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FERRELL: To what extent can you establish the abruptness of the drop in the apparent gap and to what extent do these various theories predict any abruptness?

F. REIF, *University of California:* At the present time I cannot establish the abruptness too well. One thing I can say is that the negative resistance region disappears at a rather small concentration range. Beyond this it just seems to broaden out. In order to get better information we would have to plot in detail the density of states. The Suhl theory, if I understand it correctly, would not predict anything terribly sudden. I think the other theory predicts something more sudden.

MEISSNER: I would like to caution that even if you evaporate at low temperatures, you may during the evaporation of the second film actually shoot atoms into the first film. The atoms are coming from a fairly high temperature source and if the metal underneath is something as soft as indium, then the atoms could penetrate for quite some distance.

G. v. MINNIGERODE, *University of Göttingen:* We did an experiment superimposing two films of tin and indium. In such a system of indium and tin, an alloy of the two components has a higher transition temperature than either of the components. These films were superimposed at helium temperature and the transition temperature of the sandwich was between pure tin and pure indium. There was no alloying effect. If we warmed up this sandwich to a temperature of about 200°K, suddenly the alloying process starts and then we found a transition temperature of about 5.6°. We are sure in the low-temperature region there is no alloying effect. We tried another system too–lead and bismuth.

THEORY

CHAIRMAN: *J. R. Schrieffer*

The Existence of a Superconducting State in Semiconductors

MARVIN L. COHEN*†

Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago 37, Illinois

Despite the scarcity of published work on superconductivity in semiconductors, degenerate semiconductors have been examined for superconducting properties both experimentally and theoretically. The results of these investigations have not on the whole been encouraging.

The main reason for finding a degenerate semiconductor with superconducting properties is to use this semiconductor as a tool for investigating electron–electron and electron–phonon interactions in both the normal and the superconducting states. A semiconductor of this type could also be used to give further information about the band structure of semiconductors and might possibly yield new insight into the phenomenon of superconductivity.

The band structures of many semiconductors have been determined quite accurately, and the effects on the band structure arising from uniaxial strain, hydrostatic pressure, and alloying are also known. By using these methods, the band structure of a semiconductor can be changed for a fixed concentration of impurities, and if the small effects of the doping on the band structure are neglected, the number of carriers can be changed for a given band structure by changing the doping. The carrier concentration and band structure of a degenerate semiconductor can therefore be varied independently of one another and, if a semiconductor were in a superconducting state, the superconductivity could then be observed as a function of band-structure changes and changes in the number of carriers alone.

The band-structure model used for previous theoretical investigations was that of a single-valley conduction band and valence band. Because this model

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* Shell Graduate Fellow (1962–63) and NASA Research Assistant (Summer 1963).

† Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.

yields a very small density of states at the Fermi energy for electrons, the primary aim of these investigations became the determination of the conditions under which the largest intravalley electron–phonon interaction would exist to maximize the "$N(0)V$" parameter of the BCS[1] theory. It was concluded that a very strong intravalley electron–phonon coupling was necessary to produce a transition into a superconducting state.[2]

We have reopened this problem and have used a many-valley model for the semiconductor band structure. Intervalley phonon processes were expected to be even more important than intravalley phonon processes, since these involve large momentum transfers and would therefore not be screened appreciably; also, the existence of a larger number of valleys in a degenerate semiconductor would give a larger number of states into which an electron could scatter through an intervalley process.

To obtain a quantitative understanding of the contribution of intervalley and intravalley phonon processes to superconductivity in semiconductors, we have examined degenerate Ge with a carrier concentration $n = 10^{20}$ carriers/cc. We assume the BCS theory and solve the BCS gap equation after making the appropriate changes to include both intravalley and intervalley processes.

For the attractive phonon interaction we assume a Bardeen–Pines[3] interaction and the repulsive Coulomb interaction is computed by using a dynamic dielectric function modeled after the dielectric function first derived by Lindhard.[4] This dielectric function is also used to evaluate the screening of the intravalley phonon modes. The intravalley electron–phonon matrix elements appearing in the Bardeen–Pines interaction are computed by expressing them in terms of the crystal deformation potentials which are then taken from experiment. The intervalley electron–phonon matrix element is evaluated by expressing this interaction in terms of an intervalley electron–phonon coupling constant ξ which is obtained from an analysis[5] of the temperature dependence of the semiconducting energy gap.

