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XVI-1. Superconductivity in Degenerate Semiconductors*

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A discussion of recent developments in the field of superconductivity in degenerate semiconductors is presented. The application of the BCS theory to degenerate semiconductors and the calculation of the electron-electron interaction is discussed.

Some current experimental results are discussed along with the theory.

§ 1. Introduction

Superconductivity in degenerate semiconductors arises basically from the same mechanisms(1,2) as superconductivity in metals. The electron-lattice interaction is the dominant interaction causing the superconducting transition, and the properties of these materials are consistent with the BCS(3) theory of superconductivity.

Unlike metals, it is possible to change the normal state properties of extrinsic semiconductors radically and to explore the dependence of the superconducting properties on the normal-state system. Band structure effects in superconductivity can be explored since it is possible to change the band structure of many semiconductors in a predictable way by alloying or by applying stress. In a doped semiconductor the carrier concentration can be changed by orders of magnitude and the influence of this change on the superconductivity can be measured. Studies(4) of this type have already yielded information about the mechanisms of superconductivity.

The first successful experimental searches for superconductivity in semiconductors were stimulated by theoretical predictions,(1,2) and the first semiconductors to exhibit superconducting properties were GeTe,(5) $SrTiO_3$(6) and SnTe.(7) These materials are superconducting below .5°K and they all have similar properties.

Originally some skepticism existed about the bulk properties of these samples. It was suggested that the observed superconducting properties arose from superconducting filaments of dense Te in GeTe, Ti in $SrTiO_3$ and Sn in SnTe. It can be argued that such filaments might obscure electrical resistivity and magnetic susceptibility experiments. To dispel all doubt, heat capacity measurements(8~10) were made for all three materials. The results of these experiments showed that the bulk of all three semiconductors were superconducting as opposed to some small concentration of impurity filaments.

Early experimental work on intrinsic semiconductors was not successful at all. This was not surprising since these materials were not even reasonable conductors at low temperatures. The BCS theory explained the negative results since for even a very low transition temperature one needed a reasonably large density of states. In the pure semiconductor case the density of states is so small that a transition at an experimentally measurable temperature is unlikely.

A degenerate semiconductor at first glance doesn't appear too hopeful either. The BCS model solution of the gap equation gives

$$T_C=1.14T_De^{-1/N(0)V}\ , \tag{1}$$

where $N(0)$ is the density of states at the Fermi energy and V is the effective, attractive, electron-electron interaction. The density of states $N(0)\sim m^*n^{1/3}$ and therefore in a typical two band semiconductor one expects 1/10−1/100 of the density of states in a metal. One possibility which was suggested(13) was to look at strong electron-phonon interactions as might occur in a polar semiconductor like InSb. Another suggestion was to look at many-valley semiconductors and very polar ferroelectric-type materials like $SrTiO_3$.(2) The advantage of many-valley systems is that one can get a larger density of states and a larger effective electron-electron interaction. A larger density of states exists because of the distribution of electrons among many valleys instead of one and because masses for bands away from $k=0$ in the Brillouin zone are usually larger than $k=0$ masses. In addition, the attractive electron-intervalley phonon-electron interaction can be large since intervalley scattering involves large momentum transfers which are difficult to screen for low carrier densities.

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For these reasons many-valley semiconductors appear favorable and the three superconducting materials mentioned earlier are believed to be of the many-valley type.

It should be noted that the resistivity of highly doped semiconductors approaches that of semimetals. One would distinguish the latter by the existence of overlapping bands. The theory to be described would apply to a doped (*n* type or *p* type) semiconductor or semimetal.

§ 2. Theory

To compute the superconducting properties of a semiconductor the BCS integral equation must be solved for a specific semiconductor band structure. Neglecting renormalization and lifetime effects this equation has the form

$$\Delta_k = -\frac{1}{2}\sum_{k'}\frac{V_{kk'}\Delta_{k'}}{E_{k'}}\tanh\left(\frac{E_{k'}}{2k_BT}\right), \qquad (2)$$

where Δ_k is the superconducting energy gap, $E_k=(\varepsilon_k{}^2+\Delta_k{}^2)^{1/2}$ is the superconducting quasiparticle energy, ε_k is the normal-state electron energy measured from the Fermi energy E_F, T is the temperature, k_B is Boltzmann's constant and $V_{kk'}$ is the matrix element for electron-electron scattering from the state k to the state k'.

