Model for an Exciton Mechanism of Superconductivity

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The exciton mechanism of superconductivity is discussed with respect to a particular model, a thin metal layer on a semiconductor surface. In this model, the metal electrons at the Fermi surface tunnel into the semiconductor gap where they interact with virtual excitons, producing a net attractive interaction among the electrons in direct analogy with the phonon mechanism of superconductivity. The physical requirements for successful realization of the exciton mechanism in a metal-semiconductor system are explored in detail, and the relevant parameters are described. Estimates are made for electron tunneling and band-bending effects, and an electron-exciton coupling constant is defined and estimated. Finally, an appropriately modified integral equation for the superconducting energy gap is solved numerically to yield transition temperatures both for a pure-exciton mechanism and for the exciton and phonon mechanisms acting simultaneously.

I. INTRODUCTION

There has long been an interest in the so-called exciton mechanism of superconductivity, in which the effective attractive interaction between electrons comes from virtual excitation of excitons (electron-hole pairs) rather than phonons. Ginzburg,\(^4\,4\) in particular, has emphasized the importance of this mechanism because of the possibility of obtaining higher transition temperatures than can be realized through the phonon mechanism. While there is at present no experimental evidence for the exciton mechanism, no studies have been carried out on well-defined systems where theory suggests it should be observed. At the University of Illinois, we have initiated a parallel experimental and theoretical study to try to establish the possibilities and limitations of the proposed mechanism. In this paper we discuss the theoretical aspects.

A favorable medium for the exciton mechanism is a narrow-gap semiconductor, such as Ge, InSb, or PbTe. In the pseudopotential approximation, the valence electrons can, in many cases, be regarded as if in a free-electron metal in which the gaps are introduced at the Brillouin-zone boundaries to make the crystal insulating or semiconducting. For example, it is known that the plasma frequencies of many semiconductors do not differ markedly from free-electron values obtained using the density of valence electrons. We shall show that favorable materials for the exciton mechanism are those with their average gap frequency small compared to their plasma frequency. In the exciton mechanism, all initial states as well as all wave-vector differences between the interacting electrons are involved, so it is the average gap width throughout the zone that is important. Some indication of the value of the average width is the position of the peak in a plot of the imaginary part of the dielectric function \(\varepsilon_\infty(q, \omega)\) vs frequency \(\omega\).

To obtain a high transition temperature \(T_s\), one needs a high concentration of mobile carriers in the superconductor. Doping of a semiconductor to get a high concentration of carriers tends to wash out the gap. A sandwich structure consisting of alternate layers of metal and semiconductor has been suggested.\(^1\) If the layers are very thin (~10 Å) and if there is intimate contact between the metal and semiconductor, the metal electrons can tunnel into the gap region of the semiconductor and interact with the excitons. An important parameter is the fraction of time the metal electrons spend in the semiconductor gap.

Such sandwich structures require rather exacting conditions and would be difficult to fabricate. To try to establish the exciton mechanism rather than achieve a high \(T_s\), we have decided to look first at a single interface between a metal and semiconductor. Under favorable conditions, a very thin layer of metal can be deposited on a clean semiconductor surface. Some enhancement of \(T_s\) can be expected if the metal electrons have an appreciable probability of penetrating into the semiconductor gap.

Two questions needing consideration are: How far are the metal electrons near the Fermi surface expected to tunnel into the semiconductor gap, and what is the effective interaction constant in the semiconductor due to exciton effects? The first question is fairly straightforward, and the answer is of the order of 5 Å. There has been considerable controversy with regard to the second. One may write the effective attractive interaction constant for the exciton mechanism in the form

\[
N(0)\gamma^2 k_\varepsilon - \mu, \tag{1.1}
\]

where \(N(0)\) is the density of states at the Fermi level of one spin, \(\mu\) is the density of states times an average of the screened Coulomb interaction, extending to energies above the Fermi surface of
the order of the Fermi energy \( \omega_F \), and \( \lambda_{ex} \) is the electron-exciton coupling constant, to be defined and discussed at length later. Arguments have been given\(^3\) that \( \lambda_{ex} < \mu \), at least as \( \omega \rightarrow 0 \). These are based on the concept that the effective interaction may be written

\[
V(G, \omega = 0) = 4\pi\varepsilon_0^2/q^2 \varepsilon(G, \omega = 0), \tag{1.2}
\]

where \( \varepsilon \) is the wave vector and frequency-dependent dielectric function. Stability requires that \( \varepsilon(G, 0) > 0 \) and thus that \( \lambda_{ex} < \mu \). The same arguments could be used for the relation between the phonon coupling constant \( \lambda_p \) and \( \mu \). However, it is known that \( \lambda_p \) can be much larger than \( \mu \). The explanation is that umklapp processes are involved and that \( \varepsilon \) is really a tensor in reciprocal lattice vectors. All this is intimately involved with the fact that the local field at an ion can be considerably different than the average field in that lattice cell.\(^4,5\) We shall show that the situation is similar for the exciton mechanism and that in favorable cases one can also have \( \lambda_{ex} > \mu \). Physically, the exciton-induced interaction comes from polarization of the valence bonds within the unit cell.

