

Number-Phase Fluctuations in Two-Band Superconductors

A. J. LEGGETT

*Magdalen College, Oxford, England and
Department of Physics, Kyoto University, Kyoto*

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It is shown that in a clean two-band (transition-metal) superconductor there appears a collective excitation corresponding to small fluctuations of the relative phase of the two "condensates". In contrast to the transverse collective excitations in ordinary superconductors, the energy of this mode can be derived directly from existing experimental data; for Nb it lies about at the middle of the smaller single-particle gap. Direct experimental detection of this resonance is estimated to be rather beyond the limits of available techniques, but its effect on the ultrasound dispersion curve should be easily observable. The phenomenon is used to elucidate the physical nature of excitons in superconductors in general.

§ 1. Introduction

It was long ago suggested¹⁾ that, if sufficiently purified, the transition metal superconductors should be describable by a 'two-gap' theory of superconductivity, which is the appropriate generalization of the usual BCS theory²⁾ to the case when the Fermi surface intersects two bands. In such a theory Cooper pairs are formed in each band separately, but under the influence of a self-consistent field arising from the pairs in both bands. Earlier experimental work on the transition metals failed to show the expected 'two-gap' behaviour, probably because the samples were too dirty, but recent specific-heat measurements on niobium³⁾ appear to be in good agreement with the theory⁴⁾ and we may therefore accept that two-gap superconductors do exist in nature. A number of authors⁵⁾ have discussed the thermal, electrodynamic and transport properties of such superconductors; generally speaking, the results are qualitatively analogous to those well-known in the one-band case.

In this paper we shall investigate a phenomenon which, at first sight at least, does *not* have an analogue in the one-band case: the existence of a collective oscillation corresponding to small fluctuations of the relative phases of the two 'condensates'. Such an oscillation arises because the total energy of the system depends not only on the relative phase of the two condensates but also on the canonically conjugate variable, the relative density of electrons in the two bands; in a sense it may be thought of as an internal second-order Josephson effect. From another point of view, its existence is a

consequence^{*)} of the fact that under realistic conditions the coupled gap equations for the two-band system have more than one nontrivial solution. This of course is also true in the usual single-band theory if other spherical harmonics of the pairing interaction besides the zeroth are attractive; thus, in principle, the effect we shall discuss here does have an analogue in the $l \neq 0$ 'exciton' modes investigated within the framework of the BCS theory by many authors.⁶⁾ However, in practice there is the following important difference: in the single-band case, with realistic values of the parameters, any unstable solutions of the gap equations have a condensation energy small compared to that of the BCS solution, so that the corresponding exciton modes lie very close to the top of the gap. On the other hand, both theoretical⁷⁾ and experimental^{3),4)} investigations indicate that the opposite is likely to be true in the case of two bands: there exists an unstable solution whose condensation energy is very little smaller than that of the true ground state, and as a result the corresponding exciton may lie well below the smaller of the two gaps. This feature not only makes its possible experimental consequences of greater interest but permits a rather clearer physical picture of the collective excitation than is usually available in the one-band case. In fact, we shall use it to try to shed some light on the latter.

The experimental detection of this resonance would be of great value in confirming the basic hypotheses of the two-gap theory of transition metal superconductors. We shall find that in spite of the advantageous feature that it is well separated from the two-particle continuum, its direct observation probably lies rather beyond the limit of present experimental possibility, even under rather favourable conditions. The basic difficulty is that, in a charged system, the only physical response function in which it appears as a pole is the response function of the relative density of the electrons in the two bands, and no external probe will couple directly to this quantity in the long-wavelength limit. The most promising method of dynamic detection seems to be indirect neutron scattering via a virtual intermediate phonon, but an order of magnitude estimate suggests that this is rather beyond the limits of available experimental technique. On the other hand it turns out to be possible to measure the excitation spectrum indirectly by observing its effect on the ultrasound dispersion relation; such an experiment is estimated to be well within current experimental feasibility. The existence of this excitation may also have a marked effect on the specific heat at very low temperatures, but the absolute magnitude of the effect is probably rather beyond the limit of present experimental accuracy, though not hopelessly so. It should perhaps be mentioned that Geilikman⁸⁾ has recently suggested that some transition metals or ordered alloys might become superconducting at room temperature or above under favourable conditions; although the mechanism

^{*)} In the simplified model usually used. See the footnote to Eq. (3.12) below.

he considers most favourable does *not* lead to a 'two-gap' superconducting state, he concludes that such a state cannot be ruled out. If this were the case, it should be comparatively easy to detect the corresponding collective excitation directly; however, such a hypothesis must be regarded as very speculative at present.

In the next section we shall present a simple physical argument, based on the number-phase uncertainty relation, which demonstrates the existence of a collective excitation and enables us to calculate its energy in the long-wavelength limit under a certain approximation which is probably quite realistic. In § 3 the problem is attacked under general conditions by field-theoretic methods and the dispersion relation is obtained in some physically interesting limits. In § 4 we make a quantitative estimate of the parameters of the excitation for niobium and discuss the possibility of experimental detection. Section 5 considers various aspects of the results obtained: the relation to the Josephson effect and to the $l \neq 0$ excitons in a one-band superconductor is elucidated, and an interpretation is given in terms of a quasi-hydrodynamic model of the two-condensate system. Section 6 is a brief conclusion.

§ 2. Number-phase fluctuations

We shall work with a two-band Hamiltonian of the standard type:^(1),5)

$$\begin{aligned} \hat{H} = & \sum_{k\sigma} \varepsilon_{k\sigma}^{(1)} a_{k\sigma}^+ a_{k\sigma} + \sum_{q\sigma} \varepsilon_{q\sigma}^{(2)} b_{q\sigma}^+ b_{q\sigma} \\ & - \sum_{kk'} V_{kk'} a_{k\uparrow}^+ a_{k'\downarrow}^+ a_{-k'\downarrow} a_{-k\uparrow} - \sum_{qq'} U_{qq'} b_{q\uparrow}^+ b_{q'\downarrow}^+ b_{-q'\downarrow} b_{q\uparrow} \\ & - \sum_{kq} (J_{kq} a_{k\uparrow}^+ a_{-k\downarrow}^+ b_{-q\downarrow} b_{q\uparrow} + \text{H.c.}). \end{aligned} \quad (2.1)$$

Here and subsequently the notation is as follow: $a_{k\sigma}^+$ and $b_{q\sigma}^+$ create, respectively, an electron in the first and second band, with energy $\varepsilon_{k\sigma}^{(1)}$ and $\varepsilon_{q\sigma}^{(2)}$. We shall denote the operator of the total number of electrons in the j -th band by \hat{N}_j , and the density of states of *both* spins at the Fermi surface by ρ_j :

$$\rho_j = p_{Fj}^2 / \pi^2 v_j \quad (2.2)$$

when p_{Fj} is the Fermi momentum in the j -th band and v_j the corresponding Fermi velocity. Here we have chosen units so that $\hbar=1$ and assumed that the Fermi surface is isotropic in both bands (an unlikely assumption in practice but one which is unlikely to lead to qualitative error in the results). We shall also choose a BCS-type form for the pairing interactions U , V and J :

$$\begin{aligned} V_{kk'} &= V, \text{ if } |\varepsilon_k^{(1)}|, |\varepsilon_{k'}^{(1)}| < \tilde{\omega}, = 0 \text{ otherwise,} \\ U_{qq'} &= U, \text{ if } |\varepsilon_q^{(2)}|, |\varepsilon_{q'}^{(2)}| < \tilde{\omega}, = 0 \text{ otherwise,} \\ J_{kq} &= J, \text{ if } |\varepsilon_k^{(1)}|, |\varepsilon_q^{(2)}| < \tilde{\omega}, = 0 \text{ otherwise.} \end{aligned} \quad (2.3)$$

In (2.3) the energies are measured from the Fermi energy in the normal state. Thus, we have omitted a constant term $N\varepsilon_F$ in the Hamiltonian (2.1) (We work in this paper with a fixed total number of particles—see below). Again, the relaxation of the rather artificial assumption of the same cutoff for all three interactions is unlikely to change the results qualitatively. Rather more questionable, possibly, is the assumption of symmetry of the interaction with respect to the Fermi surface; we shall assume that the effects of relaxing it will be essentially no different from those arising in the one-band problem and will in any case be negligible in the weak-coupling limit, to which we shall restrict ourselves. We notice that while V and U are completely fixed by the physics of the problem, the phase of J is a matter of convention (corresponding to the choice of the relative phases of the Bloch waves in the two bands). We shall take advantage of this to choose J to be real and positive. For the moment we make no particular assumptions about the signs of U or V or their magnitudes relative to J . Finally, we shall always deal with pure specimens and work at zero temperature unless explicitly otherwise stated.

Before starting on the calculations we should make two remarks about the Hamiltonian (2.1). First, it does not include a chemical potential term $-\mu\hat{N}$, where $\hat{N}\equiv\hat{N}_1+N_2$ is the total number of electrons in the system; this feature makes the subsequent argument somewhat clearer, but it means that strictly speaking we must always choose the wave function explicitly to be an eigenfunction of \hat{N} . This introduces no special difficulties and we shall simply assume it is done at the necessary points in the argument without always mentioning it explicitly; this point is further discussed at the end of this section. Secondly, there are no terms in (2.1) corresponding to interactions diagonal in the quasiparticle occupation number ("Fermi-liquid" terms). In a real system such terms certainly exist, and if they are large may change the quantitative results quite considerably (cf. reference 9) where their effect on $l\neq 0$ excitons in one-band superconductors is discussed). However, if we can calculate the appropriate correlation functions for the system described by the Hamiltonian (2.1)—which is easy to do by the methods of § 3, though we do not actually carry out the calculation*)—then it is trivial to incorporate the effects of such 'Fermi-liquid' terms (cf. reference 10)). Since they certainly do not change the results by more than a factor of order unity, we shall not consider them in this paper.

