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Interface exciton modes and superconducting transition temperature of a metal in contact with a semiconductor

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Abstract. The problem of superconductivity in a metal-semiconductor system has been studied, using the dielectric formulation of superconductivity. The charge redistribution due to the quantum penetration of the metallic electrons to the semiconductor side is approximated by a simple exponential function. The interface exciton modes are obtained within the framework of classical electrostatics, and their effect in modifying the effective electron-electron interaction near the interface is investigated. It is found that the strength of the excitonic term is small, and by itself, insufficient to lead to superconductivity. Nevertheless, it can alter the superconducting transition temperature of a metal, if it is already superconducting due to some other mechanism. This has been studied as a function of the various parameters entering in the problem.

Keywords. Interface excition; superconductivity; semi-conductor; metal.

1. Introduction

It has been speculated (Ginzburg 1970; Ginzburg and Kirzhnits 1972) in recent years that high temperature superconductivity can be obtained if the attractive phonon exchange mechanism in conventional superconductors is replaced by exchange of some electronic excitation, which has a much higher characteristic energy, and in particular, by the exchange of excitons in a semiconductor. A composite system of a metal and a semiconductor is expected to be most ideal for the occurrence of the exciton mechanism of superconductivity. This is primarily so because of the high density of conduction electrons in metals and the weak damping of excitons in semiconductors. Still, there has been a divergence of opinions as to the strength of the exciton-mediated term in such a system. A recent model calculation by Allender, Bray and Bardeen (ABB) (1973) predicts appreciably high values of the superconducting transition temperature (T_c) in a thin layer of a metal (thickness $L \sim 10$ Å) deposited over a semiconductor. ABB use the exciton-mediated interaction valid for the bulk semiconductor to calculate the effective interaction between electrons tunnelled from the metal side to the semiconductor side. A more careful treatment of semiconductor should, of course take into account the charge redistribution and the considerable modification of the interaction in the neighbourhood of the interface. The estimates on T_c in ABB treatment may not, therefore, be reliable. In fact, Inkson and Anderson (1973) have already pointed out that there is a considerable double

counting of the excitonic effects in the ABB calculation and if those are corrected properly the predicted enhancement in T_c disappears. However, see the reply of Allender *et al* (1973 *b*).

There have been a few other treatments (Inkson 1974; Rangarajan 1974; Uspenskii and Zharkov 1974) of the metal semiconductor system with regard to superconductivity. Inkson (1974) has included the effect of surface plasmons and concludes that there will be no increase in T_c. Rangarajan (1974) has calculated the exciton coupling constant completely neglecting the quantum-mechanical tunnelling and has thereby estimated the amount by which the T_c of a metal is already superconducting will be enhanced. It must be noted that recent experiments (Tsuei and Johnson 1974; Miller *et al* 1973) related to this problem seem to be rather inconclusive.

In order to obtain a more reliable estimate of the extent to which the exciton mediated interaction can alter the existing values of T_c, it becomes essential to investigate the nature of the modified interaction between the electrons in the neighbourhood of the interface. The exchange of the interface excitons rather than purely bulk excitons and their contribution to the effective interaction between the metal electrons near the Fermi surface have to be carefully included. Our object in this paper is to treat the problem semi-classically and include the tunnelling effects neglected in the previous treatment (Rangarajan 1974). We approximate the tunnelling charge density by a simple model expression and study the modification of the interaction in the interface region; the regions far away from the interface being described by phenomenological expressions for the dielectric function. The interface exciton modes are properly included in our treatment. Once the interaction between two electrons in the metallic film of the sandwich is obtained it is approximated by a suitable effective local dielectric function, and T_c is solved for.

It must be mentioned that our treatment is still within an assumed model for the bulk dielectric function for the metal and for the semiconductor. In particular, we have neglected the dispersion of the bulk exciton mode in the semiconductor. In case this dispersion is large, our conclusions may get greatly altered. Tunnelling effects are included only to the extent of the model charge density redistribution. It would be a reasonably good approximation only if the virtual excited states involved lie close to the ground state in energy. Still, our treatment should provide some understanding of the nature of, and the role played by the interface exciton modes in altering the superconducting transition temperature of the metal.

In section 2 of this paper we consider a model expression for the tunnelling charge density, and suitably modify the electrostatic equations to include the effects of the charge redistribution. We then obtain the interface exciton modes, and study them for a few model systems. In section 3 we investigate the effective electron-electron interaction in the metal side of the metal-semiconductor system, and derive the Coulomb, exciton and phonon parts of the kernel of the integral equation for the determination of T_c. For this purpose the dielectric function formalism for superconducting transition temperature has been developed in the Appendix. In particular, we also obtain in this section the exciton coupling constant and compare it with the repulsive Coulomb coupling constant. Section 4

discusses the calculation of T_c and presents the variation of the relative enhancement in T_c with respect to various parameters. In section 5 we summarise our main conclusions.

2. Interface exciton modes

We consider a composite system of a metal and a semiconductor and take $x = 0$ as the surface of separation. The bulk semiconductor ($x < 0$) is described by the one-oscillator model dielectric function with the real part

$$\epsilon_s(\omega) = 1 + \frac{\omega_0^2(\epsilon_0 - 1)}{\omega_0^2 - \omega^2} \tag{2.1}$$

where ϵ_0 is the static dielectric constant and $\hbar\omega_0$ is an energy of the order of the energy gap of the semiconductor. We take for the bulk metal ($x > 0$) the dielectric function

$$\epsilon_m(q) = 1 + \frac{q_{s0}^2}{q^2} \tag{2.2}$$

where $q_{s0}^2 = 6\pi ne^2/E_F$ is the square of Fermi–Thomas screening wave number. This correctly describes the static screening in the metal, the inclusion of which is essential for the calculation of the repulsive Coulomb coupling constant.

The neglect of spatial dispersion in eq. (2.1) for the bulk semiconductor dielectric function is a crucial approximation. It could have a vital bearing on our conclusions if for frequencies close to the surface exciton modes, the spatial dispersion is large. To investigate this qualitatively, let us consider two classical media described by dielectric constants ϵ_2 and ϵ_1, separated by an interface at $x = 0$. Because of the image term, the total classical interaction energy between two electrons at points $\boldsymbol{r}$ and $\boldsymbol{r}'$ in the first medium on the right is given by

$$V_{\text{CLASSICAL}}(\boldsymbol{r}, \boldsymbol{r}') = \frac{e^2}{\epsilon_1 |\boldsymbol{r} - \boldsymbol{r}'|} + \frac{e^2(\epsilon_1 - \epsilon_2)}{\epsilon_1(\epsilon_1 + \epsilon_2)} \frac{1}{|\boldsymbol{r} - \boldsymbol{r}' + 2x'|}$$

The image term (second term) is attractive whenever $\epsilon_1 < \epsilon_2$, and repulsive otherwise. For the case when the media are described by $\boldsymbol{q}$ and ω-dependent dielectric functions, one may, to a certain crude approximation, compare $\epsilon_M(q, \omega)$ for the metal with $\epsilon_S(q, \omega)$ for the semiconductor for each q and ω, in order to see the range of $\boldsymbol{q}$ vectors over which the image term in the metal side would be attractive. With the inclusion of rapid spatial dispersion in ϵ_s, it may so happen that for $|\boldsymbol{q}|$ close to the Fermi momentum k_F of the metal, the interaction remains repulsive, *i.e.* $\epsilon_S(k, \omega) < \epsilon_M(k_F, \omega)$ for ω equal to the interface mode frequency. In such a case, it cannot, of course, aid the onset of superconductivity.

In a composite system of the type considered here, there will appear new collective modes localised in the interface region, in contrast to the bulk exciton mode included in eq. (2.1). These interface exciton modes are expected to play a crucial role in determining the superconductivity of the system, as is evident from the expression for the kernel of the integral equation for T_c (see appendix; eq. A. 19) which requires a knowledge of the dispersion relation of these modes.

