seen by the results reported here, V_{ax} at an Fe^{3+} site in beryl is considerably smaller than for the other three crystals.

ACKNOWLEDGMENTS

We are particularly grateful to Professor C. S. Wu of Columbia University for the use of the facilities of her laboratory during the early stages of this experiment. We are also indebted to E. Friedman for experimental aid and for verifying the calculation of Watanabe with respect to the contribution to V_{ax}^2, to J. Kucza for help in sample preparation, and to N. Stemple for x-ray analysis.

PHYSICAL REVIEW VOLUME 129, NUMBER 6 15 MARCH 1963

Dielectric Constant of a Superconductor*

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(Received 7 November 1962)

The longitudinal dielectric constant has been calculated for the extended Bardeen-Cooper-Schrieffer model of a superconductor. An explicit formula is obtained which has been evaluated numerically. The competition between collective and single-particle effects is pronounced, so that the dielectric function differs remarkably from the most elementary approximations to it. However, the dielectric function of the superconductor does not differ greatly from that in the normal metal in either the high-frequency or static limit, regardless of the wavelength. This prevents the modifications due to superconductivity from being readily observed. In particular, the shift in the static polarizability should cause very small shifts in the phonon speed, so small that no effect on the lattice specific heat should be observed.

I. INTRODUCTION

THE dielectric function of a metal is of fundamental interest not only for its direct experimental relevance, but because of its close relationship to the correlation structure and excitation system of the metal. In a "normal" metal, the dielectric function is believed to be determined primarily by the single-particle excitations. In a superconductor, on the other hand, there exists a strong competition between the single-particle and collective effects, especially in the longitudinal dielectric function. We have studied the longitudinal dielectric function of a superconductor, in order to exhibit these collective effects, as well as to clarify some points which we shall mention below.

Anderson[1] and Rickayzen[2] have previously studied the dielectric function, and they have obtained the fundamental equations. More recently, Nishiyama[3] has discussed limiting cases of these equations. We have obtained numerical values for the dielectric function, and thus are in a position to discuss the dielectric function quite generally.

An elementary approximation to the dielectric function is obtained by restricting the possible excitations to those of two quasi-particles. In the normal case, this leads to the Lindhard[4] formula. We shall consider the irreducible polarization part, rather than the dielectric function. The wave number and frequency-dependent dielectric function is related to the irreducible polarization part, $N\Lambda(q,\omega)$, by

$$\epsilon(q,\omega)=1+v(q)N\Lambda(q,\omega), \tag{1}$$

where $v(q)$ is the Fourier transform of the Coulomb potential,

$$v(q)=4\pi e^2/q^2=3(\omega_p/v_0q)^2/N. \tag{2}$$

We have introduced the notation ω_p for the classical frequency, $\omega_p{}^2=4\pi ne^2/m$, and v_0 for the Fermi velocity. The density of states at the Fermi surface is denoted by $N=mp_0/\pi^2$. The irreducible polarization part is slightly more convenient to discuss theoretically than the dielectric constant itself. The function $\Lambda(q,\omega)$ is to a first approximation independent of the coupling. It depends weakly on the Coulomb potential $v(q)$, being much more strongly influenced by the "average" attractive force.

It, of course, should be realized, that ω_p/v_0q is very large for wavelengths of interest, namely, wavelengths such that $v_0q\lesssim k_B\Theta$ for $\Theta\lesssim 100$°K. As a result of this large, direct Coulomb coupling, great experimental difficulties stand in the way of a direct observation of the dielectric constant.

The polarization part is given by the sum of all irreducible graphs shown in Fig. 1. An irreducible graph is one which cannot be separated into two pieces by

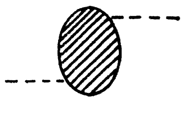

FIG. 1. General structure of the polarization part. The shaded area represents the sum of all graphs which cannot be separated into two disjoint graphs by breaking a single Coulomb line.

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* Supported in part by the U. S. Air Force Office of Scientific Research.

[1] P. W. Anderson, Phys. Rev. **112**, 1900 (1958).

[2] G. Rickayzen, Phys. Rev. **115**, 795 (1959).

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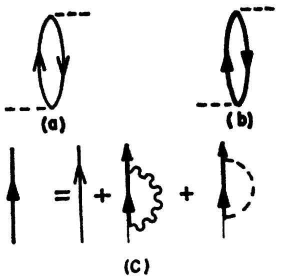

FIG. 2. (a) Lowest order bubble graph. (b) Lowest order bubble graph in the theory of superconductivity. Heavy directed lines represent propagators for "dressed" electrons, i.e., quasi-particles. (c) Approximate self-energy corrections used in defining the quasi-particle operators. A graphical representation of the integral equation.

cutting either a single Coulomb line (denoted by the dashes) or a phonon line (denoted by the wavy line). The Lindhard formula can be obtained by retaining the graph of Fig. 2(a) alone.

The dielectric constant which we have written down here is the electronic contribution to the complete dielectric function. To it must be added the ionic contribution which in the ion plasma approximation takes simple form, $-(\Omega_p/\omega)^2$, where Ω_p is the ionic plasma frequency. The inverse of the complete dielectric function takes into account correctly all of the polarization graphs, both reducible and irreducible. We shall not concern ourselves with the refinements possible in calculating the ionic contribution, but shall concentrate on the electronic part only.