Let us rewrite the Hamiltonian (2.1) (with the simplifications (2.3)) in the following identically equivalent form:

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{J} + \hat{L}, \\ \hat{H}_0 &= \sum_{k\sigma} \varepsilon_{k\sigma}^{(1)} a_{k\sigma}^\dagger a_{k\sigma} + \sum_{q\sigma} \varepsilon_{q\sigma}^{(2)} b_{q\sigma}^\dagger b_{q\sigma} - V \sum_{kk'} a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger a_{-k'\downarrow} a_{k'\uparrow} \\ &\quad - U \sum_{qq'} b_{q\uparrow}^\dagger b_{-q\downarrow}^\dagger b_{-q'\downarrow} b_{q'\uparrow} - \hat{E}_0(\hat{N}_1, \hat{N}_2),\end{aligned}\tag{2.4}$$

*) Cf. also Eqs. (5.35-6).

$$\hat{J} = -J \sum_{kq} (a_{k\uparrow}^+ a_{-k\downarrow}^+ b_{-q\downarrow} b_{q\uparrow} + b_{q\uparrow}^+ b_{-q\downarrow}^+ a_{-k\downarrow} a_{k\uparrow}),$$

$$\hat{L} = \hat{E}_0(N_1, N_2).$$

Here the operator $\hat{E}_0(\hat{N}_1, \hat{N}_2)$ is defined by its matrix elements in the representation in which \hat{N}_1, \hat{N}_2 are diagonal; in this representation \hat{E}_0 is also diagonal with elements equal to the normal-state ground state energy*) of $\hat{H}_0 + \hat{E}_0$ for the values of \hat{N}_1, \hat{N}_2 in question (we note that \hat{H}_0 commutes with \hat{N}_1 and \hat{N}_2 separately), i.e. we have defined \hat{E}_0 so that the normal-state ground state energy of \hat{H}_0 is identically zero for arbitrary values of N_1 and N_2 . In practice (because of the boundary conditions, various residual scattering processes, etc.) the values $N_1^{(0)}, N_2^{(0)}$ of N_1, N_2 in the real groundstate, whether normal or superconducting, of $\hat{H}_0 + \hat{E}_0$ are fixed by the conditions

$$N_1 + N_2 = N = \text{const}, \quad \partial E_0 / \partial N_1 = \partial E_0 / \partial N_2. \tag{2.5}$$

Let us write

$$\hat{N}_1 - \hat{N}_2 - (N_1^{(0)} - N_2^{(0)}) \equiv \hat{K} \tag{2.6}$$

and expand \hat{E}_0 in powers of \hat{K} . For the simplified model considered (here, if desired, we could easily incorporate the effects of ‘Fermi-liquid’ terms) we have

$$\hat{L} \equiv \hat{E}_0(\hat{N}_1, \hat{N}_2) = E_{ng} + \gamma \hat{K}^2, \quad \gamma \equiv \frac{1}{8} (\rho_1^{-1} + \rho_2^{-1}) \tag{2.7}$$

where E_{ng} is the normal groundstate energy of the real physical system, which is fixed by (2.5). It should be noted that in writing (2.7) we have assumed we will eventually consider only states with a fixed value of N ; otherwise we should have had to include terms not only in $(\hat{N} - N_0)^2$ but also in $(\hat{N} - N_0) \hat{K}$.

In Eq. (2.4) the operator \hat{H}_0 commutes, of course, not only with \hat{N} but also with \hat{K} . Moreover, the eigenvalues are by construction independent of \hat{K} (or \hat{N}). (This is strictly true only so long as we can neglect the shift of the limits of integration which is effectively introduced when the Fermi surfaces of the two bands are shifted (cf. (2.3)) and also the fact that the density of states ρ_j may depend on the position of the Fermi surface. We shall assume this to be the case.) Thus, by writing (2.1) in the form (2.4) we have lumped all the dependence of \hat{H} on \hat{K} into the operator \hat{L} .

The Hamiltonian H_0 (Eq. (2.4)) is simply the sum of two commuting BCS-like Hamiltonians referring to the two bands separately, and can be diagonalized by any of the standard methods. Let us restrict ourselves to the subspace spanned by functions of the BCS type:²⁾

$$\Phi(A_1, A_2) = \prod_k [u_k + v_k a_{k\uparrow}^+ a_{-k\downarrow}^+] \prod_q [u'_q + v'_q b_{q\uparrow}^+ b_{-q\downarrow}^+] |\Phi_0\rangle \tag{2.8}$$

*) I.e. the ‘‘ground state energy’’ obtained by ordinary perturbation theory without anomalous pairing.

where $|\Phi_0\rangle$ is the vacuum state and

$$\begin{aligned} |u_k|^2 + |v_k|^2 &= 1, & |u'_q|^2 + |v'_q|^2 &= 1, \\ u_k v_k^* &= \frac{A_1}{2\{(\epsilon_k^{(1)})^2 + |A_1|^2\}^{1/2}}, & u'_q v'_q^* &= \frac{A_2}{2\{(\epsilon_q^{(2)})^2 + |A_2|^2\}^{1/2}}, \end{aligned} \quad (2.9)$$

where A_1, A_2 are complex constants which we allow for the moment to take arbitrary values and the energies are measured from the Fermi energy. In the limit $N \rightarrow \infty$ the functions $\Phi(A_1, A_2)$ defined by (2.8) are effectively orthogonal for different values of the complex parameters A_1, A_2 (that is, the normalization integral becomes δ -function-like). If we define operators

$$\hat{\Psi}_1 \equiv \sum_k a_{k\uparrow}^+ a_{k\downarrow}^+, \quad \hat{\Psi}_2 \equiv \sum_q b_{q\uparrow}^+ b_{q\downarrow}^+ \quad (2.10)$$

(the sum being understood to be limited by the cutoff (2.3)), then within the subspace and in the representation defined by (2.8), $\hat{\Psi}_1$ and $\hat{\Psi}_2$ are diagonal in the limit $N \rightarrow \infty$; their eigenvalues are given by

$$\Psi_j = \frac{1}{2} \rho_j A_j \ln(2\tilde{\omega}/|A_j|) \quad (j=1, 2) \quad (2.11)$$

so that we can equally well label the states (2.8) by their Ψ_j values. The Hamiltonian \hat{H}_0 (Eq. (2.4)) is also diagonal within the representation (2.8) in the appropriate limit; we can write, in fact,

$$\hat{H}_0 = f_1(|\Psi_1|^2) + f_2(|\Psi_2|^2) - V|\Psi_1|^2 - U|\Psi_2|^2, \quad (2.12)$$

where $f_j(|\Psi_j|^2)$ corresponds to the kinetic energy of the electrons in the j -th band. We see, then, that the energy depends only on the magnitudes of Ψ_1 and Ψ_2 and not on their phases, either absolute or relative. Minimization of (2.12) in fact leads to two independent 'one-band' gap equations; in our notation they read simply

$$A_1 = V\Psi_1, \quad A_2 = U\Psi_2. \quad (2.13)$$

(They reduce to the conventional form if we use (2.11).) If we write

$$\Psi_j = |\Psi_j| \exp i\phi_j, \quad (2.14)$$

then within the subspace corresponding to given $|\Psi_1|, |\Psi_2|$ all the wave functions corresponding to different values of the phases ϕ_1 and ϕ_2 separately are degenerate. Since by an appropriate superposition of states with different values of ϕ_j we can construct an eigenfunction of $\hat{N}_j^{(1)}$, we can therefore choose the eigenstates of \hat{H}_0 to be also eigenstates of \hat{N} and/or \hat{K} if we wish.

Now we add to \hat{H}_0 the term \hat{J} (Eq. (2.4)). The resultant Hamiltonian \hat{H} is essentially that used in the previous treatments of two-band superconductors, since in these treatments \hat{E}_0 is implicitly treated as a constant. In the representation (2.8) the extra term can be written

$$J = -J(\Psi_1^* \Psi_2 + \Psi_1 \Psi_2^*) = -2J|\Psi_1||\Psi_2| \cos(\phi_1 - \phi_2) \quad (2.15)$$

and hence the total Hamiltonian becomes

$$\hat{H}' = f_1(|\Psi_1|^2) + f_2(|\Psi_2|^2) - V|\Psi_1|^2 - U|\Psi_2|^2 - 2J|\Psi_1||\Psi_2| \cos(\phi_1 - \phi_2). \quad (2.16)$$

Since this expression depends explicitly on the relative phase of the two 'condensates' ($\phi_1 - \phi_2$), we cannot choose ϕ_1 and ϕ_2 independently in the groundstate. In fact the condition for the energy to have an extremum gives the familiar coupled gap equations^{1),7)}

$$\begin{aligned} \Delta_1 &= V\Psi_1 + J\Psi_2, \\ \Delta_2 &= U\Psi_2 + J\Psi_1. \end{aligned} \quad (2.17)$$

Equations (2.17) always have one nontrivial solution unless $V < 0$, $U < 0$ and $J^2 < UV$.¹²⁾ However, if $V > 0$, $U > 0$, $J^2 < UV$ they have *two* nontrivial solutions, of which one corresponds to the true groundstate and the other to a saddlepoint of the energy. The stable solution must have $\phi_1 = \phi_2$, as is obvious from (2.16) (we recall that J is positive by convention); the unstable one has $\phi_1 - \phi_2 = \pi$. Note that in general the addition of \hat{J} to \hat{H}_0 not only fixes the relative phases but changes the equilibrium values of $|\Psi_j|$ from those given by (2.13). However, if U and V are positive and J is small, the relative change of $|\Psi_j|$ is only of order $(J/UV\rho_1)(\Delta_2/\Delta_1)$, where ρ_1 is the smaller of the densities of states, which in general is associated with the smaller gap. Thus far, our results are in complete agreement with those of previous treatments.

However, we still have to take into account the term \hat{L} of Eq. (2.4). In the general case this leads to a rather complicated problem, which is best handled by field-theoretic methods from the start (see next section); however in the case $U > 0$, $V > 0$, $J \ll UV\rho_1(\Delta_2/\Delta_1)$ we can give a very simple and illuminating treatment. Therefore for the rest of this section we shall consider only this case, which, as will be shown later, is actually quite realistic from a physical point of view.

Going back, then, to Eq. (2.16) we see that under the conditions we have assumed the term in \hat{J} may be treated as a small perturbation on \hat{H}_0 (Eq. (2.12)). Applying first-order perturbation theory and denoting the values of $|\Psi_j|$ obtained from (2.13) by Ψ_j^0 (without the modulus sign), we can therefore approximate (2.16) by

$$\hat{H}' = W_0 + 2J\Psi_1^0\Psi_2^0(1 - \cos(\phi_1 - \phi_2)) \approx W_0 + J\Psi_1^0\Psi_2^0(\phi_1 - \phi_2)^2, \quad (2.18)$$

where W_0 is the true groundstate energy of \hat{H}' and we have expanded the cosine for small values of $\hat{\phi}_1 - \hat{\phi}_2$ (which, we must remember, is an operator in the subspace of interest to us; this latter, within our approximation, is now the subspace corresponding to the minimum value of $|\Psi_j|$ but arbitrary ϕ_j). If now we add the term in \hat{L} (Eq. (2.4)) we can finally write the full Hamiltonian \hat{H} , within the subspace of interest, in the form

$$H = E_{00} + J\Psi_1^0\Psi_2^0(\hat{\phi}_1 - \hat{\phi}_2)^2 + \gamma\hat{K}^2 \quad (E_{00} \equiv W_0 + E_{ng}), \quad (2.19)$$

where $\hat{\phi}_1 - \hat{\phi}_2$ is the operator of the relative phase of the two condensates and \hat{K} the operator of their relative density fluctuation. Let us examine the commutation relation of these two operators. According to the definition (2.10) we have

$$[\hat{N}_i, \hat{\Psi}_j] = 2\delta_{ij}\hat{\Psi}_j \quad (2.20)$$

and hence, using (2.14) and the fact that $|\Psi_j^0|$ is a c -number (equal to Ψ_j^0) in our subspace, we get the 'number-phase uncertainty relation'

$$[\hat{K}, \hat{\phi}_1 - \hat{\phi}_2] = -4i. \quad (2.21)$$

The derivation of (2.21) sketched here is of course far from rigorous. It is by no means obvious *prima facie* either that (2.20) remains true when the intermediate states are restricted to our subspace, or that (2.21) is a necessary as well as sufficient condition for (2.20). Physical arguments can, in fact, be given to support both these assumptions, but since this section is anyway not intended as a rigorous demonstration we shall not pause to do so here.

