

completely unsettled. Even if the skin depth is comparable to the dimension of the specimen, there will be coupling between the microwave magnetic field and all of the spin waves in the pathological region. No technique for calculating the skin-depth width has occurred

to us which would not require the diagonalization of the Hamiltonian. We have in fact verified that in a case of practical importance in metallic ferromagnetic resonance, i.e., the flat-plate specimen, position dependence does also occur in the dipole-wave sums.

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Electron-Phonon Interaction in Metals*

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The role of electron-electron interactions in determining the electron-phonon interaction in metals is investigated by extending the Bohm-Pines collective description to take into account the ionic motion. Collective coordinates are introduced to describe the long-range electron-ionic correlations, and it is shown by a series of canonical transformations that these give rise to plasma waves and to coupled electron-ion waves which correspond to longitudinal sound waves. The dispersion relation for the sound waves is identical with that derived by Toya and Nakajima by self-consistent field methods. The velocity of these sound waves is calculated from first principles for sodium and is found to be in

good agreement with experiment. The effective matrix element for the electron-phonon interaction is determined and is found to be identical for long wavelengths with that found earlier by Bardeen using a self-consistent field method which neglects exchange and correlation effects. The agreement with the earlier work is explained by the fact that the residual electron-electron interaction is of quite short range, so that an independent-particle treatment is rather well justified. The effects of Coulomb correlations on superconductivity are likewise shown to be small, so that the neglect of Coulomb interactions in the formulation of the superconductivity problem is justified.

1. INTRODUCTION

IN the coupled motion of electrons and ions in a metal, the tendency of the electrons to screen out the field of the ions is of primary importance. This screening greatly influences the effective matrix element for the electrical conductivity of the metal; it is also determining for the longitudinal sound wave velocity. The extent and effectiveness of this screening depend, in turn, on the electron-electron interaction in the metal. The usual theories of metallic electrical conduction treat these electron interactions on an independent-particle model in which each electron is assumed to move independently in a self-consistent field determined by the ions and the other electrons. Often no attempt is made to determine this self-consistent field; instead an empirical constant is introduced to describe the electron-lattice interaction. In 1937, one of us extended the self-consistent field method to take into account the motion of the ions, and thus to determine the matrix element for electron-lattice interactions.¹ The electron-electron interactions were treated in the Hartree approximation. More recently Nakajima² has given a simple field-theoretic treatment of this problem which also invokes the Hartree approximation and which leads to results essentially equivalent to A .

The independent-particle model has been successfully applied to a wide variety of problems. This success is somewhat surprising, because the marked correlations in electronic positions due to Coulomb interaction and exchange have been neglected. One of the main objects of this paper is to give a justification for this approach to the theory of conductivity.

The question of electronic correlations is of particular importance in the theory of superconductivity. Here one would expect that the large Coulomb correlation energy would play a more important role than the relatively small electron-lattice interaction energy in determining the transition from the normal to the superconducting state. However, experimentally this is not the case, as is shown by the isotope effect. We shall show why this is to be expected on theoretical grounds, and thereby justify the application of the independent-particle model to the formulation of this problem.

The physical basis for the unimportance of electron-electron correlations in conductivity and superconductivity arises from the tendency of the electrons to stay apart from one another in such a way that the field of a given electron is screened out within a distance of the order of the inter-particle spacing. Bohm and one of the authors have established this by showing that the long-range part of the Coulomb interaction leads only to coherent plasma oscillations of the electron gas and may be described in terms of these oscillations.³ Energies of the plasma quanta are so high that the

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¹ J. Bardeen, *Phys. Rev.* **52**, 688 (1937), hereafter referred to as A .

² S. Nakajima, *Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, September, 1953* (Science Council of Japan, Tokyo, 1954).

³ D. Bohm and D. Pines, *Phys. Rev.* **82**, 625 (1951); **85**, 338 (1952); **92**, 609 (1953); and D. Pines, *Phys. Rev.* **92**, 626 (1953), hereafter referred to as BP I, BP II, BP III, and P IV respectively.

oscillations are not excited thermally. There remains the short-range screened interaction between the aforementioned electrons. This analysis shows why electron-electron collisions are not important for either thermal or electrical conduction in metals. Abrahams⁴ has estimated the collision cross section and mean free path for electrons interacting via the screened Coulomb interaction in alkali metals. While the cross sections are of a reasonable order of magnitude ($\sim 10^{-15}$ cm²) the scatterings possible are so greatly restricted by the exclusion principle that collisions are infrequent. The electron-electron mean free path is long compared with the electron-phonon mean free path at all temperatures of interest.

The BP collective description is extended here to treat the coupled system of moving electrons and ions. Plasma coordinates are introduced to take into account the effect of electron-electron interactions on the electron-ion system. It is found that the effect of the long-range interactions may then be described rather simply, and explicit expressions are derived for the effective electron-phonon matrix element and for the sound wave frequencies. There remains the short-range electron-electron interaction which, as we have mentioned, does not influence the motion of a given electron appreciably, so that it is not surprising that superconductivity is little affected by the electronic Coulomb correlations.

The results we obtain for the influence of the electronic response on the electron-phonon interaction are in good agreement with those obtained in A. This problem has also been treated from another point of view by Bohm and Staver,⁵ who describe the ions and electrons as a set of coupled plasmas. They used a semi-classical approach closely related to BP II, and obtained the phonon dispersion relation. Our dispersion relation reduces to theirs in the appropriate limit.

The foregoing collective description is not applicable in the short wavelength region (corresponding to Fourier components of the electron-electron or electron-phonon interaction of wave vector greater than about the inverse particle spacing). Here the electron response to the ionic motion is probably best accounted for using the formulation of Nakajima. However, this formulation should be extended to include exchange effects, for it is precisely in this region (distances comparable or small compared to an electron de Broglie wavelength) that exchange begins to play an important role. We discuss the Nakajima method with exchange, but do not attempt to apply it to a detailed calculation because of the mathematical difficulties encountered in so doing.

2. DERIVATION OF HAMILTONIAN

We shall derive here for a monatomic crystal the Hamiltonian which will be used in the subsequent dis-

cussion. A number of approximations are made in order to simplify the calculations. It is assumed, as is usually done in the Bloch theory, that the matrix elements of the electron-lattice and Coulomb interactions depend only on the difference in wave vectors of the initial and final states. Another approximation is that lattice waves are either longitudinal or transverse, and that the electrons interact only with the longitudinal component. Both of these amount to neglect of anisotropic effects which greatly complicate the equations are probably important only for detailed quantitative calculations.

The general Hamiltonian is of the form

$$H = \sum_i (\mathbf{p}_i^2/2m) + \sum_{i,j} v(\mathbf{x}_i - \mathbf{X}_j) + H_{\text{ion-ion}} + H_{\text{Coul}}. \quad (2.1)$$

where i runs over the valence electrons, j over the ions, $v(\mathbf{x}_i - \mathbf{X}_j)$ represents the electron-ion interaction, $H_{\text{ion-ion}}$ includes the Coulomb and exchange repulsion of the ion cores and H_{Coul} the Coulomb interaction of the electrons. There are $n_0 = ZN$ electrons/cm³ where Z is the valency and N the ionic density. In order to eliminate infinities which appear in the separate terms of (2.1) (although not in the sum) we suppose there is subtracted from the electron-ion interaction the interaction of each electron with a uniform positive charge, from the electron-electron interaction the self-energy of a uniform negative charge, and from the ion-ion interaction the self-energy of a uniform positive charge. The sum of these adds to zero, so that the energy is unchanged. The ion-ion interaction energy less the self-energy of a uniform positive charge is equivalent to the energy of the ions in a uniform negative sea, including the self-energy of the negative charge.

