Superconducting transition temperature for semimetals like bismuth

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Abstract. The superconducting transition temperature T_c for semimetals like bismuth has been calculated as a function of the density n_c of the electron and hole charge carriers. A simplified two-band model for describing the longitudinal dielectric function for such a system has been used in our model calculation. We find that the attractive interaction responsible for the instability of the normal ground state comes not only from the exchange of lattice phonons, but also from the electron-hole sound mode, provided the ratio of the averaged hole to electron mass, $m_h/m_e \neq 1$. We have compared our theoretical values of $T_c(n_c)$ with experimental results for bismuth under hydrostatic pressure, and find reasonable agreement if m_h/m_e is assumed to have a value which is only slightly larger than that at atmospheric pressures. A linear variation of the negative band gap as a function of pressure has been assumed for the sake of this comparison.

1. Introduction

In a recent paper (Bhattacharyya and Jha 1978, hereafter referred to as I) the possibility of an excitonic insulator transforming under pressure into a superconductor rather than into a semimetal has been considered. There it was found that even on neglecting the usual lattice-phonon induced electronic attraction, a large transition temperature T_c (~100°K) could be obtained provided the ratio of the hole mass to the electron mass m_h/m_e, or its inverse, is much greater than one, and the effective 'carrier' density $n_c > 10^{19}$ cm^{-3}. The mechanism leading to such large transition temperatures can be roughly understood in analogy with the ionic-phonon mechanism.

Imagine a metal being made up of an equal number of ions and conduction electrons. If these two fluids do not interact with each other, there are collective excitations at the electronic and ionic plasma frequencies ω_{pe} and ω_{pI}, respectively. If now, the electron-ion interaction is switched on, ω_{pe} is only slightly perturbed, but ω_{pI} is strongly affected. The ionic plasma frequency is renormalised by the screening of the conduction electrons, and becomes an acoustic mode (longitudinal lattice phonons) with a linear dispersion for long wavelengths. Note that nowhere in this argument do we demand the ions to be localised, because of their heavy mass, at lattice sites. Of course, the localisation at lattice sites leads to additional acoustic modes which are transverse. Clearly, a similar situation appears in an interacting electron-hole plasma if $m_h \neq m_e$, and one gets an additional sound-like longitudinal collective mode in such systems. This can be called the electron-hole sound (EHS)

mode. There is, however, one important difference here: both the holes and the electrons may degenerate nonlocalised charge carriers. If $m_h \gg m_e$, then the density of states at the Fermi-surface (for one spin) $N_h(0) \gg N_e(0)$, and the total superconducting effective BCS coupling constant g is determined by g_{hh}, the hole coupling constant. Similarly, for $m_e \gg m_h$, g_{ee}, the electron coupling constant is dominant. This, after appropriate renormalisation, leads to an effective g which is of the same order as in an ordinary metal. However, the range ω_m of the attractive BCS interaction is set by the frequency of the EHS mode at $q \sim 2k_F$, which is about $\omega_{ph} \simeq (4\pi n_c e^2/m_h)^{\frac{1}{2}}$, and is, therefore, much larger than ω_D, the Debye frequency. Hence it is possible for the transition temperature $k_B T_c \sim \hbar\omega_m \exp(-1/g)$ to be much larger than that expected on the basis of the lattice phonon mechanism. It was further shown that this EHS exchange mechanism by itself, cannot lead to superconducting transitions if m_h/m_e (or m_e/m_h when $m_e > m_h$) $\lesssim 5$; when $m_h/m_e = 1$, the new mode of course does not exist. The present work addresses itself to the question whether a similar mechanism is already partially operative in semimetals and, in particular, whether it is possible to explain the pressure dependence of T_c in such systems.

In the conventional picture within the jellium model, the attractive lattice phonon coupling constant λ_{ph} is equal to the repulsive Coulomb coupling constant μ. It decreases with increasing electron density n, from a maximum value of 0·5 in the very low density region. If $dn/dP > 0$, we should then normally expect $dT_c/dP < 0$, in contrast with the experimental behaviour where T_c first increases with pressure, e.g. in bismuth and its alloys (Il'ina and Itskevich 1970, Il'ina 1976), and then decreases at high pressures (see figure 1). This, we believe, is a direct indication of the inadequacy of the lattice-phonon jellium model and it has led us to ask whether a resolution of this discrepancy may be found in the model that was proposed in I or it is due to other band-structure effects neglected in the jellium model. In fact, we find that we can reproduce the behaviour of T_c mentioned earlier, within a model similar to I, but extended to include the polarisation of the lattice, i.e. with the inclusion of
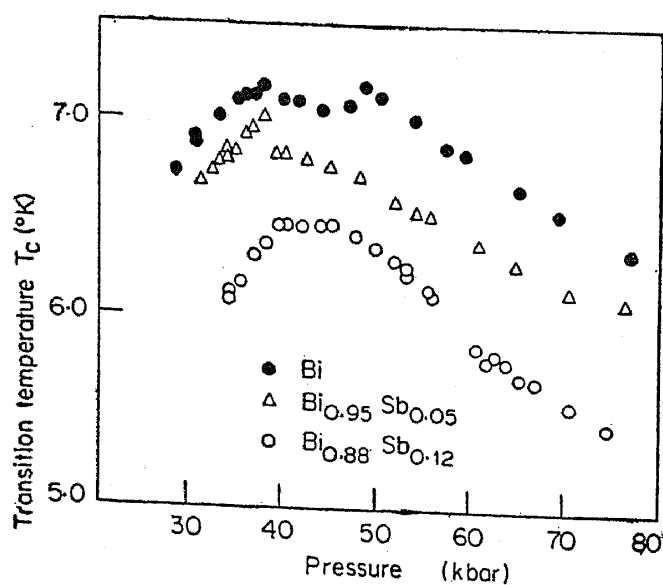

Figure 1. Experimental results on the pressure dependence of the superconducting transition temperatures of bismuth and its alloys with antimony (Il'ina 1976).

both lattice sound and EHS exchange mechanisms. We have made here, a more careful study of bismuth, simply because there are more experimental data on T_c (P) available for this material than for the other semimetals.