The results of Lindhard may, for our purposes, be summarized most easily, by noting that the absorptive part of $\Lambda(q,\omega)$, which we denote by $\Lambda_2(q,\omega)$, is given by

$$\begin{aligned}\Lambda_2{}^{(L)}(q,\omega) &= \pi\omega/2v_0q, & \omega &< v_0q \\ &= 0, & \omega &> v_0q.\end{aligned} \tag{3}$$

We are assuming throughout that $\hbar v_0 q$ is much smaller than the Fermi energy. The dispersive (real) part of $\Lambda(q,\omega)$ is given by the Kramers-Kronig relation,

$$\Lambda_1(q,\omega) = (2/\pi)\int_0^\infty \omega' d\omega'\, \Lambda_2(q,\omega')/(\omega'^2-\omega^2) \tag{4}$$

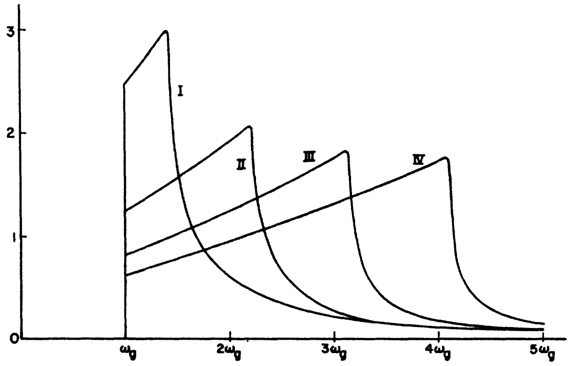

FIG. 3. Function $B_2(q,\omega)$, defined in the text, vs frequency. (I) $q=\omega_g/v_0$; (II) $q=2\omega_g/v_0$; (III) $q=3\omega_g/v_0$; (IV) $q=4\omega_g/v_0$.

which is generally valid. Furthermore, the sum rule,

$$\int_0^\infty \omega\Lambda_2(q,\omega)d\omega = \pi(v_0q)^2/6, \tag{5}$$

and the property

$$\Lambda_2(q,\omega) \geq 0, \quad \omega > 0 \tag{6}$$

hold for any permissible polarization part, be it for a superconductor or for a normal metal.

The most striking effect of superconductivity is the introduction of an energy gap into the spectrum of $\Lambda_2(q,\omega)$. Thus, we naively expect that for a superconductor, $\Lambda_2(q,\omega)$ will vanish for frequencies below a gap frequency ω_g. The "oscillator strength" thus removed from the gap region must be replaced at higher frequencies, according to (5). Consequently, in a superconductor, $\Lambda_2(q,\omega)$ might appear as in Figs. 3 and 4.

We have plotted in Fig. 3 the function $B_2(q,\omega)$, where $B(q,\omega)$ is the polarization part connected with Fig. 2(b) in which the propagators are associated with the quasi-particles of the theory of superconductivity. In the matrix Green's function notation of Nambu,[5] we have

$$\begin{aligned}B(q,\omega) &= (i/N)(2\pi)^{-4}\,\mathrm{Tr}\int d^4k\, \boldsymbol{\tau}_3\mathbf{G}(k-\tfrac{1}{2}q,\, k_0-\tfrac{1}{2}\omega)\boldsymbol{\tau}_3\mathbf{G}(k+\tfrac{1}{2}q,\, k_0+\tfrac{1}{2}\omega) \\ &= \frac{2}{N}\int \frac{d^3k}{(2\pi)^3}[u(k+\tfrac{1}{2}q)v(k-\tfrac{1}{2}q)+u(k-\tfrac{1}{2}q)v(k+\tfrac{1}{2}q)]^2 \frac{E(k+\tfrac{1}{2}q)+E(k-\tfrac{1}{2}q)}{[E(k+\tfrac{1}{2}q)+E(k-\tfrac{1}{2}q)]^2-\omega^2}.\end{aligned} \tag{7}$$

This formula and all subsequent ones are based on the approximation,

$$\omega_g = 2\phi = \text{constant}.$$

We have denoted the energy gap by ϕ. The u's, v's, and E's are the usual Bogoliubov functions.[6]

Now B is not an approximation to the polarization part consistent with gauge invariance. In particular, the sum rule (6) is not satisfied. Insofar as ϕ is a constant, in fact, the total oscillator strength of $B(q,\omega)$ by itself is infinite, since the high-frequency tail of B_2 is proportional to $(\phi/\omega)^2$. Consequently, it is essential to include the collective effects for this reason alone.

II. EXISTENCE OF COLLECTIVE EXCITATIONS

We now proceed to show that at sufficiently long wavelengths there necessarily are contributions to $\epsilon_2(q,\omega)$ and therefore to $\Lambda_2(q,\omega)$ at very low frequencies. Indeed, we must have

$$\epsilon(q,\omega) \to \infty, \quad q \to 0 \tag{9}$$

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[5] Y. Nambu, Phys. Rev. 117, 648 (1960). This notation is reviewed in the Appendix.

[6] N. N. Bogoliubov, Zh. Eksperim. i Teor. Fiz. 34, 85 (1958) [translation: Soviet Phys.—JETP 7, 41 (1958)].

since we are dealing with conductors rather than insulators. It is easy to see that this condition is incompatible with

$$\epsilon_2(q,\omega)=0, \quad \omega<\omega_g. \tag{10}$$

Since one can find the bound

$$\epsilon(q,0)\leq 1+(\omega_p/\omega_g)^2 \tag{11}$$

by using the conditions (4) and (5). Thus, the strict energy gap (10), cannot be correct. In fact, it turns out that there is a pole in ϵ, i.e., a δ function in $\epsilon_2(q,\omega)$, at a frequency $\omega=\omega(q)$, where $\omega(q)$ is proportional to q in the long-wavelength limit.

III. CALCULATION OF THE POLARIZATION PART

It is well known that, in order to maintain gauge invariance, one cannot keep an arbitrary selection of graphs in calculating the response to an electric field. Just as in ordinary quantum electrodynamics, along with every graph, one must also include all those graphs in which the external field interacts with every charge carrying line.

Accordingly, following Nambu, we must include not only the graphs of Fig. 2(a), which contain "self-energy" corrections, but all the "ladders" as in Fig. 5. This remark applies equally well to the corrections to the Lindhard formula in the normal case. Glick[7] has studied this selection of graphs in the theory of the electron gas with repulsive interactions. The procedure we are following is practically the same as that adopted by Anderson and Rickayzen, who in effect kept only those ladders giving the scattering of particles of opposed spin. We choose to approximate this sum of graphs slightly differently than was done by Anderson and Rickayzen, however.

