SOVIET PHYSICS JETP VOLUME 25, NUMBER 2 AUGUST, 1967

THE PHONON SPECTRUM OF METALS

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Submitted to JETP Editor, August 22, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 52, 557–574 (February, 1967)

The problem of the validity of the adiabatic approximation for the analysis of oscillations of the electron-ion system in metals is considered. Determination of the phonon spectrum reduces to solution of an equation of the Born-Karman type; the part of the dynamic matrix related to the electrons and responsible for long-range interaction is found explicitly. Two particle and many-particle interionic interactions are analyzed. The method developed by the authors for separating long-range and short-range forces between ions is employed for calculating the phonon spectrum of tin. The five required parameters can be found in terms of the three elastic moduli and two characteristic spectrum frequencies. The spectrum of the purely ionic tin lattice is calculated. The contribution of the covalent part of the interaction is analyzed. The role of electrons in determining the shape of the tin spectrum is discussed. The results are compared with those of the experiments.

1. INTRODUCTION

UP to recent times, information relative to the spectrum of oscillations of crystalline lattices can be found only from quantities that are integrated over the spectrum, such as specific heat; these allow one to determine only certain averaged phonon characteristics. However, a method which has been intensively developed in recent years, based on the scattering of cold neutrons, allowed one to obtain the differential characteristics such as dispersion curves for definite directions in the crystal.

For the theoretical analysis of the results and the construction of the phonon spectrum in all phase space, it is customary to use the model of lattice vibrations of the Born-Karman type. Here an assumption is made that the strong interactions between the atoms are quickly damped with distance, and the small number of independent constants entering into the equation is determined by experiment. Such an approach, which is valid for dielectrics, is shown to be actually of little use for metals. This was recently shown especially clearly in the study of comparatively complicated lattices with two atoms per unit cell (Zn[1] and Sn[2]). The analysis made by the authors[3] shows that for a reasonable description of the spectrum of the phonons in the tin lattice, it is necessary to take the interaction into account with at least six coordination spheres.

Such a long-range interaction actually appears as a reflection of the important role of electrons in the formation of the phonon spectrum of metals. In the framework of the Born-Karman theory[4], it leads to correlation between the force constants which correspond to different coordination spheres, and they cease to be independent. Therefore, the natural idea arises of isolating of this long-range interaction in explicit form. Then the only force constants which correspond to the nearest neighbors will be independent force constants that are subject to determination by experiment.

The accomplishment of such a program is to a great extent connected with the possibility of reducing the interaction in the electron-ion system to an effective interaction between the separate atoms, in essence, this is equivalent to the use of the adiabatic approximation. Although adiabaticity in the trivial sense does not hold for electrons in a metal, nevertheless, as will be shown below, the presence of the small parameter ω/ϵ_F together with the Pauli principle leads to the result that the adiabatic approximation is realized with great accuracy. Furthermore, it is shown to be possible to separate systematically the "adiabatic" phonons, the renormalization of which (due to the electron phonon interaction) is negligibly small, and also the form of the matrix element for this interaction. This is the more important since, in the use of a Hamiltonian of the Fröhlich type, in which there is no possibility of giving the "bare" frequency of the phonon or the constant of electron-phonon interaction, an illusion arises about the strong renormalization of the phonons[5] (see also[6]), which also leads to instability of the lattice in some cases.

As a result, we obtain a systematic method of analysis of the phonon spectrum in metals, using a very limited number of parameters. The effectiveness of this method is demonstrated in the last section of the work, where results are given of the calculation of the phonon spectrum of tin, the most complicated spectrum of the metals investigated to date.

2. THE VALIDITY OF THE ADIABATIC APPROXIMATION IN METALS

As the initial Hamiltonian of the many-particle problem, which describes the electron-ion system of the metal, we choose the following:

$$H = \sum_i \frac{\mathbf{P}_i^2}{2M_i} + \frac{1}{2}\sum_{ij}{}' \frac{Z^2e^2}{|\mathbf{R}_i - \mathbf{R}_j|} + \frac{1}{2}\sum_{ij} \varphi(\mathbf{R}_i, \mathbf{R}_j)$$

$$+ \sum_\nu \frac{\mathbf{p}_\nu^2}{2m} + \frac{1}{2}\sum_{\nu\nu'}{}' \frac{e^2}{|\mathbf{r}_\nu - \mathbf{r}_{\nu'}|} + \sum_{i\nu} V(\mathbf{r}_\nu - \mathbf{R}_i). \quad (2.1)$$

Here standard notation is used for the coordinates and momenta of the ions and the conduction electrons.

In the expression for the Hamiltonian in Eq. (21), we assume that the internal electrons are localized close to the nucleus, forming an ion "core" rigidly connected to them. These electrons, together with the nuclei, create an effective potential for the conduction electrons (the last term in (2.1)). The direct Coulomb interaction between the ions (second term) is separated in explicit form and the interaction between them is of a different nature (third term).

Furthermore, carrying out the usual procedure for the adiabatic Born-Oppenheimer approximation (see, for example, [4]), we first separate the problem for electrons in the fixed potentials of the ions:

$$[H_e(\mathbf{r}) + H_{ei}(\mathbf{r}, \mathbf{R})]\Psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R})\Psi_m(\mathbf{r}, \mathbf{R}). \quad (2.2)$$

(Here symbolic notation is used for the different terms of the Hamiltonian (2.1).) Then the oscillations of the nuclei will be described by the set of equations

$$[H_i(\mathbf{R}) + E_n(\mathbf{R})]\Phi_n(\mathbf{R}) + \sum_m C_{nm}\Phi_m(\mathbf{R}) = E\Phi_n(\mathbf{R}), \quad (2.3)$$

where

$$C_{nm} = A_{nm} + B_{nm},$$

$$A_{nm} = -\frac{1}{M}\int d\mathbf{r}\, \Psi_n^*(\mathbf{r}, \mathbf{R}) \nabla_\mathbf{R} \Psi_m(\mathbf{r}, \mathbf{R}) \nabla_\mathbf{R},$$

$$B_{nm} = -\frac{1}{2M}\int d\mathbf{r}\, \Psi_n^*(\mathbf{r}, \mathbf{R}) \nabla_\mathbf{R}^2 \Psi_m(\mathbf{r}, \mathbf{R}). \quad (2.4)$$

If we neglect the diagonal terms C_{nm}, then we get an "adiabatic" equation for the determination of the energy levels α of the vibrational problem for fixed values of n ($E_{n\alpha}^0$). For the clarification of the role of correction terms in (2.3), it is customary to make a rough estimate of their contribution to the total energy of the electron-ion system. However, we shall be interested in the explicit form of the renormalization of the frequencies of the "adiabatic" phonon spectrum (for arbitrary value of the wave vectors). Simultaneously, the renormalization of the electron spectrum will be found in explicit form.

For this purpose, it is necessary to calculate the matrix elements $A_{n\nu; m\beta}$ and $B_{n\nu; m\beta}$ of the adiabatic equation ((2.3) with $C_{nm} = 0$). The integrals in Eqs. (2.4) are not difficult to transform. We let the operator ∇_R act on the left and right sides of Eq. (22) and, multiplying by $\Psi_n^*(\mathbf{r}, \mathbf{R})$, we integrate over the coordinates of all the electrons. Then we get for $m \neq n$,

$$[\nabla_\mathbf{R}]_{nm} = -\frac{[\nabla_\mathbf{R} H_{ei}(\mathbf{r}, \mathbf{R})]_{nm}}{E_n(\mathbf{R}) - E_m(\mathbf{R})}. \quad (2.5)$$

For the calculation of the energy correction, it is sufficient to limit ourselves to the first term of the expansion of this matrix element in $\mathbf{R} - \mathbf{R}_0$, setting $\mathbf{R} = \mathbf{R}_0$ in it. Then we can construct the many-particle wave function of the electrons from ordinary single-particle Bloch functions, which we shall characterize by the wave vector **k**. Using the explicit form for the operator $H_{ei}(\mathbf{r}, \mathbf{R})$, it is easy to see that the only matrix elements in (2.5) that differ from zero correspond to one-electron transitions. Departing further from the symbolic notation, we make the substitution

$$\nabla_\mathbf{R} \to \sum_j \nabla_{\mathbf{R}_j}$$

and get

$$A_{\mathbf{k}\nu;\, \mathbf{k}'\beta} = \frac{1}{M}\sum_j \frac{[\nabla_{\mathbf{R}_j} V(\mathbf{r}, \mathbf{R}_j)]_{\mathbf{k}\mathbf{k}'}}{E_\mathbf{k} - E_{\mathbf{k}'}} \int \Phi_\nu^{0*}(\mathbf{R})\, \nabla_{\mathbf{R}_j} \Phi_\beta^0(\mathbf{R})\, d\mathbf{R}. \quad (2.6)$$

In writing down this expression, we have neglected the change in the vibrational spectrum, which arises upon excitation of the individual electron.

