Effect of conduction-electron band structure on the phonon spectrum of a metal

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The effect of coherent restructuring of the energy spectrum of conduction electrons on the phonon spectrum of transition metals is analyzed. Using a representation of the dynamic matrix in terms of the generalized susceptibility, a convenient procedure of calculating the dispersion curves with allowance for the band structure is proposed. The scale of the band corrections to the polarizability is established on the basis of a simple band model of the electron energy spectrum; the order of magnitude of these corrections does not exceed the (3/2) power of the energy gap. The band structure influences most strongly the acoustic region of the phonon spectrum. It is found that the sound velocity can become considerably renormalized if the Fermi level lands in certain phase-space regions within the band gap. The results are confirmed by concrete calculations of the group velocities of phonons in aluminum and cadmium, and agree well with the available experimental data.

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1. INTRODUCTION

The recent progress in the study of the properties of transition metals is closely related to the multiparticle perturbation theory in terms of the electron-ion interaction. This approach is particularly effective in an analysis of the phonon spectra of metals with simultaneous determination of their static properties under identical approximations (see, e.g., Ref. 1). It was found that the electrons play a substantial role in the formation of the phonon spectrum, and determine both the spectrum as a whole and the appearance of singularities peculiar only to metals. These singularities are connected with the abrupt edge of the electron distribution in momentum space, which leads to a certain Kohn anomaly in the phonon spectrum when account is taken of the paired indirect interaction of the ions via the conduction electrons,[2] and to multiparticle singularities when the nonpair indirect interaction is taken into account.[1,3]

Until recently, coherent restructuring of the electron energy spectrum near the faces of the Brillouin zone (BZ) were not taken explicitly into account in the multiparticle theory of metals. In most cases, the influence of the BZ on the metal properties integrated over the electron states, at $\tilde{V}_{\mathbf{G}} \ll 1$, $\tilde{V}_{\mathbf{G}} = V_{\mathbf{G}}/\varepsilon_F$ ($V_{\mathbf{G}}$ is the Fourier component of the electron-ion potential and is calculated at point $\mathbf{G}$ of the reciprocal lattice, while ε_F is the Fermi energy) is negligible compared with the smoothed allowance for the change of the spectrum and density, a change typical of the multiparticle perturbation theory.

There exist, however, definite situations wherein the fine structure of the phonon spectrum may turn out to be quite sensitive to the restructuring of the electron spectrum near the faces of the BZ. This pertains primarily to multiparticle singularities and to the ensuing Kohn anomalies of nondiametral type. Both types of singularity are localized in the same region of phonon wave-vector values (see below). This raises the question of their relative contribution to the fine structure of the phonon spectrum. As will be shown presently, the contribution of the nondiametral Kohn anomaly is always small compared with the contribution of the non-pair interaction.[1,3,15] It is just this circumstance which predetermined the possibility of observing it directly in aluminum.[4]

Of particular importance is the electron-spectrum restructuring near the BZ edges, which leads to vanishing of parts of the Fermi surface over definite faces (in the extended-band scheme). In this case there appears in the phonon spectrum an anomaly corresponding to the wave vector $\mathbf{q}$ which is a multiple of the reciprocal-lattice vector $\mathbf{G}$; this is equivalent to the onset of a unique Kohn anomaly in the sound. Although this anomaly does not lead to a divergence, in view of the finite energy gap in the electron spectrum, it turns out to be strong enough to change the speed of sound by an amount of the order of its value. This anomaly was recently observed in an experimental investigation of the group velocity of phonons in cadmium,[5] where the situation noted above is realized precisely for one of the face types.

In the analysis of the phonon-spectrum fine structure due to restructuring, near the BZ faces, of both the energy spectrum and the electron wave functions, it is necessary to go outside the framework of perturbation theory. One can use here the known representation of the dynamic matrix in terms of the generalized susceptibility of the electron subsystem (see, e.g., Ref. 6), using for the explicit determination of the latter an iteration procedure with allowance for the small parameter $\tilde{V}_G$. As a result we obtain a relatively simple representation that goes over directly, if the coherent restructuring of the electron spectrum is neglected, into the known perturbation-theory expression. The dynamic matrix obtained thereby permits not only to determine the properties of the singularities in the phonon spectrum, but actually analyze the scale of the infiuence of the band structure on the

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spectrum in the entire region in which the wave vectors are defined.

2. DYNAMIC MATRIX

It is known (see, e.g., Ref. 1) that for nontransition metals one can represent the dynamic matrix, assuming validity of the adiabatic approximation, as a sum of contributions of the direct and indirect ion-ion interactions:

$$D^{\alpha\beta}(\mathbf{q}) = D_i^{\alpha\beta}(\mathbf{q}) + D_e^{\alpha\beta}(\mathbf{q}) \tag{2.1}$$

(α and β are Cartesian indices). We shall not indicate the sublattice indices, assuming for simplicity a monatomic lattice. Taking the translational symmetry into account, it is convenient to represent each contribution in the form

$$D^{\alpha\beta}(\mathbf{q}) = \overline{D}^{\alpha\beta}(\mathbf{q}) - \overline{D}^{\alpha\beta}(0). \tag{2.1a}$$

The most important is the electron contribution to the dynamic matrix; it is expressed in the general case in terms of the generalized susceptibility χ (the response function) of the electron gas (see, e.g., Ref. 6)

$$\overline{D}_e^{\alpha\beta}(\mathbf{q}) = \frac{1}{MN}\sum_{\mathbf{G}_1\mathbf{G}_2} (\mathbf{q}+\mathbf{G}_1)^{\alpha}(\mathbf{q}+\mathbf{G}_2)^{\beta} V_{\mathbf{q}+\mathbf{G}_1} V_{-\mathbf{q}-\mathbf{G}_2} \chi \times (\mathbf{q}+\mathbf{G}_1, \mathbf{q}+\mathbf{G}_2). \tag{2.2}$$

Here M is the mass of the atom and N is the number of atoms in the crystal. The matrix of the response function that connects the induced electron density with the external potential is given by[7]

$$\chi(\mathbf{k}_1, \mathbf{k}_2) = \sum_{n\neq 0} \frac{\langle 0|\exp(-i\mathbf{k}_1\mathbf{r})|n\rangle\langle n|\exp(i\mathbf{k}_2\mathbf{r})|0\rangle}{E_0 - E_n}, \tag{2.3}$$

where E_n and $|n\rangle$ are the exact energy and exact wave function of the n-th state of the multielectron system. It will be more convenient to work with the irreducible part (polarizability $\tilde{\chi}$) of a generalized susceptibility defined by the Dyson equation

$$\chi(\mathbf{k}_1, \mathbf{k}_2) = \tilde{\chi}(\mathbf{k}_1, \mathbf{k}_2) + \sum_{\mathbf{k}'} \tilde{\chi}(\mathbf{k}_1, \mathbf{k}') v_{\mathbf{k}'} \chi(\mathbf{k}', \mathbf{k}_2), \tag{2.4}$$

where $v_{\mathbf{k}} = 4\pi e^2/k^2\Omega$ (Ω is the volume of the crystal). The simplest approximation for the polarizability is that of Hartree

$$\tilde{\chi}_0(\mathbf{k}_1, \mathbf{k}_2) = 2\sum_{\mathbf{p},\mathbf{p}'} \frac{n_{\mathbf{p}} - n_{\mathbf{p}'}}{\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{p}'}} \langle \mathbf{p}|\exp(-i\mathbf{k}_1\mathbf{r})|\mathbf{p}'\rangle\langle \mathbf{p}'|\exp(i\mathbf{k}_2\mathbf{r})|\mathbf{p}\rangle, \tag{2.5}$$

where $|\mathbf{p}\rangle$ is a one-electron state with energy ε_p, and n_p are the occupation numbers. If the electron-electron interaction is taken into account in the local-field approximation, as in the calculation of multipoles in perturbation theory (see Ref. 1), we have directly

$$\tilde{\chi}(\mathbf{k}, \mathbf{k}) \approx T(\mathbf{k})\tilde{\chi}_0(\mathbf{k}, \mathbf{k}), \tag{2.6}$$

$$\tilde{\chi}(\mathbf{k}_1, \mathbf{k}_2) \approx T(\mathbf{k}_1)\tilde{\chi}_0(\mathbf{k}_1, \mathbf{k}_2)T(\mathbf{k}_2), \quad \mathbf{k}_1 \neq \mathbf{k}_2; \tag{2.7}$$

$$T(\mathbf{k}) = [1 + v_{\mathbf{k}} f(\mathbf{k})\tilde{\chi}_0(\mathbf{k}, \mathbf{k})]^{-1}. \tag{2.8}$$

