PHYSICAL REVIEW B VOLUME 8, NUMBER 9 1 NOVEMBER 1973

Comment on "Model for an Exciton Mechanism of Superconductivity"

J. C. Inkson
Cavendish Laboratory, Cambridge CB2 3RQ, United Kingdom

P. W. Anderson*
Cavendish Laboratory, Cambridge CB2 3RQ, United Kingdom
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 2 March 1973)

The excitonic mechanism of superconductivity in a metal-semiconductor system is studied from the point of view of the complete electron-electron interaction. It is shown that recent calculations of an enhancement of the superconducting transition temperature by way of virtual excitons involves a double counting of these processes. Once this is taken into account the enhancement disappears. The local-field effects in the semiconductor are discussed but it is shown that the off-diagonal elements of the interaction are no help in recovering the enhanced superconductivity.

There has been a recent flurry of interest in what might be called the superconducting Schottky barrier.[1] In this system, enhancement of the superconducting critical temperature of a metal is achieved by placing it in intimate contact with a semiconductor. The electrons in the metal interact by way of virtual excitons in the semiconductor so that an extra attractive interaction is obtained. This system has been aired previously[2] but a recent detailed analysis by Allender, Bray, and Bardeen[1] (hereafter referred to as ABB) suggests that a real effect does exist and should be observable. They derived an expression for the exciton coupling constant to be included in the BCS equation in which the average band gap of the semiconductor (ω_g) appeared thus:

$$\lambda_{ex} \propto \omega_p^2/\omega_g^2 , \tag{1}$$

ω_p being the plasmon energy. This equation would suggest that as the average band gap decreased and our semiconductor tended towards a free-electron metal, the coupling constant would shoot off to large values and astronomically high superconducting transition temperatures would be achieved; quite the opposite of what we would expect to happen. This is of course unfair in that the approximations of AAB's method would break down long before this. We believe in fact, however, that a large amount of double counting has taken place in deriving the above expression. When this is taken into account the anomaly disappears as does, unfortunately, the possibility of real enhancement of the metal superconducting transition temperature.

The model we are concerned with is this[1]: On placing a metal in contact with the semiconductor, metal electrons near the Fermi level tunnel into the semiconductor band gap, where they interact with each other by way of virtual excitons. The depth of penetration of the electrons is, at most, a few angstroms,[3] so that we are in a region where the electron-electron interaction is highly nonlocal.[4] We will ignore this, as ABB have done, and assume that when in the semiconductor the electrons interact by way of the Coulomb interaction reduced by the semiconductor dielectric function $\epsilon_s(\vec{q}, \omega)$. In the metal we have

$$V_c(\vec{q}, \omega) = 4\pi e^2/q^2 \epsilon_m(\vec{q}, \omega) , \tag{2}$$

which leads, by averaging over momentum transfers over the Fermi sphere, to the required parameter $\mu(\omega) = N(0)\langle V_c \rangle$. The symbols have their usual meaning, and of course $\mu(\omega)$ is then approximated by a square-well interaction in energy for the purposes of the BCS equation.[5] In a similar way the electron-phonon interaction is characterized by the parameter λ_{ph}. The total, in favorable circumstances, is an attractive interaction, and superconductivity occurs. We assume in the present model that λ_{ph} is the same for semiconductor and metal. Now we have to include the exciton effects, and here we differ from ABB. It is not enough just to add them onto the μ and λ_{ph} for the metal. The excitons are included in the semiconductor dielectric function, so what we shall look at first is

$$V_{cs}(\vec{q}, \omega) = 4\pi e^2/q^2 \epsilon_s(\vec{q}, \omega) . \tag{3}$$

If we average this in the normal way over the Fermi surface, we get an awkward answer for defining an "effective" μ. Because $\epsilon_s(0, 0)$ is finite we get a logarithmic divergence in $\langle V_{cs} \rangle$ for low energies reflecting the residual long-range repulsion in semiconductors. This of course would be disastrous for any form of superconductivity. This logarithmic divergence will be cut off by screening by the metal layer and may not be particularly strong. On the other hand, we find, upon detailed analysis, that enough remains so that the net effect of the semiconductor layer is to