For calculation of the remaining matrix element in (2.6), it is convenient to transform to the representation of second quantization for phonons. Writing down the momentum operator of the ion ∇_{R_j} in this representation, we find directly

$$\frac{1}{M}\int \Phi_\nu^{0*}(\mathbf{R})\, \nabla_{\mathbf{R}_j} \Phi_\beta^0(\mathbf{R})\, d\mathbf{R}$$

$$\to \pm\, \omega_{\mathbf{q}\lambda}(2M\omega_{\mathbf{q}\lambda}N)^{-1/2} \mathbf{e}_{\mathbf{q}\lambda} (N_{\mathbf{q}\lambda} + 1/2 \mp 1/2)^{1/2} \exp\{\pm i\mathbf{q}\mathbf{R}_j^0\}. \quad (2.7)$$

Here we use the usual notation of $\omega_{q\lambda}$, $\mathbf{e}_{q\lambda}$, $N_{q\lambda}$ for frequency, polarization vector, and occupation number of phonons of momentum **q** and branch number λ (for simplicity of writing, we consider the case of a single-atom lattice). As is seen from (2.7), the matrix element corresponds to single-phonon transition; the upper sign corresponds to absorption of a single phonon and the lower emission.

As a result, carrying out summation over $\mathbf{R}_j^0$, we can transform (2.6) to its final form:

$$A_{\mathbf{k}N_{\mathbf{q}\lambda}\mp 1;\,\mathbf{k}'N_{\mathbf{q}\lambda}} = \mp\frac{\omega_{\mathbf{q}\lambda}}{E_{\mathbf{k}}-E_{\mathbf{k}'}} \times M_{\mathbf{k}\mathbf{q}\lambda}\sqrt{N_{\mathbf{q}\lambda}+\frac{1}{2}\mp\frac{1}{2}}\,\Delta(\mathbf{k}-\mathbf{k}'\mp\mathbf{q}). \tag{2.8}$$

Here the delta function describes the law of conservation of momentum with accuracy up to a vector of the reciprocal lattice, while $M_{kq\lambda}$ represents the ordinary Bloch matrix element

$$M_{\mathbf{k}\mathbf{q}\lambda} = \left(\frac{N}{2M\omega_{\mathbf{q}\lambda}}\right)^{1/2}\int \psi_{\mathbf{k}}^*(\mathbf{r})\,[\mathbf{e}_{\mathbf{q}\lambda}\nabla_{\mathbf{r}}V(\mathbf{r})]\,\psi_{\mathbf{k}'}(\mathbf{r})\,d\mathbf{r}. \tag{2.9}$$

We now find the matrix element which corresponds to the operator B. Making use of the complete electron functions, and also Eq. (2.5), we transform the inner integral in (2.4) in the following fashion:

$$\int \psi_n^*(\mathbf{r},\mathbf{R})\,\nabla_{\mathbf{R}}^2\psi_m(\mathbf{r},\mathbf{R})\,d\mathbf{r} \equiv [\nabla_{\mathbf{R}}^2]_{nm} = \sum_p \frac{[\nabla_{\mathbf{R}}H_{ei}(\mathbf{r},\mathbf{R})]_{np}\,[\nabla_{\mathbf{R}}H_{ei}(\mathbf{r},\mathbf{R})]_{pm}}{[E_n(\mathbf{R})-E_p(\mathbf{R})]\,[E_p(\mathbf{R})-E_m(\mathbf{R})]}\,. \tag{2.10}$$

Setting $\mathbf{R} = \mathbf{R}_0$ as before, and carrying out integration over the ion coordinates, we obtain the result that the matrix element $B_{n\nu;\,m\beta}$ differs from zero only for diagonal transitions in the vibrational spectrum. So far as transitions in the electron spectrum are concerned, $B_{n\nu;\,m\beta}$ differs from zero for $n = m$ too. Therefore, the operator B give the energy corrections in the first order perturbation theory, whereas the operator A obviously gives them only in the second.

We calculate the diagonal matrix element of B, using both the single-electron representations above and also the identity

$$\sum_\lambda e_{\mathbf{q}\lambda}^{\alpha}e_{\mathbf{q}\lambda}^{\beta} = \delta_{\alpha\beta}.$$

After simple transformations, we find

$$B_{\mathbf{k}\nu;\,\mathbf{k}\nu} = \sum_{\mathbf{q}\lambda}\omega_{\mathbf{q}\lambda}|M_{\mathbf{k}\mathbf{q}\lambda}|^2(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})^{-2}. \tag{2.11}$$

We now determine the energy correction of the adiabatic state connected with the operator A. Using second-order perturbation theory and the explicit form of Eq. (2.8), we get

$$\Delta E_A = \sum_{\mathbf{q}\lambda}\sum_{\mathbf{k}}|M_{\mathbf{k}\mathbf{q}\lambda}|^2\left(\frac{\omega_{\mathbf{q}\lambda}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}\right)^2\left\{\frac{N_{\mathbf{q}\lambda}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}+\omega_{\mathbf{q}\lambda}}\right.$$

$$\left.+\frac{N_{\mathbf{q}\lambda}+1}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}-\omega_{\mathbf{q}\lambda}}\right\}n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}}).$$

This result can be directly transformed to the form

$$\Delta E_A = \sum_{\mathbf{q}\lambda}\left(N_{\mathbf{q}\lambda}+\frac{1}{2}\right)\sum_{\mathbf{k}}\left(\frac{\omega_{\mathbf{q}\lambda}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}\right)^2|M_{\mathbf{k}\mathbf{q}\lambda}|^2 \times\frac{2(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}})}{(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})^2-\omega_{\mathbf{q}\lambda}^2} + \sum_{\mathbf{q}\lambda}\sum_{\mathbf{k}}\left(\frac{\omega_{\mathbf{q}\lambda}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}\right)^2|M_{\mathbf{k}\mathbf{q}\lambda}|^2\frac{\omega_{\mathbf{q}\lambda}n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}})}{(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})^2-\omega_{\mathbf{q}\lambda}^2}. \tag{2.12}$$

We proceed to the calculation of the energy correction associated with the operator B. Taking it into account here that the operator B, as was shown, gives the energy shift even in first order perturbation theory, and using (2.11), we get

$$\Delta E_B = \sum_{\mathbf{k}}\sum_{\mathbf{q}\lambda}\frac{|M_{\mathbf{k}\mathbf{q}\lambda}|^2\omega_{\mathbf{q}\lambda}n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}})}{(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})^2}. \tag{2.13}$$

Finally, for the energy correction of the adiabatic state, we get the following expression:

$$\Delta E = \Delta E_A + \Delta E_B = \sum_{\mathbf{q}\lambda}\left(N_{\mathbf{q}\lambda}+\frac{1}{2}\right) \times\sum_{\mathbf{k}}|M_{\mathbf{k}\mathbf{q}\lambda}|^2\left(\frac{\omega_{\mathbf{q}\lambda}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}\right)^2 \times\frac{2(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}})}{(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})^2-\omega_{\mathbf{q}\lambda}^2} + \sum_{\mathbf{q}\lambda}\sum_{\mathbf{k}}\frac{|M_{\mathbf{k}\mathbf{q}\lambda}|^2\omega_{\mathbf{q}\lambda}n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}})}{(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})^2-\omega_{\mathbf{q}\lambda}^2}. \tag{2.14}$$

