direction of propagation of the sound wave are no longer transverse, the above results can be generalized by using the appropriate expression for the σ_{xx} component of the conductivity tensor.

V. DISCUSSION

Our calculations have shown that there is a dependence of the velocity of sound in a semiconductor or semimetal on an applied dc electric field. We have found that the velocity of sound has either a maximum or minimum value as a function of electric field when $V_d=S_0$. This results because the maximum interaction between the conduction electrons and the sound wave occurs when the electrons have a net drift velocity in the direction of propagation which is equal to the velocity of sound. We can use the zero-field value of the velocity of sound in all our expressions, since the corrections resulting from the field are small compared to S_0.

The question now arises as to the conditions under which the change in the velocity of sound is measurable. It is possible, at present, to measure velocity changes by one part in 10^5 using the conventional pulse technique.[14] It is estimated, that when the present techniques are improved, a measurement of velocity changes of one part in 10^7 would be possible. Since the maximum effect of the dc electric field on the velocity of sound occurs when $V_d=S_0$, and the attenuation due to the sound-wave conduction electron interaction vanishes at this point, there would be no complications arising from a large attenuation or amplification of the wave.

The change of velocity to be measured is that between the value at zero dc field and at the field where $V_d=S_0$. In an extrinsic semiconductor with $N_0=10^{14}$ electrons/cm^3, $m=10^{-28}$ g and $C=10$ eV the maximum change of $\Delta S/S_0\sim10^{-5}$ occurs for $ql<1$, while for $ql>1$, the maximum change would only be $\Delta S/S_0\sim10^{-9}$. For $ql<1$, the maximum change should be measurable and occur for ω between 10^8 and 10^{10} cycles/sec. The change when $ql>1$ would not be measurable under present conditions. For a semimetal, with a density of $N_0=5\times10^{17}$ electrons/cm^3 and a deformation potential of 10 eV, the change of velocity in the crossed fields would be $\Delta S/S_0\sim10^{-1}$ and should easily be measurable.

[14] J. G. Mavroides, B. Lax, K. J. Button, and Y. Shapira, Phys. Rev. Letters **9**, 451 (1962).

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Superconductivity in Many-Valley Semiconductors and in Semimetals*

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It is shown that the attractive electron-electron interaction arising from the exchange of intravalley and intervalley phonons can be larger than the repulsive Coulomb interaction in many-valley semiconductors and semimetals and can cause these materials to exhibit superconducting properties. The importance of observing a superconducting transition in these materials and the properties required of a semiconductor or semimetal to maximize its superconducting transition temperature are discussed.

I. INTRODUCTION

IN early work on materials below 1°K, nondegenerate semiconductors were tested along with metals for superconductivity; however, none were found to exhibit a superconducting transition. In particular, Ge and Si were examined, and these semiconductors were found to remain in a normal state down to 0.05°K [1] and 0.073°K,[2] respectively.

When one considers the small number of free carriers available in a nondegenerate semiconductor below 1°K, these results are not surprising and are consistent with the Bardeen-Cooper-Schrieffer (BCS)[3] theory of superconductivity.

However, even after the advent of the BCS theory, the question of the existence of a superconducting state in a degenerate semiconductor or a semimetal remained unanswered,[4] and, despite the paucity of published work on this problem, it has been frequently explored both theoretically and experimentally.

In previous theoretical investigations, only intravalley processes in a single-valley conduction band and a single-valley valence band had been considered, and

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[1] N. Kurti and F. Simon, Proc. Roy. Soc. (London) **A151**, 610 (1935).
[2] N. E. Alekseevskii and L. Migenov, J. Phys. (USSR) **11**, 95 (1947).
[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[4] D. Pines, Phys. Rev. **109**, 280 (1958).

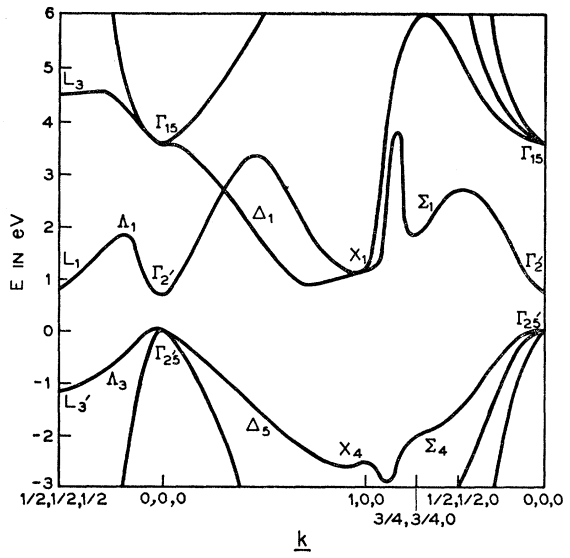

FIG. 1. The band structure of germanium; D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters **9**, 94 (1962).

these investigations have not on the whole yielded encouraging results. The obvious obstacle which appears in an analysis based on the above model is the small density of states at the Fermi energy. The primary aim of these investigations, therefore, 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 theory. A good example of the results of this approach to the study of superconductivity in semiconductors is the interesting work of Gurevich,[5] Larkin, and Firsov, who concluded that a very strong electron-phonon coupling was necessary to produce a transition into a superconducting state.

Because the band structure and electron-phonon coupling constants have been determined quite accurately for many semiconductors we have chosen semiconductors rather than semimetals for our calculations, and in the present work we will therefore limit our discussion to semiconductors. Semimetals will be discussed further in Sec. IV.