When the metal and the semiconductor are brought in intimate contact, there is a quantum penetration of the metal electrons to the semiconductor side. If one uses the effective-mass approximation for the Bloch states in the semiconductor, the modification of the charge density can be calculated by demanding continuity of the single particle wave function and its derivative at the interface $x = 0$. We can of course describe the conduction electrons in the metal in the free-electron approximation. The Fermi energy of the metal is taken to lie against the middle of the forbidden gap of the semiconductor. Under these assumptions, the density of electrons which penetrate into the semicondutor forbidden gap is given by (Pellegrini, 1974)

$$n_b(x) = \frac{2}{\pi^2} \int_0^\infty \int_0^\infty \theta(E_F - E)\,\theta(E - E_{0b}) \times \frac{k_1^2 m_b^{*2}}{m(m - m_b^*) k_t^2 + \frac{2m_b^* E_{0b} m^2}{\hbar^2} - m_b^*(m - m_b^*) k_1^2} \times \exp\left\{2x \sqrt{k_t^2 \left(1 - \frac{m_b^*}{m}\right) - \frac{m_b^*}{m} k_1^2 + \frac{2m_b^* E_{0b}}{\hbar^2}}\right\} dk_1 k_t dk_t \quad (2\cdot3)$$

where $b = c, v$ is the band index, m_b^* is the isotropic effective mass for the band b, m is the free electron mass and E_{0b} is the energy of the bottom of the 'b' band as measured from the bottom of the metal conduction band.

Approximately, we can express the above density of metal electrons tunnelling to the semiconductor side by means of a sufficiently accurate sum of two exponentials (Pellegrini 1974), *viz.*

$$n(x) = n_{v0}\, e^{q_v x} + n_{c0}\, e^{q_c x}. \quad (2.4)$$

Moreover, for the typical systems we are interested in, $n_{c0} \ll n_{v0}$ so that we are justified in retaining only the first term in eq. (2.4). Further, for the depth of penetration to be appreciable, the transverse energy $E_T \equiv \frac{\hbar^2 k_t^2}{2m}$ has to be small, and so, we introduce a cut-off $\bar{E}_T$, taken to be

$$\bar{E}_T \equiv \frac{\sqrt{3}}{2} \frac{|m_v^*|}{m} \left(\frac{m_c^* E_g}{|m_v^*| + m_c^*}\right) \quad (2.5)$$

where $E_g \equiv E_{c0} - E_{0v}$ is the band gap. We obtain for n_{v0} and q_v appearing in eq. (2.4), the expressions (Pellegrini 1974):

$$n_{v0} = \frac{8\sqrt{2}\pi m^{3/2} \bar{E}_T}{h^3} \frac{m_v^* E_g}{\sqrt{E_F}\,(|m_v^*| + m_c^*)}$$

$$q_v = \frac{4\sqrt{2}}{3\hbar} \sqrt{\frac{m + |m_v^*|}{m_c^* + |m_v^*|}}\, \sqrt{m_c^*}\, \sqrt{E_g} \quad (2.6)$$

The numerical values of (n_{v0}, q_v) for GaAs–Ga, PbTe–Pb and Ge–Al systems turn out to be $(2.29 \times 10^{20}\ \text{cm}^{-3},\ 0.358\ \text{Å}^{-1})$, $(1.60 \times 10^{20}\ \text{cm}^{-3},\ 0.246\ \text{Å}^{-1})$ and $(2.895 \times 10^{20}\ \text{cm}^{-3},\ 0.456\ \text{Å}^{-1})$, respectively. It should be noted that in reality the use of the effective mass approximation for this calculation in most of these materials is inappropriate, as it is not valid for the high values of the transverse momentum of the matching wave functions. For example, for Ge it may be meaningless to use the value of m_c^* for the L-band minimum and of m_v^* for the Γ-point maximum in our expression. However, the numerical values obtained in the effective mass approximation at least give us some rough idea of the magnitude of the tunneling charge density. In any case in actual calculation we will vary the tunnelling parameters n_{v0} and q_v in a wide range, to investigate their effects on the enhancement of T_c.

The charge redistribution on the metal side is confined only to the immediate vicinity of the interface, and is as shown in figure 1 (*a*). We have checked for one particular value of the parameters that the small amount of charge redistribution on the metal side, with continuously varying density across the interface [figure 1 (*b*)], is indeed unimportant for the calculation of T_c. Therefore, we take the electronic charge density in the metal to be uniform [figure 1 (*c*)], readjusting its value so that the total charge is conserved, Thus, we have

$$n(x) = n_{v0} e^{q_v x} \theta(-x) + n_0 \theta(x)\, \theta(L - x) \tag{2.7}$$

where

$$n_0 = N_0 - \left(\frac{n_{v0}}{q_v L}\right) \tag{2.8}$$

N_0 being the conduction electron density in the bulk metal and L being the extension of the metal region perpendicular to the interface.

Since now the metal electron density is a function of x, we define a local value for the screening wave number q_S through

$$q_S^2(x) = \frac{12\pi e^2 m}{\hbar^2 (3\pi^2)^{\frac{1}{3}}}\, n^{\frac{1}{3}}(x). \tag{2.9}$$

The interfacial collective excitations are obtained by the nontrivial solution of the electrostatic equations:

$$\left(\frac{\partial^2}{\partial x^2} - p^2\right) V_1(q_t, x) = 0, \quad \text{for } x > 0 \tag{2.10}$$

and

$$\left[\epsilon(\omega)\frac{\partial^2}{\partial x^2} - \epsilon(\omega)\, q_t^2 - q_{SD}^2\, e^{\frac{1}{3} q_v x}\right] V_2(q_t, x) = 0, \quad \text{for } x < 0 \tag{2.11}$$

where

$$p^2 \equiv q_t^2 + q_{SO}^2, \tag{2.12}$$

$$q_{SO}^2 = \frac{12 m \pi e^2}{\hbar^2 (3\pi^2)^{\frac{1}{3}}}\, n_0^{\frac{1}{3}}, \tag{2.13}$$

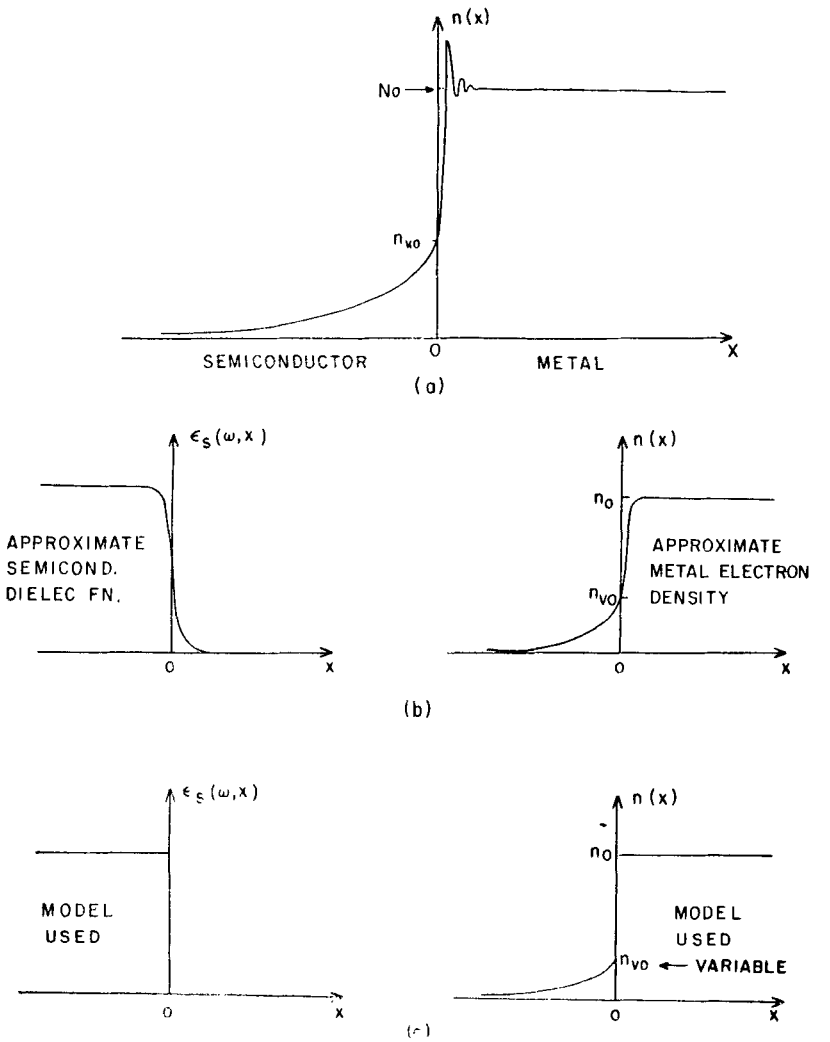

Figure 1. (*a*) A sketch showing the variation of the electron density n as a function x. N_0 is the density in the metal side if tunnelling is neglected. (*b*) Approximate semiconductor dielectric function $\epsilon_s(\omega, x)$ and approximate metal electron density $n(x)$. (*c*) $\epsilon_s(\omega, x)$ and $n(x)$ used in our model.

$$q_{SD}^2 = \frac{12m\pi e^2}{\hbar^2 (3\pi^2)^{\frac{1}{3}}} n_{VO}^{\frac{1}{3}}, \tag{2.14}$$