The plan of the paper is as follows: in § 2, we extend the method of Ginzburg and Kirzhnits (1972) for calculating T_c for a single band system to the problem at hand, involving two bands and three different interaction kernels due to the ionic-sound, the electron-hole sound and the direct Coulomb repulsion, with asymmetric frequency cut-offs. In § 3, we describe our model dielectric function for a semimetal, and show how to obtain the respective superconducting interaction kernels. Finally, in § 4, we give the results of our calculations, particularly for Bi and similar semimetals, and discuss their significance.

2. Formulation of the superconducting interaction

For a single band of carriers the superconducting transition temperature T_c is determined from the nontrivial solution of the linearised integral equation (Ginzburg and Kirzhnits 1972).

$$\Phi(\mathbf{k}) = - \int \frac{d^3k'}{(2\pi)^3} W(\mathbf{k}, \mathbf{k}') \frac{\tanh(\beta_c \xi_{k'}/2)}{2 \xi_{k'}} \Phi(\mathbf{k}'), \quad \beta_c = \frac{1}{k_B T_c}, \tag{1}$$

where

$$W(\mathbf{k}, \mathbf{k}') = \frac{4\pi e^2}{|\mathbf{k} - \mathbf{k}'|^2} \left[1 - 2 \int_0^\infty \frac{d\omega' \, \rho(\mathbf{k} - \mathbf{k}', \omega')}{\omega' + (|\xi_\mathbf{k}| + |\xi_{\mathbf{k}'}|)/\hbar} \right], \tag{2}$$

and $\rho(\mathbf{q}, \omega)$ is the spectral representation function of the effective electron-electron interaction $V_{eff}(\mathbf{q}, \omega)$. The function $W(\mathbf{k}, \mathbf{k}')$ can be thought of as the effective superconducting interaction corresponding to the usual interaction causing the transition in which the Cooper pair $\mathbf{k}' \uparrow$ and $- \mathbf{k}' \downarrow$ changes to $\mathbf{k} \uparrow$ and $- \mathbf{k} \downarrow$, respectively, with momentum transfer $\hbar \mathbf{q} = \hbar \mathbf{k} - \hbar \mathbf{k}'$ and energy transfer $\hbar \omega = \xi_\mathbf{k} - \xi_{\mathbf{k}'}$, ξ_k being the energy measured from the Fermi energy E_F. For a homogeneous isotropic system, the spectral representation function $\rho(\mathbf{q}, \omega)$ is given by (Kirzhnits *et al* 1973)

$$\rho(\mathbf{q}, \omega) = -\frac{1}{\pi} \frac{q^2}{4\pi e^2} \text{Im} \, V(\mathbf{q}, \omega) = -\frac{1}{\pi} \text{Im} \, \epsilon^{-1}(\mathbf{q}, \omega), \tag{3}$$

where $\epsilon(\mathbf{q}, \omega)$ is the longitudinal dielectric response function of the system. If one carries out an angular average over θ, the angle between $\mathbf{k}$ and $\mathbf{k}'$, or equivalently over $q = (k^2 + k'^2 - 2kk' \cos \theta)^{1/2}$, and changes the variables from $\mathbf{k}$ and $\mathbf{k}'$ to ξ and ξ', one obtains

$$\Phi(\xi) = - \int_{-\infty}^\infty \frac{d\xi'}{2\xi'} \tanh(\beta_c \xi'/2) K(\xi, \xi') \Phi(\xi'), \tag{4}$$

where the kernel $K(\xi, \xi')$ is given by

$$K(\xi, \xi') = \frac{4\pi e^2 N(\xi)}{k(\xi) k'(\xi')} \int_{|k(\xi)-k'(\xi')|}^{k(\xi)+k'(\xi')} \frac{dq}{2q} \left[1 + \frac{2}{\pi} \int_0^\infty \frac{d\omega' \, \mathrm{Im} \, \epsilon^{-1}(q, \omega')}{\omega' + (|\xi| + |\xi'|)/\hbar} \right]. \quad (5)$$