We have reopened this problem because of the potential utility of a semiconductor in a superconducting state. A semiconductor in which such a transition can occur can be used as a tool to investigate electron-electron and electron-phonon interactions in both the normal and superconducting state, the band structure of semiconductors, and the properties of the superconducting state itself in a manner which was not possible before. The band structure and carrier concentration of a degenerate semiconductor can be accurately determined and varied independently of one another, allowing an investigation of the superconducting state as a function of changes in either of these parameters alone.[6]

In recent years many advances have been made in experimental work on both semiconductors and superconductors. High carrier concentrations $> 10^{20}$ carriers/cc can be achieved in semiconductors[7,8] and superconductors are being found with transition temperatures below 20 millidegrees.[9] The chemistry of semiconductors has also advanced considerably so that the band structure of semiconductors can be easily changed through alloying. These advances remove many of the experimental limitations which have previously existed and allow us to suggest experimental investigations of semiconductors with specific band structures in the high-concentration range and at very low temperatures.

The semiconductors examined in the present work are considered to be of the many-valley type. Using this many-valley band-structure model, we have evaluated the attractive and repulsive electron-electron interactions arising from both intravalley and intervalley processes. Although the latter contribution has been neglected in previous work, we have considered it in detail as it was expected that within the framework of the BCS theory, intervalley phonon processes would give a large attractive electron-electron contribution for the following reasons:

1. Intervalley processes involve large momentum transfers and would, therefore, be screened less than intravalley processes.

2. The existence of a large number of valleys in a degenerate semiconductor would provide a large number of states into which an electron could scatter through an intervalley phonon process.

We find, in fact, that for reasonable values of the intervalley electron-phonon coupling, the largest contribution to the attractive electron-electron interaction in many-valley semiconductors arises from the exchange of intervalley phonons; these processes can yield an attractive electron-electron interaction which can be larger than the repulsive Coulomb interaction and hence can induce a superconducting transition.

To present a quantitative description of the role of intervalley and intravalley processes in the superconductivity of semiconductors, we have chosen degenerate Ge as our first example (Sec. II). The band structure of Ge is of the man-valley type and appears in Fig. 1. The degenerate valleys are the four L_1 valleys in the (111) direction at the Brillouin zone edge. We assume that the changes in the band structure arising from the introduction of impurities are negligible and treat the case of degenerate Ge with a carrier concen-

[5] V. L. Gurevich, A. I. Larkin, and Y. A. Firsov, Fiz. Tver. Tela **4**, 185 (1962) [English transl.: Soviet Phys.—Solid State **4**, 131 (1962)].

[6] These points are discussed in more detail in Sec. IV.

[7] W. G. Spitzer, F. A. Trumbor, and R. A. Logan, J. Appl. Phys. **32**, 1822 (1962).

[8] L. E. Howarth and J. F. Gilbert, J. Appl. Phys. **34**, 236 (1963).

[9] R. A. Hein, J. W. Gibson, and R. D. Blaugher, Phys. Rev. Letters **11**, 6 (1963).

tration $n=10^{20}$ carriers/cc using Fig. 1 as our model for the band structure. This large concentration of impurities necessitates the use of the Anderson[10] theory of "dirty" superconductors; however, in the case of Ge it will be shown that this theory predicts essentially no change in the transition temperature between the "dirty" and "clean" cases. We will also show that Ge is not a very promising semiconductor for the observance of superconductivity because the predicted estimate of the transition temperature is very small; however, intervalley[11] and intravalley[12] deformation potentials have been derived from experiment for Ge, and, therefore, a reasonably accurate analysis of this semiconductor can be made. This analysis provides the information required for an investigation of our second example (Sec. III), which is the more promising case of a Ge–Si alloy in which the six degenerate (100) Δ_1 valleys (see Si, Fig. 2) and four L_1 valleys are all degenerate in energy. Again, the Anderson theory of dirty superconductors is required, and unlike the case of Ge, it plays an important role in determining the transition temperature of this semiconductor. Estimates for the transition temperature will be presented as a function of the carrier concentration and the average intervalley deformation potential ξ, which is treated as a parameter.

With the results of our investigations of Ge and the Ge–Si alloy as guideposts, we discuss in Sec. IV the most important properties required of a degenerate semiconductor or a semimetal to maximize its superconducting transition temperature.

II. GERMANIUM

At low temperatures, intervalley scattering arises primarily from the presence of impurities. For example, in degenerate Ge with a carrier concentration $n=10^{20}$ carriers/cc the intervalley relaxation time τ is approximately 2×10^{-13} sec.[13] Since $\hbar/\tau$ is much larger than the average superconducting energy gap to be expected in a semiconductor, Ge at this concentration can be considered to be a "dirty" superconductor.

