SECOND SOUND, THE CONVECTIVE HEAT TRANSFER MECHANISM, AND EXCITON EXCITATIONS IN SUPERCONDUCTORS

V. L. GINZBURG

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor March 28, 1961; resubmitted May 3, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) 41, 828-834 (September, 1961)

The possibility of observing convective heat transfer and second sound in superconductors is discussed. The change in the single-particle excitation spectrum and, in particular, the existence in superconductors of exciton excitations can in principle greatly reduce the role played by impurity scattering. As a result, the attenuation of second sound may be substantially diminished, while the convective transfer of heat may increase markedly. Some experimental data relative to superconducting lead are discussed. A mechanism is indicated which may lead to a Knight frequency shift in superconductors in the case of small samples and strong magnetic fields.

THE possibility of the simultaneous existence in superconductors of superconducting and normal currents with densities $\mathbf{j}_s$ and $\mathbf{j}_n$ should lead to the appearance of convective thermal transport in a non-uniformly heated metal, particularly in the absence of a total current $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n$ (see [1]). A number of estimates[2-4] have led, however, to the conclusion that this effect is insignificant. This is explained, in the first place, by the strong friction opposing the movement of the normal component of the electron fluid, which is due fundamentally to the presence of a residual resistance. On this basis, one may conclude that the propagation of weakly-damped second sound in superconductors is impossible.

Actually, within the framework of two-fluid hydrodynamic theory, by analogy with the case of superfluidity[5] we obtain directly, in the linear approximation, the equations

$$\partial \frac{m}{e}\mathbf{j}/\partial t = -\nabla p - \rho_{n0}\nu\mathbf{v}_n + \frac{e}{m}\rho_0\mathbf{E}, \qquad \frac{\partial\rho}{\partial t} + \operatorname{div}\frac{m}{e}\mathbf{j} = 0,$$

$$\frac{\partial\mathbf{v}_s}{\partial t} = -\nabla\mu + \frac{e}{m}\mathbf{E}, \qquad \frac{\partial S}{\partial t} + S_0\operatorname{div}\mathbf{v}_n = 0,$$

$$\operatorname{div}\mathbf{E} = \frac{4\pi e}{m\varepsilon}(\rho - \rho_0), \qquad dp = S_0\,dT + \rho_0\,d\mu,$$

$$\frac{m}{e}\mathbf{j} = \rho_s\mathbf{v}_s + \rho_n\mathbf{v}_n, \qquad \mathbf{j}_s = \frac{e}{m}\rho_s\mathbf{v}_s, \qquad \mathbf{j}_n = \frac{e}{m}\rho_n\mathbf{v}_n. \tag{1}$$

Here the zero subscript refers to the ground-state values, and is omitted hereafter. The momentum current density is taken to be $(m/e)\mathbf{j}$, where e/m is the free electron charge-to-mass ratio; ϵ is the dielectric constant, which is not connected with the motion under consideration, and ν is a certain effective number of collisions.

If we discount the possibility that the value of ϵ may be anomalously large,[6] which in any case lies beyond the bounds of the model used, the plasma frequency $\omega_0 = \sqrt{4\pi e^2\rho_0/m^2\epsilon}$ turns out to be extraordinarily high. The system (1) for the propagation of low-frequency waves proportional to $\exp i(\omega t - \mathbf{k}\cdot\mathbf{r})$ leads therefore to the relation

$$k^2 = \omega^2\left(1 - i\frac{\rho_s}{\rho}\frac{\nu}{\omega}\right) \times \frac{\rho_n\rho\,[(\partial S/\partial T)_p(\partial\rho/\partial p)_T - (\partial S/\partial p)_T(\partial\rho/\partial T)_p]}{\rho_s S^2(\partial\rho/\partial p)_T}. \tag{2}$$

We obtain from this, for $\nu = 0$ and $(\partial S/\partial T)(\partial\rho/\partial p) \gg (\partial S/\partial p)\cdot(\partial\rho/\partial T)$, the well-known formula for the second sound velocity in He II:

$$u_2 = \sqrt{\rho_s S^2 T/\rho\rho_n C}, \tag{3}$$

where the entropy S and the specific heat C $= T\partial S/\partial T$ are referred to unit volume, ρ is the total density of the electron fluid, and ρ_s and ρ_n are the respective densities of the superfluid and normal components of the fluid.