Here, $N(\xi) = d^3k/(2\pi)^3 \, d\xi$ is the density of states for one type of spin and $k(\xi) = [2m \, (\xi + E_F)]^{\frac{1}{2}}/\hbar$. If the dielectric function $\epsilon^{-1}(q, \omega)$ is split into contributions arising from the direct electron-electron Coulomb interaction and various indirect exchange interactions, as

$$\epsilon^{-1}(\mathbf{q}, \omega) = \sum_i \epsilon_i^{-1}(\mathbf{q}, \omega), \quad (6)$$

the corresponding kernels can also be rewritten as

$$K(\xi, \xi') = \sum_i K_i(\xi, \xi'). \quad (7)$$

The determination of T_c essentially reduces to solving the generalised gap equation (4) in terms of the kernels $K_i(\xi, \xi')$. It can be shown that $K_i(\xi, \xi')$ is a smooth real function of its arguments and falls off separately in each argument. If one splits the bare Coulomb interaction term, i.e. the first term 1 within the square brackets in equation (5), in a manner consistent with the screening of long wavelength interactions due to each mode, including the Coulomb plasma mode labelled by c, one expects K_c to be repulsive for small ξ and ξ' whereas the other remaining kernels will be attractive in this region. A good estimate of T_c in such a case is usually obtained by replacing each kernel $K_i(\xi, \xi')$ by suitable square-wells. Explicitly, one assumes

$$K_i(\xi, \xi') \simeq K_i(0, 0), \text{ for } - \hbar \, \omega_{iL} \leqslant \xi \, \xi' \leqslant \hbar \, \omega_{iR} \quad (8)$$
$$= 0, \text{ otherwise}$$

where the upper frequency cut-off ω_{iR} is the frequency of the corresponding mode for $q \sim 2 k_F$, and the lower cut-off ω_{iL} is the minimum of ω_{iR} and E_F. For the Coulomb kernel, $\omega_{3R} \simeq \omega_{pe}$, the electron plasma frequency. Using equation (5) and the usual dispersion relations, the strength of the individual coupling constants can be rewritten more simply as

$$K_i(0, 0) = \frac{N(0)}{2k_F^2} \int_0^{2k_F} dq \, \frac{4\pi e^2}{q} \, \epsilon_i^{-1}(q, 0). \quad (9)$$

For a three-square-well model involving two attractive exchange mechanisms with coupling constants $\lambda_1 = - K_1(0, 0)$ and $\lambda_2 = - K_2(0, 0)$, respectively, and the direct repulsive Coulomb coupling constant $\mu = K_3(0, 0) = K_c(0, 0)$, solution of equation (4) leads to the transition temperature T_c given by

$$k_B T_c = 1 \cdot 14 \, \hbar \, \omega_{1m} \exp(-1/g_{\mathrm{eff}}), \, k_B T_c \ll \hbar \, \omega_{1m}, \quad (10)$$

where $\quad g_{\text{eff}} = \lambda_1 + \dfrac{\lambda_{23}}{1 - \lambda_{23} \ln (\omega_{2m}/\omega_{1m})}$ (11)

$$\mu^* = \mu \Big/ \left(1 + \mu \ln \frac{\omega_{3m}}{\omega_{2m}}\right), \quad \lambda_{23} = \lambda_2 - \mu^*.$$ (12)

Here, the effective range $\omega_{im} = (\omega_{iL}\,\omega_{iR})^{\frac{1}{2}}$, and we have assumed $\omega_{1m} < \omega_{2m} < \omega_{3m}$. Note that the above expression is valid only in the weak coupling limit. To take care of strong coupling effects, one can approximately change

$$\lambda_1 \to \lambda_1^* = \frac{\lambda_1}{1 + \lambda_1}, \quad \lambda_{23} \to \lambda_{23}^* = \frac{\lambda_{23}}{1 + |\lambda_{23}|},$$ (13)

in the above expression for T_c.

For carriers in two different bands, as in the case of semi-metals, a slight extension of the above method is necessary (Geilikman and Kresin 1974). Note that now we have two different Fermi energies E_{Fe} and E_{Fh}, and hence different possible ranges $\omega_{im\mu}$ ($\mu = e$ or h). In such a case, we have to first calculate g_{ee} and g_{hh} using the corresponding expressions (11) to (13). Except for the density of states factor $N_\mu(0)$ in the coupling constant $\lambda_{\mu\nu}^{(i)} = -\overline{V}_{\mu\nu}^{(i)} N_\nu(0)$ for each mode[†], if the average interaction $\overline{V}_{\mu\nu}^{(i)}$ is assumed to be the same for different carriers (see I), for the two band case one finds

$$k_B T_c = 1{\cdot}14\,\hbar\,(\omega_{1me})^{[N_e(0)]/[N_e(0) + N_h(0)]}\,(\omega_{1mh})^{[N_h(0)]/[N_e(0) + N_h(0)]}$$

$$\times \exp\left[-1/(g_{ee} + g_{hh})\right]$$ (14)

Here, for $\mu = e, h$,

$$g_{\mu\mu} = \lambda_{\mu\mu}^{(1)} + \lambda_{\mu\mu}^{(23)} \Big/ \left[1 - \lambda_{\mu\mu}^{(23)} \ln (\omega_{2m\mu}/\omega_{1m\mu})\right],$$ (15)

$$\lambda_{\mu\mu}^{(23)} = \lambda_{\mu\mu}^{(2)} + \lambda_{\mu\mu}^{(3)} \Big/ \left[1 - \lambda_{\mu\mu}^{(3)} \ln (\omega_{3m\mu}/\omega_{2m\mu})\right],$$ (16)

$$\omega_{1m\mu} = (\omega_{iL\mu}\,\omega_{iR\mu})^{\frac{1}{2}},$$ (17)

$$\omega_{iR\mu} = \omega_i\,(2k_{F\mu}), \quad \omega_{iL\mu} = \text{Min}\,(\omega_{iR\mu}, E_{F\mu}/\hbar).$$ (18)

In the next section, we discuss the application of this procedure to a simplified model of the dielectric function in simple semimetals.