We assume the BCS theory that superconductivity arises from an attractive interaction between quasiparticles and make the appropriate changes suggested by Anderson[10,14] for the case of a "dirty" superconductor with nonmagnetic impurities. We consider the problem of the wave functions of the electrons in the presence of the scatterers to be solved exactly and assume that

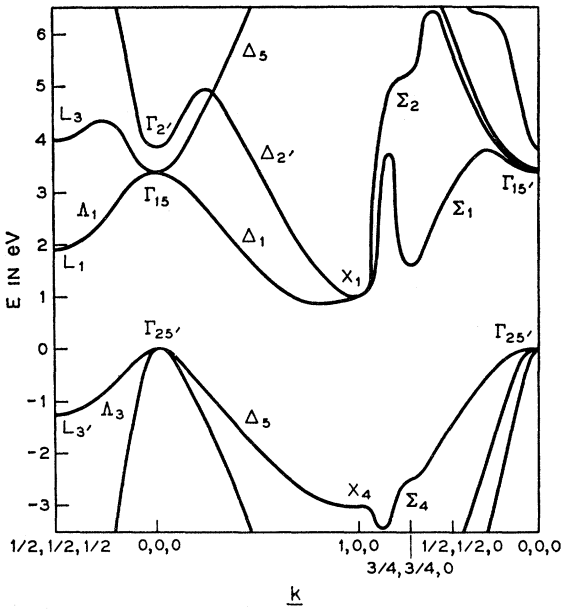

FIG. 2. The band structure of silicon: D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters **9**, 389 (1962).

the wave function and its time reversed state are[15]

$$\psi_{n\sigma}=\sum_k (n|k)\varphi_{k,\sigma}$$

and

$$(\psi_{n\sigma})^*=\sum_k (n|k)^*\varphi_{-k,-\sigma}, \tag{II.1}$$

where $\varphi_{k,\sigma}$ are the Bloch waves and the $(n|k)$'s are the unitary transformation coefficients solving the scattering problem. These new wave functions are now used to compute the electron-electron interactions and the integral equation for the superconducting energy gap Δ, which takes the form

$$\Delta_n=-\tfrac{1}{2}\sum_{n'}\frac{V_{nn'}\Delta_{n'}}{E_{n'}}\tanh\left(\frac{E_{n'}}{2k_BT}\right), \tag{II.2}$$

where $E_n=(\mathcal{E}_n^2+\Delta_n^2)^{1/2}$ is the superconducting quasiparticle energy, $\mathcal{E}_n$ is the normal-state energy of the exact one-electron states, measured from the Fermi energy, and $V_{nn'}$ is a matrix element of the effective interaction for scattering between states n and its time-reversal conjugate, and n' and its time-reversal conjugate.

We require that the $(n|k)$'s be of random phase and normalized so that

$$\sum_k |(n|k)|^2=1 \tag{II.3}$$

and

$$|(n|k)|^2=\frac{d(\mathcal{E}_n-\mathcal{E}_k)}{N^t(\mathcal{E}_n)}, \tag{II.4}$$

[10] P. W. Anderson, Phys. Chem. Solids **11**, 26 (1959).
[11] M. L. Cohen, Phys. Rev. **128**, 131 (1962).
[12] These constants will be discussed in Sec. II.
[13] W. P. Mason and T. B. Bateman, Phys. Rev. Letters **10**, 151 (1963).
[14] D. H. Douglass, Jr. and L. M. Falicov, *Progress in Low Temperature Physics* [North Holland Publishing Company, Amsterdam (to be published)].
[15] Henceforth, the spin index will be suppressed.

where $d(\mathcal{E}_n-\mathcal{E}_k)$ is a spread-out delta function with a half-width $\approx\hbar/\tau$, $\mathcal{E}_k$ is the normal-state energy, measured from the Fermi energy, of the initial plane-wave states, and $N^t(\mathcal{E}_n)$ is the total density of states for electrons of energy $\mathcal{E}_n$. Equations (II.3) and (II.4) yield the following form for $V_{nn'}$,

$$V_{nn'}=\sum_{kk'}\frac{d(\mathcal{E}_n-\mathcal{E}_k)d(\mathcal{E}_{n'}-\mathcal{E}_{k'})}{N^t(\mathcal{E}_n)N^t(\mathcal{E}_{n'})}V_{kk'}, \quad \text{(II.5)}$$

where $V_{kk'}$ is the usual BCS matrix element between plane-wave states. For the case in which the valleys are all equivalent (i.e., Ge) Eq. (II.5) reduces approximately to

$$V_{nn'}=\bar{V}_{kk'}d(\mathcal{E}_n-\mathcal{E}_k)d(\mathcal{E}_{n'}-\mathcal{E}_{k'}), \quad \text{(II.6)}$$

where $\bar{V}_{kk'}$ is an average value of $V_{kk'}$, k and k' are now considered to be the average values of k and k' in an energy shell of width $\hbar/\tau$ about the Fermi energy, and $\mathcal{E}_k$ and $\mathcal{E}_{k'}$ are the electron energies for the average wave numbers k and k' measured from the Fermi energy. In the above derivation we have implicitly assumed that the average value of the product of the superconducting energy gap and the BCS matrix element is equal to the product of the averages of these quantities taken separately.

By taking $d(\mathcal{E}_n-\mathcal{E}_k)\approx\delta(\mathcal{E}_n-\mathcal{E}_k)$ a semiconductor with ν equivalent valleys can be treated as a clean superconductor with an energy gap $\Delta(\mathcal{E}_k)$ arising from both intravalley and intervalley processes. If k space is divided into ν regions (ν valleys), Eq. (II.2) takes the following form

$$\Delta_k=-\frac{1}{2}\sum_{\substack{k'\\ k,k' \text{ in the}\\ \text{same region}}}\Delta_{k'}\frac{V_{kk'}{}^{\text{ra}}}{E_{k'}}\tanh\frac{E_{k'}}{2k_BT}$$
$$-\frac{\nu-1}{2}\sum_{\substack{k'\\ k,k' \text{ in}\\ \text{different}\\ \text{regions}}}\Delta_{k'}\frac{V_{kk'}{}^{\text{er}}}{E_{k'}}\tanh\frac{E_{k'}}{2k_BT}, \quad \text{(II.7)}$$

where superscripts ra and er mean intravalley and intervalley, respectively.

