Electron-Phonon Interactions in the Transition Metals

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A generalized version of the Bardeen-Pines approach is applied to the problem of electron-phonon coupling in a two-band metal in the long-wavelength region, particular attention being paid to the question of how far observation of the phonon spectrum will give information on the low-lying collective excitations of the electron system predicted elsewhere. It is shown that (in contrast to the situation in a one-band metal) subsidiary poles due to electronic resonances should in principle appear in the phonon spectrum, but their direct observation is estimated to be experimentally unfeasible. On the other hand the existence of these resonances should lead to comparatively large effects on the ultrasound velocity; in particular, interesting effects of an observable order of magnitude are predicted in the ultrasound dispersion curve in a clean two-band superconductor at low temperatures.

§ 1. Introduction

Among the various nontrivial examples of the many-body problem found in nature, probably the best understood from a theoretical point of view is the problem of a degenerate normal or superconducting Fermi system. The classic work of Landau\(^1\) showed how to take account of arbitrarily strong interparticle interactions in the normal state, while that of Bardeen, Cooper and Schrieffer\(^2\) (BCS) provided the key to a microscopic theory of superconductivity. It is not difficult to combine these two theories\(^3\),\(^4\) and thus give an account of the behaviour of a superfluid system with arbitrarily strong interparticle interactions. Thus we may say that we can to-day claim a qualitative understanding of the properties of any degenerate Fermi system which is normal or conventionally superfluid.

While many of the predictions of the semiphenomenological microscopic theory — e.g. the temperature dependence of the thermal and kinetic coefficients of a normal Fermi liquid, the electrodynamic and other properties of superconductors, etc., — have been tested experimentally and overwhelmingly confirmed, there remain a number of others for which no experimental check has so far been possible. In particular the theory makes unambiguous predictions about the behaviour of the various two-particle correlation functions of the system, or equivalently about its dynamic response to a space- and time-varying external field; some of the most interesting of these predictions relate to the existence of various resonances not found in a noninteracting system (zero sound, the ‘Bogolyubov-Anderson’ mode of a neutral superfluid, etc.). These have proved ex-
tremely difficult to verify. In liquid He$^3$, the only neutral Fermi liquid thought to occur in nature, the difficulties are mainly experimental; in the case of the Fermi system formed by the electrons in metals they are more fundamental. The trouble is that the conditions for the existence of 'transverse' zero sound are probably too stringent to be satisfied for these comparatively weakly interacting systems (but see reference 5)), while the longitudinal collective modes which must certainly exist at least in a superfluid neutral system are drastically screened out by the long-range Coulomb interaction. If the electrons in metals formed a completely isolated system, in fact, we should have no possibility at all of examining the 'unscreened' density-density correlation function experimentally.

In the case of real metals, however, the ions are to some extent free to move and may cancel at least some part of the Coulomb interactions. It is therefore of some interest to investigate whether as a result of this the structure of the unscreened electron density correlation function might again become observable, say as reflected in the phonon spectrum. It can be shown, however (the appropriate formulae are a special case of the results of this paper and are discussed in §4 below) that although the phonon spectrum does in principle give a certain amount of information on the unscreened electron correlation function there are the following two drawbacks: (a) most of the effects of interest are of order $(c/v)^3$, where $c$ is the physical phonon velocity and $v$ a typical electron velocity; for a free-electron model this factor is of order $(m/M)^{3/2} \approx 10^{-7}$. (b) even worse, because of the actual form of the expression for the phonon response function, it will not show up the poles of the electronic response function in any direct way; in fact if we take for the electronic function itself a simple 'phonon-like' form (which is in fact the correct form for a superfluid) then the only effect of the 'structure' of this function is to renormalize the (real) phonon velocity slightly. This second feature is a direct consequence of the fact that the basic mechanism of the ion-electron interaction is the Coulomb force (even though it may be supplemented by various short-range forces); it does not appear if we start from a Hamiltonian of the Migdal type in which the screening is assumed to be complete before the electron-phonon coupling is switched on.

In a metal with two unfilled bands, however, the situation is rather different. In the first place, in such metals (transition metals) the characteristic velocity in one band is often very low; therefore at least one characteristic ratio of the form $(c/v)^3$ may be several orders of magnitude larger than that estimated above. More importantly, however, in such metals there are two independent electronic quantities which can sustain fluctuations, corresponding (say) to the total density and the relative density of electrons in the two bands. Clearly the Coulomb interaction involves only the total density, and it is therefore worth while to investigate whether and how the phonon spectrum would show up the structure of the electronic relative density response function. This quantity
was investigated in detail for the case of a two-band superconductor in reference 8) (hereafter referred to as A), where it was shown that it should show a peculiar and characteristic resonance which illustrates rather directly the phase-coherence properties of the two-condensate system. It turns out that the only practical possibility of observing this resonance may well be through its effect on the phonon spectrum, and we shall therefore pay special attention to this problem.

In this paper, therefore, we shall discuss the general question of electron-phonon coupling in a two-band metal, following a generalized version of the approach used by Bardeen and Pines9) in the one-band case. To put it precisely, the problem we set ourselves is the following: Suppose we have a full knowledge of the appropriate electronic correlation functions of the system in the absence of the Coulomb interaction (or, strictly speaking, the long-range part of the Coulomb interaction, since exchange Coulomb terms and others may contribute to the short-range dynamics) and in the limit of infinite ion mass (but see also below). We then allow for the finite mass of the ions, which interact with one another by Coulomb and short-range interactions; then the ions themselves form an isolated dynamic system. Finally we switch on both the long-range electron-electron interaction (pure Coulomb force) and the ion-electron interaction (both Coulomb and short-range forces). The problem is to express the renormalized response functions, in particular the ion (phonon) response function, in terms of the original ‘unscreened’ electronic response functions and a few phenomenological parameters (the short-range coupling constants). Clearly this is only possible in the region of long wavelengths and low frequencies; however, this is precisely the region in which the electronic response functions are unambiguously predicted by the theory, so that we shall confine ourselves to this limit without regret. There is obviously a certain asymmetry in the above programme, in that the effect of the short-range coupling in the electron system itself is assumed to be given in the original data, while the effect of the short-range ion-electron coupling is part of the target of the calculation. We shall see however that the latter effect is usually trivial compared to the former, and indeed that we get qualitatively correct results in most cases if we neglect the short-range part of the ion-electron coupling (and of the ion-ion coupling) altogether.

To summarize the main conclusions of this paper briefly: (1) in a two-band metal poles of the electronic relative density response function do appear as subsidiary poles in the phonon spectrum; however, the amplitude of the corresponding peaks of the spectral function is probably too small to be observable by available techniques: (2) if the metal is normal (or superconducting with no interband coupling), all results for the (in practice) experimentally observable quantities—in particular the velocity shift and absorption of ultrasound—are qualitatively analogous to those for the one-band case: (3) however, if the metal
is a two-band superconductor of the type discussed in A, the velocity of ultrasound undergoes a characteristic wavelength-dependent shift at low temperatures; under probably realistic conditions this shift provides direct information on the dispersion relation of the electronic relative-density excitation discussed in A. The predicted effect is estimated to lie well within the scope of current experimental technique.

In the next section we shall choose and discuss the Hamiltonian describing our model problem. In § 3 we solve the problem of expressing the renormalized response functions in terms of the unscreened ones, using an algebraic technique which is equivalent to but perhaps simpler than the usual graphical methods. In § 4 we discuss electronic effects on the phonon spectrum in some detail, and try to estimate their order of magnitude. Section 5 is a brief conclusion.