If for normal motion in superconductors ν is of the same order as in the non-superconducting case, then there can be no possibility for propagation of low-frequency second sound.* Actually, the attenuation in (2) will be weak provided $\nu \sim v_0/l_s \ll \omega$ ($v_0 \sim 10^8$ is the velocity at the Fermi boundary,

*We note that the extremely strong attenuation of second sound in superconductors has been emphasized in a number of papers.[7,8] I. M. Khalatnikov and the author arrived at the same conclusion, independently of one another, some two years ago.

while l_S is the mean free path for scattering by impurities). This gives $l_S \gg v_0/\omega \sim 10^8/\omega$, and even for $\omega \sim 10^8$ the extremely stringent condition $l_S \gg 1$ cm must be fulfilled.

Even this condition, however, is insufficient if the inequality $\lambda = 2\pi u_2/\omega \gg l_0$, required for the application of hydrodynamic theory, is not satisfied. The effective excitation mean free path l_0 necessary for establishment of hydrodynamic flow is of the same order as the mean free path l_e for electron-electron collisions only when $l_e \ll l_S$. Further, for a normal metal $l_e \sim (1/\sigma_e n_0)\times(\epsilon_0/kT)^2 \sim 3 \times 10^{-3}(100/T)^2$, where $\sigma_e \sim 10^{-15}$, $n_0 \sim 3 \times 10^{22}$, and ϵ_0 is the energy at the Fermi boundary (see, for example, [9]). Hence, for $T \sim 3°$ we have $l_e \sim 3$ cm, while in a superconductor l_e is even larger, due to the appearance of the factor $\exp(2\Delta/kT)$ (2Δ is the width of the gap formation of two single-particle excitations). For $u_2 \sim 10^4$ (see below) and $l_e \sim 10$ we arrive at the wholly unrealistic conditions $\omega \ll l_e/2\pi u_2 \sim 10^4$ and $l_S \gg 10^8/\omega \sim 10^4 - 10^5$ cm.

Nevertheless, the possibility of the occurrence of second sound in superconductors merits more careful attention. The fact is, that the spectrum and character of the excitations in the superconducting state differ radically from those prevailing in the normal state. Thus, in the isotropic model[8] the single-particle excitations in superconductors possess the following energy and velocity:

$$E = \sqrt{\varepsilon^2 + \Delta^2}, \qquad \varepsilon = \frac{p^2 - p_0^2}{2m} = \frac{p^2}{2m} - \varepsilon_0;$$
$$v = \frac{dE}{dp} \approx \frac{v_0\varepsilon}{E}, \qquad v_0 = \frac{p_0}{m}.$$

Since in the simplest case the number of collisions is proportional to v, then in the superconducting state $\nu^{(s)} = \nu^{(n)} v/v_0$. If the Fermi surfaces are complex, one can assume that for a sufficiently large number of excitations $\nu^{(s)}$ is much smaller than $\nu^{(n)}$. It is unlikely, however, that ν should change in these circumstances by many orders of magnitude.

The situation may prove to be more favorable with regard to transverse collective excitations (excitons), which appear under certain conditions in superconductors* (see [6,8,10-13]). The scattering of excitons by impurities is diminished for a number of reasons. Thus, in the long-wave region collective excitations are in a number of cases only weakly scattered, since the energy of their interaction with impurities contains the wave vector as a factor. As an example, we may point to the scattering of phonons and long-wave excitons (photons) in non-conductors. As regards excitons in superconductors in the long-wave region, neither the character of the excitations themselves* nor their law of scattering is as yet sufficiently clear. This region, however, is of least importance, since the corresponding excitons are extremely few in number and cannot contribute significantly to ρ_n. However, for excitons having a sufficiently large wave vector q, these playing the principal role, the effective cross section for scattering by impurities can fall sharply, as a consequence of the large size of the excitons.