Cohen and Anderson\(^3\) derive for a simple model of the phonon mechanism an effective interaction of the form

\[
-\frac{N(0)}{2} \left[ \varepsilon \left( G \right) - \bar{\varepsilon} \right] \left( G \right) = \frac{\mu - \lambda_p}{\omega_p}, \tag{1.3}
\]

where \( N(0) \) is the ion plasma frequency and \( \omega_p \) the phonon frequency. The averaged term, equal to \( \lambda_p/\mu \), can be much larger than unity. We shall show that a similar expression applies to the exciton mechanism

\[
-\frac{N(0)}{2} \left( G \right) = \frac{\mu - \beta \left( \omega_p/\omega \right)}{\omega_p} = \frac{\mu - \lambda_{ex}}{\omega_p}, \tag{1.4}
\]

where \( \omega_p \) is the electron plasma frequency in the semiconductor and \( \omega_p \) the average gap frequency. Here \( \varepsilon(G) \) is a dielectric constant for a metal of equal electron density and \( \beta \) is a numerical factor, less than unity, which accounts both for the decay of the metallic electron's wave function in the semiconductor and the fraction of time the metal electrons spend in the semiconductor.

The expression for \( \lambda_{ex} \) may be rewritten

\[
\lambda_{ex} = \frac{b}{a} \frac{\omega_p^2}{\omega_p^2}, \tag{1.5}
\]

where \( b \) is the fraction of time the electron spends in the semiconductor, \( a \) is a reduction factor of order \( \frac{1}{2} \), which includes the screening factor \( 1/\varepsilon(G, \omega) \). In favorable cases, one could have \( \omega_p \sim 10 \text{ eV}, \quad \omega_p \sim 2 \text{ eV}, \quad \beta \sim 2, \quad \mu \sim \frac{1}{2}, \quad \lambda_{ex} \sim 0.2 - 0.5 \). As we shall see, such values should give substantial increases in the transition temperature of the metal film.

Numerical solutions of the superconducting energy-gap equation have been carried out for a number of cases to establish how the transition temperature \( T_c \) varies with the various parameters of the theory. For the exciton mechanism alone, \( T_c \) is a maximum of the order of \( 800 \text{ K} \) for values of \( \lambda_{ex} \sim 1.4 \), no doubt unrealistically large. A series of calculations were made for \( \lambda_{ex} = \mu \), the limiting value some predict on grounds of stability. With this limitation, \( T_c \) is noticeably enhanced, although not to more than about \( 30 \text{ K} \). However, we do not believe that this is a valid limitation, and that values of \( \lambda_{ex} > \mu \) are possible under very favorable conditions. Taking reasonable values for the parameters of the theory and allowing \( \lambda_{ex} > \mu \), we have made some calculations of \( T_c \) vs \( \lambda_{ex} \), where the exciton and phonon mechanisms act together.

II. MODEL OF METAL-SEMICONDUCTORS INTERFACE

We suppose that the metal film and semiconductor are in intimate contact with no oxide layer or other barrier separating them. This implies that there is a chemical bonding at the interface such that the tails of the wave functions of the electrons near the Fermi surface of the metal penetrate into the energy-gap region of the semiconductor.\(^6\) For optimum penetration, the Fermi level \( E_F \) of the metal should be near the center of the semiconductor gap at the interface, as illustrated in Fig. 1. Band bending due to the space charge of the metal electrons in the semiconductor should be less than the order of half of the average gap. This gives some limitation on the maximum penetration of the metal electrons one can have without getting a large concentration of free carriers in the semiconductor near the interface.

We estimate the penetration for a simple model and also calculate the band bending due to the space charge of the metal electrons in the semiconductor. We assume that the band gap \( E_g \) is small compared with the semiconductor plasma energy, so that for \( \hbar \omega < E_g = \hbar \omega_p \), the dielectric function is large. For frequencies \( \omega > \omega_p \) in first approximation, the screening is similar to that of a metal with an electron density equal to that of the valence electrons.

For simplicity we assume an isotropic energy

FIG. 1. Metal–semiconductor interface. \( E_c \) and \( E_v \) are the bottom of the conduction band and top of the valence band, respectively.
gap in the semiconductor such that the electron energy $E$ measured from midgap may be expressed in the form

$$E = \pm \left[ \frac{\hbar^2}{2m} \left( k_x^2 + k_y^2 \right) - E_F \right]^{1/2}, \quad (2.1)$$

in analogy with a superconductor with a gap $2\Delta = E_{\phi}$. Here $\epsilon$ is the free-electron energy, measured from the Fermi level at midgap,

$$\epsilon = \left( \frac{\hbar^2}{2m} \right) \left( k_x^2 + k_y^2 \right) - E_F,$$  \quad (2.2)

where $k_x^2 = k_x^2 + k_y^2$ is the square of the component of $k$ parallel to the interface. The Fermi energy may be expressed as

$$E_F = \left( \frac{\hbar^2}{2m} \right) \left( k_x^2 + k_y^2 \right), \quad (2.3)$$

where $k_{\|}$ is the value of $k_x$ required to give the energy $E_F$ for a given transverse component $k$.

$$\alpha = \left( \frac{\hbar^2}{2m} \right) k_{\|}, \quad (2.4)$$

where we have assumed $\alpha < k_{\|}$ and neglected a term of order $\alpha^2$. Solving Eq. (2.1) for $\alpha$ we obtain

$$\alpha = \frac{m |(\frac{1}{2}E_F^2 - E^2)|^{1/2}}{\hbar^2 |k_y^2 - k_y^2|^1/2}, \quad (2.6)$$

where $k_F$ is the magnitude of the Fermi wave vector.