[†]The explicit expression for $\lambda_{\mu\mu}^{(i)}$ is given in equation (35).

3. Interaction kernels in semimetals

The longitudinal dielectric function for a semimetal can be approximately written as

$$\epsilon(\mathbf{q}, \omega) = \epsilon_{core}(\mathbf{q}, \omega) + 4\pi\alpha_e(\mathbf{q}, \omega) + 4\pi\alpha_I(\mathbf{q}, \omega), \tag{19}$$

where $\epsilon_{core}(\mathbf{q}, \omega)$ corresponds to the polarisability of the core electrons and $\alpha_e(\mathbf{q}, \omega)$ is the polarisability of the valence electrons in partially filled bands. The third term $\alpha_I(\mathbf{q}, \omega)$ is the ionic polarisability. In the frequency region of interest, ϵ_{core} can be assumed to be independent of frequency and replaced by a constant.

$$\epsilon_{core}(\mathbf{q}, \omega) = \epsilon_{co} = \text{constant.} \tag{20}$$

The calculation of $\alpha_e(\mathbf{q}, \omega)$, in general, can be quite subtle (Cohen 1969). In semimetals, where one has degenerate electrons and holes, it is written, within the random phase approximation, as the sum of intra-band and inter-band contributions. The intra-band terms can be parametrised, as in the jellium model, by the plasma frequencies $\omega_{p\mu}$ ($\mu = e$ or h), and the screening wave vectors $q_{s\mu}$ which give the correct static compressibility. These are constructed to be correct in both static and high-frequency limits. In other words, we can assume

$$4\pi\alpha_{intra}(\mathbf{q}, \omega) = \frac{A_1}{y_1 - \omega^2} + \frac{A_2}{y_2 - \omega^2}, \tag{21}$$

where $A_1 \equiv \omega_{pe}^2 = 4\pi n_e e^2/m_e,$

$$A_2 \equiv \omega_{ph}^2 = 4\pi n_h e^2/m_h,$$

$$y_1 \equiv \alpha_1 q^2 = (\omega_{pe}^2/q_{se}^2) q^2, \tag{22}$$

$$y_2 \equiv \alpha_2 q^2 = (\omega_{ph}^2/q_{sh}^2) q^2.$$

The screening wavevector $q_{s\mu}$ is given by

$$q_{s\mu}^2 = (K/K_f)_\mu \, q_{FT\mu}^2 = (K/K_f)_\mu \frac{6\pi n_\mu e^2}{E_{F\mu}} \tag{23}$$

where $(K/K_f)_\mu$ is the ratio of the actual compressibility to the free compressibility of the corresponding interacting liquid. For small $r_{s\mu}$, defined by

$$r_{s\mu} = (9\pi/4)^{1/3} (m_\mu e^2/\hbar^2 k_{F\mu}), \tag{24}$$

i.e. for large density, one has

$$(K_f/K)_\mu \to (1 - \alpha r_{s\mu}/\pi), \quad \alpha = (4/9\pi)^{1/3}, \tag{25}$$

in the Hartree-Fock approximation. Its behaviour at low densities, i.e. for large $r_{s\mu}$, is not very well known (see e.g., Shastry *et al* 1978), but is expected to vanish (Wigner 1938) at some large $r_{s\mu}$. Instead of using an elaborate interpolation scheme, approximately, we assume

$$(K_f/K)_\mu \simeq 1/(1+\alpha r_{s\mu}/\pi) \tag{26}$$

in the density region of interest to us. The interband terms are also not so straightforward, but in the frequency range of interest to us, if we ignore the small excitonic effects, we can again take it to be a constant $A_3/(E_D^2/\hbar^2)$ (see I). This can be combined with the core contribution (20), the total being redefined as another constant ϵ_0. For our purpose, the ionic polarisability $4\pi\alpha_I$ (q, ω) can be replaced by its high-frequency value given by

$$4\pi\alpha_I(\mathbf{q}, \omega) = - A_4/\omega^2, \tag{27}$$

where $A_4 = 4\pi n_I Z_{\text{eff}} e^2/m_I$ is the square of the ionic plasma frequency.

Combining all the contributions, we take the model expression for the longitudinal dielectric function as

$$\epsilon(\mathbf{q}, \omega) = \epsilon_0 \left[1 + \frac{\tilde{A}_1}{y_1 - \omega^2} + \frac{\tilde{A}_2}{y_2 - \omega^2} - \frac{\tilde{A}_4}{\omega^2} \right], \quad \tilde{A}_i \equiv A_i/\epsilon_0. \tag{28}$$