In fact, to a certain approximation[12,13] an exciton can be regarded as an excited Cooper "pair" having the wave function $\Psi = e^{i\mathbf{q}\cdot\mathbf{R}}\varphi(\mathbf{r})$, where $\mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$ locates the center of mass of the pair and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ is the relative separation of its components. We shall now consider the scattering of the pairs by impurities, in which the interaction energy is

$$V = A_1 D_1(\mathbf{r}_1) + A_2 D_2(\mathbf{r}_2), \qquad \int D_{1,2}(\mathbf{r})\, d\mathbf{r} = 1.$$

Then, in the Born approximation, the transport cross section for elastic scattering of the pairs is ($M = m_1 + m_2$, $d\Omega = \sin\theta\, d\theta\, d\varphi$)

$$\sigma_{tr} = \frac{M^2}{4\pi^2\hbar^4}\int (1-\cos\theta)\left|\int\left\{A_1 D_1\left(\mathbf{R} - \frac{m_2}{M}\mathbf{r}\right) + A_2 D_2\left(\mathbf{R} + \frac{m_1}{M}\mathbf{r}\right)\right\} e^{i(\mathbf{q}-\mathbf{q}')\mathbf{R}}\,|\varphi(\mathbf{r})|^2 d\mathbf{R}\, d\mathbf{r}\right|^2 d\Omega. \tag{4}$$

The size of the pairs is characterized by the parameter a, which is of the order of or greater than $\xi_0 \sim 10^{-4} - 10^{-5}$ cm. $D_{1,2}$ can therefore be replaced by a δ-function. Setting, for simplicity, $\varphi(\mathbf{r}) = \varphi(r)$, $m_1 = m_2 = M/2$, and $A_1 = A_2 = A$ we have

$$\sigma_{tr} = \frac{32\pi M^2 A^2}{\hbar^4}\int_0^\pi\left\{\int_0^\infty \frac{\sin(qr\sin(\theta/2))\,|\varphi(r)|^2}{q\sin(\theta/2)}\, r\, dr\right\}^2 \times (1-\cos\theta)\sin\theta\, d\theta. \tag{5}$$

If $qa \ll 1$, then $\sigma_{tr} = 4M^2A^2/\pi\hbar^4$, since

$$4\pi\int|\varphi(r)|^2 r^2 dr = 1.$$

*The conclusion that the excitation spectrum of a superconductor is a mixed one, and incorporates both Fermi and Bose (photon) excitations was discussed some time ago.[6] Only the microscopic theory, however, was under consideration (the term "photon" used in[6] for electric waves in the medium is identical in present-day terminology with the term "exciton;"[14] in[6] retardation was regarded as of fundamental importance, while in[8,10-13] the excitons correspond to poles of the permittivity $\varepsilon(\omega, k)$.

*For non-conductors, it is known (see, for example,[14]) that in the long-wave region one must take retardation into account. We are not clear as to the region of applicability of the results of[12,13], especially for long waves.

For qa ≫ 1, on the other hand, the cross section σ_{tr} is, generally speaking, extremely small. At the same time, for excitons whose energy E_e is near 2Δ, the size of the pairs increases greatly, and $a \gg \xi_0$ (see [12]). To this must be added the fact that the velocity dE_e/dq of the pairs is also extremely small when q is large and $E \sim 2\Delta$ (see the dispersion equation (3.22) in [13]). There is thus an established basis for assuming that a significant fraction of the pairs is extremely weakly scattered by impurities; and the hypothesis that for excitations of the exciton type $\nu^{(s)}$ is smaller by many orders of magnitude than $\nu^{(n)}$ does not appear improbable, although it can by no means be considered as proven.