Again utilizing the notation of Nambu, we may write the polarization part as

$$\Lambda(q,\omega)=iN^{-1}(2\pi)^{-4}\,\mathrm{Tr}\int d^4k \\ \times\boldsymbol{\tau}_3\mathbf{G}(k-\tfrac{1}{2}q)\boldsymbol{\Gamma}(k-\tfrac{1}{2}q,\,k+\tfrac{1}{2}q)\mathbf{G}(k+\tfrac{1}{2}q), \tag{12}$$

where $\boldsymbol{\Gamma}(p,p')$ is the vertex part satisfying the approximate equation

$$\boldsymbol{\Gamma}(p+\tfrac{1}{2}q,\,p-\tfrac{1}{2}q) \\ =\boldsymbol{\tau}_3-i\boldsymbol{\tau}_3(2\pi)^{-4}\int d^4k\,\mathbf{G}(k+\tfrac{1}{2}q) \\ \times\boldsymbol{\Gamma}(k+\tfrac{1}{2}q,\,k-\tfrac{1}{2}q)\mathbf{G}(k+\tfrac{1}{2}q)D(p-k). \tag{13}$$

Here $D(q,\omega)$ is the sum of the Coulomb and phonon propagators, i.e.,

$$D(q,\omega)=4\pi e^2/q^2+g^2h^2(q)/[\omega^2-(cq)^2]. \tag{14}$$

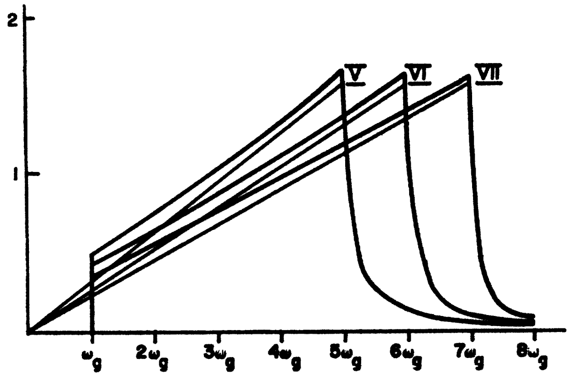

FIG. 4. Function $B_2(q,\omega)$ vs frequency. Heavy lines: (V) $q=5\omega_g/v_0$; (VI) $q=6\omega_g/v_0$; (VII) $q=7\omega_g/v_0$. Light lines: $\Lambda^{(L)}(q\omega)$ at corresponding wavelengths.

In this equation g is the electron-phonon coupling constant, $h(q)$ is the form factor associated with this coupling, and c is the phonon velocity.

We recall that the energy gap equation, in this notation, is

$$\boldsymbol{\tau}_2\phi=(2\pi)^{-4}\int d^4k\,\boldsymbol{\tau}_3\mathbf{G}(k)\boldsymbol{\tau}_2\phi\mathbf{G}(k)\boldsymbol{\tau}_3D(p-k). \tag{15}$$

In order to study Eq. (13) it is customary to suppose that $\mathbf{G}(k)$ has the structure

$$\mathbf{G}(k)=i/[k_0-\boldsymbol{\tau}_3(k^2/2m-\mu)-\boldsymbol{\tau}_1\phi]. \tag{16}$$

More importantly, $D(q,\omega)$ is replaced by a frequency-independent shell potential V, which vanishes outside a shell of width ω_0 around the Fermi surface and is constant within.[8]

This set of approximations has been questioned recently.[9] The final results are at present unclear. It seems safe to say, however, that the ordinary approximation is quite satisfactory for many purposes.

The use of a shell potential is, of course, not strictly speaking gauge invariant. However, it is well known that the shell potential leads to small deviations from gauge invariance as long as the width of the shell is large compared with the energy gap.

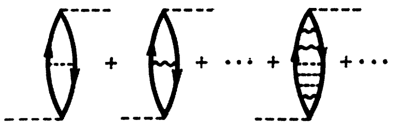

Fig. 5.

FIG. 5. Ladder graphs included in higher approximations.

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[7] A. Glick, Phys. Rev. **129**, 1399 (1963).

[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

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In order to solve Eq. (13), having made this simplification, we make the substitution

$$\boldsymbol{\tau}_3\boldsymbol{\Gamma}\boldsymbol{\tau}_3=\boldsymbol{\tau}_3=h_0+\boldsymbol{\tau}_1h_1-i\boldsymbol{\tau}_2h_2+\boldsymbol{\tau}_3h_3. \tag{17}$$

It may be readily verified that the components h_0, and h_1, satisfy homogeneous equations. In order to show this, the symmetry under the exchange $k+\frac{1}{2}q\rightarrow -k+\frac{1}{2}q$ must be exploited. One must further take advantage of the thinness of the effective interaction region around the Fermi surface ($\omega_0\ll p_0^2/2m$) by noting that one may reflect through the Fermi surface as if it were flat. We thus have symmetry under the reflection $k^2/2m-\mu\rightarrow-(k^2/2m-\mu)$ (μ is the chemical potential). We may therefore suppose that h_0 and h_1 vanish. With the substitution (17), we obtain from (13) the result,

$$h_3=-NV\left(m+\frac{NVn^2}{1-NVl}\right)\bigg/\left(1+NVm+\frac{NVn^2}{(1-NVl)}\right), \tag{18}$$

where

$$m=\tfrac{1}{2}B(q,\omega), \tag{19a}$$

$$n=\frac{1}{N}\int\frac{d^3k}{(2\pi)^3}\omega\frac{u(k-\frac{1}{2}q)v(k-\frac{1}{2}q)+u(k+\frac{1}{2}q)v(k+\frac{1}{2}q)}{[E(k+\frac{1}{2}q)+E(k-\frac{1}{2}q)]^2-\omega^2}, \tag{19b}$$

$$l=\frac{1}{N}\int\frac{d^3k}{(2\pi)^3}\frac{[u(k-\frac{1}{2}q)u(k+\frac{1}{2}q)+v(k-\frac{1}{2}q)v(k+\frac{1}{2}q)]^2[E(k+\frac{1}{2}q)+E(k-\frac{1}{2}q)]}{[E(k+\frac{1}{2}q)+E(k-\frac{1}{2}q)]^2-\omega^2}. \tag{19c}$$

We thus have

$$\Lambda(q,\omega)=\left[B(q,\omega)+\frac{2NVn^2}{1-NVl}\right]\bigg/\left[1+NV\left(m+\frac{NVn^2}{1-NVl}\right)\right]. \tag{20}$$

We now proceed to an evaluation and discussion of formula (20). Unfortunately, although the functions m, n, and l, are relatively simple, it is not easy to see even the gross features of the final formula except by numerical methods. Before giving the numerical results, however, we shall discuss some of the salient features.

