epsilon)=H_{i,p}^{jk}\epsilon_{jk}(\mathbf{R}) \ , \tag{6}$$

$$u_i^{(2)}(\mathbf{R})=u_{i,p}^{(2)}=N_{i,p}^{jkl}\frac{\partial\epsilon_{jk}}{\partial x_1} \ , \tag{7}$$

where p enumerates the atoms in the cell, $\underline{H}$ and $\underline{N}$ may be expressed in terms of bulk microscopic quantities (see Appendix). The change of the crystal polarization induced by the moving of crystal particles is given by

$$\delta P=(V')^{-1}\sum_{\{R'\}}Q(\mathbf{R}')\mathbf{R}'-V^{-1}\sum_{\{R\}}Q(\mathbf{R})\mathbf{R} \ , \tag{8}$$

where V and V' are volumes of the crystal before and after the deformation, $Q(\mathbf{R})$ is the charge of a particle at $\mathbf{R}$ and where summations over the whole set of crystal charges are done. Inserting expression (5) into (8) we find the final form for the polarization change:

$$\begin{aligned}\delta P_i=\epsilon_{ij}(0)P_j^0-\epsilon_{jj}(0)P_i^0+V^{-1}\sum_{\{R\}}Q(\mathbf{R})u_i^{(1)}(\mathbf{R})\\ +\frac{1}{6}Q_{jk}\frac{\partial\epsilon_{ij}}{\partial x_k}+\frac{I}{2}\frac{\partial\epsilon_{ij}}{\partial x_j}+V^{-1}\sum_{\{R\}}Q(\mathbf{R})u_i^{(2)}(\mathbf{R}) \ ,\end{aligned} \tag{9}$$

$$\mathbf{P}^0=V^{-1}\sum_{\{R\}}Q(\mathbf{R})\mathbf{R} \ , \tag{10}$$

$$Q_{ij}=V^{-1}\sum_{\{R\}}Q(\mathbf{R})(3R_iR_j-\delta_{ij}R^2) \ , \tag{11}$$

$$I=V^{-1}\sum_{\{R\}}Q(\mathbf{R})R^2 \ , \tag{12}$$

where $\mathbf{P}^0$ is the average dipole moment density of the crystal and $\underline{Q}$ is the average quadrupolar moment density.

The first three terms of (9) are equal to Eq. (3), if it were derived with the help of the rigid-ion model. They are related to piezoelectricity and have been discussed in the previous section. The last three terms of (9) describe the polarization change produced by the strain gradient, or, in other words, the flexoelectricity. As we have shown in the previous section only the last of the piezoelectric terms is genuine and the first two ones are spurious. It is an accurate definition of piezoelectricity that gives us an opportunity to distinguish the genuine term. But in the case of flexoelectricity there is no such a definition. Therefore, if we want to give a reasonable interpretation of the flexoelectric terms of (9), we have to define the flexoelectricity as clearly as possible. Let us define the flexoelectric constant as the polarization partial derivative with respect to strain gradient in the absence of macroscopic electric field. For the case of a uniform strain gradient in a finite crystal it means that all multipole electric moments of the crystal in the absence of strain must be zero, because if this condition is not fulfilled, the macroscopic electric field does not vanish. Thus, we have to set in (9) $P^0=0$ and $\underline{Q}=0$ and, using Eq. (7), we find the final form for the flexoelectric response,

$$P_i^{(\mathrm{fl})}=\frac{I}{2}\frac{\partial\epsilon_{ij}}{\partial x_j}+v^{-1}Q_pN_{i,p}^{jkl}\frac{\partial\epsilon_{jk}}{\partial x_1} \ , \tag{13}$$

where v is the unit-cell volume and Q_p is the pth ion charge.[17]

The second term of (13) relates to internal strains and corresponds to the bulk contribution to the polarization. The origin of the first term of (13) is similar to that of the spurious fourth term of (9), but this term cannot be eliminated with the help of the condition of the macroscopic electric field vanishing, because a distribution of charge with all multipole moments being zero and $I\neq0$ does not create a macroscopic electric field. As it may be seen from definition of I, (12),[18] I is very sensitive to an electrical structure of the crystal surface, so is the contribution to polarization, corresponding to the first term of (13). That is why we shall refer to this contribution as the *surface flexoelectric contribution.* One can obtain a rough estimate for I: $I\sim e/a$ (e is the charge of electron, a is an atomic dimension). Taking into account the estimate for the bulk contribution to flexoelectricity[11–14] [in expression (2) $f\sim e/a$], we see that in ordinary dielectrics bulk and surface contributions to flexoelectricity are of the same order of magnitude.[19]