Equations (2.19) and (2.21) simply define the problem of the simple harmonic oscillator. The frequency of the characteristic vibration is

$$\omega_0 = 8(\gamma J\Psi_1^0\Psi_2^0)^{1/2} \quad (2.22)$$

or, using the values of Ψ_j^0 given by (2.13) and the definition of γ (Eq. (2.7)),

$$\omega_0 = 4\left\{\frac{1}{2}(\rho_1^{-1} + \rho_2^{-1})(J/UV)A_1A_2\right\}^{1/2}. \quad (2.23)$$

In practice it is very likely⁴⁾ that $\rho_1 \ll \rho_2$, $A_1 \ll A_2$. Then the ratio of ω_0 to the smaller threshold for single-particle excitations $2A_1$ is given by

$$(\omega_0/2A_1)^2 = \frac{2J(A_2/A_1)}{\rho_1UV} \equiv \alpha'. \quad (2.24)$$

A realistic value of α' is probably of order 0.5 (see § 4). Thus the collective excitation is well separated from the single-particle threshold. Strictly speaking, for such a value of α' the derivation used above is invalid, but we shall see in § 4 that the error involved is not great.

Thus, in the limit $k=0$ there exists in the two-band system a collective oscillation corresponding to small fluctuations of the relative phase (or relative density) of the two condensates. In the limit $N \rightarrow \infty$, $V \rightarrow \infty$, $N/V = \text{const}$, the zero-point root-mean-square fluctuation of the relative phase decreases as $N^{-1/2}$ while that of the relative number increases as $N^{1/2}$; the zero-point energy of the oscillation remains constant in this limit. Thus the conventional results for the groundstate and one-particle excitation spectrum are not modified.

It may be asked whether the frequency ω_0 given by (2.23) is in fact the correct limit of $\omega(k)$ as $k \rightarrow 0$ (clearly we expect the collective excitation to exist also for long but finite wavelengths). The question arises because in setting

up the problem we assumed $N = \text{const}$; this is of course strictly true for $k = 0$ for a closed system, but for arbitrarily long but finite wavelengths fluctuations of the total density are possible and it might be thought they would affect the results (since in general the Hamiltonian contains a cross-term $\hat{N}\hat{K}$). Actually, in a real metal this problem does not arise, because the Coulomb forces screen out fluctuations of the total density perfectly in the limit $k \rightarrow 0$. However, it is also not difficult to show that even in a neutral system (2.23) is the correct limit of $\omega(k)$ as $k \rightarrow 0$; in this limit the problem is completely analogous to that of a harmonic oscillator of finite mass coupled to another whose mass tends to infinity.

The validity of the above treatment is limited by the assumption that the weak interband coupling is a small perturbation on a superconducting state already established by the stronger intra-band forces, and is also restricted to the limit $k = 0$. In the next section we remove these restrictions by a more general field-theoretic approach.

§ 3. Field-theoretic discussion

We shall look for the collective oscillation by investigating the poles of the scattering amplitude for two particles of nearly opposite momentum. We start with the case of a neutral system; then we may neglect the coupling of two-particle states to particle-hole states (this is equivalent to neglecting the Fermi-liquid terms). If the two particles are initially in (say) the first band they may as a result of the scattering either both remain in the first band or both be transferred to the second band; for small total momentum there are no processes in which the two particles end up in different bands.⁸⁾ Thus, provided we are going to be interested only in the even harmonics of the scattering amplitude, the relevant equations may be written in the form (cf. references 13) and 14))

$$\Gamma_{\alpha\beta} = \Gamma_{\alpha\beta}^{\phi} + \frac{1}{2} \Gamma_{\alpha\gamma}^{\phi} (-GG^{-} - FF)_{\gamma} \Gamma_{\gamma\beta}. \tag{3.1}$$

Here α, β may take the values 1 or 2 (corresponding to the two bands); summation over repeated indices is implied. $\Gamma_{\alpha\beta}$ is the complete amplitude for the process in which a pair in band α is transferred to band β , and $\Gamma_{\alpha\beta}^{\phi}$ is the corresponding irreducible amplitude, in the usual terminology. We introduce the factor $1/2$ so that the sum implicit in (3.1) may be taken to include a sum over spins—a convention we shall use consistently throughout this section. Thus, Eq. (3.1) written out explicitly is

$$\begin{aligned} \Gamma_{\alpha\beta}(\mathbf{p}\mathbf{p}' : \mathbf{k}\omega) &= \Gamma_{\alpha\beta}^{\phi}(\mathbf{p}\mathbf{p}' : \mathbf{k}\omega) - \frac{1}{2} \sum_{\gamma} \sum_{\mathbf{p}''} \sum_{\sigma''} \int \frac{d\varepsilon''}{2\pi i} \Gamma_{\alpha\gamma}^{\phi}(\mathbf{p}\mathbf{p}'' : \mathbf{k}\omega) \\ &\times \{G_{\gamma}(-\mathbf{p}'' + \mathbf{k}/2, -\varepsilon'' + \omega/2) G_{\gamma}(\mathbf{p}'' + \mathbf{k}/2, \varepsilon'' + \omega/2) \\ &+ F_{\gamma}(-\mathbf{p}'' + \mathbf{k}/2, -\varepsilon'' + \omega/2) F_{\gamma}(\mathbf{p}'' + \mathbf{k}/2, \varepsilon'' + \omega/2)\} \times \Gamma_{\gamma\beta}(\mathbf{p}''\mathbf{p}' : \mathbf{k}\omega), \end{aligned} \tag{3.2}$$

where to simplify the notation we have already assumed that Γ^ϕ and Γ do not depend on the energies ε and ε' analogous to \mathbf{p} and \mathbf{p}' . In Eq. (3.1) the notation is the standard one, i.e. (3.1) is the Bethe-Salpeter equation for scattering of two particles of nearly opposite momenta $\mathbf{p} + \mathbf{k}/2$, $-\mathbf{p} + \mathbf{k}/2$ (and energies $\varepsilon + \omega/2$, $-\varepsilon + \omega/2$) to states $\mathbf{p}' + \mathbf{k}/2$, $-\mathbf{p}' + \mathbf{k}/2$. If we confine ourselves to the simple BCS-type theory of the last section, we must make the identifications

$$\begin{aligned} \Gamma_{11}^\phi(\mathbf{p}\mathbf{p}' : \mathbf{k}\omega) &= \text{const} = -V, \\ \Gamma_{22}^\phi(\mathbf{p}\mathbf{p}' : \mathbf{k}\omega) &= \text{const} = -U, \\ \Gamma_{12}^\phi(\mathbf{p}\mathbf{p}' : \mathbf{k}\omega) &= \Gamma_{21}^\phi(\mathbf{p}\mathbf{p}' : \mathbf{k}\omega) = \text{const} = -J. \end{aligned} \quad (3.3)$$

If we substitute the forms of G and F appropriate to the superfluid phase, the integrals over ε'' and \mathbf{p}'' are easily carried out;¹³⁾ we can then write Eq. (3.1) explicitly in the form

$$\begin{aligned} \Gamma_{11} &= -V + V\xi_1\Gamma_{11} + J\xi_2\Gamma_{21} \\ \Gamma_{21} &= -J + J\xi_1\Gamma_{11} + U\xi_2\Gamma_{21} \end{aligned} \quad (3.4)$$

(and similar equations for Γ_{12} , Γ_{22}), where

$$\begin{aligned} \xi_j(k, \omega) &\equiv \frac{1}{2} \rho_j \ln(2\tilde{\omega}/|A_j|) + \theta_j(k, \omega) \\ \theta_j(k, \omega) &\equiv \frac{1}{2} \rho_j \int \frac{d\Omega}{4\pi} \frac{\beta_j \arcsin \beta_j}{(1 - \beta_j^2)^{1/2}}, \quad \beta_j(\mathbf{k}, \omega) \equiv \frac{\omega^2 - (\mathbf{k} \cdot \mathbf{v}_j)^2}{4|A_j|^2}, \end{aligned} \quad (3.5)$$

where v_j is the Fermi velocity in the j -th band. The vertex parts therefore have a pole when

$$\begin{aligned} (1 - V\xi_1)\Gamma_{11} - J\xi_2\Gamma_{21} &= 0, \\ -J\xi_1\Gamma_{11} + (1 - U\xi_2)\Gamma_{21} &= 0 \end{aligned} \quad (3.6)$$

or

$$(1 - V\xi_1)(1 - U\xi_2) - J^2\xi_1\xi_2 = 0. \quad (3.7)$$

Before proceeding, we emphasize once again that (3.7) is a correct description of the exciton mode we are looking for only for a neutral system (and in the limit that 'Fermi-liquid' terms may be neglected). For a charged system Eqs. (3.1) and hence (3.7) must be generalized; see below. However, we investigate the formally simpler neutral case first to bring out the main features of the problem.

Equations (3.6) always have a solution for $k = \omega = 0$ (when $\theta_j = 0$). With the convention, which we continue to use in this section, that J is positive, this solution gives the same sign for Γ_{11} and Γ_{21} ; it is in fact just equivalent to the gap equations (2.17). Correspondingly, there will always be a solution for small k and ω , with ω proportional to k ; this is just the Bogolyubov-Anderson

mode corresponding to a fluctuation of the total density. However, under certain conditions there will also be a second solution, in which Γ_{11} and Γ_{21} have opposite signs; at sufficiently long wavelengths this solution corresponds to a fluctuation of the relative density in the two bands, i.e. to the collective excitation we are looking for.

To see this, we subtract from (3.7) its value for $k=\omega=0$, i.e. the determinantal equation of the gap equations (2.17). This gives

$$\begin{aligned} & \{V + (J^2 - UV)^{\frac{1}{2}} \rho_2 \ln(2\tilde{\omega}/|A_2|)\} \theta_1(k, \omega) \\ & + \{U + (J^2 - UV)^{\frac{1}{2}} \rho_1 \ln(2\tilde{\omega}/|A_1|)\} \theta_2(k, \omega) \\ & + (J^2 - UV) \theta_1(k, \omega) \theta_2(k, \omega) = 0. \end{aligned} \quad (3.8)$$

Substituting (2.12) and using the gap equations (2.17), we can reduce (3.8) to the form

$$(A_1/A_2) \theta_1(k, \omega) + (A_2/A_1) \theta_2(k, \omega) + J^{-1}(J^2 - UV) \theta_1(k, \omega) \theta_2(k, \omega) = 0 \quad (3.9)$$

with $\theta_j(k, \omega)$ given by (3.5).