§ 2. Model Hamiltonian

The approach we shall use is a generalization of that applied by Bardeen and Pines to the problem of a free electron gas interacting with the crystal ions. First, we hold the ion cores fixed in their equilibrium positions and neglect all electron-electron interactions. Then we have essentially a one-body problem; the electronic wave functions are Bloch waves specified by their pseudomomentum $\mathbf{p}$ and band index $n$:

$$\psi_{mn}(\mathbf{r}) = \exp(i\mathbf{p} \cdot \mathbf{r}) u_{mn}(\mathbf{r}),$$

where the functions $u_{an}(\mathbf{r})$ are periodic within a unit cell. Here and subsequently we choose the volume of the crystal to be unity and normalize the electronic wave functions within that volume. We shall at once introduce the approximation of complete spherical symmetry; this is, in fact, highly dubious for the transition metals, but it is unlikely to introduce qualitative error into the results. The Bloch energies $\varepsilon_{an}(\mathbf{p})$ will therefore be taken to be independent of the direction of $\mathbf{p}$. By hypothesis, two bands $a$ and $b$ overlap and the Fermi energy $\varepsilon_{F}$ is such that the equation

$$\varepsilon_{F} = \varepsilon_{a}(p_{Fa}) = \varepsilon_{b}(p_{Fb})$$

is satisfied for some pseudomomenta $p_{Fa}$, $p_{Fb}$ which do not lie on the zone boundaries. We will assume that $p_{Fa}$ and $p_{Fb}$ do not lie close together, and furthermore that any regions of the Fermi surface such that $p_{Fa}$ is close to $p_{Fa} + K$, where $K$ is a reciprocal lattice vector, are negligibly small; if this is not so a number of special complications are introduced. The number of impurities, lattice imperfections and so on is assumed to be so small that we can neglect scattering due to them. Thus far, then, the one-electron Green function is diagonal in both the momentum $\mathbf{p}$ and the band index $n$. 
Now we switch on the electron-electron interactions. Anticipating somewhat, we include in these already terms due to the exchange of virtual phonons, which may be necessary to cause superconductivity but can usually be neglected for other purposes. We shall assume that as the net result of this process we can describe the low-lying states of the electron system by a Hamiltonian which is the sum of three terms: (1) a Hamiltonian describing two ‘Landau-type’ neutral Fermi liquids in the two bands separately (but with the energy of a quasiparticle in one band depending in general on the quasiparticle distribution in both bands) (2) some residual short-range terms describing both interband and intraband scattering (3) the long-range part of the Coulomb interaction. Provided we consider only times short compared to the quasiparticle lifetime (we shall do so generally in this paper unless otherwise stated) the only terms we need to keep in (2) are those which may lead to superconductivity, i.e. the terms describing the scattering of particles of equal and opposite momentum; putting (1) and (2) together, therefore, we can write down a Hamiltonian $H_{\text{el}}$ of the superfluid Fermi-liquid form:

$$H_{\text{el}} = \sum_p \varepsilon(p, i) \delta n(p, i) + \frac{1}{2} \sum_{pp'ii} f(pp', ij) \delta n(p, i) \delta n(p', j) + \sum_{\delta} V_{\delta \delta}(pp') \alpha_{\delta}^\dagger \alpha_{\delta} \alpha_{-\delta}^\dagger \alpha_{-\delta} + \text{c.c.},$$

(2.3)

where $\alpha_{\delta}$ is the creation operator of a quasiparticle of momentum $p$ in band $i$ and $\delta n(p, i) = \alpha_{\delta}^\dagger \alpha_{\delta} - \langle \alpha_{\delta}^\dagger \alpha_{\delta} \rangle$. As it stands the Hamiltonian (2.3) is of course not gauge-invariant and both the second and third terms should be generalized to allow for small but finite momentum transfer $k$; we have not written this out explicitly so as not to obscure the general nature of $H_{\text{el}}$. Provided we deal only with processes which involves small momentum transfer $q$, there are no terms in the generalized form of $H_{\text{el}}$ with $k \leq q$ which can scatter a particle from a state $p$ in one band to a state $p+k$ in a different band (since by hypothesis $p_{\text{pa}} - p_{\text{pb}}$ is not small); hence we can put $i = j$, $k = l$ in the third term of (2.3). It then reduces to a generalization of the Hamiltonian usually used in the theory of two-band superconductors (see, e.g. reference 8)).

The basic quantities in terms of which the results of this paper will be expressed are the ‘bare’ response functions $\chi_{\delta\delta}^{(0)}$ calculated from $H_{\text{el}}$. To define these quantities we imagine that a couple of infinitesimally small external potentials $\delta U_a(r, t)$ and $\delta U_b(r, t)$ which couple to the density fluctuations of the electrons in the $a$- and $b$-bands respectively are allowed to act on the system. Then the perturbation operator has the form

$$\delta \hat{H}(t) = \int \delta U_a(r, t) \delta N_a(r, t) \, dr + \int \delta U_b(r, t) \delta N_b(r, t) \, dr,$$

(2.4)

where

$$\delta N_i(r, t) = \sum_p \delta n(p, r, t: i)$$

(2.5)
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(here we have used the semiclassical quasiparticle description which is valid at long wavelengths). Taking the Fourier transforms of $\delta U$ and $\delta n$ with respect to the spatial coordinates, we can write

$$
\delta \hat{H}(t) = \sum_{k\lambda} \delta U_{kl}(t) \rho_{-kl}(t),
$$

(2.6)

where

$$
\rho_{kl}(t) = \frac{\delta \langle \rho_{kl}(t) \rangle}{\delta U_{kl}(t)}.
$$

(2.7)

etc. Finally, taking the Fourier transform with respect to time also, we define the bare response functions $\chi^{(0)}_{klj}$ by

$$
\chi^{(0)}_{klj}(k, \omega) = \langle \rho_{klj} \rangle.
$$

(2.8)

It can be shown that under appropriate boundary conditions $\chi^{(0)}_{klj}$ is identical to the retarded Green function of $\rho_{kl}$ and $\rho_{-kl}$:

$$
\chi^{(0)}_{klj}(k, \omega) = \langle \rho_{klj} \rangle(\omega),
$$

(2.9)

where the notation is the standard one. Since $\delta N_i(r)$ is a Hermitian operator and the system is assumed to be reflection-invariant, we have the symmetry relation

$$
\chi^{(0)}_{klj}(k, \omega) = \chi^{(0)}_{klj}(k, \omega).
$$

(2.10)

We shall assume that the quantities $\chi^{(0)}_{klj}(k, \omega)$ have been calculated from $\hat{H}_{e,0}$ by any of the possible techniques; our task in this paper is to express the real electron and phonon response functions in terms of them.

To get the full Hamiltonian of the electron system in the limit of infinite ion mass we must add the long-range Coulomb term. It is easy to show that over distances large compared to the interatomic spacing the average total charge density is simply $e$ times the sum of the local densities of quasiparticles in the two bands. Hence the long-range Coulomb term (which by definition is that part of the Coulomb energy coming from the interaction of the charge density over regions large compared to the interatomic spacing) can be written

$$
H_c = \int e^2 \delta N(r) \delta N(r') \frac{dr dr'}{|r-r'|}, \quad \delta N(r) = \sum_i \delta N_i(r).
$$

(2.11)

Introducing the notation $\rho_k = \sum_r \rho_{kr}$, we can therefore write the total electron Hamiltonian

$$
\hat{H}_e = \hat{H}_{e,0} + \sum_{k<\kappa} v_k \rho_k \delta_{-k}, \quad v_k = \frac{4\pi e^2}{k^2},
$$

(2.12)

where by definition we incorporate in $\hat{H}_{e,0}$ components of the Coulomb potential with $|k|$ larger than a cut off value $\kappa$ (see below).
Now we must allow for the finite mass of the ions. Following Bardeen and Pines, we first neglect the ion-electron interactions and allow the ions to interact only with one another. We adopt the usual adiabatic model in which the ions are treated as structureless ‘elementary’ particles with a certain effective interaction potential; at long distances this has the Coulomb form

$$V_{\text{eff}}(r) = Ze^2/|r|,$$

where $Z$ is the effective charge on an ion (equal to the number of conduction electrons per atom), but at short distances it may of course deviate very considerably from this behaviour. If we allow the ions to perform small vibrations around their equilibrium positions, then at sufficiently long wavelengths the ‘longitudinal’ vibrations will be harmonic with frequency $\Omega(k)$, where

$$\Omega^2(k) = \Omega_0^2 - c^2 k^2, \quad \Omega_0^2 = 4\pi N Ze^2/M.$$  

In (2.14) $M$ is the ion mass and $N$ the number of ions per unit volume. The coefficient $c^2$ is generally of order $a^2 \Omega_0^2$, where $a$ is the interatomic spacing. The transverse oscillations of the ion system do not couple to the electron system in the long-wavelength limit and we shall therefore ignore them. To formulate the description of the bare ion system in parallel to that of the electron system, we use instead of the usual normal coordinates the ion density fluctuation operators

$$Q_k = i k \sum_l \exp(i k \cdot R_l) u_l,$$

where $u_l$ is the component of the displacement of the $l$-th atom (at site $R_l$) parallel to $k$. Then if we apply to the system an infinitesimal potential $V_k$ which couples only to the ionic density fluctuation, so that

$$\delta \hat{H}(t) = V_k Q_{-k},$$

then the bare ionic response function is defined by

$$W_k(k, \omega) = \frac{\langle Q_k \rangle(\omega)}{\delta V_k} = \langle Q_k : Q_{-k} \rangle(\omega).$$

