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 $n_e$ 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, $m_h/m_e = 0.1$. We have compared our theoretical values of $T_c(n_e)$ 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.

Keywords. Superconductivity; transition temperature; semi-metals; electron-hole sound mechanism.

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 $T_c$ ($\sim 100^\circ$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 $n_e > 10^{19}$ 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 $\omega_{pe}$ and $\omega_{pl}$, respectively. If now, the electron-ion interaction is switched on, $\omega_{pe}$ is only slightly perturbed, but $\omega_{pl}$ 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 $m_h/m_e$, 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 $\omega_m$ of the attractive BCS interaction is set by the frequency of the EHS mode at $q \sim 2k_F$, which is about $\omega_{ph} \sim (4\pi n_e e^2/m_h)^{1/2}$, and is, therefore, much larger than $\omega_D$, the Debye frequency. Hence it is possible for the transition temperature $k_BT_c \sim \hbar\omega_m \exp(-1/g)$ 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 $m_e > m_h$) $\leq 5$; 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 $\lambda_{ph}$ is equal to the repulsive Coulomb coupling constant $\mu$. 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 (II'in and Itskevich 1970, II'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

![Graph](image)

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

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

where

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

and $\rho(\mathbf{q}, \omega)$ is the spectral representation function of the effective electron-electron interaction $V_{\text{eff}}(\mathbf{q}, \omega)$. 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 $\hbar \omega = \xi_k - \xi_{k'}$, $\xi_k$ 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)

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

where $\epsilon(\mathbf{q}, \omega)$ is the longitudinal dielectric response function of the system. If one carries out an angular average over $\theta$, 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 $\xi$ and $\xi'$, one obtains

$$\Phi(\xi) = - \int \frac{d\xi'}{2\xi'} \frac{\tanh (\beta_c \xi'/2)}{2 \xi'} K(\xi, \xi') \Phi(\xi'),$$
where the kernel $K(\xi, \xi')$ is given by

$$K(\xi, \xi') = \frac{4\pi e^2 N(\xi)}{k(\xi) k'(\xi')} \int \frac{dq}{2q} \left[ \frac{1}{k(\xi)-k'(\xi')} \right]^{k(\xi)+k'(\xi')} \Gamma + \int_0^{\infty} \frac{d\omega'}{\omega'} \Im \epsilon^{-1}(q, \omega').$$  

(5)

Here, $N(\xi) = d^3 k/(2\pi)^3 \, d\xi$ is the density of states for one type of spin and $k(\xi) = [2m (\xi + E_F)]^{1/2}/\hbar$. 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

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

(6)

the corresponding kernels can also be rewritten as

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

(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 $\xi$ and $\xi'$ 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

$$K_i(\xi, \xi') \approx K_i(0, 0), \text{ for } -\hbar \omega_{IL} \leq \xi, \xi' \leq \hbar \omega_{IR}$$  

(8)

$$= 0, \text{ otherwise}$$

where the upper frequency cut-off $\omega_{IR}$ is the frequency of the corresponding mode for $q \sim 2k_F$, and the lower cut-off $\omega_{IL}$ is the minimum of $\omega_{IR}$ and $E_F$. For the Coulomb kernel, $\omega_{IR} \approx \omega_{pe}$, 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

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

(9)

For a three-square-well model involving two attractive exchange mechanisms with coupling constants $\lambda_1 = -K_3(0, 0)$ and $\lambda_2 = -K_3(0, 0)$, 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

$$k_B T_c = 1.14 \hbar \omega_{1m} \exp(-1/\mu_{eff}), \quad k_B T_c < \hbar \omega_{1m} .$$  

(10)
where
\[ g_{\text{eff}} = \lambda_1 + \frac{\lambda_{23}}{1 - \lambda_{23} \ln \left( \frac{\omega_{2m}}{\omega_{1m}} \right)} \tag{11} \]

\[ \mu^* = \mu \left( 1 + \mu \ln \frac{\omega_{2m}}{\omega_{1m}} \right), \quad \lambda_{23} = \lambda_2 - \mu^*. \tag{12} \]

Here, the effective range \( \omega_{1m} = (\omega_{iL} \omega_{iR})^{1/2} \), and we have assumed \( \omega_{1m} < \omega_{2m} < \omega_{2m} \).