The solution of (3.9) in the general case requires rather tedious calculations, in view of the complicated form of $\theta_j(k, \omega)$. Here we shall examine some limiting cases of physical interest. First, let us examine the (improbable) case of complete symmetry between the two bands, i.e. $\rho_1 = \rho_2$, $v_1 = v_2$, $V = U$. We recall that while J is positive by definition, U may be positive or negative. Then we have $A_1 = A_2 = A$, $\theta_1 = \theta_2 = \theta$; if we neglect the solution $\theta(k, \omega) = 0$ which corresponds to the Bogolyubov-Anderson mode, (3.9) reduces to

$$\theta(k, \omega) = \frac{2J}{U^2 - J^2}, \quad (3.10)$$

where

$$\theta(k, \omega) = \frac{1}{2} \rho \int \frac{d\Omega}{4\pi} \frac{\beta \arcsin \beta}{(1 - \beta^2)^{1/2}}, \quad \beta^2 = \frac{\omega^2 - (\mathbf{k} \cdot \mathbf{v})^2}{4A^2}. \quad (3.10a)$$

In the limit $k=0$ the function $\theta(k, \omega)$ is proportional to $(\omega^2/4A^2)$ for small ω and tends to infinity as $\omega \rightarrow 2A$. For $\omega > 2A$ it becomes imaginary, indicating the possibility of real processes in which two quasiparticles are excited. We see that a collective mode can exist only if $U^2 > J^2$. If U were negative, such a condition would mean that the superconducting state could not exist,¹²⁾ while if U is positive, it is just the necessary and sufficient condition for the existence of a second nontrivial solution to the gap equations (2.17). Indeed, the situation is entirely analogous to that encountered in the theory of excitons in a one-band superconductor. We can see this more clearly if we rewrite (3.10) in the form

$$\theta(k, \omega) = \frac{1}{U - J} - \frac{1}{U + J}.$$

In corresponding notation the equation determining the frequencies of the $l \neq 0$ excitons in a one-band superconductor in the approximation of no Fermi-liquid interactions is⁶⁾ (in the limit $k \rightarrow 0$)

$$\theta(k, \omega) = \frac{1}{V_l} - \frac{1}{V_0}, \quad (3.11)$$

where V_0 is the S -wave part of the pairing interaction which binds the true ground state and V_l is the appropriate higher harmonic of the interaction. The analogy is further discussed in § 5. It is not difficult to see from (3.9) that these qualitative considerations hold under general conditions; the general necessary and sufficient condition for the existence of a collective excitation is

$$U, V > 0, \quad J^2 < UV \quad (3.12)$$

which again is just the condition for the gap equations to have an unstable solution.*)

Next we consider the case discussed in the last section, where $\rho_1 \neq \rho_2$, $U \neq V$, etc., but where $U, V > 0$ and $J \ll UV\rho_1(\Delta_1/\Delta_2)$ (we again assume by convention that ρ_1 is the smaller density of states; then usually Δ_1 will be the smaller of the gaps). In this case we may look for a solution of (3.9) with $\omega, v_j k \ll \Delta_1$. Expanding $\theta_j(k, \omega)$ in powers of ω^2 and k^2 , we have

$$\theta_j(k, \omega) = \frac{1}{2} \rho_j (\omega^2 - \frac{1}{3} k^2 v_j^2) / 4\Delta_j^2 + \dots, \quad (3.13)$$

whence (3.9) can be written

$$\begin{aligned} \rho_1 (\omega^2 - \frac{1}{3} k^2 v_1^2) + \rho_2 (\omega^2 - \frac{1}{3} k^2 v_2^2) \\ - Q (\omega^2 - \frac{1}{3} k^2 v_1^2) (\omega^2 - \frac{1}{3} k^2 v_2^2) = 0, \end{aligned} \quad (3.14)$$

where

$$Q \equiv \rho_1 \rho_2 (UV - J^2) / 8J\Delta_1\Delta_2. \quad (3.15)$$

Equation (3.14) is valid to zeroth order in $\omega/\Delta_1, vk/\Delta_1$ but to all orders in $\omega/\omega_0, vk/\omega_0$ (this makes sense because under the conditions assumed here $\omega_0 \ll \Delta_1$). (ω_0 is defined below.)

Equation (3.14) has the general solution

$$\begin{aligned} \omega^2 = \frac{1}{2} \left\{ \omega_0^2 + (c_1^2 + c_2^2) k^2 \right. \\ \left. \pm \left[\omega_0^4 + (c_1^2 - c_2^2)^2 k^4 - 2\omega_0^2 \left(\frac{\rho_1 - \rho_2}{\rho_1 + \rho_2} \right) (c_1^2 - c_2^2) k^2 \right]^{1/2} \right\}, \end{aligned} \quad (3.16)$$

where

$$\omega_0^2 \equiv Q^{-1} (\rho_1 + \rho_2) \equiv 8 (\rho_1 + \rho_2) J\Delta_1\Delta_2 / \rho_1 \rho_2 (UV - J^2) \quad (3.17)$$

*) However, the significance of this coincidence should not be overstressed. It appears to fail when 'Fermi-liquid' terms are present.

and for brevity we have written $\frac{1}{3} v_j^2 = c_j^2$.

We see that in the limit $k \rightarrow 0$ ($v_j k \ll \omega_0$) one branch of (3.16) has the sound-wave-like dispersion relation

$$\omega^2 = c^2 k^2, \quad c^2 = (\rho_1 c_1^2 + \rho_2 c_2^2) / (\rho_1 + \rho_2), \quad (3.18)$$

while the other is of exciton type:

$$\omega^2 = \omega_0^2 + v^2 k^2, \quad v^2 = (\rho_1 c_2^2 + \rho_2 c_1^2) / (\rho_1 + \rho_2). \quad (3.19)$$

In the limit $k \rightarrow \infty$ (i.e. for our purposes, $\omega_0 \ll v_j k \ll 2\Delta_1$, in the unlikely case that such a criterion can be satisfied for both v_j simultaneously), the first and second solutions go over respectively into

$$\omega^2 = c_2^2 k^2, \quad \omega^2 = c_1^2 k^2, \quad (3.20)$$

where we have assumed that $c_1 > c_2$.

Equations (3.18)–(3.20) are easily interpreted if we regard the two ‘condensates’ as perfect hydrodynamic liquids; this is discussed in § 5. Since we have always been working in the weak-coupling approximation and have already assumed $J \ll UV\rho_1(\Delta_1/\Delta_2)$, we should neglect J^2 in comparison to UV in (3.17). Thus the result (3.19) agrees with (2.23) of the last section.

Let us now consider the case of a real superconductor, where the Coulomb field prevents long-range oscillations of the total density at low energies. To apply the field-theoretic technique to this case it is necessary to generalize it so as to include the coupling between two-particle states and particle-hole states. Such a generalization has been developed by a number of authors; here we follow the notation of reference 14). Consider first the one-band case. In the formalism of reference 14), we are interested in the low-energy poles of the matrix $1 - \hat{\Gamma}^\circ \hat{g}$, where $\hat{\Gamma}^\circ$ and \hat{g} are given explicitly by Eqs. (13) and (12) of reference 14) respectively; $\hat{\Gamma}^\circ$ is a matrix describing the irreducible particle-particle (pairing) and particle-hole scattering amplitudes and \hat{g} a matrix describing the various possible combinations of G and F functions. We must now take the particle-hole irreducible scattering amplitude to be the Coulomb potential:

$$\Gamma^\circ = 4\pi e^2 / k^2. \quad (3.21)$$

For simplicity we neglect, as usual, any short-range (‘Fermi-liquid’) terms. This means that $\Gamma^\circ(\mathbf{p}, \mathbf{p}')$ is isotropic on the Fermi surface. Since we have already taken $\Gamma^\phi(\mathbf{p}, \mathbf{p}')$ to be isotropic, and since the quantities $(G^-F - FG)$ (k, ω) and $(G^-G^- - GG)$ (k, ω) which enter into Eq. (12) of reference 14) are odd with respect to k , they vanish on integration over the Fermi surface and the third row and column of the matrix \hat{g} may be ignored. For the same reason we may write $\frac{1}{2}(GG + G^-G^-)$ as simply GG . Thus we are left with the following two equations, where Γ as before represents the two-particle scattering amplitude and Z the amplitude for two particles to be converted into a particle-

hole pair :*)

$$\begin{aligned} \Gamma &= \Gamma^\phi + \frac{1}{2} \Gamma^\phi \{(-GG^- - FF)\Gamma + (G^-F + FG)Z\}, \\ Z &= \Gamma^\omega \{(GG^- - FF)Z + (G^-F + FG)\}. \end{aligned} \quad (3.22)$$

The problem is therefore determined by a knowledge of the quantities

$$\begin{aligned} \frac{1}{2}(-GG^- - FF)(k\omega) &\equiv -\xi(k\omega), & (\text{cf. (3.5)}) \\ 2^{-1/2}(G^-F + FG)(k\omega) &\equiv \phi(k\omega), & (3.23) \\ (GG^- - FF)(k\omega) &\equiv \psi(k\omega). \end{aligned}$$

(The peculiar-looking factor of $2^{-1/2}$ is due to our convention that all integrals include a spin sum; cf. the remark on Eq. (3.1)). It is easy to see that if Γ^ω has the form (3.21), the condition for the existence of a low-energy collective oscillation is

$$1 + \Gamma^\phi \{\xi(k\omega) + [\psi(k\omega)]^{-1}[\phi(k\omega)]^2\} = 0 \quad (3.24)$$

or using the gap equation,

$$\phi(k\omega)\theta(k\omega) + \{\phi(k\omega)\}^2 = 0 \quad (3.25)$$

with $\theta(k\omega)$ given by (3.10). However, (3.25) has no solution, at least for small k and ω , and hence in the simple one-band model considered no low-energy collective oscillation is possible.**)

Turning now to the two-band case, we easily see that Eqs. (3.22) are still valid provided that we regard Γ , Γ^ϕ , Z and Γ^ω as matrices in the 'space' of the two bands and $(-GG^- - FF)$, etc., as diagonal matrices in this space (cf. Eq. (3.1)). Explicitly, we have

$$\begin{aligned} \Gamma^\phi &= -\begin{pmatrix} V & J \\ J & U \end{pmatrix}, & \Gamma^\omega &= 4\pi e^2/k^2 \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} & (3.26) \\ \xi &= \begin{pmatrix} \xi_1 & 0 \\ 0 & \xi_2 \end{pmatrix}, & \xi_j &= (-GG^- - FF)_j \end{aligned}$$

and similar definitions for ϕ and ψ . Substituting the second of Eqs. (3.22) and dropping the inhomogeneous term, we get the matrix equation

$$\Gamma = \Gamma^\phi \{-\xi + \phi(1 - \Gamma^\omega \phi)^{-1} \Gamma^\omega \phi\} \Gamma \quad (3.27)$$

which determines the frequency of the collective excitation for our model two-

*) In reference 14) the factor $\frac{1}{2}$ was omitted in the first line. This is simply equivalent to a redefinition of Γ^ϕ , which does not appear in the final results of that reference.