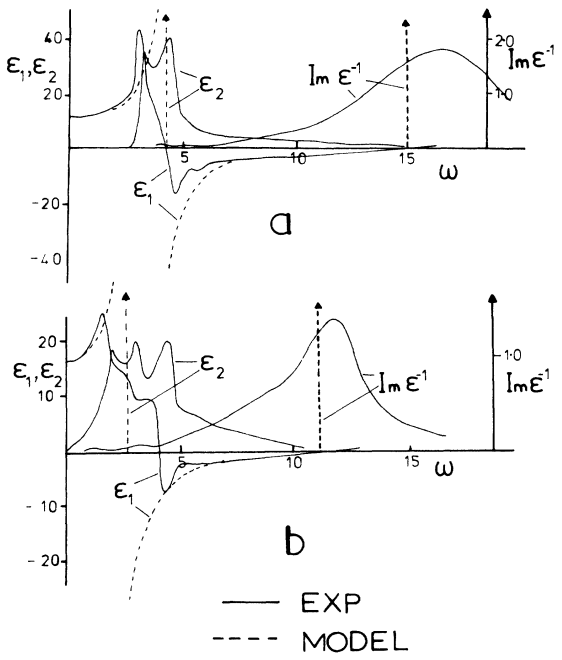

FIG. 1. Comparison of the long-wavelength model dielectric function with the experimental results of Ehrenreich and Phillipp: (a) silicon; (b) indium antimonide.

increase the repulsion, not the attraction. There is a simple form of semiconductor dielectric function which illustrates this[4];

$$\epsilon_s(\vec{q},\omega)=1+\frac{\epsilon_0-1}{1+(q^2/k^2)\epsilon_0-(\omega^2/\omega_R^2)\epsilon_0}\,, \qquad (4)$$

where

$$\gamma^2=k^2\frac{\epsilon_0}{\epsilon_0-1},\quad \omega_R^2=\omega_p^2\frac{\epsilon_0}{\epsilon_0-1}\,,$$

and k^{-1} and ω_p are the screening length and plasmon energy of the equivalent electron density metal. This dielectric function satisfies the sum rules; it has the plasmon peak in Im $[1/\epsilon(\vec{q},\omega)]$ and an "exciton" peak in Im $\epsilon(\vec{q},\omega)$ and also contains the essentials of the structure of the experimental[6] and theoretical[7] semiconductor dielectric functions that we have (Fig. 1). We feel that Eq. (4) is entirely accurate enough for qualitative purposes. Inserting this into Eq. (4), we find that

$$V_{cs}(\vec{q},\omega)=\frac{4\pi e^2}{q^2}\frac{1}{\epsilon_0}+\frac{\epsilon_0-1}{\epsilon_0}\left(\frac{4\pi e^2}{q^2}\right)\frac{1}{\epsilon_M(\vec{q},\omega)}, \qquad (5)$$

where $\epsilon_M(\vec{q},\omega)$ is the metallic dielectric function within the same approximation.[4]

One essential point here is that, as we already remarked, the "excitons" and other excitations are poles of the dielectric function, but these are *zeros* of the interaction because that involves $1/\epsilon$. The main pole of $1/\epsilon$ is at the plasma frequency, just as in a metal.

If we averaged Eq. (5) we would have the normal μ factor reduced by $(\epsilon_0-1)/\epsilon_0$, but what we are left with to add on is the long-range Coulomb repulsion, which only disappears as we go to the metallic limit $\epsilon_0\to\infty$. This leaves us with the conclusion that the effect of the presence of the semiconductor will be to suppress rather than enhance the pair attraction.

What about the excitonic effect of ABB? Let us look at it in more detail. The mechanism is illustrated in Fig. 2(a). We have interactions involving the emission and absorption of virtual excitons. This is second order in perturbation theory and, so, of course, is attractive. By various approximations ABB were available to evaluate the matrix elements and obtain the result of Eq. (1). Consider now the similar process which occurs in the metal—the interaction by way of virtual excitation of electron-hole pairs [Fig. 2(b)]. Obviously there is no essential difference between the two processes. In diagrammatic form the second process corresponds to that shown in Fig. 3(a), and in Fig. 3(b) we show how this process fits into the total Coulomb interaction by a simple resumming of the RPA diagrams for the interaction. We see that if we take out this process we leave the *bare* Coulomb interaction (modified by the third term in the series). By adding it onto the screened interaction, we would have serious double counting of this process. Of course in the metal case this is not done, but we see that this is just what has happened in the semiconductor.