Now, for the determination of the frequency shift of the phonon with wave vector $\mathbf{q}$ and branch number λ, it is necessary to vary the occupation number of the phonons $N_{q\lambda}$. As a result, after simple transformations, we have

$$\Delta\omega_{\mathbf{q}\lambda} = \sum_{\mathbf{k}}|M_{\mathbf{k}\mathbf{q}\lambda}|^2\left(\frac{\omega_{\mathbf{q}\lambda}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}\right)^2\frac{2(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}})}{(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})^2-\omega_{\mathbf{q}\lambda}^2} = \sum_{\mathbf{k}}|M_{\mathbf{k}\mathbf{q}\lambda}|^2\frac{n_{\mathbf{k}}-n_{\mathbf{k}+\mathbf{q}}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}-\omega_{\mathbf{q}\lambda}} - \sum_{\mathbf{k}}|M_{\mathbf{q}\lambda}|^2\frac{n_{\mathbf{k}}-n_{\mathbf{k}+\mathbf{q}}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}. \tag{2.15}$$

The meaning of the latter expression is not difficult to understand. The second term in it actually describes the adiabatic contribution of the electrons to the phonon frequency, i.e., the contribution associated with account of the electron energy $E_n(\mathbf{R})$ in the expression. However, the nonadiabatic renormalization proper is already very weak. Actually, computing the integrals in (2.15), we obtain, in the principal region of phase space[1]

$$\Delta\omega_{\mathbf{q}\lambda} \sim \omega_{\mathbf{q}\lambda}(\omega_0/\varepsilon_F)^2. \qquad (2.16)$$

For this reason, in particular, it is necessary to use the so-called Fröhlich Hamiltonian with care if we are dealing with analysis of the phonon spectrum. Actually, introducing the bare phonons, as is usually done[5], (see also[6,7]), and then renormalizing them from the electron-phonon interaction with the matrix element $M_{kq\lambda}$, we actually take the contribution [which is equivalent to the second terms in (2.15)] into account twice in the renormalization of the frequency. Just this circumstance creates a representation of the strong renormalization of the phonon spectrum ($\sim\omega$) at the expense of the electron-phonon interaction and leads, in particular, to conclusions on the possible instability of the lattice[7,8].

Returning to the renormalization of the electron system, we vary the expression (2.14) with respect to the occupation numbers of the electrons. As a result, we get

$$\Delta E_{\mathbf{k}} = \sum_{\mathbf{q}\lambda} |M_{\mathbf{k}\mathbf{q}\lambda}|^2 \left\{ \left(N_{\mathbf{q}\lambda} + \frac{1}{2}\right) \frac{2(E_{\mathbf{k}} - E_{\mathbf{k}+\mathbf{q}})}{(E_{\mathbf{k}} - E_{\mathbf{k}+\mathbf{q}})^2 - \omega_{\mathbf{q}\lambda}{}^2} \right.$$
$$\left. \times \left(\frac{\omega_{\mathbf{q}\lambda}}{E_{\mathbf{k}} - E_{\mathbf{k}+\mathbf{q}}}\right)^2 + \frac{\omega_{\mathbf{q}\lambda}(1 - 2n_{\mathbf{k}+\mathbf{q}})}{(E_{\mathbf{k}} - E_{\mathbf{k}+\mathbf{q}})^2 - \omega_{\mathbf{q}\lambda}{}^2} \right\}. \qquad (2.17)$$

Computing Eq. (2.17) for the shift in the chemical potential, we get

$$\Delta E_{\mathbf{k}_F} \sim \omega(\omega/\varepsilon_F). \qquad (2.18)$$

Thus, the renormalization of the chemical potential as a result of electron-phonon interaction is a small quantity in comparison with ω. At the same time, it follows from (2.17) that the renormalization of the velocity of the electrons close to the Fermi surface is appreciable, in agreement with the result obtained by Migdal[5].

We note that (2.16) and (2.18) are direct evidence that the usual vertex of the electron-phonon interaction is determined not by the matrix element $M_{kq\lambda}$, but by the quantity $M_{kq\lambda}\omega_{q\lambda}/(E_k - E_{k+q})$, which is important for virtual processes. For real processes, when $E_k - E_{k+q} = \pm\omega_{q\lambda}$, all the results (damping, electron-phonon scattering cross section in the kinetic coefficients, and so forth) are the same as in the use of the Fröhlich Hamiltonian.

Inasmuch as electrons with $E_k - E_{k+q} \lesssim \omega_{q\lambda}$ take part in the pairing which takes place as the result of the virtual exchange of phonons and which leads to superconductivity, the effective electron-electron interaction is also unchanged in comparison with the ordinary one.

3. DETERMINATION OF THE ELECTRON ENERGY

As follows from the previous section, for the determination of the phonon frequencies it is necessary to compute the energy levels of the electron system in the field of the fixed ions, i.e., $E_n(\mathbf{R}_1, \ldots, \mathbf{R}_n)$ in Eq. (2.3). Here one must take into account the interaction of the conduction electrons with the ion cores, which by itself is not weak. However, if the method of pseudopotential is used, which is actually the basis of the model of almost free electrons, then in place of the real interaction with the ion there appears a certain effective interaction, for which one can develop a perturbation theory.[9-11]

In this method, the wave function of the conduction electron is represented in the form of a smooth function and a function which oscillates rapidly inside the ion core. The elimination of the oscillating part leads to the appearance in the Schrödinger equation for the smooth function of an effective repulsive potential which acts in the region of the core and in significant measure compensates the initial attractive potential. The resulting potential $V^*(\mathbf{r}\cdot\mathbf{r}')$ (it can be replaced with great accuracy by the local potential $V^*(\mathbf{r})$[10,11]) is shown to be so weak that it is a characteristic smallness parameter V_k^*/ϵ_F (V_k^* is the Fourier component of the pseudopotential, and $\mathbf{K}$ is one of the vectors of the reciprocal lattice of the crystal).

In a metal, where it is necessary to consider the electron-electron interaction, the principal contribution in the corresponding matrix elements is made only by the smooth parts of the wave functions. Moreover, even the single electron spectrum can be found from the equation which includes only smooth parts (with the replacement of the real potential by the pseudopotential). Therefore, we get for the effective Hamiltonian in the representation of second quantization in plane waves (the total volume of the system is set equal to unity throughout):

$$H = \sum_{\mathbf{k}} \frac{\mathbf{k}^2}{2m} a_{\mathbf{k}}{}^{+} a_{\mathbf{k}} + \sum_{\mathbf{k}\mathbf{q}}{}' V_{\mathbf{q}} a^{+}_{\mathbf{k}+\mathbf{q}} a_{\mathbf{k}} + \frac{1}{2} \sum_{\substack{\mathbf{k}\mathbf{k}' \\ \mathbf{q}}}{}' \frac{4\pi e^2}{\mathbf{q}^2} a^{+}_{\mathbf{k}-\mathbf{q}} a^{+}_{\mathbf{k}'+\mathbf{q}} a_{\mathbf{k}'} a_{\mathbf{k}}. \qquad (3.1)$$

Here we introduce the notation

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[1] In a very narrow range of momenta, where $|q - 2k_F|/k_F \sim \omega/\epsilon_F$, the smallness of the renormalization is shown to be weaker: $\Delta\omega_{p\lambda} \approx \omega_{p\lambda}(\omega_0/\epsilon_F)$.

$$V_{\mathbf{q}} = \sum_l v_{\mathbf{q}}^* e^{i\mathbf{q}\mathbf{R}_l}, \qquad v_{\mathbf{q}}^* = V_{\mathbf{q}}^* \sum_s e^{i\mathbf{q}\boldsymbol{\rho}_s}. \quad (3.2)$$

The coordinate $\mathbf{R}_l$ describes the elementary cell of the crystal, and $\boldsymbol{\rho}_s$ the basis vectors of the atom in the unit cell. We have limited ourselves to the case of one-component metals, and therefore V_q^* does not depend on $\dot{s}$. Furthermore, if in the Hamiltonian (2.1) we transform to the Fourier representation, then the terms with $q = 0$ in the potential energy are mutually canceled, which is a consequence of the electrical neutrality of the system. Keeping this in mind, we have omitted the corresponding terms in the Hamiltonian (3.1) (sums with the prime).