Here $f(\mathbf{k})$ is a function that takes effectively into account the exchange and correlation interelectron interaction in the local approximation. Substituting (2.6) and (2.7) in (2.4), we transform the Dyson equation for χ into

$$\chi(\mathbf{k}, \mathbf{k}) = \frac{\tilde{\chi}_0(\mathbf{k}, \mathbf{k})}{\tilde{\varepsilon}(\mathbf{k})} + \frac{1}{\tilde{\varepsilon}(\mathbf{k})}\sum_{\mathbf{k}'\neq\mathbf{k}} \tilde{\chi}_0(\mathbf{k}, \mathbf{k}') T(\mathbf{k}') v_{\mathbf{k}'} \chi(\mathbf{k}', \mathbf{k}), \tag{2.9}$$

$$\chi(\mathbf{k}_1, \mathbf{k}_2) = \frac{\chi_0(\mathbf{k}_1, \mathbf{k}_2)}{\tilde{\varepsilon}(\mathbf{k}_1)\tilde{\varepsilon}(\mathbf{k}_2)} + \frac{1}{\tilde{\varepsilon}(\mathbf{k}_1)}\sum_{\mathbf{k}'\neq\mathbf{k}_1,\mathbf{k}_2} \tilde{\chi}_0(\mathbf{k}_1, \mathbf{k}') T(\mathbf{k}') \times v_{\mathbf{k}'} \chi(\mathbf{k}', \mathbf{k}_2) + \frac{\tilde{\chi}_0(\mathbf{k}_1, \mathbf{k}_2)}{\tilde{\varepsilon}(\mathbf{k}_1)\tilde{\varepsilon}(\mathbf{k}_2)} T(\mathbf{k}_2) v_{\mathbf{k}_2} \sum_{\mathbf{k}'\neq\mathbf{k}_2} \tilde{\chi}_0(\mathbf{k}_2\ \mathbf{k}') T(\mathbf{k}') v_{\mathbf{k}'} \chi(\mathbf{k}', \mathbf{k}_2). \tag{2.10}$$

The function $\tilde{\varepsilon}$ is defined in the usual manner:

$$\tilde{\varepsilon}(\mathbf{k}) = 1 - v_{\mathbf{k}}(1 - f(\mathbf{k}))\tilde{\chi}_0(\mathbf{k}, \mathbf{k}). \tag{2.11}$$

When the parameter $\tilde{V}_G$ tends to zero, only the first term of the right-hand side of (2.9) remains, and

$$\tilde{\chi}_0(\mathbf{k}, \mathbf{k}) = -\Omega\pi_0(\mathbf{k}), \tag{2.12}$$

where $\pi_0(\mathbf{k})$ is the known Lindhard function. The next term of the expansion of $\chi(\mathbf{k},\mathbf{k})$ is quadratic in the parameter $\tilde{V}_G$.

Expansion of the off-diagonal elements of the generalized susceptibility begins with the term that is linear in $\tilde{V}_G$ and is connected with the first term in (2.10). In this limit (see Sec. 3) we obtain

$$\tilde{\chi}_0(\mathbf{k}, \mathbf{k}+\mathbf{G}) = 6\Omega \frac{V_{\mathbf{G}}}{\tilde{\varepsilon}(\mathbf{G})} \Lambda_0^{(3)}(\mathbf{k}, -\mathbf{k}-\mathbf{G}, \mathbf{G}), \tag{2.13}$$

where $\Lambda_0^{(3)}$ is a three-pole—a simple ring diagram with three external-field ends (see Ref. 1). For $\chi(\mathbf{k}_1,\mathbf{k}_2)$ the next terms of the series are also quadratic in $\tilde{V}_G$.

The presence of a small parameter $\tilde{V}_G$ typical of nontransition metals makes it possible to make effective use of an iteration procedure for the solution of Eqs. (2.9) and (2.10). If the resultant series is substituted in (2.2) and if ε_p and $|\mathbf{p}\rangle$ are replaced in $\tilde{\chi}$ (2.5) by expressions derived within the framework of the one-electron perturbation theory, we obtain, taking (2.8) and (2.11) into account, the previously obtained representation for the dynamic matrix in the form of a series in the indirect multi-ion interaction (see, e.g., Ref. 1).

For most nontransition metals it suffices to retain the first terms of (2.9) and (2.10), whose contributions to the dynamic matrix (2.2) are equivalent to $\overline{D}_e^{(2)}$ and $\overline{D}_e^{(3)}$ in multiparticle perturbation theory.[1] In comparison with the latter, however, it becomes possible to take into account the correct structure of the spectrum and of the wave functions of the electrons, and to analyze the influence of the coherent restructuring of the electron spectrum near the faces of the BZ on the singularities of the phonon spectrum, as well as in general on the formation of the fine structure of the dispersion curves. It is clear from (2.2), (2.9), (2.10), and (2.8) that this influence is directly connected with the properties of the polarizability $\tilde{\chi}_0$ (2.5). We shall pay principal attention hereafter to the analysis of this function.

3. POLARIZABILITY OF A METAL IN THE BAND MODEL

In a regular crystal, the one-electron wave function can be represented in the form

$$|\mathbf{p}\rangle = \frac{C_\mathbf{p}}{\Omega^{1/2}} \sum_\mathbf{G} \alpha_\mathbf{p}(\mathbf{G}) \exp(i(\mathbf{p}-\mathbf{G})\mathbf{r}), \quad \alpha_\mathbf{p}(0)=1. \tag{3.1}$$

The band index is not indicated here, as in the model of expanded bands. In (3.1) we have separated the normalization factor

$$|C_\mathbf{p}|^2 = \left(\sum_\mathbf{G} |\alpha_\mathbf{p}(\mathbf{G})|^2 \right)^{-1}. \tag{3.2}$$

Substituting (3.1) in (2.5) we obtain directly an explict expression for the polarizability

$$\tilde{\chi}_0(\mathbf{k}, \mathbf{k}+\mathbf{G}) = 2 \sum_{\mathbf{p},\mathbf{G}_1} \frac{n_\mathbf{p} - n_{\mathbf{p}+\mathbf{k}+\mathbf{G}_1}}{\varepsilon_\mathbf{p} - \varepsilon_{\mathbf{p}+\mathbf{k}+\mathbf{G}_1}} \Big[|C_\mathbf{p}|^2 |C_{\mathbf{p}+\mathbf{k}+\mathbf{G}_1}|^2$$
$$\times \Big(\sum_{\mathbf{G}'} \alpha_\mathbf{p}^*(\mathbf{G}') \alpha_{\mathbf{p}+\mathbf{k}+\mathbf{G}_1}(\mathbf{G}'+\mathbf{G}_1) \Big)$$
$$\times \Big(\sum_{\mathbf{G}''} \alpha_\mathbf{p}(\mathbf{G}''+\mathbf{G}) \alpha_{\mathbf{p}+\mathbf{k}+\mathbf{G}_1}^*(\mathbf{G}''+\mathbf{G}_1) \Big) \Big]. \tag{3.3}$$

Before we proceed to analyze the polarizability, we note that the calculation of $\tilde{\chi}_0$ in the representation (3.3) can be carried out in principle if one knows the one-electron energies ε_p and the coefficients $\alpha_p(\mathbf{G})$ of the expansion of the wave function (3.1), which are obtained from the solution of a system of linear equations of high order. It is easy to show, however, that the momentum space region connected with the immediate vicinity of the intersection of several BZ faces, where waves with different $\mathbf{G}$ interfere (see (3.1)) and accordingly two and more coefficients $\alpha_p(\mathbf{G})$ are simultaneously of the order of unity, is proportional to $\tilde{V}_G^2$ at the edges of the BZ and to the cube of this parameter at the vertices of the BZ. In the principal region in which $\mathbf{p}$ is defined we have $\alpha_p(\mathbf{G}) \propto \tilde{V}_G$. In the general case, therefore, the contribution to (3.3) from the interference regions will be smaller at most by a factor $\tilde{V}_G^{-1}$ than from the coherent restructuring of the electronic states in the vicinity of each face of the BZ.