Since degenerate semiconductors are dirty in the Anderson[14] sense, *i.e.* electron or hole scattering times are shorter than $\hbar/\Delta$, the above form of the BCS equation must be modified. This can be done by forming a new basis set which includes the scattering by impurities. Matrix elements are then computed using the new eigenfunctions.[14,2]

After making the above modification, eq. (2) becomes

$$D_k = -\int\frac{D_{k'}}{E_{k'}}K(c,\,\delta)\tanh\left(\frac{E_{k'}}{2k_BT}\right)d\varepsilon_{k'}, \qquad (3)$$

where $D_k \equiv c\Delta_k$, $c=k/k_F$, $\delta=(\varepsilon_{k'}-\varepsilon_k)/E_F$, and the kernel $K(c,\,\delta)$ of the integral equation roughly gives a measure of the "$N(0)V$" parameter of the BCS theory. The kernel contains electron-electron matrix elements $V^{\rm intra}$ and $V^{\rm inter}$ arising from intravalley and intervalley processes. The kernel has the form

$$K(c,\,\delta)=\frac{\Omega k_F{}^3}{4\pi^2E_F}\frac{1}{(\delta+c^2)}$$
$$\times\left[\int_{(\frac{1}{2})|c-(\delta+c^2)^{1/2}|}^{(\frac{1}{2})|c+(\delta+c^2)^{1/2}|}V^{\rm intra}(\beta,\,\delta)\beta d\beta\right.$$
$$\left.+(\nu-1)\int_{(\frac{1}{2})|c-(\delta+c^2)^{1/2}|}^{(\frac{1}{2})|c+(\delta+c^2)^{1/2}|}V^{\rm inter}(\beta_0,\,\beta,\,\delta)\beta d\beta\right], \qquad (4)$$

where $\beta=|k-k'|/2k_F$, β_0 is the wavevector separation of the valleys divided by $2k_F$, ν is the number of valleys, and Ω is the crystal volume.

For the case of a non-polar semiconductor the intravalley interaction[2] $V^{\rm intra}$ contains the repulsive intravalley Coulomb interaction and the attractive interaction caused by the coupling of electrons to the various intravally phonon modes. The Coulomb interaction has the form

$$V^{\rm intra}_{\rm Coulomb}=\frac{4\pi e^2}{(2k_F)^2\Omega\beta^2\varepsilon(\beta,\,\delta)}, \qquad (5)$$

where $\varepsilon(\beta,\,\delta)$ contains the static dielectric function plus a dynamic dielectric function to account for the screening caused by the free electrons. The free electron screening can be estimated by computing the dielectric function based on the Lindhard[15,2] model. This model gives a good approximation to the actual dielectric function for many cases since r_s, the electron gas parameter, can be small in a doped semiconductor.

The attractive interaction can be modeled after a Bardeen-Pines[16] interaction

$$V^{\rm intra}_{\rm phonon}=-\sum_\lambda\frac{2\hbar\omega^\lambda_{k'-k}|M^\lambda_{k'-k}|^2}{(\hbar\omega_{k'-k})^2-(\varepsilon_{k'}-\varepsilon_k)^2}, \qquad (6)$$

where the sum is over λ phonon modes, $\omega^\lambda_{k-k'}$ is the phonon frequency of wavevector $|k'-k|$, and $M^\lambda_{k'-k}$ is the matrix element for scattering an electron from k to k' by a phonon. The matrix elements $M^\lambda_{k'-k}$ can be wavevector-dependent and they can be expressed in terms of deformation potential constants. Values for these constants can then be obtained from normal-state transport experiments.

It should be emphasized at this point that the screening of the electron-phonon interaction by the free electrons is crucial. The deformation potential constants obtained from intrinsic semiconductor experiments must be considered to be "bare" couplings which are weakened by the screening of the free electrons. This is especially important for intravalley processes since small momentum transfers are involved which can be screened by low carrier densities. The screening of the electron-phonon-electron interaction is in general critical since these processes are screened by the square of the dielectric function (once at each vertex).