The zeros of the above function give the different longitudinal modes of the system. It would become clear later that for large q, the low-frequency ionic-sound mode frequency is approximately equal to $\tilde{A}_4^{\frac{1}{2}}$. This should correspond approximately to the Debye frequency ω_D, so that we can identify A_4/ϵ_0 by

$$A_4/\epsilon_0 \equiv \tilde{A}_4 \simeq \omega_D^2, \tag{29}$$

and use the corresponding experimental values. Since we are interested in separating out contribution to ϵ^{-1} (q, ω) from different longitudinal modes, we can invert (28) in the form

$$\epsilon^{-1}(\mathbf{q}, \omega) = \epsilon_0^{-1} \left[1 + \sum_{i=1}^{3} \tilde{f}_i(\mathbf{q})/(\omega^2 - \Omega_i^2(\mathbf{q})) \right], \tag{30}$$

where $\Omega_i(\mathbf{q})$ are the frequencies of the three longitudinal modes obtained by solving the cubic equation

$$\Omega^2(y_1 - \Omega^2)(y_2 - \Omega^2) + \tilde{A}_1\Omega^2(y_2 - \Omega^2)$$

$$+ \tilde{A}_2\Omega^2(y_1 - \Omega^2) - \tilde{A}_4(y_1 - \Omega^2)(y_2 - \Omega^2) = 0, \tag{31}$$

and the oscillator strengths $\tilde{f}_i$ (q) given by

$$\tilde{f}_i(\mathbf{q}) = \Omega_i^2(\Omega_i^2 - y_1)(\Omega_i^2 - y_2) \Big/ \pi \underset{j \neq i}{(\Omega_i^2 - \Omega_j^2)}. \tag{32}$$

It is easy to see that the following sum rules are valid:

$$\sum_{i=1}^{3} \Omega_i^2(q) = \tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4 + y_1 + y_2, \tag{33a}$$

$$\sum_{i=1}^{3} \tilde{f}_i(q) = \tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4, \tag{33b}$$

$$\sum_{i=1}^{3} \tilde{f}_i(0) / \Omega_i^2(0) = 1, \tag{33c}$$

where $\tilde{f}_i(0)/\Omega_i^2(0)$ is to be understood as the limiting value of $\tilde{f}_i(q)/\Omega_i^2(q)$ as $q \to 0$. To take care of screening of the long wavelength part of the interaction, one is therefore allowed to rewrite equation (30) in the final form

$$\epsilon^{-1}(q, \omega) = \sum_{i=1}^{3} \epsilon_i^{-1}(q, \omega), \quad \epsilon_i^{-1}(q, \omega) = \epsilon_0^{-1} \left[\frac{\tilde{f}_i(0)}{\Omega_i^2(0)} + \frac{\tilde{f}_i(q)}{\omega^2 - \Omega_i^2(q)} \right]. \tag{34}$$

This separation uniquely ensures that each $\epsilon_i^{-1}(q, 0)$ goes to zero as $q \to 0$, and the integration of the type (9) is well behaved at the lower limit. The above expression can be used directly in equations similar to (9) to calculate the kernels $K_i(0, 0)$ once $\Omega_i^2(q)$ and $\tilde{f}_i(q)$ are known. In the two-band model for electrons and holes, for each mode the coupling constants $\lambda_{\mu\mu}^{(i)}$ and the kernels $K_{\mu\mu}^{(i)}(0, 0)$ for $\mu = e, h$, of course have to be rewritten as

$$\lambda_{\mu\mu}^{(i)} = - K_{\mu\mu}^{(i)}(0, 0) = - \frac{q_{FT\mu}^2}{4k_{F\mu}} \int_0^{2k_{F\mu}} (dq/q) \, \epsilon_i^{-1}(q, 0), \tag{35}$$

where ϵ_i^{-1} is given by (34).

In general, equation (31) has complicated analytic expressions for its roots, except in some limiting cases. In the small q-limit, we find

$$\Omega_1^2(q) = \frac{1}{2} \left[y_1 + y_2 - \frac{y_1 \tilde{A}_1 + y_2 \tilde{A}_2}{\tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4} \right] - \frac{1}{2} \left[\left(y_1 + y_2 - \frac{y_1 \tilde{A}_1 + y_2 \tilde{A}_2}{\tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4} \right)^2 \right.$$
$$\left. - \frac{4 \tilde{A}_4 y_1 y_2}{\tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4} \right]^{\frac{1}{2}}, \tag{36a}$$

$$\Omega_2^2(q) = \frac{1}{2} \left[y_1 + y_2 - \frac{y_1 \tilde{A}_1 + y_2 \tilde{A}_2}{\tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4} \right] + \frac{1}{2} \left[\left(y_1 + y_2 - \frac{y_1 \tilde{A}_1 + y_2 \tilde{A}_2}{\tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4} \right)^2 \right.$$
$$\left. - \frac{4 \tilde{A}_4 y_1 y_2}{\tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4} \right]^{\frac{1}{2}} \tag{36b}$$

$$\Omega_3^2(q) = \tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4 + (y_1 \tilde{A}_1 + y_2 \tilde{A}_2)/(\tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4), \tag{36c}$$

where we recall that $y_1 = a_1 q^2 = (\omega_{pe}^2 / q_{se}^2) q^2$ and $y_2 = a_2 q^2 = (\omega_{ph}^2 / q_{sh}^2) q^2$. Here, Ω_1 corresponds to the lattice-phonon mode, Ω_2 to the EHS mode and Ω_3 to the Coulomb plasma mode. In this limit, we also find

$$\tilde{f}_1(\mathbf{q}) \xrightarrow[q \to 0]{} a_1 q^4, \quad \tilde{f}_2(\mathbf{q}) \xrightarrow[q \to 0]{} a_2 q^4 \text{ and } \tilde{f}_3(\mathbf{q}) \xrightarrow[q \to 0]{} a_3 = \text{const.} \tag{37}$$

