

Pyroelectric, piezoelectric, flexoelectric, and thermal polarization effects in ionic crystals

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An analysis has been made of the linear response of polarization to a uniform change in temperature, in its gradient (thermal polarization effect), in macroscopic deformation and in its gradient (flexoelectric effect). It has been shown how the use of some definitions of polarization widespread in the literature can lead to essentially incorrect results in the analysis of piezo- and flexoelectric effects in the field of elastic deformations of an acoustic wave. It has also been shown that in calculating the above responses in the case of a spatially uniform disturbance in a sample of finite size two classes of contributions arise: 1) contributions depending on the microscopic properties of the lattice, and 2) contributions depending only on changes in the distortion tensor accompanying the response, and on multipole moments of the charge distribution of the whole unperturbed crystal. In this connection it was established that the former contributions are bulk effects while the latter ones are surface or false contributions (which are not manifested in the generally accepted experimental arrangements for measurements). The special features of the manifestation of the flexoelectric and thermal polarization effects are discussed in detail.

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1. INTRODUCTION

The present paper provides a theoretical description of the pyroelectric, piezoelectric, flexoelectric and thermal polarization effects. The first two have been investigated thoroughly both experimentally and theoretically. The other two are relatively new and have been studied much less. They represent a linear response of the polarization to strain and temperature gradients and are primarily of interest because they describe the appearance of a polarization in a nonpiezoelectric crystal under the action of a "nonelectric" disturbance.

To the best knowledge of the author, the possibility of appearance of a polarization under the influence of a strain (deformation) gradient was first pointed out by Mashkevich and Tolpygo.^{1,2} They derived a microscopic expression for the relationship between the amplitudes of the polarization and of the strain gradient in an acoustic wave for structures of the diamond type. The first step in the development of a phenomenological description of this effect was made by Kogan.³ Some symmetry aspects of the description proposed by Kogan³ were discussed by Indenbom, Loginov, and Osipov.⁴ They also provided a microscopic description of the flexoelectric effect in the case of a static strain gradient. The effect was investigated experimentally by Zheludev and Lik-

hacheva.^{5,6} The experimentally determined coefficient of proportionality between the polarization and the strain gradient was found to be four orders of magnitude greater than the rough theoretical estimate obtained in Ref. 4.

The thermal polarization effect was predicted from phenomenological considerations by Marvan.⁷ A phenomenological description was refined by Gurevich and Tagantsev,^{8,9} who also developed a theory of the phonon mechanism of the effect. Experimental confirmation of the effect was obtained by Kholkin, Trepakov, and Smolenskii¹⁰ for centrosymmetric crystals of lead magnoniobate, which is a ferroelectric with a broad phase transition. This effect has not yet been investigated very thoroughly, but the values of the coefficient of proportionality¹¹ between the temperature gradient and the polarization are in reasonable agreement with the theoretical estimates.¹² There is as yet no microscopic theory of the thermal polarization effect for ferroelectrics exhibiting order-disorder phase transitions, although the experimental data for crystals of this type (triglycine sulfate) have already been obtained by Strukov *et al.*¹³

A theoretical description of the flexoelectric and thermal polarization effects has certain special features. However, at the present level of development of theoretical physics there should be no fundamental difficulties. It is therefore surprising that in the process of microscopic calculations

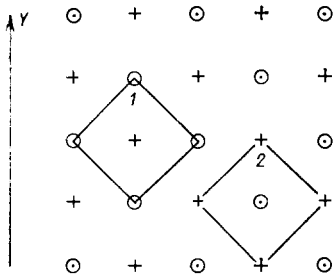


FIG. 1. Planar square diatomic lattice. Two types of unit cells of maximum symmetry are shown: 1) with a positive ion at the center; 2) with a negative ion.

these effects have foundered on a "reef." This is manifested in the simplest analysis of, for example, the flexoelectric effect. We shall illustrate it by considering an example.

We shall discuss the appearance of a polarization in the flexoelectric effect in a planar square lattice of the NaCl type shown in Fig. 1. We shall analyze qualitatively the process of appearance of a polarization in such a lattice under the influence of constant longitudinal strain gradients $\partial U_{yy} / \partial y > 0$. We shall do this by considering changes in the dipole moment of a unit cell as a result of inhomogeneous deformation. We shall select the unit cell to be electrically neutral with the maximum symmetry and the minimum volume (area). Such a cell contains a whole ion of one sign at the center of the square and four quarters of ions of the opposite sign at the corners of the square. We can see from Fig. 1 that there are two kinds of such cells: with a positive ion at the center and with a negative one. We shall first consider a unit cell of the first type. In an undeformed crystal the centers of gravity of positive and negative charges of the cell coincide, so that its dipole moment is zero. If the deformation is homogeneous, the centers of gravity of the charges continue to coincide and there is no dipole moment. However, in the case of inhomogeneous deformation the distances from the "upper" and "lower" quarters of ions (Fig. 2) to the central ion become different so that the centers of gravity of the positive and negative charges no longer coincide. Consequently, the cell becomes polar and the polarization is (as can be seen from

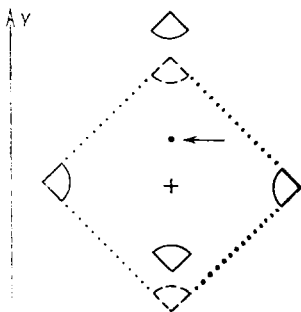


FIG. 2. Displacement of quarters of negative ions relative to a positive ion in the case of inhomogeneous deformation. The dashed lines are the positions of the upper and lower quarters in an undeformed cell. The horizontal arrow indicates the position of the center of gravity of a negative charge of the cell after deformation.

Fig. 2) opposite to the strain gradient. However, if we select a cell with a negative ion at the center (which is labeled 2 in Fig. 1) and repeat the above discussion, we find that the direction of the resultant polarization coincides with the direction of the strain gradient. This means that in this approach the flexoelectric coefficient (which is the coefficient of proportionality between the strain gradient and the polarization) changes its sign depending on the selection of the unit cell. We can thus see that our simple clear analysis yields a result which is absurd from the point of view of formulation of a problem.

The absurdity of this result is a consequence of a "collision with an underwater reef" mentioned above. The only paper known to the present author in which a direct calculation is made of the polarization response to a constant strain gradient is that of Indenbom, Osipov, and Loginov⁴ and it *does not avoid this difficulty*: The microscopic expression obtained by these authors for the flexoelectric coefficient depends on the way that the unit cell is selected. It has been found that the "underwater reef," the influence of which we have just demonstrated, appears not only in the description of such exotic phenomena as the flexoelectric and thermal polarization effects, but also when the old and thoroughly studied pyroelectric and piezoelectric effects are considered. In the latter case the "reef" is more hidden, but a "collision" with it gives the same paradoxical answers. Born and Huang¹⁴ analyzed the pyroelectric effect and considered not only the intrinsic contribution, but also fictitious contributions which do not appear in the experiments carried out in accordance with the crystallophysical definition of the effect. This vanishing of the fictitious contributions becomes obvious after the paradox mentioned above is resolved.

An analysis of the piezoelectric effect in pyroelectrics given in the book of Born and Huang¹⁴ and in the paper of Martin¹⁵ suffers from a similar shortcoming.

We shall now define the aim of the present paper and the way we shall pursue this aim. In Sec. 2 we shall use the example of pyroelectricity and piezoelectricity in the simplest model situation to show how to resolve a paradox similar to that described above. In Sec. 3 we shall discuss the piezoelectric effect in the field of strains created by an acoustic wave, and also carry out a critical analysis of various definitions of the polarization. We shall use the approach developed in the study of the pyroelectric and piezoelectric effects to analyze the flexoelectric and thermal polarization effects in Secs. 3–5. In Sec. 6 we shall formulate phenomenological descriptions of the bulk contributions to these effects. In Sec. 7 we shall summarize briefly the results and identify the reasons why our results differ from those given in Refs. 4, 14, and 15.

We shall be interested in these effects in insulators characterized by a strong localization of the valence electrons so that we shall consider only the ionic contribution to the polarization and ignore the electronic contribution. One of the problems considered below (specifically the pyroelectric and piezoelectric effects in a sample of finite dimensions) has been discussed in the literature^{16–21} in a situation characterized by a high degree of delocalization of the valence electrons. We shall not join this discussion, but simply point out that the results summarizing this discussion and given by Kallin and Halperin²¹ are not in conflict with our conclusions.

2. PYROELECTRIC AND PIEZOELECTRIC EFFECTS IN SPATIALLY HOMOGENEOUS MATERIALS

We shall consider three crystal structures consisting of point ions with lattices of the NaCl, sphalerite, and GeTe types in the ferroelectric phase. In all these structures the same ions form fcc lattices. In a structure of the NaCl type the sublattices of ions with different signs are shifted along a threefold axis by half the body diagonal of the cube. The symmetry group of the resultant lattice is then O_h . In the second structure the sublattices are shifted in the same direction, but by a quarter of the body diagonal (point symmetry group T_d). In the paraelectric phase the compound GeTe has the NaCl structure. In the ferroelectric phase the lattice of GeTe differs from the high-temperature structure by a slight shift along the threefold axis (point group C_{3v}).¹⁾ In each of these structures we shall mentally select thin plates perpendicular to the c_3 axis. It is shown in Fig. 3 that in all three structures such plates consist of parallel layers of ions of the same sign, but shifted by different amounts relative to one another. We shall assume that the sample is electrically neutral, so that negative ions appear on one face and positive ions on another. We shall consider pyroelectric and piezoelectric properties of plates prepared in this way. In accordance with the symmetry of the lattices from which they are cut, the first plate (O_h) should not have pyroelectric or piezoelectric properties, the second (T_d) should exhibit piezoelectric but not pyroelectric properties, and the third (C_{3v}) should exhibit both pyroelectric and piezoelectric properties. We shall now consider how the properties of plates match the point symmetry of the original lattices and the experimentally observed effects.

We shall find the response of the polarization to a change in temperature. Using the definition that the polarization is the specific dipole moment²² and Fig. 3, we can write down the heating-induced change in the polarization δP in the form

$$\delta P = \frac{P'}{V'} - \frac{P}{V} = P^0 \left[\frac{1 + (\delta a/a)}{1 + (\delta V/V)} - 1 \right], \quad (2.1)$$

where

$$P^0 = \frac{NaQ}{V}, \quad \delta V = V' - V, \quad \delta a = a' - a;$$

P , V , and a , and P' , V' , and a' are, respectively, the dipole moments, volumes of the plates, and lattice parameters (Fig. 3) before and after heating; Q is the charge of a positive ion; N is the number of pairs of ions in a plate. Using Eq. (2.1),

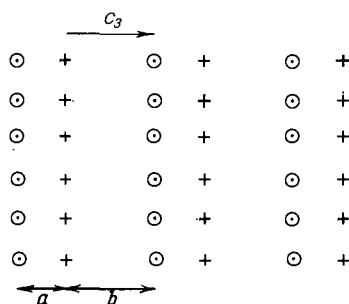


FIG. 3. Three model crystal structures (shown schematically at right angles to the c_3 axis): $a = b$ for NaCl, $3a = b$ for ZnS, and $a = \lambda b$ for GeTe.

we can readily find the "pyroelectric" response of such a plate. We are using quotes for the word "pyroelectric" because such a response is exhibited by all three plates, including those made of nonpyroelectric structures. In fact, in the case of the first two structures we find from the law of thermal expansion that, in the linear approximation, the change in the polarization is

$$\delta P = -P^0 \cdot 2\alpha \delta T, \quad (2.2)$$

where α is the thermal expansion coefficient. For the structure of the GeTe type, we obtain

$$\delta P = -P^0 \cdot 2\alpha_1 \delta T + \frac{NQ}{V} \frac{ab}{a+b} \frac{\delta \lambda}{\lambda}, \quad \lambda = \frac{a}{b}, \quad (2.3)$$

where α_1 is the thermal expansion coefficient at right-angles to the c_3 axis.