We describe the electron wave function in second quantization by occupation numbers of a set of Bloch functions. It is assumed that the individual electrons move in a potential $V(\mathbf{x})$ which is the potential of the ions compensated by a uniform negative charge:

$$V(\mathbf{x}) = \sum_j v(\mathbf{x} - \mathbf{X}_j) + \text{comp. charge}. \quad (2.2)$$

The Bloch equation is

$$[(\mathbf{p}^2/2m) + V(\mathbf{x})]\psi_{\mathbf{k}} = E_{\mathbf{k}}\psi_{\mathbf{k}}. \quad (2.3)$$

We have used the extended zone scheme, so that \mathbf{k} is not necessarily in the first Brillouin zone. A discrete set of \mathbf{k} values is obtained in the usual way by introduction of periodic boundary conditions, with N the number of atoms in a fundamental period of unit volume. Creation and destruction operators, $c_{\mathbf{k}s}^*$, $c_{\mathbf{k}s}$, are defined in the usual way and obey commutation laws for Fermi particles:

$$[c_{\mathbf{k}'s'}^*, c_{\mathbf{k}s}]^+ = \delta_{\mathbf{k}\mathbf{k}'}\delta_{ss'}. \quad (2.4)$$

We shall omit the spin index s except where necessary for clarity.

The departure of the ions from equilibrium positions,

$$\delta\mathbf{X}_j = \mathbf{X}_j - \mathbf{X}_j^0, \quad (2.5)$$

⁴ E. Abrahams, Phys. Rev. **95**, 839 (1954).

⁵ D. Bohm and T. Staver, Phys. Rev. **84**, 836 (1952); T. Staver, Ph.D. thesis, Princeton University, 1952 (unpublished).

may be expressed in terms of normal coordinates, $q_{k\sigma}$ ($\sigma=1, 2, 3$):

$$\delta \mathbf{X}_j = (NM)^{-\frac{1}{2}} \sum_{k\sigma} q_{k\sigma} \mathbf{e}_{k\sigma} \exp[i\mathbf{k} \cdot \mathbf{X}_j^0], \quad (2.6)$$

in which $\mathbf{e}_{k\sigma}$ is a unit vector in the direction of polarization of the lattice waves, taken in the same sense for \mathbf{k} and $-\mathbf{k}$ so that $q_{-\mathbf{k}} = q_{\mathbf{k}}^*$. We assume that one of these directions is longitudinal and two transverse, and that the transverse frequencies are determined entirely from ion-ion interactions. These assumptions are not really valid, particularly for short wavelengths for which the distinction between longitudinal and transverse waves is no longer sharp. While much of the analysis can be carried through without making these assumptions, the slight additional generality gained does not seem warranted by the increase in complexity of the equations. We shall use the symbol q_k without polarization subscript to denote the longitudinal mode. In some of the summations, \mathbf{k} may run out of the first zone. In such a case, we always mean the q_k for the corresponding \mathbf{k} in the first zone. The phonon Hamiltonian is

$$H_{\text{ph}} = \frac{1}{2} \sum_{\text{zone}} (p_k^* p_k + \Omega_k^2 q_k^* q_k), \quad (2.7)$$

where Ω_k^2 is determined solely from ion-ion interactions. Calculation of the correct frequency, ω_k , which requires inclusion of the electron-lattice interactions, is discussed later.

The remaining parts of the Hamiltonian are expressed in terms of the c_k 's. The electron-lattice interaction may be written

$$\sum_{i,j} v(\mathbf{x}_i - \mathbf{X}_j) = \sum_{i,j} v(\mathbf{x}_i - \mathbf{X}_j^0) - (NM)^{-\frac{1}{2}} \sum_k \mathbf{e}_k \cdot \nabla v(\mathbf{x} - \mathbf{X}_j^0) q_k \exp[i\mathbf{k} \cdot \mathbf{X}_j^0]. \quad (2.8)$$

The first term may be combined with the kinetic energy of the electrons to give

$$H_{\text{el}} = \sum_i [(\mathbf{p}_i^2/2m) + V(\mathbf{x}_i)] = \sum_{ks} E_k c_{ks}^* c_{ks}. \quad (2.9)$$

The second term of (2.8) may be expressed in terms of the matrix elements,

$$v_k^i = - (NM)^{-\frac{1}{2}} \int \psi_{\kappa+k}^* \{ \sum_j \mathbf{e}_k \cdot \nabla v(\mathbf{x}_i - \mathbf{X}_j^0) \times \exp[i\mathbf{k} \cdot \mathbf{X}_j^0] \} \psi_{\kappa} d\tau, \quad (2.10)$$

assumed to be independent of κ , to give

$$H_{\text{int}} = \sum_{\kappa ks} c_{\kappa+k, s}^* c_{\kappa, s} q_k v_k^i = \sum_k q_k v_k^i \rho_{-k}, \quad (2.11)$$

where

$$\rho_k = \sum_{\kappa s} c_{\kappa-k, s}^* c_{\kappa, s}; \quad \rho_{-k} = \sum_{\kappa s} c_{\kappa, s}^* c_{\kappa-k, s}. \quad (2.12)$$

The sum over \mathbf{k} and κ extend over all values; q_k refers to the reduced vector in the first zone. Note that $(v_k)^* = v_{-k}^i$. The Coulomb interaction may be expressed in the form

$$H_{\text{Coul}} = \frac{1}{2} \sum_k M_k^2 \rho_{-k} \rho_k, \quad (2.13)$$

where for free electrons, $M_k^2 = 4\pi e^2/k^2$. It has again

been assumed that the matrix elements depend only on the vector difference between initial and final states.

The Hamiltonian is now expressed in the form

$$H = E_{\text{ion-ion}} + H_{\text{tr}} + H_1,$$

where

$$H_1 = H_{\text{el}} + H_{\text{ph}} + H_{\text{int}} + H_{\text{Coul}}, \quad (2.14)$$

and $E_{\text{ion-ion}}$ is the ion-ion interaction energy for the ions in equilibrium positions, H_{tr} is the Hamiltonian for transverse phonons, and the terms in H_1 are given by (2.7), (2.9), (2.11), and (2.13). From now on, we shall be concerned with the Hamiltonian H_1 . In Sec. III, we discuss earlier methods for calculation of the electron-lattice interaction by self-consistent field methods and in Sec. 4 we introduce plasma coordinates to treat the long-range part of the Coulomb interaction.

3. EARLIER METHODS FOR THE CALCULATION OF v_k AND ω_k

We are concerned in this section with a review of calculations which have been made of the effect of the shielding of the valence electrons on the interaction potential and on the sound-wave vibrational frequencies. For long wavelengths, the interaction of a given electron with the ionic motion is radically altered by the field due to the other electrons, which in the course of responding to the ionic motion move in just such a way as to produce a field which very nearly cancels the ionic field. The effective matrix element for the electron-lattice interaction, v_k , may be written as the sum of v_k^i due to the motion of the ions and v_k^e due to the motion of the electrons:

$$v_k = v_k^i + v_k^e. \quad (3.1)$$

In A, v_k^e was computed by what amounts to a Hartree self-consistent field calculation. It was assumed that the wave functions of the individual electrons change adiabatically with the ion motion. Recently Toya has determined the longitudinal sound wave frequency, ω_k , using this same model.⁶ We here give a simple derivation of the effect of the electron response on v_k and ω_k which agrees in the long wavelength limit with the foregoing calculations. Our treatment parallels in some respects that of Bohm and Staver.

According to (2.14) the equation of motion of the k th sound wave amplitude is

$$\ddot{q}_k + \Omega_k^2 q_k = -v_{-k}^i \rho_k. \quad (3.2)$$

The electronic density fluctuation ρ_k consists of two parts; one, ρ_k^0 , associated with the motion of electrons in the absence of a sound wave, and another, $\delta\rho_k$ which represents the motion of the electrons associated with the sound wave. For pure Coulomb interactions between free electrons $\delta\rho_k$ is related to the Fourier component of that part of the effective one-electron interaction potential v_k associated with the electronic re-

⁶ T. Toya, *Busseiron Kenkyu* **59**, 179 (1952).

sponse v_k^p , by Poisson's equation; $k^2 v_k^p q_k = 4\pi e^2 \delta \rho_k$, or more generally,

$$v_k^p q_k = M_k^{-2} \delta \rho_k. \quad (3.3)$$

Thus we may write for our sound-wave, q_k ,

$$\ddot{q}_k + \omega_k^2 q_k = -v_{-k}^i \rho_k^0, \quad (3.4)$$

with ω_k specified by the dispersion relation

$$\omega_k^2 = \Omega_k^2 + M_k^{-2} v_{-k}^i v_k^p. \quad (3.5)$$

Equation (3.4) describes the interaction of the sound waves with the *independently* moving electrons (here described in terms of their density fluctuation ρ_k^0) and in principle the resistance may be calculated from it.

