Effect of a magnetic field on phase transitions in vibronic ferroelectrics

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The effect of a magnetic field on the spontaneous polarization, the soft-mode frequency, and the Curie temperature of a ferroelectric phase transition is considered within the framework of the vibronic theory of ferroelectricity, in which the structural phase transitions are attributed to the cooperative Jahn-Teller pseudoeffect (the mixing of the electronic bands by the transverse optical vibrations). In contrast to previous investigations, the dispersion of the vibronic constants and the mixing of the electronic states by the magnetic field are taken here into account; the influence of these effects on antiferroelectric phase transitions is also analyzed. Estimates in the two-band model show that the Curie-point shift can attain a value of several degrees in 10-T fields, and may have opposite signs in ferro- and antiferroelectrics.

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§1. INTRODUCTION

The electronic-vibrational character of the structural phase transitions that occur in certain classes of crystals has now been reliably established (see, for example, Refs. 1 and 2). These phase transitions have characteristic features due to the important role played by the electron subsystem. In particular, such phase transitions are significantly affected by external fields, which act directly on only the electron subsystem.

Of special interest is the change in the properties of vibronic ferro- and antiferroelectrics in strong magnetic fields. In these crystals the symmetric-lattice-configuration instability that induces the soft mode and the ferroelectric phase transition is due to the strong interband electron-phonon (vibronic) interaction. The possibility of using a magnetic field as a test for the verification of the actuality of the vibronic mechanism of lattice instability in specific compounds was first pointed out in Ref. 3 (see also Ref. 4 for a review). A magnetic-field-induced ferroelectric-phase-transition-temperature shift was first observed indirectly in the compound $Pb_{1-x}Ge_xTe$ by Murase *et al.*[5] The systematic experimental investigation of the effect of a magnetic field directly on the permittivity, the spontaneous polarization, and the Curie temperature of a number of ferro- and antiferroelectrics has just begun.[6-9]

Theoretically, the question of the effect of a magnetic field on the properties of ferroelectric crystals is considered in Refs. 3 and 10–15. In these papers, however, individual particular cases are considered; and, as will be shown below, some of the assumptions used in these papers, in particular, the neglect of the dispersion of the vibronic constant, are not always valid.

In the present paper we derive on the basis of perturbation theory expressions for the quadratic—in the magnetic field—corrections to the ferroelectric characteristics under certain quite general assumptions about the structure of the electronic spectrum and the dispersion of the vibronic constant. These general expressions are analyzed within the framework of the two-band model of the vibronic ferroelectric for a number of actual particular cases. The effect of a magnetic field on antiferroelectric phase transitions is also considered.

§2. CALCULATION OF THE QUADRATIC—IN THE MAGNETIC FIELD—CORRECTIONS TO THE POLARIZATION OPERATOR

We cannot, in considering the effect of a uniform magnetic field H on the electron subsystem of a crystal, use the standard perturbation theory. This is due to the fact that the operator representing the interaction between the uniform magnetic field and the electron subsystem contains explicitly the vector potential, which diverges at large distances. To obviate the complications connected with the occurrence of singular perturbation matrix elements, let us use a method that has been used to analyze the diamagnetic susceptibility of solids.[16,17] Let us consider the behavior of ferroelectrics in an inhomogeneous magnetic field $(H\|z)$ described by the periodic vector potential $\mathbf{A}=(-Hp^{-1}\sin py, 0, 0)$; by passing in the final expressions to the limit $p\to 0$, we obtain the corrections to the ferroelectric characteristics in a homogeneous magnetic field.

The Hamiltonian of a vibronic ferroelectric located in an inhomogeneous magnetic field can be represented in the following form:

$$\mathscr{H}=H_0+H_1+H_2, \tag{1}$$

where H_0 is the Hamiltonian in the absence of external fields and H_1 and H_2 describe the linear and quadratic—in the vector potential—interactions of the electron subsystem with the inhomogeneous magnetic field. The Hamiltonian H_0 is given in the second-quantization representation by the following expression[3]:

$$H_0=\sum_{k,\nu}\varepsilon_k{}^\nu a_k{}^{+\nu}a_k{}^\nu+\sum_q\hbar\omega_q b_q{}^+b_q+\sum_{k,q,\nu,\nu'}B_{k,k-q}^{\nu\nu'}(q)\,a_k{}^{+\nu}a_{k-q}^{\nu'}(b_q+b_{-q}{}^+), \tag{2}$$

where the first two terms describe the energies of the noninteracting electron and phonon subsystem; ε_k^ν and $\hbar\omega_q$ respectively denote the electronic and phonon spectra; $a_k^{+\nu}$ and d_k^ν are respectively the creation and annihilation operators for the electrons in the ν-th band with wave vector k; b_q^+ and b_q are the creation and annihilation operators for the transverse optical pho-

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nons with wave vector q. The last term in (2) describes the interband electron—phonon interaction, $B_{k,k-q}^{\nu\nu'}(q)$ being the vibronic constant, which, in the general case, depends on the incoming and outgoing momenta of the scattered electron.