Since the problem of the bare ion system is a simple harmonic-oscillator problem, it is easy to show that

$$W_k(k, \omega) = \frac{N k^2}{M (\omega^2 - \Omega^2(k))}$$

with $\Omega(k)$ given by (2.14). We notice that anharmonic effects may safely be neglected provided $ka \ll 1$.

Finally we switch on the electron-ion interaction. To first order in the ionic displacements this is given by

$$\hat{H}_{\text{int}} = \sum_i \int \psi^+(\mathbf{r}) \phi(\mathbf{r}) \nabla V(\mathbf{r} - \mathbf{R}_i) \cdot \mathbf{u}_i(\mathbf{R}_i) \, d\mathbf{r},$$
where \( V(r - R) \) is the effective potential between an electron at point \( r \) and the ion at site \( R \). Although this term involves only the total electron density at the point \( r \), it would be quite wrong to assume that it can be expressed for our purposes in terms of the total density fluctuation \( \rho_k \) only. To clarify this point, let us consider first the case when the electron system can be treated as a noninteracting gas of particles in Bloch states. In that case we should have

\[
\hat{H}_{\text{int}} = \sum_{p \neq j} a_{p+k,i}^* a_{p,j} \frac{Q_{-k}}{Q} M_{jk}^M
\]

where the matrix element \( M_{jk}^M \) is given by

\[
M_{jk}^M = (ik)^{-1} \int \hat{k} \cdot \nabla V(r) \exp (-ik \cdot r) u_{p+k,i}^*(r) u_{p,j}(r) \, dr
\]

where \( \hat{k} \) represents a unit vector in the direction of \( k \). The functions \( u_{p,j}^*(r) \) are orthonormal within the volume of the crystal, therefore we have in particular

\[
\int u_{p,i}^*(r) u_{p,j}(r) \, dr = N^{-1} \delta_{ij}
\]

if the integral is taken over a single unit cell. It follows, then, that the long-range part of the matrix element does indeed depend only on the total density fluctuation \( \rho_k \). However, because of the various screening processes involved in the electron-phonon interaction, it turns out that the ‘short-range’ part (which comprises not only the contribution from the deviation of the effective potential from Coulomb form at short distances but also, in general, a contribution from the nonorthogonality of \( u_{p+k,i}^* \) and \( u_{p,j} \)) is equally important for our purposes. Since we are going to deal with wavelengths so long that we can neglect the possibility of interband scattering, we need consider only the terms in (2.21) with \( i = j \). Then it is easily seen that the short-range part of \( M_{jk}^M \) does in general depend both on the band index \( i \) and on the momentum index \( p \). We may estimate it to be of the order of magnitude of \( \varepsilon_p / N \). Again we shall neglect the possible dependence of \( M_{jk}^M \) on \( p \) and \( k \), and write the short-range part simply as \( C_i \). Then we have

\[
\hat{H}_{\text{int}} = \sum_{k,i} \left( -\frac{4\pi Ze^2}{k^2} + C_i \right) \rho_{k,i} Q_{-k}.
\]

We can see that similar arguments will be qualitatively valid even in the case when the electrons interact strongly among themselves. That is, it will in general be possible to separate the electron-ion interaction into a long-range part which depends only on the total density fluctuation and a short-range part which is in general different for the two bands. Thus it can be written in the general form (2.23). The interaction Hamiltonian (2.23) does not of course claim to be a complete description of the ion-electron interaction; it describes
only the interaction of the electron system with the long-wavelength fluctuations of the ion density (roughly speaking, fluctuations with wavelength long compared to a lattice period). For the purposes of this paper we shall assume that any important effects arising from interaction with shorter-wavelength vibrations of the ion system have already been incorporated into the effective electron Hamiltonian; in particular, the interband and intraband attraction arising from exchange of virtual phonons is already included in $H_{0,c}$. Thus the sum over $k$ in (2.23) is assumed to be cut off at some value of $k$ which is much smaller than both the inverse lattice spacing and the smaller Fermi momentum, though not necessarily smaller than the inverse superconducting coherence length.

We therefore write our total Hamiltonian in the form:

$$\hat{H} = \hat{H}_0 + \sum_{|k| < k_c} V_k \rho_{k} \rho_{-k} + \sum_{|i| < k_i} \left( -\frac{4\pi Z e^2}{k^2} + C_i \right) \rho_{k_i} Q_{-k}$$ (2.24)

where $\hat{H}_0$ is $H_{0,c}$ plus the Hamiltonian describing the bare ion system. Our problem is to express the true response functions of the system in terms of the bare response functions

$$\chi_{ij}^{(0)} = \left[ \frac{\delta \langle \rho_{k_i} \rangle (\omega)}{\delta U_{kj}} \right]_{H_0}, \quad W_k = \left[ \frac{\delta \langle Q_{k} \rangle (\omega)}{\delta V_{k}} \right]_{H_0}.$$ (2.25)

Before we start on the calculations, one last point should be made. As it stands, the electron-electron Coulomb interaction in (2.24) will drastically affect not only the particle-hole scattering amplitude (which is what enters the density response function directly) but also at least part of the amplitude for scattering of two particles of nearby equal and opposite momentum, which will be equally important in the superconducting case. We are going to assume that all such effects have already been taken into account self-consistently in $H_0$ and can therefore be neglected hereafter; the response functions $\chi^{(0)}$ are therefore to be calculated using the two-particle scattering amplitude for pairs of equal and opposite momentum which follows from a consistent treatment of the whole problem. Our approach is therefore completely phenomenological: since in practice it is almost impossible to determine the pairing amplitude theoretically, we simply regard it as a parameter to be fitted from experiment. The point is that the functional form of the response functions $\chi_{ij}^{(0)}$ is completely determined by the statement that the system is superfluid (or normal,* as the case may be), without reference to the original form of the Hamiltonian; on the other hand the true response functions $\chi_{ij}$ are completely determined by $\chi_{ij}^{(0)}$ and the interaction terms in (2.24). This point is further discussed in § 5.

* This is strictly speaking only true so long as we ignore Fermi-liquid terms, as we shall do.
§ 3. Response functions

To solve the problem of expressing $\chi_{ij}$ in terms of $\chi^{(0)}_{ij}$ we could, of course, use conventional field-theoretic techniques (since the $\chi$'s are just field-theoretic Green functions—cf. (2·9)). It is, however, conceptually a good deal simpler (and less liable to numerical errors!) to use the technique which will now be explained; let us call this the ‘generalized molecular field method.’