Similarly, for large q-values, when $\tilde{A}_4 < \tilde{A}_1, \tilde{A}_2$, one has

$$\Omega_1^2(\mathbf{q}) = \tilde{A}_4, \quad \Omega_2^2(\mathbf{q}) = y_2 + \tilde{A}_2, \quad \Omega_3^2(\mathbf{q}) = y_1 + \tilde{A}_1, \tag{38}$$

if $m_h > m_e$; otherwise the expressions for modes 2 and 3 get interchanged. For arbitrary values of q, we have solved equation (31) numerically to obtain $\Omega_i^2(\mathbf{q})$. This also allows us to obtain $\tilde{f}_i(\mathbf{q})$, and hence $\epsilon_i^{-1}(\mathbf{q}, \omega)$ and $\lambda_{\mu, i}^{(i)}$, for each mode, by using equations (32), (34) and (35), and numerical integration methods. We have calculated these for various sets of parameters $n_{ec} = n_h = n_c$ (which is a function of pressure), m_e, m_h, ω_D, etc. on a computer. Further, we can take the upper cut-off frequencies

$$\omega_{1R\mu} \simeq \tilde{A}_4^{\frac{1}{2}}, \quad \omega_{2R\mu} \simeq \text{Min}\,(\tilde{A}_1^{\frac{1}{2}}, \tilde{A}_2^{\frac{1}{2}}) \text{ and } \omega_{3R\mu} = \Omega_3\,(2k_{F\mu}).$$

For the purpose of illustration, the dispersion relations obtained for the three modes, i.e. the frequency as the function of the wave vector, have been plotted in figure 2, with parameters $n_c = 2 \cdot 75 \times 10^{17}$ cm^{-3}, $m_e/m = 0 \cdot 045$, $m_h/m = 0 \cdot 141$, $\epsilon_0 = 1 \cdot 0$ and $\theta_D = (\hbar \, \omega_D/k_B) = 120°$K. (Here the average mass $m_\mu = (m_1 m_2 m_3)_\mu^{\frac{1}{3}}$ where m_i's are the
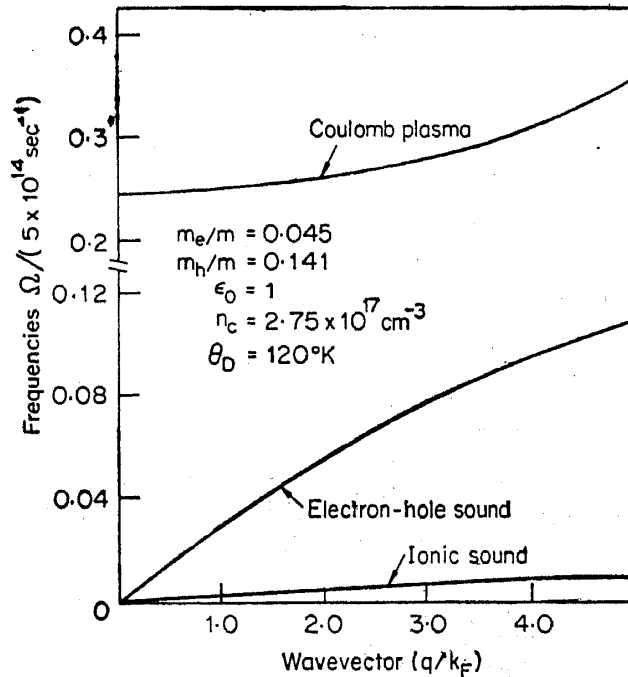

Figure 2. Dispersion relations for (i) the ionic sound, (ii) the electron-hole sound and (iii) the Coulomb plasma modes in a bismuth-like semimetal.

effective mass values evaluated at the Fermi surface). These parameters correspond to the case of bismuth at the atmospheric pressure (Dresselhaus 1971). The two lower modes, i.e. the ionic sound mode Ω_1 and the electron-hole sound mode Ω_2, are sound-like with ω^2 proportional to q^2 for small q-values. The Coulomb plasma mode Ω_3, however, tends to a constant $(\tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4)^{\frac{1}{2}}$ as $q \to 0$.

In general, we find that the interaction kernels due to the ionic sound mode and the electron-hole sound mode are attractive for low frequencies. The Coulomb plasma mode, however, is repulsive for low frequencies corresponding to the repulsive direct Coulomb interaction in the jellium model. Now that the coupling constants $\lambda_{\mu\mu}^{(i)}$ and the cut-off frequencies are known, the procedure explained in § 2 can be carried out to obtain g_{ee} and g_{hh} and the corresponding superconducting transition temperature T_c for any given set of parameters. This will be discussed in detail in the next section.

4. Results and discussions

In the last two sections, we have described how we can calculate the coupling constants $\lambda_{\mu\mu}^{(i)}$ for each of the three modes in our two-band model for the semimetal, and consequently how to determine the corresponding T_c, using equations (14) to (19). Fro bismuth at atmospheric pressure, the carrier density is $n_c \equiv n_e = n_h \simeq 2.75 \times 10^{17}$ cm^{-3}, the average electron mass is $m_e \simeq 0.045$ times the bare electron mass m, the average $m_h/m_e \simeq 3.2$ and the Debye temperature $\theta_D \simeq 120°$K. With $\epsilon_0 \simeq 1$, this set of parameters leads to a T_c, in our model, which is less than 10^{-3} °K. This is consistent with the experiment where no transition has been observed at low pressures. In fact, in this case, since the mass ratio m_h/m_e is less than 5, as already noted in I, there is no superconducting transition if the attractive ionic sound mode 1 is completely ignored in our calculations (i.e. when $A_4 \to 0$). However, because of the fact that the contribution due to EHS-mode is a sensitive function of m_e/m_h, and increase with this ratio, if we include both the ionic-sound and the EHS contributions, one expects an observable T_c at higher densities, even when m_h/m_e is less than 5. In such a model, the coupling constants and the transition temperature T_c are not monotonically decreasing functions of n_c, as in the lattice phonon jellium model; but there is an initial increase with n_c before these start decreasing. Since, on application of pressure, n_c is expected to generally increase in semimetals, we expect that inclusion of the EHS mode may allow us to explain the observed variation of T_c of the type shown in figure 1.