We now transform the sum over k' to integrals over $q=|k'-k|$ and $\mathcal{E}_{k'}$, and, after making the appropriate changes to include both intravalley and intervalley processes Eq. (II.7) becomes

$$\Delta_k=-\frac{\Omega}{2(2\pi)^2}\int\frac{\Delta_{k'}}{E_{k'}}\left[\frac{1}{v\hbar}\int_{|k-k'|}^{|k+k'|}qV^{\text{ra}}(\mathcal{E}_k,\mathcal{E}_{k'},q)dq\right.$$
$$\left.+\frac{(\nu-1)}{v\hbar}\int_{|k-k'|}^{|k+k'|}qV^{\text{er}}(\mathcal{E}_k,\mathcal{E}_{k'},q+q_0)dq\right]$$
$$\times\tanh\frac{E_{k'}}{2k_BT}d\mathcal{E}_{k'}, \quad \text{(II.8)}$$

where q_0 is the separation of the valleys in k space, Ω is the crystal volume and v is the velocity $\hbar k/m^*$, m^* being the density-of-states effective mass of these valleys which are assumed to be sphericalized. We follow the BCS theory and assume that $V^{\text{ra}}(\mathcal{E}_k,\mathcal{E}_{k'},q)$ and $V^{\text{er}}(\mathcal{E}_k,\mathcal{E}_{k'},q+q_0)$ are each composed of an attractive phonon induced interaction and a repulsive, screened-Coulomb interaction.

Before we discuss these interactions, we will make some convenient changes in our integral equation. Letting $D_k=(k/k_F)\Delta_k$ and $D_{k'}=(k'/k_F)\Delta_{k'}$ Eq. (II.8) becomes

$$D_k=-\int\frac{D_{k'}}{E_{k'}}K(c,\delta)\tanh\left(\frac{E_{k'}}{2k_BT}\right)d\epsilon_{k'}. \quad \text{(II.9)}$$

The kernel[16] $K(c,\delta)$ of the integral equation corresponds to the "$N(0)V$" parameter of the BCS theory and is defined by

$$K(c,\delta)=K^{\text{ra}}(c,\delta)+K^{\text{er}}(c,\delta), \quad \text{(II.10)}$$

$$K^{\text{ra}}(c,\delta)=\left(\frac{k}{k'}\right)\frac{\Omega}{2(2\pi)^2}\frac{1}{v\hbar}\int_{|k-k'|}^{|k+k'|}qV^{\text{ra}}(\mathcal{E}_k,\mathcal{E}_{k'},q)dq$$
$$=\frac{\Omega k_F{}^3}{4\pi^2E_F}\frac{1}{(\delta+c^2)^{1/2}}\int_{(1/2)|c-(\delta+c^2)^{1/2}|}^{(1/2)|c+(\delta+c^2)^{1/2}|}V^{\text{ra}}(\beta,\delta)\beta d\beta, \quad \text{(II.11)}$$

and

$$K^{\text{er}}(c,\delta)=\frac{(\nu-1)\Omega k_F{}^3}{4\pi^2E_F}\frac{1}{(\delta+c^2)^{1/2}}$$
$$\times\int_{(1/2)|c-(\delta+c^2)^{1/2}|}^{(1/2)|c+(\delta+c^2)^{1/2}|}\beta V^{\text{er}}(\beta,\delta)d\beta, \quad \text{(II.12)}$$

where $c=k/k_F$, $\beta=q/2k_F$, $\delta=\hbar\omega/E_F=(\mathcal{E}_k-\mathcal{E}_{k'})/E_F$ and E_F and k_F are the Fermi energy and wave number of the L_1 valley for a given carrier concentration.

The largest contribution to $K^{\text{ra}}(c,\delta)$ arises from the screened, intravalley Coulomb interaction $V_C{}^{\text{ra}}$. We evaluate this contribution using the formalism of Englert[17–20] which yields

$$V_C{}^{\text{ra}}=\frac{4\pi e^2}{(2k_F)^2\Omega\beta^2\epsilon(\beta,\delta)\epsilon_0}, \quad \text{(II.13)}$$

where $\epsilon(\beta,\delta)$ is a dynamic dielectric function modeled after the dielectric function derived first by Lindhard.[21] The Lindhard dielectric function is a good approximation to the actual dielectric function for degenerate Ge,

[16] In the remainder of the paper the term kernel will refer to the gap independent part of the integral equation Eq. (II.9).
[17] F. Englert, Phys. Chem. Solids **11**, 78 (1959).
[18] F. Englert, *Proceedings of the International Conference on Semiconductor Physics, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961/Academic Press Inc., New York, 1961).
[19] J. W. Garland, Jr., Phys. Rev. Letters **11**, 111 (1963).
[20] J. W. Garland, Jr. (to be published).
[21] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **28**, 8 (1954).

as can be seen by examining the parameter r_s for the case of degenerate Ge. Since the static dielectric constant ϵ_0 for Ge is 15.8 and $m^*=0.22m_0$, the value for r_s at a carrier concentration n of 10^{20} carriers/cc is $r_s=(3/4\pi n)^{1/3}(m^*e^2/\hbar^2\epsilon_0)\approx 0.35$. We are, therefore, dealing with a high-density electron gas and expect the Lindhard dielectric function to give the Gell-Mann and Brueckner[22] result for the correlation energy to a good approximation.[23–26]