In connection with what has been said, let us suppose that there can exist a group of excitations, most probably excitons, possessing low friction. These excitations, then, could make a considerable contribution to the transport processes, and make possible as well the propagation of second sound in superconductors (the latter, of course, being less likely). If we assume that the exciton mean free path satisfies certain conditions, which are evident from what has already been said at the beginning of this article, then the second sound velocity $u_{2e} = \sqrt{\rho_s S_e^2 T/\rho\rho_{ne} C_e}$, where S_e, C_e and ρ_{ne} are the contributions these excitations make to S, C, and ρ_n (as before, however, ρ_s and ρ refer to all of the conduction electrons, and, of course, $\rho \neq \rho_s + \rho_{ne}$).

As we pass from one metal to another ρ_{ne}, S_e and C_e will obviously change greatly; only for Pb and Hg among the metals studied are these quantities relatively large. Anomalous behaviour of the specific heat is, in fact, observed in Pb and Hg,[15] and microwave absorption sets in for $\hbar\omega < 2\Delta$ (see [16,17]). These two effects, if they are to be associated with exciton excitations, cannot be explained within the framework of the theory of weak binding of the electrons with the lattice.[8,12] In both Pb and Hg, on the other hand, the binding is relatively strong, and the usual approximation is probably not applicable (we note that for Pb, Hg and Sn, respectively, the ratio $10^3 T_c/\theta_D$ has the values 76, 52, and 19 (see [17]); here T_c and θ_D are the critical and Debye temperatures respectively). From the point of view of this hypothesis, second sound propagation may most probably occur in Pb and Hg. If all of the values for Pb are taken for the simplest model of a superconductor*, then, from Eq. (3), $u_2 = 2.2 \times 10^4$ at $T = 3.9°$. It may be presumed that u_{2e} does not differ from u_2 by more than an order of magnitude, since the quantity $S_e^2/\rho_{ne}C_e$ is considerably less sensitive to changes in the various parameters than ρ_{ne}, S_e, or C_e themselves.

If a group of excitations having sufficiently small friction exists at all, then propagation of second sound is possible in principle, even for extremely small values of ρ_{ne} and S_e, although in the latter case this sound would be more difficult to excite and detect. As regards Pb and Hg, one may expect an appreciable contribution by the exciton excitations to the thermal conductivity, as well as to the specific heat, resulting from convective heat transfer. The possibility of such an effect for Pb was discussed some time ago,[18,19,2,3] but seemed highly unlikely on theoretical grounds. On the other hand, an alternative explanation of the experiments with Pb — Bi alloys, based upon consideration of the part played by the thermal conductivity of the lattice, meets with difficulties[3] (in order to explain the data of [19], the lattice thermal conductivity for an alloy containing 0.5% Bi, to take one example, would have to be higher than for an alloy with 0.02% Bi).

In the light of the ideas advanced above, it seems probable to us that convective heat transport has actually been observed in Pb. We note that in non-cubic metals (here, mercury is of especial interest) under certain conditions a total current j must flow during the heat transfer process, and, consequently, that magnetic measurements are also possible.[1] During convective heat transport the normal fluid is transformed at the boundary of the superconductor into superfluid; as in the case of He II, therefore, a temperature discontinuity can arise.

We should also point out another possible role of the convective mechanism, viewed as an explanation of the peculiar behavior of the thermal conductivity in the intermediate state.[3,18,19] With the density ρ_n there is associated a charge $(e/m)\rho_n$; on the other hand, the mean free path of the excitons may be large. Their contribution, therefore, to the "normal conductivity" and to the surface impedance Z might be significant even for small ρ_{ne}. In this view, attention is drawn to the fact that in a number of cases the quantity R = ReZ exceeds the value calculated without taking exciton excitations into account;[20] the complicated dependence of Z upon an external magnetic field[21]

*The following values have been used:[8] $\rho = mn = 1.8 \times 10^{-5}$ ($\lambda_L(0) = 3.7 \times 10^{-6}$), $\gamma T_c = C_0 = 1.22 \times 10^4$, $T/T_c = 0.54$, $S/C_0 = 0.17$, $C/C_0 = 0.59$, $\rho_n/\rho = 1 - \rho_s/\rho = 0.21$. For Sn: $C_0 = 4.1 \times 10^3$, $\rho = 2.05 \times 10^{-5}$ ($\lambda_L(0) = 3.55 \times 10^{-6}$), and $u_2 = 8.6 \times 10^3$ cm/sec (for $T/T_c = 0.54$, $T = 2°$).

also remains unclear. (In computing the effect of a field upon the current in a superconductor, Miller[22] made use of an assumption which was tantamount to neglecting transverse excitons).