The operator representing the interaction between the electron subsystem and the inhomogeneous magnetic field has, in the second-quantization representation, the form

$$H_1=-\frac{i\hbar\Omega_c}{2p}\sum_{k,\nu,\nu'}\left(\Gamma_{k,k-p}^{\nu\nu'}a_k^{+\nu}a_{k-p}^{\nu'}-\Gamma_{k,k+p}^{\nu\nu'}a_k^{+\nu}a_{k+p}^{\nu'}\right), \tag{3}$$

$$H_2=\frac{m\Omega_c^2}{8p^2}\sum_{k,\nu,\nu'}\left[2\delta_{\nu\nu'}a_k^{+\nu}a_k^{\nu'}-S_{k,k-2p}^{\nu\nu'}a_k^{+\nu}a_{k-2p}^{\nu'}-S_{k,k+2p}^{\nu\nu'}a_k^{+\nu}a_{k+2p}^{\nu'}\right], \tag{4}$$

where $\Omega_c=eH/mc$ and m is the mass of the free electron. The parameters $\Gamma_{k,k'}^{\nu\nu'}$ and $S_{k,k'}^{\nu\nu'}$ in (3) and (4) are defined by the relations

$$\Gamma_{k,k'}^{\nu\nu'}=k_x'S_{k,k'}^{\nu\nu'}+P_{kk'}^{\nu\nu'}, \tag{5}$$

$$S_{kk'}^{\nu\nu'}=\frac{1}{v_0}\int_{v_0}U_k^{\nu*}U_{k'}^{\nu'}\,dr, \tag{6}$$

$$P_{kk'}^{\nu\nu'}=-\frac{i}{v_0}\int_{v_0}U_k^{\nu*}\frac{\partial}{\partial x}U_{k'}^{\nu'}\,dr, \tag{7}$$

where v_0 is the volume of the unit cell and the U_k^{ν} are the Bloch amplitudes.

Let us consider the renormalization by the magnetic field of the soft-optical-mode frequency, which is given by the expression

$$\Omega_q^2=\omega_q^2[1+\Pi_q]. \tag{8}$$

The polarization operator Π_q can, under the assumption that the electronic bands are nondegenerate and are separated by a gap that significantly exceeds the Debye phonon frequency and the cyclotron quantum, be represented in the form of an expansion in powers of the vibronic constant[18]:

$$\Pi_q=\Pi_q^{(2)}+\Pi_q^{(4)}+\dots, \tag{9}$$

where $\Pi_q^{(2)}$, $\Pi_q^{(4)}$, etc. are respectively the polarization operators of second, fourth, etc. orders in the electron—phonon interaction constant. In the absence of a magnetic field, the second-order polarization operator for a vibronic ferroelectric described by the Hamiltonian H_0 is negative. If we limit ourselves in the expansion (9) to the consideration of the first term, then the symmetric configuration of the system becomes unstable upon the fulfillment of the condition $|\Pi_q^{(2)}|>1$. The temperature dependence of $\Pi_q^{(2)}$ is determined by the temperature dependence of the electronic occupation numbers. Therefore, in systems with wide forbidden bands, i.e., for $E_g\gg kT_c$, the second-order polarization operator practically does not depend on temparature. The fourth-order polarization operator is positive. Its temperature dependence, in contrast to the temperature dependence of $\Pi_q^{(2)}$, is determined by the phonon occupation numbers, a fact which allows us to explain the observed temperature dependence of the phonon spectra of ferroelectrics. As the temperature rises, the stabilizing contribution from $\Pi_q^{(4)}$ increases. If $\Pi_q^{(4)}$ turns out to be equal to $|1+\Pi_q^{(2)}(0)|$ at some temperature $T=T_c$, then the symmetric configuration of the system will be stable at $T>T_c$, i.e., the system will undergo a phase transition from the ferro- into the paraelectric phase.

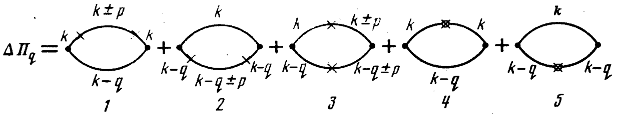

FIG. 1. The diagrams determining the corrections, quadratic in the field and the vibronic interaction, to the polarization operator (the solid circles denote the electron—phonon vertex; the crosses and the crossed open circles, the interactions linear and quadratic in the magnetic field).

The polarization operator changes by an amount $\Delta\Pi_q$ in a magnetic field. Let us assume that the fourth-order polarization operator depends linearly on the temperature in the high-temperature region ($kT>\hbar\omega_q$), and determine the phase transition temperature T_c in a magnetic field from the condition that the soft-mode frequency vanish at this temperature. As a result, we obtain for the relative phase-transition-temperature shift the following expression:

$$\Delta T_c/T_c(0)=-\Delta\Pi_q/|1+\Pi_q^{(2)}(0)|, \tag{10}$$

where $\Delta T_c=T_c(H)-T_c(0)$. Notice that the quantity $|1+\Pi_q^{(2)}(0)|$ is significantly smaller than unity. This circumstance allows us to obtain appreciable shifts in the phase transition temperature for relatively small changes in the polarization operator. Earlier[11] we showed that the magnetic-field-induced corrections to the fourth-order polarization operator contain an additional smallness parameter ($\hbar\omega_0/E_g$) in comparison with the corrections to $\Pi_q^{(2)}$. Therefore, below by $\Delta\Pi_q$ in (10) we shall mean the magnetic-field-induced correction to the second-order polarization operator. Figure 1 shows the diagrams that determine the quadratic—in the magnetic field—corrections to the polarization operator. The diagrams 1 and 2 describe the corrections to the polarization operator that are due to the renormalization by the linear—in the magnetic field—coupling of the electron Green functions. The diagram 3 corresponds to the renormalization of the electron-phonon vertices by this coupling. The diagrams 4 and 5 describe the corrections due to the quadratic—in the magnetic field—interaction H_2. The analytic expression corresponding to these diagrams have the form