IV. FLEXOELECTRICITY: SOUND WAVE OF FINITE WAVELENGTH IN AN INFINITE CRYSTAL

Consider a long-wave acoustic phonon mode of wave vector $\mathbf{K}$ in an effectively infinite crystal, i.e., K^{-1} much less than the crystal dimensions, but $K^{-1}\gg a$, the atomic displacements associated with this mode being written

$$r_{i,p}^{\mathbf{n}}=u_{i,p}e^{i\mathbf{K}\cdot\mathbf{R}_p^{\mathbf{n}}-i\omega t} \ , \tag{14}$$

where $\mathbf{n}$ numbers the cells. In this case only longitudinal polarizations are experimentally detectable. The longitudinal polarization is most easily discussed in terms of the induced charge-density variation $\delta\rho$ related to $\mathbf{P}$ by

$$\frac{\partial P_i}{\partial x_i}=-\delta\rho(\mathbf{x}) \ . \tag{15}$$

In the rigid-ion model

$$\rho(\mathbf{x})=\sum_{\mathbf{n},p}Q_p\delta(\mathbf{x}-\mathbf{R}_p^{\mathbf{n}}) \ , \tag{16}$$

and it is easy to show, using Eqs. (14)–(16) that the amplitude of the longitudinal polarization wave associated with the sound wave in question may be written as

$$\mathbf{P}^{\|}_{\mathbf{K}} = v^{-1} Q_p \mathbf{u}^{\|}_p \,, \tag{17}$$

where

$$\mathbf{u}^{\|}_p = \mathbf{K}(\mathbf{u}_p \cdot \mathbf{K})/K^2 \,.$$

It is well known[1] that for the acoustic phonon mode in the limit $K \to 0$ and $\omega \to 0$, $\mathbf{u}_p = \mathbf{w}$, which does not depend on p. But for a real mode with $K \neq 0$ and $\omega \neq 0$ the spatial and the frequency dispersion effects reveal themselves, and we have to take into account waves of internal strains, following the "pure" acoustic wave with amplitude w. The lowest spatial-dispersion-induced contributions to $\mathbf{u}_p$ can be written with the help of Eqs. (6) and (7). The frequency dispersion reveals itself in contributions to $\mathbf{u}_p$, being proportional to even powers of ω, because here we are not interested in dissipative phenomena. Then we can find a $(Ka)^2$-order expansion in series for u_p in the form

$$u_{i,p} = w_i + iH^{jk}_{i,p} w_j K_k - N^{jkl}_{i,p} w_j K_k K_l - G^{j}_{i,p} w_j \omega^2 \,. \tag{18}$$

A microscopic expression for $\underline{G}$ is derived in the Appendix.

Inserting the two first terms of expression (18) into (17), we see that there is no contribution from the first term and that the second one given an ordinary piezoelectric contribution to polarization. Substituting the third and the fourth terms of expression (18) into (17) leads to the desired relation for the flexoelectric response to a sound wave:

$$(\mathbf{P}^{\|}_{\mathbf{K}})_i = -v^{-1} Q_p (G^{\|j}_{i,p} \omega^2 + N^{\|jkl}_{i,p} K_k K_l) w_j \,, \tag{19}$$

where longitudinal components of $\underline{G}$ and $\underline{N}$, $\underline{N}^{\|}$, and $\underline{G}^{\|}$, are defined as in the case of $\mathbf{u}^{\|}$. As one can see, both terms of (19) give contributions to the flexoelectric constant for a sound wave, for in such a wave $\omega^2 \propto K^2$. If we compare the expressions for flexoelectric response in the case of a uniform strain gradient in a finite crystal, Eq. (13), and in the "sound" case, Eq. (19), we can note that only the second terms correspond to each other. These terms relate to the contribution, which we shall refer to as *static bulk flexoelectricity*. The first term of (19) corresponds to the contribution, not arising in the case of a static strain gradient. That is why we shall refer to this contribution as *dynamic bulk flexoelectricity*. Using the estimates for $\underline{N}$ and $\underline{G}$ from the Appendix, it is easy to show that in the sound case static and dynamic bulk contributions to flexoelectricity are of the same order of magnitude.