$q_t = +\sqrt{q_y^2 + q_z^2}$ and $\epsilon_S(\omega)$ is given by eq. (2.1). Eqs (2.10) and (2.11) are to be solved subject to the matching conditions

$$V_1(q_t, x = O^+) = V_2(q_t, x = O^-) \tag{2.15}$$

and

$$\frac{\partial V_1}{\partial x}(q_t, x = O^+) = \epsilon_S(\omega) \frac{\partial V_2}{\partial x}(q_t, x = O^-). \tag{2.16}$$

The solution shows that the interface exciton modes and their dispersion can be obtained as the solution of the transcendental equation (Rangarajan 1975)

$$\frac{J_{\eta+1}(v)}{J_\eta(v)} = \frac{6q_t}{vq_v} - \frac{pq_v v}{6q_{SD}^2} \tag{2.17}$$

where

$$\eta = \frac{6q_t}{q_v} \tag{2.18}$$

and

$$v^2 = -\frac{36\, q_{SD}^2}{q_v^2 \epsilon_S(\omega)} \tag{2.19}$$

The real solution exists only in the range of frequencies $\omega_0 < \Omega < \sqrt{\epsilon_0}\,\omega_0$; Ω being the frequency of the interface mode. We have shown in figure 2 the dispersion relations of the first few of the interface modes for Ge–Al system. The behaviour of these modes is similar in GaAs–Ga and PbTe–Pb systems, the other two systems which were studied. The lowest mode lies quite close to, and just below the interface mode obtained with the neglect of tunnelling, *i.e.*, $n_{v0}/n_0 = 0$, shown dotted in figure 2. In fact, it may be obtained from the latter by a perturbative calculation, with n_{v0}/n_0 as the perturbation parameter. All the other modes appear only when tunnelling is included. Whereas the lowest mode has the behaviour $\Omega^2(q_t \to \infty) = (\epsilon_0 + 1)\ \omega_0^2/2$, all other modes are such that $\Omega^2(q_t \to \infty) = \epsilon_0 \omega_0^2$, *i.e.*, they tend to the value corresponding to the bulk semiconductor mode. The appearance of the several modes is due to the smearing of the metal electron density in the interface region, rather than being sharply cut off at $x = 0$. This is reminiscent of the bulk normal modes of an inhomogeneous plasma. It is to be noted, however, that all these new modes contribute, to be shown later, very little to the exciton coupling constant compared to the contribution from the lowest mode. It is also expected that these additional modes give only small dips in the optical reflectivity function relative to the large dip due to the lowest mode.

3. Effective electron-electron interaction in the metal

The expression for the kernel of the integral equation for the determination of T_C has been derived in Appendix A in terms of the imaginary part of the effective local inverse dielectric function. Within our model [eq. (2.2)] for the dielectric function of the bulk metal, the Coulomb part of the kernel $K_C(\xi, \xi')$, given by eq. (A. 18), can be written as

$$K_C(\xi, \xi') = \frac{q_{SO}^2}{4K_F^2} \int_{\frac{|\xi - \xi'|}{\hbar v_F}}^{2K_F} \frac{q\,dq}{q^2 + q_{SO}^2} \tag{3.1}$$

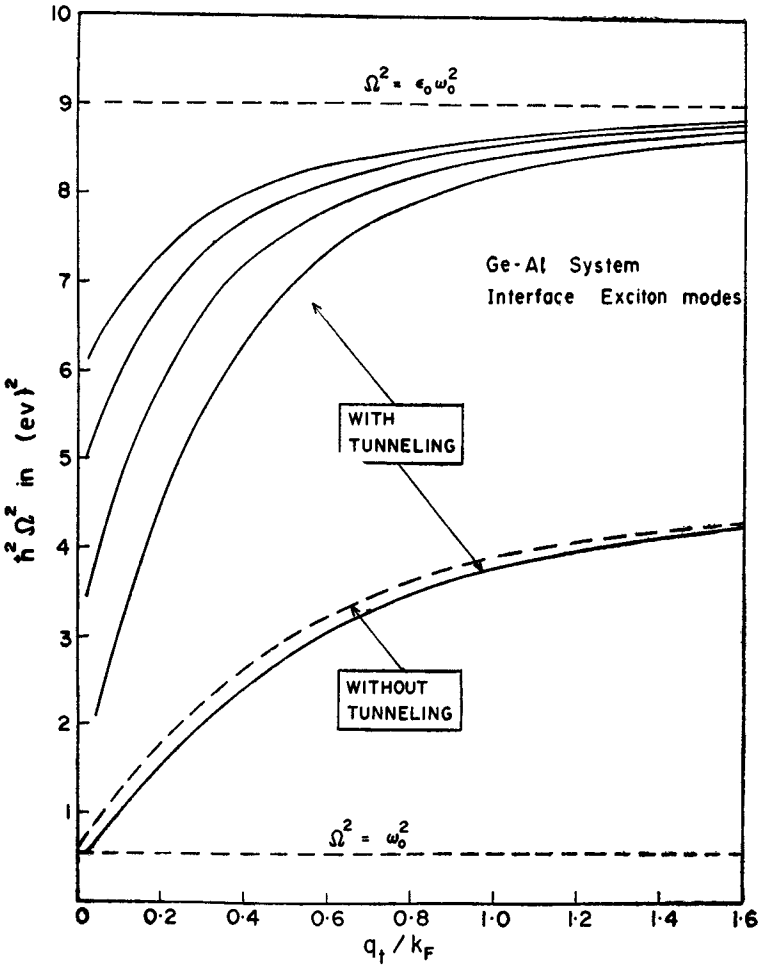

Figure 2. Dispersion relations of the first few interface exciton modes for Ge-Al-system with $k_FL = 1{\cdot}6528$. Dashed line shows the ' image mode ', for comparison.

where v_F is the Fermi velocity. An estimate on the strength of the Coulomb repulsion is provided by the Coulomb coupling constant, *viz.*,

$$\mu \equiv K_C(0, 0) = \frac{q_{SO}^2}{8K_F^2} \ln\left(1 + \frac{4K_F^2}{q_{SO}^2}\right) \tag{3.2}$$

For obtaining the $K_{ex}(\xi, \xi')$ part of the kernel, we have to study the interaction between two electrons in the metal in the presence of the model metal electron density given by eq. (2.7). The transverse Fourier transform of the interaction potential when an external charge $-e$, is placed at r' in the metal, satisfies the equation

$$\frac{d}{dx}\left(\epsilon(\omega, x)\frac{dV}{dx}\right) - q_t^2\,\epsilon(\omega, x)\,V - q_s^2(x)\,V = 4\pi e\delta(x - x') \tag{3.3}$$

where

$$\epsilon(\omega, x) = \epsilon_s(\omega)\,\theta(-x) + \theta(x) \tag{3.4}$$

and $V \equiv V(q_t, x, x')$. Once the Coulomb part $K_e(\xi, \xi')$ is separated out, the kernel in eq. (A. 17) involves only the singular part of the interaction potential arising from the exchange of excitons. It is, therefore, sufficient to solve for only the singular part of V from eq. (3.3).

For this purpose we consider a more general problem given by

$$[\mathcal{L}(\delta) - \nu]\, \mathcal{G}_\nu(x, x'; \delta) = \delta(x - x') \tag{3.5}$$

where $\mathcal{L}(\delta)$ is the operator on the left hand side of eq. (3.3) *viz.*,

$$\mathcal{L}(\delta) \equiv \mathcal{L}_1 - \delta \mathcal{L}_2 \tag{3.6}$$

with

$$\mathcal{L}_1 = \frac{d^2}{dx^2} - q_t^2 - q_e^2(x) \tag{3.7}$$

$$\mathcal{L}_2 = \omega_0^2(\epsilon_0 - 1)\left[q_t^2\,\theta(-x) + \delta(x)\frac{d}{dx} - \theta(-x)\frac{d^2}{dx^2}\right] \tag{3.8}$$

and

$$\delta = \frac{1}{\omega_0^2 - \omega^2}. \tag{3.9}$$

We have the expansion (Morse and Feshbach 1953)

$$\mathcal{G}_\nu(x, x'; \delta) = \sum_n \frac{\phi_n^*(x'; \delta)\,\phi_n(x; \delta)}{\nu_n - \nu} \tag{3.10}$$

where

$$\mathcal{L}(\delta)\,\phi_n(x; \delta) = \nu_n\,\phi_n(x; \delta). \tag{3.11}$$