The physical meaning of these formulas is simple. When the first two structures expand, the ratio of the two distances in a unit cell remains constant, so that the parameter a varies strictly in accordance with the thermal expansion law and the relative change in the dipole moment of the investigated crystal is $\alpha \delta T$. The relative change in the volume is $3\alpha \delta T$. Consequently, the polarization changes by an amount δP described by Eq. (2.2). In the last structure the parameter a and the change in the dipole moment of the whole crystal with a do not obey the law of thermal expansion. Only the quantities $a + b$ obey this law. The ratio $a/b = \lambda$ is no longer determined (in contrast to the first two cases) by the crystal symmetry and, therefore, it depends on temperature. In this situation Eq. (2.2) contains not only a term due to pure thermal expansion, but also a term which appears because of the temperature dependence of λ .

Therefore, all three plates formally exhibit pyroelectric properties, and this applies to a plate formed from the centrosymmetric structure of the NaCl type. The result is paradoxical. Larmor²³ was the first to draw attention to this paradox. However, this paradox does not apply to the quantity usually determined experimentally, which is the pyroelectric charge. This could be demonstrated by carrying out a pyroelectric measurement in a thought experiment. We shall assume that electrically neutral electrodes are deposited on the large faces of the plates and that the circuit is closed by a galvanometer. It is then obvious that before closing of the circuit there is a homogeneous depolarizing electric field $4\pi P^0$ in the plates. After closure of the circuit the macroscopic field in the capacitor vanishes because of the field of charges on the electrodes. We can readily show that compensation of the depolarizing field requires transfer of a charge $QMa/(a+b)$ (where M is the number of atoms in a monatomic layer perpendicular to the c_3 axis), i.e., a charge $Qa/(a+b)$ per each atom reaching an electrode.

We shall now vary the temperature of a sample and determine the change in the polarization from the pyroelectric current. In the first plate there is no such current to within a/L (where L is the thickness of the plate). In fact, since the macroscopic field in the plate is zero, the whole crystal can be divided into dipole-free cells (with the possible exception of the surface layers of thickness of the order of a , which are electrically neutral when we bear in mind the charges on the electrodes). During heating the nonpolar middle part of the sample remains unaffected, so that the dipole moment does not appear in this region. There may be

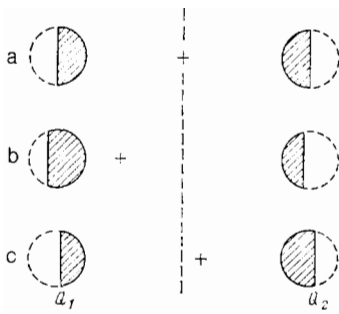


FIG. 4. Schematic form of dipole-free unit cells in the case of three model structures: NaCl (a), ZnS (b), and GeTe (c). The magnitudes of the outer charges are selected bearing in mind the relationship between a and b .

a change in the dipole moment in the surface layer, but this contribution is extremely small, of the order of $P^0\alpha\delta T/L$ when converted to the average density.

In the case of the second plate there is no pyroelectric signal within the same limits as in the first case. Once again we shall demonstrate this by the division described above, but a dipole-free cell is now obtained in a different way. In the first case in our projection this is the cell consisting of an ion of one sign in the middle and half the ions of the other signs at the edges (Fig. 4a). Now the central ion is located asymmetrically and the charges of the outer ions are $Q/4$ and $3Q/4$ (Fig. 4b). However, it is important that the relationship $3a = b$ is maintained by the symmetry and, consequently, the cell remains dipole-free when temperature is varied. We can now repeat the discussions used in the first case and obtain the same answer.

We shall try to apply the above discussion to a plate cut from a "true" pyroelectric structure of the GeTe type. The initial division into nonpolar (dipole-free) cells is still possible, but the charges at the edges should be selected as $bQ/(a+b)$ and $aQ/(a+b)$ (Fig. 4c). The fundamental difference from the preceding cases is that division is now temperature-dependent. Therefore, the initially dipole-free middle of a crystal acquires a dipole moment as temperature is varied. The corresponding change in the polarization is described by the second term in Eq. (2.3) and can be written in the form

$$\delta P = \frac{NQ}{V} \frac{ab}{a+b} \frac{\partial}{\partial T} \ln \frac{q}{b} \cdot \delta T. \quad (2.4)$$

This is the true pyroelectric effect. We shall now draw attention to the formal attribute which distinguishes the true pyroelectric effect from the apparent one. If Eqs. (2.2) and (2.3) are derived for a plate cut in a different way (from the point of view of the signs of the ions emerging on the surface), the formulas become modified as in the case of the substitutions $a \rightleftharpoons b$ and $Q \rightarrow -Q$, and then the apparent contributions change their sign, whereas the true pyroelectric effect is not affected.²⁾

We shall now consider piezoelectric properties of our plate. We shall apply mentally a uniaxial stress along the c_3 axis. A slight modification of the reasoning which yielded Eqs. (2.2) and (2.3) above allows us to show that the piezoelectric response is finite and of the same order for all three plates. As in the case of the pyroelectric effect, this response contains the contributions of the apparent and true effects.

We can separate them by a thought experiment involving piezoelectric measurements using a circuit of the kind assumed above in pyroelectric measurements. We can calculate the response using the old division into dipole-free cells and an electrically neutral layer. The presence of the true piezoelectric effect depends on whether the dipole-free nature of a cell is retained under the action of uniaxial stresses. The application of a uniaxial stress to the first plate does not affect the symmetry elements ensuring that $a = b$ and the cell remains dipole-free. Therefore, we can expect a very small piezoelectric signal associated with the surface. In the second plate the application of a uniaxial stress destroys the symmetry elements that ensure the equality $3a = b$ and makes the cell dipolar. The response of the polarization to the change in the strain tensor $\delta U_{\alpha\beta}$ can in this case be described, by analogy with Eq. (2.4), in the form³⁾

$$\delta P = \frac{NQ}{V} \frac{ab}{a+b} \frac{\partial}{\partial U_{\alpha\beta}} \ln \frac{a}{b} \cdot \delta U_{\alpha\beta}. \quad (2.5)$$

In the case of the third plate the ratio $a/b = \lambda$ is not fixed by the symmetry and, consequently, it depends on the strain tensor. The piezoelectric effect which is thus generated is also described by Eq. (2.5).

We have thus obtained two different answers for the pyroelectric and piezoelectric responses by employing two different methods. At first sight the definitions of the polarization used to obtain the two answers are the same, so that we are faced with the natural question: why is the first set of answers incorrect? This is due to the fact that in the first discussion we used incorrect definitions of the pyroelectric and piezoelectric effects. We shall discuss this in greater detail in the case of the pyroelectric effect (and similar arguments apply when the piezoelectric effect is considered). According to the classical textbook of Nye,²⁴ pyroelectricity is the appearance of a dipole moment in crystals as a result of change in temperature, whereas Eqs. (2.2) and (2.3) are derived by calculating the change in the polarization, i.e., the investigated quantity is the change in the dipole moment. Our thought experiment involves measurements of the pyroelectric response using the current circuit [as assumed in the derivation of Eq. (2.4)], which corresponds exactly to the definition proposed by Nye: The dipole moment of a crystal directly before a change in the pyroelectric charge is zero. Such an apparently slight deviation from the correct definition produces a very large difference between the answers.

One further comment should be made about a phenomenological definition of pyroelectricity. When Nye says in Ref. 24 that the pyroelectric effect is manifested by the appearance of a dipole moment of crystals as a result of heating, the crystal is implied to be free (of electrodes) and its dipole moment is compensated (if it ever existed) to zero by the surface charges, i.e., the dipole moment of a crystal is understood to include the surface charges. Hence, it is clear that in the case of a crystal with electrodes the dipole moment should be calculated allowing for the induced charges (for details see Ref. 38).

It is in this sense that the definition of pyroelectricity given by Nye²⁴ can be based on the measurements in a current circuit.

We shall finish the discussion of model structures by drawing attention to the need of an exact crystallochemical definition of a pyroelectric. It follows from an analysis pre-

ceding Eq. (2.4) that we can select a unit cell with the maximum symmetry of the nonpolar phase when dealing with pyroelectricity. It is then found that the definition of a pyroelectric as a crystal with a polar unit cell is insufficient. It is therefore necessary to refine these definitions: a pyroelectric is a crystal in which it is possible to select a unit cell with the maximum symmetry of the polar nature. In our opinion the definition of a pyroelectric which represents best the essence of the effect can be formulated as follows: A pyroelectric is a crystal in which nonpolar unit cells must be selected in different ways for different (even only slightly) temperatures.

The properties of pyroelectrics and piezoelectrics discussed above in the case of specific examples can be described using the framework of a more general scheme. We shall consider a solid as a set of charges $Q(\mathbf{R})$ located at points determined by the selection of the radius vectors $\{\mathbf{R}\}$. Let us assume that homogeneous stresses created by a tensor $\sigma_{\alpha\beta}$ are induced in the investigated body and that the temperature of this body changes by δT . Then, writing down the distance traveled by each charge $\mathbf{r} = \mathbf{R}' - \mathbf{R}$ and selecting only the part corresponding to the contribution of the macroscopic deformation, we find that

$$r_{\alpha} = \varepsilon_{\alpha\beta}(\hat{\sigma}, \delta T) R_{\beta} + u_{\alpha}, \quad (2.6)$$

where $\varepsilon_{\alpha\beta}$ is the distortion tensor describing macroscopic deformations due to thermoelastic and mechanical stresses. The first term in Eq. (2.6) describes displacements considered in the elasticity theory approximation and the second represents deviations from the theory of elasticity due to the discrete structure of the lattice. In the terminology adopted by Born and Huang,¹⁴ the first and second terms in Eq. (2.6) represent external and internal deformations, respectively. We shall therefore call the displacements describing the deviation from the theory of elasticity the internal displacements. The change in the polarization due to the displacements described by Eq. (2.6) is

$$\begin{aligned} \delta P_{\alpha} &= \sum_{\alpha} Q(\mathbf{R}') R'_{\alpha} (V')^{-1} - \sum_{\alpha} Q(\mathbf{R}) R_{\alpha} V^{-1} \\ &= \varepsilon_{\alpha\beta} P_{\beta}^0 - \varepsilon_{\beta\alpha} P_{\alpha}^0 + \sum_{\alpha} Q(\mathbf{R}) u_{\alpha} V^{-1}, \end{aligned} \quad (2.7)$$

$$P_{\alpha}^0 = \sum_{\alpha} Q(\mathbf{R}) R_{\alpha} V^{-1}, \quad (2.8)$$

where the summation is carried out over all the charges. We can easily see that P^0 is the polarization of an undeformed crystal calculated allowing for all the charges, including those on the surface and on the electrodes. We have seen above that, by definition of the pyroelectric and piezoelectric effects, this quantity should be zero. The first two terms in Eq. (2.7) vanish and they represent the apparent pyroelectric and piezoelectric contributions. The term remaining in Eq. (2.7) describes the true pyroelectric and piezoelectric effects.