On application of pressure, bismuth is known to undergo polymorphic transformations, as established by Bridgman (1952) by measuring the volume compressibility and by Bundy (1958) from electrical resistance measurements. The values of the transformation pressures were, $P_{\text{I-II}} \simeq 25.3$ kbar, $P_{\text{II-III}} \simeq 27.0$ kbar, $P_{\text{III-IV}} \simeq 44.8$ kbar, $P_{\text{IV-V}} \simeq 65.0$ kbar and $P_{\text{V-VI}} \simeq 89.5$ kbar. In the transformations III-IV and IV-V, the volume-change $\Delta V/V_0$ was small, approximately 0.5%. While Bi I is not super-conducting, Bi II (Brandt and Ginzburg 1965), Bi III, Bi IV and Bi V (Il'ina and Itskevich 1970) and Bi VI (Wittig 1966) have been observed to undergo superconducting transitions. A detailed and more precise experimental study of the

pressure-dependence of T_c in bismuth in the 30-80 kbar pressure range, i.e. III-IV-V phases, has been made by Il'ina (1976) who has also studied the Bi-Sb alloy systems. But there is no detailed study of the values for n_c, m_e, m_h/m_e and ω_D and of their pressure dependences. However, it is fair to assume that, here ω_D is a slowly varying function of pressure P, the negative band gap

$$E_g \simeq \text{constant } (P), \tag{39}$$

i.e. $$n_c \simeq \beta P^{3/2} \text{ or } (n_c/10^{18} \text{ cm}^{-3}) = (P/P_0)^{3/2} \tag{40}$$

and the mass ratio m_h/m_e is only slightly different from $\simeq 3\cdot 2$, the value at low-pressure. In fact, since in our case the most sensitive parameters are m_h/m_e and n_c, in that order, we have tried to fit the experimental values for T_c in bismuth, as shown in figure 1, by assuming θ_D still to be 120°K, and using only two free parameters P_0 and m_h/m_e. We find that we get the best fit for our theoretical values of T_c with the corresponding experimental values in bismuth, if we choose $P_0 \simeq 10\cdot 55$ kbar and $m_h/m_e \simeq 4\cdot 8$, over the whole range of pressures between 30 kbar and 80 kbar for which the experimental observations are available. We point out here that equations (39) and (40) are only approximately valid. A more reasonable form to choose would be $E_g - E_{g0} \propto P$, where E_{g0} is the *extrapolated* value of E_g at low pressures. We have checked that a very good fit is obtained with $E_{g0} \ll E_g$ in the region of interest, thus validating our choice of the form given above. Note that we have neglected the damping of the EHS-mode, possibly mainly due to the interband collisions, in our analysis. This will definitely change the quantitative results of our calculations, but the basic qualitative results should remain valid.
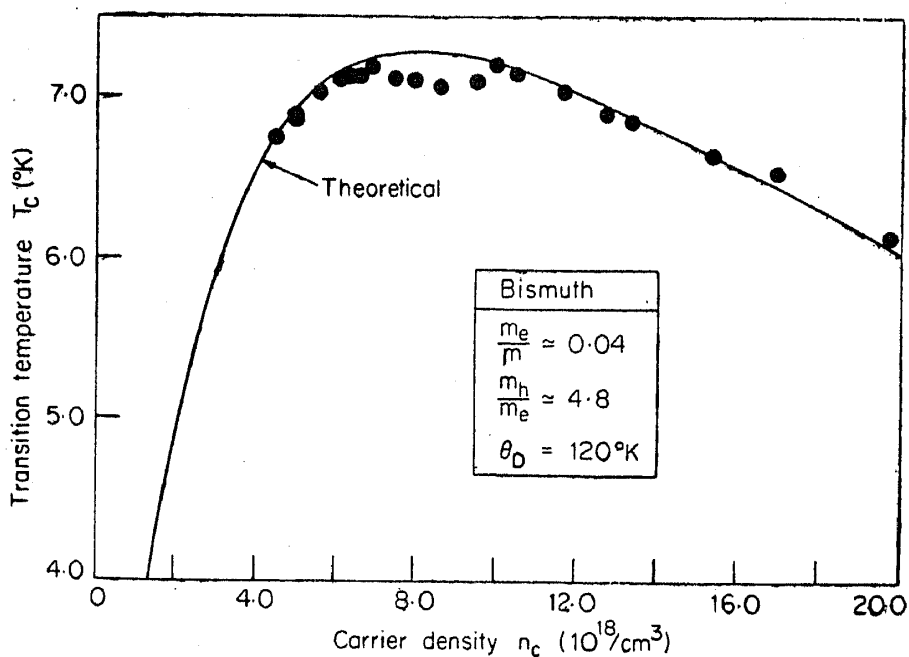

Figure 3. Theoretically calculated values of the superconducting transition temperature T_c as a function of the carrier density n_c for bismuth under pressure. The circles correspond to the experimental values for bismuth, obtained from figure 1 (see text).