To conclude this section we want to make some remarks on the nature of the two contributions discussed above. The static bulk flexoelectricity contribution arises due to effects of the spatial dispersion, or, in other words, due to discontinuity of the crystal lattice. The dynamic bulk flexoelectricity contribution arises due to effects of the frequency dispersion. It depends upon the distribution of the unit-cell mass among the ions and it vanishes, if we assume the equal masses of the ions [see Eqs. (19) and (A11)]. Therefore, one may say that this contribution arises due to a nonequal distribution of mass among the ions of the unit cell.

V. PHENOMENOLOGICAL DISCUSSION OF BULK FLEXOELECTRICITY

It is obvious that taking into account the additional term (2) in the free-energy density describes static bulk flexoelectricity only. For the description of dynamic bulk flexoelectricity we propose to add a new term in the kinetic energy phenomenological density as follows:

$$M_{ij} \dot{P}_i \dot{r}_j \,. \tag{20}$$

Using the Lagrangian density with regard to terms (2) and (20), we find equation of motion for P

$$\chi^{-1}_{ij} P_j = E_i - f_{ijkl} \frac{\partial^2 r_j}{\partial x_k \partial x_l} - M_{ij} \ddot{r}_j \,, \tag{21}$$

where $\mathbf{E}$ is the macroscopic electric field and $\underline{\chi}$ is the dielectric susceptibility tensor of the crystal.

Comparing (21) with (19), we see that term (20) in the kinetic energy phenomenological density does describe dynamic bulk flexoelectricity and we can find relations between the phenomenological tensors $\underline{f}$, $\underline{M}$ and the matrices $\underline{N}$ and $\underline{G}$, which can be expressed in terms of microscopic bulk properties of crystal lattice (see the Appendix), as

$$\chi_{ij} f_{jklm} = -v^{-1} Q_p N^{klm}_{i,p} , \quad \chi_{ij} M_{jk} = -v^{-1} Q_p G^{k}_{i,p} \,. \tag{22}$$

A simple expression for $\underline{M}$ may be written for the case of a crystal with two ions per unit cell:

$$M_{ij} = \delta_{ij}(m_1 - m_2)/2Q \,, \tag{23}$$

where m_1, m_2 and $Q, -Q$ are masses and charges of the ion, respectively. Equation (23) can be obtained with the help of Eqs. (22) and (A11) and the following expression for $\underline{\chi}$ in the rigid-ion model:[1]

$$\chi_{ij} = v^{-1} Q_p \Gamma_{ip,jp'} Q_{p'} \,,$$

where $\underline{\Gamma}$ is defined in the Appendix.

In conclusion of this section we want to point out that there is an interesting question to discuss. Is there any contradiction between a nondiagonal form of the kinetic energy density used in the phenomenological treatment and a diagonal form of the kinetic energy usually used in microscopic calculations? It has been shown in the author's previous paper[20] that there is no such contradiction.

VI. UNIFORM STRAIN GRADIENT IN A FINITE CRYSTAL: SURFACE PIEZOELECTRICITY CONTRIBUTION TO POLARIZATION

There is another effect in addition to the ones discussed in previous sections, which can provide a polarization linear response to a strain gradient in a finite crystal. That is the surface piezoelectricity. That effect is not of our special interest, because it is not of "proper" flexoelectric nature. So we shall restrict ourselves only to its brief discussion for the case of nonpiezoelectric crystals.

In the depth of a nonpiezoelectric crystal the piezoelectric constant is zero, but it may be of nonzero value in a thin layer in the vicinity of the crystal surface. It is clear that the average piezoelectric constant in that layer depends on the structure of the surface and its crystallographic orientation.[21] So surface piezoelectric constants may be different for the opposite plates of a crystal. In this situation surface piezoelectricity may imitate a flexoelectric response. One can illustrate this imitation by the simple example. Consider the thin plate cut from nonpiezoelectric crystal with effective values of surface piezoelectric constant near its two large surfaces l_1 and l_2. Let us mentally apply to the plate a longitudinal strain gradient, which is perpendicular to it and directed to its plate with surface piezoelectric constant l_1. It is easy to show that in this situation due to the surface piezoelectricity we have a contribution to the average specimen flexoelectric constant of order $(l_1-l_2)d$, where d is the thickness of the perturbated surface layer. It is natural to assume that in ordinary dielectrics $l_1 \sim l_2 \sim e/a^2$ and $d \sim a$, and therefore, $(l_1-l_2)d \sim e/a$. Thus, taking into account that in Eq. (21) $f \sim e/a$, we see that in ordinary dielectrics the surface piezoelectricity contribution to the flexoelectric constant and the "proper" contribution to it are of the same order of magnitude.