The wave functions decay as $e^{-\alpha x}$ and the electron density as $e^{-2\alpha x}$. To get the average depth of penetration $D = (1/2\alpha)$ for electrons with energies in the gap we need to average over energies and over $k_x$ values. We then find

$$D = \left( \frac{1}{2\alpha} \right) = \left( \frac{\hbar^2}{mE_F} \right) \int_{E_F/2}^{E_F} \left( \frac{1}{2}E_F^2 - E^2 \right)^{1/2} dE \times \frac{2}{\hbar} \int_{E_F/2}^{E_F} \left( k_x^2 + k_y^2 \right)^{1/2} dE \right.$$  \quad (2.7)

For $k_F = 1.5 \times 10^{10}$ cm$^{-1}$, corresponding to an electron density of $\sim 10^{23}$ cm$^{-3}$ and $E_x = 2$ eV, we find that $D$ is of the order of $5 \AA$, or about two atomic layers. We stress that this estimate of the tunneling distance assumes good matching at the two semiconductorsuperconductor interface and is thus an optimistic one. Other models of the metal-semiconductor interface are of course possible and may lead to smaller estimates of tunneling distances.

The voltage drop due to the space charge of the penetrating electrons in the gap is less than one might suppose because of the high dielectric constant of the semiconductor. The number of such electrons per unit area of semiconductor surface is

$$\sigma = \gamma N(0) E_F D, \quad (2.8)$$

where $2N(0)$ is the Fermi-level density of states for electrons of both spins in the metal, $\gamma N(0) E_F$ is the corresponding density of electrons at the interface in the energy range $-\frac{1}{2}E_F$ to $0$ of the semiconductor gap, and $D$ is the average depth of penetration. A schematic plot of the variation of density of states with $z$ is given in Fig. 2.

The electric field produced by these electrons at the interface is $4\pi\alpha_0 / \epsilon_0$, where $\epsilon_0$ is the dielectric constant and the voltage drop is of order $4\pi\alpha_0 D / \epsilon_0$. The change in electron energy due to this drop should be less than half the gap, or $\frac{1}{2}E_x$. Thus we require that

$$4\pi\alpha_0^2 \gamma N(0) E_F D^2 / \epsilon_0 < \frac{1}{2}E_x \quad (2.9)$$

or

$$8\pi\alpha_0^2 \gamma N(0) D^2 < \epsilon_0.$$

For $k_F = 1.5 \times 10^{10}$ cm$^{-1}$, $N(0) \sim 3 \times 10^{23}$ erg$^{-1}$ cm$^{-3}$, and $D = 5 \times 10^{-6}$ cm we find $\epsilon_0 / \gamma \sim 40$. For $\gamma \sim \frac{1}{2}$, $\epsilon_0$ should be of the order of 20 or larger. Such values are typical of many narrow-gap semiconductors.

Also using the relationships depicted in Fig. 2, we may define for future discussion the parameter $b = \gamma D / \hbar$, where $L$ is the thickness of the metal film and $b$ roughly signifies the fraction of the time the metal electrons spend in the semiconductor. If we take $L \sim 10-15$ A, $\gamma \sim 1$, and $D \sim 5$ A, we get $b \sim \frac{1}{4}$.

III. INTERACTION: DISCUSSION OF $\lambda_{\text{ex}}$

We now turn our attention to the interaction potential. As is well known from the BCS theory of superconductivity, an attractive interaction between electrons near the Fermi surface in a material is necessary for a superconducting state to exist. An excellent discussion of the form and properties of the interaction potential of physical systems is presented in the review article of Ginzburg and also in an article by Cohen and Anderson.

For our metal-semiconductor system, the interaction is the combination of three contributions,

$$V(\omega) = V_{\text{ph}} + V_C + V_{\text{ex}}, \quad (3.1)$$

where $V_{\text{ph}}$ is the phonon part, $V_C$ the Coulomb in-

FIG. 2. Plot illustrating the tailing of the density of states into the semiconductor gap. The density of states at the interface is given by $\gamma N(0)$. 

This content is from the paper by Allender, Bray, and Bardeen.
teration, and \( V_0 \) the exciton part. The \( \omega \) variable is an energy variable representing the energy difference between the initial and final states which occurs in the matrix elements for the scattering processes. We shall comment only briefly on the Coulomb and phonon interactions but examine the exciton contribution in some detail.

The Coulomb interaction is represented by the parameter \( \mu \). We start with the Fourier transform of the screened Coulomb potential \( V_C(\mathbf{q}, \omega) \),

\[
V_C(\mathbf{q}, \omega) = \frac{4\pi e^2}{q^2} q^2 \epsilon(\mathbf{q}, \omega)
\]

\[
\approx 4\pi e^2 \left( \frac{q^2 + q_s^2}{q^2} \right) \text{ for } \omega \ll \omega_F,
\]

(3.2)

where \( \mathbf{q}, \omega \) are the momentum and energy transfers in the electron scattering, \( \epsilon(\mathbf{q}, \omega) \) is the electronic dielectric function for a metal of equivalent electron density, and \( q_s \) is an appropriate screening wave vector. We may then define \( \mu \) to be the average of \( V_C(\mathbf{q}, \omega) \) over the Fermi surface times the density of states at the Fermi surface \( N(0) \):

\[
\mu = N(0) \langle V_C \rangle.
\]

(3.3)

The average over the Fermi surface \( \langle V_C \rangle \), may be expressed as an integral over \( q \), leaving \( \mu \) as a function of \( \omega \) only. We then choose the square–well model, in which \( \mu \) is taken to be a constant out to \( \omega = \omega_F \):

\[
\mu(\omega) = \mu \text{ for } 0 \leq |\omega| \leq \omega_F
\]

\[
= 0 \text{ otherwise.}
\]

(3.4)

It is, in general, quite difficult to predict \( \mu \) theoretically for a given material, since various approximations for the dielectric function lead to different values for \( \mu \). The authors wish to thank Allen for providing them with Fig. 3, which shows \( \mu \) as a function of \( r_s \) for the Fermi–Thomas, \( \text{Lindhard} \), and \( \text{Hubbard} \) approximations to the dielectric function.