$$\Delta\Pi_q=\frac{2T}{\hbar\omega_q}\left(\frac{\hbar\Omega_c}{2p}\right)^2\sum_{i=1}^{5}\left(I_q^i(p)+I_q^i(-p)\right), \tag{11}$$

where

$$I_q^1(p)=\sum_{k,\omega}\mathrm{Sp}[B_{k,k-q}(q)G_{k-q}\Gamma_{k-q,k-q-p}G_{k-q-p}\Gamma_{k-q-p,k-q}G_{k-q}B_{k-q,k}(-q)G_k], \tag{12}$$

$$I_q^2(p)=\sum_{k,\omega}\mathrm{Sp}[B_{k,k-q}(q)G_{k-q}B_{k-q,k}(-q)G_k\Gamma_{k,k-p}G_{k-p}\Gamma_{k-p,k}G_k], \tag{13}$$

$$I_q^3(p)=\sum_{k,\omega}\mathrm{Sp}[B_{k,k-q}(q)G_{k-q}\Gamma_{k-q,k-q-p}G_{k-q-p}B_{k-q-p,k-p}(-q)G_{k-p}\Gamma_{k-p,k}G_k], \tag{14}$$

$$I_q^4(p)=\frac{m}{2\hbar^2}\sum_{k,\omega}\mathrm{Sp}[B_{k,k-q}(q)G_{k-q}^2B_{k-q,k}(-q)G_k], \tag{15}$$

$$I_q^5(p)=\frac{m}{2\hbar^2}\sum_{k,\omega}\mathrm{Sp}[B_{k,k-q}(q)G_{k-q}B_{k-q,k}(-q)G_k^2]. \tag{16}$$

In the expressions (12)–(16) the trace is evaluated with respect to the band indices. The electron Green function G_k is a diagonal matrix with elements $G_k^{\nu\nu}=[i\omega-\varepsilon_k^\nu]^{-1}$, and the elements of the matrices $B_{k,k-q}(q)$ and $\Gamma_{k,k'}$ are defined in (2) and (5) respectively.

The corrections to the polarization operator in a homogeneous field are obtained from the relations (11)–(16) by going over to the limit $p\to 0$. To determine these corrections, let us expand the right members of (12)–(14) in powers of p, limiting ourselves to the terms quadratic in p. Then the sum over i in the formula (11) does not contain zeroth-order terms, since

$$I_q^1(0)+I_q^2(0)+I_q^3(0)=I_q^4(0)+I_q^5(0).$$

This can most easily be verified by going over in the zeroth-order terms from the Bloch representation to the Luttinger-Kohn representation in the same way as was done in the analysis of the diamagnetic susceptibility of solids.[17] There are no terms linear in p because $I_q^i(p)+I_q^i(-p)$ is an even function of p. The quadratic—in p—terms in the expansion of $I_q^i(p)+I_q^i(-p)$ give a correction in a homogeneous field:

$$\Delta\Pi_q={}^1/_2(\Delta\Pi_q{}^+ +\Delta\Pi_q{}^-), \tag{17}$$

where

$$\begin{aligned}\Delta\Pi_q{}^+ =\frac{T(\hbar\Omega_c)^2}{2\hbar\omega_q}\sum_{k,\omega}\mathrm{Sp}\Big\{&B_{k,k-q}(q)\,G_{k-q}B_{k-q,k}(-q)\,G_k\frac{\partial^2}{\partial k_{1y}{}^2}[\Gamma_{k,k_1}G_{k_1}\Gamma_{k_1,k}]\,G_k\\ &+B_{k,k-q}(q)\,G_{k-q}\frac{\partial^2}{\partial k_{1y}{}^2}[\Gamma_{k-q,k_1-q}G_{k_1-q}\Gamma_{k_1-q,k-q}]\,G_{k-q}B_{k-q,k}(-q)\,G_k\\ &+B_{k,k-q}(q)\,G_{k-q}\frac{\partial^2}{\partial k_{1y}{}^2}[\Gamma_{k-q,k_1-q}G_{k_1-q}B_{k_1-q,k_1}(-q)\,G_{k_1}\Gamma_{k_1,k}]\,G_k\Big\}_{k_1=k}.\end{aligned} \tag{17a}$$

The expression for $\Delta\Pi_q^-$ is obtained from (17a) by making the substitution $x\leftrightarrow y$.

To carry out further calculations with this formula without any assumptions about the structure of the electronic spectrum is not quite simple. But it is possible to draw certain conclusions about the mechanisms underlying the effect of a magnetic field on the dielectric properties of polar crystals on the basis of the relations (17). It can be seen from the expressions (10) and (17) that the magnetic-field-induced phase-transition-temperature shift is greatest in compounds whose electronic spectrum, vibronic constant, and $\Gamma_{k,k'}$ matrix (or at least one of these quantities) have large electron-wave-vector derivatives. Notice that it has thus far been assumed[2,10-15] that the effect of a magnetic field on the ferroelectric characteristics is strongest in compounds with small effective masses, i.e., in compounds with large derivatives of the electronic spectrum. In compounds with narrow allowed and wide forbidden bands, the corrections due to the dispersion of the electronic spectrum are small, since each differentiation of the electron Green functions yields an additional smallness parameter, α/Δ, where α is the allowed-band width and Δ is the mean band spacing. Of greater importance in the case of these compounds is the occurrence in them of the dispersion of the vibronic constant and the $\Gamma_{k,k'}$ matrices (if, of course, the derivatives of these quantities are not, for some reasons, equal to zero), since the electron-wave-vector derivatives of these quantities do not provide additional smallness parameters of this type α/Δ.