We emphasize that the Hamiltonian (3.1) is equivalent to the initial one in finding the energy levels of the system, determining at the same time only the smooth part of the real wave functions (as is the case also in the problem for the single ion [9]).

We shall carry out the calculation of the energy of the fundamental state in the form of an expansion in powers of the pseudopotential, taking into account an arbitrary power of the electron-electron interaction in each term of this expansion:

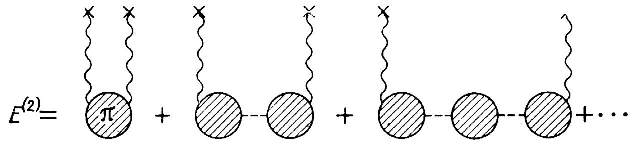
$$E = E^{(0)} + E^{(1)} + \ldots \quad (3.3)$$

If we carry out the usual analysis, using as the perturbation the last two terms in (3.1), then we can prove directly that the change of the energy of the system (relative to the energy of the free electron gas) is equal to the sum of the diagonal (in vacuum) elements of the S matrix

$$S = T \exp\left(-i \int_{-\infty}^{\infty} H'(t')\,dt'\right), \quad (3.4)$$

corresponding to bound diagrams (see, for example, [12]). Here it is necessary formally to introduce in the integrand of each term of the series the factor $i\delta(t')$—the delta function of one of the time arguments.

Using the diagram technique, one can find the expansion (3.3) in explicit form. The zeroth term of this series describes the energy of the interacting electron gas and is of no further interest. The terms linear in the pseudopotential V vanish; this is connected with the electrical neutrality of the system. For terms quadratic in V, the correction to the energy can be represented graphically as follows:



Here the effect of the external field is represented by the cross together with the wavy line; the dashed lines represent interelectron interaction and the unresolved block along the line of this interaction is denoted by π (the polarization operator).

As a result of summation of the diagrams, we find

$$E^{(2)} = \sum_{\mathbf{q}_1} \Gamma^{(2)}(\mathbf{q}_1, -\mathbf{q}_1)\,|V_{\mathbf{q}_1}|^2; \quad (3.6)$$

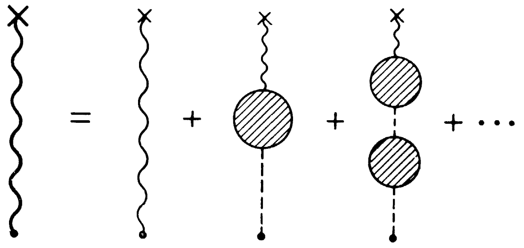
$$\Gamma^{(2)}(\mathbf{q}_1, -\mathbf{q}_1) = -\frac{1}{2}\frac{\pi(\mathbf{q}_1)}{\varepsilon(\mathbf{q}_1)}, \qquad \varepsilon(\mathbf{q}_1) = 1 + \frac{4\pi e^2}{\mathbf{q}^2 V_0}\pi(\mathbf{q}_1). \quad (3.7)$$

In similar fashion, one can write down the expression for an arbitrary n:

$$E^{(n)} = \sum \Gamma^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n) V_{\mathbf{q}_1} \ldots V_{\mathbf{q}_n} \Delta(\mathbf{q}_1 + \ldots + \mathbf{q}_n),$$

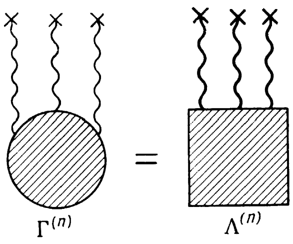
$$\Delta(\mathbf{q}) = \begin{cases} 1, & q = 0 \\ 0, & q \neq 0 \end{cases}. \quad (3.8)$$

(The law of momentum conservation in this expression appears as a consequence of the homogeneity of space.) Here the n-pole $\Gamma^{(n)}$ is determined by the set of all connected diagrams obtained from the expansion (3.4) and having n "tails" of the external field. Although the expression for $\Gamma^{(n)}$ with $n > 2$ cannot be obtained in such a simple form as (3.7), one can carry out a partial summation, introducing the "heavy" vertex of the external field with the help of the following expression:



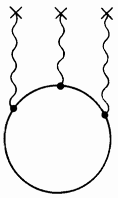
(3.9)

Then $\Gamma^{(n)}$ can be represented in the form



(3.10)

Here $\Lambda^{(n)}$ is determined by the set of diagrams with n inputs which have no parts which could be reduced to one of the "heavy" vertices of the external field. The simplest diagram of such a form is the following (the continuous lines as usual denote the electron G_0 functions (see, for example, [6]):



(3.11)

Analytically, the equation corresponding to (3.1) is written in the form

$$\Gamma^{(n)}(q_1,\ldots,q_n)=\frac{\Lambda^{(n)}(q_1,\ldots,q_n)}{\varepsilon(q_1)\ldots\varepsilon(q_n)},\quad n>2. \tag{3.12}$$

We note that the case $n = 2$ (3.7) is distinct, since only one of the two external lines can be "heavy."

4. EFFECTIVE INTERACTION BETWEEN IONS IN THE METAL

We write down the expression for an arbitrary term of the series (3.3), introducing the coordinates of the ions in explicit form, in accord with (3.2):

$$E^{(n)}=\sum_{l_1\ldots l_n}\sum_{\mathbf{q}_1\ldots\mathbf{q}_n}{}' \Gamma^{(n)}(\mathbf{q}_1,\ldots,\mathbf{q}_n)\,v_{\mathbf{q}_1}{}^{*}\ldots v\;{}_{n}^{*}$$
$$\times\exp\{i\mathbf{q}_1\mathbf{R}_{l_1}+\ldots+i\mathbf{q}_n\mathbf{R}_{l_n}\}\,\Delta(\mathbf{q}_1+\ldots+\mathbf{q}_n). \tag{4.1}$$

We are interested in the usual problem of small vibrations of the ions; therefore, representing the coordinate of the s-th atom in the unit cell in the form

$$\mathbf{r}_{ls}=\mathbf{R}_l^0+\boldsymbol{\rho}_s+\mathbf{u}_{ls}=\mathbf{r}_{ls}{}^0+\mathbf{u}_{ls},$$

We shall seek an expansion of the electron energy in powers of u_{ls}. We begin with the zeroth term. In this case, summation over l in (4.1) can be carried out in explicit form, as a result of which we get

$$E_0^{(n)}=\sum_{\mathbf{K}_1\ldots\mathbf{K}_n\neq 0}\Gamma^{(n)}(\mathbf{K}_1,\ldots,\mathbf{K}_n)\,v^*_{\mathbf{K}_1}\ldots v^*_{\mathbf{K}_n}$$
$$\times\ \Delta(\mathbf{K}_1+\ldots+\mathbf{K}_n). \tag{4.2}$$

Here K_i are the vectors of the reciprocal lattice of the crystal ($K = 2\pi b$). The series (3.3) with terms computed from (4.2) gives the value of the energy of the electron system in the case of a rigid regular lattice. It is easy to see that account of the term with $n = 2$ ($E_0^{(1)} = 0$) already leads to a dependence of the electron energy on the structure of the crystalline lattice and hence to the appearance of anisotropy in the dispersion law of the renormalized electrons.