Next we derive an estimate of the exciton–electron coupling constant \( \lambda_{pe} \). The interaction term in the Hamiltonian for a metal electron arising from the semiconductor electrons consists of a screened Coulomb–like potential, summed over all of the semiconductor valence electrons:

\[
H_{int} = \sum_i \left( \epsilon^2 / |\mathbf{T}_i - \mathbf{r}| \right)_e
\]

(3.7)

where \( \mathbf{T}_i \) is the coordinate of the metal electron and \( \mathbf{r}_i \) is the position of the \( i \)-th semiconductor–valence electron. The subscript \( e \) implies that the interaction is screened as in a metallic jellium model of equivalent electron density.

We Fourier transform to obtain, for \( \omega \ll \omega_F \),

\[
H_{int}(r) = \sum_i \sum_\omega \frac{4\pi e^2}{q^2} \left( \epsilon(\mathbf{q}, \omega = 0) \right)^2 \left( 1/|\mathbf{T}_i - \mathbf{r}| \right)
\]

(3.8)

Clearly, \( 4\pi e^2 / q^2 \epsilon \) is the Fourier coefficient of the screened interaction.

The fluctuations in potential in each cell that
give rise to the band gaps will be treated in perturbation theory. The reciprocal dielectric function \([1/\epsilon]_{\vec{q},\vec{k}}\) may be regarded as a tensor in the reciprocal lattice vectors \(\vec{R}\) and \(\vec{q}\). As shown by Adler\(^4\) and by Wiser,\(^5\) the tensor character allows for local field effects. Cohen and Anderson have shown that for the phonon mechanism, local fields permit having an effective attractive interaction \(\lambda_{\alpha}\sim\mu\) without violating stability considerations.

The same applies in an analogous way to the exciton mechanism.

We may then write
\[
H_{\text{exc}} = \sum_{\vec{q}} s(4\pi\epsilon^2/q^3)\rho_{\alpha\beta} e^{-i\vec{q}\cdot\vec{r}} \tag{3.9}
\]
where
\[
\rho_{\alpha\beta} = \sum_{\vec{r}} e^{i\vec{q}\cdot\vec{r}} \tag{3.10}
\]

The screening factor \(s\) in Eq. (3.9) is of order \(1/\epsilon\) and approximates the effects of the dielectric tensor \(1/\epsilon\). In terms of our notation in Eq. (3.2) we may write
\[
s = (1/\epsilon) = (q_\beta^2/(q_\alpha^2 + q_\beta^2)) \sim \frac{1}{2} \tag{3.11}
\]

since average \(q_\alpha\)'s are of order \(k_F\) and \(q_\beta\) of \(k_F\). The angular brackets denote an average over the Fermi surface as in Eq. (3.3).

We form the matrix element
\[
M = \langle N\vec{K}_1|H_{\text{exc}}|0,\vec{K}_2\rangle, \tag{3.12}
\]
where \(|0,\vec{K}_2\rangle\) is the initial state with no exciton and a metal electron of momentum \(\vec{K}_2\) and \(|N,\vec{K}_1\rangle\) is the final state with an exciton \(|N\rangle\) of definite momentum \(-\vec{q}\) and the metal electron scattered to \(\vec{K}_1 = \vec{K} + \vec{q}\).

If we assume plane-wave states for the metal electrons, the matrix element becomes
\[
M = \sum_{\vec{q}} s(4\pi\epsilon^2/q^3)\rho_{\alpha\beta}(q_\alpha^2)\rho_{\gamma\delta}(q_\gamma^2) \tag{3.13}
\]
where \(\rho_{\alpha\beta}(q_\alpha^2) = \langle N|\rho_{\alpha\beta}|0\rangle\). Actually only the transverse components of \(\vec{K}\) can be defined by a wave vector and there will be only a limited number of states in the \(\vec{K}\) direction, but this will not affect the order of magnitude of the estimates to be made. The range of the interaction is less than the depth of penetration into the semiconductor.

The exciton scattering process shown in Fig. 4 is second order in perturbation theory involving both the emission and absorption of a virtual exciton. Either pair electron may emit or absorb the exciton, implying an additional factor of 2. Thus for \(\omega \ll \omega_{01}\),
\[
V_{\text{ex}} = 2 \sum_{\vec{q}} \frac{|M|^2}{\omega_{\gamma\delta}}. \tag{3.14}
\]

However, this expression for \(|M|^2\) still needs to be modified by the factor that gives the fraction of time the metal electrons are in the semiconductor \(b\) and by the decreased amplitude in the penetration region \(\gamma\):
\[
V_{\text{ex}} = 2 s^2 \frac{4\pi\epsilon^2}{q^3} \sum_{\vec{q}} \gamma b \frac{4\pi\epsilon^2}{q^3} \frac{(\rho_{\alpha\beta})^2}{\omega_{\gamma\delta}}. \tag{3.15}
\]

Now approximate \(\omega_{01}\) by its average value \(\langle \omega_{01}\rangle = \omega_{\epsilon}\) the average gap width:
\[
V_{\text{ex}} = 2 s^2 \gamma b (4\pi\epsilon^2/q^3) \sum_{\vec{q}} (4\pi\epsilon^2/q^3)(\rho_{\alpha\beta})^2 \tag{3.16}
\]

We use the following two sum rules:\(^12\)
\[
\int_0^\infty \omega \epsilon_s(\omega) d\omega = \frac{1}{2} \pi \omega_p^2 = \frac{1}{2} \pi (4\pi m e^2/m), \tag{3.17}
\]
\[
\int_0^\infty \epsilon_s(\omega) d\omega = \frac{1}{2} \pi \omega_p^2 (\rho_{\alpha\beta})^2 \tag{3.18}
\]

where \(\omega_p\) is the electronic-plasma frequency, \(\epsilon_s\) is the imaginary part of the dielectric function, and \(n_e\) is the density of semiconductor valence electrons.