For a degenerate semiconductor with ν equivalent valleys, the Lindhard dielectric function takes the following form:

$$\epsilon(\beta,\delta)=\epsilon_1(\beta,\delta)+i\epsilon_2(\beta,\delta),$$

where

$$\epsilon_1(\beta,\delta)=1+\frac{\nu 3\pi e^2 n_\nu \hbar^2}{\epsilon_0 32 m^* E_F^2 \beta^3}\left\{\left[1-\left(\beta+\frac{\delta}{4\beta}\right)^2\right]\ln\left|\frac{1+\beta+(\delta/4\beta)}{1-\beta-(\delta/4\beta)}\right|+\left[1-\left(\beta-\frac{\delta}{4\beta}\right)^2\right]\ln\left|\frac{1+\beta-(\delta/4\beta)}{1-\beta+(\delta/4\beta)}\right|+4\beta\right\}$$

and

$$\epsilon_2(\beta,\delta)=-\frac{\nu 3\pi e^2 n_\nu \hbar^2}{\epsilon_0 32 m^* E_F^2 \beta^3}\times\begin{cases}\delta, & \text{when } \beta<1 \text{ and } \delta<|4\beta^2-4\beta|,\\ 1-(\beta-\delta/4\beta)^2, & \text{when } |4\beta^2-4\beta|<\delta<|4\beta^2+4\beta|,\\ 0, & \text{when } \delta>|4\beta^2+4\beta|,\\ 0, & \text{when } \beta>1 \text{ and } \delta<|4\beta^2-4\beta|;\end{cases} \tag{II.14}$$

n_ν is the carrier concentration in each valley and ϵ_0 is the static background dielectric constant.

Using Eqs. (II.11), (II.13), and (II.14), the contribution of $V_C^{\rm ra}(\beta,\delta)$ to the kernel becomes

$$K_C^{\rm ra}(c,\delta)=\frac{k_F e^2}{4\pi E_F}\frac{1}{(\delta+c^2)^{1/2}}\times\int_{(1/2)|c-(\delta+c^2)^{1/2}|}^{(1/2)|c+(\delta+c^2)^{1/2}|}\frac{\epsilon_1(\beta,\delta)}{\epsilon_0[\epsilon_1^2(\beta,\delta)+\epsilon_2^2(\beta,\delta)]}\frac{d\beta}{\beta}.$$

The above intravalley Coulomb kernel is plotted as a function of δ for $c=1$ in Fig. 3 along with the other Ge kernels. We will discuss these kernels and Fig. 3 at the end of this section.

A Bardeen-Pines[27] interaction is chosen to evaluate the attractive, electron-phonon-electron, intravalley contribution to superconductivity. This interaction has the form

$$V_{kk'}^{\rm ph}=-\frac{2\hbar\omega_{k-k'}|M_{k-k'}|^2}{(\hbar\omega_{k-k'})^2-(\mathcal{E}_k-\mathcal{E}_{k'})^2}, \tag{II.15}$$

where $\omega_{k-k'}$ is the phonon frequency of wave number, $q=|k'-k|$, and $M_{k-k'}$ is the matrix element for the scattering of an electron from k to k' by a phonon.

We consider coupling to both the acoustical and

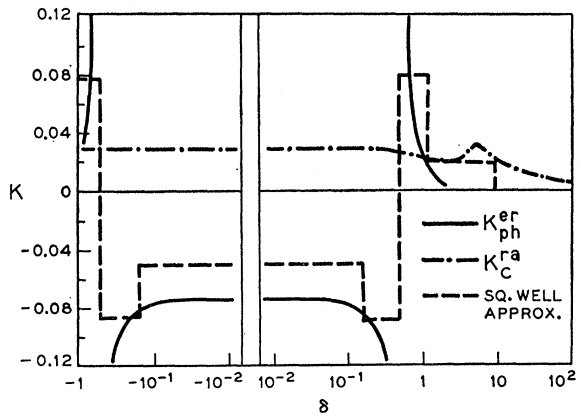

FIG. 3. Intravalley-Coulomb, intravalley-phonon, and intervalley-phonon kernels for Ge. The square-well approximation to the total kernel is also given.

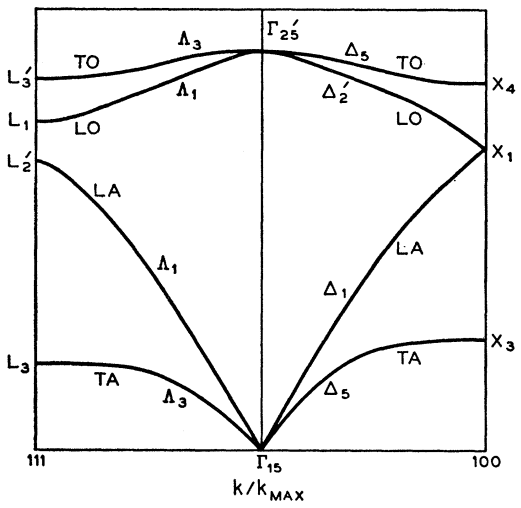

FIG. 4. The vibration spectrum of germanium: B. M. Brockhouse, and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

[22] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 181 (1957).