Let us now consider the term that is linear in the displacements;

$$E_1^{(n)}=in\sum_{ls}\sum_{\mathbf{K}_1\ldots\mathbf{K}_{n-1},\mathbf{q}}\Gamma^{(n)}(\mathbf{K}_1,\ldots,\mathbf{K}_{n-1},\mathbf{q})\,v^*_{\mathbf{K}_1}\ldots v^*_{\mathbf{K}_{n-1}}V^*_{\mathbf{q}}$$
$$\times\exp\{i\mathbf{q}(\mathbf{R}_l{}^0+\boldsymbol{\rho}_s)\}(\mathbf{u}_{ls}\mathbf{q})\,\Delta(\mathbf{K}_1+\ldots+\mathbf{K}_{n-1}+\mathbf{q}). \tag{4.3}$$

If we make use of the fact that $V_{-q}{}^* = V^*_q$, and hence, $v_{-q}{}^* = (v^*_q)_{\text{comp. conj.}}$, and also the fact that Γ remains unchanged upon replacement of all $\mathbf{K}_i$ by $-\mathbf{K}_i$, then Eq. (4.3) can be transformed to the following:

$$E_1^{(n)}=-n\sum_{\mathbf{K}_1\ldots\mathbf{K}_n\neq 0}\sum_{ls}(\mathbf{u}_{ls}\mathbf{K}_n)\,\Gamma^{(n)}(\mathbf{K}_1,\ldots,\mathbf{K}_n)$$
$$\times\,\mathbf{Im}\,(v^*_{\mathbf{K}_1}\ldots v^*_{\mathbf{K}_{n-1}}V^*_{\mathbf{K}_n}e^{i\mathbf{K}_n\rho_s})\,\Delta(\mathbf{K}_1+\ldots+\mathbf{K}_n). \tag{4.4}$$

Hence it follows immediately that in the case of a lattice with a single atom in the unit cell, E_i^n vanishes identically. This is natural, because, the total force acting on an arbitrary ion in such a lattice due to the direct interionic interaction also vanishes identically. In the case of a complicated lattice, when there is more than a single atom per unit cell, the force acting on an arbitrary ion on the part of the electronic liquid ($-\partial E_1/\partial u_{ls}$) is generally different from zero. It must be compensated by the total force acting on the given ion directly on the part of the other ions, which in this case is also different from zero. This also guarantees the equilibrium of the nonsymmetric configuration of the atomic distribution in the unit cell.

We now determine the fundamental quantity of the vibrational problem, E_2.

We find directly from Eq. (4.1) that

$$E_2^{(n)}=-\frac{n(n-1)}{2}\sum_{\substack{ll'\\ss'}}u^{\alpha}_{ls}u^{\beta}_{l's'}\sum_{\mathbf{q}\mathbf{q}_1}\sum_{\mathbf{K}_1\ldots\mathbf{K}_{n-2}}\Gamma^{(n)}$$
$$\times\,(\mathbf{K}_1,\ldots,\mathbf{K}_{n-2},\mathbf{q},\mathbf{q}_1)\,v^*_{\mathbf{K}_1}\ldots v^*_{\mathbf{K}_{n-2}}V_{\mathbf{q}}{}^*V_{\mathbf{q}_1}{}^*\mathbf{q}^{\alpha}\mathbf{q}_1{}^{\beta}$$
$$\times\,\exp\{i\mathbf{q}(\mathbf{R}_l{}^0-\mathbf{R}_{l'}{}^0)+i\mathbf{q}\boldsymbol{\rho}_s+i\mathbf{q}_1\boldsymbol{\rho}_{s'}\}$$
$$\times\Big[1-\delta_{ll'}\delta_{ss'}\sum_{l''s''}\exp\{i\mathbf{q}(\mathbf{R}_l{}^0-\mathbf{R}_{l''}{}^0)-i\mathbf{q}_1(\boldsymbol{\rho}_s-\boldsymbol{\rho}_{s''})\}$$
$$\times\Delta(\mathbf{K}_1+\ldots+\mathbf{K}_{n-2}+\mathbf{q}+\mathbf{q}_1)\Big]\equiv\frac{1}{2}\sum_{\substack{ll'\\ss'}}u^{\alpha}_{ls}u^{\beta}_{l's'}A^{\alpha\beta(n)}_{ls;\,l's'}. \tag{4.5}$$

In the derivation we used the obvious relation

$$\mathbf{q}_1\mathbf{R}_l{}^0=-\Big(\mathbf{q}+\sum_{i=1}^{n-2}\mathbf{K}_i\Big)\mathbf{R}_l{}^0=-\mathbf{q}\mathbf{R}_l{}^0+2\pi m.$$

We note that in the general expansion (3.7), the term with $E^{(n)}$ practically corresponds to the contribution to the electron energy from the n-fold scattering of electrons by the ions of the system. In the vibrational problem these terms are responsible for the n-particle interaction between the ions. Here the expression with $n = 2$ leads to effective pair interaction between the ions, since that with $n > 2$ corresponds to unpaired interaction. However, the contribution of any of these terms to the vibrational matrix $A_{ls;l's'}$, by virtue of the translational invariance, depends on the vector $\mathbf{R}_l^0 - \mathbf{R}_{l'}^0$, which is seen directly from Eq. (4.5). The effective pair interaction between the ions depends only on the modulus $|\mathbf{r}_{ls}^0 - \mathbf{r}_{l's'}^0|$. Therefore, if we limit ourselves only to terms with $n = 2$, then only those terms an interaction that is central in character will figure in the total vibrational matrix [including the direct interaction between the ions from (2.1)]. The noncentral interaction arises at once in the account of the following terms with $n = 2$, while it is easy to see that the corresponding vibrational matrices already possess the symmetries of the crystal (for $n = 2$, the circumstance introduces summation over the sites of the reciprocal lattice).

We write down the explicit expression of the vibrational matrix for $n = 2$:

$$A_{lsl's'}^{\alpha\beta(2)} = -\sum_{\mathbf{q}} \exp\{i\mathbf{q}(\mathbf{r}_{ls}{}^0 - \overset{0}{\mathbf{r}}_{l's'})\}|V_{\mathbf{q}}{}^*|^2$$

$$\times \frac{\mathbf{q}_\alpha \mathbf{q}_\beta \pi(\mathbf{q})}{\varepsilon(\mathbf{q})}\left[1 - \delta_{ll'}\delta_{ss'}\sum_{l''s''}\exp\{i\mathbf{q}(\mathbf{r}_{ls}{}^0 - \overset{0}{\mathbf{r}}_{l''s''})\}\right]. \quad (4.6)$$

It is seen immediately from Eq. (4.5) that all subsequent terms of the expansion of the matrix A will contain the extra factors V_K^*/ϵ_F. If we compare the behavior of $A^{(n)}$ and $A^{(2)}$ at large distances between the ions $\mathbf{R}_l^0 - \mathbf{R}_{l'}^0$, then we easily get the result that

$$A^{(n)}/A^{(2)} \sim (V_K^*/\varepsilon_F)^{n-1}, \quad n > 2.$$

However, as we have noted above, the ratio V_K^*/ϵ_F can be considered as a small parameter of the problem. Therefore, the long-range interaction between the ions is determined essentially by the matrix $A^{(2)}$. So far as terms with $n > 2$ are concerned, they are significant only in consideration of the vibrational matrices for nearest neighbors. If we also take it into consideration that these terms are connected with the unpaired character of the interaction, it is natural that the account is equivalent to allowance for the covalence of the interaction.

As was pointed out in connection with the result (4.2), the systematic account of scattering of the electrons by the ions (and by the "other" electrons) determines the appearance of the real dispersion law for electrons and the true form of the Fermi surface. By virtue of this fact, in the determination of the vibrational matrices, particularly in the computation of the polarization operator, it is reasonable to use the true dispersion law of the electrons. As a rule, this does not lead to a significant change in the electronic part of the vibrational matrix. However, there is one circumstance to which we should pay special attention.

As is known, the presence of a sharp boundary of the Fermi spectrum leads to the appearance of oscillating non-exponential terms in the asymptotic expression in terms of $\mathbf{r}_{ls}^0 - \mathbf{r}'_{s'}$ in the effective interionic interaction (see, for example,[13]). (We note that this result is directly contained in (4.6) and appears as a result of the nonanalytic character of the polarization operator as a function of $\mathbf{q}$.) In the case of a spherical Fermi surface, such a nonanalytic behavior arises for $q = 2k_F$ and $\pi(q)$ has a singularity of the form $(q - 2k_F)\ln(q - 2k_F)$[14]. Here the asymptotic behavior of $A^{(2)}$ will be given by

$$A_{ls;l's'}^{\alpha\beta} \sim \frac{\cos 2k_F|\mathbf{r}_{ls}{}^0 - \overset{0}{\mathbf{r}}_{l's'}|}{|\mathbf{r}_{ls}{}^0 - \mathbf{r}^0{}_{l's'}|^3}. \quad (4.7)$$

In the case of a nonspherical Fermi surface, the character of the singularity in the polarization operator can be greatly strengthened[15]. This involves a much weaker asymptotic damping of the interionic interaction in definite directions in the crystal in comparison with (4.8).