**) It is claimed by Thouless and Tilley¹⁵⁾ that Eq. (3.25) does have a solution for small k and $\omega \sim vk$ if the finite-temperature forms of θ , ϕ , ψ are substituted, and they interpret this as representing a sort of collisionless second sound wave. I believe however their results to be incorrect, owing among other things to their neglect of the imaginary parts of θ , ϕ and ψ .

band system.

Consider the matrix $(1 - \Gamma^o \phi)^{-1} \Gamma^o$, where Γ^o is given by (3.26). Even in the limit $k^2 v_j^2 \ll \omega_p^2$ (i.e. $\Gamma^o \phi \gg 1$) we cannot immediately put this equal to $-\phi^{-1}$, because the matrix Γ^o is singular. In fact, calculating the matrix for finite k and taking the limit $k \rightarrow 0$, we find that in this limit we must put

$$(1 - \Gamma^o \phi)^{-1} \Gamma^o = -(\psi_1 + \psi_2)^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}. \tag{3.28}$$

Substituting (3.20) into (3.27), we find that the frequency of the collective oscillation is determined by the equation

$$\det(1 + \Gamma^o C) = 0 \tag{3.29}$$

where the matrix C is defined by

$$C_{ij} = \xi_i \delta_{ij} + (\psi_1 + \psi_2)^{-1} \phi_i \phi_j. \tag{3.30}$$

Explicitly, (3.29) reads

$$1 - \{VC_{11} + UC_{22} + 2JC_{12}\} + (UV - J^2)(C_{11}C_{22} - C_{12}C_{21}) = 0. \tag{3.31}$$

Writing

$$\tilde{C}_{ij} = \theta_i(k\omega) \delta_{ij} + \{\psi_1(k\omega) + \psi_2(k\omega)\}^{-1} \phi_i(k\omega) \phi_j(k\omega) \tag{3.32}$$

(where $\theta_i(k\omega)$ is defined by (3.5)), and subtracting the gap equation, we can put (3.31) in the form

$$\begin{aligned} & \{V + (J^2 - UV) \frac{1}{2} \rho_2 \ln(2\tilde{\omega}/|A_2|)\} \tilde{C}_{11} + \{U + (J^2 - UV) \frac{1}{2} \rho_1 \ln(2\tilde{\omega}/|A_1|)\} \tilde{C}_{22} \\ & + 2J\tilde{C}_{12} - (UV - J^2)(\tilde{C}_{11}\tilde{C}_{22} - \tilde{C}_{12}\tilde{C}_{21}) = 0 \end{aligned} \tag{3.33}$$

which is the appropriate generalization of Eq. (3.8). Proceeding as with (3.8), we can write (3.33) in the form

$$(A_1/A_2) \tilde{C}_{11} + (A_2/A_1) \tilde{C}_{22} + J^{-1}(J^2 - UV)(\tilde{C}_{11}\tilde{C}_{22} - \tilde{C}_{12}\tilde{C}_{21}) = 0 \tag{3.34}$$

with \tilde{C}_{ij} given by (3.32). As with (3.9), the solution is complicated in the general case; again we shall consider some simple limiting cases.

First, consider the case of complete symmetry between the two bands. Then $\phi_1 \equiv \phi_2 \equiv \phi$, etc., and (3.34) reduces to

$$(\theta + \phi^2/\psi) - \frac{1}{2} J^{-1}(U^2 - J^2) \{\theta + \phi^2/2\psi\} - (\phi^2/2\psi)^2 = 0. \tag{3.35}$$

The factor $(\theta + \phi^2/\psi)$ (which cannot be zero) cancels and we are left with

$$\theta(k\omega) = 2J/(U^2 - J^2) \tag{3.36}$$

which is identical to (3.10). Hence in the special case of complete symmetry between the bands the Coulomb interaction has no effect whatever on the collective oscillation of interest to us. This is not difficult to understand physically, since in this case the Hamiltonian splits into two commuting terms referring

respectively to the total and relative density.

Next we consider the case $J \ll UV\rho_1(\Delta_1/\Delta_2)$ and expand the \tilde{C}_{ij} to lowest order in k^2 and ω^2 . We have (cf. reference 14))

$$\begin{aligned}\psi_j &= -\rho_j, & \phi_j^2 &= \frac{1}{2}(\omega/2\Delta_j)^2\rho_j^2, \\ \theta_j &= \frac{1}{2}\{(\omega^2 - \frac{1}{3}v_j^2k^2)/4\Delta_j^2\}\rho_j.\end{aligned}\quad (3.37)$$

Substituting these values, we get

$$\begin{aligned}(\Delta_1/\Delta_2)\tilde{C}_{11} + (\Delta_2/\Delta_1)\tilde{C}_{22} + 2\tilde{C}_{12} &= -(8\Delta_1\Delta_2)^{-1}(\rho_1c_1^2 + \rho_2c_2^2)k^2, \\ \tilde{C}_{11}\tilde{C}_{22} - \tilde{C}_{12}\tilde{C}_{21} &= \frac{\rho_1\rho_2}{(8\Delta_1\Delta_2)^2(\rho_1 + \rho_2)} \left\{ (\rho_1 + \rho_2)c_1^2c_2^2k^4 - (\rho_1c_1^2 + \rho_2c_2^2)k^2\omega^2 \right\},\end{aligned}\quad (3.38)$$

where again $c_j^2 \equiv \frac{1}{3}v_j^2$. Finally, substituting (3.38) into (3.34), we get

$$\begin{aligned}\omega^2 &= \omega_0^2 + v^2k^2, \\ \omega_0^2 &= \frac{8J\Delta_1\Delta_2(\rho_1 + \rho_2)}{\rho_1\rho_2(UV - J^2)}, \\ v^2 &= \frac{(\rho_1 + \rho_2)c_1^2c_2^2}{\rho_1c_1^2 + \rho_2c_2^2}.\end{aligned}\quad (3.39)$$

Equation (3.39) is valid in the whole region $vk \ll 2\Delta_1$.*) Comparing it with (3.19) and (3.20), we see that the infinite-wavelength limit ω_0 is insensitive to the Coulomb interaction but the dispersion relation is affected. The velocity v given by (3.39) is in fact just the velocity of 'quasi-hydrodynamic' sound in a system of two perfect classical liquids coupled only by the Coulomb force (see § 5).

Finally let us examine the physically very important case where we have $\rho_1 \ll \rho_2$ but not necessarily $J \ll UV\rho_1(\Delta_1/\Delta_2)$. Let us consider explicitly the neutral case, take the limit $k \rightarrow 0$ and assume for the moment that ω_0 will still be sufficiently far from $2\Delta_1$ that the function $\theta_1(k, \omega)$ (Eq. (3.10a)) is still only of order of magnitude ρ_1 . Then we may neglect the term $(\Delta_1/\Delta_2)\theta_1(k\omega)$ in (3.9), which therefore becomes

$$\theta_1(k\omega) = J(\Delta_2/\Delta_1)/(UV - J^2). \quad (3.40)$$

Thus, using Eq. (3.10a), we finally get as the equation determining ω_0

$$\begin{aligned}\omega_0^2 f(\omega_0/2\Delta_1) &= 8J\Delta_1\Delta_2/\rho_1(UV - J^2), \\ f(x) &\equiv \arcsin x/x(1-x^2)^{1/2}\end{aligned}\quad (3.41)$$

which agrees with (3.17) in the limit $\omega_0 \rightarrow 0$. We will assume without detailed calculation, on the basis of the physical argument given at the end of the last

*) Even if $v_1k \gg 2\Delta_1$. See § 5.

section, that this formula remains valid in the presence of Coulomb interactions. It is clear from a comparison of (3.41) and (3.39) that the latter expression for ω_0 is a good approximation up to quite large values of $\omega_0/2\Delta_1$. Similarly it can be seen by detailed consideration of the exact expressions for θ , ϕ and ψ (Eqs. (3.23); cf. reference 9)) that the velocity given by (3.39) is at least of the right order of magnitude until ω_0 (or vk) is very close to $2\Delta_1$. For purposes of estimation in the next section we shall therefore usually use Eq. (3.39).

To conclude this section we briefly mention the behaviour of the collective mode at finite temperature. The necessary generalization simply consists in using the appropriate finite-temperature forms of the functions θ , ϕ and ψ ; in the long-wavelength and low-frequency limit these were calculated in reference 14). In general they have finite imaginary parts even in this limit, owing to the possibility of scattering an already excited quasiparticle; however, since the maximum velocity of the quasiparticles is the higher Fermi velocity v_1 , the collective mode will not be damped in the long-wavelength region where $\omega(k) > kv_1$. Detailed examination shows that ω_0 increases relative to Δ_1 with increasing T ; at first sight we should expect the oscillation to disappear altogether at temperatures of the order of $\Delta_1(0)$, since at much higher temperatures the gap equations have only a single nontrivial solution. However, detailed examination of the one-band case shows that at finite temperature the existence of a second solution is not a necessary condition for the existence of the corresponding exciton even in the simplified model considered here; thus we can draw no conclusion without explicit calculation.

§ 4. Experimental aspects

In this section we shall, first, try to estimate the parameters of the collective excitation for niobium, the only transition metal superconductor for which sufficient experimental information is available at present, and then go on to discuss the general question of the feasibility of its experimental detection. It should be stated at once that the answer to this question is rather sensitive to the values of certain parameters of which at present we have only rather crude estimates; thus the conclusions must be regarded as somewhat tentative.