We approximate the first sum rule by assuming that \(\epsilon_s\) is sharply peaked at \(\omega = \omega_p\) and integrating just over this exciton peak:
\[
\int_0^\infty \omega \epsilon_s(\omega) d\omega \rightarrow \omega_p \int_{\text{peak}} \epsilon_s(\omega) d\omega. \tag{3.19}
\]

We may reduce \(n_e\) to some value \(n_{e\text{eff}}\) to account for integrating only over the exciton peak. Then
\[
\int \frac{1}{\omega_p} \epsilon_s(\omega) d\omega = \frac{1}{2} \pi \omega_p^2 \omega_p^2 \tag{3.20}
\]

giving
\[
V_{\text{ex}} = s^2 \gamma b (4\pi\epsilon^2/q^3)(\omega_p^2/\omega_{\epsilon}^2). \tag{3.21}
\]

The value of \(\lambda_{\alpha\beta}\) is \(N(0)\) times the average of \(V_{\text{ex}}\) over the Fermi surface:
\[
\lambda_{\alpha\beta} = N(0)\langle V_{\text{ex}} \rangle \tag{3.22}
\]
\[
= \langle N(0)|s(4\pi\epsilon^2/q^3)|\langle \epsilon\rangle \gamma b (\omega_p^2/\omega_{\epsilon}^2), \tag{3.23}
\]
which is similar to (1.5) with \(s\gamma = \alpha\).

Taking favorable estimates for parameters
\(b \sim \frac{1}{3}, \gamma \sim \frac{1}{3}, \omega_p \sim 10 \text{ eV}, \omega_{\epsilon} \sim 2 \text{ eV}\), we get
\[
\lambda_{\alpha\beta} \lesssim 0.5. \tag{3.24}
\]
IV. DISCUSSION OF CALCULATIONS

A. Integral Equation for Energy Gap Function

In order to estimate the effect of an exciton mechanism, we have obtained numerical solutions to the integral equation for the superconducting gap as used by McMillan\textsuperscript{12} for the limiting case \( T = T_c \). The integral equation for \( \Delta \) is then linear and homogeneous and \( T_c \) is determined such that there is a solution for \( \Delta \):

\[
\Delta(\omega) = [Z(\omega)]^{-1} \int_0^\infty d\omega' (\omega')^{-1} \text{Re}[\Delta(\omega')]
\times \int_0^{\omega_m} d\omega_p \alpha^2_p(\omega_p) F_p(\omega_p) \{N(\omega_p) + f(-\omega')\}
\times \left[ \frac{1}{(\omega' + \omega_p + \omega)^2 + (\omega' + \omega_p - \omega)^2} \right] - \left[ N(\omega_p) + f(\omega') \right]
\times \left[ \frac{1}{(\omega' + \omega_p + \omega)^2 + (\omega' + \omega_p - \omega)^2} \right]
\times \left[ \frac{1}{(\omega' + \omega_p + \omega)^2 + (\omega' + \omega_p - \omega)^2} \right] + \mu [Z(\omega)]^{-1} \int_0^{\omega_m} d\omega' (\omega')^{-1} \text{Re}[\Delta(\omega')]
\times \left[ 1 - 2f(\omega') \right],
\]

where \( F_p(\omega_p) \) is the phonon density of states, \( \omega_m \) is the maximum phonon frequency, \( \alpha^2_p(\omega_p) \) is an average of the electron-phonon interaction, and \( N(\omega) \) and \( f(\omega) \) are the Bose and Fermi occupation probabilities, respectively.

Several approximations were made with the dual purpose of convenient numerical solution and optimum values for the relevant parameters. Only the real part of \( \Delta(\omega) \) was considered, and \( N(\omega) \) and \( f(\omega) \) were evaluated at zero temperature. A Lorentzian was used for \( F_p(\omega) \):

\[
F_p(\omega_p) = B / \left[ \{ [\omega_p - \omega_{ph}]^2 + B^2 \} \right],
\]

where \( B \) is full width at half-maximum and \( \omega_{ph} \) is center of spectrum. The interaction \( \alpha^2_p(\omega_p) \) was assumed constant and was evaluated such that when \( \omega = \omega' = 0 \), the integral over \( \omega \) reduces to \( \lambda_{ph} \).

Finally, an exciton kernel was added to the integrand.

Thus we arrive at the form of the integral equation that was solved:

\[
\Delta(\omega) = [Z(\omega)]^{-1} \int_0^\omega m d\omega' (\omega')^{-1} \text{Re}[\Delta(\omega')]
\times (K_{ex} + K_{ph} - \mu),
\]

where

\[
K_{ph} = \int_0^{\omega_m} d\omega_p \alpha^2_p(\omega_p) F_p(\omega_p)
\times \left[ \frac{(\omega' + \omega_p + \omega)^2 + (\omega' + \omega_p - \omega)^2}{(\omega' + \omega_p + \omega)^2 + (\omega' + \omega_p - \omega)^2} \right] + \frac{\omega_{ph}}{\omega_{ph} + B}/\omega_{ph},
\]

\[
\alpha^2_p = 0.5 \lambda_{ph} (\omega_{ph} + B)/\omega_{ph}.
\]