5. DYNAMIC MATRIX OF OSCILLATIONS FOR PHONONS IN A METAL

In the foregoing section, we obtained the electron part of the vibrational matrix (4.5). The total vibrational matrix will also contain two terms $B_{ls;l's'}^{\alpha\beta}$ and $C_{ls;l's'}^{\alpha\beta}$, connected with the expansion of the direct interionic interaction in terms of small displacements, described by the second and third term, respectively, in the Hamiltonian (2.1). Here we have for the Coulomb interaction between ions,

$$B_{ls;l's'}^{\alpha\beta} = 4\pi e^2 Z^2 \sum_{\mathbf{q}}{}' \frac{\mathbf{q}_\alpha \mathbf{q}_\beta}{\mathbf{q}^2}\exp\{i\mathbf{q}(\mathbf{r}_{ls}{}^0 - \overset{0}{\mathbf{r}}_{l's'})\}$$

$$\times\left[1 - \delta_{ll'}\delta_{ss'}\sum_{l''s''}\exp\{i\mathbf{q}(\mathbf{r}_{ls}{}^0 - \overset{0}{\mathbf{r}}_{l''s''})\}\right]. \quad (5.1)$$

To find the phonon spectrum, it is necessary for us to diagonalize the dynamic matrix $D_{ss'}^{\alpha\beta}(q)$, which is defined by the usual relation (see, for example,[4])

$$D_{ss'}^{\alpha\beta}(\mathbf{q}) = \frac{1}{M}\sum_l D_{0s;ls'}^{\alpha\beta}\exp\{-i\mathbf{q}(\overset{0}{\mathbf{r}}_{ls'} - \mathbf{r}_{0s}{}^0)\},$$

$$D^{\alpha\beta}_{ls;\,l's'} = A^{\alpha\beta}_{ls;\,l's'} + B^{\alpha\beta}_{ls;\,l's'} + C^{\alpha\beta}_{ls;\,l's'}. \qquad (5.2)$$

We separate the effective pair interaction corresponding to the term (4.6) in the matrix $A^{\alpha\beta}_{ss'}(\mathbf{q})$ and we join the part which corresponds to the unpaired one (terms with $n > 2$) with the matrix $C^{\alpha\beta}_{ss'}(\mathbf{q})$, which describes the direct interaction between the ion shells. As a result,

$$D^{\alpha\beta}_{ss'}(\mathbf{q}) = D^{\alpha\beta}_{1ss'}(\mathbf{q}) + D^{\alpha\beta}_{2ss'}(\mathbf{q}). \qquad (5.3)$$

The dynamic matrix $D^{\alpha\beta}_{1ss'}(\mathbf{q})$ corresponding to the pair interaction between the ions, with account of (4.6) and (5.1), can be written down in the form (V_0 is the volume of the unit cell)

$$\begin{aligned} D^{\alpha\beta}_{1ss'}(\mathbf{q}) &= \frac{1}{MV_0}\sum_{\mathbf{K}} (\mathbf{q}+\mathbf{K})^{\alpha}(\mathbf{q}+\mathbf{K})^{\beta} \exp\{i\mathbf{K}(\boldsymbol{\rho}_s - \boldsymbol{\rho}_{s'})\} \\ &\times\left[\frac{4\pi Z^2 e^2}{|\mathbf{q}+\mathbf{K}|^2} - \frac{|V^*_{\mathbf{q}+\mathbf{K}}|^2}{\varepsilon(\mathbf{q}+\mathbf{K})}\pi(\mathbf{q}+\mathbf{K})V_0\right] \\ &- \frac{\delta_{ss'}}{MV_0}\sum_{s''}\sum_{\mathbf{K}\neq 0} \mathbf{K}^{\alpha}\mathbf{K}^{\beta}\exp\{i\mathbf{K}(\boldsymbol{\rho}_s - \boldsymbol{\rho}_{s''})\} \\ &\times\left[\frac{4\pi Z^2 e^2}{|\mathbf{K}|^2} - \frac{|V_{\mathbf{K}}{}^*|^2}{\varepsilon(\mathbf{K})}\pi(\mathbf{K})V_0\right]. \end{aligned} \qquad (5.4)$$

The matrix $D^{\alpha\beta}_{2ss'}(q)$ corresponds to the vibrational matrix describing the short-range interaction. This makes it possible to construct it by the usual method for the Born-Karman scheme. To be precise, for the description of the coupling between atoms we introduce the nearest-neighbor force constants (which are uncorrelated with one another). These satisfy only the symmetry requirements of the crystal. Knowing the pseudopotential V^*_q, we have the possibility of computing part of the dynamic matrix D_1 directly. Then the inverse problem of establishing the phonon spectrum reduces to finding the force constants entering into the matrix D_2. Here there is every reason for supposing that, inasmuch as the long-range part of the interaction is systematically taken into account in the matrix D_1, it suffices for the adequate description of the spectrum to take into account in D_1 only the interaction with nearest neighbors. In many cases the corresponding force constants can be determined simply in terms of known elastic moduli.

This scheme turns out to be extraordinarily effective even in the case of metals with a complicated lattice, which can be observed clearly in the example of the analysis of the phonon spectrum of tin, which is given in the next section.

To find the connection of the force constants with the elastic moduli, it is necessary to consider the behavior of the dynamic matrix for small $\mathbf{q}$. For the matrix D_2 one can use the "method of long waves" directly [4]. We obtain the limiting expression of the matrix D_1 for small $\mathbf{q}$ in explicit form. By expanding the elements of the matrix (5.4), and keeping terms up to second order of smallness in $\mathbf{q}$, we get

$$D^{\alpha\beta}_{1ss'}(\mathbf{q}) = \overset{0\alpha\beta}{D_{ss'}} + D^{1\alpha\beta}_{ss'} + D^{2\alpha\beta}_{ss'}, \qquad (5.5)$$

$$\begin{aligned} D^{0\alpha\beta}_{ss'} &= \frac{1}{MV_0}\sum_{\mathbf{K}\neq 0} \mathbf{K}^{\alpha}\mathbf{K}^{\beta}\varphi_{\mathbf{K}}\,[\exp\{i\mathbf{K}(\boldsymbol{\rho}_s - \boldsymbol{\rho}_{s'})\} \\ &- \delta_{ss'}\sum_{s''}\exp\{i\mathbf{K}(\boldsymbol{\rho}_s - \boldsymbol{\rho}_{s''})\}], \end{aligned} \qquad (5.6)$$

$$\begin{aligned} D^{1\alpha\beta}_{ss'} &= \frac{1}{MV_0}\sum_{\mathbf{K}\neq 0} \exp\{i\mathbf{K}(\boldsymbol{\rho}_s - \boldsymbol{\rho}_{s'})\}\,[(\mathbf{q}^{\alpha}\mathbf{K}^{\beta} + \mathbf{q}^{\beta}\mathbf{K}^{\alpha})\varphi_{\mathbf{K}} \\ &+ \mathbf{K}^{\alpha}\mathbf{K}^{\beta}\mathbf{q}_{\nu}(\partial\varphi/\partial\mathbf{f}_{\nu})_{f=\mathbf{K}}], \end{aligned} \qquad (5.7)$$

$$\begin{aligned} D^{2\alpha\beta}_{ss'} &= \frac{\mathbf{q}^{\alpha}\mathbf{q}^{\beta}}{M}\left[\frac{Z^2}{\pi(\mathbf{q}=0)} + 2bZ\right] \\ &+ \frac{1}{MV_0}\sum_{\mathbf{K}\neq 0}\exp\{i\mathbf{K}(\boldsymbol{\rho}_s - \boldsymbol{\rho}_{s'})\} \\ &\times\Big[\mathbf{q}^{\alpha}\mathbf{q}^{\beta}\varphi_{\mathbf{K}} + \mathbf{q}_{\nu}(\partial\varphi/\partial\mathbf{f}_{\nu})_{\mathbf{f}=\mathbf{K}}(\mathbf{q}^{\alpha}\mathbf{K}^{\beta} + \mathbf{q}^{\beta}\mathbf{K}^{\alpha}) \\ &+ \frac{1}{2}\mathbf{K}^{\alpha}\mathbf{K}^{\beta}\mathbf{q}^{\nu}\mathbf{q}^{\mu}\left(\frac{\partial^2\varphi}{\partial\mathbf{f}_{\mu}\partial\mathbf{f}_{\nu}}\right)_{\mathbf{f}=\mathbf{K}}\Big]. \end{aligned} \qquad (5.8)$$