Let us note another circumstance connected with the fact that the $\Gamma_{k,k'}$ matrix has, generally speaking, off diagonal—in the band indices—elements, which describe the mixing of states from different bands by the magnetic field. Thus, besides the intraband interaction with the field, which is considered in detail in Refs. 2 and 10–15, the interband interaction, which has not been considered before, makes a contribution to the expression (17). If the contribution from the intraband interaction is proportional to the allowed-band width and tends to zero as $\alpha\to 0$, the contribution of the interband mixing does not contain this parameter. In principle, the contribution of this interaction can be nonzero even in compounds with extremely narrow allowed bands. Below we shall show that in a number of cases the interband interaction with the field makes the dominant contribution to the correction to the polarization operator.

§3. ANALYSIS OF THE CORRECTIONS TO THE POLARIZATION OPERATOR IN THE TWO-BAND MODEL

The subsequent analysis of the effect of a magnetic field on ferroelectric phase transitions will be performed within the framework of the two-band model. In this case the matrices $B_{k,k-q}(q)$ and G_k are given by the expressions

$$\hat{G}_k=\begin{pmatrix}[i\omega-\varepsilon_k{}^1]^{-1}, & 0\\ 0, & [i\omega-\varepsilon_k{}^2]^{-1}\end{pmatrix},\quad \hat{B}_{k,k-q}(q)=B_{k,k-q}(q)\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}. \tag{18}$$

3.1. Absence of dispersion of the vibronic constant

A. The intraband contribution. Let us neglect the dependence of the vibronic constant on the incoming and outgoing momenta of the electron scattered on the $B_{k,k-q}(q)\approx B_q$, as well as the off-diagonal—in the band indices—elements of $\Gamma_{k,k'}$. The expression (17) contains, besides the matrices $\Gamma_{k,k'}$, the first and second electron-wave-vector derivatives $\partial^2\Gamma_{k,k'}/\partial k_y'$ and $\partial^2\Gamma_{k,k'}/\partial k_y'^2$ of these matrices. It can be shown that these derivatives are proportional to $\partial^2\varepsilon_k^\nu/\partial k_x\partial k_y$ and $\partial^3\varepsilon_k^\nu/\partial k_x\partial k_y^2$ respectively. In the case of the dispersion law (22) considered below these derivatives are equal to zero. Therefore, only the derivatives of the electron Green functions need be taken in the differentiation with respect to k_y in (17a). Taking account of the fact that $\hbar^2(k_x+P_{kk}^{\nu\nu})=m\partial\varepsilon_k^\nu/\partial k_x$, we obtain for the matrix $\Gamma_{k,k}$ the following expression:

$$\Gamma_{k,k}=\frac{m}{\hbar^2}\begin{pmatrix}\partial\varepsilon_k{}^1/\partial k_x, & 0\\ 0, & \partial\varepsilon_k{}^2/\partial k_x\end{pmatrix}. \tag{19}$$

Using the expressions for the electronic functions, the vibronic constants, and the matrices $\Gamma_{k,k}$, we compute the trace with respect to the band indices in (17), and then perform the summation over ω. As a result, we have for $\Delta\Pi_q^+$ the expression

$$\Delta\Pi_q{}^+ =\frac{(\hbar\Omega_c)^2}{2\hbar\omega_q}B_q{}^2\left(\frac{m}{\hbar^2}\right)^2\sum_k[f_q(k)+f_{-q}(k)], \tag{20}$$

where

$$
\begin{aligned}
f_q(k)={}&\frac{\partial\varepsilon_k^1/\partial k_x}{(\varepsilon_k^1-\varepsilon_{k-q}^2)^4}\left\{\frac{\partial\varepsilon_k^1}{\partial k_x}\left[\frac{\partial^2\varepsilon_k^1}{\partial k_y^2}-2\frac{(\partial\varepsilon_k^1/\partial k_y)^2}{\varepsilon_k^1-\varepsilon_{k-q}^2}\right]\right.\\
&\left.+\frac{\partial\varepsilon_{k-q}^2}{\partial k_x}\left[3\frac{\partial^2\varepsilon_{k-q}^2}{\partial k_y^2}+8\frac{(\partial\varepsilon_{k-q}^2/\partial k_y)^2}{\varepsilon_k^1-\varepsilon_{k-q}^2}-\frac{6}{\varepsilon_k^1-\varepsilon_{k-q}^2}\frac{\partial\varepsilon_k^1}{\partial k_y}\frac{\partial\varepsilon_{k-q}^2}{\partial k_y}\right]\right\}\\
&+\frac{\partial\varepsilon_k^2/\partial k_y}{(\varepsilon_{k-q}^1-\varepsilon_k^2)^4}\left\{\frac{\partial\varepsilon_k^2}{\partial k_x}\left[-\frac{\partial^2\varepsilon_k^2}{\partial k_y^2}-2\frac{(\partial\varepsilon_k^2/\partial k_y)^2}{\varepsilon_{k-q}^1-\varepsilon_k^2}\right]\right.\\
&\left.+\frac{\partial\varepsilon_{k-q}^1}{\partial k_x}\left[-3\frac{\partial^2\varepsilon_{k-q}^1}{\partial k_y^2}+8\frac{(\partial\varepsilon_{k-q}^1/\partial k_y)^2}{\varepsilon_{k-q}^1-\varepsilon_k^2}-\frac{6}{\varepsilon_{k-q}^1-\varepsilon_k^2}\frac{\partial\varepsilon_{k-q}^1}{\partial k_y}\frac{\partial\varepsilon_k^2}{\partial k_y}\right]\right\}. \qquad (21)
\end{aligned}
$$

The expressions (20) and (21) have been derived under the assumption that the valence band is completely filled, while the conduction band is empty.