The theoretical values of T_c, in our case, as a function of n_c and the corresponding experimental values obtained from figure 1 and equation (40) are plotted in figure 3. There is a close correspondence between these two results. It should be noted that the value used for m_h/m_e is not very different from its value in the low pressure phase. With the application of pressure, in the new phase there is always the possibility of compression and rearrangement of different valleys occupied by the carriers, and hence a change in the value of the average mass $m_\mu = (m_1 m_2 m_3)_\mu^{1/3}$. In this connection, it is interesting to note that for bismuth, in the phase transformations Bi III → Bi IV → Bi V, the volume changes are small compared to the change in the Bi I → Bi III transformation. This may, in a way, justify our taking m_e and m_h/m_e same in the 30–80 kbar region. Also, it should be emphasised that the final value of P_0 used to fit the data is of reasonable order in magnitude.

Our calculations and analysis can be extended to the case of arsenic and antimony also. However, the experimental data on the pressure dependence of T_c for these materials are not available in detail. It will be very hard, therefore, to carry out detailed analysis as in the case of bismuth. In figure 4, we, however, present the results of our calculations and the possible density-dependence of T_c in these materials. The parameters m_h/m_e are chosen to approximately fit the maximum observed values of T_c in arsenic (Berkman and Brandt 1969) and antimony (Wittig 1969) under pressure. It is clear from our results that T_c in arsenic is very small because there the mass ratio m_h/m_e is closer to 1 as compared to the other two materials.

Before concluding, it should be emphasised that although we have demonstrated here very explicitly that the inclusion of EHS-exchange mechanism is crucial to explain the pressure-dependence of T_c in a semimetal like bismuth, it is not clear that our explanation is unique. For example, unless complete band-structure calculations for interacting electron- and hole-fluids are performed for these semimetals, one is never sure whether the picture is complete. Nevertheless, within our simplified model,
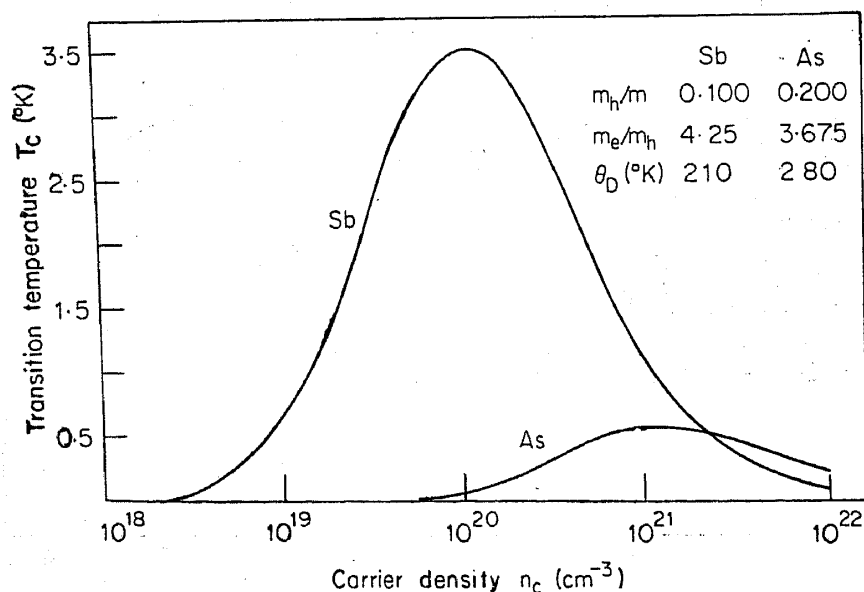

Figure 4. Theoretically calculated values of the superconducting transition tempeture T_c as a function of n_c, the carrier density, with parameters relevant to arsenic and antimony.

we have shown that the ratio of the average masses m_h/m_e is an extremely sensitive parameter in determining the superconducting transition in semimetals. This fact is expected to retain its validity even in more elaborate calculations of T_c.

A real test of the model proposed here can, of course, only be made if the electron and hole masses m_e and m_h, the Debye temperature θ_D and the carrier concentration n_c are known as functions of pressure. It should be borne in mind that given this experimental information, we have a unique way to determine T_c within the formalism. Future experiments in this regard should, therefore, be extremely interesting. If indeed the role of the EHS exchange mechanism is established, then it would be worthwhile to look for a semimetal with $m_h/m_e \gg 1$ and $n_c \sim 10^{20}$ cm^{-3} which would be expected to have a high superconducting transition temperature.

We would like to conclude with a brief comparison of our model for $m_h/m_e \gg 1$ with that of Abrikosov (1978). In our case, since the holes are delocalised, the total coupling constant is dominated by that of the holes. However, if m_h/m_e is increased still further, T_c will become comparable with the Fermi temperature of the holes. They will then form a lattice and the total coupling constant will be determined essentially by that of the electrons which, as our calculations indicate, is small. Thus, in the Abrikosov limit, T_c will be small whereas in the regime considered by us, it can be quite large ($\sim 100°$K) for suitable values of the carrier concentration n_c and the effective masses.

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