For polar semiconductors or ferroelectric type materials, the intravalley electron-optical phonon coupling can be computed[13,17] along with the intravalley Coulomb interaction. This interaction has the form

$$V_{\text{polar}}^{\text{intra}}=\frac{4\pi e^2}{\Omega(2k_F)^2\beta^2\varepsilon_T(\beta,\delta)}, \tag{7}$$

where $\varepsilon_T(\beta,\delta)$ is the total dielectric function arising from electron-electron and electron-phonon intravalley scattering. One can obtain this dielectric function by adding the polarizabilities caused by the valence electrons, the free electrons and the optical phonons. For large band gap materials the valence electron polarizability can be taken as a constant $\varepsilon_\infty-1$, where ε_∞ is the high frequency dielectric constant. The free electron polarizability can be computed using the Lindhard[15] dielectric function as in eq. (5). Lastly, the optical phonon polarizability has the form

$$\pi_{\text{phonon}}=\sum_i\frac{4\pi Z_i^2}{(\omega_i^2-\omega^2+i\gamma_i\omega)}, \tag{8}$$

where Z_i is the effective charge for the ith transverse optical phonon mode, ω_i is the frequency of this mode and γ_i is the damping constant for the mode. As an example, the form of ε_T for one optical mode t is

$$\varepsilon_T(\beta,\omega)=\varepsilon(\beta,\omega)_{\text{electrons}}+\frac{(\varepsilon_0-\varepsilon_\infty)\omega_t^2}{\omega_t^2-\omega^2}, \tag{9}$$

where ε_0 is the static dielectric function and $\varepsilon(\beta,\omega)_{\text{electron}}$ is ε_∞ plus the Lindhard free electron polarizability.

The interaction in eq. (7) can now be computed using the full dielectric function which has a form similar to eq. (9). For strong polar coupling the total interaction can be attractive and it contributes to the superconductivity. It is interesting to note that the interaction (one mode example) can be separated in the following way,

$$\begin{aligned}V_{\text{polar}}^{\text{intra}}&=\frac{4\pi e^2}{\Omega(2k_F\beta)^2}\frac{1}{\varepsilon_{\text{electron}}+\pi_{\text{phonon}}}\\&=\frac{4\pi e^2}{\Omega(2k_F\beta)^2}\Bigg[\frac{1}{\varepsilon_{\text{electron}}}\\&\qquad-\frac{\pi_{\text{phonon}}}{\varepsilon_{\text{electron}}(\varepsilon_{\text{electron}}+\pi_{\text{phonon}})}\Bigg],\end{aligned} \tag{10}$$

which becomes

$$\begin{aligned}V_{\text{polar}}^{\text{intra}}&=\frac{4\pi e^2}{\Omega(2k_F\beta)^2}\\&\quad\times\left[\frac{1}{\varepsilon_{\text{electron}}}-\frac{\{(1/\varepsilon_\infty)-(1/\varepsilon_0)\}\omega_l^2}{(\varepsilon_{\text{electron}}/\varepsilon_\infty)^2(\tilde{\omega}^2-\omega^2)}\right],\end{aligned} \tag{11}$$

where ω_l is the bare longitudinal optic frequency, $\tilde{\omega}$ is the renormalized longitudinal optical frequency given by

$$\begin{aligned}\{\omega(\beta,\omega)\}^2=\omega^2\Bigg[&\frac{\varepsilon_\infty}{\varepsilon_0}+\frac{\varepsilon_\infty}{\varepsilon(\beta,\omega)_{\text{electron}}}\\&-\frac{\varepsilon_\infty^2}{\varepsilon_l\varepsilon(\beta,\omega)_{\text{electron}}}\Bigg].\end{aligned} \tag{12}$$

In eq. (11) the repulsive Coulomb interaction and the attractive electron-phonon-electron interaction are separated corresponding to the two terms of this equation respectively. The electron phonon interaction does become screened by the square of the electronic dielectric function as was discussed above and in ref. 2).

The intervalley interactions can also be computed in a similar way. The repulsive term has the form

$$V_{\text{Coulomb}}^{\text{inter}}=\frac{4\pi e^2}{(2k_F)^2\Omega(\beta_0)^2\varepsilon(\beta,\beta_0,\delta)}, \tag{13}$$

where the dielectric function has the Lindhard form for the free electrons and the contribution of the valence electrons to the screening of the intervalley processes is modified to include wavevector dependence.[18] The electron-intervalley phonon-electron interaction can be evaluated using the Bardeen-Pines interaction as in eq. (6). Since the momentum transfer in an intervalley process is essentially constant, the electron-phonon matrix element can be taken independent of wavevector