In conclusion of this section we want to point out that in the framework of our theoretical approach the contribution discussed above and the one of the surface flexoelectricity may be easily distinguished. To make that fact understood one must take into consideration that the first contribution has to depend upon the surface value of H [see Eq. (6)], which governs the piezoelectric response, and the second one does not. The problem of an experimental discrimination of those contributions is discussed in the next section.

VII. DISCUSSION AND CONCLUSIONS

The first problem discussed in this paper is a description of piezoelectricity in pyroelectrics. We have shown that in contradiction with Refs. 1 and 8 there are no additional terms in the properly defined piezoelectric response for the case of a uniform strain in a finite pyroelectric crystal in comparison with the one for the case of a sound wave in the same crystal. We want to point out that the absence of those terms may be checked experimentally.

The second problem discussed in this paper is a linear response of polarization to a strain gradient (flexoelectricity) in solid crystalline dielectrics. As it was shown in the previous sections there are four mechanisms[22] which can provide that response: (1) dynamic bulk flexoelectricity, (2) static bulk flexoelectricity, (3) surface flexoelectricity, (4) surface piezoelectricity.

The first two give contributions for the case of a propagating sound wave, and the last three give contributions for the case of a uniform static gradient in a finite crystal. In ordinary dielectrics contributions of all mechanisms are of the same order.

Flexoelectricity is of interest for ferroelectrics with a nonpiezoelectric paraelectric phase. In the framework of the Landau second-order phase-transition theory only one coefficient in the free energy expansion is equal to zero at the phase transition temperature. For proper ferroelectrics that is one of the components of χ_{ij}^{-1}. So, generally speaking, f [see formula (2)] is nonzero at this temperature. Besides, it is very improbable to find $M_{ij}=0$ at the transition temperature. Therefore, it is clear from Eq. (21) that contributions of the bulk flexoelectric effects would have a temperature anomaly proportional to χ near the transition.[23] So one can expect that near this temperature flexoelectric constants of ferroelectrics may be 10^2-10^3 times larger than the ones of ordinary dielectrics. The surface flexoelectricity contribution is not sensitive to ferroelectric properties of crystal, for I which determines the value of this contribution [see Eq. (13)] does not depend on any dynamic characteristic of crystal lattice. So we can expect that the estimate of this contribution, obtained above, remains valid for ferroelectrics.

Thus there is no universal estimate for the surface piezoelectricity contribution to the flexoelectric constant of a ferroelectric, but it is clear that there are some causes for a temperature anomaly of this contribution. The anomaly may be induced by critical dependence of the disturbed surface layer thickness d, or by a critical dependence of the effective surface piezoelectric constants l_1 and l_2.[21]

Now we shall make some remarks on a possibility of experimental investigations of flexoelectricity.

For the "sound" case the effect reveals itself in the appearance of the polarization wave, following any sound wave. If the polarization wave is longitudinal, a macroscopic electric field wave is present too. Using an estimate for bulk flexoelectric constants obtained above and in Refs. 11–14, it is easy to show that in ordinary dielectrics a sound wave with $K=10^4$ cm^{-1} and the strain amplitude$=10^{-5}$ is followed by the electric field wave with the amplitude ~ 1 V/cm. This estimate remains valid for ferroelectrics too, because of the depolarization effect. For the sound case the contribution of the dynamic bulk effect and of the static bulk one are of the same order, therefore there is no opportunity for their separation in the framework of a dynamic experiment. For this separation the contribution of the bulk static flexoelectricity should be obtained with the help of static measurements.

Three mechanisms give contributions for the case of a uniform static strain gradient in a finite crystal: static bulk flexoelectricity, surface flexoelectricity, and surface piezoelectricity. In ordinary dielectrics the contributions of these mechanisms are of the same order, therefore experimental values of flexoelectric constants, measured in such situation, may strongly depend on the crystallographic orientation of the crystal surface and their quality. This is the main direction for experiment.