Here for convenience, we have introduced the notation

$$\varphi_{\mathbf{f}} = \frac{4\pi Z^2 e^2}{\mathbf{f}^2} - \frac{|V_{\mathbf{f}}{}^*|^2}{\varepsilon(\mathbf{f})}\pi(\mathbf{f})V_0. \qquad (5.9)$$

For the case $\mathbf{K} = 0$, we have made use of the fact that as $\mathbf{q} \to 0$ the pseudo-potential takes the form

$$V_{\mathbf{q}}{}^* \to -4\pi Z e^2/\mathbf{q}^2 V_0 + b,$$

and $\epsilon(\mathbf{q})$ is given by the expression (3.7). Then, expanding the second term in φ_q, it is easy to ascertain that the principal term of this expansion accurately cancels out with $4\pi Z^2 e^2/q^2 V_0$, which describes the direct Coulomb interaction between the ions. Therefore, the next term of the expansion, which is given in (5.8) is the important one.

It follows directly from the form of the expression (5.6) that

$$\sum_{s'} D^{\alpha\beta}_{1ss'}(\mathbf{q}=0) \equiv 0. \qquad (5.10)$$

As is well known, just this relation determines the mandatory existence of three acoustic branches, the frequencies of which vanish when $q = 0$. We note that (5.10) appears automatically only in the systematic account of the electron screening (in the opposite case, for the longitudinal branch of oscillations the ion plasma frequency appears). As a result, the condition of the form (5.10), which the total dynamic matrix (5.3) must also satisfy, is actually shifted to $D_{2ss'}^{\alpha\beta}(\mathbf{q})$.

The appearance of a term of (5.7) linear in $\mathbf{q}$ is connected with the specific lattice in the elementary cell of which there is more than a single atom. Similar terms arise in the expansion of the ordinary dynamic matrix of Born-Karman. Therefore, in finding the dispersion law for acoustic phonons, the scheme of the method of "long waves" is entirely preserved (hence, the linear terms of (5.7) enter into the expression for the squares of the frequencies, in bilinear combinations, of course).

In the case of a single atom lattice, the terms $D^{(0)}$ and $D^{(1)}$ vanish identically. Then

$$D_1^{\alpha\beta}(\mathbf{q}) = \frac{\mathbf{q}_\alpha \mathbf{q}_\beta}{M}\left[\frac{Z^2}{\pi(\mathbf{q}=0)} + 2bZ\right] + \frac{1}{MV_0}\sum_{\mathbf{K}\neq 0}\left[\mathbf{q}^\alpha \mathbf{q}^\beta \varphi_{\mathbf{K}} + \frac{1}{2}\mathbf{K}^\alpha \mathbf{K}^\beta \mathbf{q}^\nu \mathbf{q}^\mu \left(\frac{\partial^2\varphi}{\partial \mathbf{f}_\mu \partial \mathbf{f}_\nu}\right)_{\mathbf{f}=\mathbf{K}}\right]. \quad (5.11)$$

As is known, for small $\mathbf{q}$, the polarization operator is determined by a simple loop diagram (see[6])

$$\pi_0(\mathbf{q}) = \frac{1}{N}\sum_{\mathbf{k}}\frac{n_{\mathbf{k}} - n_{\mathbf{k}+\mathbf{q}}}{E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}}}. \quad (5.12)$$

Here, if we neglect Umklapp processes in (5.11), and use the spherical nature of the Fermi surface, then we obtain an expression from which the well known result of Bardeen-Pines[16,17] is obtained for the longitudinal sound velocity. In the general case, consideration of the second term in (5.11) can lead to a significant change in the value of this quantity. Furthermore, in the anisotropic crystal, account of Umklapp processes leads to a difference in the velocities of longitudinal sound in the different directions. So far as transverse sound is concerned, it follows from (5.11) that it is on the whole due to the Umklapp processes and is determined only by the third term in (5.11). In this connection, one can observe that for transverse sound, account of electron screening plays no essential role, as in the case of longitudinal,—the transverse acoustic branches arise also in the complete absence of screening.

Up to the present time, we have considered only the electron part of the dynamic matrix. Actually, account of D_2 can lead to a significant change both in the longitudinal and transverse velocities of the sound (see the following section).

In a many-atom lattice, for the analysis of the phonon spectrum for small q, it is necessary to use the general representation (5.5)—(5.9). In the special case of a two-atom lattice, if the symmetry of the crystal is sufficiently high, one can write out the explicit form for the limiting optical frequencies. Actually, if $D_{ss'}^{\alpha\beta}(\mathbf{q}=0)$ is diagonal in the cartesian indices, a resolution takes place into three independent vibrations with polarization along the chosen axes. The corresponding frequencies are equal to

$$\omega_\alpha^2(\mathbf{q}=0) = -\frac{2}{MV_0}\sum_{\mathbf{K}\neq 0}\cos(\mathbf{K}\boldsymbol{\rho})\,\varphi_{\mathbf{K}}\mathbf{K}_\alpha^2 + \omega_{2\alpha}^2(\mathbf{q}=0), \quad (5.13)$$

where the second term is connected with account of the matrix D_2.

Finally, we note that the expression (5.4) also directly contains a singularity in the phonon spectrum, noted first by Kohn[14 15], while, as follows from our consideration, this singularity is already obtained in the adiabatic approximation.

6. PHONON SPECTRUM OF TIN

A. In the present section, the scheme developed above is used for the analysis of the phonon spectrum of metallic tin. This is the most complicated case of all those metallic spectra studied to data. The complication is brought about by the presence of two atoms in the elementary cell and by virtue of the anisotropies of the lattice. The anomalies obtained in the phonon spectrum are so important that they also lead to an unusual behavior of the characteristics integrated over the spectrum (for details, see[3 18]). In the use of the traditional Born-Karman model for the description of the spectrum, it was necessary to introduce at least 14 independent constants.

B. The spectrum of the phonon frequencies is determined by the diagonalization of the summation matrix (5.3). To find its elements, it is necessary to know the Fourier component of the pseudopotential $V_{\mathbf{q}}^*$, the polarization operator $\pi(\mathbf{q})$ and the uncorrelated force constants of the matrix D_2.

The structure of the dynamic matrix D_2 in the case of tin was considered in detail in[3 18]. In the framework of our scheme, we limit ourselves to the account of the interaction only with four atoms in the nearest coordination sphere. This interaction is described by four force constants, of which only three (α, β, γ) are independent (for details, see[3]).

As to $V_{\mathbf{q}}^*$, for the determination of this quantity we could make use of values found on the basis of numerical calculations[19]. However, inasmuch as the calculations possess limited accuracy in the important region of large $\mathbf{q}$, we can pose the question of finding $V_{\mathbf{q}}^*$ in the framework of the inverse problem. With this aim, we made use of the pseudopotential in the Bardeen form:

$$V_q^* = \left(-\frac{4\pi Z e^2}{q^2 V_0} + \sigma\right)\chi(qr_s),$$

$$\chi(qr_s) = \frac{3(\sin qr_s - qr_s \cos qr_s)}{(qr_s)^3}, \qquad (6.1)$$

leaving two parameters, σ and r_s, free.

As was pointed out, for small **q**, the polarization operator has the form (5.12), which leads for the case of a spherical Fermi surface to the expression

$$\pi_0(q) = \frac{3}{2}\frac{nV_0}{\varepsilon_F}\left\{\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q}\ln\left|\frac{2k_F + q}{2k_F - q}\right|\right\}. \qquad (6.2)$$

For large values of q, this expression becomes approximate. There exist a number of schemes that improve the accuracy of (6.2) in the range of large q. These schemes (see, for example,[12, 20]) actually reduce to replacing $4\pi e^2/q^2$ in Eq. (3.7) for the dielectric constant by the quantity $4\pi e^2 q^{-2} f_q$, where

$$f_q = \left(1 - \frac{1}{2}\frac{q^2}{q^2 + \lambda k_F^2}\right), \qquad (6.3)$$

and λ can be regarded as a free parameter.