The matrix element v_k^p may be simply calculated in the Fermi-Thomas approximation.⁷ In this approximation the electron density, $\rho(\mathbf{x})$, is proportional to $[E_0 - \delta V(\mathbf{x})]^{\frac{3}{2}}$, where E_0 is the energy of an electron at the top of the Fermi distribution and $\delta V(\mathbf{x})$ is the effective potential acting on the electrons due to the ionic motion. We then have for the density change $\delta \rho(\mathbf{x})$ associated with the sound-wave potential $\delta V(\mathbf{x})$,

$$\delta \rho(\mathbf{x}) = -\frac{3 n_0}{2 E_0} \delta V(\mathbf{x}). \quad (3.6)$$

We Fourier-analyze (3.6) and apply (3.1) to obtain

$$\delta \rho_k = -\frac{3 n_0}{2 E_0} v_k q_k = -\frac{3 n_0}{2 E_0} (v_k^i + v_k^p) q_k. \quad (3.7)$$

If we now compare (3.7) with (3.3), we see that the requirement that our treatment be self-consistent yields

$$v_k^p = \frac{-v_k^i}{1 + (2E_0/3n_0 M_k^2)}. \quad (3.8)$$

For long wavelengths, M_k^2 is given by its free-electron value, $4\pi e^2/k^2$, and we have

$$v_k^p = \frac{-v_k^i}{1 + (k^2 v_0^2/3\omega_p^2)} \cong -v_k^i \left(1 - \frac{k^2 v_0^2}{3\omega_p^2} \right), \quad (3.9)$$

where v_0 is the velocity of an electron at the top of the Fermi distribution and

$$\omega_p^2 = 4\pi n e^2 / m \quad (3.10)$$

is the square of the plasma frequency. Thus we see that the effect of the field of the other electrons is to screen out the "bare" electron-ion interaction within a distance of order ω_p/v_0 . For long wavelengths the effective matrix element for electron-phonon interaction is thus drastically reduced to

$$v_k \cong (k^2 v_0^2/3\omega_p^2) v_k^i. \quad (3.11)$$

The corresponding expression for the sound-wave fre-

quencies is

$$\omega_k^2 = \Omega_k^2 - \frac{k^2}{4\pi e^2} v_{-k}^i v_k^i \left(1 - \frac{k^2 v_0^2}{3\omega_p^2} \right). \quad (3.12)$$

Our expressions (3.9) for v_k and (3.12) for ω_k agree in this limit with the corresponding results of A and of Toya.

We may obtain a quite general expression for ω_k if we neglect the effect of lattice periodicity on the Ω_k and v_k^i and consider only Coulombic electron-ion and ion-ion interactions. This corresponds to treating the positive ions as a plasma; the "bare" phonon frequency is then

$$\Omega_k^2 \cong \Omega_P^2 = 4\pi N Z^2 e^2 / M. \quad (3.13)$$

The v_k^i are given by

$$v_k^i \cong - (4\pi Z e^2 i / k) (N/M)^{\frac{1}{2}}. \quad (3.14)$$

We then have

$$\omega_k^2 = k^2 v_0^2 \Omega_P^2 / 3\omega_p^2 = m Z^2 v_0^2 k^2 / 3M. \quad (3.15)$$

Thus in this approximation the square of the phonon frequency has been reduced by the same factor as the electron-phonon interaction matrix element,⁸ the phonon frequency is altered from a constant to one linear in k , with a sound velocity c_l , which depends only on the density and which is given by

$$c_l = m Z v_0 / \sqrt{3} M. \quad (3.16)$$

Equation (3.16) was first obtained by Bohm and Staver,⁵ and as shown by Staver⁵ is in fairly good agreement with the experimental observations. The extent of this agreement ($\sim 20\%$ for the alkali metals, no worse than a factor of two for any metal) indicates that one can get a good order of magnitude estimate, by such simple Coulombic considerations. In Appendix A, we discuss the results obtained with our more accurate dispersion relation (3.12). It is interesting to note that this same simplified model leads to a Sommerfeld-Bethe interaction constant $C = E_F/\sqrt{2}$.

Nakajima's field-theoretic derivation for v_k^p and ω_k goes somewhat beyond the adiabatic approximation but gives nearly equivalent results. We sketch his derivation here because as we shall see, it offers the best framework for the treatment of the short wavelength electron-phonon interaction. Frohlich⁹ has used a field-theoretic method which differs in some respects. He used an individual particle model which did not include Coulomb interactions between the electrons. His choice of creation and destruction operators and method of analyzing is such as to give the correct result for his problem when the change in the frequency from electron-phonon interactions is small. However, his dis-

⁸ The same shielding factor occurs because in the limit we are considering we may write $\omega^2 = n k^2 v_k^i (v_k^i + v_k^p) / m$, so that the sound wave frequencies are proportional to the effective matrix element v_k .

⁹ H. Frohlich, Proc. Roy. Soc. (London) **A215**, 291 (1952).

⁷ See also A. W. Overhauser, Phys. Rev. **89**, 689 (1953).

persion relation is not correct when the change in frequency is large.

Nakajima writes the Hamiltonian, H_1 , in a form equivalent to the following:

$$H_1 = \sum_{\kappa s} E_{\kappa} c_{\kappa s}^* c_{\kappa s} + \frac{1}{2} \sum_{\text{zone}} (p_k^* p_k + \omega_k^2 q_k^* q_k) + \sum_k v_k q_k \rho_{-k} + \frac{1}{2} \sum_k M_k^2 \rho_k \rho_{-k} + \sum_k (v_k^i - v_k) q_k \rho_{-k} + \frac{1}{2} \sum_{\text{zone}} (\Omega_k^2 - \omega_k^2) q_k^* q_k. \quad (3.17)$$

A canonical transformation is made to eliminate the first linear term in q_k . The interaction v_k is determined so as to eliminate the second linear terms in q_k , the second line, and ω_k^2 is chosen so as to cancel diagonal terms in $q_k^* q_k$ in the last line.

The transformed Hamiltonian is

$$H_1' = e^{-iS/\hbar} H_1 e^{iS/\hbar} = H_1 + i\hbar^{-1} [H_1, S] - \frac{1}{2} \hbar^{-2} [[H_1, S], S] + \text{etc.} \quad (3.18)$$

For S we take

$$S = i \sum_{\kappa \kappa'} c_{\kappa}^* c_{\kappa-k} [f(\mathbf{k}, \kappa) q_k - ig(\mathbf{k}, \kappa) p_{-k}]. \quad (3.19)$$

The required commutators are:

$$[\sum_{\kappa} E_{\kappa} c_{\kappa}^* c_{\kappa}, S] = i \sum (E_{\kappa} - E_{\kappa-k}) c_{\kappa}^* c_{\kappa-k} \times [f(\mathbf{k}, \kappa) q_k - ig(\mathbf{k}, \kappa) p_{-k}]. \quad (3.20)$$

$$[\frac{1}{2} \sum (p_k^* p_k + \omega_k^2 q_k^* q_k), S] = i \sum c_{\kappa}^* c_{\kappa-k} \times \{-i\hbar p_{-k} f(\mathbf{k}, \kappa) + \hbar \omega_k^2 q_k g(\mathbf{k}, \kappa)\}. \quad (3.21)$$

$$[\rho_{-k} \rho_k, S] = \rho_{-k} [\rho_k, S] + [\rho_{-k}, S] \rho_k. \quad (3.22)$$

$$[\rho_k, S] = i \sum_{\kappa, \kappa', \kappa''} \{\delta_{\kappa \kappa'} c_{\kappa-k}^* c_{\kappa'-k} - \delta_{\kappa'-k, \kappa-k} c_{\kappa}^* c_{\kappa'}\} \times \{f(\mathbf{k}', \kappa') q_{k'} - ig(\mathbf{k}', \kappa') p_{-k'}\}. \quad (3.23)$$