We can use Eq. (2.7) to write down readily explicit expressions for the pyroelectric and piezoelectric responses via microscopic characteristics of the crystal lattice. We shall be interested in those responses when a macroscopic electric field E in a sample is zero. This condition is satisfied automatically when measurements are carried out using the current circuit described above. Clearly, if a change in the strain or temperature makes the field E different from zero, the polarization response will be different than for $E = 0$.

However, the corresponding renormalization of the response allowing for the shape of the sample and for electrical boundary conditions on its surfaces can be carried out using the framework of macroscopic electrostatics of insulators. In the case of homogeneous deformations the internal displacements can be written in the form

$$u_{\alpha, p}^{(1)} = H_{\alpha, p}^{\beta\gamma} \varepsilon_{\beta\gamma}, \quad (2.9)$$

where p is the number of an atom in a unit cell. In the case under discussion when the macroscopic electric field is zero, the tensor $H_{\alpha, p}^{\beta\gamma}$ is symmetric in respect of the upper pair of indices, so that the real internal displacements depend only on the symmetric part of the distortion tensor, i.e., on the strain tensor.^{14,15} The internal displacements responsible for the pyroelectric response in an acoustically clamped lattice can be written in the form

$$u_{\alpha, p}^{(pyr)} = B_{\alpha, p} \delta T. \quad (2.10)$$

Both $H_{\alpha, p}^{\beta\gamma}$ and $B_{\alpha, p}$ are generally different in the bulk of a crystal and near its surface. However, in an analysis of the kind made here we can ignore the inhomogeneity of the distribution of these quantities in the interior of a crystal, since the contribution made to the last of the sums in Eq. (2.7) by the surface regions (where \hat{H} and \hat{B} are different from the bulk values) is negligible due to the smallness of the ratio of the volume of these regions to the volume of the whole crystal. Using Eqs. (2.7), (2.9), and (2.10), we finally obtain the following expressions for the piezoelectric and pyroelectric responses:

$$\delta P_{\alpha}^{(pie)} = v^{-1} Q_p H_{\alpha, p}^{\beta\gamma} \varepsilon_{\beta\gamma}, \quad (2.11)$$

$$\delta P_{\alpha}^{(pyr)} = v^{-1} Q_p \left(B_{\alpha, p} + H_{\alpha, p}^{\beta\gamma} \frac{\partial \varepsilon_{\beta\gamma}}{\partial T} \right) \delta T, \quad (2.12)$$

where Q_p is the charge of the p th ion in a unit cell; v is the volume of this cell; \hat{H} and \hat{B} are the bulk values. We can easily see that Eqs. (2.11) and (2.12) are not affected by the selection of the unit cell.

The first term in Eq. (2.12) describes the contribution of what is known as the primary pyroelectric effect.²⁵ In the case of a mechanically free crystal the second term of Eq. (2.12) describes the contribution of the secondary pyroelectric effect,²⁵ when the derivative of the distortion tensor with respect to temperature can be replaced by the thermal expansion tensor. In the case of partial mechanical clamping this derivative with respect to temperature can be calculated allowing for the boundary conditions and then the last term in Eq. (2.12) will also describe the contribution of the tertiary pyroelectric effect.²⁵

The bulk values of the quantities \hat{B} and \hat{H} which occur in Eqs. (2.11) and (2.12) can be found by the standard calculation of the equilibrium properties of the crystal lattice (see, for example, Refs. 14 and 26). In our discussions their actual form is unimportant.

We shall conclude this section by noting that the discussion of the pyroelectric and piezoelectric effects given above for spatially homogeneous materials differs fundamentally from the discussions known to the authors and given in Refs. 14 and 15. The difference is the main result obtained above, which is the separation of the apparent pyroelectric and piezoelectric contributions. We shall consider the reasons for this difference in the final section of the present paper.

3. PIEZOELECTRIC AND FLEXOELECTRIC EFFECTS IN THE FIELD OF AN ACOUSTIC WAVE

In the preceding section we analyzed the response of the volume-average polarization to a homogeneous change in the temperature and to homogeneous deformation. In such cases we need not use the "primary" definition of the polarization²²

$$\operatorname{div} \mathbf{P} = -\bar{\rho} \quad (3.1)$$

($\bar{\rho}$ is the average density of the bound charges), but can employ an obvious consequence of Eq. (3.1):

$$\int \mathbf{P} d^3x = \int \mathbf{x} \bar{\rho} d^3x + \oint \mathbf{x} (d\mathbf{S} \cdot \mathbf{P}). \quad (3.2)$$

Since we are interested in the volume-average polarization, the integration indicated in Eq. (3.2) can be carried out over the volume surrounding the body in question, so that the surface integral vanishes. Therefore, in the preceding section the polarization was defined as the dipole moment per unit volume of an insulator. This was in agreement with the definition of the polarization adopted by Landau and Lifshitz.²²

However, we must bear in mind that if we are interested in the polarization averaged over some internal volume of an insulator, the surface integral of Eq. (3.2) does not vanish. Therefore, the conclusion reached in Ref. 22 on the basis of Eq. (3.2) that the polarization is the density of the dipole moment is incorrect. Other definitions of the polarization are used in the literature^{26,27} and some of them are also incorrect. However, it is found that if we confine our attention to the phenomena which occur in the zeroth order with respect to the spatial dispersion, such as the polarization of an insulator in an electric field, then all the definitions of the polarization give the same answer (to a high degree of accuracy). In an analysis of the piezoelectric and flexoelectric effects in the field of an acoustic wave it is found that various "secondary" definitions of the polarization generally give very different answers.

The purpose of the present section is to analyze the piezoelectric and flexoelectric effects in the field of an acoustic wave starting from the primary definition of the polarization given by Eq. (3.1) and then to demonstrate how the widely used but not fully correct definitions of the polarization can give rise to qualitative errors in the description of these phenomena. Therefore, we shall divide the present section into three subsections: a) internal displacements in the field of an acoustic wave; b) description utilizing the "primary" definition; c) descriptions utilizing other definitions of the polarization.

3.1. Internal displacements in the field of an acoustic wave

We shall consider an acoustic wave of wavelength $2\pi/K$ much greater than the characteristic interatomic distance a , but much smaller than the size of a crystal L . In general, the displacements of the lattice sites in such a wave can be written in the form

$$\mathbf{r}_p = \exp(i\mathbf{k}\mathbf{R}_p^n - i\omega t) \mathbf{u}_p(\mathbf{k}, \omega), \quad \mathbf{R}_p^n = \mathbf{n} + \mathbf{x}_p, \quad (3.3)$$

where \mathbf{n} is the lattice vector and \mathbf{x}_p is the radius vector of the p th atom in a cell. It is known that in the limit $K \rightarrow 0$ and $\omega \rightarrow 0$ the amplitude u_p is independent of p so that to a high

degree of accuracy we can assume that in the case of our wave the amplitude \mathbf{u}_p is equal to the vector \mathbf{w} which is independent of p . The wave characterized by $\mathbf{u}_p = \mathbf{w}$ represents an acoustic wave in the theory of elasticity approximation in the sense that the displacements in such a wave are determined entirely by the value of the phase factor in Eq. (3.3), i.e., exactly as in the definition of the displacements in a wave traveling in an elastic continuum. In the case of a real wave in a crystal we find that \mathbf{u}_p differs from \mathbf{w} . A wave with the amplitude $\mathbf{u}_p - \mathbf{w}$ will be called a wave of internal displacements, because it describes the difference of real displacements of the lattice sites from those obtained for an acoustic wave considered in the theory of elasticity approximation (for definitions of internal displacements, see Sec. 2). A wave of internal displacements appears because of manifestations of spatial and temporal dispersions. Its amplitude is proportional to w because of the linearity of the problem. The spatial dispersion is manifested in the form of corrections to the approximation of the theory of elasticity in powers of the parameter Ka . The temporal dispersion is manifested (because we are considering a nondissipative situation) only in the form of corrections in even powers of the parameter ω/ω_0 (ω_0 is the characteristic frequency of an optical phonon). When lower corrections are allowed for, the amplitude \mathbf{u}_p can be written in the form

$$u_{\alpha, p} = w_{\alpha} + iH_{\alpha, p}^{\beta\gamma} w_{\beta} K_{\gamma} - N_{\alpha, p}^{\beta\gamma\delta} w_{\beta} K_{\gamma} K_{\delta} - G_{\alpha, p}^{\beta} w_{\beta} \omega^2 u_{\beta}. \quad (3.4)$$

Since ω and \mathbf{K} for an acoustic wave satisfy the relationship

$$w_{\alpha} \rho \omega^2 = c_{\alpha\beta\gamma\delta} w_{\gamma} K_{\beta} K_{\delta}, \quad (3.5)$$

where ρ is the density and \hat{c} is the tensor of the elastic moduli, the term in Eq. (3.4) associated with the temporal dispersion can be excluded formally by the substitution

$$\hat{N} \rightarrow \tilde{N}_{\alpha, p}^{\beta\gamma\delta} = N_{\alpha, p}^{\beta\gamma\delta} + \rho^{-1} G_{\alpha, p}^{\gamma} c_{\nu\gamma\beta\delta}.$$

The general method which allows us to calculate \hat{H} and \tilde{N} using the matrix of the force constants of a crystal,⁴⁾ was formulated in the book of Born and Huang.¹⁴ A microscopic expression for \hat{H} used in the description of the piezoelectric effect was also obtained by Born and Huang. Moreover, it was assumed in Ref. 14 that the tensor \hat{H} can also be used to describe the response of internal displacements to static deformation, i.e., that \hat{H} in Eqs. (2.9) and (3.4) is the same quantity. The validity of this conclusion can be demonstrated rigorously.²⁸ The microscopic expressions for the tensors \hat{N} and \hat{G} were obtained by the present author²⁸ and the tensor \tilde{N} was defined so that the response of internal displacements $\mathbf{u}_p^{(2)}$ to a static strain gradient is described by the same tensor, i.e.,

$$u_{\alpha, p}^{(2)} = N_{\alpha, p}^{\beta\gamma\delta} \frac{\partial e_{\beta\gamma}}{\partial x_{\delta}}. \quad (3.6)$$

Clearly, this selection of \hat{N} corresponds to a correct separation of the contribution of the spatial dispersion to internal displacements of the second order in Ka .