We remark immediately, that if the simplifications of symmetry about the Fermi surface and reflection symmetry are made, the approximations of Anderson and Rickayzen correspond exactly to the expression

$$\Lambda^{(A)}=B(q,\omega)+2NVn^2/(1-NVl). \tag{21}$$

In some senses, this is as meaningful an approximation to the correct polarization part as the formula (20). As the energy gap vanishes, while the coupling strength NV remains fixed, $\Lambda^{(A)}$ approaches the Lindhard approximate value. Thus, we can regard $\Lambda^{(A)}-\Lambda^{(L)}$ as giving the difference between the value of the polarization part in the normal and superconducting states.

We shall therefore discuss first the expression (21). The first term of this expression, $B(q,\omega)$, as has already been mentioned, may be regarded as the contribution of the quasi-particles alone, whereas the second provides the corrections arising from the collective effects. As might be anticipated, the contribution of the independent quasi-particles dominates for wavelengths shorter than the coherence length ($qv_0/\omega_g\gg1$). The collective oscillations predominate for long wavelengths, ($qv_0/\omega_g<1$), and are competitive for wavelengths such that $qv_0/\omega_g\lesssim7$.

The quasi-particle term has the properties

$$B_2(q,\omega)=0,\quad \omega<\omega_g \tag{22a}$$

$$B_2(q,\omega)-\Lambda_2^{(L)}(q,\omega)>0,\quad \omega>\omega_g \tag{22b}$$

$$\Lambda^{(A)}(q,0)=B(q,0). \tag{22c}$$

However, as noted before, there is too much oscillator strength in B_2 alone, so that the sum rule is not satisfied. Property (c) is particularly important, namely, that the collective excitations have no influence on the static polarizability.

IV. STATIC POLARIZABILITY

We have just seen that the excitation of independent quasi-particles determines the zero-frequency polarizability. This is particularly important since the static polarizability determines the effect of the electron screening on the phonon spectrum. [The phonon frequency is determined by the zero of the complete dielectric constant, $1-v(q)N\Lambda(q,\omega)-(\Omega_p/\omega)^2$, which is to a good approximation at $\omega^2=\Omega_p^2/v(q)N\Lambda(q,0)$.]

A shift of the phonon spectrum can be observed by measuring the specific heat of the lattice. However, it turns out that the static polarizability depends very weakly on the energy gap, i.e., it does not depend strongly on whether or not the superconducting transition has taken place, so that the lattice specific heat should not undergo an observable change.

It is easy to demonstrate that the static polarizability is insensitive to the superconducting transition once it is realized that the entire contribution to it comes from the independent quasi-particle excitations. Indeed, it is easy to see that $B(q,0)$ may be expanded as

$$B(q,0)\simeq 1+a(v_0q/\mu)+b(\omega_g/\omega_0)^2+\cdots, \tag{23}$$

where a and b are constants. In particular, there are no terms depending on the ratio v_0q/ω_g. The values of the constants as given by (7) are not particularly meaningful, however, since the whole approximation scheme is based on the supposition that ω_g/ω_0 and v_0q/μ are small. Thus, we reach the conclusion that the static polarizability and, consequently, the sound speed are practically independent of the energy gap, for all wavelengths, and especially for wavelengths comparable with the coherence length, $\xi_0=2v_0/\pi\omega_g$.

Consequently, we find especially, that the experiment of Bryant and Keesom[10] cannot be explained on the basis of a shift in the sound speed, as proposed by Ferrell.[11] (The static polarizability would have to increase by a fraction of order ω_g/v_0q when this fraction is in the neighborhood of 1/7 if the experiments of Bryant and Keesom are to be explained on this basis.)

V. COLLECTIVE EFFECTS

The second term of (21) can be regarded as deriving from collective effects. The denominator, $d(q,\omega)$ vanishes at a frequency $\omega(q)$. It is not difficult to study the vanishing of the denominator in the long-wavelength limit. The result is the well-known one, $\omega(q)=qv_0/\sqrt{3}$, $q\xi_0\ll 1$.

In this limit, all of the oscillator strength of the polarization propagator is associated with the collective pole. Consequently, we find that

$$\epsilon(q,\omega)\rightarrow 1-\omega_p^2/[\omega^2-(v_0q)^2/3], \quad q\xi_0\ll 1. \tag{24}$$

It should be realized that collective states of the system are given by the singularities of $1/\epsilon(q,\omega)$ which according to (24) consist of a pole at $\omega\approx\omega_p$. The pole of the dielectric function itself does not have such a direct meaning, although it is a manifestation of a collective response.

In a neutral fermion superfluid, there would exist actual states at a frequency approximately determined by the vanishing of the denominator. Even in a charged system, these states are of interest, since it is usually convenient to regard the system as consisting of an underlying one with effectively short-ranged forces, and then to take into account later the effects of the long-range forces on the density fluctuations. Thus, we see that the ghost of the collective state of the underlying neutral system remains to haunt the dielectric constant of the charged system.

In a neutral fluid the collective states have a simple classical interpretation. They are simply the states of ordinary sound which can persist because in the presence of an energy gap there is no way in which they can decay. The sound speed is related to the compressibility in the usual way. Thus, in the weak-coupling limit we obtain the sound speed for a perfect Fermi liquid, $v_0/\sqrt{3}$. It is possible to obtain corrections to this sound speed in the case of weak coupling.