To evaluate the sums entering into (20), we must make assumptions about the dispersion of the electronic spectrum. Let us consider the correction to the polarization operator in the case when the electronic spectrum is given by the expression

$$\varepsilon_k^{1(2)}=\pm(E_g/2+\hbar^2k^2/2\tilde{m}). \qquad (22)$$

where $\tilde{m}$ is the effective mass. Performing the summation over k in (20), we obtain for $\Delta\Pi_0$ the following expression:

$$
\begin{aligned}
\Delta\Pi_0 &\approx\frac{\pi}{48}\frac{(\hbar\Omega_c)^2}{E_g^{3/2}E_0^{1/2}}=\frac{1}{48\pi^3}\left(\frac{E_0}{E_g}\right)^{3/2}\left(\frac{a}{R}\right)^4, \quad E_g\ll E_0,\\
\Delta\Pi_0 &\approx\frac{2}{5}\frac{E_0}{E_g}\left(\frac{\hbar\Omega_c}{E_g}\right)^2=\frac{2}{5\pi^4}\left(\frac{E_0}{E_g}\right)^3\left(\frac{a}{R}\right)^4, \quad E_g\gg E_0,
\end{aligned}
\qquad (23)
$$

where $E_0=\hbar^2\pi^2/\tilde{m}a^2$, $R^2=c\hbar/He$, and a is the lattice constant. In deriving these relations, we took into account the fact that $|\Pi_0^{(2)}(0)|\approx 1$. The expressions (23) coincide with the results of the earlier calculations,[10-15] in which the Landau basis was used in the case when $\hbar\Omega_c\ll E_0, E_g$.

Generally speaking, the dispersion law (22) is typical only in the vicinity of the extrema of ε_k. The contribution to the polarization operator is determined by the states in the entire Brillouin zone; therefore, it is necessary to use the approximation of ε_k that takes account of the main characteristics of the spectrum over the entire zone. In particular, it is necessary to remember that the derivatives $\partial\varepsilon_k/\partial k_x$ change sign when we go from $k=0$ to $k=\pi/a$. This turns out to be especially important in the analysis of the antiferroelectric transitions induced by the vibronic mixing of the states whose wave vectors differ by π/a. In view of this, let us consider the corrections to the polarization operator in the case when the electronic spectrum is given by the expression

$$\varepsilon_k^{1(2)}=\pm[{}^1/_2\Delta-\alpha(\cos k_xa+\cos k_ya+\cos k_za)]. \qquad (24)$$

The anisotropy of the electronic spectrum (24) gives rise to a situation in which the correction to the polarization operator in a magnetic field depends on the orientation of the magnetic field with respect to the crystallographic axes of the crystal. For an arbitrary orientation of the field the electron-wave-vector derivatives of the matrices $\Gamma_{k,k'}$ in (17a) are generally nonzero, which significantly complicates the final expressions for $\Delta\Pi_q$. We shall consider the simpler situation in which the field is oriented along one of the principal crystallographic axes. In this case the assumptions within the framework of which the expression (20) was derived remain valid. The summation over k in (20) with the spectrum (24) can, when $\alpha\ll\Delta$, easily be performed after expanding $f_q(k)$ in a power series in the ratio α/Δ. As a result, we obtain for $\Delta\Pi_0$ the expression

$$\Delta\Pi_0\cong 2(\alpha/\Delta)^4(a/R)^4. \qquad (25)$$

The terms proportional to $(\alpha/\Delta)^3$ are equal to zero in this case because of the fact that they are proportional to an integral whose integrand is a derivative of a function that is periodic over the Brillouin zone.

The corrections to the polarization operator in the case of nonzero values of the phonon wave vector (the antiferroelectric situation) depend essentially on the mutual orientation of the magnetic field H and the wave vector q. The correction coincides with the expression (25) when the magnetic field is parallel or antiparallel to q. In this case, however, we took into account the fact that $|\Pi_q^{(2)}(0)|\approx 1$, where q is the limiting phonon momentum. When the components of the wave vector q in the plane perpendicular to the field $(H||z)$ are nonzero, the corrections to the polarization operator have the form

$$1)\ \mathbf{q}=(\pi/a,0,\pi l/a)\ \text{ or }\ \mathbf{q}=(0,\pi/a,\pi l/a),\quad \Delta\Pi_q\cong-{}^1/_2(\alpha/\Delta)^4(a/R)^4,$$
$$2)\ \mathbf{q}=(\pi/a,\pi/a,\pi l/a),\quad \Delta\Pi_q\cong 0.$$

The expressions for the corrections to the polarization operator are completely determined by specifying the component $q_\perp$, and does not depend on $q_\parallel$. This is because the magnetic field does not reconstruct the electronic states along the field.