A comparison of eqs (3.3) and (3.5) yields the result

$$\mathrm{Re}\, V(x, x'; \delta) = 4\pi e\, \mathcal{G}_{\nu=0}(x, x'; \delta). \tag{3.12}$$

As we are interested only in the exciton part, Im ϵ_{ee}^{-1}, in order to obtain the $K_{ee}(\xi, \xi')$ part of the kernel, we can construct the imaginary part of $V(x, x', \delta)$ due to exciton exchange by Kramers-Kronig relation. This yields

$$\mathrm{Im}\, V(x, x'; \delta) = \frac{4\pi e}{\pi} P \int_{-\infty}^{+\infty} \frac{d\omega'}{\omega - \omega'} \sum_n \frac{\phi_n^*(x'; \delta')\,\phi_n(x; \delta')}{\nu_n(\delta')} \tag{3.13}$$

$$\delta' = \frac{1}{\omega_0^2 - \omega'^2}$$

Inspection of eq. (3.13) shows that the zeros of ν_n in the ω'^2 plane will determine the exciton exchange contribution to the integral in the right hand side. Let us fix one value of n and study ν_n as a function of δ. Let $\delta = \delta_i$ be such that

$$\nu_n(\delta_i) = 0 \tag{3.14}$$

Then, from eq. (3.11)

$$\mathcal{L}(\delta_i)\,\psi_i(x) = 0 \tag{3.15}$$

where

$$\psi_i(x) = \underset{\delta \to \delta_i}{\mathcal{L}\text{im}}\ \phi_n(x;\delta). \tag{3.16}$$

The residues at the poles ω_i, where ω_i are given by

$$\delta_i = \frac{1}{\omega_0^2 - \omega_i^2} \tag{3.17}$$

can be found by a first order perturbation theory, with $(\delta_i - \delta)$ as the perturbation parameter. This leads to the result (Rangarajan 1975)

$$\text{Im } V(x, x';\ \omega) = 4\pi e \sum_i \frac{\psi_i^*(x')\,\psi_i(x)}{a_i} \times \frac{\pi}{2\omega_i} \times (\omega_0^2 - \omega_i^2)^2 \times [\delta(\omega - \omega_i) - \delta(\omega + \omega_i)] \tag{3.18}$$

where

$$a_i = (\omega_0^2 - \omega_i^2) \int_{-\infty}^{+\infty} dx\, \psi_i^*(x) \left\{ \frac{d^2}{dx^2} - q_t^2 - q_e^2(x) \right\} \psi_t(x) \tag{3.19}$$

Thus, numerically solving the eigen value problem in eq. (3.15), and constructing the matrix element a_i according to eq. (3.19), we obtain Im $V(x, x', \omega)$ *via* eq. (3.18).

We can, therefore, write the singular part of the interaction between two electrons due to the exchange of interface excitons as

$$\text{Im} V_{ex}(r, r', \omega) = -e^2 \int_0^\infty dq_t\, q_t\, J_0(q_t r_t) \frac{e^{-p|z-z'|}}{p} \times \left[\sum_i \left(\psi_i^*(x')\,\psi_i(x)\, e^{p|z-z'|} \right) \times \frac{\pi p}{a_i \omega_i} (\omega_0^2 - \omega_i^2)^2 \times \{\delta(\omega - \omega_i) - \delta(\omega + \omega_i)\} \right] \tag{3.20}$$

To get an effective local interaction, the x and x' dependent part within the square brackets in eq. (3.20) is replaced by an average over the length of the metal region. Defining

$$\beta_i(q) = \langle \psi_i^*(x))\,\psi_i(x)\, e^{p|z-z'|} \rangle \tag{3.21}$$

we obtain

$$\text{Im } \epsilon_{ex}^{-1}(q, \omega) = -\frac{1}{\epsilon_M(q)} \sum_i \beta_i(q) \frac{\pi \bar{p} [\omega_0^2 - \omega_i^2(q)]^2}{a_i(q)\,\omega_i(q)} \times \{\delta[\omega - \omega_i(q)] - \delta[\omega + \omega_i(q)]\} \tag{3.22}$$

where p has been replaced by $\bar{p} = +\sqrt{\bar{q}_t^2 + q_{e0}^2}$; $\bar{q}_t^2 = \frac{2}{3} q^2$. It should be emphasized that our final results and conclusions are insensitive to the exact method of averaging the nonlocal interaction.

When the quantum mechanical tunnelling is neglected (*i.e.*, $n_{v0}/n_e = 0$), we obtain only eigenvalue given by

$$\omega_1^2 = \frac{\omega_0^2(\bar{p} + \epsilon_0 \bar{q}_t)}{(\bar{p} + \bar{q}_t)} \tag{3.23}$$

and

$$a_1 = \bar{q}_t\, \omega_0^2 (\epsilon_0 - 1); \quad \beta_t = e^{-2\bar{p}L/3}. \tag{3.24}$$

in this case we obtain

$$\text{Im}\ \epsilon^{-1}_{\text{image}}(q, \omega) = -\frac{1}{\epsilon_M(q)} \frac{\pi}{\omega_1} \frac{\bar{p}\,\bar{q}_t\, \omega_0^2 (\epsilon_0 - 1)\, e^{-2\bar{p}L/3}}{(\bar{p} + \bar{q}_t)^2} \times \{\delta(\omega - \omega_1) - \delta(\omega + \omega_1)\} \tag{3.25}$$

Equation (3.25) could have been, of course, directly obtained within the image approximation' (Rangarajan 1974).

In general, substitution of eq. (3.22) in eq. (A. 19) leads to the exciton part of the kernel as

$$K_{ex}(\xi, \xi') = -N(\xi') \int d(\cos\theta) \frac{8\pi e^2}{q^2 + q_{s0}^2} \times \sum \frac{\beta_i(q)\bar{p}}{a_i(q)\,\omega_i(q)} [\omega_0^2 - \omega_i^2(q)]^2 \times \frac{1}{\left[\omega_i(q) + \frac{1}{\hbar}(|\xi| + |\xi'|)\right]}. \tag{3.26}$$

The exciton coupling constant λ_{ex} can be written as

$$\lambda_{ex} = -K_{ex}(0, 0) \equiv \sum_i \gamma_i \tag{3.27}$$

where

$$\gamma_i = \frac{q_{s0}^2}{2K_F^2} \int_0^{2K_F} \frac{qdq}{q^2 + q_{s0}^2} \times \frac{\beta_i(q)\bar{p}}{a_i(q)\,\omega_i(q)} [\omega_0^2 - \omega_i^2(q)]^2 \tag{3.28}$$

We find that γ_i decreases rapidly as i increases, as shown in figure 3, ensuring convergence of eq. (3.27). Thus, retaining only the first few values of i guarantees a sufficiently accurate value for λ_{ex}. In figure 4 is shown the dependence of λ_{ex} on q_{s0}/k_F for different values of $q_{s0}L$. The Coulomb coupling constant μ is also plotted for comparison. It is seen that for reasonable values of L, the attractive λ_{ex} is found to be much smaller than μ and so this mechanism, by itself, cannot bring about superconductivity in the system. For nontrivial solution of the integral equation for T_c, the net coupling constant must be attractive.

In order to study the extent to which this additional attractive term can alter the bulk value of the superconducting transition temperature of the metal, we include a phonon term in the kernel. For this purpose, we assume a model expressions for $\text{Im}\ \epsilon^{-1}_{ph}(q, \omega)$ given by

$$\text{Im}\ \epsilon^{-1}_{ph}(q, \omega) = \frac{-C}{\epsilon_M(q)} \times \frac{D}{(\omega - \omega_{p0})^2 + D^2} \tag{3.29}$$

where C is a suitable normalisation constant, ω_{p0} is the central frequency of the