Let us first consider an arbitrary system in which there is no long-range order; let the characteristic correlation length of the system be of order $\xi$. Let us consider a set of quantities $\rho_a(r)$ (‘generalized densities’) which are locally conserved or nearly conserved. Any quantity whose space integral commutes with the Hamiltonian (such as the particle density or spin density) will automatically form a generalized density in this sense, but other choices are also possible. For instance in a Landau-type Fermi liquid at sufficiently low temperatures the quantity

$$\sum_p \rho_a(p) \delta n(p, r)$$

constitutes a generalized density for most purposes (where $\delta n(p, r)$ has the usual meaning of the variation of the local quasiparticle occupation number) even though it does not, strictly speaking, commute with the full Hamiltonian. Now let us suppose that we can write the Hamiltonian in the form

$$\hat{H} = \hat{H}_0 + \sum_{a, b} C_{a, b}^{(k)} \rho_{K_{-a}, b} \rho_{K_{+a}, b}$$

(3·1)

where $\rho_{K_{-a}, b}$ is the appropriate Fourier transform of $\rho_a(r)$, and the cutoff $k_c$ is taken to be much less than $1/\xi$. Suppose further that we know the response functions defined by $\hat{H}_0$:

$$\chi^{(0)}_{a, b}(k, \omega) = \langle \partial_{K_{-a}, b} \rho_{K_{-a}, b} \rangle_{H_0}(\omega) = \left[ \frac{\delta \langle \rho_{K, a} \rangle(\omega)}{\delta U_{K, b}} \right]_{H_0}$$

(3·2)

in the notation of § 2. We wish to calculate the true response functions.

$$\chi_{a, b}(k, \omega) = \left[ \frac{\delta \langle \rho_{K, a} \rangle(\omega)}{\delta U_{K, b}} \right]_{\hat{H}}$$

(3·3)

If we transform the Hamiltonian (3·1) into position space, it takes the form

$$\hat{H} = \hat{H}_0 + \sum_{a, b} \int dr dr' f_{a, b}(r - r') \rho_a(r) \rho_b(r')$$

(3·4)

where $f_{a, b}(r - r')$ is some function whose characteristic range of variation is $k_c^{-1}$, which by hypothesis is much greater than the correlation length $\xi$. As a result the expectation value of the second term in any state close to the equilibrium state can be expressed in terms of $\langle \rho_a(r) \rangle$: 

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\[ \langle \rho_{a} \rangle = \sum_{\beta} \chi_{a\beta}^{(0)}(k\omega) U_{k\beta}^{\ast}, \]

\[ U_{k\beta}^{\ast} = U_{k\beta} + M_{k\beta}, \]

\[ M_{k\beta} = \sum_{\gamma} C_{\gamma\beta}^{(0)} \langle \rho_{\gamma} \rangle. \]  

(3.7)

From these equations and the definitions of \( \chi \) and \( \chi^{(0)} \) it follows straightforwardly that

\[ \chi_{a\beta} - \sum_{\gamma} \chi_{a\gamma}^{(0)} C_{\gamma\beta} = \chi_{a\beta}^{(0)}, \]  

(3.8)

where summation over repeated indices is implied. This solves the problem.

In the case of a superfluid system the decomposition (3.5) is not prima facie valid; in general we should expect a term of the form

\[ \int d\mathbf{r} d\mathbf{r'} f_{a\alpha}(|\mathbf{r} - \mathbf{r'}|) \langle \psi_{a}^{+}(\mathbf{r}) \psi_{a}^{+}(\mathbf{r'}) \rangle. \]  

(3.9)

However, in the case of interest in this paper we have explicitly stipulated that all such terms have already been taken into account in \( \hat{H}_0 \) (see the last paragraph of § 2 and also § 5); hence the results go through unchanged.

In the special case of the electron gas the above method is well known (cf., e.g. reference 10); it reduces to the simple random-phase approximation if \( \chi \) is taken to be the function appropriate to a free Fermi gas. It seems to be less generally appreciated, however, that the whole of the theory of the normal or superfluid Fermi liquid is simply an example of this method, which is completely equivalent to the much more complicated-looking graph technique. On this, see reference 11).

Before applying this method to the interacting electron-ion system, let us make a slight change of variables and write

\[ \rho = \rho_{t} + \rho_{r}, \quad \sigma = \rho_{t} - \rho_{r}. \]  

(3.10)

The appropriate response functions are given by (here \( 't' \) stands for total density, \( 'r' \) for relative density)
The matrix of the coupling constants corresponding to \( C_{\alpha\beta} \) then takes the form (the rows and columns are numbered in the order corresponding to \( \rho, \sigma, Q \))

\[
\begin{pmatrix}
v_k & 0 & v_k' \\
0 & 0 & C_r \\
v_k' & C_r & 0
\end{pmatrix}
\]  

(3.12)

where the constants \( C_t, C_r \) are defined by

\[ C_t = \frac{1}{2} (C_1 + C_2), \quad C_r = \frac{1}{2} (C_1 - C_2) \]  

(3.13)

and

\[ v_k = 4\pi e^2/k^2, \quad v_k' = -Zv_k + C_t. \]  

(3.14)

In the same notation the bare response function matrix is

\[
\begin{pmatrix}
\zeta_{tt}^{(0)} & \zeta_{tr}^{(0)} & 0 \\
\zeta_{rt}^{(0)} & \zeta_{rr}^{(0)} & 0 \\
0 & 0 & W_0
\end{pmatrix}
\]  

(3.15)

and the full response function, which is the object of the calculation, is

\[
\begin{pmatrix}
\zeta_{tt} & \zeta_{tr} & \phi_t \\
\zeta_{rt} & \zeta_{rr} & \phi_r \\
\phi_t & \phi_r & W
\end{pmatrix}
\]  

(3.16)

(which defines the quantities \( \phi_t(k, \omega), \phi_r(k, \omega) \)).

Inserting (3.12–16) into (3.8), we find the expressions for the full response functions. For completeness we shall give all six independent quantities, although we shall not need all of these subsequently;

\[
\begin{align*}
\zeta_{tt} &= D^{-1} \{ \zeta_{tt}^{(0)} - C_t W_0 \det \zeta^{(0)} \}, \\
\zeta_{tr} &= \zeta_{rt} = D^{-1} \{ \zeta_{tr}^{(0)} + C_r W_0 v_k' \det \zeta^{(0)} \}, \\
\zeta_{rr} &= D^{-1} \{ \zeta_{rr}^{(0)} - (v_k + W_0 v_k'') \det \zeta^{(0)} \}, \\
\phi_t &= D^{-1} W_0 \{ v_k' \zeta_{tt}^{(0)} + C_t \zeta_{tr}^{(0)} \}, \\
\phi_r &= D^{-1} W_0 \{ v_k' \zeta_{rt}^{(0)} + C_r \zeta_{rr}^{(0)} - v_k C_r \det \zeta^{(0)} \}, \\
W &= D^{-1} W_0 \{ 1 - v_k \zeta_{tt}^{(0)} \},
\end{align*}
\]  

(3.17)

where

\[
\det \zeta^{(0)} = \zeta_{tt}^{(0)} \zeta_{rr}^{(0)} - \zeta_{tr}^{(0)} \zeta_{rt}^{(0)}
\]
Electron-Phonon Interactions in the Transition Metals

and

\[ D = \left( 1 - v_k \chi^{(0)} \right) + W_0 \{ C_r v_k \det \chi^{(0)} - v_k^2 \chi^{(0)} - 2C_r v_k \chi^{(0)} - C_r \chi^{(0)} \}. \]  

(3.18)

Let us expand these quantities to lowest order in \( \omega^2/\Omega_0^2 \), \( k^2/\Omega_0^2 \). Using (3.13), (3.14) and (3.18), we have to this order

\[ v_k + v_k' W_0 = -(M/NZ^2 k^2) (\omega^2 + \alpha^2 k^2) + 2C_r Z^{-1}, \]

\[ v_k' W_0 = Z^{-1}, \]

\[ v_k W_0 = -Z^{-1}. \]  

(3.19)

Thus we have

\[ \chi_{tt} = D^{-1} \chi^{(0)}; \]

\[ \chi_{tt} = \chi_{tt} = D^{-1} \{ \chi^{(0)} - Z^{-1} C_r \det \chi^{(0)} \}, \]

\[ \chi_{rr} = D^{-1} \{ \chi^{(0)} + [(M/NZ^2 k^2) (\omega^2 + \alpha^2 k^2) - 2C_r Z^{-1}] \det \chi^{(0)} \}, \]

\[ \phi_t = D^{-1} Z^{-1} \chi^{(0)}; \]

\[ \phi_t = D^{-1} (Z^{-1} \chi^{(0)} + Z^{-2} C_r \det \chi^{(0)}), \]

\[ W = D^{-1} Z^{-2} \chi^{(0)}. \]  

(3.20)

and to this order \( D \) is given by

\[ D = 1 + Z^{-1} \left\{ \frac{MK^2}{Nk^2} (\omega^2 + \alpha^2 k^2) - [2Z(C_r \chi^{(0)} + C_r \chi^{(0)} + C_r^2 \det \chi^{(0)}]) \right\}, \]  

(3.21)

where \( \alpha \) was defined in (2.14).