3.2. Description utilizing "primary" definition of polarization

In the preceding subsection we used an expansion of the displacements of the lattice sites in an elastic wave employing lower orders in respect of the spatial and temporal dis-

persions. Now, in a microscopic description of the piezoelectric and flexoelectric effects we have to define the response of the polarization to such displacements. We shall use the primary definition of the polarization given by Eq. (3.1). However, it is more convenient to transpose the commuting operations of averaging and differentiation, i.e., it is more convenient to define the change in the polarization $\delta\mathbf{P}$ caused by an acoustic wave as a solution of the equation

$$\operatorname{div} \delta\mathbf{P}_{\text{mic}} = -\delta\rho. \quad (3.7)$$

averaged over a scale which is large compared with the lattice constant; $\delta\rho$ is the change in the density of the bound charge induced by the elastic wave. When using this definition to describe the piezoelectric response to displacements in an acoustic wave, we shall follow the work of Martin¹⁵ and then generalize his results to the case of the flexoelectric response.

Let us assume that displacements in an acoustic wave are described by Eq. (3.3). Then a linear response of the density of the bound charge to such displacements is

$$\delta\rho(\mathbf{x}) = \sum_{\{\mathbf{R}\}} Q_p (\mathbf{u}_p \nabla_{\mathbf{x}}) \delta(\mathbf{x} - \mathbf{R}) e^{i\mathbf{k}\mathbf{R}}, \quad (3.8)$$

here, $\{\mathbf{R}\}$ denotes summation over all the vectors \mathbf{R}_p^n . Substituting Eq. (3.8) into Eq. (3.7), we obtain the solution of the latter in the form⁵⁾

$$\delta\mathbf{P}_{\text{mic}}(\mathbf{x}) = \sum_{\{\mathbf{R}\}} Q_p \mathbf{u}_p \delta(\mathbf{x} - \mathbf{R}) e^{i\mathbf{k}\mathbf{R}}. \quad (3.9)$$

After summation over the lattice vectors the Fourier component $\delta\mathbf{P}_{\text{mic}}$ becomes

$$\mathbf{P}_{\mathbf{k}}^{\text{mic}} = V^{-1} \int d^3x e^{-i\mathbf{k}\mathbf{x}} \delta\mathbf{P}_{\text{mic}}(\mathbf{x}) = v^{-1} \sum_{\mathbf{b}} Q_p \mathbf{u}_p e^{i\mathbf{b}\mathbf{x}} \Delta_{\mathbf{k}+\mathbf{b}, \mathbf{k}}, \quad (3.10)$$

(\mathbf{b} is the reciprocal lattice vector and $\Delta_{\mathbf{k}\mathbf{k}'}$ is the Kronecker delta). We shall now carry out the averaging. In the summation over \mathbf{b} in Eq. (3.10) we need to retain only the term with $\mathbf{b} = 0$, because the other values of \mathbf{b} correspond to contributions oscillating with wavelengths smaller than or of the order of the lattice constant. Consequently, the amplitude of a macroscopic polarization wave $\mathbf{P}_{\mathbf{k}}$ which accompanies sound is given by

$$\mathbf{P}_{\mathbf{k}} = v^{-1} Q_p \mathbf{u}_p. \quad (3.11)$$

Now, using the results of Sec. 2, we can obtain the contributions made to the polarization that accompanies an acoustic wave and we can do this in the zeroth, first, and second orders in respect of the spatial dispersion. Substituting \mathbf{w} instead of \mathbf{u}_p in Eq. (3.11), we can demonstrate that in the elasticity theory approximation the contribution to the polarization which accompanies sound is absent for crystals of any symmetry. This is ensured by the electrical neutrality of a unit cell and corresponds to the result of Sec. 2 where only apparent contributions are obtained in the elasticity approximation.

Using Eqs. (3.4), (3.5), and (3.11), we find that the amplitudes of the polarization which accompany sound are given by the following expressions which are valid in the first and second orders in Ka :

$$(\mathbf{P}_{\mathbf{k}})_{\alpha}^{(\text{pie})} = v^{-1} Q_p H_{\alpha, p}^{\beta\gamma} i w_{\beta} K_{\gamma}, \quad (3.12)$$

$$(\mathbf{P}_{\mathbf{k}})_{\alpha}^{(\text{fe})} = -v^{-1} Q_p (\rho^{-1} G_{\alpha, p}^{\beta\gamma} + N_{\alpha, p}^{\beta\gamma\delta}) w_{\beta} K_{\gamma} K_{\delta}. \quad (3.13)$$

Clearly, $iK_p W_{\alpha}$ and $-K_p K_{\gamma} W_{\alpha}$ are the Fourier components of the distortion tensor and of its gradient in an acoustic wave, so that Eq. (3.12) is in agreement with Eq. (2.11) and describes the piezoelectric effect in the elastic field of this wave. However, Eq. (3.13) describes the response of the polarization to a strain gradient in an acoustic wave, i.e., it describes the flexoelectric effect.

We have thus obtained a relationship between the polarization and the strain as well as its gradient in an elastic wave. This was done using the "primary" definition of the polarization given by Eq. (3.1). We shall now see what description of these effects can be obtained employing other definitions of the polarization found frequently in the literature.

3.3. Descriptions utilizing other definitions of polarization

The following definition of the polarization corresponding to the macroscopic electric field of zero intensity is used in the book by Vaks²⁶:

$$\mathbf{P}(\mathbf{x}) = \frac{\mathbf{d}(\mathbf{x})}{v}, \quad (3.14)$$

where $\mathbf{d}(\mathbf{x})$ is the dipole moment of a unit cell and v is the unperturbed volume of this cell. Since Vaks did not give a microscopic description of the effects which appear when higher orders of the spatial dispersion are considered, the use of Eq. (3.14) gave no paradoxical or incorrect results.

We shall show that in the description of the piezoelectric and flexoelectric effects this definition generally gives incorrect results. We shall assume that displacements in an acoustic wave are given in the form of Eq. (3.3) and then, using Eq. (3.14), we shall show that the amplitude of the polarization wave which accompanies sound is described not by Eq. (3.11) but by

$$\mathbf{P}_{\mathbf{k}} = v^{-1} Q_p \mathbf{u}_p e^{i\mathbf{k}\mathbf{x}} \mathbf{p}. \quad (3.15)$$

Equations (3.15) and (3.11) differ only by the presence of an additional phase factor, but the responses described by them are qualitatively different: According to Eq. (3.11) the displacements corresponding to the zeroth order in respect of the spatial dispersion do not create a polarization wave, whereas according to Eq. (3.15), such displacements do create a wave. In fact, substituting \mathbf{w} instead of \mathbf{u}_p in Eq. (3.15) and expanding the exponential function in a series, we obtain the piezoelectric contribution in the first order in Ka and the flexoelectric contribution in the second order in terms of the same quantity:

$$v(\mathbf{P}_{\mathbf{k}})_{\alpha} = iM_{\beta}^{(1)} K_{\beta} w_{\alpha} - M_{\beta\gamma}^{(11)} K_{\beta} K_{\gamma} w_{\alpha} + \dots, \quad (3.16)$$

$$M_{\alpha}^{(1)} = Q_p x_{\alpha, p}, \quad M_{\alpha\beta}^{(11)} = \frac{1}{2} Q_p x_{\alpha, p} x_{\beta, p}, \dots \quad (3.17)$$

It should be noted that the contribution to the polarization described by Eq. (3.16) is physically meaningless. For example, it is well known that the selection of a unit cell to ensure that it is as symmetric as possible simplifies calculation of any bulk property of a solid, but the same results should be obtained irrespective of the selected unit cell. However, the piezoelectric and flexoelectric coefficients obtained with the aid of Eq. (3.16) clearly depend on such selection because the sums $M^{(1)}$ and $M^{(11)}$ in terms of which

these coefficients are expressed depend on the selected unit cell. It should be noted that such apparent piezoelectric effects should not generally be compensated by inclusion of higher terms of the expansion in Eq. (3.4), because the apparent effect is independent of the properties of the matrix of the force constants of the crystal, whereas the terms in question do depend on these properties. We have encountered a similar paradox earlier in an analysis of the piezoelectric effect when considering a spatially homogeneous material. We can readily show that the expression describing the apparent piezoelectric effect in Eq. (3.16) is identical with the Fourier transform of the first term in Eq. (2.7), if \mathbf{P}^0 is understood to be the average density of the dipole moment in a unit cell.

As pointed out above, the correct answers are obtained from Eq. (3.13) in the zeroth order in respect of the spatial dispersion. We can therefore expect Eq. (3.14) to represent only the first term of the expansion. We shall write down the whole series and show how the terms corresponding to the apparent effects of the (3.16) type are compensated. It is shown in Ref. 27 that the expression for the microscopic value of the polarization can be written in the form

$$P_{\text{mic}}^{\alpha}(\mathbf{x}) = \sum_n (\delta(\mathbf{x} - \mathbf{n}) M_{\alpha}^{(I)} - \delta_{\beta}^{\prime}(\mathbf{x} - \mathbf{n}) M_{\alpha\beta}^{(II)}) + \delta_{\beta\gamma}^{\prime\prime}(\mathbf{x} - \mathbf{n}) M_{\alpha\beta\gamma}^{(III)} - \dots, \quad (3.18)$$

where $M^{(III)}$ and the other tensors $M^{(IV)}$ etc. are defined in the same way as $M^{(I)}$ and $M^{(II)}$ in Eq. (3.17). It should be pointed out that the tensors $M^{(I)}$, $M^{(II)}$, etc. correspond to the definition of multipole moments of a unit cell adopted in Ref. 27. The required expansion will be obtained in the Fourier representation. This can be done by attributing all the displacements of the lattice sites in an acoustic wave, described by Eq. (3.3), to a change in \mathbf{p}_p (and not a change in the lattice vector \mathbf{n}) and then substituting Eq. (3.3) into Eq. (3.17) as well as Eq. (3.17) into Eq. (3.18), linearizing with respect to \mathbf{u}_p , using the Fourier transform, and averaging in the same way as was done in the derivation of Eq. (3.11). We then obtain

$$v(\mathbf{P}_{\mathbf{K}})_{\alpha} = M_{\alpha}^{(I)}(\mathbf{K}) - iK_{\beta} M_{\alpha\beta}^{(II)}(\mathbf{K}) - K_{\beta} K_{\gamma} M_{\alpha\beta\gamma}^{(III)}(\mathbf{K}) + \dots, \quad (3.19)$$

where

$$M_{\beta}^{(I)}(\mathbf{K}) = \frac{\partial M_{\beta}^{(I)}}{\partial x_{\alpha, p}} u_{\alpha, p} e^{i\mathbf{K}\mathbf{x}_p}, \text{ etc.} \quad (3.20)$$

are the amplitudes of waves of multipole moments of unit cells defined in accordance with Eq. (3.17).

We can readily see that the first term in Eq. (3.19) does indeed correspond to Eq. (3.15) and, consequently, agrees with the definition of Eq. (3.14). Since in contrast to Eq. (3.15), the formula given by Eq. (3.19) is obtained from first principles, it naturally gives the same longitudinal component of the polarization as Eq. (3.11). Direct calculation can show that a series obtained for $(\mathbf{K}, \mathbf{P}_{\mathbf{K}})$ from Eq. (3.19) sums to a form which can be obtained from Eq. (3.11). The difference between the values of the transverse component of the polarization given by Eqs. (3.11) and (3.19) is to be expected, because there is some indeterminacy in the determination of these components in the course of derivation of these formulas. However, since macroscopic electrostatics

deals only with the longitudinal components of P , this difference does not give rise to any contradictions.