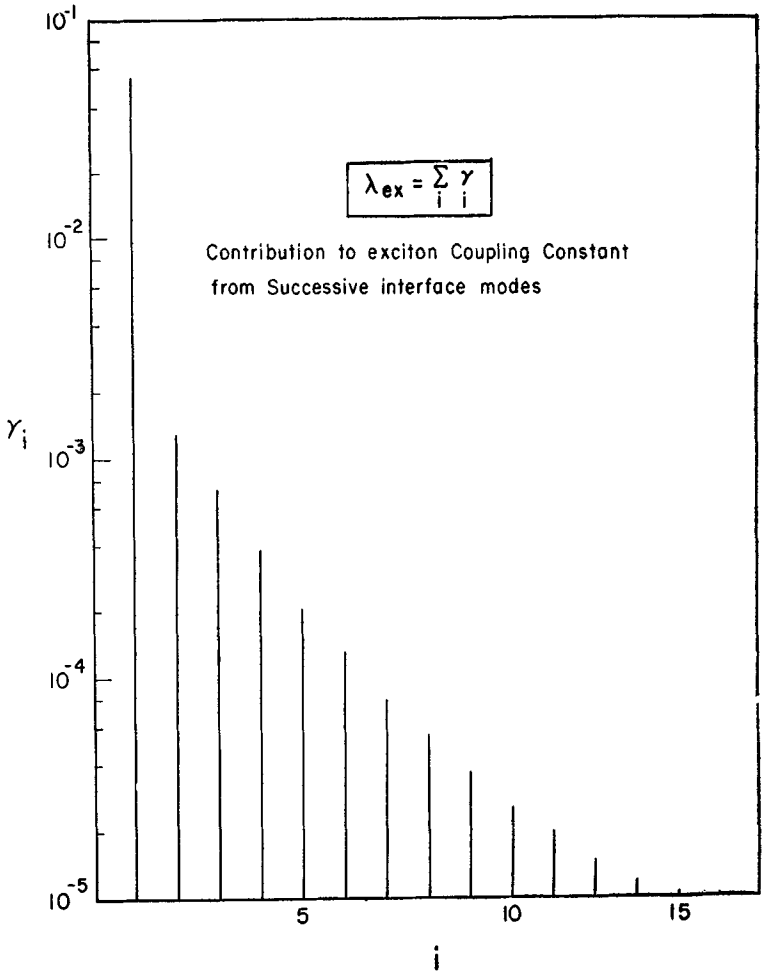

Figure 3. The relative contribution from successive eigenvalues to the exciton coupling constant.

phonon spectrum and D is the full width of the spectrum at half maximum. This choice is equivalent to assuming a Lorentzian for the phonon density of states and treating the electron-phonon interaction function to be a constant. Substituting eq. (3.29) in eq. (A. 19), we obtain

$$K_{ph}(\xi, \xi') = -\frac{2\mu C}{\pi}\int_0^\infty d\omega \frac{D}{\left\{(\omega - \omega_{p0})^2 + D^2\right\}\left\{\omega + \frac{1}{\hbar}(|\xi| + |\xi'|)\right\}} \tag{3.30}$$

where μ is the Coulomb coupling constant. The constant C is to be evaluated such that

$$K_{ph}(0, 0) = -\lambda_{ph} \tag{3.31}$$

λ_{ph}, being the experimentally phonon coupling constant. We choose ω_{p0} to be $k_B \theta_D/2\hbar$, where θ_D is the Debye temperature, and D to be $0{\cdot}1\ \omega_{p0}$.

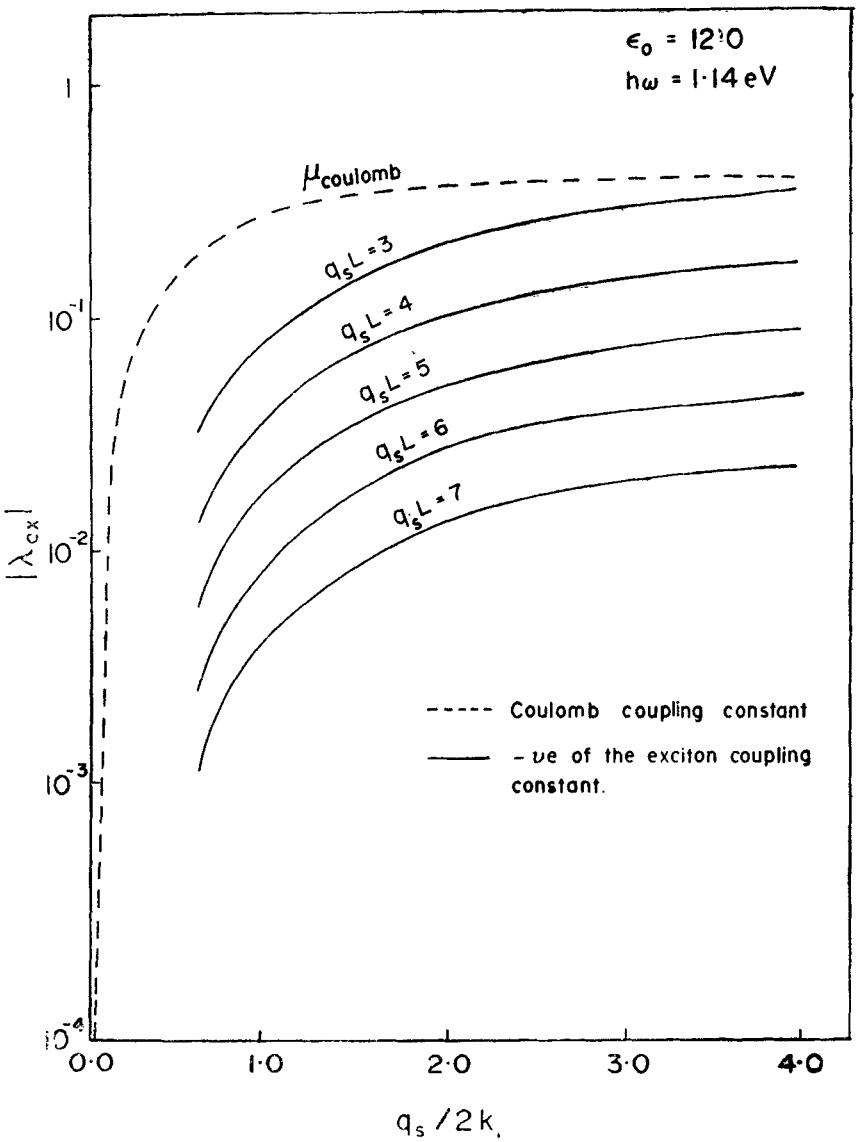

Figure 4. Dependence of the attractive exciton coupling constant on $q_{s0}/2k_F$ for various values of $q_{s0}L$. The repulsive Coulomb coupling constant μ is shown for comparison.

4. Calculation of superconducting transition temperature

We have derived in Appendix A an expression for T_c in terms of a function $\eta(x)$, which satisfies an inhomogeneous integral equation (A. 22) with a real, smooth kernel. Once the Coulomb, phonon and exciton parts of the kernel are evaluated from eqs (3.1), (3.30) and (3.26), respectively, the calculation of T_c is straightforward. We convert eq. (A 22) into a set of linear algebraic equations, by expanding $\eta(\xi)$ and $K(\xi, 0)$ in terms of Legendre polynomials. We find that six polynomials in the expansion give a reasonable stability in the value of T_c so obtained. The necessary integrals were performed by a multiple use of the

16-point Gauss-Legendre quadrature formula, demanding a relative accuracy of 10^{-6}.

The superconducting transition temperature for the bulk metal was first obtained by substituting

$$K(\xi, \xi') = K_e(\xi, \xi') + K_{ph}(\xi, \xi') \tag{4.1}$$

Then, we solve for T_c with the inclusion of the excitonic part of the kernel, *i.e.*, by considering

$$K(\xi, \xi') = K_e(\xi, \xi') + K_{ph}(\xi, \xi') + K_{ex}(\xi, \xi') \tag{4.2}$$

so that we obtain the relative enhancement in the transition temperature over the bulk value.

The strongest dependence of the relative enhancement $\triangle T_c/T_c$ is on the length of the metal region, as represented by the parameter $k_F L$. Figure 5 shows the variation with respect to $k_F L$ for the three model systems, Ge–Al, GaAs–Ga and PbTe–Pb. In all the three cases the dependence is nearly exponential, with the slope increasing slightly as $k_F L$ decreases. The dependence on the other metal parameter, *viz*., q_{s0}/k_F, which is related to the Fermi energy through

$$E_F = \frac{8me^4}{\pi^2 \hbar^2} \frac{1}{(q_{s0}/k_F)^4} \tag{4.3}$$

is not so strong. We have depicted in figure 6 the dependence of $\triangle T_C/T_C$ on the Fermi energy E_F of the metal. The rather weak dependence on this parameter justifies our use of the model dielectric function (2.2) for the metal, which is valid only in the long wavelength limit ($q \ll q_{s0}$)., whereas the integral in eq. (3.28) extends up to $q = 2k_F$. It would have been necessary to generalise the expression as

$$\epsilon_M(q, 0) = 1 + \frac{q_{s0}^2}{q^2} \langle \delta_M \rangle \tag{4.4}$$

where $\langle \delta_M \rangle$ is a suitable average factor. $\langle \delta_M \rangle = 1$ for $q \ll q_{s0}$ and $\langle \delta_M \rangle \sim \frac{1}{2}$ for $q \sim k_F$. Since we now find that $\triangle T_C/T_C$ has only a weak dependence on q_{s0}/k_F the neglect of the $\langle \delta_M \rangle$ factor in eq. (4.4) is indeed unimportant.