With an intervalley coupling constant $\xi = 8\text{eV}$, we find that the largest contribution to the attractive electron–electron interaction arises from the exchange of intervalley phonons and this contribution is larger than the repulsive Coulomb interaction and hence induces a transition into a superconducting state. A rough estimate of the transition temperature for Ge with $n = 10^{20}$ carriers/cc and $\xi = 8\text{eV}$ is 5 mdeg, indicating that Ge is not a promising choice of a semiconductor for observing a superconducting transition. However, the calculation for Ge serves to point out the important properties required of a good choice. In particular, a large number of degenerate valleys are desired to enhance the attractive intervalley phonon contribution.

We have therefore investigated the case of a Ge–Si alloy with ten degenerate valleys as an example of a more promising semiconductor. We again solve the BCS gap equation after making the changes suggested by Anderson[6] for the case of a "dirty" superconductor with nonmagnetic impurities. Although the Anderson theory predicts essentially no change in the transition temperature of Ge between the "dirty" and "clean" cases, it does have a large effect in the case of the Ge–Si alloy and therefore must be considered.

The results of this analysis appear in Fig. 1 where we have plotted isotherms for three values of the transition temperature T_c: $T_c = 0.002°\text{K}$, $T_c = 0.16°\text{K}$, and $T_c = 1.5°\text{K}$. The transition temperature is a strong function of the carrier concentration n and the average intervalley coupling constant ξ, as is expected. For $\xi = 8\text{eV}$ and $n = 10^{20}$ carriers/cc, which were the values we chose for Ge, the transition temperature of the Ge–Si alloy is $0.16°\text{K}$. Although these values of T_c should be considered to be approximate, we note that in the high concentration region, T_c is still in the $0.01°\text{K}$ to $0.1°\text{K}$ range for an average coupling constant ξ, 25%

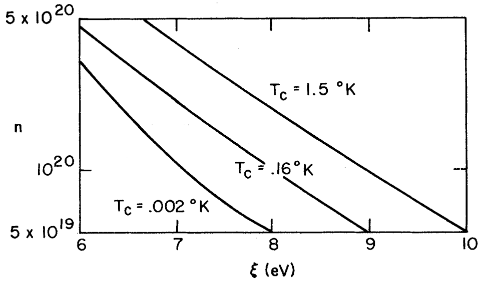

FIG. 1. Approximate isotherms for the superconducting transition temperature T_c of the Ge–Si alloy are drawn as a function of the carrier concentration n and the intervalley coupling constant ξ.

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less than that expected for Ge. This indicates that at high concentrations of impurities, the Ge–Si alloy is a promising choice for a superconducting semiconductor.

Our analysis of Ge and the Ge–Si alloy yields a knowledge of the important properties required of a semiconductor in which a superconducting transition is expected to occur. These properties are best illustrated by discussing the band-structure parameters of the semiconductor and considering them adjustable variables which, when maximized, enhance the superconducting transition temperature.

A maximization of the carrier concentration n is essential. The larger n, the larger the density of states at the Fermi surface, $N(0)$. A large $N(0)$ is important for two reasons: (a) It increases the number of states available for scattering and this is equivalent to effectively increasing the "$N(0)V$" parameter of the BCS theory, mainly through the increase of the attractive intervalley phonon contribution; and (b) it makes the dielectric screening more complete, reducing the repulsive Coulomb interaction.

The number of degenerate valleys should also be maximized in order to contribute as many intervalley processes as possible. The presence of more valleys also increases the density of states at the Fermi energy which, as we have stated, is desirable.

The density of states and the screening of the Coulomb interaction are also increased by maximizing the effective mass of each valley and the static dielectric constant.

Finally, to enhance the attractive intervalley phonon contribution, the intervalley coupling constant and the number of intervalley phonons should both be as large as possible. The latter can be determined by a group-theoretical analysis[7] of intervalley scattering in the crystal. The intervalley coupling constant is difficult to measure but can be obtained[6] from measurements of the temperature dependence of the semiconducting energy gap.

As we have shown, the Ge–Si alloy is an example of a semiconductor having some of the desired properties. A few other examples of semiconductors having some of these properties are: (a) the GaAs–GaP alloy with eleven degenerate valleys, (b) n-type or p-type Bi_2Te_3 which is a many-valley semiconductor with a large static dielectric constant, and (c) hexagonal SiC which is of the many-valley type with a large effective mass.[8] This short list of examples is in no way intended to represent the result of a complete study of semiconductors which may exhibit superconductivity.

We hope our work will encourage experimental investigation of many-valley semiconductors. High impurity concentrations[9,10] have been achieved in these semiconductors and superconductors have been found[11] below 20 mdeg suggesting that the experimental techniques involved in observing superconductivity in semiconductors are probably among those presently available.