Note that the above expression is valid only in the weak coupling limit. To take care of strong coupling effects, one can approximately change

\[ \lambda_1 \to \lambda_1^* = \frac{\lambda_1}{1 + \lambda_1}, \quad \lambda_{23} \to \lambda_{23}^* = \frac{\lambda_{23}}{1 + \lambda_{23}}. \tag{13} \]

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 (Gellikman and Kresin 1974). Note that now we have two different Fermi energies \( E_F e \) and \( E_F h \), and hence different possible ranges \( \omega_{im\mu} (\mu = e, h) \). 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 \( \lambda_{1(1)}^{(i)} \) \( V_{\mu
u}^{(ii)} N_{\nu} (0) \) for each mode, if the average interaction \( \mathcal{V}_{\mu
u}^{(i)} \) is assumed to be the same for different carriers (see I), for the two band case one finds

\[ k_B T_c = 1.14 \times 10^{-4} \left( \frac{\omega_{1me}}{N_e(0)/[N_e(0) + N_h(0)]} \right) (\omega_{2mh}/[N_e(0)/N_e(0) + N_h(0)]) \times \exp \left[ -1/(g_{ee} + g_{hh}) \right] \tag{14} \]

Here, for \( \mu = e, h, \)

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

\[ \lambda_{2(23)}^{(i)} = \lambda_{2(23)}^{(i)} + \lambda_{1(1)}^{(i)} \left[ 1 - \lambda_{1(1)}^{(i)} \ln \left( \frac{\omega_{2m\mu}}{\omega_{1m\mu}} \right) \right], \tag{16} \]

\[ \omega_{im\mu} = (\omega_{iL\mu} \omega_{iR\mu})^{1/2}, \tag{17} \]

\[ \omega_{iR\mu} = \omega_i (2k_F \mu), \quad \omega_{iL\mu} = \text{Min} \left( \omega_{iR\mu} E_{F\mu} / \hbar \right). \tag{18} \]

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

\[ {\text{\textsuperscript{+}}\text{The explicit expression for } \lambda_{1(1)}^{(i)} \text{ is given in equation (35).}} \]
3. Interaction kernels in semimetals

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

$$\varepsilon(q, \omega) = \varepsilon_{\text{core}}(q, \omega) + 4\pi\alpha_e(q, \omega) + 4\pi\alpha_f(q, \omega),$$  \hspace{1cm} (19)

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

$$\varepsilon_{\text{core}}(q, \omega) = \varepsilon_{\text{co}} = \text{constant.}$$  \hspace{1cm} (20)

The calculation of $\alpha_e(q, \omega)$, 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 $\omega_{\mu k} (\mu = e \text{ or } h)$, 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

$$4\pi\alpha_{\text{intra}}(q, \omega) = \frac{A_1}{y_1 - \omega^2} + \frac{A_2}{y_2 - \omega^2},$$  \hspace{1cm} (21)

where

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

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

$$y_1 = \alpha_e q^2 = (\omega_{pe}^2/q_{pe}^2) q^2,$$

$$y_2 = \alpha_e q^2 = (\omega_{ph}^2/q_{ph}^2) q^2.$$  \hspace{1cm} (22)

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

$$q_{s\mu}^2 = (K/K_f)_{\mu} q_{F\mu}^2 = (K/K_f)_{\mu} \frac{6m_{\mu} e^2}{E_{F\mu}},$$  \hspace{1cm} (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

$$r_{s\mu} = (9\pi/4)^{1/3} \left( m_{\mu} e^2/n^2 k_{F\mu} \right),$$  \hspace{1cm} (24)

i.e. for large density, one has

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

\[
(K_f/K)_\mu \simeq 1/(1 + \alpha r_{s\mu}/\pi)
\]  

(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 \( A_0/(E^2_f/\hbar^2) \) (see I). This can be combined with the core contribution (20), the total being redefined as another constant \( \epsilon_0 \). For our purpose, the ionic polarisability \( 4\pi a_\mu(q, \omega) \) can be replaced by its high-frequency value given by

\[
4\pi a_\mu(q, \omega) = -\frac{A_4}{\omega^2},
\]

(27)

where \( A_4 = 4m_F Z_{\text{eff}} e^2/m_F \) is the square of the ionic plasma frequency.