Substituting \mathbf{w} instead of \mathbf{u}_p in Eq. (3.20) and then substituting Eq. (3.20) into Eq. (3.19), we can see how the apparent piezoelectric and flexoelectric contributions originating from the first term in Eq. (3.19) cancel out or, which is equivalent, when this happens in the case of the contributions obtained from the expansion of Eq. (3.16): The apparent piezoelectric contribution cancels the contribution due to the second term of Eq. (3.19), and the apparent flexoelectric contribution cancels out two contributions arising from the second and third terms. Therefore, if we wish to use the expansion of Eq. (3.19) for the description of piezoelectricity, we must take account not only of a wave of dipole moments of unit cells, but also of a wave of their quadrupole moments. Similarly in the description of flexoelectricity we need to allow for a wave of octupole moments.

We can now see the results of the use of the definition of the polarization as the average density of the dipole moment.²² We must point out that Eq. (3.14) does not follow strictly this definition, because it does not allow for the change in the unit cell volume. A rigorous correspondence with the definition of Ref. 22 can be obtained by rewriting Eq. (3.14) in the form

$$\mathbf{P}(\mathbf{x}) = \frac{d(\mathbf{x})}{v'(\mathbf{x})}, \quad (3.21)$$

where $v'(\mathbf{x})$ is the volume of the cell deformed by the acoustic wave. In the approximation which is linear in respect of the elastic displacement in a wave \mathbf{w} , this volume can be written in the following complex form:

$$v'(\mathbf{x}) = v(1 + i(\mathbf{K}\mathbf{w})e^{i\mathbf{K}\mathbf{x}}), \quad (3.22)$$

Using Eqs. (3.21) and (3.22), we find that the amplitude of a polarization wave which accompanies a displacement wave of Eq. (3.3), is described by the following expression obtained in the linear approximation

$$\mathbf{P}_{\mathbf{K}} = v^{-1} Q_p [\mathbf{u}_p e^{i\mathbf{K}\mathbf{x}_p} - i\mathbf{x}_p (\mathbf{K}\mathbf{w})]. \quad (3.23)$$

We can readily show that Eq. (3.23) is "better" than Eq. (3.15) in the sense that the additional term in the former cancels out the apparent piezoelectric contribution to the longitudinal component of the polarization. Therefore, Eq. (3.23), and, consequently, Eq. (3.21) can be used to describe the piezoelectric effect. However, the apparent flexoelectric contribution remains so that in describing the effects of the second or higher orders in respect of the spatial dispersion, we still find that Eq. (3.23) is unsuitable.

We shall now consider qualitatively the reasons for such a difference between the consequences of Eqs. (3.21) and (3.14). We shall consider a crystal which can be divided into unit cells with a dipole moment $\mathbf{M}^{(I)}$ and assume that a longitudinal acoustic wave is propagating in the crystal parallel to $\mathbf{M}^{(I)}$. Clearly, the dipole moment decreases in the case of those cells which experience compression, whereas it increases for the cells which become elongated. In the elasticity theory approximation the relative change in the length of a dipole is equal to the corresponding component of the strain tensor. Consequently, an acoustic wave considered in the elasticity approximation is accompanied by a wave of dipole moments of unit cells and the amplitude of this wave is $\mathbf{M}^{(I)} (\partial r_{\alpha} / \partial x_{\alpha})$.

According to Eq. (3.14), this wave of dipole moments creates a polarization wave which is the source of the apparent piezoelectric effect. This approach reveals the origin of the surprising properties of the apparent piezoelectric effect: 1) its occurrence in the case of centrosymmetric structures; 2) the dependence of its magnitude on the selection of a unit cell. In fact, any structure can be divided into polar units cells and hence the first property follows, whereas the dipole moment of a unit cell depends on the way the cell is selected, giving rise to the second property.

According to (3.21) a wave of dipole moments of unit cells is insufficient for the creation of a polarization wave, because we must have a wave of the density of dipole moments of unit cells. However, in the case of the wave under consideration we find that in the elasticity theory approximation the relative changes in the dipole moment of a unit cell and of its volume are the same and, consequently, waves of the density of dipole moments do not appear. Therefore, we find no apparent piezoelectric effect if we use Eq. (3.21).

The fact that the relationship (3.21) can correctly describe the piezoelectric effect but not the flexoelectric effect, suggests that Eq. (3.21) and consequently Eq. (3.23) are the first terms of some expansion based on the spatial dispersion parameter. In contrast to Eq. (3.19), such an expansion should not contain contributions of the amplitudes of waves of multipole moments of unit cells, but contributions made by amplitudes of the waves of multipole densities of moments. This expansion can readily be obtained from Eq. (3.18). The derivation is similar to the derivation of Eq. (3.19) except that now some of the displacements of the lattice sites [described by Eq. (3.3)] equal to $\delta \mathbf{n} = \mathbf{w} e^{i\mathbf{k}\mathbf{n}}$ should be attributed to the change in \mathbf{n} and not in \mathbf{x}_p . Consequently, in the Fourier representation this gives rise to a series which differs from Eq. (3.19) by the replacement

$$M^{(N)} \dots (\mathbf{K}) \rightarrow \tilde{M}^{(N)} \dots (\mathbf{K}) \\ = \frac{\partial M^{(N)} \dots}{\partial x_{\alpha, p}} (u_{\alpha, p} e^{i\mathbf{K}\mathbf{x}_p} - w_{\alpha}) - i (\mathbf{K}\mathbf{w}) M^{(N)} \dots$$

We can see from the above formula that the series now obtained is in terms of the spatial derivatives of multipole densities and its first term corresponds to Eq. (3.23) and, consequently, to Eq. (3.21). In contrast to the series (3.19), a correct description of the piezoelectric effect can be provided if we include only the first term, whereas the first two terms are needed for the correct description of the flexoelectric effect.

4. FLEXOELECTRIC EFFECT IN SPATIALLY HOMOGENEOUS MATERIALS

In this section we shall consider the response of the polarization averaged over a sample to a homogeneous strain gradient which is independent of time. We shall do this in a manner similar to that used above to deal with the piezoelectric effect.

We shall find the linear response of the average polarization of a crystal to an inhomogeneous strain distribution described by the following distortion tensor:

$$\varepsilon_{\alpha\beta}(\mathbf{x}) = \varepsilon_{\alpha\beta}(0) + \frac{\partial \varepsilon_{\alpha\beta}}{\partial x_{\gamma}} x_{\gamma}, \\ \varepsilon_{\alpha\beta}(0) = V^{-1} \int_V \varepsilon_{\alpha\beta}(\mathbf{x}) d^3x. \quad (4.1)$$

In the vector describing the displacements due to the field of elastic strains of Eq. (4.1) we can distinguish the contribution corresponding to strains considered in the elasticity theory approximation from internal displacements $\mathbf{u}^{(1)}$ and $\mathbf{u}^{(2)}$ which appear in the first and second orders in respect of the spatial dispersion and represent the response to a strain and its gradient:

$$\mathbf{r}_{\alpha} = \varepsilon_{\alpha\beta}(0) R_{\beta} + \frac{1}{2} \frac{\partial \varepsilon_{\alpha\beta}}{\partial x_{\gamma}} R_{\beta} R_{\gamma} + u_{\alpha}^{(1)} + u_{\alpha}^{(2)} + \dots \quad (4.2)$$

Since the volume-average polarization is equal to the volume-average density of the dipole moment, we can find the change in the former from the change in the latter. Consequently, using Eqs. (4.2) and (2.7), we obtain: 1) three terms corresponding to the apparent and true piezoelectric effects [they are given in Eq. (2.7)]; 2) the terms of interest to us and associated with the flexoelectric effect:

$$\delta P_{\alpha} = \frac{1}{6} Q_{\beta\gamma} \frac{\partial \varepsilon_{\alpha\beta}}{\partial x_{\gamma}} + \frac{I}{2} \frac{\partial \varepsilon_{\alpha\beta}}{\partial x_{\beta}} + V^{-1} \sum Q(\mathbf{R}) u_{\alpha}^{(2)}, \quad (4.3)$$

$$Q_{\alpha\beta} = V^{-1} \sum Q(\mathbf{R})(3R_{\alpha}R_{\beta} - \delta_{\alpha\beta}R^2), \quad (4.4)$$

$$I = V^{-1} \sum Q(\mathbf{R}) R^2. \quad (4.5)$$

Summation in all three formulas is carried out over all the charges in a crystal, including the surface charges.

In the relationship (4.3), as in the case of the piezoelectric effect, two terms out of three appear in the elasticity theory approximation [compare with Eq. (2.7)]. However, in contrast to Eq. (2.7) only the first term from Eq. (4.3) corresponds to the apparent contribution, whereas the second corresponds to the real contribution and is generally not small. We shall now demonstrate this.

We can separate the apparent (not experimentally observable) contributions from the true piezoelectric effect if we compare our theoretical relationships with the crystallophysical definitions of the piezoelectric effect. In the case of the flexoelectric effect the corresponding concept has not yet been formulated clearly, since the effect has not yet been studied experimentally. Therefore, we shall first give the definition of the flexoelectric effect based on the same principles as that on which the definition of the piezoelectric effect is based. We recall that, according to Nye,²⁴ the piezoelectric effect is the appearance of a polarization in a homogeneously deformed solid, i.e., it is the appearance of the dipole moment in a deformed crystal and this moment is zero in the undeformed state. We shall define the flexoelectric effect as the appearance of a polarization under the influence of a strain gradient in a solid whose quadrupole moment is zero in the undeformed state.⁶⁾ We shall show why precisely this definition of the flexoelectric effect corresponds to the adopted definition of the piezoelectric effect. We shall do this by first elucidating why the dipole moment of an undeformed crystal is assumed to be zero in the definition of the piezoelectric effect. This is due to the fact that the macroscopic field around and inside such a crystal is zero if it is under constant external conditions for a sufficiently long time. A nonzero dipole moment of all the charges in a crystal, including the surface charges (captured by the surface from air and those on the electrodes, if the latter exist), would have been in conflict with zero value of the macroscopic field. In the definition of the piezoelectric effect it is important only that the dipole moment should be zero, so that higher moments are not mentioned. However, it is clear

that not only the dipole moment of a crystal, but all the higher multipole moments should be zero. Therefore, the expression (4.3) for the flexoelectric contribution to the polarization includes the average density of the quadrupole moment of a crystal and the vanishing of the quadrupole moment of a crystal in its initial state should be reflected in the definition of the flexoelectric effect.