The sound frequency is the frequency at which there is a pole in the *improper* polarization propagator. The improper propagator is defined as the sum of all graphs of the type shown in Fig. 1, including those in which a connection is made by means of a single interaction line. It is readily related to the proper polarization part by the formula

$$\Lambda_{\text{improper}}=\Lambda/(1-NV\Lambda). \tag{25}$$

The pole of this expression may be readily studied in the limit in which both the frequency and wave number vanish. In this limit the functions defined in (19) have the form

$$m\rightarrow\tfrac{1}{2}, \tag{26a}$$

$$n\rightarrow\omega/2\omega_g, \tag{26b}$$

$$(NV)^{-1}-l\rightarrow[\tfrac{1}{3}(qv_0)^2-\omega^2]/2\omega_g^2. \tag{26c}$$

By using these expressions together with (20) and (25), we find the speed of ordinary sound in the neutral Fermi liquid to be $a^2=\frac{1}{3}v_0^2(1+\frac{3}{2}VN)$. This result differs from that of Anderson,[1] and is somewhat more general in that we have included the ladder graphs as well as the "bubble" contributions.

At shorter wavelengths such that $qv_0\gtrsim 3\omega_g$ the collective pole practically disappears. In $\Lambda^{(A)}(q,\omega)$, the pole at the zero of $d(q,\omega)$ never completely disappears. Rather, the position of the pole approaches the gap frequency, approximately as $\omega_g-\omega(q)\sim\omega_g e^{-(qv_0/\omega_q)\beta}$, where β is a number of order unity. The residue at the pole vanishes exponentially also. However, in the more complete expression (20), there is no pole for these shorter wavelengths. In expression (20), the absorptive part of the polarization-propagator is modified so that instead of jumping discontinuously at the gap frequency, it rises continuously from zero at that point. The rise occurs over a region exponentially small in size, however.

Even though the pole itself is unimportant, the collective effects are strongly felt for wavelengths with $qv_0\lesssim 7\omega_g$ and are important for considerably shorter wavelengths. In general, the collective effects tend to increase the oscillator strength at lower frequencies, at the expense of oscillator strength at greater frequencies. The high-frequency tail of the absorption due to independent quasi-particles is, of course, completely eliminated.

We may raise the question of whether there are any collective states, that is, whether there are any zeros of the dielectric function (other than at the plasma frequency). When there is a pole in the dielectric function, the function will be negative for frequencies just greater than the frequency of the pole. On the other hand, the absorptive part of the dielectric function rises very abruptly at the energy gap. If this rise were infinitely

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[10] C. A. Bryant and P. H. Keesom, Physica 4, 460 (1960).

[11] R. A. Ferrell, Phys. Rev. Letters 6, 541 (1961).

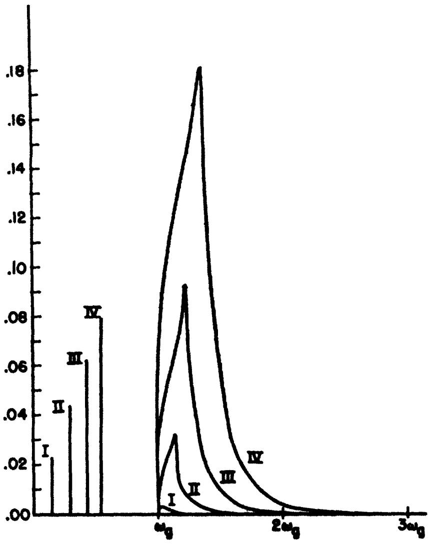

FIG. 6. Function $\Lambda_2^{(A)}(q,\omega)$, defined in the text, vs frequency. Vertical lines represent δ-function contributions. (I) $q=\omega_g/4v_0$, (II) $q=\omega_g/2v_0$, (III) $q=3\omega_g/4v_0$, (IV) $q=\omega_g/v_0$.

steep, it would produce a large positive contribution to the dielectric function just below the gap frequency. In between the frequency of the pole and the gap frequency would lie a zero of the dielectric function.

The dielectric function is not discontinuous at the frequency of the energy gap. According to the formula (20), the behavior of $\Lambda_2(q,\omega)$ for frequencies just greater than the gap frequency is

$$\Lambda_2(q,\omega)=a/[\ln(\omega-\omega_g)]^2,$$

where a is weakly dependent upon the frequency. This behavior is just mild enough that it does not lead to a large positive contribution to $\Lambda(q,\omega)$ for frequencies near ω_g. Consequently, the sign of the polarization part just below the gap frequency will depend predominantly on the absorption well away from the gap edge. According to the numerical evaluation of Eq. (20), the dielectric function never actually vanishes in the gap region. We can thus conclude that there is no (s-wave) collective state.

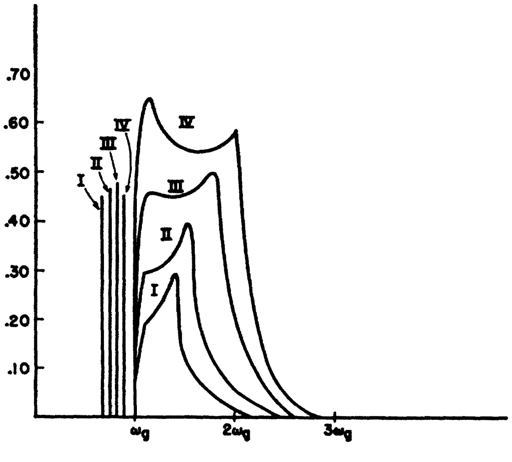

FIG. 7. Function $\Lambda_2^{(A)}(q,\omega)$ vs frequency. Vertical lines represent δ-function contributions. (I) $q=5\omega_g/4v_0$, (II) $q=3\omega_g/2v_0$, (III) $q=7\omega_g/4v_0$, (IV) $q=2\omega_g/v_0$.

VI. NUMERICAL RESULTS

In this section we deal with numerical results for representative values of the wavelengths. The results were obtained by numerical integration of formulas (22). The absorptive parts of the functions, m, n, and l, can be found in closed form. Expressions for these absorptive parts are given in the Appendix. This leaves one-dimensional principal-value integrals to be performed numerically. It is estimated that these formulas were evaluated with an accuracy such that the difference $\Lambda^{(A)}-\Lambda^{(L)}$ is correct to 1%. The accuracy is less good when this difference is itself very small.