Thus, the intraband corrections to the polarization operator in the absence of dispersion of the vibronic constant stabilize the symmetric configuration of the ferroelectric, and shift the ferroelectric phase transition temperature toward the region of low temperatures. The effect of a magnetic field on antiferroelectric phase transitions in the presence of intraband interaction with the field has a more complicated character. In the final analysis, the sign and magnitude of the effect are determined by the mutual orientation of the magnetic field and the wave vector along which the antiferroelectric ordering occurs.

B. The interband contribution. Let us now consider the question how important the off-diagonal—in the band indices—elements of $\Gamma_{k,k'}$ are in comparison with the intraband interaction, for which purpose we retain only the off-diagonal—in the band indices—elements in the $\Gamma_{k,k'}$ matrix. The dispersions of the $\Gamma_{k,k'}$ matrices and the vibronic constant $B_{k,k-q}(q)$ are interrelated, and are determined by the dispersion of the Bloch amplitudes. Therefore, we must set the electron-wave-vector derivatives of the $\Gamma_{k,k'}$ matrices in (17) equal to zero, assuming that there is no dispersion of the vibronic constant. Using the explicit forms of the vibronic constant, the electron Green functions, and the $\Gamma_{k,k'}$ matrix, we compute the trace with respect to the band indices and perform the summation over ω. The expression thus obtained for $\Delta\Pi_q$ for arbitrary q has quite an unwieldy form. The expression for the correction to the polarization operator is significantly simpler in the case of ferroelectric phase transitions ($q=0$):

$$\Delta\Pi_0^+=\frac{2B_0^2}{\hbar\omega_0}(\hbar\Omega_c)^2\sum_k\frac{|P_{k,k}^{12}|^2}{(\varepsilon_k^1-\varepsilon_k^2)^4}\left\{-3\frac{\partial^2\varepsilon_k^1}{\partial k_y^2}+3\frac{\partial^2\varepsilon_k^2}{\partial k_y^2}+\frac{1}{\varepsilon_k^1-\varepsilon_k^2}\left[\left(\frac{\partial\varepsilon_k^1}{\partial k_y}\right)^2+\left(\frac{\partial\varepsilon_k^2}{\partial k_y}\right)^2\right]-\frac{6}{\varepsilon_k^1-\varepsilon_k^2}\frac{\partial\varepsilon_k^1}{\partial k_y}\frac{\partial\varepsilon_k^2}{\partial k_y}\right\}. \tag{26}$$

Let us analyze this expression further, using the *f*-sum rule[19]:

$$\frac{\partial^2\varepsilon_k^\nu}{\partial k_x^2}=\frac{\hbar^2}{m}+2\frac{\hbar^4}{m^2}\sum_{\mu\neq\nu}\frac{|P_{k,k}^{\mu\nu}|^2}{\varepsilon_k^\nu-\varepsilon_k^\mu}. \tag{27}$$

The dominant contribution to the sum over μ in the relation (27) is made by the states close in energy to ε_k^ν. Within the framework of the two-band model, the dominant contribution will be connected with the transitions between the conduction and valence bands, i.e., between the bands, the interband electron-phonon mixing of which leads to the instability of the symmetric configuration of the system. Taking account of the foregoing, we obtain from the relation (27) for $|P_{k,k}^{12}|^2$ the following expression:

$$|P_{k,k}^{12}|^2\approx\frac{m^2}{4\hbar^4}(\varepsilon_k^1-\varepsilon_k^2)\left(\frac{\partial^2\varepsilon_k^1}{\partial k_x^2}-\frac{\partial^2\varepsilon_k^2}{\partial k_x^2}\right). \tag{28}$$

This relation is fulfilled with a good degree of accuracy in compounds with a narrow forbidden band.[19] Substituting (28) into (26), we obtain for $\Delta\Pi_0$ the expression

$$\Delta\Pi_0=-\frac{3B_0^2}{2\hbar\omega_0R^4}\sum_k\left[\frac{\partial^2\varepsilon_k^1}{\partial k_x^2}-\frac{\partial^2\varepsilon_k^2}{\partial k_x^2}\right]\left[\frac{\partial^2\varepsilon_k^1}{\partial k_y^2}-\frac{\partial^2\varepsilon_k^2}{\partial k_y^2}\right](\varepsilon_k^1-\varepsilon_k^2)^{-3}+O\left(\frac{\alpha^4}{\Delta^4}\right). \tag{29}$$

In the case when the electronic spectrum is given by the expression (22), it is easy to obtain the following approximate expression for $\Delta\Pi_0$:

$$\begin{aligned}\Delta\Pi_0&\approx-\frac{3}{32\pi^3}\left(\frac{E_0}{E_g}\right)^{3/2}\left(\frac{a}{R}\right)^4, \quad E_g\ll E_0,\\ \Delta\Pi_0&=-\frac{3}{2\pi^4}\left(\frac{E_0}{E_g}\right)^2\left(\frac{a}{R}\right)^4, \quad E_g\gg E_0.\end{aligned} \tag{30}$$

It can be seen from this that the dependence of the correction $\Delta\Pi_0$ on the parameters of the spectrum in compounds with narrow forbidden bands is the same as in the case of the intraband interaction, but the numerical coefficient is almost five times greater. In compounds with wide forbidden bands, the magnetic-field-induced correction to the polarization operator contains the square of the small parameter E_0/E_g, whereas in the case of the intraband interaction the correction is proportional to the cube of this parameter. The sign of the correction is negative. This means that the interband interaction with the magnetic field increases the instability in the system, and shifts the ferroelectric phase transition temperature toward the high-temperature region.