It follows therefore that a reasonable model for the analysis of band effects in the dynamic problem at $\tilde{V}_G \ll 1$ is one in which the one-electron energy and the wave function in the vicinity of each BZ face corresponding to the vector $\mathbf{G}$ are determined only by the value of V_G. The electron dispersion law can then be represented in the form

$$\varepsilon_\mathbf{p} \approx \varepsilon_\mathbf{p}^{(0)} + \sum_{\mathbf{G}\neq 0} \Delta\varepsilon_\mathbf{p}(\mathbf{G}), \quad \varepsilon_\mathbf{p}^{(0)} = {}^1/_2 p^2, \tag{3.4}$$

$$\Delta\varepsilon_\mathbf{p}(\mathbf{G}) = {}^1/_2 \operatorname{sign}(x) [(x^2 + 4|V_\mathbf{G}|^2)^{1/2} - |x|], \quad x = \varepsilon_\mathbf{p}^{(0)} - \varepsilon_{\mathbf{p}-\mathbf{G}}^{(0)}. \tag{3.5}$$

Here and below we use atomic units: the energy in hartress, and the momentum in units of $(1/a_B)$ where a_B is the Bohr radius. In (3.5) and elsewhere V_G is taken to mean the screened potential $V_G/\tilde{\epsilon}(\mathbf{G})$, which determines in fact the band structure. The coefficients of the expansion (3.1) are correspondingly approximated by the first term of their iteration series

$$\alpha_\mathbf{p}(\mathbf{G}) \simeq V_\mathbf{G} / (\varepsilon_\mathbf{p} - \varepsilon_{\mathbf{p}-\mathbf{G}}^{(0)}). \tag{3.6}$$

The next term of the series is known to contain, at any value of $\mathbf{p}$, the additional small factor $\tilde{V}_G$.

The approximation corresponding to (3.4) and (3.6) introduces into the polarizability $\tilde{\chi}$ an error of the order of $\tilde{V}_G^2$. Since the representation of the generalized susceptibility by means of the first terms of (2.9) and (2.10) is of the same accuracy, one can certainly determine the dynamic matrix by using expressions (3.4) and (3.6) and obtain an accuracy at least equivalent to full allowance for the contributions $\overline{D}_e^{(2)}$ and $\overline{D}_e^{(3)}$ to the usual scheme. Actually we attain a better accuracy, as will be shown in the sequel.

We analyze now the diagonal elements of $\tilde{\chi}_0$ (3.3) and show that we can disregard in their calculation, at the same accuracy, the restructuring of the wave function and confine ourselves to the change of only the energy spectrum. We consider the behavior of the integrand in different regions of momentum space. If the arguments $\mathbf{p}$ and $(\mathbf{p}+\mathbf{k}+\mathbf{G}_1)$ of the coefficients $\alpha(\mathbf{G})$ lie far from the BZ faces, the leading term in $\tilde{\chi}_0$ is determined by the condition $\mathbf{G}_1 = \mathbf{G}' = \mathbf{G}'' = 0$, at which the expression in the square brackets (see (3.3)) can be replaced by unity. In this case all the remaining terms are at least as small as $\tilde{V}_G^2$.

We consider the case when one of the arguments, say $\mathbf{p}$, lies near the BZ face corresponding to $\mathbf{G}_0$:

$$\left| \frac{\mathbf{p}\mathbf{G}_0}{G_0} - \frac{G_0}{2} \right| \leqslant \varkappa, \quad \varkappa \equiv \varkappa_{\mathbf{G}_0} = V_{\mathbf{G}_0} \Big/ \frac{G_0}{2}, \tag{3.7}$$

and $(\mathbf{p}+\mathbf{k})$ is far from the BZ faces. In this case a noticeable contribution is made only by terms corresponding in (3.3) to $\mathbf{G}' + \mathbf{G}_1 = 0$, $\mathbf{G}'' + \mathbf{G}_1 = 0$ and ($\mathbf{G}_1 = 0$ or $\mathbf{G}_1 = -\mathbf{G}_0$). The corresponding integrand reduces then to

$$2|C_\mathbf{p}|^2 \left(\frac{n_\mathbf{p} - n_{\mathbf{p}+\mathbf{k}}}{\varepsilon_\mathbf{p} - \varepsilon_{\mathbf{p}+\mathbf{k}}} + \frac{n_\mathbf{p} - n_{\mathbf{p}+\mathbf{k}-\mathbf{G}_0}}{\varepsilon_\mathbf{p} - \varepsilon_{\mathbf{p}+\mathbf{k}-\mathbf{G}_0}} |\alpha_\mathbf{p}(\mathbf{G}_0)|^2 \right). \tag{3.8}$$

It is necessary to consider simultaneously the symmetrical region of $\mathbf{p}$ corresponding to

$$|\mathbf{p}\mathbf{G}_0 + {}^1/_2 G_0^2| \leqslant \varkappa G_0,$$

in which the integrand is determined in analogy with (3.8) but with $\mathbf{G}_0$ replaced by $(-\mathbf{G}_0)$. Replacing in this region $\mathbf{p}$ by $(-\mathbf{p})$, we reduce the integral to the first region. Grouping in the resultant expression the second term with the first of (3.8), and the first respectively with the second, and recognizing that ε_p, n_p, and $|C_p|^2$ are even functions of $\mathbf{p}$, and

$$\alpha_{-\mathbf{p}}(-\mathbf{G}_0) = \alpha_\mathbf{p}^*(\mathbf{G}_0),$$

we can verify that at $(\mathbf{p}\cdot\mathbf{G}_0) = \frac{1}{2}G_0^2$ the term of the form $(n_p - n_{-p+k})/(\varepsilon_p - \varepsilon_{p+k})$ can be taken outside the parentheses. The expression remaining in the parentheses is then cancelled by $|C_p|^2$ accurate to $\tilde{V}_{G_0}^2$. At $(\mathbf{p}\cdot\mathbf{G}_0) \neq \frac{1}{2}G_0^2$ this cancellation takes place already with accuracy linear in $\tilde{V}_{G_0}$. However, if it is recognized that the relative volume of the integration region near the BZ faces, where the wave function is effectively restructured, is of the order of $\tilde{V}_{G_0}$, all the corrections to the result are again of the order of $\tilde{V}_{G_0}^2$. Therefore in this case, too, the expression in the square brackets of (3.3) can be set equal to unity and only the term with $\mathbf{G}_1 = 0$ remains.

We consider finally the case when both arguments $\mathbf{p}$ and $(\mathbf{p}+\mathbf{k})$ lie in the immediate vicinity of BZ faces with respective indices $\mathbf{G}_0$ and $\mathbf{G}_0'$. If $\mathbf{G}_0'$ is not collinear with $\mathbf{G}_0$, the

picture remains exactly the same as in the preceding case, since the integration along one of the faces of the BZ automatically takes the second argument out of the region where the corresponding $\alpha_{\mathbf{p}+\mathbf{k}+\mathbf{G}_1}(\mathbf{G}_0+\mathbf{G}_1)$ is of the order of unity. On the other hand the integration region where both wave-function expansion coefficients are of the order of unity is certainly small as $\tilde{V}_G^2$.

If $\mathbf{G}_0'$ is parallel to $\mathbf{G}_0$, this corresponds in fact to $(\mathbf{k}\cdot\mathbf{G}_0)\approx\frac{1}{2}\mathbf{G}_0(\mathbf{G}_0'-\mathbf{G}_0)$, i.e., $\mathbf{k}$ lies near one of the BZ faces parallel to the face with index $\mathbf{G}_0$. This is the only case when it may be necessary to take into account the restructuring of the wave function in the diagonal matrix elements of the polarizability (see Sec. 6).

Thus, at arbitrary $\mathbf{k}$, with exception of only the particular case noted above, expression (3.3) for the diagonal polarizability elements reduces, accurate to terms of order $\tilde{V}_G^2$, to

$$\tilde{\chi}_0(\mathbf{k},\mathbf{k})\equiv\tilde{\chi}_0(\mathbf{k})=2\sum_{\mathbf{p}}\frac{n_{\mathbf{p}}-n_{\mathbf{p}+\mathbf{k}}}{\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}+\mathbf{k}}}. \tag{3.9}$$

It is interesting that, within the framework of the considered approximation, $\tilde{\chi}(k)$ has the same structure as for a homogeneous electron gas, only with $\varepsilon_p^{(0)}$ replaced by ε_p and with the occupation numbers $n_p^{(0)}$ replaced by n_p, which are equal to unity for the states below the true Fermi surface.