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

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

(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 \( \tilde{A}_4 \). This should correspond approximately to the Debye frequency \( \omega_D \), so that we can identify \( A_4/\epsilon_0 \) by

\[
\frac{A_4}{\epsilon_0} \equiv \tilde{A}_4 \simeq \omega_D^2,
\]

(29)

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

\[
\epsilon^{-1}(q, \omega) = \epsilon_0^{-1} \left[ 1 + \sum_{i=1}^{3} f_i(q)/(\omega^2 - \Omega_i^2(q)) \right],
\]

(30)

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

\[
\Omega^2(y_1 - \Omega^2)(y_2 - \Omega^2) + \tilde{A}_1 \Omega^2(y_2 - \Omega^2) \\
+ \tilde{A}_2 \Omega^2(y_1 - \Omega^2) - \tilde{A}_4 (y_1 - \Omega^2)(y_2 - \Omega^2) = 0,
\]

(31)

and the oscillator strengths \( f_i(q) \) given by

\[
\tilde{f}_i(q) = \Omega_i^2(\Omega_i^2 - y_j)/\pi (\Omega_i^2 - \Omega_j^2).
\]

(32)
It is easy to see that the following sum rules are valid:

\[ \sum_{i=1}^{3} \Omega_i^2(q) = \tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4 + y_1 + y_2, \]  
\[ \sum_{i=1}^{3} \tilde{f}_i(q) = \tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4, \]  
\[ \sum_{i=1}^{3} \tilde{f}_i(0) / \Omega_i^2(0) = 1, \]

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

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

(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 \( K_{\mu}(0, 0) \) 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 \( \lambda_{\mu}^{(i)} \) and the kernels \( K_{\mu}(0, 0) \) for \( \mu = e, h \), of course have to be rewritten as

\[ \lambda_{\mu}^{(i)} = - K_{\mu}^{(i)}(0, 0) = - \frac{q^2}{4k_F} \int_0^{2k_F} (dq) \epsilon_i^{-1}(q, 0), \]  
\[ \lambda_{\mu}^{(i)} = - K_{\mu}^{(i)}(0, 0) = - \frac{q^2}{4k_F} \int_0^{2k_F} (dq) \epsilon_i^{-1}(q, 0), \]

(35)

where \( \epsilon_i^{-1} \) 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

\[ \Omega_1^2(q) = \frac{1}{2} \left[ y_1 + y_2 - \frac{y_1 \tilde{f}_1 + y_2 \tilde{f}_2}{A_1 + A_2 + A_4} \right] - \frac{1}{2} \left[ \left( y_1 + y_2 - \frac{y_1 \tilde{f}_1 + y_2 \tilde{f}_2}{A_1 + A_2 + A_4} \right)^2 \right. \]
\[ - \frac{4 \tilde{f}_1 y_1 y_2}{A_1 + A_2 + A_4} \right], \]
\[ \Omega_2^2(q) = \frac{1}{2} \left[ y_1 + y_2 - \frac{y_1 \tilde{f}_1 + y_2 \tilde{f}_2}{A_1 + A_2 + A_4} \right] + \frac{1}{2} \left[ \left( y_1 + y_2 - \frac{y_1 \tilde{f}_1 + y_2 \tilde{f}_2}{A_1 + A_2 + A_4} \right)^2 \right. \]
\[ - \frac{4 \tilde{f}_1 y_1 y_2}{A_1 + A_2 + A_4} \right], \]
\[ \Omega_3^2(q) = \tilde{A}_1 + \tilde{A}_2 + \tilde{A}_4 + (y_1 \tilde{f}_1 + y_2 \tilde{f}_2)/(A_1 + A_2 + A_4), \]