The exciton kernel is written in analogy with the phonon part:

\[
K_{ex} = \int_0^{\omega_m} d\omega_p \alpha^2_p(\omega_p) F_p(\omega_p)
\times \left[ \frac{(\omega' + \omega_p + \omega)^2 + (\omega' + \omega_p - \omega)^2}{(\omega' + \omega_p + \omega)^2 + (\omega' + \omega_p - \omega)^2} \right],
\]

where \( \alpha^2_p = 0.5 \lambda_{ex} (\omega_{ex} + A)/\omega_{ex} \), \( \lambda_{ex} = \) maximum exciton frequency, \( F_p(\omega_p) = A/[\pi(\omega_p - \omega_{ex})^2 + A^2] \). It is seen that a Lorentzian of width \( A \) and centered at the average gap width \( \omega_p \) is used for the excitons. \( \alpha^2_p \) is evaluated such that \( K_{ex} = \lambda_{ex} \) when \( \omega = \omega' = 0 \).

It should be noted that a Lorentzian is a fairly good approximation to the peak in the exciton spectrum. Experimental curves of \( \varepsilon_p(\omega) \) vs \( \omega \) show that \( A = 0.5 \omega_p \) at least.\textsuperscript{11} On the other hand, a Lorentzian approximation of a real phonon spectrum is not good in general.

The renormalization function \( Z(\omega) \) was taken to be

\[
Z(\omega) = \begin{cases} 1, & \omega > \omega_m \\ 1 + \lambda_{ex}, & \omega_m > \omega > \omega_p \\ 1 + \lambda_{ex} + \lambda_{ph}, & \omega_p > \omega. \end{cases}
\]

(4.5)

The values of \( \omega_m \) and \( \omega_p \) were regarded as non-critical and may be taken as a full width beyond the center of their respective Lorentzians.

A final approximation involves evaluating the Fermi and Bose distribution functions at \( T = 0 \), but taking a lower bound on the integral over \( \omega' \) so as to get the correct \( T_c \). The analog in BCS theory is given as follows. The BCS gap equation is

\[
1 = N(0)V \int_0^\theta d\epsilon \frac{\tanh[(\epsilon^2 + \Delta^2)^{1/2} / 2kT]}{\left( \epsilon^2 + \Delta^2 \right)^{1/2}},
\]

where \( \Delta \) is the superconducting energy gap, \( V \) is the effective interaction constant, and \( \theta \) is the maximum phonon temperature. To get \( T_c \) we let \( \Delta = 0 \), \( T = T_c \) and solve Eq. (4.6) to get

\[
T_c = 1.13 \theta e^{-1/\pi N(0)V}.
\]

(4.7)

If, in analogy with letting \( f(\omega) = N(\omega) = 0 \) in Eq. (4.1), we set \( T = 0 \) in Eq. (4.6), then we find that we must replace the lower limit 0 by \( T_{ex}/1.13 \) to recover Eq. (4.7):

\[
1 = N(0)V \int_{T_{ex}/1.13}^\theta d\epsilon \frac{d\epsilon}{\epsilon} \quad \text{[giving Eq. (4.7)].}
\]

(4.8)

McMillan\textsuperscript{12} shows that the BCS gap equation is a good approximation to Eq. (4.1) for small \( \lambda_{ex} \), and therefore we solve our singularity problem by replacing the lower limit 0 in Eq. (4.3) by \( T_{ex}/1.13 \). Equation (4.3) was solved by a computer-iterative procedure. \( \Delta(0) \) was fixed to be one in order to set the scale. The initial guess was a four-step function where the four steps were taken alternately positive and negative on the intervals \( \omega < \omega_{ph}, \omega_{ph} < \omega < 5 \omega_{ph}, 5 \omega_{ph} < \omega < \omega_p, \omega_p < \omega < \omega_{ex} \).

The values of the four steps were non-critical but the general feature of four steps did seem important to convergence. The next approximation for \( \Delta \) was obtained via Eq. (4.4), and one of the parameters was adjusted until \( \Delta(0) = 1 \) again. This process is repeated until \( \Delta(\omega) \) has converged. After convergence one has obtained a set of nine parameters \( \lambda_{ex}, \lambda_{ph} \), etc.
\( \mu, T_c, \omega_{F}, \omega_{p}, A, \omega_{p0}, B \), which are self-consistent within the framework of Eq. (4.3).

We note that many others\(^{12,15,16} \) have obtained solutions to Eq. (4.1) with less restrictive approximations. We have made the aforementioned approximations because we are more interested in the relative effect of the exciton mechanism than in very accurate values for transition temperatures. Also, the values of many of the parameters which are input into the theory are quite difficult to estimate.

### B. Exciton Mechanism Alone

Results for the exciton mechanism alone are calculated by letting \( \lambda_{ph} = 0 \). The gap equation then returns six self-consistent parameters \( (\lambda_{exc}, \mu, T_c, \omega_{F}, A, \omega_{p}) \). Figures 5-7 show results for various parameter values when \( \lambda_{exc} = \mu \), the upper limit for \( \lambda_{exc} \) if umklapp processes are neglected. For this case, one notes that for reasonable parameter values the \( T_c \)'s obtained are not higher than those normally encountered for the phonon mechanism. As noted by Cohen and Anderson, the optimum values for \( \omega_f \) for fixed \( \omega_{p} \) are not far from the usual range of phonon frequencies.