Let us consider the order of magnitude of the quantities involved in (3.20) and (3.21). For present purposes we may treat the ratio of electron and ion masses as small, while ignoring the difference between the real electron mass and the effective masses. In this spirit we take all electron correlation functions \( \chi^{(0)} \) to be of order \( N/mv^2 \), where \( v \) is a characteristic electron velocity. We saw that \( C_r \) and \( C_r \) are expected to be of order \( \epsilon_r/N \), that is of the order inverse to \( \chi^{(0)} \). Also we estimated that \( \alpha^2 \) is of order \( a^2 \Omega^2 \), which under normal conditions is of order \( (m/M) v^2 \). From these considerations we conclude that we can write \( D \) in the general form

\[ D = -\left( \omega^2/c^3 k^3 - f(k, \omega) \right), \]  

(3.22)

where \( c \) is a velocity of order \( (m/M)^{1/2} v \) and \( f(k, \omega) \) is a dimensionless function which has singularities, if at all, only in the region \( \omega \sim v k \), and tends to 1 for \( \omega \ll v k \). Thus, \( c \) is the velocity of the sound to zeroth order in \( (c/v)^2 \).

From (3.20) we see that in the limit of infinite ion mass all response functions except \( \chi_{rr} \) tend to zero. This is of course natural; the ions themselves are then fixed and fluctuations of the total charge density are completely screened out by the Coulomb forces. Fluctuations of the relative density of electrons in
the two bands, without change of the total charge density, are however still possible; if we denote the limiting value of $\chi_{rr}$ as $M \to \infty$ by $\tilde{\chi}$, we have

$$\tilde{\chi} = \left\{ \chi_{rr}^{(0)} - \frac{\chi_{tt}^{(0)} \chi_{tt}^{(0)}}{\chi_{tt}^{(0)}} \right\}.$$  \hspace{1cm} (3.23)

It was precisely $\tilde{\chi}(k, \omega)$ (or rather its poles) which was investigated in detail in A. We see that poles of $\tilde{\chi}$ arise from zeros of $\chi_{rr}^{(0)}$ (the converse is not obvious but is in fact true except in pathological cases); thus instead of investigating $\tilde{\chi}$ itself in order to show up the collective resonances of the electron system, we could equally well investigate $1/\chi_{tt}^{(0)}$. This fact will be used to simplify the calculations in the next section.

For $M$ large but finite all correlation functions involving the electrons, except for $\chi_{rr}$, are of order $(m/M)$ relative to their 'bare' values $\chi^{(0)}$. Since direct measurement of these quantities is not very easy in the low-energy region anyway, we shall henceforward ignore them and concentrate on the ion response function $W$, which is in principle directly accessible in neutron scattering experiments over the whole range of $k$ and $\omega$.

According to (3.20) and (3.21), we can write

$$W(k, \omega) = \frac{Nk^2}{M} \left\{ \omega^2 + \frac{Nk^2}{M \chi_{tt}^{(0)}(k, \omega)} \left[ Z^2 - 2Z(C_t - M\alpha^2/N)\chi_{tt}^{(0)}(k, \omega) \right. \right.$$

$$\left. - 2Z \chi_{tt}^{(0)} C_r - C_r^2 \det \chi^{(0)} \right\}^{-1}$$  \hspace{1cm} (3.24)

or in the form (3.22)

$$W(k, \omega) = \frac{Nk^2/M}{\omega^2 - c^2 k^2 f(k, \omega)}.$$  \hspace{1cm} (3.25)

Armed with Eq. (3.24), we shall go on in the next section to calculate the effects of the 'structure' of the electronic functions on the phonon spectrum; in particular we shall investigate the small ultrasound velocity shifts and absorption and the possible occurrence of 'reflected' poles of $f(k, \omega)$ in the phonon spectrum. From the considerations given above it is obvious that the shifts will be of relative order $(c/v)^3$, while the amplitude of the 'reflected' poles, if any, relative to the primary pole at $\omega \sim c k$ will be of order $(c/v)^4$. However, more detailed investigation is needed in order to determine the order of magnitude of the effective $v$ in each case. This will be given in the next section.

§ 4. Electronic effects on the phonon spectrum

In this section we shall have to consider the electronic bare response functions in rather more detail. Generally speaking, the parameters entering these
response functions\(^*\) will be the densities of states at the Fermi surface in the two bands, \(\rho_1\) and \(\rho_2\), and the two Fermi velocities \(v_1\) and \(v_2\) (in this section we shall always apply the label ‘1’ to the band with the lower density of states (s-band); generally speaking this band will also have the higher Fermi velocity). In the case of a two-band superconductor, we will always assume we are in the ‘quasi-hydrodynamic’ region \(\nu k \ll \Delta_1\) (where \(\nu\) is a characteristic velocity of the electronic system and \(\Delta_1\) the smaller gap—see A for a detailed discussion); then in addition to the above four parameters we need the frequency \(\omega_0\) of coherent transfer of pairs between the two bands.

Let us tabulate the forms of \(\chi^{(0)}_{ij}(k, \omega)\) for reference for various cases of interest. In the case of two normal non-interacting bands, we have

\[
\chi^{(0)}_{11} = \rho_1 \, \omega \, (\omega / v_1 k), \quad \chi^{(0)}_{22} = \rho_2 \, \omega \, (\omega / v_2 k),
\]

\[
\chi^{(0)}_{12} = \chi^{(0)}_{21} = 0,
\]

where

\[
\omega(s) = \left( \frac{s}{2} \ln \left| \frac{1 + s}{1 - s} \right| - 1 \right) + i \pi s \delta'(1 - s).
\]

In the case of two non-interacting superconducting bands (i.e. the case of no inter-band pairing) we have

\[
\chi^{(0)}_{11} = \frac{\rho_1 \mu_1^2 k^2}{\omega^2 - u_1^2 k^2}, \quad \chi^{(0)}_{22} = \frac{\rho_2 \mu_2^2 k^2}{\omega^2 - u_2^2 k^2},
\]

\[
\chi^{(0)}_{12} = \chi^{(0)}_{21} = 0,
\]

where

\[
u_i^2 = \frac{1}{2} v_i^2.
\]

Equations (4·3) is also a correct description of a normal two-band system in the frequency region where \(\omega^{-1}\) is long compared to the time for establishment of thermal equilibrium within a band but short compared to the characteristic inter-band scattering time—a region which may be appreciable in very clean specimens. Finally in the case of a two-band superconductor with interband coupling the functions \(\chi^{(0)}(k\omega)\) were calculated in A (Eqs. (5·35))

\[
\chi^{(0)}_{11} = Q^{-1}(k, \omega) \left\{ \frac{\rho_1 \omega_0^2}{\rho_1 + \rho_2} \left( \rho_1 \, \omega^2 - \rho_1 \, u_1^2 k^2 - \rho_2 \, u_2^2 k^2 \right) + (\omega^2 - u_3^2 k^2) \rho_1 \, u_1^2 k^2 \right\},
\]

\[
\chi^{(0)}_{12} = \chi^{(0)}_{21} = Q^{-1}(k, \omega) \left\{ - \frac{\omega^2 \omega_0^2 \rho_1 \rho_2}{\rho_1 + \rho_2} \right\},
\]

where

\(^*\) For simplicity we shall at once make the approximation of neglecting all ‘Fermi-liquid’ effects. Taking these into account would complicate the notation without changing the results in any essential way.
\[ Q(k, \omega) = \omega^4 - \{\omega_n^2 + (u_1^2 + u_2^2)k^2\} \omega^2 + \omega_0^2 k^2 \left\{ \frac{\rho_1 u_1^2 + \rho_2 u_2^2}{\rho_1 + \rho_2} \right\} + u_1^2 u_2^2 k^4. \quad (4.6) \]