Finally, let us turn to the problem of the Knight frequency shift in superconductors. Experimental data[23,24] testify to the fact that for $T \ll T_c$ the Knight shift is smaller by only 20—30% than in the normal state. At the same time, it follows from theory that at $T = 0$ this shift must be equal to zero.[8,25,26] In view of this contradiction, Abrikosov and Gor'kov[26] not only criticized certain hypotheses concerning the origins of the Knight shift in superconductors, but also expressed general doubts concerning the reality of the effect itself. It seems to us, however, that as regards the experiments[24] discussed in [26] these objections do not apply at all. In these experiments the samples (fine particles of Sn) were of graded dimensions, much smaller (by tens of times) than the field penetration depths. Furthermore, while the fields employed exceeded 1200 oersteds, they were nevertheless considerably below the critical field [$H_c(0) \approx 2.5 \times 10^4$]. There is no basis, therefore, for assuming that superconductivity was destroyed in parts of the samples. Despite the small sizes of the particles, their critical temperature was 3.71°, which is lower by only 0.02° than the T_c of bulk Sn. It must therefore be presumed that the fundamental state of the superconductor in the particles investigated in the absence of a field was the same as in the bulk metal, and conformed to the representation of the contemporary theory of superconductivity, which for Sn agrees well with experiment.[8]

An attempt can be made to explain the presence of a Knight shift as due to the effect of the strong magnetic field used in these experiments[23,24] upon the exciton levels. From the constancy of T_c noted above it may be presumed that for small samples these levels are close to the levels in the bulk superconductor (the smallest particle size in reference 24 is ~ 40 A, which is still considerably greater than the electron wavelength at the Fermi boundary $\hbar/p_0 \sim 1$ A). In the particles, however, it is inappropriate to speak of the motion of the exciton center of mass, and the energy of interaction of the exciton with the field **H** is

$$-\frac{e}{2m_{\text{eff.}}c}\mathbf{HL} + \frac{e^2}{16m_{\text{eff.}}c^2}([\mathbf{Hr}])^2. \quad *$$

Here, **L** is the angular momentum of the exciton, which, it is assumed, is composed of two

*$\mathbf{HL} = \mathbf{H}\cdot\mathbf{L}$; $[\mathbf{Hr}] = \mathbf{H}\times\mathbf{r}$.

identical quasi-particles of charge e and mass m_{eff}. Due to the small size of the samples the diamagnetic effect is inconsequential; thus, even for a particle of dimensions $\sim 3 \times 10^{-6}$ cm

$$\Delta E \sim (e^2/16mc^2)\,H^2\overline{r^2} \sim 10^{-24}H^2.$$

At the same time, the depression, associated with paramagnetism, of the lower of the Zeeman sublevels of the exciton level is $\Delta E = -e\hbar l H/2m_{\text{eff}}c$, where $\hbar l$ is the angular momentum of the exciton. Even for $l = 1$ and $m_{\text{eff}} = m$ we have $\Delta E \approx 10^{-20}H > 10^{-17}$, for $H > 10^3$. If the lower exciton level is sufficiently low ($E_e \ll 2\Delta \sim 10^{-15}$), $m_{\text{eff}} \ll m$, or excitons are present with $l \gg 1$, then in the fields used ($H > 10^3$) the lower Zeeman sublevel may reach the energy of the ground state. The latter thereby becomes unstable, and another state should arise which may show paramagnetic susceptibility.