Now, using the adopted definition and the relationship (4.3), we shall obtain the final expression for the flexoelectric response. The quantity $VQ_{\alpha\beta}$ is the quadrupole moment of all the charges in a crystal and, in accordance with the adopted definition, it should be equated to zero. Therefore, the first term in Eq. (4.3) vanishes. By analogy with the piezoelectric effect, we can say that such a term corresponds to the apparent contribution. The second term in Eq. (4.3) depends on I [see Eq. (4.5)] and does not vanish, because the macroscopic field around and inside a crystal is independent of I (see, for example, Ref. 29). In the last term in Eq. (4.3) the summation over all the charges in a crystal can be replaced (which is accurate to within the order of the ratio of the volume of the distorted surface region to the total volume of a crystal) with summation over the part of the crystal unperturbed by the influence of the surface, exactly in the same way as was done in the derivation of Eq. (2.11). Using Eqs. (4.3) and (3.6) for the flexoelectric response in the presence of a static strain gradient in a bounded crystal, we finally obtain

$$\delta P_{\alpha}^{(ne)} = \frac{I}{2} \frac{\partial \epsilon_{\alpha\beta}}{\partial r_{\beta}} + v^{-1} Q_{\beta} N_{\alpha, \nu}^{\beta\gamma\delta} \frac{\partial \epsilon_{\beta\gamma}}{\partial r_{\delta}}. \quad (4.6)$$

The nature of the contribution corresponding to the second term in Eq. (4.6) is quite obvious: It is governed by internal displacements caused by a strain gradient, by analogy with the situation when the piezoelectric effect is governed by internal displacements caused by the strain itself. The nature of the contribution corresponding to the first of Eq. (4.6) is not so obvious. We shall now try to give a qualitative interpretation of this term.

We shall begin by considering the physical meaning of the quantity I . Although a macroscopic field E created by a system of charges in a crystal is independent of I , the potential of this field may depend on I . In fact, according to Eq. (4.5), $I/2$ is the trace of a tensor of the average density of the quadrupole moment which is subtracted from this tensor on transition from the definition used in Ref. 27, $M_{\alpha\beta}^{(II)}/v$ [see Eq. (3.17)], to the traceless definition adopted in Eq. (29), $Q_{\alpha\beta}$ [see Eq. (4.4)]. If we assume that I corresponds to the constant density of the trace within a solid, we can readily show that the potential created by this density is

$$\varphi(\mathbf{x}) = \frac{I}{2} \int_{V'} \frac{\partial^2}{\partial r_{\alpha}^2} \frac{1}{|\mathbf{x} - \mathbf{x}'|} d^3x' = -2\pi I \int_{V'} \delta(\mathbf{x} - \mathbf{x}') d^3x'.$$

Hence it follows that the jump of the potential on the surface of a solid is $2\pi I$. Strictly speaking, we can apply this result to a crystal only after further justification. However, it is known that the distribution of the potential obtained for a continuous distribution of the density, which corresponds to the tensor $Q_{\alpha\beta}$, is in reasonable agreement with the experimental results.³⁰ We can therefore hope that the proportionality between I and a discontinuity of the potential on the surface will remain true also in the case of a discrete distribution of the charge. Clearly, for a real crystal, such a jump

occurs at a double electric layer on the atomic scale.⁷⁾ This layer naturally forms as a result of compensation of multipole moments of the original crystal by surface charges. Since the jump across this double layer is governed primarily by the structure of the surface, the contribution corresponding to the first term in Eq. (4.6) is of surface origin. The mechanism responsible for its appearance can be described as follows. In the case of the original crystal the average dipole moment of a double layer on the surface is zero. In the case of an inhomogeneous strain, the layer is displaced together with the surface and this gives rise to a finite dipole moment.

We shall conclude this section by comparing the properties of the piezoelectric and flexoelectric effects. The "general" properties of the piezoelectric effects are based on two observations: the absence of a significant surface charge and the identity of the relationship between internal displacements and the macroscopic strain in the case of an acoustic wave and static deformation [compare Eqs. (2.9) and (3.4)]. They can be formulated as follows: 1) the effect appears in the same way under conditions of homogeneous static deformation and in the presence of a traveling acoustic wave; 2) the effect is essentially a bulk phenomenon, i.e., when the change in the total polarization of a sample of finite dimensions is measured, the contribution of the surface is small because of the relative smallness of the volume of the distorted surface layer. The flexoelectric effect has none of these "general" properties. In fact, if we compare the expressions for the flexoelectric response under the conditions of static inhomogeneous deformation of Eq. (4.6) and in the presence of a traveling acoustic wave of Eq. (3.13), we can see that there is a correspondence only in the last terms of these equations. The contribution represented by these terms will be called the *bulk static flexoelectric effect*. The first term in Eq. (3.13) appears only under transient conditions and we shall call it the *bulk dynamic flexoelectric effect*. As pointed out already, the first term in Eq. (4.6) is of surface origin and, therefore, it is natural to call it the *surface flexoelectric effect*. The simplest estimates for the usual insulator indicate that all three contributions are generally of the same order of magnitude and the coefficient of proportionality between a strain gradient and the polarization is of the order of e/a for all the contributions (e is the electron charge). This corresponds to an estimate of the effect obtained in Refs. 1-4.

To complete the picture of the response of the polarization to a strain gradient we must point out a further effect that can simulate the flexoelectric response and which is the surface piezoelectric effect, i.e., the effect which occurs in the surface layer of a crystal where the lattice is distorted by the influence of the surface³¹ and the tensor \hat{H} of Eq. (2.9) is not equal to the bulk value. We shall consider how this can occur in a plane parallel plate cut from a centrosymmetric crystal with opposite faces which are identical in the crystallophysical sense. It follows from symmetry considerations (for a detailed discussion of such situations see Ref. 31) that the components of the surface piezoelectric modulus for the opposite faces, associated with the normal component of the polarization, differ in sign. In this situation a change in the corresponding components of the total dipole moment of a crystal is proportional to the difference between the strains of its opposite faces and is independent of its thickness.

Clearly, such a change in the polarization simulates the flexoelectric response and in the case of an ordinary insulator the coefficient of proportionality between the change in the average polarization and the average strain gradient is of the same order of magnitude as in the case of the true effect.

The piezoelectric effect exhibits an anomaly at a phase transition in a ferroelectric and this anomaly is proportional to the lattice susceptibility χ . A similar anomaly may be exhibited also by the bulk flexoelectric contributions.²⁸ This can again be shown by employing the phenomenological description given in Sec. 6. The surface flexoelectric contribution does not have an anomaly because the value of I which describes this anomaly is completely insensitive to the dynamic properties of the lattice. The surface piezoelectric effect may have an anomaly in the case of bulk or surface phase transitions.³¹ The temperature dependences of the contribution of this effect to the response of the polarization of a ferroelectric crystal to a strain gradient has not been analyzed in detail. There are simply indications²⁸ that this contribution exhibits an anomaly, but in some cases it may be weaker than the bulk flexoelectric contributions.

5. THERMAL POLARIZATION EFFECT

As pointed out before, the thermal polarization effect represents a linear response of the polarization to a temperature gradient. A general description must be made more precise in order to give an unambiguous definition of the effect. Firstly, we must exclude trivial nonlocal contributions to the polarization of an inhomogeneously heated body associated with the long-range macroscopic electrostatic and elastic forces, i.e., this response will be considered for zero values of the macroscopic field E and elastic stresses. Secondly, since there is a contribution to the effect associated with the inhomogeneity of elastic deformation,⁸ we shall match the definition of the thermal polarization effect to that of the flexoelectric effect, i.e., we shall require that in the case when the polarization is deduced from the change in the average density of the dipole moment of a sample, the dipole and quadrupole moments of the original crystal are zero.

As in the case of the effects analyzed earlier, our discussion will be split into two stages: the definition of displacements of lattice sites in the case of inhomogeneous heating and calculation of the change in the polarization from such displacements.

Among the displacements defined in the first stage we can distinguish components of different origin:

$$\mathbf{r} = \mathbf{u}^{(el)} + \mathbf{u}^{(1)} + \mathbf{u}^{(2)} + \mathbf{u}^{(pyr)} + \mathbf{u}^{(t)} + \mathbf{u}^{(k)}. \quad (5.1)$$

The first four contributions can appear in bodies other than those inhomogeneously heated. They are as follows:

$\mathbf{u}^{(el)}$ is the displacement considered in the elasticity theory approximation and generally described by an integral of the distortion tensor,³² and in the case of a constant gradient it corresponds to the first two terms of Eq. (2.4) where the distortion tensor should be found by solving the corresponding problem in the theory of elasticity;

$\mathbf{u}^{(1)}$ and $\mathbf{u}^{(2)}$ are the internal displacements responsible for the piezoelectric and bulk flexoelectric responses, which are described by Eqs. (2.9) and (3.6);

$\mathbf{u}^{(pyr)}$ is the internal displacement responsible for the primary pyroelectric effect and described by Eq. (2.10).

The last two terms in Eq. (5.1) represent the contribu-

tions made to displacements of the lattice sites solely because of the spatial inhomogeneity of the temperature distribution. They are as follows:

$\mathbf{u}^{(t)}$ due to a temperature gradient considered in terms of quasiequilibrium thermodynamics, but after subtraction of the contribution already included in $\mathbf{u}^{(2)}$;

$\mathbf{u}^{(k)}$ is the internal displacement known as kinetic and is due to nonequilibrium of the phonon system.

Determination of the last two contributions is the main task of a microscopic theory of the thermal polarization effect. In the case of an ideal weakly anharmonic insulator this was done by Gurevich and the present author.^{8,9,33}

We shall not be interested in details of the description of the individual contributions to the effect, but we shall simply classify them.

We shall consider the simplest situation when all the change in the polarization of an insulator in the presence of a temperature gradient is due to the thermal polarization effect, in accordance with the adopted definition: we shall discuss a mechanically free nonpyroelectric crystal in which a homogeneous (over the whole sample) temperature gradient is established⁸ and the macroscopic field E is controlled.

When the problem is formulated in this way, we can distinguish the surface contributions to the thermal polarization effect (representing the displacements $\mathbf{u}^{(el)}$, $\mathbf{u}^{(1)}$ and $\mathbf{u}^{(pyr)}$) and the bulk contributions ($\mathbf{u}^{(2)}$, $\mathbf{u}^{(t)}$, and $\mathbf{u}^{(k)}$). We shall begin with the surface contributions. The elastic displacements $\mathbf{u}^{(el)}$ make a contribution to the polarization which is proportional to the temperature gradient and this contribution is due to the surface flexoelectric effect [first term in Eq. (4.6)]. In the case of a nonpyroelectric crystal neither $\mathbf{u}^{(1)}$ nor $\mathbf{u}^{(pyr)}$ make a bulk contribution to the polarization. However, the surface piezoelectric effect still simulates the flexoelectric response, which ensures a corresponding surface contribution to the thermal polarization effect. The surface pyroelectric effect can also simulate the response of the polarization to a temperature gradient in the same way as the surface piezoelectric effect simulates the flexoelectric effect (as discussed at the end of Sec. 4).

One of the bulk contributions corresponding to $\mathbf{u}^{(2)}$ reduces, like the surface contributions, to the effects already considered: It is the contribution of the bulk flexoelectric effect due to inhomogeneous strains created by a temperature gradient. The bulk contributions to the thermal polarization effects which cannot be reduced to other effects appear because of the displacements $\mathbf{u}^{(t)}$ and $\mathbf{u}^{(k)}$. The contribution due to the displacement $\mathbf{u}^{(k)}$ is known as kinetic because it appears only if an allowance is made for nonequilibrium in a crystal. The combination of the contributions due to displacements $\mathbf{u}^{(t)}$ and $\mathbf{u}^{(k)}$ is known as the thermodynamic contribution, because it can be deduced within the framework of quasiequilibrium thermodynamics.