It appears that for the "static" case the most interesting crystals for investigation are ferroelectrics. First, for the case of a uniform static gradient in a finite crystal we can eliminate the depolarization effect by measuring with a shorted-capacitor set up, and therefore in ferroelectrics we may deal with effects which are 10^2-10^3 times more extreme than in ordinary dielectrics. Second, in ferroelectrics the contribution of surface flexoelectricity is negligibly small and the contributions of surface piezoelectricity and static bulk flexoelectricity may have different temperature dependences. So, it is ferroelectrics that give us an opportunity to distinguish the contributions of mechanisms of flexoelectricity.

Note, that the high susceptibility of the flexoelectric effect to the properties of crystal surface may make this effect an effective method of surface investigation.

To the author's knowledge, no systematic experimental investigations of flexoelectricity in solid dielectrics have been made. The first attempts of such investigation are discussed in Ref. 11.

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APPENDIX

In this Appendix we shall obtain a microscopic expression for a linear response of internal strains to a gradient of macroscopic strain in the absence of macroscopic electric field E.

We shall proceed from the equation of motion for atomic displacements $r^{n}_{i,p}$

$$m_p \ddot{r}^{\mathbf{n}}_{i,p} = -\Phi^{\mathbf{nn}'}_{ip,i'p'} r^{\mathbf{n}'}_{i',p'} , \tag{A1}$$

where m_p is the mass of the pth atom in the cell and $\underline{\Phi}$ is the matrix of the crystal potential energy second partial derivatives with respect to atomic displacements, with the macroscopic field contribution being excluded.

For the case of a propagating sound wave the response in question may be obtained with the help of "the method of long waves."[1] Following this method let us write $r^{\mathbf{n}}_{i,p}$ in form (14), insert (14) into (A1), and consider the long-wave acoustic solutions of the resulting equation for $\mathbf{u}$. As it was shown,[1] this equation can be solved by the perturbation method with respect to the small parameter Ka. The perturbation equations for contributions to $\mathbf{u}$ in the zeroth, first, and second orders $(\mathbf{u}^{(0)},\mathbf{u}^{(1)},\mathbf{u}^{(2)})$ are

$$A^{(0)}_{ip,i'p'} u^{(0)}_{i',p'} = 0 . \tag{A2}$$

$$A^{(0)}_{ip,i'p'} u^{(1)}_{i',p'} = -iK_j A^{(1)}_{ip,i'p'} u^{(0)}_{i',p'} , \tag{A3}$$

$$A^{(0)}_{ip,i'p'} u^{(2)}_{i',p'} = -iK_j A^{(1)}_{ip,i'p'} u^{(1)}_{i',p'} - \frac{K_j K_l}{2} A^{(2)jl}_{ip,i'p'} u^{(0)}_{i',p'} + \omega^2 m_p u^{(0)}_{i,p} , \tag{A4}$$

where

$$A^{(0)}_{ip,i'p'} = \sum_{\mathbf{n}'} \Phi^{\mathbf{nn}'}_{ip,i'p'} ,$$

$$A^{(1)j}_{ip,i'p'} = \sum_{\mathbf{n}'} \Phi^{\mathbf{nn}'}_{ip,i'p'} (\mathbf{R}^{\mathbf{n}}_p - \mathbf{R}^{\mathbf{n}'}_{p'})_j ,$$

$$A^{(2)jl}_{ip,i'p'} = -\sum_{\mathbf{n}'} \Phi^{\mathbf{nn}'}_{ip,i'p'} (\mathbf{R}^{\mathbf{n}}_p - \mathbf{R}^{\mathbf{n}'}_{p'})_j (\mathbf{R}^{\mathbf{n}}_p - \mathbf{R}^{\mathbf{n}'}_{p'})_1 .$$