In the present case, we have not considered the correction (6.3), which transfers the center of gravity of the inverse problem to a determination of the parameters of the pseudopotential. Therefore, the general solution of the inverse problem reduces to the determination of five quantities: α, β, γ, σ, and r_s.

C. For their determination, we used the following choice of experimental quantities: 1) the limiting value of the optical frequency (ω_1) for $q = (0, 0, 2\pi/c)$ with polarization along the z axis; 2) the limiting value of the optical frequencies (ω_2) for $q = 0$ with polarization along the z axis; 3) the elastic modulus c_{33}, corresponding to the longitudinal sound velocity along the [001] axis; 4) the elastic-modulus combination $c_{11} + c_{12}$, corresponding to the longitudinal sound velocity along the [110] axis; 5) the elastic modulus c_{66}, corresponding to the transverse sound velocity along the [100] axis. The numerical values of the frequencies ω_1 and ω_2 were obtained from experiments on neutron scattering[2], while the elastic moduli were obtained from[21].

As a result of this solution of the inverse problem, the following values of the parameters were obtained:

$$\alpha = 2.87\cdot 10^3 \text{ dyne/cm}, \quad \beta = 1{,}34\cdot 10^3 \text{dyne/cm},$$

$$\gamma = 1{,}24\cdot 10^3 \text{ dyne/cm},$$

$$\sigma = 1{,}61 \text{ eV}, \quad r_s = 0{,}48\cdot 10^{-8} \text{ cm}. \qquad (6.4)$$

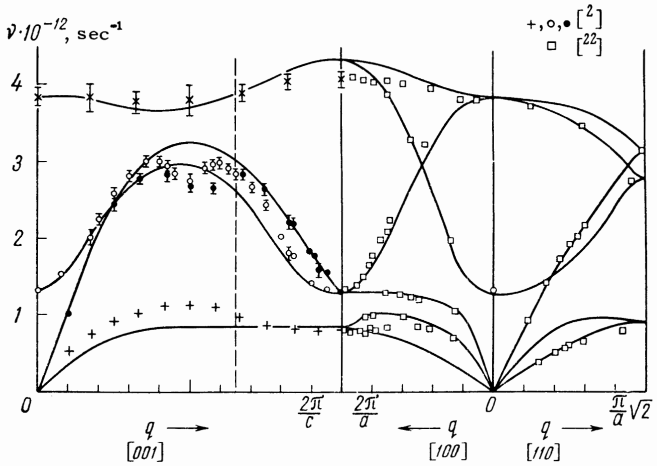


FIG. 1

D. The calculation of the vibration spectrum was carried out on a high-speed computer. Here, for the determination of the matrix D_1 according to (5.4), we used about 2000 sites of the reciprocal lattice in the summation over K. The results of the calculations for three principal directions of the wave vector, corresponding to the parameters of (6.4), are given in Fig. 1. Here, the experimental points used were from[2, 22]. As is seen, the agreement of theory with experiment is very good, especially if we consider the extraordinary nontrivial character of the behavior of the optical and acoustical branches and the abundance of information which is given by the dispersion curves for the three directions of the wave vector.

Figure 2 shows the pseudopotential for the tin ion, constructed by means of (6.1) and (6.12) for the parameters found above, and also the pseudopotential computed in[19]—the dashed curve. The agreement between the results is excellent, closer even than the values of the characteristic point corresponding to a change of sign of V_q^*. Therefore, we could have used the computed pseudopotential, and then the number of necessary parameters would be generally reduced to three. On the other hand, the obtained agreement shows

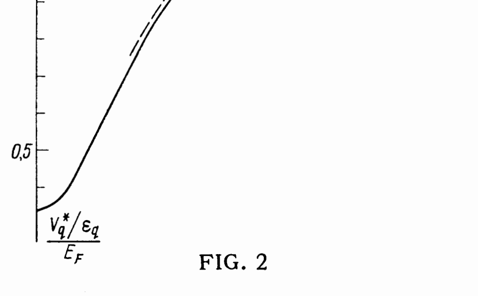


FIG. 2

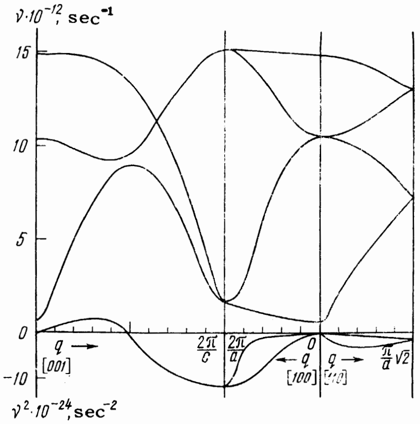


FIG. 3

the pseudopotential of the electron-ion interaction can be effectively replaced by the phonon spectrum of the metal.

E. Let us analyze the relative role of the long-range and short-range forces in the formation of the spectrum of white tin. For this purpose, we put forward the results of the calculation of the phonon spectrum corresponding to vibrations of the ion lattice of the tin, placed in the neutral field of a homogeneous negative charge (Fig. 3). (For the reduction of (5.4) to a rapidly converging series, use was made of a method similar to the well known method of Ewald.)

We note that the frequency of longitudinal optical vibrations (two ions vibrate in phase) does not go zero as $\mathbf{q} \rightarrow 0$, but to the value of the ion plasma oscillation frequency $\omega_0 = (2.4\pi Z^2 e^2/MV_0)^{1/2}$ (an extra factor of 2 arises from the presence of two atoms per unit cell). Then the combined shift of ions as $\mathbf{q} \rightarrow 0$ corresponds to motion of the optical type of the entire ionic lattice relative to a motionless phonon. It is essential that the ionic lattice is shown to be unstable—the phonon frequencies in the entire region of phase space become imaginary.

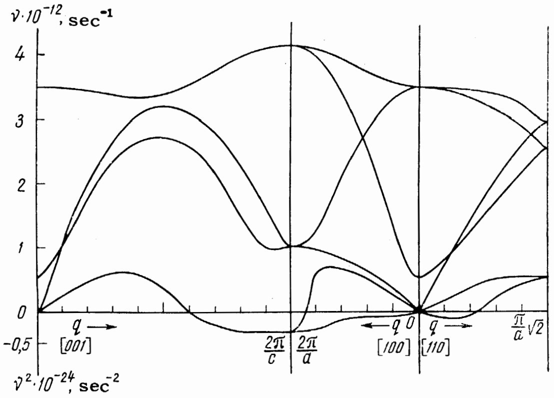


FIG. 4

Figure 4 shows the dispersion curves with allowance for the electron contribution to the long-range part of the interaction (but without introduction of covalency). Comparison with Fig. 3 shows that the screening of the ionic motion plays a very important role; in particular, the vibration frequencies fall off sharply in magnitude, a longitudinal acoustic branch of vibrations appears, and so forth.

By comparing the result with Fig. 1, we see that the obtained spectrum already bears many marks of the final one, especially for the optical branches. Yet the frequencies in several entire regions differ quantitatively from their true values. Moreover, the lattice as a whole is still unstable. The latter circumstance is not surprising, because the purely central interaction between ions could not lead to such a complicated crystalline structure as exists in the case of tin. Thus, in the complicated structure of tin, the stability is achieved only with the introduction of the short-range forces of the convalent type. This is a very interesting circumstance, sharply distinguishing the complicated crystals from the simple, for example, the alkali crystals.

Turning again to long-range interaction, we note that a detailed analysis shows the important and indeed, decisive role of Umklapp processes (terms with $\mathbf{K} \neq 0$) in tin. This leads to a sharp difference of frequencies of longitudinal and transverse optical branches for $q = 0$, to an unusual behavior of longitudinal vibrations with $\mathbf{q} \parallel [001]$, the frequencies of which pass through a maximum inside the Brillouin zone, and so forth. Such a specific role of terms with $\mathbf{K} \neq 0$ is not observed in simple metals, and therefore the dispersion curves in them have a very simple character.

More detailed results of the calculation of the phonon spectrum of tin will be published in a special paper.

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Translated by R. T. Beyer
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