We can gain an idea of the relationship between the contributions by obtaining order-of-magnitude estimates and considering the problem of feasibility of their separation in experiments. We shall confine our attention to high temperatures (which are higher than or of the order of the Debye temperatures) when the thermal polarization effect is large.

From the experimental point of view the least favorable situation is that in an ordinary centrosymmetric insulator. The simplest estimates indicate that in this case all the con-

tributions to the effect are generally of the same order of magnitude and the effect is very small (the coefficient of proportionality between the polarization and the temperature gradient, known as the thermal polarization coefficient, is of the order of k_B/e , where k_B is the Boltzmann constant).

In the case of a noncentrosymmetric nonferroelectric crystal the ability to separate the contributions depends on the intensity of the phonon-impurity scattering.⁸ If this scattering can be ignored, then all the contributions are of the same order of magnitude exactly as in the preceding case. It was shown by Gurevich⁸ that enhancement of the phonon-impurity scattering increases the kinetic contribution, which reaches its maximum at an approximately 1% concentration of defects, and then decreases on further increase in this concentration. The other contributions are generally dependent on the concentration of defects. Therefore, for the optimal concentration of defects, the kinetic contribution may exceed all the others by one or two orders of magnitude.⁸ This situation is convenient for the determination of the effect (which is then large) and also from the point of view of selection of the most interesting of the contributions which is the kinetic one. However, there is a difficulty involving maintenance of a homogeneous temperature gradient with a high degree of precision so as to avoid the influence of a strong background signal due to the tertiary pyroelectric effect.²⁵

Convenient materials for the investigation of the thermal polarization effect are ferroelectrics firstly because of the large magnitude of the effect and, secondly, because it is possible to separate effectively the surface and bulk contributions. This is demonstrated by the following considerations. The bulk contributions to the effect have an anomaly at a phase transition^{7,9,11} and are approximately a factor of χ (χ is the lattice susceptibility) higher than for ordinary insulators. The contribution associated with the surface flexoelectric effect is unimportant in ferroelectrics since, as pointed out above, the surface flexoelectric effect has no anomalies in the case of ferroelectrics. The question of the anomaly of the contributions to the thermal polarization effect, which is due to the surface pyroelectric and piezoelectric effects, has not been studied systematically, but as shown by Strukov *et al.*³⁵ these contributions are approximately $\chi^{1/2}$ times greater than the bulk contributions in the case of a uniaxial ferroelectric.

6. PHENOMENOLOGICAL DESCRIPTION OF BULK CONTRIBUTIONS TO FLEXOELECTRIC AND THERMAL POLARIZATION EFFECTS

The bulk static flexoelectric effect can be described by analogy with the piezoelectric effect using a term in the expression for the free energy density first proposed by Kogan³:

$$f_{\alpha\beta\gamma\delta} P_{\alpha} \frac{\partial^2 r_{\beta}}{\partial x_{\gamma} \partial x_{\delta}}. \quad (6.1)$$

The bulk dynamic flexoelectric effect (representing the difference between the bulk contributions to the effect in the case of a propagating acoustic wave and a static inhomogeneous strain) cannot obviously be described by introducing new terms in the expansion of the free energy. However, such a description can be provided if we include the term

$$\mu_{\alpha\beta} \dot{P}_{\alpha} \dot{r}_{\beta} \quad (6.2)$$

in the phenomenological expression for the kinetic energy density. In fact, using the standard macroscopic density of a Lagrangian, to which the terms (6.1) and (6.2) are added, we obtain the equation of motion for the polarization

$$\chi_{\alpha\beta}^{-1} \dot{P}_{\beta} = E_{\alpha} - f_{\alpha\beta\gamma\delta} \frac{\partial^2 r_{\beta}}{\partial x_{\gamma} \partial x_{\delta}} - \mu_{\alpha\beta} \dot{r}_{\beta}, \quad (6.3)$$

which corresponds to the above microscopic description of the bulk flexoelectric effect [compare Eq. (3.13) and (4.6)]. A comparison of Eqs. (6.3) and (3.13) and an allowance for Eq. (3.5) gives, in the approximation of rigid ions, the relationship between the phenomenological tensors f and $\hat{\mu}$ and the quantities describing the microscopic properties of the lattice:

$$\begin{aligned} \chi_{\alpha\nu} f_{\nu\beta\gamma\delta} &= -v^{-1} Q_{\nu} N_{\alpha,\nu}^{\beta\gamma\delta}, \\ \chi_{\alpha\beta} \mu_{\beta\gamma} &= -v^{-1} Q_{\nu} G_{\alpha,\nu}^{\gamma}. \end{aligned}$$

As shown in Ref. 28, the tensor μ becomes particularly simple in the case of a diatomic crystal with masses and charges of the ions m_1, Q , and $m_2, -Q$, respectively:

$$\mu_{\alpha\beta} = \frac{\delta_{\alpha\beta} (m_1 - m_2)}{2Q}.$$

In the case of this phenomenological description we may encounter the problem how to relate the phenomenological off-diagonal kinetic energy density to the diagonal form of the kinetic energy usually employed in microscopic calculations. We shall explain this contradiction as follows. The Jacobi coordinates are usually employed in microscopic calculations (see, for example, Ref. 26) and then the coordinate of the center of gravity of a unit cell considered in the long-wavelength limit is identified with the acoustic displacement vector \mathbf{r} . When this definition is used, the microscopic density of the potential energy of a crystal, considered as a function of the normal phonon coordinates \mathbf{P} and of the spatial derivatives of \mathbf{P} and \mathbf{r} , depends on the distribution of the masses of atoms in a unit cell. Clearly, the definition of the potential energy dependent on the distribution of these masses is incorrect. However, this problem is not encountered in lower orders in respect of the spatial dispersion: the elastic constants and piezoelectric moduli exhibited in the classical approximation using this potential energy are independent of the distribution of masses. However, if we calculate the flexoelectric response, this incorrectness is manifested because the static flexoelectric coefficient is found to depend on the distribution of masses in a unit cell. Therefore, in describing the flexoelectric effect we can no longer identify \mathbf{r} with the position of the center of gravity of a unit cell and we have to redefine \mathbf{r} so that the physically meaningless dependence of the static coefficient on the distribution of masses disappears. Clearly, such a redefinition generally makes the kinetic energy off-diagonal. In this situation we can quite justifiably accept off-diagonal terms in the phenomenological expression for the kinetic energy density.

In the phenomenological description of the bulk thermal polarization effect we shall, for the sake of simplicity, consider only a static temperature gradient.

Historically the first to predict a kinetic contribution to the thermal polarization effect was Marvan⁷ and he used a phenomenological approach. Marvan⁷ obtained the rate of increase of the entropy density \dot{S} in the form

$$\dot{S} = -\frac{J_\alpha}{T^2} \frac{\partial T}{\partial x_\alpha} + \frac{E_\alpha - \chi_{\alpha\beta}^{-1} P_\beta}{T} \dot{P}_\alpha, \quad (6.4)$$

where J is the heat flux. Then, he used the Onsager formalism to write down the phenomenological relationships satisfying the principle of symmetry of the transport coefficients:

$$-J_\alpha = -\chi_{\alpha\beta} \frac{\partial T}{\partial x_\beta} + T b_{\alpha\beta} \dot{P}_\beta, \quad (6.5)$$

$$E_\alpha - \chi_{\alpha\beta}^{-1} P_\beta = -b_{\beta\alpha} \frac{\partial T}{\partial x_\beta} + v_{\alpha\beta} \dot{P}_\beta. \quad (6.6)$$

We can readily see that the relationship (6.6) does indeed describe the thermal polarization effect, i.e., the appearance of a polarization proportional to a temperature gradient when the macroscopic field is zero. The relationship (6.5) describes an effect conjugate (in accordance with Onsager) to the thermal polarization, i.e., the existence of a heat flux proportional to the rate of change of the polarization.

The thermodynamic contribution to the thermal polarization effect could naturally be described in terms of a quasiequilibrium free energy density, i.e., the density of that free energy which admits the possibility of a coordinate dependence of the temperature of a sample. Thus, the flexoelectric contribution to the effect can be described¹¹ by introducing a term of the (6.1) type into the expansion for the free energy density. The "nonflexoelectric" part of the thermodynamic contribution, corresponding to terms $u^{(i)}$ in Eq. (5.1), can be described only if we include in this expansion a term of the type³⁵

$$g_{\alpha\beta}(T) \frac{\partial P_\alpha}{\partial x_\beta}.$$

We must draw attention to the fact that this term contributes to the equation of motion of the polarization only in the case of an inhomogeneous temperature distribution in a sample, because otherwise it transforms into a surface integral. On the whole, the thermodynamic contribution to the effect can be written in the form

$$\chi_{\alpha\beta}^{-1} P_\beta = \left[(f_{\alpha\beta\gamma\delta} - 2f_{\alpha\delta\gamma\beta}) a_{\gamma\delta} + \frac{\partial g_{\alpha\beta}}{\partial T} \right] \frac{\partial T}{\partial x_\beta}, \quad (6.7)$$

where \hat{a} is the thermal expansion tensor. In writing down the first term in Eq. (6.7) we used the familiar relationship⁴ between the gradients of the distortion and strain tensors.

We shall conclude this section by drawing attention to the special role of the kinetic contribution to the effect: It corresponds to an inverse effect (in the sense of the Onsager relationships), because a nondissipative heat flux proportional to the rate of change of the polarization appears, whereas the other contributions have no inverse effects. One of the manifestations of the inverse thermal polarization effect is the appearance of an oscillatory (on the time scale) difference between the temperatures at the opposite faces of a crystal when it is subjected to an alternating homogeneous electric field. Near a phase transition in a ferroelectric this effect may be quite easily noticeable. For example, if an electric field of amplitude 1 kV/cm and of 1 MHz frequency is applied to a crystal with a permittivity of the order of 10^4 , the simplest estimates indicate that we can expect an amplitude of a temperature gradient of the order of 0.1 K/cm.

7. CONCLUSIONS

We analyzed the pyroelectric, piezoelectric, and thermal polarization effects by considering first a spatially ho-

mogeneous material and a sample of finite dimensions, and also the piezoelectric and flexoelectric effects in the field of an acoustic wave (using the method of long wavelengths).

The following are the most interesting features from the methodological point of view.

In Sec. 3 it is shown how the use of the widely employed definitions of the polarization described by Eqs. (3.14) and (3.21) may give seriously wrong results in an analysis of the piezoelectric and flexoelectric effects by the method of long wavelengths.