The solutions of Eqs. (A2)—(A4) were investigated and the following properties of those solutions were obtained in Ref. 1. Equation (A2) has nontrivial solutions of the form[24]

$$\mathbf{u}^{(0)}_p = \mathbf{w} , \tag{A5}$$

where $\mathbf{w}$ can be any arbitrary vector in space. The condition for solubility, Eqs. (A3) and (A4), is the requirement that their right-hand members summed over p must vanish. After inserting (A5) into (A3) the condition for solubility (A3) is identically fulfilled. The solution of (A3) is

$$u^{(1)}_{i,p} = -\sum_{p''} \Gamma_{ip,i'p'} A^{(1)j}_{i'p',i''p''} iK_j w_{i''} , \tag{A6}$$

where $\underline{\Gamma}$ is the inverse matrix, defined in a special way, to the singular matrix $\underline{A}^{(0)}$. The condition for solubility (A4) [after inserting (A5) and (A6) into (A4)] is the equation for the long acoustic lattice waves. It may be written as

$$\sum_{p,p'} (\omega^2 m_p \delta_{pp'} \delta_{ii'} - K_j K_l T^{jl}_{ip,i'p'}) w_{i'} = 0 , \tag{A7}$$

where

$$T^{jl}_{ip,i'p'} = A^{(1)j}_{ip,i''p''} \Gamma_{i''p'',i'''p'''} A^{(1)l}_{i'''p''',i'p'} + \tfrac{1}{2} A^{(2)jl}_{ip,i'p'} .$$

It is obvious that Eq. (A6) describes the internal strain response to macroscopic strain.

Our interest in the internal strain response to a macroscopic strain gradient makes us calculate $\mathbf{u}^{(2)}$. Inserting (A5) and (A6) into (A4) and taking into account the condition for solubility (A4), we can find the solution of (A4) in the form

$$u^{(2)}_{i,p} = \sum_{p''} \Gamma_{ip,i'p'} (\omega^2 \mu_{p'} \delta_{p'p''} \delta_{i'i''} - K_j K_1 \widetilde{T}^{jl}_{i'p',i''p''}) w_{i''} , \tag{A8}$$

where

$$\widetilde{T}^{jl}_{ip,i'p'} = T^{jl}_{ip,i'p'} - \frac{\delta_{pp'}}{s} \sum_{p'',p'''} T^{jl}_{ip'',i'p'''} ,$$

$\mu_p = m_p - M$, $M = s^{-1} \sum_p m_p$, s is the number of atoms per unit cell of the crystal.

Comparing (18) with (A5), (A6), and (A8) we can write microscopic expressions for $\underline{N}$, $\underline{H}$, and $\underline{G}$:

$$H^{lj}_{i,p} = -\sum_{p''} \Gamma_{ip,i'p'} A^{(1)j}_{i'p',lp''} , \tag{A9}$$

$$N^{jkl}_{i,p} = \sum_{p''} \Gamma_{ip,i'p'} \widetilde{T}^{kl}_{i'p',jp''} , \tag{A10}$$

$$G^{j}_{i,p} = -\Gamma_{ip,jp'} \mu_{p'} . \tag{A11}$$

It is easy to show that in ordinary dielectrics $\underline{H} \sim a$, $\underline{N} \sim a^2$, $\underline{G} \sim \omega_0^{-2}$ (ω_0 is the optic mode frequency).

There are many ways to divide up the right-hand term of (A8) into the ω-dependent and the K-dependent parts, for $\mathbf{K}$ and ω must satisfy Eq. (A7). Therefore, there is some arbitrariness in the definition of $\underline{N}$ and $\underline{G}$ in the framework of "the method of long waves." This arbitrariness may be eliminated with the help of the requirement that the matrix $\underline{N}$ must be the same as in the expression for the internal strains response in the static case (7). Let us show that $\underline{N}$ defined by (A10) just satisfies this condition.

We proceed from the equation of static equilibrium of crystal lattice:

$$\Phi^{\mathbf{nn}'}_{ip,i'p'} r^{\mathbf{n}'}_{i',p'} = 0 \ . \tag{A12}$$

Consider a macroscopic strain $\epsilon_{ij}(\mathbf{x})$, unsymmetrized, which is a smooth function of coordinates. The problem is to find internal strains $\mathbf{u}_p(\mathbf{x})$ as a smooth function of coordinates, which being summed with macroscopic displacements of the lattice sites provide equilibrium in the lattice, i.e.,

$$\begin{gathered} r^{\mathbf{n}'}_{i,p'} = \int_0^{\mathbf{R}'} \epsilon_{ij}(\mathbf{x}) dx_j + u_{i,p'}(\mathbf{R}') \ , \\ \mathbf{R} \equiv \mathbf{R}^{\mathbf{n}}_p, \quad \mathbf{R}' \equiv \mathbf{R}^{\mathbf{n}'}_{p'} \ , \end{gathered} \tag{A13}$$