Diagonal terms are obtained if $\mathbf{k}' = \mathbf{k}$. If we keep only these, we may treat $[\rho_k, S]$ as a c -number. This is the procedure which Nakajima used, and is essentially equivalent to the Hartree approximation since there are evidently diagonal exchange terms in $\rho_{-k} [\rho_k, S]$ which are neglected. In this approximation, then,

$$\frac{1}{2} \sum_k M_k^2 [\rho_{-k} \rho_k, S] = i \sum_{\kappa, \kappa'} M_k^2 \rho_{-k} \{n(\kappa - \mathbf{k}) - n(\kappa)\} \times \{f(\mathbf{k}, \kappa) g_k - ig(\mathbf{k}, \kappa) p_{-k}\}. \quad (3.24)$$

Elimination of linear terms in q_k and p_{-k} in the first line gives the following for f and g :

$$g(\mathbf{k}, \kappa) = -\frac{\hbar f(\mathbf{k}, \kappa)}{E_{\kappa} - E_{\kappa-k}}, \quad (3.25)$$

$$f(\mathbf{k}, \kappa) = \frac{\hbar (E_{\kappa} - E_{\kappa-k}) v_k}{(E_{\kappa} - E_{\kappa-k})^2 - \hbar^2 \omega_k^2}. \quad (3.26)$$

Principal parts are to be taken in the sums over the energy denominators. Elimination of linear terms in q_k from the second line then gives

$$\sum_{\kappa, s} M_k^2 \{n(\kappa - \mathbf{k}) - n(\kappa)\} f(\mathbf{k}, \kappa) = \hbar (v_k^i - v_k), \quad (3.27)$$

or, substituting for $f(\mathbf{k}, \kappa)$,

$$v_k^i - v_k = -M_k^2 v_k \sum_{\kappa, s} \frac{(E_{\kappa} - E_{\kappa-k})(n(\kappa) - n(\kappa - \mathbf{k}))}{(E_{\kappa} - E_{\kappa-k})^2 - \hbar^2 \omega_k^2} = M_k^2 v_k \sum_{\kappa, s} \frac{n(\kappa) - n(\kappa - \mathbf{k})}{E_{\kappa-k} - E_{\kappa} + \hbar \omega_k}. \quad (3.28)$$

which can be solved readily to give v_k . Terms in p_{-k} vanish for a symmetrical distribution, such that $n(\kappa) = n(-\kappa)$.

Finally, elimination of diagonal terms in $q_k^* q_k$ gives the following equation for ω_k^2 :

$$\Omega_k^2 - \omega_k^2 = -S v_{-k}^i v_k \sum_{\kappa, s} \frac{n(\kappa - \mathbf{k}) - n(\kappa)}{E_{\kappa-k} - E_{\kappa} + \hbar \omega_k}. \quad (3.29)$$

The κ on the left refers to the reduced vector in the first Brillouin zone. The sum s on the right is over all \mathbf{k} which correspond to this same reduced wave vector, so that transitions due to Umklapp processes may be included. Contributions of electrons from different bands, if treated separately should also be added to the right-hand side. An alternative expression is

$$\Omega_k^2 - \omega_k^2 = S M_k^{-2} v_{-k}^i (v_k^i - v_k). \quad (3.30)$$

This is of the same form as Eq. (3.5). Equation (3.28) for the matrix element agrees with the 1937 result if $\hbar \omega_k$ in the denominator is neglected. Since $\hbar \omega_k \sim 10^{-4} E_F$, where E_F is the Fermi energy, the term will have practically no effect on the matrix element or frequency.

It should be noted that the Coulomb interaction between electrons still appears in the transformed Hamiltonian and we are still left with the problem of taking into account correlation effects on electron motion. The transformation does serve to introduce a set of oscillators which to second order are not coupled with the individual electrons. Scattering of electrons by oscillators is accounted for by interactions which conserve energy; i.e., those with zero energy denominators in the expansion. When summed by taking principal parts, these give a negligible contribution to the matrix element.

The exchange terms which Nakajima neglects are considered in Appendix B. Perhaps the most important effect of these terms is to add an exchange energy, W_{κ} , to the individual particle energy. It is known that such a term leads to an abnormally small density of states at the Fermi surface, and a correspondingly small low-temperature specific heat, which is contrary to observation.¹⁰ This has been explained by the collective description in which the fields of the individual electrons are effectively screened by the other electrons. The exchange terms are drastically reduced, and one finds that the calculated specific heat is not far from the free-electron value neglecting exchange.¹¹ It is

¹⁰ J. Bardeen, Phys. Rev. **50**, 1098 (1936).

¹¹ See P IV for a derivation of this result.

likely that inclusion of the unshielded exchange energy in the Nakajima calculation would lead to an incorrect electron-lattice interaction for long wavelengths. We shall show in Sec. 4 that the collective description is such as to introduce a shielded interaction into the calculation of the short-wavelength exchange terms, and no exchange effects at all appear for long wavelengths.

There remains the question of convergence of the expansion of the canonical transformation in a power series in v_k . The transformation is such as to introduce new individual particle wave functions which depend on the q_k 's. The expansion coefficients are, neglecting $\hbar^2\omega_k^2$ in the denominator,

$$\hbar^{-1}f(\mathbf{k}, \kappa) \cong \frac{v_k q_k}{E_{\kappa-k} - E_\kappa}. \quad (3.31)$$

One may expect that the expansion will converge rapidly if

$$\sum_k \frac{v_k^* v_k q_k^* q_k}{(E_{\kappa-k} - E_\kappa)^2} \ll 1. \quad (3.32)$$

The v_k are small and difficulty arises only from the terms for which the energy denominators are correspondingly small.

We shall now show that since principal parts are used, terms with small energy denominators contribute a negligible amount to the calculation of the matrix elements and frequency. Our analysis is similar to that of Frohlich⁹ who suggested omitting from the transformation those $f(\mathbf{k}, \kappa)$ which have small energy denominators, i.e., those for which

$$|E_{\kappa-k} - E_\kappa| < \Delta E. \quad (3.33)$$

When the same is done in our calculation, we find that we can choose ΔE large enough so that (3.32) is satisfied and small enough to have a negligible effect on the self-consistent field. To estimate the orders of magnitude involved, let us replace the matrix element by an average value, so that (3.32) becomes

$$|v_k q_k|_{Av}^2 \left\{ \int_0^{E_\kappa - \Delta E} \frac{N(E) dE}{(E - E_\kappa)^2} + \int_{E_\kappa + \Delta E}^{E_F} \frac{N(E) dE}{(E - E_\kappa)^2} \right\} \ll 1, \quad (3.34)$$

where $N(E)$ is the density of states in energy. This is roughly equivalent to

$$N(E_\kappa) |v_k q_k|_{Av}^2 \ll \Delta E. \quad (3.35)$$

If terms which satisfy (3.33) are omitted, what is the effect on the principal parts summation? The integral is of order:

$$\int_0^{E_F} \frac{N(E) dE}{E - E_\kappa} \sim N(E). \quad (3.36)$$

The omitted terms contribute roughly

$$\int_{E_\kappa - \Delta E}^{E_\kappa + \Delta E} \frac{N(E) dE}{E - E_\kappa} \cong 2 \frac{dN}{dE} \Delta E. \quad (3.37)$$

The relative error is thus of order

$$\frac{2}{N(E)} \frac{dN}{dE} \Delta E \sim \frac{\Delta E}{E_F}. \quad (3.38)$$

The left-hand side of (3.35) is of order $\hbar\omega_{\max} \sim 10^{-4} E_F$ for most metals. Thus if one takes $\Delta E \sim 10^{-2} E_F$, one may satisfy (3.32) and at the same time not affect appreciably the calculation of the matrix element and vibrational frequency.