3.2. Allowance for the dispersion of the vibronic constant

A. The intraband contribution. To analyze this situation, let us neglect in the expression (17) the wave-vector derivatives of the electron Green functions and the constants $\Gamma_{k,k'}$ and, furthermore, retain only the diagonal—in the band indices—elements in the $\Gamma_{k,k'}$ matrix. Then for $\Delta\Pi_q$ we easily obtain the following expression

$$\Delta\Pi_q^+=\frac{1}{\hbar\omega_qR^4}\sum_k B_{k,k-q}(q)\frac{\partial^2}{\partial k_y^2}(B_{k-q,k}(-q))\times\left[\frac{(\partial\varepsilon_k^1/\partial k_x)(\partial\varepsilon_{k-q}^2/\partial k_x)}{(\varepsilon_k^1-\varepsilon_{k-q}^2)^3}+\frac{(\partial\varepsilon_{k-q}^1/\partial k_x)(\partial\varepsilon_k^2/\partial k_x)}{(\varepsilon_{k-q}^1-\varepsilon_k^2)^3}\right]. \tag{31}$$

The electron-wave-vector derivative of the vibronic constant entering into the relation (31) can be estimated, using the expressions obtained in Ref. 20 for $B_{k,k-q}(q)$ in the tight-binding approximation. If we limit ourselves in the expressions for $B_{k,k-q}(q)$ to the consideration of the interaction with the immediate surroundings, then we obtain for the second derivative of the vibronic constant the expression

$$\partial^2(B_{k,k-q}(q))/\partial k_y^2\approx-a^2B_{k,k-q}(q).$$

For the subsequent estimates of the correction to the polarization operator, the dispersion of the vibronic constant is no longer so important. Therefore, in computing the sum over k in (31), we replace $|B_{k,k-q}(q)|^2$ by some mean value B_q^2. Using the electronic spectrum given by the expression (24), we obtain for $\Delta\Pi_q$ (for $\alpha\ll\Delta$) the expressions

$$\Delta\Pi_q|_{q=0}=\frac{1}{4}\left(\frac{\alpha}{\Delta}\right)^2\left(\frac{a}{R}\right)^4, \quad \Delta\Pi_q|_{q=\pi/a}=-\frac{1}{4}\left(\frac{\alpha}{\Delta}\right)^2\left(\frac{a}{R}\right)^4. \tag{32}$$

Hence it is clear that, in the case of narrow allowed and wide forbidden bands, the corrections to the polarization operator in the presence of dispersion of the vibronic constant and intraband interaction with the field are significantly greater than the intraband corrections in the absence of dispersion of $B_{k,k-q}(q)$, since they contain only the square of the small parameter α/Δ. The corrections in the case of ferro- and antiferroelectrics are opposite in sign. This is due to the fact that the derivative product $(\partial\varepsilon_k^1/\partial k_x)(\partial\varepsilon_{k-q}^2/\partial k_x)$ in (31) changes sign on going from $q=0$ to $q=\pi/a$.

B. The interband contribution. Let us consider the situation in which the allowed-band widths are significantly smaller than the energy distance between the bands. In this case we can neglect the diagonal—in the band indices—$\Gamma_{k,k'}$-matrix elements, which are proportional to the allowed-band widths. Furthermore, let us neglect the derivatives of the electron Green functions in (17), since the differentiation of G_k yields an additional smallness parameter (α/Δ). With allowance for the foregoing, we compute the trace with respect to the band indices, and perform the summation over ω in (17a). As a result, we obtain the following expression for $\Delta\Pi_q$:

$$\begin{aligned}\Delta\Pi_q^+=\frac{(\hbar\Omega_c)^2}{\hbar\omega_q\Delta^3}\sum_k\Big\{&B_{k,k-q}(q)\frac{\partial^2}{\partial k_{1y}^2}[B_{k_1-q,k_1}(-q)\\&\times(\Gamma_{k-q,k_1-q}^{12}\Gamma_{k_1,k}^{12}+\Gamma_{k-q,k_1-q}^{21}\Gamma_{k_1,k}^{21})]+|B_{k,k-q}(q)|^2\\&\times\frac{\partial^2}{\partial k_{1y}^2}[\Gamma_{k,k_1}^{12}\Gamma_{k_1,k}^{21}+\Gamma_{k,k_1}^{21}\Gamma_{k_1,k}^{12}+\Gamma_{k-q,k_1-q}^{12}\Gamma_{k_1-q,k-q}^{21}+\Gamma_{k-q,k_1-q}^{21}\Gamma_{k_1-q,k-q}^{12}]\Big\}_{k_1=k}.\end{aligned} \tag{33}$$

Here we neglected the dispersion of the electronic spectrum, replacing the energy denominators by the mean distance Δ between the bands.

For further analysis of the expression (33) we need to know the dependence of the vibronic constant and the $\Gamma_{k,k'}$-matrix elements on the electron wave vector. These dependences can be established in the tight-binding approximation if we have specified the symmetry of the crystal lattice and the structure of the atomic states from which the bands active in the phase transition are derived. Such an analysis shows that the correction to the polarization operator in the case of ferroelectric phase transitions is negative and equal in order of magnitude to

$$\Delta\Pi_0 \cong -\frac{E_p E_0}{\Delta^2}\left(\frac{a}{R}\right)^4, \tag{34}$$

where $E_p = \hbar^2 P_{12}^2/m$ and P_{12} is the band-averaged value of the interband matrix element of the momentum operator P^{12}. Notice that the parameter $E_p E_0/\Delta^2$ can be greater than unity.