$$|M^{\text{inter}}|^2=\frac{\alpha\hbar^2(2k_F\beta_0)^2\xi^2}{2MN\hbar\omega_{\text{inter}}}, \tag{14}$$

where α is the degeneracy of the intervalley phonon mode, ω_{inter} is the frequency of the phonon, N is the number of unit cells, M is the ionic mass and ξ is the intervalley deformation potential to be determined from experiment. There are selection rules which limit the number of intervalley phonons which can transfer electrons between degenerate valleys. These selection rules and the degeneracy factor α can be computed using group theoretic methods.[19] The intervalley deformation potential ξ must be known accurately since the superconducting transition temperature depends exponentially upon this parameter. Optical measurements of the fundamental band gap show this gap to be temperature dependent and to depend upon the coupling of electrons to intervalley phonons. Analysis[20] of this data can give this coupling constant for some semiconductors. These values should again be considered to be "bare" couplings to be screened by the free electrons.

Using the above mentioned matrix elements, the kernel (4) can be computed. This kernel can then be used to solve eq. (3) for the gap function and superconducting transition temperature. Equation (3) can be solved either by square-well methods[2)] or by iteration. The resulting transition temperature is probably an over-estimate since renormalization and lifetime effects[21)] have not been considered.

§ 3. Applications of the Theory and Discussion

The theory of the previous section was first applied using semiconductor band structures modeled after Ge and Ge-Si alloys. These materials were chosen because the normal state properties of these semiconductors are well known. The results of these calculations illustrated the importance of considering many valley systems since a rough estimate of the transition temperature of Ge with $\xi=8$ eV and $n_c=10^{20}$ carriers/c.c. was five millidegrees while computations for a Ge-Si alloy with ten degenerate valleys gave a transition temperature roughly in the tenth of a degree range for the same density of carriers.

A plot of the kernels for the Ge-Si alloy appears in Fig. 1. The attractive intervalley phonon kernel K_{ph}^{er} is larger than the repulsive Coulomb kernel K_C^{ra} for an assumed average deformation potential ξ of 8 eV and a carrier concentration of $n_c=10^{20}$ carriers/c.c. The dependence of the transition temperature on carrier concentration and deformation potential was also computed and the results appear in Fig. 2. This plot contains isotherms of transition temperature as a function of n_c and ξ, and it illustrates the strong dependence of the transition temperature on ξ and n_i. It is worth noting that for a high n_c the value of ξ could be 20% lower than expected and the transition temperature would still be in a measurable range.

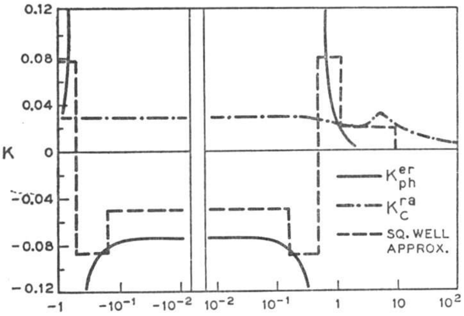

Fig. 1.

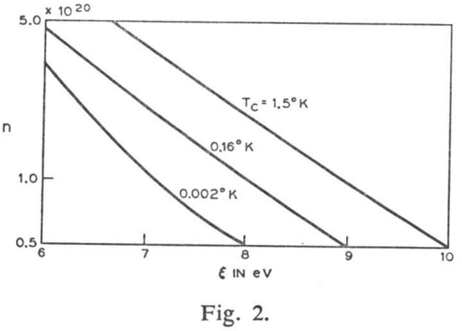

Fig. 2.

This calculation also indicated the most important parameters to maximize for superconductivity were m^*, n_c, ξ, α, ν and ε_0. If these normal state parameters are large then effectively the density of states is large (*i.e.* ν, m^*, n_c) and the attractive interaction is large (*i.e.* α, ξ, ν).

It was also pointed out that these materials should be type II[2)] superconductors, because the effective coherence length is short (short mean free path) and the penetration depth is large (low density) yielding a large Landau-Ginsburg Kappa for a semiconductor. All three superconducting semiconductors are type II superconductors. In fact, $SrTiO_3$ appears to have an anomalously large penetration depth.[22,23)] This may arise from a lower carrier density near the surface of the sample where oxidation might occur. In general the type II properties are in good agreement with the GLAD theory as pointed out by Schooley.[23)]

The application of the theory to a specific material is difficult because the normal state properties must be known very accurately before the superconducting properties can be calculated. In fact, it is expected that insufficient knowledge about the normal-state properties of superconducting semiconductors will hinder theoretical calculations more than the problems associated with superconductivity calculations.