It is, however, just these omitted terms which are all important in the theory of superconductivity.¹² In fact, the criterion for the occurrence of superconductivity is roughly that

$$N(E) |v_k q_k|_{Av}^2 > \hbar\omega_{\max}. \quad (3.39)$$

The conclusion is that even though the electron-lattice interaction is so large as to give superconductivity, one may still use the expansion in powers of v_k for those terms which give almost the entire contribution to the matrix element and vibrational frequency. This is true because the virtual transitions which give difficulty are only a very small fraction of the total and do not contribute abnormally.

4. COLLECTIVE DESCRIPTION OF ELECTRON-ION INTERACTION

In this section we wish to treat the electron response to the ionic motion by describing the electrons in terms of the appropriate plasma variables. As pointed out by BP, such a description of the electrons is only appropriate for long wavelengths, corresponding to $k < k_c$, where k_c is a critical wave vector (or the order of k_0) which is determined by minimizing the total system energy as discussed in BP III. In this section we shall therefore only apply the collective description to the long-wavelength phonons, their interaction with the electrons, and the long-range electron-electron interactions (all corresponding to Fourier components with wave vectors less than k_c). We follow a procedure closely related to that used by one of us in dealing with the electron-electron interaction problem in the absence of ionic motion.¹³

Our basic aim in the collective description is the introduction of a new set of field variables which describe the independent plasma oscillations of the system as a whole. We may do this by first introducing a new field into our basic Hamiltonian, and then carrying out a series of canonical transformations which enable us to relate this field variable to the plasma oscillations we

¹² H. Frohlich, Phys. Rev. **79**, 845 (1950); J. Bardeen, Revs. Modern Phys. **23**, 261 (1951).

¹³ D. Pines, Report to the Tenth Solvay Conference, Brussels (1954).

wish to describe. As a first step, we add a field-energy term to our initial Hamiltonian, (2.14) so that our Hamiltonian is now

$$H = H_1 + \frac{1}{2} \sum_{|\mathbf{k}| < k_c} P_k^* P_k. \quad (4.1)$$

The P_k are here a quite arbitrary set of field variables, as yet undefined, which commute with all operators appearing in H_1 . In order that the energy and number of degrees of freedom of our system remain unchanged by this field, we must further impose a set of subsidiary conditions on our combined system wave function:

$$P_k \Psi = 0 \quad (|\mathbf{k}| < k_c). \quad (4.2)$$

We now wish to transform to a representation in which the P_k will describe independent plasma oscillations. In the absence of ionic motion, the ρ_k in the long-wavelength limit describe almost free collective oscillation, and the appropriate transformation would relate the P_k to the ρ_k . In our case, since the electrons also interact with the phonons, we would expect that it is only some linear combination of density fluctuations and phonon field variables which would carry out uncoupled collective plasma oscillation. Thus we are led to try a canonical transformation which relates the P_k to both ρ_k and the q_k . The first transformation we consider is generated by

$$S = \sum_{|\mathbf{k}| < k_c} (-iM_k \rho_{-k} + u_k q_{-k}) Q_k, \quad (4.3)$$

where Q_k is the coordinate conjugate to the plasma field momentum P_k , and u_k is a real constant to be determined. After this transformation our subsidiary condition, (4.2) becomes

$$e^{-iS/\hbar} P_k e^{iS/\hbar} \Psi = [P_k - iM_k \rho_{-k} + u_k q_{-k}] \Psi = 0. \quad (4.4)$$

Our Hamiltonian (4.1) is transformed to

$$\begin{aligned} H = & \sum_{\kappa} E_{\kappa} c_{\kappa}^* c_{\kappa} + \frac{1}{2} \sum_{|\mathbf{k}| < k_c} \{ p_k^* p_k + (\Omega_k^2 - \omega_k^2) q_k^* q_k \} \\ & + \frac{1}{2} \sum_{|\mathbf{k}| < k_c} \{ P_k^* P_k + (\omega_p^2 + u_k^2) Q_k^* Q_k \} \\ & + \sum_{|\mathbf{k}| < k_c} \{ v_k^i - iM_k u_k \} q_k \rho_k + \sum_{|\mathbf{k}| < k_c} u_k \rho_k^* Q_k \\ & - \sum_{|\mathbf{k}| < k_c, \kappa} \frac{\hbar \mathbf{k}}{m} \cdot (\boldsymbol{\kappa} - \frac{1}{2} \mathbf{k}) c_{\kappa}^* c_{\kappa - \mathbf{k}} Q_k \\ & + \frac{1}{2} \sum_{|\mathbf{k}| > k_c} \{ p_k^* p_k + \Omega_k^2 q_k^* q_k \} + \sum_{|\mathbf{k}| > k_c} v_k^i q_k \rho_{-k} \\ & + \frac{1}{2} \sum_{|\mathbf{k}| > k_c} M_k^2 \rho_{-k} \rho_k. \end{aligned} \quad (4.5)$$

In obtaining this expression we have made use of the new subsidiary condition, (4.4), and we have applied the "random phase" approximation of BP.¹⁴ We have

¹⁴ If the phonon terms in (4.5) are suppressed (and $u_k = 0$), it may be seen that the form of (4.5) is identical with the Hamiltonian used in BP III as the starting point for the collective description.

also applied the effective mass approximation, $E(\boldsymbol{\kappa}) = \hbar^2 \boldsymbol{\kappa}^2 / 2m$.¹⁵

The first three terms of our new Hamiltonian, (4.5), describe the one-electron energy levels, the phonon field, and the plasma field. The next three describe the electron-phonon interaction, plasma-phonon interaction, and plasma-electron interaction, while the remaining terms describe the short-wavelength phonons, their interaction with the electrons, and the short-range electron-electron interaction. We see that we have here redescribed the long-range electron-electron interactions in terms of the plasma oscillations, which however are not yet "isolated," in the sense that there remains a plasma-electron and plasma-phonon interaction, and the plasma field variable still appears in the subsidiary condition. The effect of the electron-electron interactions on the effective interaction matrix element and on the sound wave frequency is contained in the u_k , which as we see measure the coupling between the plasma waves and the phonons. The u_k are simply related to the v_k^p we introduced in the preceding section to describe the effect of electron shielding on the v_k ; we have

$$v_k^p = -iM_k u_k. \quad (4.6)$$

Our remaining problem is thus the determination of u_k and the new sound wave frequencies.

We may actually do this without explicitly solving for the effect of the electron-plasma interaction and plasma-phonon interaction on the problem at hand. For, as is the case in the absence of ionic motion, the coupling between the electrons and the plasma oscillations is weak. Furthermore, because of the great disparity between the plasma frequencies and phonon frequencies (a disparity of order m/M), the coupling between the plasma waves and the phonons is likewise weak. Both of these interactions may easily be taken into account by appropriate canonical transformations; however because of the weakness of the coupling, such transformations will leave the relevant terms in our Hamiltonian essentially unaltered, so we do not need to carry them out explicitly here.

How, then, do we choose the u_k ? It is clear from the discussion of the preceding section that we must choose the u_k in such a way that our treatment is self-consistent. The requirement of self-consistency appears in the following guise. In our problem the electrons and phonons are coupled not only in the Hamiltonian (4.8) but in the subsidiary condition (4.9) as well. The requirement of self-consistency is then just the requirement that the coupling via the subsidiary condition be completely equivalent to the coupling via the Hamil-

¹⁵ The use of the effective mass approximation for this problem is discussed by J. Hubbard, Proc. Phys. Soc. (London) **A67**, 1058 (1954); P. Wolff, Phys. Rev. **95**, 56 (1954). E. N. Adams II [Phys. Rev. **98**, 947 (1955)] has pointed out that interband transitions may have an important effect. N. F. Mott [Proceedings of the Tenth Solvay Conference, Brussels (1954)] has given reasons for expecting that the free electron mass rather than an effective mass would appear in many cases.

tonian. This guarantees that we introduced the correct admixture of phonon coordinates (as determined by the electron-phonon interaction) in the plasma oscillation amplitude. We obtain an explicit solution for the u_k and the sound-wave frequencies ω_k by carrying out a canonical transformation which eliminates to a given order of accuracy the electron-phonon interaction terms in the Hamiltonian, (4.5). Our self-consistency requirement is then that to this same order of accuracy there be no coupling of the sound waves to the electrons in the transformed subsidiary condition; this will be the case if the phonon variable no longer appears in the transformed subsidiary condition in this order.