[23] J. Hubbard, Proc. Roy. Soc. (London) **A243**, 336 (1957).

[24] K. Sawada, Phys. Rev. **106**, 364 (1957).

[25] K. Sawada, K. A. Brueckner, N. Fukada, and R. Brout, Phys. Rev. **108**, 507 (1957).

[26] R. Brout, Phys. Rev. **108**, 515 (1957).

[27] J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

optical phonon modes (see Fig. 4). The electron-phonon matrix elements involved in calculating these contributions via Eq. (II.15) are evaluated by expressing the matrix elements in terms of the approximate deformation potentials, the values of which are then taken from experiment.

For the acoustical phonon modes we take a q-dependent matrix element of deformation potential theory[28]

$$|M_q|_{\mathrm{Ac}}{}^2=\frac{\alpha_i\hbar^2q^2E_i^2}{2MN\hbar\omega_q}, \tag{II.16}$$

where E_i is the coupling constant for the ith mode, α_i is the degeneracy of the mode, N is the total number of unit cells in the lattice, and M is the ion mass. The coupling constants E_{LA} and E_{TA} can be expressed in terms of the crystal deformation potentials Ξ_u and Ξ_d by taking the appropriate angular averages of these constants.[29] The values for these constants were taken to be $\Xi_u=19$ eV [30] and $\Xi_d=-5.8$ eV.[31] These values for the deformation potentials, and hence the E_i's, are reduced because of the screening of the electron-phonon interaction by the free carriers of the crystal. Because intravalley phonon processes involve small momentum transfer, the screening of these processes is not negligible and must be accounted for. The reduction of the magnitudes of the deformation potentials arising from the screening can be evaluated by treating the phonon wave as an external perturbation of the nearly free-electron system and thus by multiplying the intravalley electron-phonon interaction by $|\epsilon(\beta,\delta\mathrm{ph})|^{-2}$, where $\epsilon(\beta,\delta\mathrm{ph})$ is the dynamic dielectric function described by Eq. (II.14) and $\delta\mathrm{ph}$ is the energy of the phonon wave in units of the Fermi energy.

The resulting intravalley contribution to the kernel arising from acoustic phonons is

$$K_{\mathrm{Ac}}{}^{\mathrm{ra}}(c,\delta)=\frac{k_F{}^3}{4\pi^2E_F}\left(\frac{\hbar^2\Omega}{MN}\right)\left(\frac{E_{\mathrm{LA}}{}^2}{\hbar^2u_{\mathrm{LA}}{}^2}\frac{1}{(\delta+c^2)^{1/2}}\int_{(1/2)|c-(\delta+c^2)^{1/2}|}^{(1/2)|c+(\delta+c^2)^{1/2}|}\frac{\beta^3d\beta}{|\epsilon(\beta,\delta_{\mathrm{LA}})|^2(\beta^2-\eta_{\mathrm{LA}}{}^2\delta^2)}\right.$$
$$\left.+\frac{2E_{\mathrm{TA}}{}^2}{\hbar^2u_{\mathrm{TA}}{}^2}\frac{1}{(\delta+c^2)^{1/2}}\int_{(1/2)|c-(\delta+c^2)^{1/2}|}^{(1/2)|c+(\delta+c^2)^{1/2}|}\frac{\beta^3d\beta}{|\epsilon(\beta,\delta_{\mathrm{TA}})|^2(\beta^2-\eta_{\mathrm{TA}}{}^2\delta^2)}\right), \tag{II.17}$$

where

$$\eta_{\mathrm{LA}}=\frac{E_F}{2\hbar u_{LA}k_F},\quad \eta_{\mathrm{TA}}=\frac{E_F}{2\hbar u_{TA}k_F},$$

$$\delta_{\mathrm{LA}}=\frac{\beta}{\eta_{\mathrm{LA}}},\quad \text{and}\quad \delta_{\mathrm{TA}}=\frac{\beta}{\eta_{\mathrm{TA}}}.$$

We have assumed a spherical Debye distribution for our model of the acoustical phonons with u_{LA} and u_{TA} as the sound velocities for the longitudinal acoustical and transverse acoustical phonon modes, respectively.

For the optical phonon modes we choose a q-independent matrix element[32,33] similar in form to Eq. (II.16)

$$|M_q|_{\mathrm{op}}{}^2=\alpha_i\frac{\hbar^2R^2}{2MN}\frac{E_i^2}{\hbar\omega_{\mathrm{op}}}, \tag{II.18}$$

where R is a reciprocal lattice vector, ω_{op} is the frequency of the longitudinal and transverse optical modes for $q\to 0$; these are degenerate at $q=0$ (see Fig. 4). The coupling parameter $R^2E_i^2$ can be expressed as a function of the optical deformation potential D_0. Although this deformation potential has not been accurately measured for Ge, we use the value $D_0=0.5\times10^9$ eV/cm which is consistent with most experimental measurements.[34–41] This value for the deformation potential will also be screened by the free carriers of the crystal, and again this effect is computed by using the dynamic dielectric function $\epsilon(\beta,\delta)$, yielding the following expression for the intravalley optic contribution to the kernel

$$K_{\mathrm{op}}{}^{\mathrm{ra}}(c,\delta)=\frac{k_F{}^3}{4\pi^2E_F{}^3}\left(\frac{\hbar^2\Omega}{MN}\right)\frac{R^2(E_{\mathrm{LO}}{}^2+2E_{\mathrm{TO}}{}^2)}{\delta_{\mathrm{op}}{}^2-\delta^2}\frac{1}{(\delta+c^2)^{1/2}}$$
$$\times\int_{(1/2)|c-(\delta+c^2)^{1/2}|}^{(1/2)|c+(\delta+c^2)^{1/2}|}\frac{\beta d\beta}{\epsilon_1{}^2(\beta,\delta_{\mathrm{op}})+\epsilon_2{}^2(\beta,\delta_{\mathrm{op}})}, \tag{II.19}$$