Let us label the 's'-band (that is, the band with the lower density of states) 1, as in the last section; in practice this band will almost certainly also have the smaller gap, and probably though not certainly also the higher Fermi velocity. We suppose, as is almost certainly the case in practice, that $\rho_1 \ll \rho_2$. Then the parameter ω_0 is given by (3.41):

$$(\omega_0/2\Delta_1)^2 f(\omega_0/2\Delta_1) = \frac{2J(\Delta_2/\Delta_1)}{\rho_1(UV - J^2)} \equiv \alpha. \quad (4.1)$$

Since the condition $J^2 \ll UV$ is almost certainly fulfilled in practice,^{4),7)} α is equivalent to the parameter α' defined in (2.24). Moreover, it is identical to

the parameter α defined by Sung and Shen;^{4),*)} they show that its value can be obtained from the specific heat data and find that for niobium the best fit corresponds to $\alpha=0.5$. We should remark that Sung and Shen's method of obtaining α is certainly not valid in general, since they tacitly assume in proceeding from their Eq. (4) to Eq. (8) that the temperature variation of the larger gap can be neglected in the region where the smaller gap is fast varying (which they use to fit the data to the theory). It seems probable that this assumption is justified for Nb, but it would be desirable to check the value of α , which is a fundamental parameter of the theory, by fitting the exact theoretical specific-heat curve to the data without approximations (unfortunately this requires the numerical solution of two rather unpleasant simultaneous equations). For present purposes we shall use Sung and Shen's value of α with appropriate reservations. Putting this value into (4.1), we find

$$(\omega_0/2\Delta_1) \sim 0.6. \quad (4.2)$$

Thus, in niobium the collective excitation should be well separated from the two-particle threshold. It is reasonable to hope that in some other transition metals α will be smaller and the excitation may even lie near the bottom of the smaller gap. We notice, in any case, that even for the comparatively large value of ω_0 given by (4.2) Eq. (3.39) is not a bad approximation. Hence we shall generally use (3.39) rather than (4.1) in this section.

Equally important to ω_0 from the point of view of experimental detection is the velocity v of the excitation, which is given by (3.29). We see that v is of the order of the *smaller* of the quantities v_1 , $(\rho_2/\rho_1)^{1/2}v_2$:

$$v \sim \min(v_1, (\rho_2/\rho_1)^{1/2}v_2). \quad (4.3)$$

Unfortunately experimental information on the values of v_1 and v_2 for the transition metals seems to be rather scanty at present. To get an order-of-magnitude estimate we may assume with Vasudevan and Sung⁵⁾ that the Fermi momenta in the two bands are of the same order of magnitude. In this case $\rho_2/\rho_1 \sim v_1/v_2$, so we have

$$v \sim (v_1v_2)^{1/2} \sim 0.1v_1. \quad (4.4)$$

This estimate should however be treated with a certain amount of reserve; if anything it will probably underestimate v relative to v_1 .

Turning now to the problem of experimental detection, we consider first the thermodynamic consequences of our collective mode. We use the dispersion relation (3.39):**)

*) The equation defining α in reference 4) is presumably misprinted and should read

$$\alpha = -[\Delta_d(0)/\Delta_s(0)] \times J/N_s(J_s J_d - J^2).$$

We recall that our ρ_1 is twice N_s and our J has the opposite sign by convention.

***) The temperature dependence of ω_0 and v is sufficiently weak to be neglected for $k_B T \ll \Delta_1$.

$$\omega^2 = \omega_0^2 + v^2 k^2 \quad (4.5)$$

which is valid for $vk \ll 2\Delta_1$; we therefore confine our attention to the region $k_B T \ll \Delta_1$. We shall assume (hopefully) that there are transition metal superconductors for which $\omega_0 \ll \Delta_1$ ($\alpha \ll 1$), and thus consider both the regions $k_B T \ll \omega_0$ and $\omega_0 \ll k_B T \ll \Delta_1$. The specific heat due to a boson with the dispersion relation (4.5) is easily calculated in these limits; for $k_B T \ll \omega_0$ we have (here and below C_1 , C_2 and C_3 are constants of order unity)

$$C(T) = C_1 \left(\frac{\omega_0}{v} \right)^3 \left(\frac{\omega_0}{k_B T} \right) \exp(-\omega_0/k_B T) \quad (4.6)$$

while for $k_B T \gg \omega_0$,

$$C(T) = C_2 \left(\frac{\omega_0}{v} \right)^3 \left(\frac{k_B T}{\omega_0} \right)^3. \quad (4.7)$$

On the other hand, for $k_B T \ll \Delta_1$ the specific heat due to the quasi-particle excitations is

$$C_{qp}(T) = C_3 \Delta_1 \rho_1 \left(\frac{\Delta_1}{k_B T} \right)^{3/2} \exp(-\Delta_1/k_B T). \quad (4.8)$$

Then (since for purposes of estimation ω_0 , $k_B T$ and Δ_1 may be taken as of the same order) the characteristic factor occurring in the ratio of the boson and the s -electron specific heats is just $(\Delta_1^2/v_1^3 \rho_1) (v_1/v)^3$. The first factor is probably of order $10^{-7} - 10^{-8}$; thus, if we use the estimate (4.4), to detect the effect of the collective mode on the specific heat we should have to be able to measure quantities of the order of $10^{-4} - 10^{-5}$ of the s -electron specific heat in the normal state. This is certainly beyond the reach of present experimental technique, but not unthinkably so. It should be emphasized that if $\omega_0 < \Delta_1$, which requires a value of α only slightly smaller than that found for niobium, the collective mode will dominate the electronic specific heat at ultra-low temperatures—a situation which is very unlikely to occur in ordinary one-band superconductors since in them ω_0 is expected to be close to 2Δ . We see however that the above estimates are very sensitive to the value of v .

Next we consider the possibility of exciting the resonance by an external probe. We see at once that no external potential which varies over a distance large compared to the lattice spacing will be able to excite it. This is because such a potential cannot 'see' which are the s -electrons and which the d -electrons; mathematically speaking, the matrix element of the total electron density Fourier transform

$$\rho(\mathbf{k}) = \int \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}$$

to which an external scalar potential couples, is identical in the limit of small k to the Fourier transform of the sum of the 'Bloch wave densities' in the two

bands (i.e. what we have been referring to throughout this paper as the total density operator); thus it cannot involve the relative density. This would not matter in a neutral system, since the relative and total densities are not decoupled for $\nu k \sim \omega_0$ and a fluctuation of the total density would excite a fluctuation of the relative density; however in a real metal the total-density response is strongly screened out at long wavelengths and thus to excite a fluctuation of the relative density one must couple to it directly. So far, we have considered an isotropic model; however, for a crystal with arbitrary symmetry and for an arbitrary direction of wave propagation, the transverse total current will in general couple to the longitudinal 'relative' current and hence to the relative density. Thus, in principle a pole corresponding to our collective excitation should appear in the transverse current response function, and one could then in principle detect it by electromagnetic absorption or transmission experiments (cf. reference 9)). Since this effect is likely to be small and there are a large number of theoretical and experimental complications, we have not attempted to make a detailed estimate; but it should be noted that in any case this pole will not appear until $\nu k \sim \omega_0$ (for reasons connected with the fact that the relative density does not obey a continuity equation—see next section), and this alone may well put electromagnetic detection out of the question. We conclude therefore that no external probe of long wavelength is likely to be able to detect the excitation.

Therefore we must find some probe of the electron system which varies strongly over a unit cell and thus can 'tell the difference' between *s*- and *d*-electrons. The most promising candidate is the crystal ions or nuclei; the nucleus can clearly discriminate the two bands since in general the densities of the corresponding electronic wave functions at its site are different. Generally speaking, the nucleus can interact with the electrons either through its translational motion (electron-phonon coupling) or by changing its internal state, as in nuclear spin relaxation for instance. The second kind of interaction is not very useful for our purposes; the energy of interest is ω_0 , which is of the order of 1°K, and to get a splitting of the nuclear levels of this magnitude by the Zeeman effect would need a magnetic field many times larger than the superconducting critical field. In general the nuclear energy scale is either much too small (as here) or much too large (as, say, in the Mössbauer effect) to be useful for this purpose.

What, then, of the translational motion of the nucleus? The effects of electron-phonon coupling in a two-band metal will be considered in detail elsewhere; here we just quote the main results. As to the possibility of direct detection of the resonance, say by a neutron scattering experiment, it turns out that a subsidiary pole does indeed appear in the phonon propagation function at about the frequency of the electronic resonance (in contrast to the case of a one-band metal), but the amplitude of the corresponding peak in the neutron scattering cross-section relative to that of the 'primary' (real-phonon) peak is

only of order $(\rho_2/\rho_1)(c/v)^3$ where c is the phonon velocity. The value of this quantity is subject to considerable uncertainty but it seems unlikely to be much greater than 10^{-4} . Hence detection by neutron scattering does not seem feasible, unless some revolutionary advance in sample preparation and/or resolution is made. However, the possibility of observing the subsidiary resonance directly by ultrasound transmission experiments cannot be entirely ruled out, though here too the practical difficulties are likely to be formidable.

It turns out, however, that the existence of the electronic collective resonance has a quite appreciable effect on the velocity of propagation of ultrasound. Indeed, under probably realistic conditions the shift of the ultrasound dispersion curve at very low temperatures in the region $k \sim \omega_0/v$ gives a direct measure of the (inverse of) the excitation energy $\omega(k)$ of the electronic resonance. The relative magnitude of this effect is of order $(\rho_2/\rho_1)(c/v)^2$; even under very unfavourable conditions this quantity can hardly be smaller than 10^{-4} , and it may even be as large as 10^{-2} in some cases. Since the (theoretical!) absorption of ultrasound is negligible even in the region $\Delta_1 \ll k_B T \ll \Delta_2$, the detection of a shift of the predicted order of magnitude as the temperature is lowered below Δ_1 should be well within the power of current experimental technique. In order that the effect give a direct measure of $\omega(k)$ it is probably necessary that the parameter α should be small; however, there should be an unambiguous shift in the ultrasound velocity even when this is not so. It would therefore be of great interest to detect this effect even in niobium. Details of the theory will be given elsewhere.

We conclude, therefore, that indirect detection of the proposed electronic collective resonance is certainly experimentally feasible at present and that 'direct' detection (by specific heat measurements or, possibly, ultrasound transmission) is not hopelessly beyond reasonable expectation for the future. More quantitative estimates require, in particular, knowledge of the excitation velocity v , and hence of v_1 and v_2 ; in principle these quantities are obtainable from any one of a number of experiments on the pure two-band superconductor in question, and it is to be hoped that good values will become available in the near future.

§ 5. Discussion

In this section we shall try to elucidate the connection of the results of this paper with certain other phenomena in the theory of superconductivity.