Our desired canonical transformation is just that generated by (3.19), since we have identified v_k with $v_k^i - iM_k \rho_{-k}$. As before $f(\mathbf{k}, \kappa)$ and $g(\mathbf{k}, \kappa)$ are defined through (3.25) and (3.26), and as discussed in the preceding section a perturbation theory expansion in powers of v_k is valid. Our transformed Hamiltonian is¹⁶

$$\begin{aligned} H = & \sum_{\kappa} E_{\kappa} c_{\kappa}^* c_{\kappa} + \frac{1}{2} \sum_{|\mathbf{k}| < k_c} \{ p_k^* p_k + \omega_k^2 q_k^* q_k \} \\ & + \frac{1}{2} \sum_{|\mathbf{k}| < k_c} \{ P_k^* P_k + (\omega_p^2 + u_k^2) Q_k^* Q_k \} \\ & - \sum_{|\mathbf{k}| < k_c, \kappa} \frac{\hbar \mathbf{k}}{m} \cdot (\kappa - \frac{1}{2} \mathbf{k}) c_{\kappa}^* c_{\kappa-k} Q_k \\ & + \frac{1}{2} \sum_{|\mathbf{k}| > k_c} (p_k^* p_k + \Omega_k^2 q_k^* q_k) + \sum_{|\mathbf{k}| > k_c} v_k^i q_k \rho_{-k} \\ & + \frac{1}{2} \sum_{|\mathbf{k}| > k_c} M_k^2 \rho_k \rho_{-k} \\ & - \frac{1}{2} \sum_{|\mathbf{k}| < k_c, \kappa} v_{-k} \rho_k c_{\kappa}^* c_{\kappa-k} g(\mathbf{k}, \kappa). \quad (4.7) \end{aligned}$$

The dispersion relation for our "uncoupled" phonons is

$$\omega_k^2 = \Omega_k^2 - u_k^2 + v_k^2 \sum_{\kappa} \frac{n(\kappa - \mathbf{k}) - n(\kappa)}{\hbar \omega_k + E_{\kappa-k} - E_{\kappa}}. \quad (4.8a)$$

We further find, using (3.23) that our self-consistency requirement that q_k no longer appear in the subsidiary condition yields:

$$u_k = -iM_k v_k \sum_{\kappa} \frac{n(\kappa - \mathbf{k}) - n(\kappa)}{\hbar \omega_k + E(\kappa - \mathbf{k}) - E(\kappa)}. \quad (4.8b)$$

On applying (4.6) we see that this choice of u_k (or v_k) is in complete agreement with the result of Nakajima (3.28). Furthermore, on combining (4.8a) with (4.8b) we obtain the by now familiar dispersion relation (3.5).

A transformation similar to that of Nakajima may be used to eliminate the terms linear in q_k for $|\mathbf{k}| > k_c$. The result of both transformations is to replace the electron-lattice interaction by an interaction between electrons:

$$\begin{aligned} H_2 = & -\frac{1}{2} \sum_{\kappa, |\mathbf{k}| < k_c} v_{-k} \rho_k c_{\kappa}^* c_{\kappa-k} g(\mathbf{k}, \kappa) \\ & - \frac{1}{2} \sum_{\kappa, |\mathbf{k}| > k_c} v_{-k}^i \rho_k c_{\kappa}^* c_{\kappa-k} g(\mathbf{k}, \kappa). \quad (4.9) \end{aligned}$$

¹⁶ We have omitted the weak plasma-phonon interaction term.

Note that the unshielded interaction, v_{-k}^i , appears from the Nakajima transformation. Since v_{-k}^i becomes infinite while v_{-k} approaches zero as $\mathbf{k} \rightarrow 0$, the difference is particularly important when \mathbf{k} is small.

The interaction term, H_2 , is similar to one derived by Frohlich⁹ without explicit introduction of Coulomb interactions. His interaction constant is to be identified with the shielded interaction, v_k . As he points out, the usual second-order perturbation theory expression for the electron-lattice interaction energy is the sum of the diagonal component of H_2 (which Frohlich calls E_2) and the change in zero-point energy of the oscillators. It is the true frequency, ω_k , rather than Ω_k , which enters into these expressions.

There are several other important differences between our treatment and that of Nakajima. In (4.7) the long-range Coulomb interactions no longer appear, but have been redescribed by the high-frequency plasma oscillations. There remains the weak plasma-electron interaction but this may be easily transformed away, as is done in BP III, and it may then be seen that only effective residual electron-electron interaction is that described by

$$H_{s.r.} = \frac{1}{2} \sum_{|\mathbf{k}| > k_c} M_k^2 \rho_k \rho_{-k}.$$

Thus the long-range electron-electron correlations have been described in terms of the plasma oscillations, and are seen explicitly not to affect the electron response to the long wavelength phonons. We further note that no exchange effects are associated with the long-range part of the electron-electron interactions, so that the use of the Hartree approximation in determining v_k for $|\mathbf{k}| < k_c$ is completely justified.

There remains the complication introduced by the transformed subsidiary condition, which on applying (4.8b) agrees with that for the electron-plasma system in the absence of ionic motion:

$$(P_k - iM_k \rho_{-k}) \Psi = 0. \quad (4.10)$$

This complication has been discussed in BP III. The same transformation which eliminates the plasma-electron interaction in the Hamiltonian (4.7) also eliminates the plasma momentum from the subsidiary condition (4.10). There remains then a subsidiary condition acting on the electrons alone. As shown in BP III this subsidiary condition will be automatically satisfied for the lowest state of the system. It will influence the excited states in such a way as to reduce the effective number of electronic degrees of freedom slightly, but because the number of plasma degrees of freedom is relatively small (of order 5%-10%) this reduction should be correspondingly small.

We still have in our Hamiltonian (4.7) the short-wavelength terms corresponding to $|\mathbf{k}| > k_c$; the short-wavelength phonons, their interaction with the electrons, and the short-range part of the electron-electron interaction. As mentioned earlier, these terms may be

treated by the method of Nakajima in order to determine the effective electron-lattice interaction and sound wave frequencies. As discussed in Appendix B, for this wavelength region exchange effects are of importance. However, they are in principle calculable and should not lead to anomalous results, since the effective electron interaction is screened. Because of the mathematical complexity of the system of coupled equations obtained in Appendix B, we have not been able to obtain an explicit solution for the short wavelength v_k and ω_k when exchange effects are included.

The short-range electron-electron interaction occurring in (4.7) will not have an appreciable effect on the electronic wave functions. For as is shown in P IV, the range of this interaction is of the order of the interparticle spacing, and it may consequently in fact be treated as a relatively small perturbation on the electronic motion, and thus on the electronic wave functions.

5. CONCLUSIONS

We are led to the following physical picture of the coupled motion of ions and electrons in a metal. As the ions move, the electrons tend to follow their motion so as to screen out the ion field in a distance comparable with the interparticle spacing. Thus the fluctuations in potential caused by the motion of the ions are greatly reduced. The effective matrix element for electron-lattice interaction is determined by a screened field which can be calculated rather accurately for long wavelengths by elementary considerations. The positions of the electrons are correlated so that the field of a given electron is also screened out in a distance of the order of the interparticle spacing. Long-range correlation effects, according to the collective description, give rise to plasma waves and to coupled ion-electron waves which correspond to longitudinal sound waves. The remaining short-range interactions can be taken into account in a satisfactory way by the individual particle model.