For the off-diagonal elements, the expression in the square brackets of (3.3) reduces, with the same accuracy as in (3.9), to a linear combination of the functions $\alpha_p(G)$, and as a result we obtain the simple representation

$$\tilde{\chi}_0(\mathbf{k},\mathbf{k}+\mathbf{G})=2\sum_{\mathbf{p}}\left[\frac{n_{\mathbf{p}}-n_{\mathbf{p}+\mathbf{k}}}{\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}+\mathbf{k}}}(\alpha_{\mathbf{p}}(\mathbf{G})+\alpha^*_{\mathbf{p}+\mathbf{k}}(-\mathbf{G}))\right.$$
$$\left.+\frac{n_{\mathbf{p}}-n_{\mathbf{p}+\mathbf{k}+\mathbf{G}}}{\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}+\mathbf{k}+\mathbf{G}}}(\alpha_{\mathbf{p}}^*(-\mathbf{G})+\alpha_{\mathbf{p}+\mathbf{k}+\mathbf{G}_1}(\mathbf{G}))\right]. \tag{3.10}$$

It is easy to show that when the energy gap tends to zero the representation (3.10) corresponds to the limiting expression (2.13) containing a three-pole diagram (see also Ref. 8).

4. BAND CORRECTIONS TO THE POLARIZABILITY $\tilde{\chi}_0(\mathbf{k})$. NONDIAMETRAL KOHN SINGULARITIES

In the analysis of the contribution of coherent restructuring of the electron spectrum to the polarizability we are primarily interested in two problems: of the scale of the band corrections to $\tilde{\chi}_0$, and of the intensity of the so-called nondiametral Kohn singularities, which are known to be absent in the approximation with a spherical Fermi surface. Their intensity should therefore be uniquely determined by the character of the restructuring of the Fermi surface near the faces of the BZ.

In (3.9), in the principal region of variation of $\mathbf{p}$, the band correction is of the order of $\tilde{V}_G^2$. It is obvious that a large contribution can be expected only from regions directly adjacent to the BZ faces, where $\Delta\varepsilon_p\sim V_G$. From the form of expression (3.9) for χ_0 it is clear that the restructuring of the spectrum can be nontrivial in those cases when simultaneously $\varepsilon_p\approx\varepsilon_{p+k}\approx\varepsilon_F$. Thus, a noticeable band contribution should be expected at those $\mathbf{k}$ which connect states near the Fermi surface, and at least one of them must belong to the restructured region of the spectrum. In particular, the nondiametral Kohn singularities are realized just under similar conditions.

It is clear that if $\mathbf{k}$ joins simultaneously two restructured regions near the Fermi surface (with the exception of $\mathbf{k}\sim\mathbf{G}$, see Sec. 6), the character of the obtained band corrections remains the same. We therefore carry out for simplicity an analysis corresponding to the case when the second end of the wave vector lands on an almost spherical part of the Fermi surface; the first lies then on the Fermi surface in the vicinity of the restructured spectrum near a BZ face. Retaining in the representation (3.4) for ε_p the correction from only one face and introducing a cylindrical coordinate system with the axis along $\mathbf{G}$, and recognizing also that $\Delta\varepsilon_p$ depends only on p_z, the triple integral in (3.9) reduces easily to a single integral

$$\tilde{\chi}_0(\mathbf{k})=-\frac{\Omega}{\pi^2 k_\perp^2}\int_{-p_0}^{p_0}dp_z[\psi(p_z)-\operatorname{sign}(\psi)\,\theta(F(p_z))F^{1/2}(p_z)], \tag{4.1}$$

where we have introduced the notation (see Fig. 1):

$$F(p_z)=\psi^2(p_z)-k_\perp^2\rho^2(p_z),\ \rho^2(p_z)=2\varepsilon_F-p_z^2-2\Delta\varepsilon_{p_z}(\mathbf{G}),$$
$$\psi(p_z)=\tfrac{1}{2}k^2+k_zp_z-\Delta\varepsilon_{p_z}(\mathbf{G}). \tag{4.2}$$

$\theta(x)$ is the standard unit step function. We have left out of $\psi(p_z)$ the band correction $\Delta\varepsilon_{p_z+k_z}$, since it is inessential in the analysis that follows. The integration limits p_0 are determined from the condition $\rho^2(p_0)=0$. In the general case

$$|p_0-p_{F0}|/p_{F0}\sim\tilde{V}_G^2,\ p_{F0}=(2\varepsilon_{F0})^{1/2}.$$

An exception is the case when

$$|p_{F0}-\tfrac{1}{2}G|/p_{F0}\lesssim\tilde{V}_G,$$

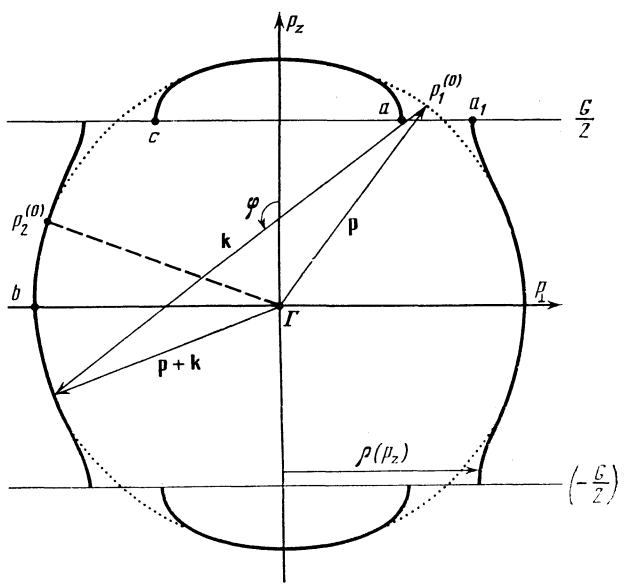

FIG. 1. Intersection of the Fermi surface with a plane passing through the vectors $\mathbf{k}$ and $\mathbf{G}$, in the expanded-band scheme with account taken of the energy gaps only on the BZ faces with indices $\mathbf{G}$ and $-\mathbf{G}$. The points correspond to the Fermi surface of the free electrons.

and then

$$|p_0-p_{F0}|/p_{F0}\sim\tilde{V}_G.$$

We begin with an analysis of the second term in the square brackets in (4.1). The region where $F(p_z)>0$ is bounded by values of p_z that are roots of the equation

$$F(p_z)=0. \tag{4.3}$$

If we use the central intersection of the Fermi distribution with the plane passing through **k** and **G** (as in Fig. 1), it is easy to verify that solutions of (4.3) are two values of p_z such that **p** and (**p** + **k**) lie simultaneously on the Fermi surface. For free electrons we obtain

$$p_{1,2}^{(0)}=-\frac{1}{2}k_z\pm\frac{k_\perp}{k}\left(2\varepsilon_{F0}-\frac{1}{4}k^2\right)^{1/2}. \tag{4.4}$$

In this geometry we can confine ourselves to a discussion of only one root, say p_1^0 corresponding to the plus sign. A nonzero contribution from the second term in (4.1) is obtained then in the region $p_z>p^{(0)}$. For Bloch electrons, the corresponding root of Eq. (4.3) is then shifted:

$$p_1=p_1^{(0)}+\Delta p_1,\quad \Delta p_1\sim\Delta\varepsilon_{p_1}^{(0)}. \tag{4.5}$$

If $p_1^{(0)}$ lands in the band-restructuring region, then $\Delta p_1\sim p_{F_0}\tilde{V}_G$. Denoting by F_0 the value of the function $F(p_z)$ for free electrons, the contribution of the second term to (4.1) and the change of the polarizability $\tilde{\chi}_0$ on account of the band structure can be written in the form

$$\Delta\tilde{\chi}_0(\mathbf{k})$$

$$\approx\frac{\Omega}{\pi^2k_\perp^2}\left(\int_{p_1^{(0)}}^{p_0}dp_z(F^{1/2}-F_0^{1/2})+\int_{p_1}^{p_1^{(0)}}dp_zF^{1/2}-\int_{p_0}^{p_{F0}}dp_zF_0^{1/2}\right). \tag{4.6}$$

At the point $p_1^{(0)}$ and in a region of order Δp_1 around it we have $F(p_z)\sim V_G$. From this we see immediately that both the first and the second integral make a contribution proportional to $(\tilde{V}_G)^{3/2}$. In the case when the relation $|p_0-p_{F_0}|/p_{F_0}\sim\tilde{V}_G^2$, is valid, the last integral is negligibly small, and in the case $|p_{F_0}-\frac{1}{2}G|/p_{F_0}\sim\tilde{V}_G^2$, when p_0 and p_{F_0} actually lie in the vicinity of $p_1^{(0)}$, we have $F(p_z)\sim V_G$ and the third integral also becomes proportional to $(\tilde{V}_G)^{3/2}$.