is consistent with Eq. (A12). Only the members with $|\mathbf{n}-\mathbf{n}'|$ small is of importance for (A12), so it is useful to expand (A13) with respect to $\mathbf{X} = \mathbf{R}' - \mathbf{R}$, i.e.,

$$\begin{aligned} r^{\mathbf{n}'}_{i,p'} = {} & \int_0^{\mathbf{R}} \epsilon_{ij}(\mathbf{x}) dx_j + \epsilon_{ij}(\mathbf{R}) X_j + \frac{1}{2} \frac{\partial \epsilon_{ij}(\mathbf{R})}{\partial x_1} X_j X_1 \\ & + \cdots + u_{i,p'}(\mathbf{R}) + \frac{\partial u_{i,p'}(\mathbf{R})}{\partial x_j} X_j + \cdots \ . \end{aligned} \tag{A14}$$

Inserting (A14) into (A12) and carrying out the sum over all $\mathbf{n}'$, we obtain a differential equation as follows:

$$\begin{aligned} \cdots + A^{(1)j}_{ip,i'p'} \frac{\partial u_i{}',p'}{\partial x_j} + A^{(0)}_{ip,i'p'} u_{i',p'} & \\ = - \sum_{p'} A^{(1)j}_{ip,i'p'} \epsilon_{i'j} + \tfrac{1}{2} \sum_{p'} A^{(2)jl}_{ip,i'p'} \frac{\partial \epsilon_{i'j}}{\partial x_l} + \cdots \ . & \end{aligned} \tag{A15}$$

This equation can be solved by a perturbation method with respect to the small parameter a/l, l being a characteristic distance of the ϵ_{ij} variation. The two first perturbation equations can be written in the form

$$A^{(0)}_{ip,i'p'} u^{(1)}_{i',p'} = - \sum_{p'} A^{(1)j}_{ip,i'p'} \epsilon_{i'j} \ , \tag{A16}$$

$$A^{(0)}_{ip,i'p'} u^{(2)}_{i',p'} = - A^{(1)j}_{ip,i'p'} \frac{\partial u^{(1)}_{i',p'}}{\partial x_j} + \tfrac{1}{2} \sum_{p'} A^{(2)jl}_{ip,i'p'} \frac{\partial \epsilon_{i'j}}{\partial x_1} \ , \tag{A17}$$

the condition for solubility, Eq. (A16), being the same as the one for Eq. (A3), is identically fulfilled. The solution of Eq. (A16) is given by (6), where $\underline{H}$ comes from (A9). The condition for solubility, Eq. (A17) [after inserting (6)], is the equation for static elastic dispacement [compare with (A7)]:

$$\sum_{p,p'} T^{jl}_{ip,i'p'} \frac{\partial \epsilon_{i'j}}{\partial x_1} = 0 \ .$$

It is easy to show that the solution of Eq. (A17) is given by (7), where $\underline{N}$ comes from (A10). This concludes the proof.

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[17] It can be shown that this equation is still valid for the flexoelectric response measured with the help of the scheme discussed in the end of Sec. II, if we take into account the consideration given there.

[18] In (12) the summation over the whole set of crystal charges, including the surface ones, is suggested.

[19] It is clear that it is impossible to give a quantitative description of surface flexoelectricity in the framework of the scheme used. But we believe that the order-of-magnitude estimate of the effect suggested is valid.

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[22] The distinguishing of the four mechanisms has not been made before (Refs. 11—14). We believe that the errors in the microscopical treatment of flexoelectricity in Ref. 11 were made due to the absence of this distinguishing. These errors have been discussed in Ref. 20.

[23] For the case of ferroelectrics of displacement type the anomaly in question may also be derived with the help of expressions (22), (A10), (A11), and (34.14) from Chap. 5 (Ref. 1). Skipping over the detailed derivation (we believe that it is not of interest for this paper), yet we point out that it is the singularity of Γ which causes the anomaly. The singularity of Γ is provided by the term proportional to $1/\omega^2_{\mathrm{SM}}$ (ω_{SM} is the soft mode frequency).

[24] We use variables which are slightly different from the ones used in Ref. 1. So the properties of Eqs. (A2)—(A4), being cited by us, do not coincide with the original in detail.