In the collective description, extra coordinates are introduced to describe the plasma oscillations, and introduction of these requires that the system wave function satisfy supplementary conditions. A series of canonical transformations is made in order to isolate the plasma oscillations and the longitudinal sound waves. The effective matrix element for electron-phonon interaction is thereby determined and found to be identical for long wavelengths with that found earlier by self-consistent field methods which neglect effects of exchange and correlation. There remain in the transformed Hamiltonian terms which describe individual particles which interact with each other with a screened Coulomb force and are coupled with the phonon field in the usual way. The screened interaction is sufficiently weak so that it can be treated by perturbation methods and does not have a large effect on the particle wave

functions. In this way we see that the usual empirical individual-particle model is justified.

An expression is derived for phonon frequencies of long wavelength and is found to be identical with that derived by Toya and Nakajima by self-consistent field methods. An explicit calculation for monovalent metals, given in an appendix, yields, when applied to Na, good agreement with values calculated from observed elastic constants. Our calculation makes use of matrix elements derived in A by the self-consistent field method. The elastic constants may also be obtained by a direct calculation of the energy of a distorted crystal, as has been done by Fuchs. The close agreement both with the observed values and with the direct calculation makes one confident that the general method for calculating matrix elements and vibrational frequencies is correct.

The calculation of the matrix elements and vibrational frequencies for short wavelengths is less reliable, because we have not been able to take into account the influence of exchange on these quantities. Perhaps the best procedure in calculations of conductivity at room temperatures, where short wavelength phonons and Umklapp processes are important, is to introduce an empirical scattering factor, as has recently been suggested by Ziman.¹⁷

In the formulation of the superconductivity problem, it is probably a reasonably good approximation to use an empirical interaction constant, v_k , and to omit explicit introduction of Coulomb interaction terms, as has been done by Frohlich and by Bardeen. The fact that v_k^i rather than v_k appears in the interaction Hamiltonian, H_2 , in (4.9) for $|\mathbf{k}| > k_c$ raises some doubt about this procedure, but the difference is not large for these short wavelengths.

Except for terms which correspond to transitions which nearly satisfy the conservation of energy,

$$|E_{k'} - E_k \pm \hbar\omega_k| < \Delta E, \quad (5.1)$$

the electron-lattice interaction can be eliminated by a canonical transformation such that in the final Hamiltonian the lattice oscillators are not coupled with the electrons. It is the remaining interaction terms which do satisfy (5.1) that are responsible for scattering of electrons and also presumably account for superconductivity. The value of ΔE always can be chosen sufficiently small so that these terms have a negligible effect on the electron-lattice matrix element and on the vibrational frequency. On the other hand, they cannot be treated by perturbation theory, and so can have a pronounced effect on the electron wave functions.

In the theory of superconductivity, then, one need only consider virtual transitions which satisfy an expression of the form (5.1). This approach was followed by one of the authors,¹² with ΔE chosen to be of the order of the electron-lattice interaction energy resulting

¹⁷ J. M. Ziman, Proc. Roy. Soc. (London) **A226**, 432 (1954).

from these virtual transitions. This gives [see Eq. (3.35)]

$$\Delta E \sim N(E) \langle |v_k q_k|^2 \rangle_{Av}, \quad (5.2)$$

which is an order of magnitude or so larger than kT_c (T_c = transition temperature) for most superconductors. If one assumes that these interactions contribute to the superconducting state, but not to the normal state, one would have far too large an energy difference between the two phases. About the correct order of magnitude for this energy difference is obtained if we arbitrarily take $\Delta E \sim kT_c$; that is if electrons with energies within $\sim kT_c$ of the Fermi surface have their energies lowered by $\sim kT_c$. Undoubtedly the virtual transitions determined by (5.2) contribute to both the normal and superconducting states, and only a very small fraction of the interaction energy is involved in the change of state. It is evident that better pictures of both the normal and superconducting phases are required. The equations we have presented here should provide a good basis for development of an adequate theory.

APPENDIX A: CALCULATION OF ω_k FOR A MONOVALENT METAL

We give here an explicit calculation of the sound-wave frequencies for the long wavelength limit, $k \rightarrow 0$, by making use of the matrix elements of the electron-lattice interaction in Eq. (3.12). The Nakajima expression, Eq. (3.30), gives equivalent results in this limit. The matrix elements used are those derived originally for a calculation of the conductivity of monovalent metals.

Determining the frequencies for long wavelengths is equivalent to calculating the elastic constants, which are usually obtained by a direct calculation of the energy of a distorted crystal. Compressibilities of monovalent metals have been determined by a Wigner-Seitz calculation of the energy as a function of volume. Fuchs¹⁸ has shown that the shear constants of the alkali metals are given quite closely by the Coulomb interactions of the ions in a uniform negative sea. Although important for the noble metals, repulsion between the closed shells is almost negligible for the alkalis.

It is most convenient to determine the sum of the squares of the frequencies for the three different directions of polarization, since this sum is independent of the direction of propagation. Kohn¹⁹ has shown that the sum for the Coulomb interactions of the ions alone is just the square of the plasma frequency for a gas of the same density:

$$\sum_{\sigma=1,2,3} \Omega_{k\sigma}^2 = \frac{4\pi N e^2}{M}. \quad (A1)$$

Only the longitudinal component is affected by the electron-lattice interaction, so that, from Eq. (3.12),

$$\sum_{\sigma} \omega_{k\sigma}^2 = \sum_{\sigma} \Omega_{k\sigma}^2 - \frac{k^2}{4\pi e^2} |v_k^i|^2 \left(1 - \frac{k^2 E_F}{6\pi N e^2} \right), \quad (A2)$$

where

$$E_F = \hbar^2 k_0^2 / 2m \quad (A3)$$

is the Fermi energy. In terms of the elastic constants

$$\sum_{\sigma} \omega_{k\sigma}^2 = NM k^2 (c_{11} + 2c_{44}). \quad (A4)$$

The expression for the matrix element v_k^i is taken from reference 1,

$$v_k^i = -\frac{ik}{(NM)^{1/2}} \left\{ \frac{4\pi N e^2}{k^2} + \gamma (V_0(r_s) - E_0) \right\} \times \left\{ \frac{3(\sin kr_s - kr_s \cos kr_s)}{(kr_s)^3} \right\}, \quad (A5)$$

where r_s is the radius of a sphere of atomic volume, $V_0(r_s) \cong 0$ is the potential at the boundary of the s -sphere, E_0 is the energy of the lowest state, and $\gamma = |\psi_0(r_s)|^2 / \langle \psi_0(r)^2 \rangle_{Av}$. Both V_0 and E_0 refer to a potential in which the field of the ions is compensated by a uniform negative charge. Wigner and Seitz calculated the energy, \mathcal{E}_0 , for a cell in which the field is that of the bare ion at the center. If $v_0(r_s)$ is the corresponding potential, there is the approximate relation

$$V_0(r_s) - E_0 = v_0(r_s) - \mathcal{E}_0 - 0.2e^2/r_s. \quad (A6)$$

There is also the following relation, originally derived by Frohlich:

$$\frac{r_s}{3} \frac{d\mathcal{E}_0}{dr_s} = \gamma (v_0(r_s) - \mathcal{E}_0). \quad (A7)$$

An expansion of (A5) in a power series in k is

$$v_k^i = -i \frac{4\pi e^2}{k} \left(\frac{N}{M} \right)^{1/2} \left\{ 1 + \frac{k^2 \gamma}{4\pi N e^2} [V_0(r_s) - E_0] - \frac{1}{10} k^2 r_s^2 + \dots \right\} \\ = -i \frac{4\pi e^2}{k} \left(\frac{N}{M} \right)^{1/2} \left[1 + \frac{k^2}{4\pi N e^2} \times \left[\gamma [V_0(r_s) - E_0] - \frac{3}{10} \frac{e^2}{r_s} \right] + \dots \right], \quad (A8)$$

where we have used $N = 3/4\pi r_s^3$. Substitution of (A8) into (A2) gives after some reduction

$$\sum_{\sigma} \omega_{k\sigma}^2 = \frac{k^2}{M} \left\{ \frac{2}{3} E_F + \frac{6e^2}{10r_s} - 2\gamma [V_0(r_s) - E_0] + \dots \right\},$$

¹⁸ K. Fuchs, Proc. Roy. Soc. (London) **153**, 662 (1936); **157**, 444 (1936).