\( \chi^{(0)}_{ii}(k, \omega) \) is obtained from \( \chi^{(0)}_{kk} \) by interchanging the indices 1 and 2. In the limit \( \omega_0 \rightarrow 0 \), (4.6) reduces of course to (4.3). The functions \( \chi^{(0)}_{ii} \), \( \chi^{(0)}_{kr} \), etc., are obtained from the \( \chi^{(0)}_{ij} \) according to (3.11). We tabulate for reference the quantities we shall need in what follows:

\[
\begin{align*}
[\chi^{(0)}_{ii}(k, \omega)]^{-1} & = (\rho_1 + \rho_2)^{-1}(\omega^2 - \omega_k^2)^{-1} \left\{ \omega_k^2 + \frac{\rho_1 + \rho_2}{\rho_1 u_1^2 + \rho_2 u_2^2} \frac{\omega^2}{k^2} \right\}, \\
\chi^{(0)}_{ii}(k, \omega) / \chi^{(0)}_{kk}(k, \omega) & = \frac{\rho_2 - \rho_1}{\rho_2 + \rho_1} \frac{\omega_k^2 + \lambda \omega^2}{\omega_k^2 - \omega^2}, \\
\det \chi^{(0)} / \chi^{(0)}_{kk}(k, \omega) & = \frac{4 \rho_1 \rho_2}{\rho_1 + \rho_2} \frac{\omega_k^2}{\omega^2 - \omega_k^2} (\equiv \tilde{F}(k, \omega)). \quad (4.7)
\end{align*}
\]

Here we use the notation

\[
\begin{align*}
\omega_k^2 = \frac{1}{2} \varphi_t^2, \quad \omega_0^2 = \omega_n^2 + v^2 k^2, \quad \omega^2 = \frac{(\rho_1 + \rho_2) u_1^2 u_2^2}{\rho_1 u_1^2 + \rho_2 u_2^2}, \\
\lambda = \left( \frac{\rho_1 + \rho_2}{\rho_2 - \rho_1} \right) \frac{\rho_1 u_1^2 - \rho_2 u_2^2}{\rho_1 u_1^2 + \rho_2 u_2^2}. \quad (4.8)
\end{align*}
\]

As was shown in A, the equation \( \omega = \omega_k \) defines the frequency of the collective oscillation of the electronic relative density oscillation characteristic of a two-band superconductor. (compare the third of Eqs. (4.7) with (3.23)). The frequency \( \omega_0 \) is of the order of but smaller than the smaller gap \( \Delta_1 \). For the moment we defer the question of the order of magnitude of \( \nu \); we note however that independently of this question, \( \lambda \) will be of order unity and furthermore that the quantity (which we shall need later)

\[
\mu = \frac{\rho_1 u_1^2 + \rho_2 u_2^2}{\rho_1 u_1^2 + \rho_2 u_2^2} \quad (4.9)
\]

will be of the order of the smaller of the quantities \( (\rho_1 / \rho_2) \), \( (u_1^2 / u_2^2) \).

According to Eq. (3.24), the phonon propagator has the form (here we write \( C_t' = C_t - M \alpha^2 / N \))

\[
W(k, \omega) = \frac{N k^2}{M} \left\{ \omega^2 + \frac{N k^2}{M \chi^{(0)}_{kk}(k, \omega)} \left[ Z^2 - 2 Z (C_t' \chi^{(0)}_{kk}(k, \omega) + C_t \chi^{(0)}_{kk}(k, \omega)) \right] - C_t^2 \chi^{(0)}_{kk}(k, \omega) \right\}^{-1}. \quad (4.10)
\]

Let us examine the relative order of magnitude of the effects of the various terms in the square brackets on the phenomena we are going to consider. Since
we have no reason to expect the order of magnitude of $C_t'$ to be different from that of $C_n$, the condition of the stability of the lattice (that is, the condition that the expression in the square brackets should be positive for $\omega = 0$) implies that $|C_t'| \leq Z(\rho_1 \rho_2)^{1/2}$. The phonon velocity itself is determined mainly by the zero-frequency limit of the $\chi$'s; the relative order of magnitude of the contributions of the three terms in the square brackets is given by the ratio $1: (\rho_1 |\rho_2|)^{1/2}: \leq 1$. The value of the relative shift in the ultrasound velocity, and the attenuation coefficient per unit wavelength, depend on the first coefficients of the expansion of the $\chi$'s for small $\omega^2/k^2$. Using the expressions (4.7) (of which (4.3) is a special case, while (4.1) clearly gives analogous results to (4.3)) we find the appropriate ratio of the contributions is $\mu: \leq (\rho_1/\rho_2)^{1/2}: \leq 1$. (where $\mu$ is given by (4.9)). Finally the amplitude of the reflected pole in the phonon spectrum will depend on the values of the expressions (4.7) (or the similar expressions obtained from (4.1) or (4.3)) near their poles; the appropriate ratio is found to be $\mu: \leq (\rho_1/\rho_2)^{1/2}: \leq 1$. Now it appears very unlikely that $\mu$ is an order of magnitude smaller than $(\rho_1/\rho_2)^{1/2}$ (this would imply, roughly speaking, a ratio of the Fermi momenta $(p_F/\rho_2) \sim 1/8$); hence the effect of the first term is quite comparable to that of the others except possibly in defining the absolute speed of sound. Hence we shall for simplicity keep only the first term from now on. It is to be emphasized that our estimates for the relative velocity shift and absorption of ultrasound, expressed in terms of the zero-order velocity $c_0$ obtained in this approximation, will be valid whether or not $c_0$ is actually a good approximation to the absolute velocity of sound. The same applies to the estimates given for the absolute amplitude of the reflected poles in the phonon spectrum.

Thus, from now on we shall write (dropping the superscript and subscripts on $\chi^{(0)}$)

$$W(k, \omega) = \frac{Nk^2}{M} \left[ \omega^2 + \frac{Z^2Nk^2}{M \chi(\omega)} \right]^{-1}. \quad (4.11)$$

In all cases the zero-frequency limit of $\chi(\omega)$ is simply $[-(\rho_1 + \rho_2)]$. Thus to zeroth order the ultrasound velocity $c_0$ is unaffected by the structure of the electronic spectrum (this result of course remains true if we use the complete expression (4.10)); it is given by

$$c_0^2 = \frac{Z^2N}{M(\rho_1 + \rho_2)} \approx \frac{Z^2N}{M\rho_2}. \quad (4.12)$$

However, as pointed out above, this result may be wrong by a factor of order up to $(\rho_1/\rho_2)^{1/2} \sim 10$.

Next we investigate effects of relative order $(m/M)$—the small shifts in the

*) We note that stability considerations prevent $\alpha^2$ from being too large.
phonon velocity in the superconducting state and the ultrasonic absorption. First let us consider wave vectors such that \(\mathbf{vk}'\mathbf{p} 0\) and so use Eqs. (4.3) for the superconducting state. If we divide the low-temperature region into (I) the region above the superconducting transition temperature (II) the region \(\Delta_s(T)  \mathbf{t} \Delta(T)\) (III) the low-temperature 'fully superconducting' region \(\Delta_s(T)  \mathbf{t} T\), omitting the transition regions, then in region I we must use Eqs. (4.1), in III Eqs. (4.3), while in II we must use (4.1) for the s-band and (4.3) for the d-band. If we define the quantity

\[
\Delta c/c_0 = \frac{1}{2} \left( 1 - \frac{\chi(k; \mathbf{c}_0 \mathbf{k})}{\chi(k; 0)} \right) = \alpha + i\beta, \tag{4.13}
\]

then \(\alpha\) gives the relative shift in the velocity of ultrasound due to electronic dynamical effects and \(\beta\) gives the ultrasonic absorption per unit wavelength. We easily obtain:

Region I: \(\alpha = \frac{1}{2} \frac{(\rho_1 v^2_s + \rho_2 v^2_1)c^2_o}{(\rho_1 + \rho_2)v^2_1} \), \(\beta = \frac{\pi}{4} \frac{(\rho_1 v^2_s + \rho_2 v^2_1)c^2_o}{(\rho_1 + \rho_2)v^2_1}\).