We consider now the first term in the square brackets of (4.1). The band correction $\Delta\tilde{\chi}_0$ connected with this term is due on the one hand to the value

$$\psi(p_z)-\psi_0(p_z)=-\Delta\varepsilon_{p_z}(\mathbf{G})$$

(see (4.2), and on the other hand to the change of the upper limit p_0. The first contribution is obviously always quadratic in $\tilde{V}_G$. The second term has the same smallness if the following relation holds

$$|p_0-p_{F0}|/p_{F0}\sim\tilde{V}_G^2,$$

while in the case

$$|p_{F0}-{}^1/_2G|/p_{F0}\sim\tilde{V}_G$$

since

$$\psi_0=({}^1/_2k^2+k_zp_z)\sim k_\perp V_G^{1/2}$$

in the intregration interval (p_0, p_{F_0}), the change of the polarizability is proportional to $(\tilde{V}_G)^{3/2}$.

We arrive thus at the important result that at arbitrary **k** the maximum correction to the polarizability, due to restructuring of the electron spectrum near the BZ faces, obeys the law

$$\Delta\tilde{\chi}_0\infty\tilde{V}_G^{3/2}. \tag{4.7}$$

An explicit expression for $\Delta\tilde{\chi}$ under the assumption $|p_{F_0}-\frac{1}{2}G|/p_{F_0}\gg\tilde{V}_G$ can be represented in the form

$$\frac{1}{\Omega}\Delta\tilde{\chi}_0(\mathbf{k})=-\frac{(\Delta p_1)^{3/2}}{\pi^2k_\perp^2}(k^2|k_z+2p_1^{(0)}|)^{1/2}\Phi(\mathbf{k}/G,\varkappa/G)+O(\tilde{V}_G^2). \tag{4.8}$$

Here Δp_1, obtained accurate to $\tilde{V}_G^2$, is of the form

$$\Delta p_1=\Delta\varepsilon_{p_1}(\mathbf{G})\frac{{}^1/_2k^2-k_\perp^2+k_zp_1^{(0)}}{k^2(k_z+2p_1^{(0)})}. \tag{4.9}$$

The dimensionless function Φ is a sum of two integrals with finite limits, which stem from the first two terms in (4.6) and depend only on dimensionless parameters. At arbitrary **k**, the function Φ changes little and is close to unity in order of magnitude. Therefore the factor that precedes Φ, written out in explicit form, makes it possible to track the **k**-dependence of the coefficient of the parameter $\tilde{V}_G^{3/2}$ in (4.7) and the vanishing of this contribution when departing from the region of the spectrum restructuring near a BZ face. In the latter case Δp_1 itself becomes proportional to $\tilde{V}_G^2$.

The region of **k** where $\Delta\tilde{\chi}_0$ behaves in accordance with (47) is, naturally, small. In the basic phase space volume, $\Delta\tilde{\chi}_0$ is proportional to $\tilde{V}_G^2$. This is clearly seen from Fig. 2, where plots of $\Delta\tilde{\chi}_0/V_G^2$ are shown for two values of V_G, 0.028 and 0.056 Ry (the first value corresponds to $|\mathbf{G}_{111}|=1.428$ and $p_{F_0}=0.930$). This are the values for aluminum. In the basic interval of variation of **k**, the two curves are almost indistinguishable. In the interval $k/p_{F_0}=1.7$–1.9 the two curves are different and their ratio is $\sqrt{2}$, in accord with the obtained law (4.7). The position of the nondiametral Kohn singularity is marked in Fig. 2 by the arrow k_1. The arrow k_2 in the same figure shows the position of the kink typical of the singularity corresponding to $\mathbf{k}_0$ which joins the points "a_1" and "b" (see Fig. 1) belonging to sections with different curvatures of the Fermi surface (see Ref. 9).

Near a definite $\mathbf{k}_0$ that corresponds to a nondiametral Kohn singularity ($\mathbf{k}_0$ joins two Fermi-surface points having strictly antiparallel values of the group velocity, see Ref. 10), the function Φ will contain a nonanalytic addition of the form $x\ln|x|$, due to the second term of (4.6). This anomalous addition is localized in the narrow interval $\Delta\mathbf{k}=|\mathbf{k}-\mathbf{k}_0|\lesssim\varkappa$. We obtain the explicit form of this anomalous contribution to the polarizability, choosing by way of example the $\mathbf{k}_0$ that joins the points a and b in Fig. 1. To this end, we consider the second integral in (4.6) and expand the function $F(p_z)$ in powers of the small deviation $x=p_z-p_1(\mathbf{k})$ near the lower integration limit

$$F(p_z)=A_1(\mathbf{k})x+A_2(\mathbf{k})x^2+\ldots. \tag{4.10}$$

Choosing the direction of the change $\Delta\mathbf{k}$ along the face ($\Delta k\,\|\mathbf{k}_1$), we expand the analytic function $A_1(\mathbf{k})$ in powers of

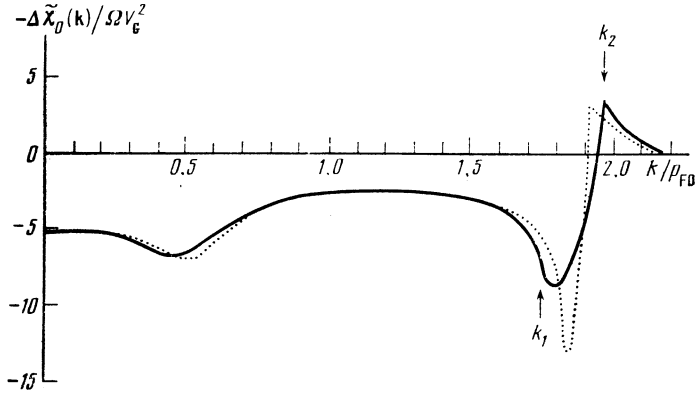

FIG. 2. Band corrections to the diagonal elements of the polarizability, referred to the square of the energy-gap parameter V_G ($\varphi = 120°$; dashed—$V_G = 0.028$ Ry, solid—$V_G = 0.056$ Ry).

$|\Delta\,\mathbf{k}|$. It is easy to verify that $A_1(\mathbf{k}_0)$, the first term of the expansion, is exactly equal to zero. Taking (4.2) into account, we obtain for A_1

$$A_1(\mathbf{k}) \approx \frac{G}{2} k^2 \left[\frac{4}{G} \left| \frac{\Delta k}{\varkappa} \right| \left(p_{F0}^2 - \frac{1}{4} G^2 \right)^{1/2} \right]^{1/2}. \quad (4.11)$$

The next terms of the series contain additional powers of the small parameter $\varkappa$. We retain for A_2 only the term that is leading at sufficiently small $|\Delta\,\mathbf{k}|$ and stems from terms that contain second derivatives of $\Delta\varepsilon_{p_z}$ with respect to p_z:

$$A_2(\mathbf{k}) \approx Gk^2/2\varkappa. \quad (4.12)$$

After determining the contribution to the integral from the narrow interval $0 \leqslant x \leqslant \varkappa$, we obtain

[SB::anom]

$$\Delta\tilde{\chi}_{\text{anom}}(\mathbf{k}) \approx -\frac{\Omega}{\pi^2 k_\perp^2} k \frac{G}{2} \left[p_{F0}^2 - \frac{1}{4} G^2 \right]^{1/2} \left(\frac{2\varkappa}{G} \right)^{3/2} \left| \frac{\Delta k}{\varkappa} \right| \times \ln \left| \frac{1}{G} \left[p_{F0}^2 - \frac{1}{4} G^2 \right]^{1/2} \frac{\Delta k}{\varkappa} \right|. \quad (4.13)$$

The anomalous contribution is of the already noted smallness scale (4.7). The derivative of (4.13) with respect to $|\Delta\,\mathbf{k}|$ has the usual logarithmic singularity

$$\partial\Delta\tilde{\chi}_{\text{anom}}/\partial\Delta k \sim (\varkappa/G)^{1/2} \ln |\Delta k/\varkappa|. \quad (4.14)$$

The coefficient of the logarithm, however, has an additional small parameter $\sim \tilde{V}_G^{1/2}$ compared with the diametral Kohn singularity. This, in conjunction with the fact that the anomaly is localized in a very narrow interval $\Delta k \lesssim \varkappa$ outside of which the very character of the analytic $\Delta\tilde{\chi}_0(k)$ dependence changes, explains why it is difficult to discern the nondiametral Kohn singularities in the phonon spectra of metals.

It is clear that the structure of the expression for $\Delta\tilde{\chi}_{\text{anom}}$ (4.13) remains the same for any other geometry of the nondiametral Kohn singularity.