First, we consider how the effects investigated here are related to the Josephson effect.¹⁶⁾ A treatment of the latter which is in many ways similar to the discussion of § 2 has been given by Wallace and Stavn.¹⁷⁾ They show that the Hamiltonian of two superconductors coupled by a Josephson junction in the absence of an external field can be written

$$\hat{H} = \hat{H}_L + \hat{H}_R - 2T \cos(\hat{\phi}_L - \hat{\phi}_R) (\Delta_L \Delta_R / V_L V_R), \quad (5.1)$$

when \hat{H}_L and \hat{H}_R are the Hamiltonians of the systems to left and right of the junction in the absence of the coupling, ϕ_L and ϕ_R are the phases of the corresponding 'condensates' and T is the coupling matrix element. This expression should be compared with our equation (2.16); in our notation (Δ_L/V_L) would be Ψ_L , etc. It should be pointed out that, strictly speaking, (5.1) cannot be correct for a closed system; as in our problem, there should be a term proportional to $(\hat{N}_L - \hat{N}_R)^2$ (where \hat{N}_L is the deviation of the number of electrons on the left-hand side of the barrier from its equilibrium value, etc.), and in principle this should give rise to harmonic oscillations of the current in zero external field. The basic difference between our case and that of a Josephson junction is, of course, that in the latter case the coefficient of $(\hat{N}_L - \hat{N}_R)^2$ is inversely proportional to the mutual capacitance of the two systems and so goes to zero with increasing volume, whereas the coupling matrix element T is determined by the size and geometry of the junction and is independent of the size of the two superconductors. Thus the frequency of the harmonic current is usually negligibly small. Now when we create an external potential difference between the two systems (say by applying a voltage V) the total Hamiltonian can be written

$$H = H_0 - 2T(\Delta_L \Delta_R / V_L V_R) \cos(\hat{\phi}_L - \hat{\phi}_R) + eV(\hat{N}_L - \hat{N}_R) \quad (5.2)$$

with the commutation relation (cf. (2.21))

$$[\hat{N}_L - \hat{N}_R, \hat{\phi}_L - \hat{\phi}_R] = -4i. \quad (5.3)$$

Because there is now no 'restoring force' proportional to $(\hat{N}_L - \hat{N}_R)$, it is not legitimate to expand the second term in (5.2) to lowest order in $(\hat{\phi}_L - \hat{\phi}_R)^2$. Thus, in the Josephson case the relative phase performs steady rotation, whereas in our case it performs small vibrations around the equilibrium position.

Next we consider the analogy to the problem of $l \neq 0$ excitons in a one-band superconductor. We shall consider only even- l (spin-zero) excitons and make the rather artificial assumption that one of the higher harmonics of the pairing interaction $U(\mathbf{n}, \mathbf{n}')$, say the second, is comparable in magnitude to the zeroth harmonic which actually binds the physical groundstate. We introduce the quantity

$$\sum_{|\mathbf{k}|} a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+ \equiv \Psi(\mathbf{n}), \quad (5.4)$$

where \mathbf{n} is a unit vector specifying the direction on the Fermi surface. We confine ourselves to states of the type (cf. (2.8))

$$\Phi\{\Delta(\mathbf{n})\} = \prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+) |\Phi_0\rangle, \quad (5.5)$$

where $|\Phi_0\rangle$ is the vacuum state, and $u_{\mathbf{k}}, v_{\mathbf{k}}$ satisfy

$$|u_k|^2 + |v_k|^2 = 1, \tag{5.6}$$

$$u_k v_k^* = \frac{\Delta(\mathbf{n})}{2\{\varepsilon_k^2 + |\Delta(\mathbf{n})|^2\}^{1/2}},$$

where $\Delta(\mathbf{n})$ is a complex function of \mathbf{n} . Then we have

$$\Psi(\mathbf{n}) = \frac{1}{2} \rho \Delta(\mathbf{n}) \ln(2\tilde{\omega}/|\Delta(\mathbf{n})|). \tag{5.7}$$

The total Hamiltonian can be written (cf. (2.16))

$$\hat{H} = \int f |\Psi(\mathbf{n})|^2 \frac{d\Omega}{4\pi} - \frac{1}{2} \iint U(\mathbf{n}, \mathbf{n}') \left\{ \Psi^*(\mathbf{n}) \Psi(\mathbf{n}') + \Psi(\mathbf{n}) \Psi^*(\mathbf{n}') \right\} \frac{d\Omega d\Omega'}{16\pi^2}, \tag{5.8}$$

where the first term represents the kinetic energy. In the groundstate we have

$$\Psi(\mathbf{n}) = \text{const} \equiv \Psi_0 = \Delta_0/U_0 \tag{5.9}$$

where Δ_0 is the value of the gap determined by the BCS equation and U_0 is the zeroth harmonic of the pairing interaction. If for the moment we assume that in the states we are going to consider the ‘best’ value of $|\Psi(\mathbf{n})|$ for a given functional form of $\arg \Psi(\mathbf{n}')$ is only slightly different from Ψ_0 (this is equivalent, roughly speaking, to the assumption that the second harmonic U_2 is close to U_0 —cf. below) then we can take the magnitude of $\Psi(\mathbf{n})$ to be equal to Ψ_0 in these excited states too, and write

$$\Psi(\mathbf{n}) = \Psi_0 \exp(i\phi(\mathbf{n})). \tag{5.10}$$

Then we can write part of (5.8) in the form (where E_0 is the BCS groundstate energy)

$$E_0 + \Psi_0^2 \left\{ U_0 - \iint U(\mathbf{n}, \mathbf{n}') \cos[\phi(\mathbf{n}) - \phi(\mathbf{n}')] d\Omega d\Omega' / 16\pi^2 \right\}. \tag{5.11}$$

However, we must also take into account a term corresponding to \hat{L} in Eq. (2.4)—that is, a term corresponding to the fact that the ‘average’ Fermi surface may be distorted (while the total volume enclosed by it must of course remain constant). This term has the form

$$\hat{L} \equiv \frac{1}{2} \rho^{-1} \int \left\{ \delta N(\mathbf{n}) \right\}^2 d\Omega / 4\pi, \tag{5.12}$$

where ρ is the density of states at the Fermi surface and

$$\delta N(\mathbf{n}) \equiv \sum_{|k|} a_k^+ a_k - \theta(k_F - k) \tag{5.13}$$

(we note that $\delta N(\mathbf{n})$ when acting on the BCS groundstate gives zero identically). Adding this term to (5.11) and expanding the cosine to second order in its argument, we finally put the Hamiltonian in the form

$$\hat{H} = E_0 + \frac{1}{2} \rho^{-1} \int \{\delta N(\mathbf{n})\}^2 d\Omega / 4\pi + \frac{1}{2} \iint U(\mathbf{n}, \mathbf{n}') \{\phi(\mathbf{n}) - \phi(\mathbf{n}')\}^2 d\Omega d\Omega' / 16\pi^2. \quad (5.14)$$

From (5.4) and (5.13) we have the commutation relation

$$[\delta N(\mathbf{n}), \phi(\mathbf{n}')] = (-i/2\pi) \delta(\mathbf{n} - \mathbf{n}'). \quad (5.15)$$

Now let us assume for $\phi(\mathbf{n})$ and $\delta N(\mathbf{n})$ the forms

$$\phi(\mathbf{n}) = \phi Y_{2m}(\mathbf{n}), \quad \delta N(\mathbf{n}) = \delta N Y_{2m}(\mathbf{n}), \quad (5.16)$$

where $Y_{2m}(\mathbf{n})$ is a normalized spherical harmonic, and expand $U(\mathbf{n}\mathbf{n}')$ in Legendre polynomials:

$$U(\mathbf{n}\mathbf{n}') = \sum_l U_l P_l(\mathbf{n}\mathbf{n}'). \quad (5.17)$$

Then the Hamiltonian (5.14) becomes

$$\hat{H} = E_0 + \frac{1}{2} \rho^{-1} (\delta N)^2 + \Psi_0^2 (U_0 - U_2) \phi^2 \quad (5.18)$$

with the commutation relation

$$[\delta N, \phi] = -2i. \quad (5.19)$$

Thus, from (5.18) and (5.19), δN and ϕ oscillate with the harmonic frequency

$$\omega_0^2 = 8(U_0 - U_2) \Psi_0^2 / \rho \quad (5.20)$$

or using (5.9)

$$\omega_0^2 = 8(U_0 - U_2) \Delta^2 / U_0^2 \rho. \quad (5.21)$$

Finally, defining a dimensionless quantity $V_l \equiv \rho U_l / 2$ to agree with the definition of g_l of Bardasis and Schrieffer,⁹⁾ we can write (5.21) as

$$\omega_0^2 / 4\Delta^2 = (V_0 - V_2) / V_0^2. \quad (5.22)$$

If $V_0 - V_2 \ll V_0^2$ this agrees with the usual results.⁹⁾ Now the above argument was based on the assumption that there exist unstable solutions of the gap equation for which $|\Psi(\mathbf{n})|$ is not much different from Ψ_0 ; the condition for this assumption to hold is precisely $V_0 - V_2 \ll V_0^2$ (cf. below), thus our argument is consistent.

Of course, this assumption is very unlikely to be satisfied in practice; the virtue of the above argument is simply that it gives a rather simple picture of the physical nature of excitons, which should be qualitatively valid under more general conditions. We see that excitons in superconductors correspond to a coherent distortion of the shape of the "average" Fermi surface, accompanied by a small fluctuation of the relative phase of the pairs in different regions of the Fermi surface. In a sense, therefore, they are the analogue of the anisotropic zero sound vibrations which may be possible in the normal phase;¹⁸⁾ however,

the conditions for their existence are much less stringent. One may say that the $l \neq 0$ collective modes in a superconductor foreshadow the breakdown of the "rigidity" of the condensate wave function, since they correspond to a distortion of its spherical symmetry. From this point of view it is also easy to see why "Fermi-liquid" terms must affect their frequencies quite strongly;⁹⁾ indeed, it is trivial to take these terms into account in the above method.

Before leaving the subject of excitons in one-band superconductors, we should perhaps draw attention to one slightly embarrassing point. According to (5.22) the frequency of the collective excitation becomes imaginary, signalling the instability of the groundstate chosen, as soon as $V_2 > V_0$. On the other hand Anderson and Morel¹⁹⁾ found that the binding energy of the D -wave-paired state does not become equal to that of the S -wave-paired state until V_2 is somewhat greater than V_0 . A similar difficulty was noted by Balian and Werthamer²⁰⁾ for the case of P -wave pairing; they claimed to have resolved it by showing that if one takes into account all spin components of the triplet pairing interaction one gets an isotropic triplet state whose binding energy exceeds that of the BCS state as soon as $V_1 > V_0$. Unfortunately the exciton instability occurs at $V_1 = V_0$ whether or not one considers all spin components of the pairing interaction, and in any case no such explanation is available for the instability with respect to D -wave pairing. The most likely resolution of the apparent contradiction is that (contrary to the estimate of reference 19)) the true groundstate is neither pure S -wave nor pure D -wave over a considerable range of the coupling constant ratio (V_2/V_0); actually, this is necessary for the argument given above, since it was supposed that if $V_0 - V_2 \ll V_0^2$ there exist low-lying unstable solutions of the gap equation with $|\Psi(\mathbf{n})|$ almost constant, and presumably these should go over into the stable solution as soon as $V_2 > V_0$. To the present author's knowledge this problem has never been satisfactorily cleared up. In our case no such difficulty arises, since there are no geometrical factors entering the expressions for the binding energies of the stable and unstable solutions.