The suggestion just advanced seems to us scarcely probable, but it deserves attention in view of the fact that the experiments of [23,24] have not been explained. Moreover, the hypothesis concerning the role of Zeeman splitting of the exciton levels can be checked; from this viewpoint superconductors should show no Knight shift in a sufficiently weak field.

The problem of excitons in superconductors is among those which have been least studied, while for the most interesting case of metals of the type of Pb and Hg no theory exists at all. For this reason, therefore, it seemed appropriate to us to devote the present article to questions of merely hypothetical character. Moreover, even if our suggestions turn out to correspond only in part to reality, then the part played by excitons in superconductors may be considered to be as great as in the case of semiconductors. Here, evidently, a whole province is laid open for new experimental and theoretical investigations.

In conclusion, I take this opportunity to thank G. P. Motulevich for discussing the question she has raised concerning the possibility of observing second sound in superconductors, and L. P. Gor'kov for his comments.

[1] V. L. Ginzburg, JETP **14**, 177 (1944), J. Phys. U.S.S.R. **8**, 148 (1944); Sverkhprovodimost' (Superconductivity), AN SSSR, 1946.

[2] V. L. Ginzburg, JETP **21**, 979 (1951).

[3] P. G. Klemens, Handbuch der Physik **14**, 198 (1956); Proc. Phys. Soc. **A66**, 576 (1953).

[4] B. T. Geĭlikman, JETP **34**, 1042 (1958), Sov. Phys. JETP **34**, 721 (1958).

[5] L. D. Landau and E. M. Lifshitz, Mekhanika sploshnykh sred (Mechanics of Continuous Media), Gostekhizdat 1953, ch. 16.
[6] V. L. Ginzburg, Usp. Fiz. Nauk **48**, 25 (1952), Fortschr. Phys. **1**, 101 (1953).
[7] C. J. Gorter, Progr. in Low Temperature Physics (Amsterdam) **1**, 1 (1955).
[8] J. Bardeen and J. R. Schrieffer, Progr. in Low Temperature Physics, (Amsterdam) **3**, 170 (1961).
[9] V. L. Ginzburg and V. P. Silin, JETP **29**, 64 (1955), Sov. Phys. JETP **2**, 46 (1956).
[10] Bogolyubov, Tolmachev, and Shirkov, Novyĭ metod v teorii sverkhprovodimosti (New Method in Superconductivity Theory), AN SSSR, 1958.
[11] P. W. Anderson, Phys. Rev. **112**, 1900 (1958).
[12] T. Tsuneto, Phys. Rev. **118**, 1029 (1960).
[13] A. Bardasis and J. R. Schrieffer, Phys. Rev. **121**, 1050 (1961).
[14] Ginzburg, Rukhadze, and Silin, FTT **3**, 1835 (1961), Sov. Phys. Solid State **3**, 1337 (1961).
[15] Decker, Mapother, and Shaw, Phys. Rev. **112**, 1888 (1958).
[16] D. M. Ginsberg and M. Tinkham, Phys. Rev. **118**, 990 (1960).
[17] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).
[18] K. Mendelssohn, Progr. in Low Temperature Physics (Amsterdam) **1**, 184 (1955).
[19] J. L. Olsen, Proc. Phys. Soc. **A65**, 518 (1952).
[20] Abrikosov, Gor'kov, and Khalatnikov, JETP **37**, 187 (1959), Sov. Phys. JETP **10**, 132 (1960).
[21] M. Spiewak, Phys. Rev. **113**, 1479 (1959).
[22] P. B. Miller, Phys. Rev. **121**, 435 (1961).
[23] F. Reif, Phys. Rev. **106**, 208 (1957).
[24] G. M. Androes and W. D. Knight, Phys. Rev. **121**, 779 (1961).
[25] K. Yosida, Phys. Rev. **110**, 769 (1958).
[26] A. A. Abrikosov and L. P. Gor'kov, JETP **39**, 480 (1960), Sov. Phys. JETP **12**, 337 (1961).

Translated by S. D. Elliott
144