§4. CONCLUSION

It follows from the above-performed analysis that a magnetic field should be expected to have an appreciable effect on ferro- and antiferroelectric phase transitions when there is strong dispersion of the electronic spectrum and (or) the vibronic constants and the matrix elements of the momentum operator, which dispersion is determined by the dispersion of the Bloch amplitudes. In compounds with narrow forbidden and wide allowed bands, the dominant contribution to the second-order polarization operator is made by the states close to the forbidden band. The dispersion of the spectrum in this interval is strong, whereas that of the Bloch amplitudes is weak. In compounds with wide forbidden and narrow allowed bands, the contribution to the polarization operator is made by the states in the entire Brillouin zone. The dispersion of the electronic spectrum in this case is weak, while that of the Bloch amplitudes is strong. Thus, in compounds with $E_0 \gg E_g$, the dominant mechanism underlying the effect of a magnetic field on the dielectric properties of polar crystals is connected with the interband interaction with the field and the strong dispersion of the electronic spectrum (Subsec. 3.1B). In compunds with $E_0 \ll E_g$, the dominant contribution to the correction to the polarization operator is determined by the interband interaction with the field and the dispersion of the vibronic constant of the matrix elements of the momentum operator (Subsec. 3.2B).

The conclusion concerning the relative actuality of the interband interactions with the field can be drawn on the basis of the following arguments. Since the stability of the symmetric configuration of the system is due to the interband electron-phonon coupling, irrespective of the intraband and interband interactions with the field, the correction to the polarization operator contains one and the same power of the energy gap in the denominator (the cases 3.1A, 3.1B and 3.2A, 3.2B). In this situation the question which interaction makes the dominant contribution to the correction $\Delta\Pi_q$ reduces to the question of the relative magnitude of the intraband and interband matrix elements of the perturbation. In compounds with narrow forbidden and wide allowed bands this relation is most easily understood within the framework of the $\mathbf{k}\cdot\mathbf{p}$ method, in which the dispersion of the electronic spectrum is determined by the interband matrix element P_{12} of the momentum operator. In this case it turns out that both the intraband and interband interactions with the field are proportional to P_{12}, but the intraband matrix elements of the perturbation contain a coefficient of the type

$$\hbar^2 P_{12} k/m[E_g{}^2 + (\hbar^2 P_{12} k/m)^2]^{1/2} < 1.$$

It can be shown that the interband interaction predominates over the intraband interaction in compounds with narrow allowed bands as well because of the smallness of the allowed-band width. Indeed, as a comparison of the expressions obtained above for $\Delta\Pi_q$ shows, the greatest T_c shifts occur in the situations 3.1B and 3.2B. It follows from the formulas (30) and (34) that $\Delta\Pi_q$ is of the order of $(a/R)^4$ in these cases. It follows from this that, in fields of intensity 10 T, the relative phase transition temperature shifts range from 0.1 to 1% ($a \sim 4$ Å, $|1+\Pi_0^{(2)}| \sim 10^{-2}-10^{-3}$). The absolute shifts can then attain values of several degrees.

The general expression (17) for the correction to the polarization operator was derived in the quadratic—in the magnetic field—approximation. It is clear that this does not impose any serious limitations on the field strength. Indeed, the expressions obtained are the first terms of the expansion of the polarization operator in a power series in the ratio $(a/R)^4$, and for the attainable field intensities $10-10^2$ T this parameter is significantly smaller than unity.

Notice, however, that the electron (hole) gas in compounds with a high concentration of free electrons (holes) is degenerate in sufficiently high fields. The corrections to the polarization operator then have an oscillatory component as a result of the passage of the Landau level through the Fermi surface. Experimentally, this effect has apparently been observed in the compound $Pb_{1-x}Sn_xTe$ in fields of intensity higher than 8 T (Ref. 5). The analysis performed allows an adequate description of the monotonic component ($\sim H^2$) of the correction; the analysis of the oscillatory effects requires approximations of higher orders in the field.

Furthermore, we neglected the possibility degeneracy and Zeeman splitting of the bands. It is not difficult to show that allowance for the degeneracy in the determination of the integrated—over the electronic spectrum—corrections to Π_q leads to a change in the final results equal to $(k_0 a)^3$, where k_0 is the dimension of that region in k space where the cyclotron quantum is either greater than, or equal to, the band spacing. Allowance for the Zeeman splitting of the bands may turn out to be important in the case when the g factors in the conduction and valence bands are opposite in sign and the spin splitting of the bands is greater than the cyclotron quantum. This effect is considered in Ref. 15, and used to explain the shift, experimentally observed in the compound $Pb_{1-x}Ge_xTe$, of the phase transition temperature toward the region of high temperatures. This explanation cannot be considered to be satisfactory, since in the lead chalcogenides the observed values of the spin splitting of the bands are roughly two times smaller than the cyclotron quantum.[21] The shift of the phase transition temperature toward the high-temperature region in these compounds should apparently be interpreted with allowance made for the above-considered mixing of states from different bands by the magnetic field (Subsec. 3.1B).

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