5. OFF-DIAGONAL POLARIZABILITY ELEMENTS. THREE-PARTICLE SINGULARITY

From the form of expression (3.10) for the off-diagonal polarizability elements, in conjunction with (3.6), it follows directly that $\chi_0(\mathbf{k},\mathbf{k}+\mathbf{G})$ contains compared with $\chi_0(\mathbf{k})$ (see (3.9)) the first power of the small parameter $\tilde{V}_G$. With account taken of the results of the preceding section, it follows directly that the contribution made to the phonon spectrum by the off-diagonal polarizability elements is always substantially larger than that of the band corrections to $\chi_0(\mathbf{k})$, since the quantity $\Delta\tilde{\chi}_0$ will contain an extra small factor $\tilde{V}_G$, in an overwhelming range of variation of $\mathbf{k}$ and the parameter $\tilde{V}$ in a narrow singled out region Δk. It is clear that allowance for $\Delta\chi_0(\mathbf{k})$ is meaningful only if the off-diagonal elements (3.10) are included in the dynamic matrix. To illustrate the foregoing, Fig. 3 shows $\tilde{\chi}_0(\mathbf{k},\mathbf{k}+\mathbf{G})$ and $\Delta\chi_0(\mathbf{k})$ calculated with the parameters corresponding to Fig. 2.

Allowance for the energy gap in the electron spectrum has little effect on the general form of $\chi_0(\mathbf{k},\mathbf{k}+\mathbf{G})$ (cf. curves *a* and *c* of Fig. 3, where curve *c* corresponds to expression (2.13) for the free electron gas). The true band structure be-

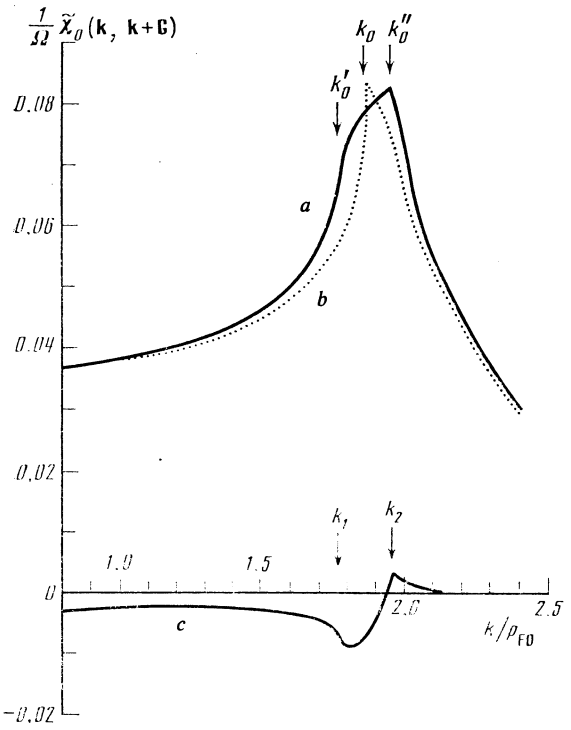

FIG. 3. Off-diagonal element of polarizability as a function of $\mathbf{k}$: *a*) $\chi_0(\mathbf{k},\mathbf{k}+\mathbf{G})$ with allowance for the band structure (see (3.10)) ($\varphi = 120°$, $V_G = 0.056$ Ry); *b*) band correction $\Delta\tilde{\chi}_0(\mathbf{k})$; *c*) result of perturbation theory.

comes essential only in the analysis of the three-particle singularity typical of $\tilde{\chi}_0(\mathbf{k},\mathbf{k}+\mathbf{G})$ (Ref. 1).

It is known that in the case of a free electron gas such a singularity appears in $\tilde{\chi}_0(\mathbf{k}_1,\mathbf{k}_2)$ when the three vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $-(\mathbf{k}_1+\mathbf{k}_2)$ form an acute triangle whose vertices lie on the Fermi surface.[1,3] The anomalous contribution behaves then like

$$\tilde{\chi}_{\text{anom}}(\mathbf{k},\mathbf{k}+\mathbf{G}) \propto \begin{cases} [(k_0-k)/k_0]^{1/2}, & k<k_0; \\ 0, & k\geqslant k_0. \end{cases} \qquad (5.1)$$

This results in a substantially stronger singularity compared with the Kohn anomaly.

The dynamic matrix (2.2), however, contains off-diagonal elements of χ_0, a feature of which is that one of the vectors of the triangle must be a reciprocal-lattice vector that connects directly states on the Fermi-surface sections reconstructed from the Fermi sphere. To analyze the properties of the singularity it becomes necessary to include the restructuring of the electron spectrum explicitly in the off-diagonal elements (3.10). As a result the secondary energy denominator that stems from (3.6) does not vanish at any value of $\mathbf{k}$, and remains of the order of V_G in the in the restructuring region. As a result, the root singularity (5.1) in the derivative of $\tilde{\chi}_0(\mathbf{k},\mathbf{k}+\mathbf{G})$ with respect to $\mathbf{k}$ becomes smeared out in this interval, even though outside this interval its square-root character is fully preserved. On the other hand the presence of denominators in the two terms of (3.10), typical of $\chi_0(\mathbf{k})$, leads to the appearance, in the same region of $\Delta\mathbf{k}$, of non-smeared Kohn anomalies of the nondiametral type (the arrows k_0' and k_0'' in Fig. 3.). A similar comparison was first cited in Brovman's dissertation.[11]

In the immediate vicinity of $\mathbf{k}_0'$ the derivative $\partial\chi_0(\mathbf{k},\mathbf{k}+\mathbf{G})/\partial\mathbf{k}$ has a behavior similar to that of $\partial\Delta\tilde{\chi}_0(\mathbf{k})/\partial\mathbf{k}$ near a nondiametral Kohn singularity (the amplitude at the logarithm is also proportional to $(V_G/\varepsilon_F)^{1/2}$). However, the smallness of $\Delta\chi_0(k)$ compared with $\tilde{\chi}_0(\mathbf{k},\mathbf{k}+\mathbf{G})$, in conjunction of preservation of the $(\Delta k/k_0)^{-1/2}$ dependence outside the interval $\Delta k\sim\varkappa$ makes the singularity of the off-diagonal elements to be integrally much more strongly pronounced than in $\Delta\chi_0(\mathbf{k})$. It must be stated right away that in the phonon spectrum this difference can be even more strongly pronounced because of the presence, in high-symmetry crystals, of a contribution of off-diagonal elements of $\tilde{\chi}_0$ from the entire group of equivalent pairs of reciprocal-lattice vectors $\mathbf{G}_1$ and $\mathbf{G}_2$ (see (2.2)), which determine the singularity at one and the same $\mathbf{k}_0$. This is particularly clearly demonstrated by the example of transverse phonon branches, which are determined only by those terms of (2.2) with $\mathbf{G}_1$, $\mathbf{G}_2\neq 0$. All these circumstances were used for an experimental observation of a three-particle singularity in aluminum.[4]

Figure 4 shows the group velocities $\partial\omega/\partial\mathbf{q}$ for the transverse branch in aluminum at $\mathbf{q}$ parallel to the [100] axis. Curve 1 corresponds to calculation of the phonon spectrum with allowance, in the electronic part of the dynamic matrix, for only the diagonal elements of the polarizability. Curve 2 corresponds to inclusion of the off-diagonal elements in the form (3.10). It is clear form this figure that the anomaly in the

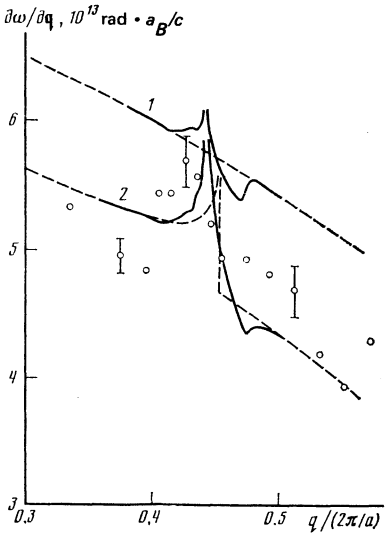

FIG. 4. Group velocity of phonons in aluminum: 1) only diagonal elements $\chi(\mathbf{k},\mathbf{k})$ taken into account in the dynamic matrix, 2) result of inclusion of both diagonal and off-diagonal elements $\chi(\mathbf{k}_1,\mathbf{k}_2)$ ($\mathbf{q}\|[100]$, points—from Ref. 4, dashed curves—perturbation theory, solid—band model).

aluminum phonon spectrum, observed in Ref. 4 at $q/q_{\max}=0.43$, is a singularity due to three-particle interaction.