Region II: \(\alpha = \frac{1}{2} \frac{(\rho_1 v^2_s - 3\rho_2 v^2_1)c^2_o}{(\rho_1 + \rho_2)v^2_1} \), \(\beta = \frac{\pi}{4} \frac{(\rho_1 c_0)}{(\rho_1 + \rho_2)v^2_1}\).

Region III: \(\alpha = \frac{3}{2} \frac{\rho_1 v^2_s + \rho_2 v^2_1}{(\rho_1 + \rho_2)v^2_1} \), \(\beta = 0\). \tag{4.14}

We see, therefore, that measurements of \(\alpha\) and \(\beta\) in the various regions should give at least an order of magnitude estimate of the parameters \(v_1\) and \(v_2\). Notice that in this wavelength region the shift in the ultrasound velocity between regions II and III is very small, in fact probably undetectably so.

Thus far the results are essentially a trivial generalization of the one-band case. However, let us now consider a two-band superconductor in the wavelength region \(kv\sim \omega_s\), in the temperature region III. Expanding the first of Eqs. (4.7) to first order in \(\omega^2/k^2\), we find

\[
1 - \frac{\chi(k, 0)}{\chi(k, \omega)} = \frac{\omega^2}{\mathbf{k}^2} \left\{ \frac{(\rho_1 u^s_1 + \rho_2 u^s_1) k^2 + (\rho_1 + \rho_2) \omega^2_s}{(\rho_1 u^s_1 + \rho_2 u^s_1) \omega^2_s} \right\}. \tag{4.15}
\]

Hence the relative shift \(\alpha\) in the velocity of ultrasound is given by:

\[
\alpha = - \frac{c^2_o}{2\omega^2_s} \left\{ \frac{\mathbf{m} k^2 + (\frac{\rho_1 + \rho_2}{\rho_1 u^s_1 + \rho_2 u^s_1}) \omega^2_s}{(\rho_1 u^s_1 + \rho_2 u^s_1) \omega^2_s} \right\}. \tag{4.16}
\]

Using the formula (4.8) for \(\omega_n\), we see that in the limit of short wavelengths \((v\mathbf{k} \gg \omega_s)\) (4.16) reduces to (4.14 III), while in the limit \(k \to 0\) we have

\[
\alpha = - \frac{1}{2} \frac{c^2_o (\rho_1 + \rho_2)}{\rho_1 u^s_1 + \rho_2 u^s_1}. \tag{4.17}
\]

If \(u_1\) is much larger than \(v\), which we shall suggest below is likely to be the
case, we have an intermediate region \( u_1 k' > \omega_0, \nu k < \omega_0 \) where

\[
\alpha = - \mu \left( \frac{c_0^2 \kappa^2}{\omega_0^2} \right) = - \frac{\mu}{2} \frac{c_0^2 \kappa^2}{\omega_0^2 + \nu^2 \kappa^2}.
\]  

(4·18)

Thus, provided the coefficient \( \mu \) is sufficiently large, measurement of the ultrasound velocity shift in this range should provide a direct test of the theory developed in A.

From (4·18), the relative effect is of order \( (\mu c_0^2/\nu^2) \), and we saw above that this estimate is valid even if \( c_0 \) is not the true zero-order velocity of sound. Let us try to estimate this parameter. Using (4·8), (4·9) and (4·12), we have

\[
\frac{\mu c_0^2/\nu^2}{Z^2N} = \frac{Z^2N}{M \rho s^2} \left( \frac{\rho_1 u_3^2 + \rho_1 u_1^2}{u_1^2 u_3^2} \right).
\]

To obtain an order-of-magnitude estimate of the quantity \( \rho_1 u_3^2 \), we use a parabolic-band model with effective mass \( m_2^* \). Then we have simply \( \rho u_3^2 = N_2/m_2^* \), where \( N_2 \) is the number of \( d\)-electrons, which is of order \( ZN \). Thus we finally arrive at the estimate

\[
\mu c_0^2/\nu^2 \sim Z m_2^*/M \sim 10^{-3}.
\]

(4·19)

This value is surprisingly large, but since the only approximations we have made in deriving it are \( \rho_1 \ll \rho_2 \) (which is almost certainly true) and the estimate \( \rho u_3^2 \sim N_2/m_2^* \) there seems no reason to think it is wrong by more than a factor of ten or so at most. Thus, since the absorption of ultrasound should be negligibly small in the low-temperature region (cf. (4·14)), the effect predicted by Eq. (4·18) should be comparatively easily observable.\(^*\)

What we should look for, then, is a shift in the ultrasound velocity in the region of wavelengths \( k \sim \omega_0/\nu \). If we take \( \omega_0 = 0.1 \degree K \), the appropriate phonon frequency range should be of the order of a few megacycles. In this region anharmonic and other extraneous effects on the phonon spectrum should be very small, but in any case they could be subtracted by comparing the results in the regions II and III (it is very plausible that in region II the expression (4·14 II) should be valid at all wavelengths, though this point really should be investigated in detail. At any rate it will be valid for \( \nu k \gg \Lambda_1(T) \)).

All the results of A which have been used above were derived on the assumption that \( \omega_0 \ll 2 \Lambda_1 \). This condition, however, is not well fulfilled for niobium, the only transition metal superconductor for which there is yet definite evidence for a two-gap theory (see A). However, we may expect the formula (4·17) for the velocity shift at zero wave vector to remain valid:

\(^*\) In principle a similar effect should occur in one-band superconductors at wavelengths \( \nu k \sim 2 \Lambda \). However, the functional form is a good deal more complicated in this case and in addition the magnitude of the effect is usually much smaller.
where at the last stage we again used a parabolic-band model and assumed $N_1 \sim N$. Comparing $|\alpha(0)|$ as given by (4.20) with its value (essentially (4.19)) in region II, we see that the former is an order of magnitude smaller. Hence we reach the following rather surprising conclusion: the speed of sound in a two-band superconductor in the infinite-wavelength limit goes down as the $d$-electrons become superconducting but goes up again as the $s$-electrons become superconducting, though the magnitude of the second shift is only 3/4 that of the first. Again this effect is expected to be of order $10^{-2} - 10^{-3}$.

It should also be interesting to examine the change of the speed of sound in transition metal superconductors with alloying. On intuitive grounds it seems reasonable that the density response function of a dirty two-band superconductor should be essentially given by an expression of the form (4.3) with $\rho \sim \rho_n$, $v \sim v_s$. Then it will lead to an $\alpha$ of essentially the same order of magnitude as (4.14) and thus we can predict that the effect of alloying on a pure two-band superconductor is essentially the same as raising the temperature through the region $T \sim A_1(T)$.

Finally, let us examine the question of 'reflected' poles in the phonon spectrum. First we digress for a moment to consider the one-band case. If we use for $X(k, \omega)$ the superconducting form (4.3) we find simply

$$W(k, \omega) = \frac{\varepsilon^2 NK^2/M}{\omega^2 - \varepsilon^2 c^2 k^2}, \quad \varepsilon^2 = (1 + \varepsilon^2/c^2)^{-1/2}$$

so that the only effect of the 'structure' of the electronic function is to renormalize the phonon velocity. If we use another form of $X$, e.g. (4.1), the effect is more complicated but it remains true that no pole will appear in $W(k, \omega)$ unless there is a corresponding zero in $X$. One can show that $\chi(k, \omega)$ can have no zero in the normal state or in the superconducting state at any temperature (cf. Eq. (3.25) of A and the associated discussion), provided isotropic Fermi-liquid theory applies. (Clearly, sufficiently strong anisotropy would lead to effects qualitatively similar to those in the two-band theory.) Thus, even in principle, the structure of the phonon spectrum will not be particularly sensitive to electronic effects in the one-band case. It is to be emphasized that this result is a consequence of using a Bardeen-Pines type of approach; if we used an approach of the Migdal type, in which the initial Hamiltonian describes the interaction of screened phonons with screened electrons, quite different results would emerge. The point is that while it is legitimate to lump the effects of the various screening processes into a couple of constants (the renormalized velocity of sound and the electron-phonon coupling constant) at energies $\omega \sim c k$ where the electronic response is practically constant, it is by no means correct
to do this at energies $\omega \sim \nu_F k$ where it has considerable structure.