Finally, we shall show that the results of § 3 for the dispersion relation of the collective excitation can be easily interpreted from a "quasi-hydrodynamic" point of view; that is, we treat the two-condensate system as a system of two perfect hydrodynamic liquids coupled by an unusual type of coherent transfer interaction. We consider first the case of a neutral system. Then the equation of motion of the current in the j -th band is the usual hydrodynamic one

$$\frac{d\mathbf{J}_j}{dt} = -c_j^2 \nabla N_j, \quad c_j^2 \equiv \frac{1}{3} v_j^2. \quad (5.23)$$

Here N_j is the deviation of the local number density in the j -th band from its equilibrium value; we have neglected terms connected with the nonconservation of N_j in the two bands separately as being of second order in the deviation in

(5.23). However, these terms are of first order in the equation of motion of N_j itself. This does not affect the total density, which is conserved:

$$\frac{d(N_1+N_2)}{dt} = -\text{div}(\mathbf{J}_1+\mathbf{J}_2). \quad (5.24)$$

In considering the equation of motion of the relative density fluctuation (N_1-N_2) we must take into account (a) the possibility of incoherent conversion of an s -electron into a d -electron, say by impurity scattering (b) the possibility of *coherent* conversion of a pair of s -electrons into a pair of d -electrons by the "internal Josephson effect" discussed in the body of the paper. We shall neglect the first, since we have always considered pure samples in this paper. To incorporate the effect of the second we argue as follows. First, in the limit that $N_1+N_2=\text{const}$ (e.g. in the very long wavelength limit) we must recover the results of § 2, i.e. we must have

$$\frac{d^2}{dt^2}(N_1-N_2) = -\omega_0^2(N_1-N_2) \quad (5.25)$$

with ω_0 given by (2.23). Secondly, in the general case the part of the equation of motion arising from this effect must be nondissipative, that is it must be a second-order differential equation, and furthermore we expect the driving force to be proportional to the deviation of the local energy from the equilibrium value for the given local value of (N_1+N_2) ; that is, this term should have the general form

$$\begin{aligned} \frac{d^2}{dt^2}(N_1-N_2) &= -A \left\{ \rho_1^{-1}N_1 + \rho_2^{-1}N_2 - \frac{2}{\rho_1+\rho_2}(N_1+N_2) \right\} \\ &= -A'(\rho_2N_1 - \rho_1N_2). \end{aligned} \quad (5.26)$$

Comparing (5.26) with (5.25), we can make the identification $A' = 2\omega_0^2/(\rho_1 + \rho_2)$. Finally, there is an additive contribution to the acceleration of (N_1-N_2) from the influx of particles into the region, which is given by the analogue of (5.24) together with (5.23). Combining these results, we finally get the equation of motion of (N_1-N_2) :

$$\frac{d^2}{dt^2}(N_1-N_2) = -2\omega_0^2 \left(\frac{\rho_2N_1 - \rho_1N_2}{\rho_1 + \rho_2} \right) + (c_1^2 - c_2^2) \nabla^2(N_1-N_2). \quad (5.27)$$

Substituting (5.23) into (5.24) and taking the Fourier transforms of the resulting equation and (5.27), we find:

$$\begin{aligned} \omega^2(N_1-N_2) &= \frac{2\omega_0^2}{\rho_1+\rho_2}(\rho_2N_1 - \rho_1N_2) + k^2(c_1^2N_1 - c_2^2N_2), \\ \omega^2(N_1+N_2) &= k^2(c_1^2N_1 + c_2^2N_2). \end{aligned} \quad (5.28)$$

Equations (5.29) have a nontrivial solution if the following equation is satisfied:

$$\omega^4 - \{\omega_0^2 + (c_1^2 + c_2^2)k^2\}\omega^2 + \omega_0^2 k^2 \left\{ \frac{\rho_1 c_1^2 + \rho_2 c_2^2}{\rho_1 + \rho_2} \right\} + c_1^2 c_2^2 k^4 = 0. \quad (5.29)$$

This is just Eq. (3.14). We see that at long wavelengths ($v_j k \ll \omega_0$) the motion of the relative density is largely decoupled from that of the total density and governed mainly by the coherent transfer effect; at short wavelengths ($v_j k \gg \omega_0$), on the other hand, the two bands are themselves decoupled and behave as independent classical liquids (it goes without saying, of course, that we assume $v_j k \ll \Delta_1$; if $\omega_0 \ll v_2 k \ll \Delta_1$, $v_1 k \sim \Delta_1$ then only one hydrodynamic wave will persist).

In the Coulomb case it is tempting but incorrect to assume $N_1 + N_2 = 0$ from the start. Instead we should replace Eq. (5.22) by

$$\frac{d\mathbf{J}_j}{dt}(\mathbf{r}) = -c_j^2 \nabla N_j(\mathbf{r}) - \nabla \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} (N_1 + N_2)(\mathbf{r}') d\mathbf{r}'. \quad (5.30)$$

This leads to the following equations in place of (5.28):

$$\begin{aligned} \omega^2 (N_1 - N_2) &= \frac{2\omega_0^2}{\rho_1 + \rho_2} (\rho_2 N_1 - \rho_1 N_2) + k^2 (c_1^2 N_1 - c_2^2 N_2) + \omega_-^2 (N_1 + N_2), \\ \omega^2 (N_1 + N_2) &= k^2 (c_1^2 N_1 + c_2^2 N_2) + \omega_+^2 (N_1 + N_2), \end{aligned} \quad (5.31)$$

where

$$\omega_{\pm}^2 = (\rho_1 c_1^2 \pm \rho_2 c_2^2) 4\pi e^2. \quad (5.32)$$

Since $\omega_+^2 \gg \omega_0^2$, $c_j^2 k^2$ we may substitute $N_1 = -N_2$ everywhere in the first equation except in the term containing ω_-^2 ; in the latter we must put

$$N_1 + N_2 = (c_2^2 - c_1^2) k^2 N_1 / \omega_+^2. \quad (5.33)$$

Then the first of Eqs. (5.31) gives the dispersion relation

$$\begin{aligned} \omega^2 &= \omega_0^2 + \frac{1}{2} k^2 (c_1^2 + c_2^2) + \frac{1}{2} (\omega_- / \omega_+)^2 (c_2^2 - c_1^2) k^2 \\ &= \omega_0^2 + k^2 \left\{ \frac{(\rho_1 + \rho_2) c_1^2 c_2^2}{\rho_1 c_1^2 + \rho_2 c_2^2} \right\} \end{aligned} \quad (5.34)$$

in agreement with (3.39). Again the long-wavelength behaviour is governed by the coherent transfer effect while the short-wavelength behaviour is that of two classical liquids coupled by the Coulomb force.

We can use this approach to show that the formula (5.34) is approximately correct throughout the whole region $v k \ll \Delta_1$, even if $v_1 k \gg \Delta_1$. In this case we cannot of course treat the s -band as a perfect hydrodynamic liquid. However, the behaviour of the collective excitation is essentially determined by the unscreened density response functions in the two bands. Provided $\omega \ll v_1 k$, these are not changed much in the process of passing from $v_1 k \ll \Delta_1$ to $v_1 k \gg \Delta_1$; indeed in the limit $\omega \rightarrow 0$ the unscreened density response function for $v_1 k \gg \Delta_1$ is essentially the normal-state compressibility (of a fictitious neutral system) which is well-known to be identical to the superfluid-state compressibility to

order $(\Delta/\varepsilon_F)^2$. In the limit $vk \gg \Delta$, $\omega \gg \Delta$, however, no collective excitation can be propagated except under very artificial assumptions.

It is obvious, incidentally, that even in a normal two-band system a "hydrodynamic" wave of the relative density will be able to propagate in a certain frequency region provided that the establishment of thermodynamic equilibrium within each band is very much faster than the establishment of equilibrium between the two bands, as is likely to be the case in a pure specimen. Such a wave would have the velocity v given by (3.39), with a frequency which goes to zero with k instead of tending to the finite limit ω_0 . It is possible that the experimental observation of this wave would be rather easier than that of the effect discussed in this paper, and it would in itself be of some interest.

To conclude this discussion we write down for reference the forms of the various response functions of the particle densities in the two bands; more precisely, the retarded Green functions

$$\chi_{ij}(k, \omega) = \langle\langle N_i : N_j \rangle\rangle(k, \omega)$$

in the standard notation. These response functions may be straightforwardly obtained by adding appropriate driving terms representing external potentials to Eqs. (5.28) or (5.31); it is essential to remember that these will affect the term containing ω_0^2 as well as the terms in $c_j^2 k^2$. After a short calculation we get for the neutral case

$$\begin{aligned} \chi_{11} &= \left[\frac{\rho_1 \omega_0^2}{\rho_1 + \rho_2} \{ \rho_2 \omega^2 - \rho_1 c_1^2 k^2 - \rho_2 c_2^2 k^2 \} + (\omega^2 - c_2^2 k^2) \rho_1 c_1^2 k^2 \right] Q^{-1}(k\omega), \\ \chi_{12} = \chi_{21} &= \left(- \frac{\omega^2 \omega_0^2 \rho_1 \rho_2}{\rho_1 + \rho_2} \right) Q^{-1}(k, \omega), \end{aligned} \quad (5.35)$$

where $Q(k\omega)$ is the quantity on the left-hand side of (5.29). χ_{22} is obviously obtained from χ_{11} by interchanging the suffices 1 and 2. Notice that in the static limit all the correlation functions are independent of k . For the Coulomb case we have the simpler result

$$\chi_{11} = \chi_{22} = -\chi_{12} = -\chi_{21} = \frac{\rho_1 \rho_2}{\rho_1 + \rho_2} \frac{\omega^2(k)}{\omega^2 - \omega^2(k)}, \quad (5.36)$$

when $\omega^2(k)$ is the quantity on the right-hand side of (5.34). It follows from (5.36) that any correlation function in which the total density $N_1 + N_2$ appears must be zero, as we should expect.

§ 6. Conclusion

In this paper we have shown that in a clean two-band superconductor the dependence of the energy on the relative phase of the two condensates as well as on their relative density gives rise to a peculiar kind of collective excitation.

Although this excitation is in principle analogous to the transverse collective excitations in ordinary superconductors, it has a number of distinguishing features. First, it is probably the only case in which a reasonable estimate of the frequency of a collective mode in a superconductor can be made from available experimental data (we have no way of estimating the higher harmonics of the pairing interaction in an ordinary superconductor from experiment). Secondly, it is well separated from the single-particle excitation threshold; we saw that for niobium $\omega/2\Delta_1 \sim 0.6$. Thirdly, it is possible to give a very clear physical picture of the nature of the excitation; it corresponds to small fluctuations of the relative phase of the two condensates around its equilibrium value (or, equivalently, to small fluctuations of the canonically conjugate variable, the relative density). In view of these points it is of considerable interest from a theoretical point of view.

From the point of view of experiment, we have seen that although direct observation of the resonance itself is probably not feasible at present, its effect on the ultrasound velocity should be easily observable and, under favourable conditions, yield its dispersion curve. Such an experiment would provide an extremely interesting confirmation of the basic hypotheses of the two-band theory of superconductivity.

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