Some calculations have been done for $SrTiO_3$ to explain the measurements of Schooley[4)] *et al.* on the dependence of the transition temperature on doping. The most recent data kindly supplied by Dr. Schooley of the National Bureau of Standards appears in Fig. 3. The general characteristic of this curve is that the transition temperature T_c first rises, reaches a maximum, and then falls. To explain the general features of this curve, eq. (3) was solved for the transition temperature as a function of carrier concentra-

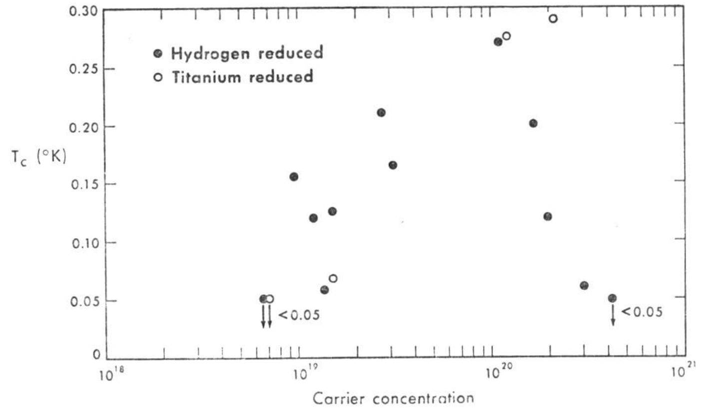

Fig. 3.

tion and the results are in good agreement with the experimental observations if intervalley processes are assumed to dominate over most of the carrier concentration range. At low carrier concentration T_c is increasing with n_c because the density of states is increasing. At high carrier concentration the free carriers are able to screen the intervalley processes and therefore reduce the effective attractive electron-electron interaction. The results of these calculations will be presented elsewhere.

To do a good job on the superconducting properties we have to know the band structure of the material we are considering very accurately. If you permit me to speculate, we have done pseudopotential calculations for SnTe and GeTe and in both materials we find a maxima along the (110) direction slightly below the maxima at L. These maxima are much lower in the lead salts which are not superconducting. It is interesting to speculate that these maxima provide a larger density of states and make more-intervalley processes possible. Since our band structure results are preliminary and there are more differences between the lead salts and SnTe or GeTe than the one mentioned, this statement should be considered to be only speculation at this time.

It should be remarked that superconductivity should not be limited to just the three existing superconducting semiconductors. Other materials should be tried. Preliminary calculations indicate that doped semimetals like Bi, Sb, As and their alloys are interesting candidates.

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DISCUSSION

Harbeke, G.: Do you think that the strong electron-phonon interaction causing the existence of superconductivity in $SrTiO_3$ is due to the low-lying Cochran-mode ?

Cohen, M. L.: No, all phonons contribute, especially at low densities, but the intervalley phonons appear to dominate.

Paul, W.: The non-observance of superconductivity in PbTe is interesting in view of its occurrence in SnTe. There are band structure differences between the two in addition to the extra maximum in the (110) direction in SnTe that you mentioned. Thus there appears to be a band structure inversion at the *L*-point of the states defining the conduction and valence bands. Clearly, measurements on PbTe-SnTe alloys are required.

Cohen, M. L.: I agree ! Work on PbTe-SnTe alloys could be very interesting. This work might prove that the occurrence of superconductivity in SnTe and GeTe and not in the lead salts is a band structure effect.

Herman, F.: What are the prospects for obtaining superconducting semiconductors having somewhat higher transition temperatures than present values ? Could you or Prof. Cohen comment, please ?

Cohen, M. L.: I think that the prospects are very good. Semiconductors with larger electron.phonon coupling constants would, of course, be interesting to investigate. Alloys or mixed crystals of existing superconducting semiconductors (*i.e.* strontium titanate) might be promising. Strain might also be a useful tool. One may even see increases in the transition temperature for certain carrier densities resulting from the shape of the kernels of the gap equation. We are exploring this latter point by attempting to find the most favourable ways of using the Coulomb interaction. We find an enhancement of the superconducting transition temperature whenever resonances in the Coulomb kernel coincide with resonances in the phonon kernel. We are working hard on this problem, but it's tricky.