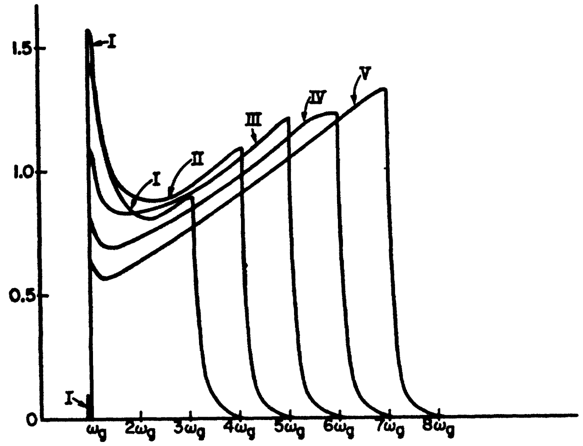

FIG. 8. Function $\Lambda_2^{(A)}(q,\omega)$ vs frequency. Vertical line represents δ function contribution. (I) $q=3\omega_g/v_0$, (II) $q=4\omega_g/v_0$, (III) $q=5\omega_g/v_0$, (IV) $q=6\omega_g/v_0$, (V) $q=7\omega_g/v_0$.

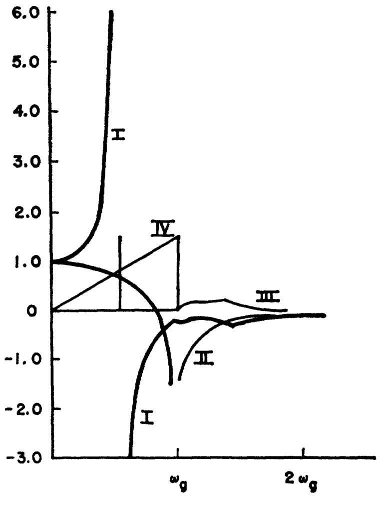

FIG. 9. Functions $\Lambda^{(L)}$ and $\Lambda^{(A)}(q,\omega)$ vs frequency, $q=\omega_g/v_0$. (I) $\Lambda_1^{(A)}$; (II) $\Lambda_1^{(L)}$; (III) $\Lambda_2^{(A)}$; (IV) $\Lambda_2^{(L)}$.

Figures 6, 7, and 8 contain plots of $\Lambda_2^{(A)}(q,\omega)$ as a function of frequency for several values of the wavelength. The competition of the independent quasiparticle and the collective effects can be seen. Figures 9 and 10 contain plots of the real part of the polarization part as compared with the Lindhard formula, for two values of the wavelength. The real part is strikingly changed in the transition. However, it should be remembered that the inverse of the dielectric constant is more readily observed, and in the inverse dielectric constant the difference is much less striking.

We have also obtained by numerical integration the values of the first few moments of the absorptive part of the polarization propagator. The moments are defined by

$$\mu_n(q)=(2/\pi)\int_0^\infty \omega^{n+1}\Lambda_2^{(A)}(q,\omega)d\omega/(qv_0)^{n+2}. \qquad (26)$$

The "moment" μ_{-2} is just the static polarizability. This turns out to be independent of q over the range of wavelengths here considered. It has the same value as in the normal case, as was previously remarked, namely, $\mu_{-2}=1$. The zeroth moment is fixed by the sum rule. With our normalization it should be

$$\mu_0=\tfrac{1}{3}.$$

Numerical integrations of the formulas for μ_{-2} and μ_0 agree with the theoretical values to about one part in 10^4 or 10^3, respectively. Most of the error occurs in the numerical integration of the frequency region in the neighborhood of v_0q.

TABLE I. Position and residue of the pole of $\Lambda^{(A)}(q,\omega)$ are listed as a function of wavelength. Also listed are the "moments" of the oscillator strength. The symbols are defined in the text.

v_0q/ω_g	$\omega(q)/\omega_g$	r_c/ω_g	μ_{-1}	μ_1	μ_2
0.25	0.142	0.227	0.578	0.206	0.21
0.50	0.282	0.443	0.570	0.219	0.20
0.75	0.412	0.640	0.563	0.225	0.20
1.00	0.529	0.810	0.560	0.229	0.20
1.25	0.634	0.928	0.555	0.234	0.20
1.50	0.724	0.968	0.548	0.236	0.20
1.75	0.798	1.002	0.547	0.238	0.20
2.00	0.853	0.969	0.550	0.241	0.20
3.00	1.0	0.437	0.524	0.250	0.20
4.00	···	···	0.519	0.249	0.20
5.00	···	···	0.516	0.242	0.20
6.00	···	···	0.510	0.244	0.20
7.00	···	···	0.509	0.245	0.20

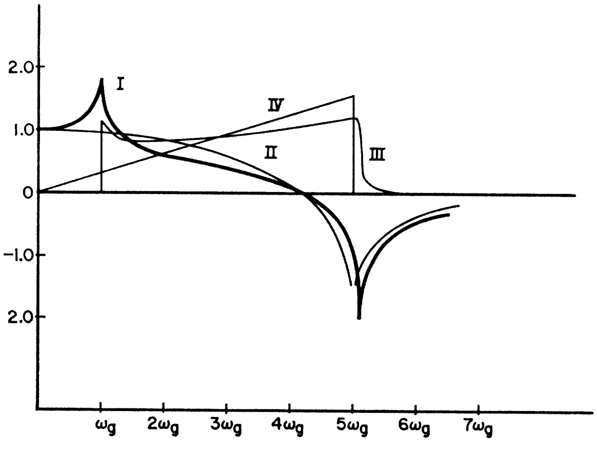

FIG. 10. Functions $\Lambda^{(L)}$ and $\Lambda^{(A)}(q,\omega)$ vs frequency: $q=5\omega_g/v_0$. (I) $\Lambda_1^{(A)}$; (II) $\Lambda_1^{(L)}$; (III) $\Lambda_2^{(A)}$; (IV) $\Lambda_2^{(L)}$.