Within the one-oscillator model for the semiconductor dielectric function, the effect of the semiconductor enters only through ϵ_0 and ω_0, where ϵ_0 is the static dielectric constant and $\hbar\omega_0$ is the energy gap. For fixed values of $(\epsilon_0 - 1)\ \omega_0^2 \equiv \omega_p^2$, the dependence of $\triangle T_c/T_c$ on ϵ_0 is shown in figure 6. There is an increase in $\triangle T_c/T_c$ by about a factor 2 when ϵ_0 increases from 5 to 15. As ω_P^2 is increased, there is a decrease in the value of $\triangle T_c/T_c$. This explains why the excitonic effect is more pronounced in Ge–Al system than in GaAs–Ga system (see figure 5), the value of $\hbar^2\ \omega_P^2$ being 8.47 $(\text{eV})^2$ and 25·75 $(\text{eV})^2$, respectively. For the same value of ϵ_0, as $\hbar\omega_0$ decreases, the relative enhancement in T_c becomes larger. When, on the other hand, $\hbar\omega_0$ is kept fixed, there is a slight increase in $\Delta T_c/T_c$ as ϵ_0 is increased. These conclusions are in qualitative agreement with recent experiments (Miller *et al* 1973; Meunier *et al* 1968) on the same metal being deposited over different semiconductors.

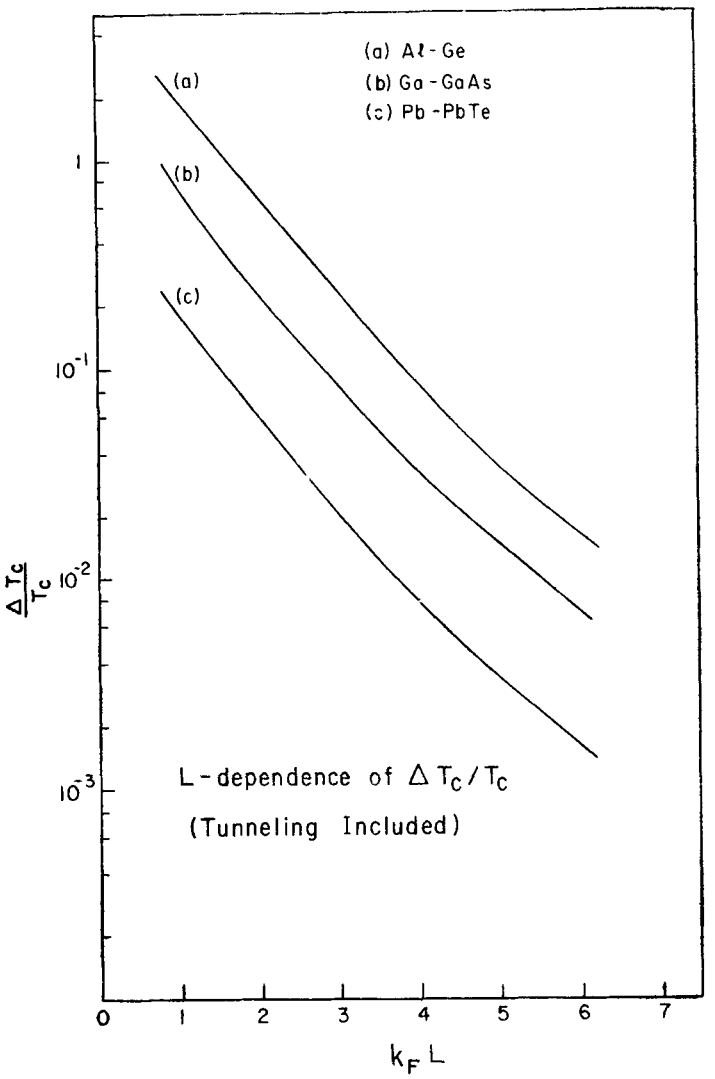

Figure 5. The relative enhancement in T_c plotted as a function of $k_F L$ for three different systems (i) Ge–Al, (ii) GaAs–Ga and (iii) PbTe–Pb.

Within our model, the metal charge density in the semiconductor side is approximated by a single exponential function and hence the dependence on the tunnelling charge density can be studied through the variation of the parameters n_{v0}/N_0 and q_v. On both of these parameter, the relative enhancement in T_c depends very weakly. As the exponential decay parameter q_v decreases, *i.e.*, when the depth of penetration into the semiconductor increases, there is a slight increase of $\Delta T_c/T_c$. For the same value of q_v, if n_{v0}/N_0 increases, there is found an increase in $\Delta T_c/T_c$ by a small amount.

In figure 7 is shown the dependence of $\Delta T_c/T_c$ on the ratio n_{v0}/n_0, where n_0 is determined from eq. (2.8). We have studied the dependence right up to the value $n_{v0}/n_0 = 1$. The choice of n_{v0}/n_0 as the independent variable is suggested

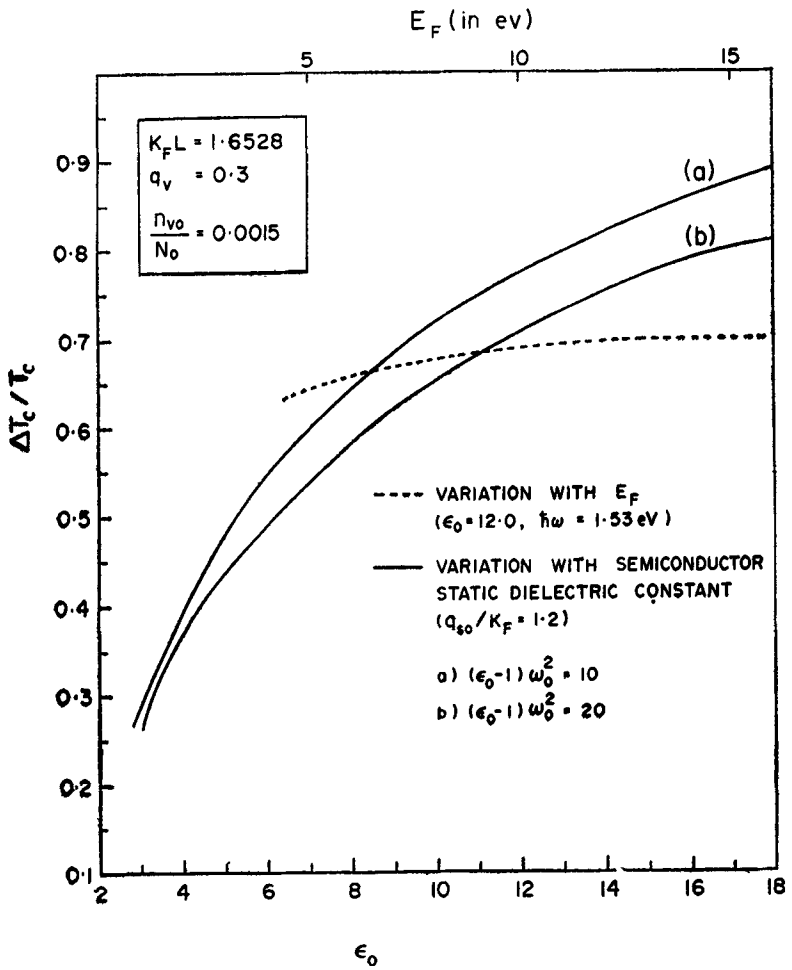

Figure 6. (i) $\Delta T_c/T_c$ as a function of the Fermi energy E_F of the metal. (ii) Dependence of $\Delta T_c/T_c$ on ϵ_0 for fixed values of $(\epsilon_0 - 1)\,\omega_0^2$. Curve (*a*) is for $(\epsilon_0 - 1)\,\omega_0^2 = 10$ (eV)^2 and curve (*b*) is for $(\epsilon_0 - 1)\,\omega_0^2 = 20$ (eV)^2.

by the fact that at the value $n_{v0}/n_0 = 1$, the charge density $n(x)$ happens to be continuous at $x = 0$. This value of n_{v0}/n_0 corresponds to $n(x)$ as shown in figure 1 (*b*), but with the profile displaced slightly to the left. As is seen from figure 7, the relative enhancement does not vary markedly with n_{v0}/n_0. The absence of an appreciable dependence on this parameter now provides the justification for the validity of the use of the model charge density shown in figure 1 (*c*).