It can thus be stated that the presence of nondiametral Kohn singularities does not prevent observation of three-particle anomalies. On the contrary, in the general case the latter mask considerably the weaker nondiametral singularities, whose observation calls for a very particular choice of experimental conditions.

6. KOHN ANOMALY IN SOUND

Of particular interest is the case when the chemical potential ε_F of the electrons is inside the energy cap corresponding to a definite $\mathbf{G}_0$ (such a case takes place, for example, in cadmium at $\mathbf{G}_0=[101]$ and vectors equivalent to it). The corresponding upper band is then empty, and the boundary of the electron distribution in momentum space has flat sections congruent with the faces of the BZ. The situation in this case is equivalent to the giant Kohn anomaly produced in the phonon spectrum when the Fermi surface has flat sections.[12] In the latter case the logarithmic singularity appears in the dispersion law itself, owing to the large phase space occupied by the states at the boundary of the distribution of the electrons displaced by a definite wave vector into other states that likewise belong the distribution boundary. But this is precisely the situation in the case considered here. The only difference is that the energies of the states adjacent to opposite sides of the distribution boundary differ from one another by the value of the energy gap $2V_{G_0}$. In the latter case there is singularity in the mathematical sense, but at small V_{G_0} a very strong anomaly can occur in the phonon spectrum.[16]

The condition $\mathbf{k}=\mathbf{G}_0$ means that such an anomaly should occur in the spectrum as $\mathbf{q}\to 0$, i.e., in the speed of sound or in the limiting optical frequencies, as well as in the

initial part, corresponding to small values of the wave vector **q**, of the phonon spectrum.

To determine the character of this anomaly one must turn to the general expression for the diagonal elements of the polarizability $\tilde{\chi}_0(\mathbf{k})$ (3.3). As already noted in Sec. 3, at $\mathbf{k}\|\mathbf{G}_0$ we are unable in the general case to replace the expression in the square brackets by unity if **k** is close to $(G_0' - G_0)/2$. In our case this means that the coefficients $\alpha_p(\mathbf{G})$ must be retained for values of **G** equal to zero, $\mathbf{G}_0$, and $-\mathbf{G}_0$. We must now integrate (3.3) with respect to **p**, retaining $\alpha_p(\mathbf{G})$ and the corresponding $|C_{p+k+G}|^2$.

We restrict ourselves to $\mathbf{k} = \mathbf{G}_0 + \Delta\mathbf{k}(\Delta\mathbf{k}\|\mathbf{G}_0)$ with $|\Delta\mathbf{k}|$ smaller than $\varkappa$, and find the first three terms of the expansion of $\tilde{\chi}_0$ in $|\Delta\mathbf{k}|$:

$$\tilde{\chi}_0(\mathbf{k}) = \tilde{\chi}_0(\mathbf{G}_0) + B_1\Delta k + B_2(\Delta k)^2 + \dots . \tag{6.1}$$

The integrals obtained are quite unwieldy in the general case. If, however, we determined beforehand the first and second derivatives of the integrals in (3.3) with respect to **k**, then at $\Delta\mathbf{k} = 0$ the integrals can be calculated directly. We present here only the result:

$$\begin{aligned}
\tilde{\chi}_0(\mathbf{G}_0) &= -\Omega\frac{G_0}{2\pi^2}\left(\frac{1}{2} - \frac{1}{8}\xi + \frac{1}{4}\xi\ln\frac{2G_0}{\varkappa}\right),\\
\frac{1}{\Omega}B_1 &= -\frac{1}{\pi^2}\left(\frac{1}{4} - \frac{1}{4}\ln\frac{2G_0}{\varkappa}\right),\\
\frac{1}{\Omega}B_2 &= \frac{G_0}{24\pi^2}\frac{\xi}{\varkappa^2}.
\end{aligned} \tag{6.2}$$

We have used here the notation

$$\xi = (\varepsilon_F - \varepsilon^{(0)}_{\mathbf{G}_0/2})/\varepsilon^{(0)}_{\mathbf{G}_0/2}.$$

For comparison, we present the expression for the polarizability of free electrons

$$\tilde{\chi}_0^{(0)}(\mathbf{G}_0) = -\Omega\frac{G_0}{2\pi^2}\left(\frac{1}{2} + \frac{1}{4}\xi + \frac{1}{4}\xi\ln\left|\frac{4}{\xi}\right|\right). \tag{6.3}$$

Recognizing that in (6.1) $\Delta k \lesssim \varkappa$ and $\xi \sim \varkappa/G_0$, it can be easily seen that restructuring of the electron spectrum changes the order of $\tilde{V}_{G_0}$ in the polarizability. The band effects thus manifest themselves in this case most strongly, as follows from a comparison with the general situation (4.7). In fact, these effects turn out to be much stronger in the phonon spectrum. As can be seen from (6.1) and (6.2), the first and second derivatives are proportional to $\tilde{V}^0_{G_0}$ and $1/\tilde{V}_{G_0}$, respectively. Turning to the expression for the dynamic matrix in the long-wave limit (see Ref. 1), in which we retain only the leading contribution from the diagonal elements of the polarizability

$$\begin{aligned}
D^{\alpha\beta}(\mathbf{q}) &= \frac{6}{M}q^\alpha q^\beta\varphi(0)\\
&\quad + \frac{1}{M}\sum_{G\neq 0}\Big[\, q^\alpha q^\beta\varphi(\mathbf{G}) + (q^\alpha G^\beta + G^\alpha q^\beta)\, q^\gamma\frac{\partial\varphi(\mathbf{G})}{\partial G^\gamma}\\
&\quad + \frac{1}{2}G^\alpha G^\beta q^\gamma q^\delta\frac{\partial^2\varphi(\mathbf{G})}{\partial G^\gamma\partial G^\delta}\Big],\\
\varphi(\mathbf{k}) &= \frac{4\pi z^2e^2}{k^2\Omega_0} + \frac{\Omega_0}{\Omega}\tilde{\chi}_0(\mathbf{k})\,|V_{\mathbf{k}}|^2/\bar{\varepsilon}(\mathbf{k}), \quad \Omega_0 = \Omega/N,
\end{aligned} \tag{6.4}$$

we see right away that the acoustic region of the phonon spectrum depends on

$$(\partial^2\tilde{\chi}_0/\partial k_i\partial k_j)_{\mathbf{k}=\mathbf{G}}.$$

The corresponding terms in (6.4) contain in place of the usual factor V_G^2 in this case V_G raised only the the first power. This effect should manifest itself particularly strongly for transverse phonons, since their dynamic matrix does not contain a first term (see (6.4)) and the indirect interaction due to the electrons is determined only by the polarizability Fourier components with $\mathbf{k} = \mathbf{G} \neq 0$. It must be taken into account here that what is larger is precisely the second derivative $\partial^2\tilde{\chi}_0/\partial k_z^2$ (the z axis is parallel to **G**). At the same time

$$\begin{aligned}
\frac{\partial^2\tilde{\chi}_0}{\partial k_x^2}\Big|_{\mathbf{k}=\mathbf{G}} &= \frac{\partial^2\tilde{\chi}_0}{\partial k_y^2}\Big|_{\mathbf{k}=\mathbf{G}}\\
&= -\Omega\frac{2}{\pi^2G}\left(\frac{1}{8} + \frac{1}{12}\left(\frac{G\xi}{4\varkappa}\right)^2 - \frac{1}{8}\ln\left(\frac{2G}{\varkappa}\right)\right),
\end{aligned} \tag{6.5}$$

(i.e., of the order of $(\tilde{V}_G)^0$. Therefore an anomalous contribution to the transverse sound is always present when the wave vector **q** is nonparallel and nonperpendicular to **G**. We note that the sign of the second derivative, B_2 in (6.2), is determined by whether the chemical potential is higher or lower than the middle of the energy gap. In sound velocity increases in the former case and decreases in the latter.

Naturally, the considered anomalous contributions pertains to only one group of reciprocal-lattice vectors that are equivalent with respect to the crystal symmetry, whereas the expression for the sound velocity contains the sum over all the vectors **G**. In addition, since the contribution of the ion lattice is not at all sensitive to the electron spectrum, an anomaly in the sound is realized against the background of other normal contributions. It must therefore manifest itself substantially if, as is frequently the case in polyvalent metals, the electron contribution cancels substantially the contribution of the ion lattice, especially in anisotropic metals. It was just this circumstance that manifested itself strongly in cadmium.