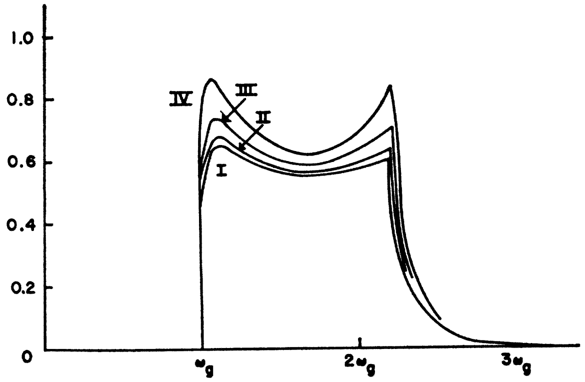

FIG. 11. Functions $\Lambda_2(q,\omega)$ and $\Lambda_2^{(A)}(q,\omega)$ vs frequency for $q=2\omega_g/v_0$. (I) $\Lambda_2^{(A)}$; (II) Λ_2, $NV=0.1$; (III) Λ_2, $NV=0.31$; (IV) Λ_2, $NV=0.72$.

The remaining moments are listed in Table I. Also given is the position $\omega(q)$ and residue r_c of the pole of the polarization part. This fixes the δ-function contribution to the absorptive part of $\Lambda_2(q,\omega)$ as $r_c\delta(\omega-\omega(q))$.

The listed moments may be compared with those of the Lindhard formula, which are $\mu_n^{(L)}=1/(n+3)$. We also note the moments obtained in the long-wavelength limit, i.e., for $\omega(q)=v_0q/\sqrt{3}$, $r_0=v_0q/\sqrt{3}$. In this case $\mu_n^{(c)}=\frac{1}{3}(\sqrt{3})^{-n}$. It should be noted that the continuum contribution already makes a significant contribution to μ_2 at $qv_0=\omega_g/4$.

VII. NORMAL CORRECTIONS TO THE DIELECTRIC FUNCTION

Equation (20) contains, in addition to corrections to the Lindhard formula deriving from the nonvanishing

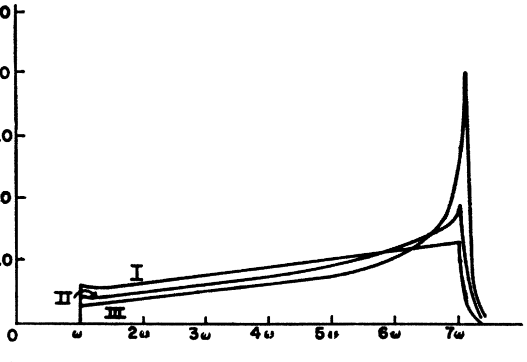

FIG. 12. Functions $\Lambda_2(q,\omega)$ and $\Lambda_2^{(A)}(q,\omega)$ vs frequency for $q=7\omega_g/v_0$. (I) $\Lambda_2^{(A)}$; (II) Λ_2, $NV=0.31$; (III) Λ_2, $NV=0.72$.

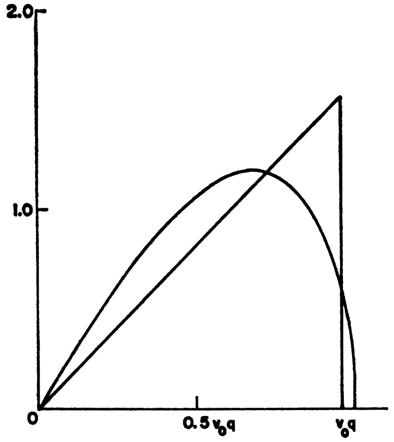

FIG. 13. Functions $\Lambda_2^{(L)}$ and normal corrections to $\Lambda_2^{(L)}$ vs frequency (after Glick).

energy gap, corrections which would be present even in the normal state. These corrections are relatively small for small coupling constant. There exist corrections to the polarization part other than those given by (20), of course, but it is believed that the ladder sums are among the most important of the corrections.

The effect of the correction is greatest whenever the approximate value of the polarization part, $\Lambda^{(A)}(q,\omega)$ is large. Consequently, the corrections will be most important near the "jumps," i.e., for frequencies in the neighborhood of ω_g and v_0q. The jump at v_0q will be particularly important, because $\Lambda^{(A)}(q,\omega)$ is large and negative there. The correction to Λ will consist of an enhancement of the absorptive part near v_0q, and a suppression near ω_g. In Figs. 11 and 12, the absorptive parts are plotted as a function of coupling constant for two values of the wavelength. As can be seen, for strong coupling, the difference is significant.

Glick[7] has found, that in the case of repulsive interactions alone, the absorptive part is enhanced at lower frequencies and suppressed at frequencies near the maximum. In addition, he finds a shift of scale arising from the self-energy correction. This shift has been neglected in our calculations. This behavior is sketched in Fig. 13. It is to be contrasted with the behavior in a superconductor. The change in sign of the effective coupling in the two cases accounts for the difference.

One should not put too much faith in the magnitude of these corrections, since the many additional corrections have not been systematically studied.

ACKNOWLEDGMENTS

The author wishes to acknowledge helpful conversations with Professor R. Ferrell, Professor A. Glick, Professor D. Falk, and Professor T. Nishiyama. The invaluable aid of Walter Daniels in assisting with the computing program is gratefully appreciated. The computations were carried out on the IBM 7090 installation at the Goddard Space Flight Center of NASA. The hospitality of the Aspen Institute of Humanistic Studies, Physics Division, at which the manuscript was prepared in part, is appreciated.

APPENDIX I

We list below the formulas for the absorptive parts of the functions m, n, and l. In these formulas we have put $\kappa=(\omega-\omega_g)/(\omega+\omega_g)$, $\sin^2\theta=[1-\omega_g^2/(\omega^2-v_0^2q^2)]\times[v_0q/(\omega-\omega_g)]^2$, and denoted by K, $F(\kappa,\theta)$ the complete and incomplete elliptic functions of the first kind. The corresponding functions of the second kind are denoted by E, $E(\kappa,\theta)$, respectively. The modulus of these functions is κ.