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where $\delta_{op}=\hbar\omega_{op}/E_F$. We have assumed an Einstein distribution for our model of the optical phonons with frequency ω_{op}. The above intravalley optical kernel is added to the intravalley acoustical kernel Eq. (II.17), and their sum K_{ph}^{ra} is plotted in Fig. 3 as a function of δ for $c=1$. The integrals involved in evaluating both the intravalley Coulomb kernel and the intravalley phonon kernel were calculated with the aid of the IBM 7094 computer of the University of Chicago computation center.

The intervalley Coulomb interaction is evaulated in the same manner as the intravalley Coulomb interaction and has the form

$$V_C^{er}=\frac{4\pi e^2}{(2k_F)^2\Omega(\beta+\beta_0)^2\epsilon(\beta+\beta_0,\delta)\epsilon_0'}, \quad \text{(II.20)}$$

where $\beta_0=q_0/2k_F$ and ϵ_0' which is less than ϵ_0 is a modified static dielectric constant. Since the intervalley Coulomb interaction involves only short range correlations, the static dielectric constant ϵ_0 which we used for the intravalley processes must be modified[42] to screen these large q processes correctly. The contribution of intervalley Coulomb interactions to the total kernel is

$$K_C^{er}(c,\delta)=\frac{(\nu-1)k_Fe^2}{4\pi E_F}\frac{1}{(\delta+c^2)^{1/2}}\int_{(1/2)|c-(\delta+c^2)^{1/2}|}^{(1/2)|c+(\delta+c^2)^{1/2}|}\frac{\epsilon_1(\beta+\beta_0,\delta)}{\epsilon_0'[\epsilon_1^2(\beta+\beta_0,\delta)+\epsilon_2^2(\beta+\beta_0,\delta)]}\frac{\beta d\beta}{(\beta+\beta_0)^2}. \quad \text{(II.21)}$$

Despite the reduction of ϵ_0' and the larger density of states for intervalley processes, $K_C^{er}(c,\delta)$ is much smaller than $K_C^{ra}(c,\delta)$ because $\beta_0\approx 10k_F$. We have, therefore, included this contribution in the intravalley Coulomb kernel plotted in Fig. 3 as a small additive constant.

The intervalley phonon processes contribute a large attractive part to the total kernel, and we have evaluated this contribution by using the Bardeen-Pines interaction given by Eq. (II.15). Since q does not vary much in an intervalley transition and is approximately q_0, we choose a q-independent electron-phonon matrix element similar to that used to describe the intravalley optical phonon modes. This matrix element has the form,[43,44]

$$|M_q|_{er}^2=\frac{\alpha\hbar^2q_0^2\xi^2}{2MN\hbar\omega_{er}}, \quad \text{(II.22)}$$

where α is a degeneracy factor to be discussed shortly, ω_{er} is the frequency of the intervalley phonon, and ξ is the intervalley deformation potential. We consider ξ to be the screened value of the intervalley deformation potential; however, the change in ξ arising from the screening of the free carriers is very small because of the large momentum transfer involved in an intervalley process. Since the contribution of the intervalley phonons is large the superconducting transition temperature is a strong function of the intervalley deformation potential ξ. This deformation potential must therefore be known accurately if it is to yield a reliable value for the transition temperature. To evaluate ξ we turn to optical measurements of the semiconducting energy gap and a calculation of the electron-phonon self-energies in Ge.[11] We identify the deformation potential derived in this way with the deformation potential required for a calculation of the contribution of intervalley processes to the superconductivity. Even though they may differ and this method does not give the very accurate value required, we have at present no better measurements of the intervalley deformation potentials. We take $\xi=8$ eV for our investigation of Ge which is consistent with the analysis of the temperature dependence of the semiconducting energy gap.[11]

The degeneracy factor α of Eq. (II.2) can be evaluated using the group-theoretic analysis of Lax and Hopfield.[45] Their work has shown that the intervalley phonons involved in transferring electrons between the L_1 valleys in Ge transform like X_1, which is composed of the LA and LO modes degenerate at the zone edge (see Fig. 4). The value of α for Ge is, therefore, 2, and the assumption is made that for a carrier concentration of 10^{20} carriers per cc the above selection rule is still essentially correct.

Because the intervalley electron-phonon matrix element M_q is assumed to be independent of q, because screening is ignored, and because we have used an Einstein phonon distribution for the intervalley phonons, $V_{ph}^{er}(\beta,\delta)$ is q-independent, and the integral in Eq. (II.12) becomes a trivial one, yielding

$$K_{ph}^{er}(c,\delta)=(\nu-1)\frac{k_F{}^3c}{4\pi^2E_F{}^3}\left(\frac{\hbar^2\Omega}{MN}\right)\frac{\xi^2q_0^2}{\delta_{er}{}^2}\frac{1}{1-(\delta/\delta_{er})^2},$$

where δ_{er} is the energy of an intervalley phonon in units of the Fermi energy. This kernel for $\xi=8$ eV, is plotted along with the intravalley kernels in Fig. 3 as a function of δ for $c=1$. It represents the largest attractive contribution to the total kernel and is larger than the Coulomb interaction, implying that a superconducting state exists for the value of $\xi=8$ eV.