Let the wave vector of a phonon in a uniaxial metal lie in the basal plane. We consider the phonon branch with polarization along the c axis. For this branch the square of the sound velocity, proportional to the elastic modulus C_{44}, can be represented in the following simple form:

$$s_{T_3}^2 = \frac{1}{\rho}C_{44} = \frac{1}{2\Omega_0\rho}\sum_{\mathbf{G}\neq 0}|S(\mathbf{G})|^2G_3^2\partial^2\varphi(\mathbf{G})/\partial G_1^2, \tag{6.6}$$

the index 1 labels the projection of **G** on the **q** direction, while the index 3 corresponds to the component of **G** along the c axis; $S(\mathbf{G})$ is the structure factor.

In the case of cadmium the Fermi surface goes off below the BZ face (the higher zone is empty) for a family of twelve equivalent faces with **G** = [101] (see, e.g., Ref. 13). We write down the anomalous contribution to $s_{T_3}^2$ from these reciprocal-lattice points:

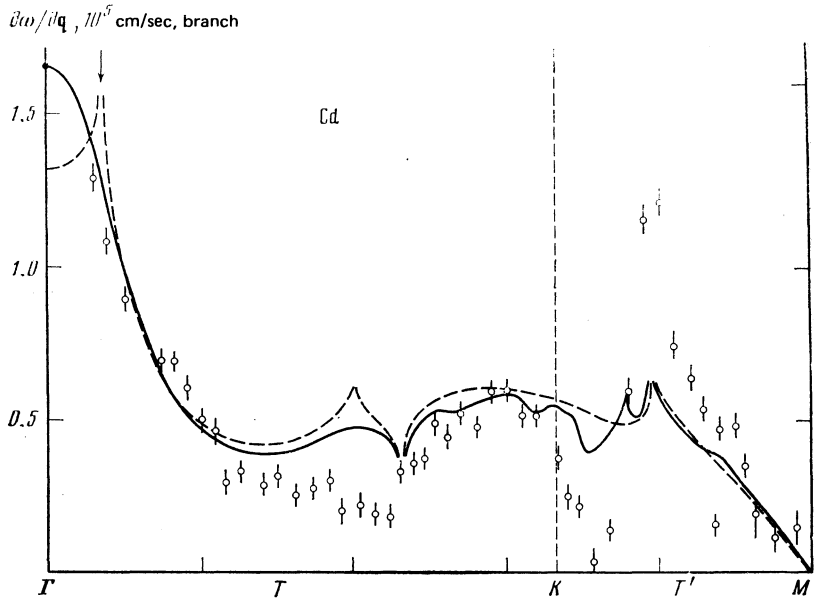

FIG. 5. Group velocity of phonons in cadmium, calculated with allowance for the presence of flat boundaries of the Fermi distribution on faces of the (101) type. The Fermi level is in this case at the upper edge of the energy gap on the indicated BZ faces (dashed curves—perturbation theory, solid—band model).

$$\Delta s_{T_3}^2 \approx \frac{1}{2\Omega_0\rho}\frac{1}{\Omega}\sum_{G\in\{101\}} G_3^2\left[V_G^2\frac{\partial^2\tilde{\chi}_0}{\partial G_1^2}+4V_G\frac{\partial\tilde{\chi}_0}{\partial G_1}\frac{\partial V_G}{\partial G_1}\right]$$

$$\sim V_G\left(\frac{\xi}{\varkappa}\right). \qquad (6.7)$$

Direct calculations shows that in the case of cadmium the chemical potential lies close to the upper edge of the gap. Taking this into account, as well as the value $V_G = 0.034$ Ry known from an analysis of the Fermi surface,[13] we obtain as an estimate of (6.7)

$$\Delta s_{T_3}^2 \approx 0.8\cdot 10^{10}\,(\text{cm/sec})^2.$$

Comparing this quantity with the experimental value

$$s_{T_3}^2 = 2.6\cdot 10^{10}\ (\text{см/с})^2,$$

we see that the anomalous contribution changes the sound velocity by an amount of the order of its value.

The anomalous contribution is localized in the interval $\Delta q \sim \varkappa$. This means that the group velocity should have a relatively narrow peak near $\mathbf{q} = 0$. Figure 5 shows the calculated values of the group velocity for the branch T_3 of cadmium, obtained by using in the dynamic matrix the polarizability in the form (3.3), which takes into account the restructuring of the spectrum and of the wave functions of the electrons near the BZ faces. This utterly unusual behavior of the group velocity was first observed in cadmium in Ref. 5. For comparison, the same figure shows the group velocity obtained within the framework of group velocity for the dynamic matrix. We note two very distinctive circumstances. First, it can be clearly seen by comparing the curves how the usual Kohn singularity (arrow in Fig. 5), which incidentally is readily observed in magnesium[14] in which the upper band above the faces with $\mathbf{G} = [101]$ is partly filled, vanishes and is replaced at $\mathbf{q} = 0$ by an anomaly whose amplitude, for reasons noted above, is finite. Second, attention must be called to the relatively large change of the sound velocity.

7. CONCLUSION

The results of the present paper allow us to formulate a number of general premises. This pertains first of all to the phonon spectrum of nontransition metals as a whole. Indeed, if the electronic part of the dynamic matrix $\bar{D}_e^{\alpha\beta}$ is represented in the form

$$\bar{D}_e^{\alpha\beta}(\mathbf{q}) = \frac{1}{MN}\left[\sum_{\mathbf{G}}(\mathbf{q}+\mathbf{G})^\alpha(\mathbf{q}+\mathbf{G})^\beta|V_{\mathbf{q}+\mathbf{G}}|^2\frac{1}{\Omega}\tilde{\chi}_0(\mathbf{q}+\mathbf{G})/\tilde{\varepsilon}(\mathbf{q}+\mathbf{G})\right.$$

$$\left.+\sum_{\mathbf{G}_1\neq\mathbf{G}_2}(\mathbf{q}+\mathbf{G}_1)^\alpha(\mathbf{q}+\mathbf{G}_2)^\beta V_{\mathbf{q}+\mathbf{G}_1}V_{-\mathbf{q}-\mathbf{G}_2}\frac{1}{\Omega}\chi_0(\mathbf{q}+\mathbf{G}_1,\mathbf{q}+\mathbf{G}_2)/\tilde{\varepsilon}(\mathbf{q}+\mathbf{G}_1)\tilde{\varepsilon}(\mathbf{q}+\mathbf{G}_2)\right],$$

where $\tilde{\chi}_0(\mathbf{q}+\mathbf{G})$ is defined in accord with (3.3), $\chi_0(\mathbf{q}+\mathbf{G}_1,\mathbf{q}+\mathbf{G}_2)$ in accord with (3.10), and the functions contained in them are defined in accord with (3.4)–(3.6), we can determine the phonon spectrum of the metal in the entire BZ, with allowance for the restructuring of the electron spectrum accurate to quantities of the order of $\tilde{V}_G^2$. This

reveals the entire phonon-spectrum fine structure due to the restructuring of the energy spectrum and of the electron wave functions both far and near the BZ faces.

In the overwhelming majority of cases, as follows from the analysis in Sec. 4, for the diagonal elements of the polarizability it suffices to use the much simpler expression (3.9). The latter, together with (3.10), takes adequate account of the role of the gaps in the band structure of the valence electrons.

In principle, by using Eqs. (2.9), (2.10), and (3.3), it is possible to obtain an iteration procedure that makes it possible to take successively into account terms of higher order in powers of (V_G/ε_F).

The restructuring of the electron spectrum near the BZ faces influences substantially the establishment of an hierarchy of singularities in the phonon spectrum of a metal. After the usual diametral Kohn anomaly, the strongest is the so-called three-particle singularity, which acquires only a slightly smoothed form because of the finite width of the gap in the band structure. Still weaker is the nondiametral Kohn singularity, which should be masked in many cases by the three-particle singularity.

Under certain conditions (see the preceding section) the band restructuring of the electron spectrum can lead to an entirely new type of anomaly—singularities in the sound or, in other words, in the phonon spectrum at $\mathbf{q} = 0$.

Although allowance for the energy gaps, as shown by analysis, influences relatively little the integral form of the phonon spectrum, it can be quite substantial in the analysis of definite region of phase space, especially when it comes to strongly anisotropic polyvalent metals such as cadmium, beryllium, or white tin (β-Sn). It seems that the difficulty of exhaustively describing the phonon spectra of these metals are caused to a considerable degree by failure to take into account the role of the energy gaps in the band structure of the valence electrons.

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