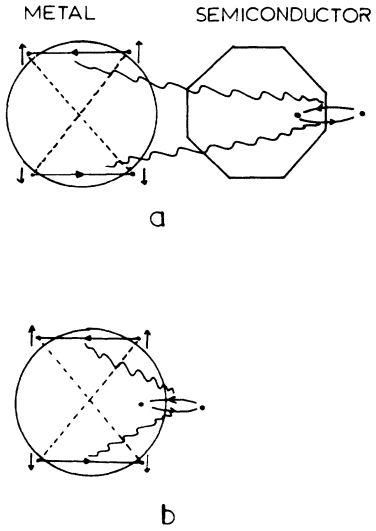

FIG. 2. Schematic representation of (a) Allender, Bray, and Bardeen's (Ref. 1) second-order virtual-exciton process; (b) the equivalent process which occurs in the metal.

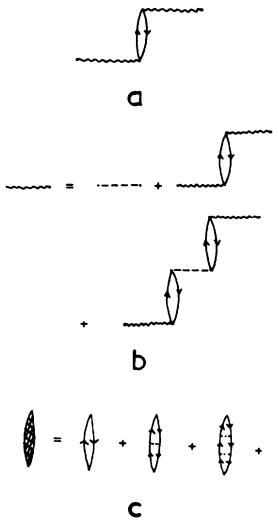

FIG. 3. Diagrammatic representation of (a) the interaction by way of a virtual "exciton"; (b) the splitting of the total Coulomb interaction; (c) the summation for the "exciton" bubble.

If we are to calculate the second-order processes in the manner of ABB, we must use essentially the unscreened interaction in calculating the μ. We now see the way the anomaly of Eq. (1) disappears: As we go towards the metal-metal situation the virtual "exciton" merges into the electron-hole excitation of the metal case, and any effect (be it enhancement or depression) will disappear.

We shall say a few words about the exciton and its contribution to the dielectric function. The excitons to which we have been referring are really electron-hole pairs with a minimum possible energy equal to about the band-gap energy. The changes owing to their being in fact bounded by the Coulomb interaction have been ignored. We would justify this by appeal to the experimental fact that in the type of semiconductors to which we are referring, i.e., those with static dielectric functions larger than about 10, true excitonic effects are very small.[8-10] In energy-loss experiments, for instance, there is no evidence for a significant exciton peak[8]: It is the plasmon-loss peak which dominates, as it is in the reflectance data of Ehrenreich *et al.*[7] (Fig. 1). The coupling between electrons and excitons is small. Even if excitons effects were large, however, our main conclusion, which is that you can not separate off the excitonic effects from the interaction without grave danger of double counting, still holds; we would just have to reinterpret the bubbles of Figs. 3(a) and 3(b) as the "excitonic" bubble obtained by summing the series of laddered bubbles as in Fig. 3(c). As the screening becomes more complete ($\epsilon_0 \to \infty$), this will tend towards the polarization bubble for the metal, and we are back where we started.

There remains one last mechanism by which the interaction is different for metals and semiconductors; that is the relative size of off-diagonal elements in the electronic dielectric function. There is a general sum rule obtained from lattice-stability requirements[11] by which the diagonal and off-diagonal elements of the static dielectric function are connected, but it does not give us actual estimates of the quantities involved. The off-diagonal elements are associated with local-field effects and give, in our case, umklapp processes involving the excitons. For this it is the relative strength of the poles in $1/\epsilon$ which is important, not their static values. We can actually calculate the off-diagonal elements by introducing nearly-free-electron wave functions in the expression for the polarization P[12];

$$P(\vec{q},\vec{q}+\vec{G},\omega)=\sum_{\vec{k},\vec{Q},\vec{Q}'}\frac{f_0(E_{\vec{Q}'}(\vec{k}+\vec{q}))-f_0(E_{\vec{Q}}(\vec{k}))}{\omega-[E_{\vec{Q}'}(\vec{k}+\vec{q})-E_{\vec{Q}}(\vec{k})]}\times\langle\vec{k}+\vec{q},\vec{Q}'|e^{+i\vec{q}\cdot\vec{r}}|\vec{k},\vec{Q}\rangle\times\langle\vec{k},\vec{Q}|e^{i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},\vec{Q}'\rangle, \quad (6)$$

where $\vec{G},\vec{Q},\vec{Q}'$ are reciprocal-lattice vectors and $|\vec{k}\vec{Q}\rangle$ is a wave function of reduced wave vector k ($\vec{k}+\vec{Q}$ in extended zone) and energy $E_{\vec{Q}}(\vec{k})$. For small $\vec{q}$ we get the approximate forms, after some algebra,

$$\epsilon(\vec{q},\vec{q}+\vec{G},\omega)\approx-\frac{\vec{q}\cdot\vec{G}}{q^2}\frac{1}{\omega^2-E_g^2}A, \quad (7a)$$

$$\epsilon(\vec{q}+\vec{G},\vec{q},\omega)\approx-\frac{\vec{q}\cdot\vec{G}}{(\vec{q}+\vec{G})^2}\frac{1}{\omega^2-E_g^2}A, \quad (7b)$$