It is shown that in calculating the response of the polarization of a crystal of finite dimensions to a homogeneous change in temperature, a temperature gradient, a homogeneous strain, or a strain gradient, we encounter two classes of terms: 1) the terms dependent on the microscopic characteristic of the crystal lattice, particularly on the matrix of its force constants; 2) the terms dependent only on the distortion tensor and various moments of the distribution of the charge of the whole unperturbed crystal, including the dipole moment, the quadrupole moment defined in a trace-free manner [see Eq. (4.4)], and the quantity I [see Eq. (4.5)] proportional to the trace of the quadrupole moment if it is defined in a manner which includes a trace. The first class of terms represents the bulk contributions to the effect and the second describes the surface or apparent effects which are not observed in the usual measurements. The influence of the apparent effects can be avoided by following rigorously the crystallophysical definitions of the effect. In the case of the pyroelectric and piezoelectric effects it follows from the definitions given by Nye²⁴ that we have to ensure that the dipole moment of a crystal should be zero before the application of thermal or mechanical perturbations. In the case of the flexoelectric and thermal polarization effects it is shown above that a reasonable definition should include zero values of the dipole and quadrupole moments of the original crystal.

The conclusions reached on the apparent contributions to the pyroelectric and piezoelectric effects are fundamentally different from those given by Born and Huang¹⁴ and by Martin.¹⁵ The authors of these theories considered contributions identical with the apparent contributions of Eq. (2.7) as the normal bulk components. We shall show why in our opinion these conclusions of Refs. 14 and 15 are incorrect. The arguments for the cases of the pyroelectric and piezoelectric effects are similar, so that we shall consider only the latter.

The terms which are of the same form as the first two terms in Eq. (2.7),

$$\varepsilon_{\alpha\beta} P_\beta^0 - P_\alpha^0 \varepsilon_{\beta\beta}, \quad (7.1)$$

are written in Refs. 14 and 15 in the form of bulk contributions to the piezoelectric effect. It is therefore assumed that P^0 in the above formula is the spontaneous polarization of a pyroelectric. A clear physical interpretation of these terms is given in Refs. 14 and 15: the former describes the change in the dipole moment of a unit cell because of its deformation within the framework of the elasticity theory, whereas the latter is due to the change in the unit cell volume.

The contribution given by Eq. (7.1) is obtained in Ref. 15 as a result of a microscopic calculation almost identical (in our approximation) to the derivation of Eq. (2.7). The only difference is that an additional modification is made in

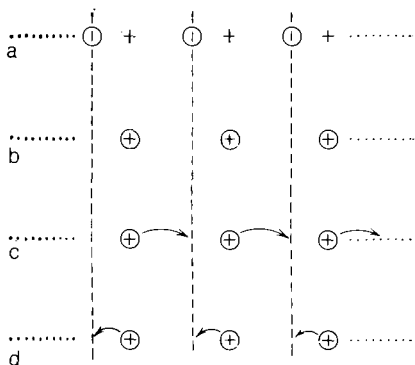


FIG. 5. a) Diatomic chain (configuration *a*); the circle identifies a negative line. b) Hypothetical state of a diatomic chain with zero density of the dipole moment (configuration *b*). c), d) Two methods (out of many) of obtaining the configuration *a* from the configuration *b*.

Ref. 15; the average specific moment of the whole crystal, given by Eq. (2.8), is replaced by the specific dipole moment of a unit cell. However, this replacement is subject to uncontrolled indeterminacy. In fact, after the volume of a crystal is split into whole unit cells, there remains in general a surface macroscopically charged layer, whose contribution to the average moment of a crystal is significant. This additional modification is the source of an error in Ref. 15: as shown in Sec. 2, the sum in Eq. (2.8) according to the definition of the piezoelectric effect should vanish, whereas in Ref. 15 this sum is replaced by a generally nonzero quantity.

In their book Born and Huang¹⁴ postulated the existence of a constant density of the dipole moment P^0 in a pyroelectric when the macroscopic electric field and the mechanical stress are zero. Then, the term of Eq. (7.1) was obtained as the change in the density of the dipole moment of a unit element of volume in the case of elastic deformation and was interpreted as the bulk contribution to the piezoelectric effect. However, the postulate adopted in Ref. 14 that it is possible to introduce a unique constant density of the dipole moment for an unbounded crystal is not satisfied. We shall now demonstrate this.

We shall use the simplest example of a linear diatomic chain to demonstrate indeterminacy of the dipole moment density P^0 . As shown in Fig. 5, a chain of this kind consists of two "subchains" of charges of opposite signs distributed with a period l : the relative shift of the "subchains" is a . First of all, we note that this indeterminacy becomes directly self-evident if we define the density of the dipole moment as the ratio of the dipole moment of a unit cell to its volume (or length). It seems to us methodologically interesting to show how this indeterminacy can be demonstrated also without using the concept of a unit cell.

A method described below can be employed to show that such a chain with fixed values of a , l , and Q (configuration *a*) can have a linear dipole moment density equal to any real number. For the sake of simplicity, we shall show that P^0 can assume the values $Q[-(a/l) + n]$, where n is an arbitrary integer. We shall adopt the following program: 1) we shall vary a and select the state of the chain to which we can ascribe in a natural manner zero value of P^0 ; 2) we shall determine the variations P^0 and δP^0 for an infinitely small change in a ; 3) we shall find the value of P^0 for any state by integration of δP^0 from the state with $P^0 = 0$ and we shall

show that the indeterminacy of P^0 follows from the indeterminacy of the integration path.

1) It is natural to select the state of the lattice with $P^0 = 0$ to be a hypothetical state (configuration *b*) for which the point charges of the opposite signs coincide (Fig. 5b).

2) The change in the average density of the dipole moment δP^0 obtained for a fixed value of l and an infinitesimally small change δa in a gives

$$\delta P^0 = -\frac{Q\delta a}{l}. \quad (7.2)$$

The relationship (7.2) is found by calculating the change in the average density of a dipole moment of any section of a chain of length $\gg l$ (including the case of a crystal which is not electrically neutral as a whole). Therefore, in the derivation of Eq. (7.2) there is no need to split a chain into electrically neutral cells.

3) The method for obtaining configuration *a* from configuration *b* is not the only one possible. Two such methods are shown in Figs. 5c and 5d. Integration of Eq. (7.2) in accordance with these methods readily shows that the first method gives $P^0 = -Qa/l$ and the second $P^0 = Q(l-a)/l$. Obviously, there is an infinitely large number of methods of obtaining the configuration *a* from *b*. It corresponds to the set of P^0 mentioned above.

This program can be easily generalized to the three-dimensional case and the result is still the same: it is not possible to introduce unambiguously the dipole moment density for an infinite medium.

In the case of a bounded crystal the average density of the dipole moment has a unique meaning, but it depends on how the crystal is cut.³⁶ Therefore, clearly the correct interpretation of the terms in Eq. (7.1) containing the quantity P indeterminate for an unbounded medium requires a study of a bounded sample. This was not done in Ref. 14 and in the opinion of the present author this is the reason for the incorrect interpretation of the terms in Eq. (7.1).

It should be noted that the question of existence of the contributions given by Eq. (7.1) to the piezoelectric effect in a pyroelectric crystal is not only of methodological interest, but also because, according to Ref. 15, the contribution of Eq. (7.1), if it exists, should be manifested only for a spatially homogeneous material and, therefore, could be deduced from the difference between the piezoelectric moduli defined for a homogeneous material and the moduli in the presence of a traveling acoustic wave.

After illustrating the impossibility of an unambiguous introduction of the dipole moment density in the case of unbounded crystals, we can naturally ask the question what is the spontaneous polarization of a ferroelectric which, among the infinite number of the values of the dipole moment density, should be ascribed to a given structure. The answer can be obtained by comparing the above discussion with the description of the process of appearance of spontaneous polarization. Its value is determined by the "method" of transition from a nonpolar state in the paraelectric phase to a given ferroelectric state. Since this approach for a given phase transition is always the same, there is no indeterminacy and the spontaneous polarization has a quite definite value. It is important to stress that the spontaneous polarization is strictly speaking a characteristic not of the structure but of the process of formation of this structure from a state

taken as nonpolar. This circumstance is important in theoretical calculations of spontaneous polarization. It was pointed out by Martin³⁷ that knowledge of the distribution of the electron density in a unit cell is generally insufficient for calculation of the spontaneous polarization, because we need to know also how the process of the redistribution of the charge takes place.⁹⁾ The properties of spontaneous polarization as a characteristic of the process of formation of a polar state are manifested also when direct measurements are made: in the course of pyroelectric measurements a crystal is converted to a nonpolar state, whereas in the case of measurements involving polarization reversal in a field, a crystal only passes through a nonpolar state.

Our results on the flexoelectric effect differ greatly from the results of Ref. 4. We shall not discuss their treatment in detail, but simply point out the reasons for the discrepancy. As shown in Sec. 4, a correct analysis of the flexoelectric effect requires a careful separation of the surface, bulk, and apparent contributions. Such a separation was not made in Ref. 4 and, because of the implicit approximations, only the surface and apparent effects were included, but they were regarded as bulk contributions. In such situations it would be natural to expect the results of Ref. 4 to disagree with those given above. We can show that the bulk contributions are not analyzed in Ref. 4 by the following simple means. According to Ref. 4, the flexoelectric tensor is proportional to a linear combination of the quadrupole moment and of the quantity

$$z = \sum_p Q_p x_p^2.$$

We can readily show that these quantities generally depend on the method of selection of a unit cell. For example, in the case of the cell shown in Fig. 1, the sign of z changes from the cell described by 1 to that labeled with 2, whereas the quadrupole moment is zero in both cases. Therefore, the flexoelectric tensor depends on the method used to select the unit cell. Clearly, this flexoelectric tensor cannot describe the bulk effect.

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¹⁾In reality, there are also additional rhombohedral distortions of the germanium and tellurium sublattices in the ferroelectric phase, but these distortions are not of fundamental importance for our analysis. Therefore, for simplicity we assume in what follows that in the ferroelectric phase the GeTe-type lattice is free of such distortions.

²⁾We note that such a replacement is equivalent to a change in the method of selection of the unit cell. This makes it possible to follow the analogy of the paradox formulated in the introduction and the apparent pyroelectric contribution.

³⁾Here and later we shall assume that repeated indices imply summation.

⁴⁾Since we are interested in the response corresponding to $E = 0$, we shall use a matrix of force constants from which the contribution of the macroscopic electric field is excluded.

⁵⁾We note that in this solution the transverse components of the polarization are defined in the usual manner (see, for example, Ref. 27).

⁶⁾Here and later we shall define the quadrupole moment as a trace-free tensor in the normalization corresponding to the definition of $Q_{\alpha\beta}$ (Ref. 29). This definition differs from that used in the preceding section. How-

ever, this should not give rise to any misunderstandings, because we shall use below only one definition and it corresponds to $Q_{\alpha\beta}$.

⁷⁾It should be noted that the constancy of a jump for any part of the surface follows also from the fact that the macroscopic field is zero around and inside the original crystal.

⁸⁾As is known from the theory of elasticity,³⁴ a homogeneous temperature gradient in a free crystal does not give rise to mechanical stresses.

⁹⁾It should be noted that this property, mentioned by Martin, is associated not with the discrete indeterminacy demonstrated above, but with the continuous indeterminacy mentioned earlier. This can be easily demonstrated. It can be done by allowing for the possibility of transfer of fractional parts of Q , for example, $0.2Q$ by the method c and $0.8Q$ by the method d .

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