For $\omega^2<\omega_g^2+(v_0q)^2$, one has

$$n_2(q,\omega)=\frac{\pi}{2}\frac{\omega_g}{v_0q}\frac{\omega}{\omega+\omega_g}K, \tag{I1}$$

$$m_2(q,\omega)=\frac{\pi}{4}\frac{\omega+\omega_g}{qv_0}E-n_2(q,\omega), \tag{I2}$$

$$l_2(q,\omega)=m_2(q,\omega). \tag{I3}$$

For $[\omega_g^2+(v_0q)^2]^{1/2}<\omega<0.5\omega_g+[(v_0q)^2+(0.5\omega_g)^2]^{1/2}$, one has

$$n_2(q,\omega)=\frac{\pi\omega_g\omega}{4v_0q(\omega+\omega_g)}[2K-F(\kappa,\theta)], \tag{I4}$$

$$m_2(q,\omega)=\frac{\pi(\omega+\omega_g)}{8v_0q}[2E-E(\kappa,\theta)-\kappa\sin\theta]-n_2(q,\omega), \tag{I5}$$

$$l_2(q,\omega)=m_2(q,\omega)+\frac{\pi(\omega-\omega_g)}{4v_0q}\sin\theta. \tag{I6}$$

For $\omega>\frac{1}{2}\omega_g+[(v_0q)^2+(\frac{1}{2}\omega_g)^2]^{1/2}$, one has

$$n_2(q,\omega)=\frac{\pi\omega_g\omega}{4v_0q(\omega+\omega_g)}F(\kappa,\theta), \tag{I7}$$

$$m_2(q,\omega)=\frac{\pi(\omega+\omega_g)}{8v_0q}[E(\kappa,\theta)-\kappa\sin\theta]-n_2(q,\omega), \tag{I8}$$

$$l_2(q,\omega)=m_2(q,\omega)+\frac{\pi(\omega-\omega_g)}{4v_0q}\sin\theta. \tag{I9}$$

APPENDIX II

We recall here for the convenience of the reader, the notation of Nambu. Let the destruction operators be redefined by $a_{k\uparrow}\rightarrow a(k)_1$, $a_{-k\downarrow}^\dagger\rightarrow a(k)_2$.

$$G_{ij}=\langle T(a(k)_i a^\dagger(k)_j)\rangle,$$

where T is the time ordering operator. It is also convenient to introduce four-dimensional notation for the momentum-frequency variables,

$$p=(p_0,\mathbf{p}).$$

Expanding $\mathbf{G}(p)$ in terms of the Pauli matrices, $\boldsymbol{\tau}_i$, $\mathbf{1}$ in the 2×2 spin space leads to the expression (16) for $\mathbf{G}$ in lowest approximation. The trace is over the spin space. The propagator $\mathbf{G}$ may be diagonalized by means of the unitary Bogoliubov transformation:

$$\mathbf{U}(\mathbf{p})\mathbf{G}(p)\mathbf{U}(p)=i/[p_0-\boldsymbol{\tau}_3(E(p)-i\eta)],$$

where $\mathbf{U}(\mathbf{p})=u(\mathbf{p})\boldsymbol{\tau}_3-v(p)\boldsymbol{\tau}_1$. Here u, v, and E are defined by

$$E(p)=[(p^2/2m-\mu)^2+\phi^2]^{1/2},$$

$$[u(p)]^2=\frac{1}{2}\left(1+\frac{p^2/2m-\mu}{E(p)}\right),$$

$$[v(p)]^2=1-[u(p)]^2.$$

PHYSICAL REVIEW VOLUME 129, NUMBER 6 15 MARCH 1963

Electronic Structure and the Properties of Metals. I. Formulation

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(Received 22 October 1962)

A method is formulated for the calculation from first principles of a variety of electronic and atomic properties of metals. The method depends upon three approximations: (1) the self-consistent-field approximation; (2) the assumption that the core states are the same as in the free atom; and (3) a perturbation solution, carried to second order, of the Hamiltonian matrix based upon orthogonalized plane waves. Only the last approximation distinguishes the method from more traditional band calculations; it is regarded as appropriate for the treatment of most polyvalent metals. The only experimental parameters which enter for a given metal are the atomic number and the atomic volume.

It is found that many electronic properties, including the Fermi surface and scattering by defects or phonons, may be calculated as for free electrons with an effective perturbing potential. The matrix elements of this potential may be written as the product of a structure factor, depending only on the ion positions, and a form factor depending only on the Hartree-Fock field of the ion and upon the atomic volume. The form factor is found to be a function only of the magnitude of the change in wave number.

It is found that for a given ion density the energy of the system may be written in terms of a central-force, two-body interaction between ions or in terms of a sum over wave number space of the Fourier transform of this interaction (the energy-wave number characteristic). The procedure for computing these functions from the Hartree-Fock field of the corresponding ion is given.

I. INTRODUCTION

EXISTING *a priori* calculations of metallic properties based on the full Hartree or Hartree-Fock treatment of the crystal potential have been, for the most part, restricted to computations of the energy bands. There are exceptions, notably calculations of the lattice distance and attempts at calculation of the cohesive energy, but for the most part properties which depend upon the details of the lattice potential and the electronic structure have been beyond the reach of available techniques.

Recent developments have given hope of going beyond these limitations in treating polyvalent metals. This hope is based on the surprising fact that the Fermi surfaces of these metals differ very little from free-electron spheres,[1] indicating a relatively weak influence of the lattice potential. This suggests that we might regard this potential as a perturbation and sufficiently simplify the analysis, in comparison to traditional band calculations, that many new aspects of the behavior of metals could be treated in some detail.

The work to be described here is part of such a program. There are two classes of properties which we wish to attack: first, atomic properties which depend upon the variation of the total energy as the atoms are rearranged; and second, electronic properties which depend on the scattering of electrons when the crystal is not perfectly ordered. For both classes of properties the computations can be carried out without the explicit determination of the energy bands. We propose to carry out a rather complete Hartree calculation (exchange is also included where it is felt to be important) for a general arrangement of the metal ions.

Certainly the most crucial approximation to be made is the self-consistent-field approximation. Because of this approximation we regard the cohesive energy, which has a large contribution from the correlation energy, as beyond our reach. Further, we might expect the change in energy associated with change in volume to have a large contribution from correlations. On the other hand, it is hoped that changes in energy when the

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[1] Extensive discussion of this point appears in the article, W. A. Harrison, Phys. Rev. **118**, 1190 (1960), and in several articles appearing in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).