¹⁹ W. Kohn (private communication). We should like to thank Professor Kohn for communicating his results to us in advance of publication.

so that, from (A4),

$$c_{11} + 2c_{44} = N \left\{ \frac{2}{3} E_F + \frac{6e^2}{10r_s} - 2\gamma[V_0(r_s) - E_0] + \dots \right\}.$$

Inserting appropriate values for sodium, with the free-electron value for E_F and $\gamma=1$, we find

$$2.6 \times 10^{22} \{3.3 + 6.6 - 0.6\} \times 10^{-12} = 2.4 \times 10^{11} \text{ ergs/cm}^3,$$

while

$$c_{11} + 2c_{44} = \{0.95 + 2(0.59)\} \times 10^{11} = 2.13 \times 10^{11} \text{ ergs/cm}^3.$$

The difference between calculated and observed values is only about 10%. This agreement gives one confidence in the method of calculation and in the values of the matrix elements for electron-lattice scattering for small k .

APPENDIX B: EXCHANGE TERMS FROM COULOMB INTERACTION

There are a number of exchange terms in the commutator of the Coulomb interaction:

$$\frac{1}{2} \sum M_{k'}^2 [\rho_{-k'} \rho_{k'}, S] = \frac{1}{2} \sum M_{k'}^2 \times \{\rho_{-k'} [\rho_{k'}, S] + [\rho_{-k'}, S] \rho_{k'}\}, \quad (\text{B1})$$

which were omitted in Nakajima's treatment. Exchange terms appear only for electrons of parallel spins. Expansion of the commutators for these gives

$$\begin{aligned} \frac{i}{2} \sum M_{k'}^2 \{ & c_{k'}^* c_{k'-k'} (c_{k-k}^* c_{k-k} - c_{k'}^* c_{k-k+k'}) \\ & + (c_{k-k}^* c_{k-k} - c_{k'}^* c_{k-k+k'}) c_{k'}^* c_{k'-k'} \} \\ & \times \{f(\mathbf{k}, \mathbf{k}) q_k - i g(\mathbf{k}, \mathbf{k}) p_{-k}\}. \end{aligned} \quad (\text{B2})$$

In the second line we have changed the sign of \mathbf{k}' .

Our problem is to find diagonal parts of the coefficients of $c_{k'}^* c_{k-k} q_k$ and corresponding terms. In addition to those for which $\mathbf{k}' = \mathbf{k}$, \mathbf{k}' arbitrary, used in obtaining (3.24), there are several others: (a) $\mathbf{k}' = \mathbf{k}$, (b) $\mathbf{k}' = \mathbf{k} - \mathbf{k}$, (c) $\mathbf{k} = \mathbf{k}' - \mathbf{k}'$, (d) $\mathbf{k}' = \mathbf{k} - \mathbf{k} + \mathbf{k}'$. The sum of these may be expressed in the form

$$\begin{aligned} \frac{1}{2} \sum M_{k'}^2 [\rho_{-k'} \rho_{k'}, S] = i \sum_{\mathbf{k}, \mathbf{k}'} \{ & \sum_{\mathbf{k}', \mathbf{s}} M_{k'}^2 \\ & \times \{n(\mathbf{k}' - \mathbf{k}) - n(\mathbf{k}')\} f(\mathbf{k}, \mathbf{k}') \\ & + \sum_{\mathbf{k}'} M_{k'}^2 \{n(\mathbf{k} - \mathbf{k} - \mathbf{k}') - n(\mathbf{k} - \mathbf{k}')\} f(\mathbf{k}, \mathbf{k}) \\ & + \sum_{\mathbf{k}'} M_{k'}^2 \{n(\mathbf{k}') - n(\mathbf{k}' - \mathbf{k})\} f(\mathbf{k}, \mathbf{k}')\} c_{k'}^* c_{k-k} q_k \\ & + \text{corresponding terms in } g(\mathbf{k}, \mathbf{k}). \end{aligned} \quad (\text{B3})$$

The first sum in the curly brackets is over both spin states, the other two only over the spin which is parallel to that of $c_{k'}^* c_{k-k}$.

When exchange terms are included, the effects of the other electrons on a given electron can no longer be expressed in terms of a potential, and it is no longer advantageous to introduce v_k . In order to eliminate linear terms in q_k and p_{-k} in the transformed Hamiltonian, $f(\mathbf{k}, \mathbf{k})$ and $g(\mathbf{k}, \mathbf{k})$ must satisfy the following equations:

$$\begin{aligned} \sum_{\mathbf{k}'} (2M_{k'}^2 - M_{k-k'}^2) [n(\mathbf{k}' - \mathbf{k}) - n(\mathbf{k}')] f(\mathbf{k}, \mathbf{k}') \\ - (W_{k-k} - W_k) f(\mathbf{k}, \mathbf{k}) + (E_k - E_{k-k}) f(\mathbf{k}, \mathbf{k}) \\ + \hbar \omega_k^2 g(\mathbf{k}, \mathbf{k}) + v_k^i = 0, \\ \sum_{\mathbf{k}'} (2M_{k'}^2 - M_{k-k'}^2) [n(\mathbf{k}' - \mathbf{k}) - n(\mathbf{k}')] g(\mathbf{k}, \mathbf{k}') \\ - (W_{k-k} - W_k) g(\mathbf{k}, \mathbf{k}) + (E_k - E_{k-k}) g(\mathbf{k}, \mathbf{k}) \\ + \hbar f(\mathbf{k}, \mathbf{k}) = 0, \end{aligned} \quad (\text{B4})$$

where W_k is the exchange energy of an electron in the state \mathbf{k} :

$$W_k = - \sum_{\mathbf{k}'} M_{k'}^2 n(\mathbf{k} - \mathbf{k}'). \quad (\text{B5})$$

The factor two multiplying $M_{k'}^2$ takes account of the sum over spins. The equations are such that for a symmetrical distribution of electrons in \mathbf{k} space, $n(\mathbf{k}) = n(-\mathbf{k})$, the solutions satisfy the relations:

$$f(\mathbf{k}, \mathbf{k} - \mathbf{k}) = -f(\mathbf{k}, \mathbf{k}); \quad g(\mathbf{k}, \mathbf{k} - \mathbf{k}) = g(\mathbf{k}, \mathbf{k}). \quad (\text{B6})$$

The direct term in the equation for $g(\mathbf{k}, \mathbf{k})$ then vanishes:

$$\sum_{\mathbf{k}'} M_{k'}^2 [n(\mathbf{k}' - \mathbf{k}) - n(\mathbf{k}')] g(\mathbf{k}, \mathbf{k}') = 0. \quad (\text{B7})$$

When the exchange terms are included, the equations cannot be solved algebraically.

There are two types of exchange terms. One simply adds the exchange energy W_k to the individual particle energy E_k . The other adds sums over $f(\mathbf{k}, \mathbf{k}')$ and $g(\mathbf{k}, \mathbf{k}')$ to the equations for f and g , and it is these which make the solution difficult. An estimate of the magnitude of the latter terms can be obtained by taking an average over \mathbf{k} . We have

$$\sum_{\mathbf{k}} M_{k-k'}^2 n(\mathbf{k}) = -W_{k'}. \quad (\text{B8})$$

An average of $W_{k'}$ is the exchange energy, $-0.92e^2/r_s$ for a monovalent metal. This is to be compared with

$$2M_{k'}^2 \sum n(\mathbf{k}) = n_0 M_{k'}^2 = 4\pi n_0 e^2 / k^2 = (3e^2/r_s) (kr_s)^{-2}, \quad (\text{B9})$$

where $n_0 = 3/4\pi r_s^3$ is the concentration of electrons. These exchange terms may be neglected when $kr_s \ll 1$, i.e., for long wavelengths. However, as discussed in the text, the exchange energies of the individual electrons, W_k , would make marked changes at long wavelengths. As the collective description shows, these should not be included.