Turning now to the two-band case, we see that for $\omega \sim \omega_0$, the first of Eqs. (4.7) can be written

$$\chi^{-1}(k, \omega) = -\frac{v}{\rho_1 + \rho_2} \cdot \frac{\omega_0^2}{\omega^2 - \omega_0^2}, \quad v = \frac{\rho_1 \rho_2 (u_1^2 - u_2^2)}{(\rho_1 u_1^2 + \rho_2 u_2^2)^2}. \quad (4.22)$$

Thus, there appears a 'reflected' pole in the phonon spectrum at $\omega = \tilde{\omega}_k$, where $\tilde{\omega}_k$ differs from $\omega_0$ by a factor of order $(m/M)$. Very near the pole we have

$$W(k, \omega) \approx \frac{(Nk^3/M) (\nu c_0^2 k^2/\omega_0^2)}{\omega^2 - \tilde{\omega}_k^2}. \quad (4.23)$$

We should compare this with the behavior in the neighbourhood of the 'primary' phonon peak:

$$W(k, \omega) = \frac{Nk^3/M}{\omega^2 - c^2 k^2} \quad (4.24)$$

(where $c$ is the true velocity of sound). Generally speaking, in a direct resonance experiment such as neutron scattering, the quantity of importance is the total strength of the resonance peak, which is proportional to the coefficient of $(\omega - \tilde{\omega}_k)^{-1}$. Thus the ratio of the strengths of the reflected and primary peaks is given by the quantity

$$R = v \left( \frac{c}{c_0} \right) \left( \frac{c_0 k}{\omega_0} \right)^3. \quad (4.25)$$

We saw above that the quantity $(c/c_0)$ is at most of order 3 or 4. If we set $\nu k \sim \omega_0$, we then have

$$R \sim v (c_0/\nu)^3 \sim \rho_1 \rho_2 \left( \frac{\rho_1}{\rho_2} \right)^{1/2} \left( \frac{\rho_1 u_1^2 - \rho_2 u_2^2}{\rho_1 u_1^2 + \rho_2 u_2^2} \right)^{1/2} u_1^2 \left( \frac{c_0}{u_2} \right)^3. \quad (4.26)$$

where so far the only approximation used has been $\rho_1 \ll \rho_2$. According to the estimate used above in connection with (4.19), $(c_0/\nu)^3 \sim 10^{-5}$. Hence $R \leq (\rho_1/\rho_2)^{1/2} \times 10^{-5} \sim 10^{-4}$. It follows therefore that neutron scattering investigation of the reflected resonances is not likely to be experimentally feasible in the foreseeable future, except possibly in exceptional cases where a number of factors combine to enhance the ratio $R$ by one or two orders of magnitude. However, the possibility of direct detection of the resonance in ultrasound transmission experiments cannot be entirely ruled out, though the practical difficulties are likely to be formidable. (Strictly speaking, the formula (4.25) cannot be applied as it stands in this case, because the response function measured in such an experiment (in distinction to neutron scattering experiments) is that of the total (ion plus electron) density, and it would be necessary to check that the ion-electron interference terms do not cancel most of the ion contribution. This can be done using Eqs. (3.20). However, since the ions and electrons con-
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tribute to the screening with opposite sign but to the density response function with the same sign it seems unlikely a priori that this would happen).

§ 5. Conclusion

In this paper we have shown that, from a theoretical point of view at least, the subject of electron-phonon coupling in a two-band metal is by no means a trivial generalization of the corresponding problem for a one-band metal. In particular we have seen that in principle the phonon spectrum can be made to yield a considerable amount of information on the properties of the electronic system, including information which may not be accessible in any other way. In practice the situation is not quite so rosy, but we have seen that under realistic conditions the phonon spectrum can still give us a good deal of interesting information.

The argument used in this paper may look suspiciously simple. Have we really ‘solved’ the complicated problem of the electron-phonon interaction in any meaningful sense? That depends on the question we set out to answer. If we had set ourselves the problem of starting from the initial Hamiltonian describing the interactions of the electrons among themselves, of the ions among themselves and of the ions with the electrons and deriving the true ion and electron response functions, then obviously the answer is no. However, it could be argued that in any case such a problem is not of practical interest since we have little quantitative information on the input data. Our question was rather: given a qualitative knowledge of the properties of the electron system which arise both from its internal dynamics and from the coupling with the ions, can we deduce anything about the behaviour of the phonon spectrum? We claim that when faced with this question, we may legitimately and profitably use the molecular-field method outlined in the text, and that the answer to the question is yes.

However, the uneasiness that the reader may feel may perhaps be formulated rather more quantitatively. Granted that we are at liberty to incorporate as much of the phonon-induced (and Coulomb-induced) short-range effects as we like into the ‘bare’ electron response functions, does it follow that having done this, we are still at liberty to describe the latter by the simple forms (4.1–9)? In writing (4.1–9) what we have done is essentially to assume, first, that the ‘bare’ electron system is described by a Landau-type normal or superfluid Fermi-liquid theory, and then to approximate the latter by a free-gas type of theory. The second step is not important; retention of the omitted quasiparticle interaction terms would merely complicate the results without changing their essential characteristics. But what exactly do we mean by the first assumption? Roughly speaking, we have assumed that the irreducible quasiparticle scattering amplitude is essentially constant over all ranges of energy and momentum transfer of
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interest to us. In particular we have implicitly assumed, in writing (4·1–9) and using them in the two regions $\omega \sim \omega k$ and $\omega \sim \omega k_c$, that the irreducible scattering amplitude has no particular singularities in these regions. Is this legitimate? For the first region the situation is essentially the same as for an isolated system of electrons and there is no particular reason to think it is not legitimate. As to the region $\omega \sim \omega k_c$: we specified that the long-range part of the Coulomb and electron-ion interactions (the Fourier components with $k < k_0$) was to be taken into account in defining the ‘bare’ response functions only in so far as it affected the pairing interaction responsible for superconductivity. Here it is essential to note that as regards the pairing interaction for pairs of total momentum $k$ (i.e. for the process $(p, -p + k \rightarrow p', -p' + k), |k| \ll |p|$, the part due to phonon exchange arises from phonons of momentum $p - p'$ rather than of momentum $k$. Thus the contribution from $k < k_0$ should be of order $(k_0/k_D)$ (where $k_D$ is the Debye wave vector) at most, and therefore we would not expect this pairing interaction when averaged over the directions of $p$ and $p'$ to be particularly sensitive to the ratio $\omega / \omega k$ for $k/k_0$. A similar argument applies to the contribution of the Coulomb interaction. Since (by construction!) the only way these ‘anticipated’ long-wavelength terms could affect the ‘bare’ response functions for wave vector $k(< k_0)$ is through the pairing interaction for total momentum $k$, we conclude that the latter are in fact likely to be well described by Fermi-liquid theory even in the region $\omega \sim \omega k$. This establishes the consistency of our procedure.

Apart from the neglect of the Fermi-liquid terms, we made two other substantial simplifications in the course of this paper. One was to neglect the short-range electron-ion coupling; however, we showed that the effects of this certainly do not change the qualitative nature of the results, and if necessary we can easily recalculate them taking explicit account of it. A more dubious approximation was the assumption of complete symmetry, which is likely to be very bad for the transition metals with their complicated $d$-band structure. Although the results of this paper (as of A) are likely because of this to be an oversimplified description of real transition metals, they should nevertheless be qualitatively correct; one must just hope that nature will not be too unkind to the theorist in this respect.

The most interesting result of this paper from the practical point of view is the prediction of a characteristic ‘structure’ in the ultrasound velocity shift in clean two-band superconductors at very low temperatures. We have estimated that this should be comparatively easily observable; this could in fact be checked by observing the shift between the regions I and II (cf. Eqs. (4·14)). The detection of the predicted effect would be of considerable interest both for the theory of electron-phonon coupling itself and for the theory of phase coherence in two-band superconductors.
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