5. Conclusions

In this paper we have studied the modification of the interaction in the neighbourhood of the metal-semiconductor interface and its bearing on the superconductivity of the metal. The interface exciton modes were obtained, and their effect was included in the calculation of the exciton part of the kernel of the integral

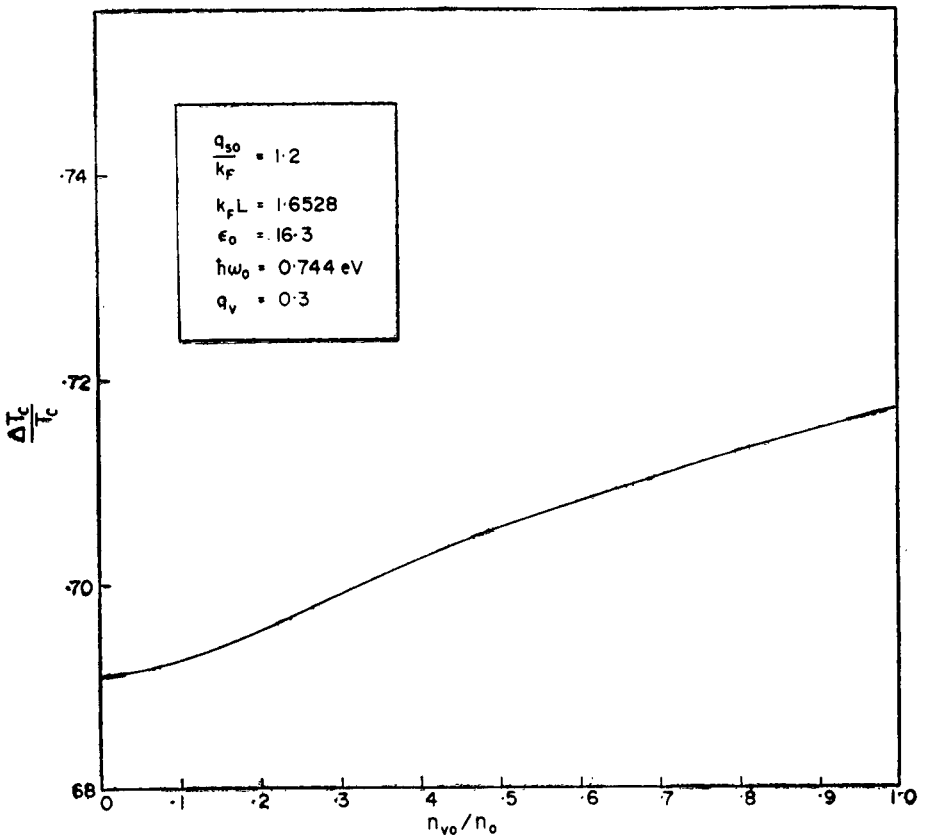

Figure 7. Dependence of $\Delta T_c/T_c$ on the ratio n_{v0}/n_0, for $q_v = 0{\cdot}3$.

equation determining T_c. We found that the strength of the exciton mediated term is small and is, by itself, insufficient to overcome the Coulomb repulsion and produce superconductivity. We, therefore, found it necessary to include a phonon term as well to study the enhancement in T_c due to the exciton mediated term.

We find that the excitonic effects can be increased significantly only by a decrease in the value of k_FL, *i.e.*, by reducing the size of the metal perpendicular to the interface. Apart from this strong and almost exponential dependence on k_FL, the relative enhancement in T_c depends rather weakly on E_F, the metal Fermi energy, ϵ_0, the static dielectric constant of the semiconductor, $\hbar\omega_0$, the energy gap in the semiconductor and on the parameters describing the tunnelling charge density. Of the three model systems, GaAs–Ga, Ge–Al and PbTe–Pb, we find that Ge–Al exhibits the largest enhancement in T_c for any given value of L. This is principally because of the large value of the Fermi energy E_F and the relatively small value of the parameter $(\epsilon_0 - 1)\,\omega_0^2$.

We conclude that a very thin film of a metal, with a large density of conduction electrons, deposited over a narrow gap semiconductor would provide the most favourable system for the occurrence of the exciton mechanism. Also, despite the L-dependence of T_c arising from many other factors, the one due to the exci-

tonic effect may be clearly distinguishable from others on account of its exponential character. In quite a few experiments (Fontaine and Meunier 1972; Dmitrenko and Skchetkin 1973), such a dependence has been observed, although the data from such experiments are still insufficient, rendering it impossible at this time for a quantitative comparison with our predictions. In any case, it is also possible that if the effect predicted by us exists in reality, it may only lead to a skin-effect type surface superconductivity, the rest of the bulk metal remaining normal.

Before concluding this article, it should be emphasized that our predictions of enhancement of the superconducting transition temperature due to virtual exchange of interface exciton modes is based on the approximation that the bulk exciton mode in the semiconductor has very little dispersion. A strong spatial dispersion in the bulk semiconductor dielectric function may lead to the opposite effect, *i.e.*, depression of T_c rather than an enhancement. In that sense one must choose semiconductors which have negligible spatial dispersion in their dynamic dielectric function, leading to almost flat bulk exciton mode.

Acknowledgement

We are very thankful to John Inkson of the Cambridge University for useful correspondence regarding this problem.

Appendix A

In this appendix, we derive the integral equation for the determination of T_c in terms of the inverse of the effective local dielectric function, $\epsilon^{-1}(q, \omega)$, of the system. We start from the anomalous Green's function $\mathcal{F}(k, n)$ defined by

$$\mathcal{F}(k, n) \equiv \mathcal{F}(k, \omega_n) = \int_0^\beta dt e^{it\omega_n t} \mathcal{F}(k, t); \quad \omega_n = \frac{(2n+1)\pi}{\hbar\beta} \tag{A.1}$$

where

$$\mathcal{F}(k, t) = -\langle T(C_{k\uparrow}(t) C_{k\downarrow}(0))\rangle, \quad \beta = 1/k_B T \tag{A.2}$$

and the symbols have their usual meaning as relevant to the finite-temperature Green's function formalism.

As $\mathcal{F}$ is expected to be zero in the normal state, the equation of motion of $\mathcal{F}$ can be linearized at $T = T_c$. Under the self-consistent Hartree Fock approximation, it satisfies the equation

$$\mathcal{F}(k, n) = \frac{-1}{\hbar^2 \omega_n^2 + \xi_k^2} \frac{1}{\beta_c} \sum_{k', n'} V_{\text{eff}}(k - k', n - n') \mathcal{F}(k', n') \tag{A.3}$$

where $\beta_c \equiv \dfrac{1}{k_B T_c}$, ξ_k is the renormalised single particle energy measured from the Fermi surface and

$$V_{\text{eff}}(q, \omega) = \frac{4\pi e^2}{q^2} \epsilon^{-1}(q, \omega). \tag{A.4}$$

We can spectral represent ϵ^{-1} and $\mathcal{F}$ as

$$\epsilon^{-1}(q, ia_n) = 1 + \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{\omega' \operatorname{Im}\epsilon^{-1}(q, \omega')\, d\omega'}{\omega'^2 + a_n^2} \; ; \; a_n = \frac{2n\pi}{\hbar\beta} \tag{A.5}$$

and

$$\mathcal{F}(k, i\omega_n) = -\int_{-\infty}^{+\infty} \frac{x dx f(k, x)}{x^2 + \omega_n^2} \tag{A.6}$$

Substitution of (A.5) and (A.6) in eq. (A.3) leads to the following integral equation for the spectral weight function $f(k, x)$;

$$\begin{aligned} f(k, x) = &-\frac{1}{2\hbar}\int \frac{d^3k'}{(2\pi)^3} \frac{4\pi e^2}{|k - k'|^2} \int_{-\infty}^{+\infty} f(k', y)\, dy \\ &\times\Bigg[\frac{\delta(|x| - |\omega_k|)}{2x} \tanh\left(\frac{\beta_e\hbar y}{2}\right) \\ &+ \frac{1}{\pi}\frac{\delta(|x| - |\omega_k|)}{4x} \int_{-\infty}^{+\infty} d\omega' \operatorname{Im}\epsilon^{-1}(k - k', \omega') \\ &\times\Bigg\{\frac{(\omega' + y)\left(\tanh\frac{\beta_e\hbar y}{2} + \coth\frac{\beta_e\hbar\omega'}{2}\right)}{(\omega' + y)^2 - \omega_k^2} \\ &+ \frac{(\omega' - y)\left(\tanh\frac{\beta_e\hbar y}{2} - \coth\frac{\beta_e\hbar\omega'}{2}\right)}{(\omega' - y)^2 - \omega_k^2}\Bigg\} \\ &- \frac{1}{2\pi}\frac{\operatorname{Sgn} x}{(x^2 - \omega_k^2)}\Big\{\operatorname{Im}\epsilon^{-1}(k - k', |x| - y) \\ &\times\left(\tanh\frac{\beta_e\hbar y}{2} + \coth\frac{\beta_e\hbar}{2}(|x| - y)\right) \\ &+ \operatorname{Im}\epsilon^{-1}(k - k', |x| + y)\left(\tanh\frac{\beta_e\hbar y}{2} - \coth\frac{\beta_e\hbar}{2}(|x| + y)\right)\Big\}\Bigg] \end{aligned} \tag{A.7}$$

where $\omega_k = \xi_k/\hbar$.