In Fig. 8 we show what critical temperatures are possible if we allow \( \lambda_{exc} > \mu \). One sees that for the parameter values chosen, \( T_c \)'s as large as 800 K may be obtained. These optimum \( T_c \)'s occur for \( \lambda_{exc} \) in the range \( 1.2 \leq \lambda_{exc} \leq 1.5 \), and this range agrees roughly with optimum values for \( \lambda_{ph} \) obtained by Hertel\(^{17} \) for the pure phonon mechanism. As indicated previously, however, for our model physically realizable values for \( \lambda_{exc} \) should be \( \leq 0.5 \). Therefore, Fig. 8 is of interest only to show that higher values of \( T_c \) may be obtained for a more nearly optimum structure. Note that in Fig. 8 we require that a relation similar to Eq. (3.23) holds among the parameters \( \lambda_{exc}, \mu, \omega_{p} \).

### C. Exciton and Phonon Mechanisms Together

So many parameters are involved when both phonon and exciton mechanisms are involved that we

**FIG. 6.** Plot of the behavior of \( T_c \) as a function of \( A/\omega_{p} \) for the exciton mechanism alone with \( \mu = \lambda_{exc} \) and \( \omega_{F} \) fixed. Note that broadening the exciton peak (i.e., increasing \( A \)) reduces \( T_c \) exponentially.

**FIG. 7.** Plot of \( T_c \) vs \( \omega_{F} \) for the exciton mechanism alone. Fixed for each curve are \( \lambda_{exc} \) (\( = \mu \), \( \omega_{p} \), and \( A/\omega_{p} \).

**FIG. 5.** Plots of \( T_c \) vs \( \lambda_{exc} = \mu \) for the exciton mechanism alone are shown with \( \omega_{F} \) and \( A \) held constant. Each curve corresponds to a given \( \omega_{p} \). Note that the transition temperature is a very steep function of \( \mu \).
show results of some typical calculations and then give an approximate formula based on a three-
square-well model that applies more generally.

In Figs. 9 and 10 are plots of $T_c$ vs $\lambda_{ex}$ for typical values of the parameters. In Fig. 9, $T_c$ for the phonon mechanism alone is about 0.6 °K and in Fig. 10 about 3.6 °K. Note that the enhancement of $T_c$ is greater in the absolute sense for larger phonon critical temperatures, but greater percentage enhancements are obtained for smaller phonon $T_c$'s. Values of $\lambda_{ex}$ of the order of 0.2–0.3 are required to get significant enhancement.

We have noted that for optimum values of the parameters a maximum $\lambda_{ex}$ of the order of 0.5 is obtained for our model of a thin metallic layer on a semiconductor surface. It would be necessary to achieve values of the order of one-half this optimum to demonstrate the exciton effect. While not easy, this may be possible.

It is desirable to be able to get a reasonable estimate for $T_c$ corresponding to a given set of parameters without solving the gap equation numerically. To this end, we neglect the exciton and phonon spectrum widths $A$ and $B$ and consider a three-square-
well approximation to the interaction potential. We define the interaction constant by

$$R = \begin{cases} 
-\lambda_{ph} - \lambda_{es} + \mu, & 0 < \omega < \omega_{ph} \\
-\lambda_{es} + \mu, & \omega_{ph} < \omega < \omega_e \\
\mu, & \omega_e < \omega < \omega_F 
\end{cases} \tag{4.9}$$

where

$$\lambda_{ph}^{*} = \lambda_{ph} / (1 + \lambda_{ph}), \quad \lambda_{es}^{*} = \lambda_{es} / (1 + \lambda_{es}).$$

This redefinition of the $\lambda$'s is suggested by McMillan's strong coupling modification of the BCS equations. We now arbitrarily apply a renormalization technique twice to obtain a BCS-like equation for $T_c$:

FIG. 9. Plot of $T_c$ vs $\lambda_{ex}$ for the combined phonon and exciton mechanisms using the indicated parameter values. The approximate formula of Sec. IV C is also shown. The critical temperature for just the phonon mechanism is 0.61 °K.

FIG. 10. Same set of plots as Fig. 9 except now the phonon critical temperature is 3.5 °K.
\[ T_0 \approx 0 e^{-1/2\mu'} \quad (4.10) \]

where

\[ \varepsilon_{\text{eff}} = \lambda_{\text{ph}} + \frac{(\lambda_{\text{ex}} - \mu')}{[1 - (\lambda_{\text{ex}} - \mu') \ln (\omega_p / \omega_p)]}, \]

\[ \mu' = \mu / [1 + \mu \ln (\omega_F / \omega_p)], \]

\[ \theta_e = \omega_p / k_B. \]

The constant of proportionality in Eq. (4.10) was determined by forcing agreement with numerical results at \( \lambda_{\text{ex}} = 0 \) and is found to be \( \sim 1/1.45 \). The approximate formula (4.10) is plotted in Figs. 9 and 10 for comparison with numerical results. Reasonable agreement is obtained, particularly for \( \lambda_{\text{ex}} \lesssim 0.45 \).

V. CONCLUSION

It has been shown that a metal-semiconductor sandwich presents a theoretically favorable situation for the observation of the exciton mechanism of superconductivity. Reasonable values for tunneling parameters and \( \lambda_{\text{ex}} \) were obtained by rough calculations. Then, using these estimates for parameters, it was demonstrated that the energy gap equation yields substantially enhanced \( T_0 \)'s for the exciton-phonon mechanism when compared to the phonon mechanism alone. We conclude that our theoretical results are sufficiently encouraging to warrant a substantial experimental effort to establish the exciton mechanism in the described manner with an ultimate goal of producing high-temperature superconductivity.