A more detailed description of the calculations discussed in the present work will be published elsewhere.

The author wishes to express his appreciation to Professor Morrel H. Cohen, Professor L. M. Falicov, and Professor J. C. Phillips for many helpful discussions. He also wishes to thank J. W. Garland, Jr. for his help with the methods of solution of the integral equation.

This research benefited directly from partial support by the ONR and NASA. It was also aided indirectly through support of solid state theory by the NSF, support of the Low Temperature Laboratory of the Institute for the Study of Metals by the NSF, and support of the Science of Materials at the University of Chicago by the AEC and ARPA.

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Discussion 37

HULM: As Dr. Marvin L. Cohen said, his theoretical work stimulated our interest in the possibility of obtaining a superconducting semiconductor. In collaboration with Hein and Gibson of the Naval Research Lab and Miller at Westinghouse, I recently examined two highly doped semiconducting compounds for superconductivity, namely SnTe and GeTe. We chose these compounds primarily because they can be obtained in a very highly doped state; doping levels can be gotten up to about 10^{21} carriers per cc. Both materials were tested magnetically down to a few millidegrees. We obtained no effect in SnTe, but in GeTe what seems like superconducting behavior was found in two samples. Unfortunately the transition temperature of the two materials are quite different—one is at 90 mdeg and the other at 270 mdeg. GeTe is rock-salt-type structure with a carrier concentration in both the samples of close to 9×10^{20}, p-type. We were unable to detect any other extraneous phase or impurity present which could be responsible for the superconductivity. Purity of the starting material for the Te was 5–9's or better and the Ge was semiconductor grade; spectroscopic analysis both before and after revealed nothing else. We are very hopeful at this time that we indeed are seeing superconductivity in GeTe.

Goodman: Would Dr. Hulm care to tell us what the GeTe was doped with?

Hulm: Self doping. The composition is actually GeTe$_{1.025}$. The solid solution formation of the compound is with excess Te and this produces *p*-type behavior. The way it forms you have a deficiency of Ge and for every Ge vacancy you have 2 *p*-type carriers. So there is nothing in there but Ge and Te. I would be unhappy if there were some other doping material present.

Autler: What is the normal resistivity of your GeTe samples?

Hulm: The resistivity has a constant term which is about 60 $\mu\Omega$ cm for this particular doping level plus a term proportional to T^2 which at room temperature adds another 60 $\mu\Omega$ cm. The conductivity, of course, varies as you vary the doping.

Influence of Impurities on the Interactions Responsible for Superconductivity

MORREL H. COHEN

Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois

I. INTRODUCTION

There is an extensive body of experimental facts[1] suggesting that certain impurities have influences upon the interactions responsible for superconductivity which cannot be encompassed within a theory based on the assumption of "normal" alloying behavior.[2]

Alloys which behave "normally" are defined as those for which the simple band and phonon pictures remain valid when supplemented by nonresonant impurity scattering, as in the Anderson theory of dirty superconductors.[3] Deviations from normal alloying behavior can thus occur in two obvious ways: (1) Instead of a smooth variation of the band structure with concentration, impurity resonances can occur at low concentrations[4,5] which can merge into impurity bands at higher concentrations.[6] (2) Similarly, impurities can produce resonant local modes in the phonon spectrum of the host material.[7,8] The purpose of the present paper is to discuss the implications of the first of these two deviations from normal alloying behavior for superconductivity.

A more subtle deviation from normal alloying behavior in superconductors arises from the series of impurities Cr through Co. These can cause either (a) impurity resonances in the spin–density wave and spin–rotation wave spectrum of the conduction electrons, or (b) stable local moments. Because the present theoretical understanding of stable local moments[9–12] and of their influence on superconductivity[13] is relatively satisfactory, we have confined our attention to the impurity resonances (a). We have found significant consequences of spin-dependent impurity resonances for superconductivity. Time does not permit the reporting of our treatment of such resonances and their consequences here. We do, however, indicate the circumstances in which the spin-independent resonances cannot be important, whereas the spin-dependent resonances can.

II. RESONANT IMPURITY LEVELS

We are concerned here with impurity-induced changes in superconducting transition temperatures for impurity concentrations of less than $\sim 10\%$. We suppose that superconductivity arises from interactions between pairs of Landau quasi-particles which consist of a phonon-induced part and a dynamically screened Coulomb part. Changes in the transition temperature thus arise from changes in the corre-

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