We define (Kirzhnits *et al* 1973) a new function $\Phi(k)$, which is a generalisation of the BCS gap function, as

$$\Phi(k) = |\omega_k| \int_{-\infty}^{+\infty} \operatorname{Sgn} x\, f(k, x)\, dx. \tag{A.8}$$

This satisfies the equation

$$\Phi(k) = -\frac{1}{\hbar}\int \frac{d^3k'}{(2\pi)^3}\frac{4\pi e^2}{|k-k'|^2}\int_0^\infty f(k', y)\, dy \tanh\left(\frac{\beta_e \hbar y}{2}\right)$$

$$\times\left[1+\frac{2}{\pi}\int_0^\infty \frac{d\omega' \mathrm{Im}\epsilon^{-1}(k-k', \omega')}{\omega'+y+|\omega_k|}\right] + R(k) \tag{A.9}$$

where

$$R(k) = -\frac{1}{\hbar}\int \frac{d^3k'\, 4\pi e^2}{(2\pi)^3 |k-k'|^2}\int_0^\infty dy f(k', y)\int_0^\infty d\omega' \,\mathrm{Im}\epsilon^{-1}(k-k', \omega')$$

$$\times\left[\left(\tanh\left(\frac{\beta_e\hbar y}{2}\right)-\coth\left(\frac{\beta_e\hbar\omega'}{2}\right)\right)\left(\frac{1}{\omega'-y+|\omega_k|\,\mathrm{Sgn}(\omega'-y)}\right.\right.$$

$$\left.\left.-\frac{1}{\omega'+y+|\omega_k|}\right)\right] \tag{A.10}$$

We note that the extra term $R(k)\to 0$ as $T_e \to 0$. Only when T_e is very large, (*i.e.*, $k_B T_C \sim E_F$) this term would be important in the solution of eq. (A.9). As we concern ourselves with $T_C \ll E_F/k_B$, we will drop this term for analytical convenience.

From eq. (A.7) it is seen that $f(k, x)$ is singular for $x = \pm\omega_k$ so that on the right hand side of eq. (A.9) we may substitute

$$f(k', y) = \frac{\Phi(k')}{2|\omega_{k'}|}\delta(y-|\omega_{k'}|) + \text{higher order terms.} \tag{A.11}$$

This leads to the required integral equation

$$\Phi(k) = -\frac{1}{\hbar}\int \frac{d^3k'}{(2\pi)^3}\frac{4\pi e^2}{|k-k'|^2}\tanh\left(\frac{\beta_e\hbar|\omega'|}{2}\right)$$

$$\times\left[1+\frac{2}{\pi}\int_0^\infty \frac{d\omega'\,\mathrm{Im}\epsilon^{-1}(k-k', \omega')}{\omega'+|\omega_k|+|\omega_{k'}|}\right]\Phi(k'). \tag{A.12}$$

For an isotropic system, angular averaging at the Fermi surface reduces the integral equation to

$$\Phi(\xi) = -\int \frac{d\xi'}{2\xi'}\tanh\frac{\beta_e\xi'}{2}K(\xi, \xi')\,\Phi(\xi') \tag{A.13}$$

where $\xi = \xi_k$, is the energy variable and the Kernel

$$K(\xi, \xi') = N(\xi')\int_{-1}^{+1} d(\cos\theta)\frac{4\pi e^2}{q^2}\left[1+\frac{2}{\pi}\int_0^\infty \frac{d\omega'\mathrm{Im}\epsilon^{-1}(q, \omega')}{\omega'+\frac{1}{\hbar}(|\xi|+|\xi'|)}\right] \tag{A.14}$$

with

$$q^2 \equiv |k - k'|^2 \equiv k^2 + k'^2 - 2kk' \cos\theta \tag{A.15}$$

The first term in eq. (A.14) is the bare Coulomb part of the kernel and the second term represents all other effects, including screening of the Coulomb interaction. However, it is convenient to separate out from the second term the part arising due to screening in the bulk metal. For this purpose, we can split up $\mathrm{Im}\,\epsilon^{-1}$ as

$$\mathrm{Im}\ \epsilon^{-1}(q, \omega) = \mathrm{Im}\ \epsilon_0^{-1}(q, \omega) + \mathrm{Im}\ \epsilon_{ex}^{-1}(q, \omega) \tag{A.16}$$

where $\epsilon_0^{-1}(q, \omega)$ is the inverse of the bulk metal dielectric function and $\epsilon_{ex}^{-1}(q, \omega)$ is the effective inverse dielectric function representing all other effects. Thus, we have

$$K(\xi, \xi') \equiv K_0(\xi, \xi') + K_{ex}(\xi, \xi') \tag{A.17}$$

where

$$K_0(\xi, \xi') = N(\xi') \int d(\cos\theta) \frac{4\pi e^2}{q^2} \left[1 + \frac{2}{\pi} \int_0^\infty \frac{d\omega'\, \mathrm{Im}\,\epsilon_0^{-1}(q, \omega')}{\omega' + \frac{1}{\hbar}(|\xi| + |\xi'|)} \right] \tag{A.18}$$

and

$$K_{ex}(\xi, \xi') = N(\xi') \int (d\cos\theta) \frac{4\pi e^2}{q^2} \frac{2}{\pi} \int_0^\infty \frac{d\omega'\, \mathrm{Im}\,\epsilon_{ex}^{-1}(q, \omega')}{\omega' + \frac{1}{\hbar}(|\xi| + |\xi'|)}. \tag{A.19}$$

For the integral equation (A.13) to have non-trivial solutions, *i.e.*, for superconductivity to exist, it is necessary that the screened Coulomb repulsion be adequately compensated by attractive interactions, arising due to exchange of phonons, excitons, etc., which enter into the $K_{ex}(\xi, \xi')$ part of the kernel. In particular, it would be required that $K_{ex}(0, 0)$ be sufficiently negative to overcome the Coulomb repulsion represented by the Coulomb coupling constant $\mu = K_c(0, 0)$.

For the numerical calculation of T_c it is convenient to set up an inhomogeneous integral equation deducible from eq. (A.13). For this purpose, we restrict the region of integration in eq. (A.13) between $(-E_F)$ and $(+E_F)$. This is quite justifiable because of the rapid decrease in the value of the kernel beyond these limits. Further, as $k_B T_C$ is expected to be much smaller than E_F, the $\tanh\frac{\beta_0 \xi'}{2}$ factor is important only in the very small region close to $\xi' = 0$. Using the result

$$\int_{-E_F}^{+E_F} \tanh\frac{\beta_0 \xi'}{2} \frac{d\xi'}{2\xi'} = \ln\left(\frac{2\gamma\, \beta_0 E_F}{\pi}\right) + \ldots. \tag{A.20}$$

where γ is the exponential of the Euler constant, and defining a new function

$$\eta(\xi) = -\frac{1}{\ln\left(\frac{2\gamma\beta_c E_F}{\pi}\right)} \frac{\Phi(\xi)}{\Phi(0)} \tag{A.21}$$

we find that $\eta(\xi)$ satisfies the inhomogeneous integral equation

$$\eta(\xi) = K(\xi, 0) - \frac{1}{2}\int_{-E_F}^{+E_F} \frac{d\xi'}{|\xi'|} [K(\xi, \xi')\eta(\xi') - K(\xi, 0)\eta(0)] \tag{A.22}$$

We have replaced the $\tanh \frac{\beta_c \xi'}{2}$ factor in the second term of eq. (A.22) by Sgn ξ', as the square-bracketed quantity vanishes for $\xi' = 0$, and is expected to be small for $\xi' \simeq 0$, if $K(\xi, \xi')$ is reasonably smooth. Once $\eta(\xi)$ is solved from eq. (A.22), using eq. (A.21), T_c is obtained as

$$T_c = \frac{2\gamma E_F}{\pi k_B} \exp\left(\frac{1}{\eta(0)}\right) \tag{A.23}$$

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