We caution again, however, that there appear to be substantial experimental problems associated with producing a sandwich structure. Adequate electron tunneling into the semiconductor gap requires both intimate contact (i.e., no surface states) at the metal-semiconductor interface and a very thin-metallic layer. Achieving good penetration of metallic wave functions into the semiconductor may be the most difficult task. It is necessary to match the work functions of the metal and semiconductor within about 0.5\( \omega_p \) so that severe semiconductor band bending with its deleterious effects upon tunneling is not encountered. Band bending due to the space charge region from the tunneling electrons may be allowed for and possibly compensated by doping of the semiconductor with a \( p \)-type impurity (Fig. 1). Very critical is the use of a narrow-gap semiconductor with a large value for the ratio of electron-plasma frequency to average gap energy.

It should be noted that several other physical arrangements for observing the exciton mechanism have been suggested and discussed. These include metal granules imbedded in a dielectric matrix, long molecules with side branches playing the role of polarizers, and various layered compounds using both organic and inorganic materials. In view of the difficulties probably associated with producing the metal-semiconductor sandwich, it is desirable to consider all possibilities for realizing the exciton mechanism. In general, every idea must involve the physical juxtaposition of a sufficient density-of-mobile charge carriers and a region where excitons are present. For instance, one might envision the deposition of cesium or another alkali metal on a semiconductor surface to bend the gap \( \sim 1-2 \text{ eV} \) below the Fermi level near the cesium-semiconductor interface. The resulting locally large accumulation of electrons above the bent portion of the gap might provide a source of electrons to tunnel into the gap to interact with the excitons. One problem with this suggestion is that the electrons tunnel only \( \sim 5-10 \text{ Å} \), while the band bending is relatively gradual \( \sim 100 \text{ Å} \). In regions where the electron density is high the bands would be bent so far that the exciton mechanism is ineffective.

Clearly, utilization of the exciton mechanism offers substantial opportunity for creative experimental suggestions. The authors believe the sandwich structure to be the most promising and should be pursued. However, it is not easy to vary the relevant parameters in such a structure. Hence we have suggested studying a single interface to try to demonstrate the exciton effect in a system in which parameters are known or can be measured so that predictions and comparisons with theory can be made. Such experimental studies are underway by Miller.

The realization of an exciton mechanism would not only be a notable achievement in itself, but could possibly lead to substantially enhanced transition temperatures. While success cannot be predicted with any certainty, the authors believe that the exciton mechanism has a firm theoretical foundation. The main problem is to try to find or build suitable structures. Conditions are exacting, but appear possible to achieve with sufficient effort.

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Electron Spin Resonance and Superconductivity in Gd$_{x}$La$_{1-x}$Al$_{3}$ Intermetallic Compounds

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Electron-spin-resonance measurements of Gd in LaAl$_3$ exhibit appreciable change of the g value and linewidth upon alloying with other nonmagnetic impurities. This indicates the existence of a “bottleneck” effect—the relaxation rate for the conduction electrons to the Gd ions $\delta_{el}$ exceeds that to the lattice $\delta_{l}$. We are able to shift the g value from $g = 2.11 + 0.01$, opening the bottleneck completely. The intermetallic compounds GdLa$_{1-x}$Al$_3$ are Abrikosov–Gorkov superconductors in the dilute limit. Measurements of the transition temperature and the upper critical field depend upon $\delta_{el}$ and $\delta_{l}$ indirectly. We are thus able to obtain parameters which determine superconducting critical-field and temperature behavior from magnetic resonance experiments.

I. INTRODUCTION

Previous electron–spin–resonance measurements of Gd in concentrated GdAl$_3$ indicate a negative g shift$^{10,11}$ which has been interpreted in terms of a negative exchange interaction between the Gd 4f and the conduction electrons. Assuming a rigid–band model, one would expect that substitution of La in place of Gd would not appreciably change the conduction–band structure, and thus the g shift. It was surprising, therefore, that the g shift of dilute (in retrospect, partially unbottlenecked) LaAl$_3$–Gd was found to be positive.$^3$ The purpose of this paper is to present new experimental data on this system. We shall demonstrate the existence of a bottleneck in the exchange relaxation mechanism. By introducing other (nonmagnetic) impurities we are able to shift the g value from $g = 2.11 + 0.01$ (a large positive shift), opening the bottleneck completely. We shall show that our experimental data, as well as the electron–paramagnetic–resonance (EPR) results of others$^{10-13}$ for the dilute and the magnetically dense GdLa$_{1-x}$Al$_3$ system, are consistent with a two–band model. This removes the experimental “discrepancy” between the EPR results for the magnetically concentrated and dilute alloys.

A condition for a bottleneck in the electron spin resonance of dilute magnetic alloys is that the conduction electrons’ relaxation rate to the paramagnetic ions $\delta_{el}$ exceeds that to the lattice $\delta_{l}$. The former can be changed by changing the concentration of the paramagnetic impurities. The latter is very sensitive to any nonmagnetic “dirt,” and therefore to the hard–to–control method of preparation. An advantage of using LaAl$_3$ as a nonmagnetic host in its superconductivity. The intermetallic compounds Gd$_{x}$La$_{1-x}$Al$_3$ (in the dilute limit) are Abrikosov–Gorkov superconductors,$^4$ so that $T_c$ measurements provide information about the concentration and exchange scattering rate of the magnetic impurities, while $H_{c2}$ measurements (upper critical field) give in addition information about the potential scattering rate of any nonmagnetic impurities. This enables us to control and measure $\delta_{el}$ directly and $\delta_{l}$ indirectly, independent of the EPR results. The correlation between these two techniques enables one to check the Hasegawa$^5$ model in a critical manner.

We shall present sample preparation and analysis in Sec. II, the EPR results in Sec. III, the superconducting behavior in Sec. IV, the interpretation in Sec. V, and the summary of our results in Sec. VI. We shall demonstrate that EPR can