A is a constant that includes band effects in the integration over $\vec{k}$ in the polarization. The off-diagonal element $\epsilon(\vec{q},\vec{q}+\vec{G},\omega)$ is *not* small compared with the diagonal element $\epsilon(\vec{q},\vec{q},\omega)$ for small $\vec{q}$ (it goes as $1/q$), but in the inversion of the matrix $\{(\epsilon)_{\vec{G},\vec{G}'}\}$ it is the product of factors like $\epsilon(\vec{q},\vec{q}+\vec{G}_1,\omega)\,\epsilon(\vec{q}+\vec{G}_2,\vec{q},\omega)$, which matters; this *is* small compared to the terms involving the diagonal element for the value of A we have estimated. A good approximation to the inverted matrix elements are

$$\epsilon^{-1}(\vec{q},\vec{q}+\vec{G},\omega)=\frac{\epsilon(\vec{q},\vec{q}+\vec{G},\omega)}{\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G},\omega)\,\epsilon(\vec{q},\vec{q},\omega)}, \quad (8a)$$

$$\epsilon^{-1}(\vec{q}+\vec{G},\vec{q},\omega)=\frac{\epsilon(\vec{q}+\vec{G},\vec{q},\omega)}{\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G},\omega)\,\epsilon(\vec{q},\vec{q},\omega)}. \quad (8b)$$

As far as the excitons are concerned, we again get a zero of the interaction [we have one factor $1/(\omega^2-E_g^2)$ on top and two below], and what we said before still holds. As we tend towards the metallic situation, the importance of these off-diagonal elements will decrease still further.[13]

In conclusion, then, we find no evidence for possible excitonic enhancement of the superconducting transition temperature for metal-semiconductor systems; rather the lack of complete

screening in the semiconductor would tend to increase the pair repulsion in that region. The mechanism suggested by ABB has been shown to be due to including the effect of virtual-"exciton" transitions twice while ignoring the incomplete screening in the semiconductor. We would suggest that if excitonic effects are to be found, it would be in a medium which offers excitons *plus* complete screening.

The authors would like to thank Dr. E. Tosatti for stimulating the discussions during the course of this work.

---

*Work at the Cavendish Laboratory supported in part by the Air Force Office of Scientific Research (AFSC), U. S. Air Force under Grant No. AFOSR 73-2449.

[1]D. Allender, J. Bray, and J. Bardeen, Phys. Rev. B **7,** 1020 (1973).

[2]V. L. Ginzberg, Usp. Fiz. Nauk **101,** 185 (1970) [Sov. Phys.-Usp. **13,** 335 (1970)].

[3]V. Heine, Phys. Rev. **138,** A1689 (1965).

[4]J. C. Inkson, J. Phys. C **5,** 2599 (1972).

[5]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106,** 162 (1957); Phys. Rev. **108,** 1175 (1957).

[6]J. P. Walter and M. L. Cohen, Phys. Rev. B **2,** 1821 (1970).

[7]H. Ehrenreich and H. R. Phillipp, Phys. Rev. **128,** 1622 (1962).

[8]C. J. Powell, Proc. Phys. Soc. Lond. **76,** 593 (1960).

[9]E. Tosatti (private communication).

[10]J. C. Phillips, Solid State Phys. **18,** 55 (1966).

[11]L. M. Pick, M. H. Cohen, and R. M. Martin, Phys. Rev. B **1,** 910 (1970).

[12]C. M. Bertoni, V. Bertoloni, C. Calandra, and E. Tosatti, Phys. Rev. Lett. **28,** 1578 (1972). (Our method of the evaluation of the expression for P differs in detail somewhat from theirs as we are interested in the energy dependence.)

[13]J. C. Phillips, Phys. Rev. **123,** 420 (1961); and Phys. Rev. **128,** 2093 (1962).