(36a) (36b) (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, \( \Omega_1 \) corresponds to the lattice-phonon mode, \( \Omega_2 \) to the EHS mode and \( \Omega_3 \) to the Coulomb plasma mode. In this limit, we also find

\[
\tilde{f}_1(q) \rightarrow a_1 q^4, \quad \tilde{f}_2(q) \rightarrow a_2 q^4 \quad \text{and} \quad \tilde{f}_3(q) \rightarrow a_3 \quad \text{as} \quad q \rightarrow 0
\]  \( (37) \)

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

\[
\Omega_4^2(q) = \tilde{A}_4, \quad \Omega_2^2(q) = \gamma_2 + \tilde{A}_2, \quad \Omega_3^2(q) = \gamma_1 + \tilde{A}_1 \quad \text{as} \quad q \rightarrow 0
\]  \( (38) \)

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

\[
\omega_{1R \mu} \simeq \tilde{A}_4^{1/2}, \quad \omega_{2R \mu} \simeq \min \left( \tilde{A}_1^{1/2}, \tilde{A}_2^{1/2} \right) \quad \text{and} \quad \omega_{3R \mu} = \Omega_3 (2k_{F\mu}).
\]

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 \( n_c = 2.75 \times 10^{17} \text{ cm}^{-3}, m_e/m = 0.045, m_h/m = 0.141, \epsilon_0 = 1 \) and \( \theta_D = (\hbar \omega_D/k_B) = 120^\circ \text{K} \). (Here the average mass \( m_\mu = (m_1 m_2 m_3)^{1/3} \) where \( m_i \)'s are the

![Figure 2](image_url) 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 $\Omega_1$ and the electron-hole sound mode $\Omega_3$, are sound-like with $\omega^2$ proportional to $q^2$ for small $q$-values. The Coulomb plasma mode $\Omega_3$, however, tends to a constant $(A_{\Omega_1} + A_{\Omega_3} + A_{\Omega_3})$ 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 $\lambda_{\mu \nu}^{(i)}$ 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 $\lambda_{\mu \nu}^{(i)}$ 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). For bismuth at atmospheric pressure, the carrier density is $n_e = n_h = n_e \approx 2.75 \times 10^{27}$ cm$^{-3}$, the average electron mass is $m_e \approx 0.045$ times the bare electron mass $m$, the average $m_h/m_e \approx 3.2$ and the Debye temperature $\theta_D \approx 120^\circ$K. With $\epsilon_0 \approx 1$, 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 $A_1 \to 0$). 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 $n_e$ as in the lattice phonon jellium model; but there is an initial increase with $n_e$ before these start decreasing. Since, on application of pressure, $n_e$ 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 I.

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, $P_{I-II} \approx 25.3$ kbar, $P_{II-III} \approx 27.0$ kbar, $P_{III-IV} \approx 44.8$ kbar, $P_{IV-V} \approx 65.0$ kbar and $P_{V-VI} \approx 89.5$ 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 superconducting, 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 $\omega_D$ and of their pressure dependences. However, it is fair to assume that, here $\omega_D$ 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 $\simeq 3.2$, 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 $\theta_D$ still to be $120^\circ\text{K}$, 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 $P_0 \simeq 10.55$ kbar and $m_h/m_e \simeq 4.8$, 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.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{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).}
\end{figure}
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 $m_\mu = (m_1 m_2 m_3)^{1/3}_\mu$. In this connection, it is interesting to note that for bismuth, in the phase transformations Bi III $\rightarrow$ Bi IV $\rightarrow$ Bi V, the volume changes are small compared to the change in the Bi I $\rightarrow$ 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 $m_\mu/m_e$ 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 $m_1/m_e$ 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,
we have shown that the ratio of the average masses $m_n/m_e$ 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 $m_n$, the Debye temperature $\theta_D$ 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 $m_n/m_e \gg 1$ 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 $m_n/m_e \gg 1$ with that of Abrikosov (1978). In our case, since the holes are delocalized, the total coupling constant is dominated by that of the holes. However, if $m_n/m_e$ 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 ($\sim 10^3$K) for suitable values of the carrier concentration $n_c$ and the effective masses.

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