The intravalley phonon kernel is smaller than the Coulomb kernel and would not, by itself, produce a superconducting transition in the case of Ge. This contribution can be larger in other semiconductors, i.e., the intravalley optical phonon modes could give a larger contribution in a polar semiconductor.[5]

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[45] M. Lax and J. J. Hopfield, Phys. Rev. **124**, 115 (1961).

The peaks appearing in the intravalley phonon and intervalley phonon kernels arise from the singularities in the Bardeen-Pines interaction. In describing the intravalley acoustical phonon modes, a Debye distribution was used resulting in a logarithmic singularity in the kernel. For the intravalley optical phonons and the intervalley phonons the singularity is of the $(1/\delta)$ type, which is a consequence of the use of an Einstein distribution for these modes. The peaks in the intravalley acoustical and optical phonon kernels do contribute to the superconductivity, but because of the small size of these kernels their contribution is very small and is therefore neglected. The intervalley phonon peaks can give a large contribution to the superconductivity and this contribution is evaluated by means of some approximations which will be discussed.

We note that in the phonon kernel presented in the present work and in other forms for this kernel resulting from more recent work (i.e., Ref. 46) the large variation of the superconducting energy-gap function in the region of the singularity in the kernel is spread out over an energy width of approximately the Debye energy. This function is to first order proportional to δ in this region and hence the product of the energy-gap function and the kernel is approximately constant. This product is equivalent to the product of a constant kernel and a constant energy gap over this region. We therefore approximate the kernel in this region by a square well of width roughly equal to the Debye energy. This approximation and the errors involved in using this procedure are discussed farther in Sec. III.

Using the square-well approximation of Fig. 4, a numerical solution to the integral equation, Eq. (II.9) can be obtained yielding a transition temperature for Ge of about five millidegrees. This value of the transition temperature should be considered to be only a rough estimate of the actual transition temperature because of the uncertainties in the kernels of Fig. 3; however, this analysis indicates, as was mentioned in Sec. I, that degenerate Ge is not a good choice of a semiconductor for observing a superconducting transition. Our investigation of Ge as a model semiconductor does, however, serve to point out the important properties required of a good choice. These properties will be discussed in detail in Sec. IV.

III. GERMANIUM-SILICON ALLOY

We have shown in Sec. II through our investigation of degenerate Ge that intervalley phonon processes contribute a large attractive electron-electron interaction in many-valley semiconductors, and that an increase in the number of available intervalley processes will enhance the superconducting transition temperature. We therefore examine in this section the superconductivity of a degenerate Ge-Si alloy with the six Δ_1 valleys (see Fig. 2) degenerate in energy with the four L_1 valleys (see Fig. 1). These valleys become degenerate in energy in alloys composed of approximately 15% Si.[47–50]

We assume that the only difference between Ge and this Ge-Si alloy is the above difference in band structure, and that the changes in the phonon dispersion curves of Ge (shown in Fig. 4) arising from the addition of Si to make the 15% Ge-Si alloy are small.[51] Consequently, we can follow the formalism described in Sec. II for Ge, making the appropriate changes arising from band structure differences between Ge and the Ge-Si alloy.

We do not investigate the intravalley phonon processes in detail in our description of the alloy as we did in the case of Ge. These processes, which were small in Ge, are even smaller in the alloy because the existence of a larger density of electron states in the alloy implies that there is more screening in this case. We can, therefore, put an upper bound on the contribution of these processes to be equal to their contribution in the Ge case, and this contribution is much smaller than that we can expect from intervalley phonon processes in the alloy. Since there are no experimental measurements of the intervalley deformation potential ξ in the alloy, ξ will be treated as a variable in this section. We can, consequently, assume that the attractive intervalley phonon contribution for a given value of ξ contains in addition the small attractive intravalley contribution.

We can describe the Δ_1 and L_1 valleys by a nearly free-electron model, characterized by the density-of-states effective masses, m_L and m_Δ. Because these valleys have different effective masses, they are not equivalent, and the Anderson theory of "dirty" superconductors yields a different kernel in the "dirty" case than in the "clean" case. Since we will be considering carrier concentrations $n \geq 5\times 10^{19}$, the Ge-Si alloy falls into the class of a "dirty" superconductor (see Sec. II) and will, therefore, be considered to have only one average superconducting energy gap Δ_n satisfying the integral equation, Eq. (II.2).

Following Sec. II, we define a new energy gap

$$D_n \equiv (k_L/k_L{}^F)\Delta_n \quad \text{and} \quad D_{n'} \equiv (k_L'/k_L{}^F)\Delta_{n'}$$

obeying the integral equation

$$D_n = -\int D_{n'} K_{nn'}(c,\delta) \tanh\frac{E_{n'}}{2k_BT} d\mathcal{E}_{n'} \quad \text{(III.1)}$$

$$K_{nn'}(c,\delta) = K_{nn'}{}^{\text{ra}}(c,\delta) + K_{nn'}{}^{\text{er}}(c,\delta), \quad \text{(III.2)}$$

where k_L, k_L', $k_L{}^F$, k_Δ, k_Δ', and $k_\Delta{}^F$ are the electron-wave vectors in the L_1 and Δ_1 valleys for energies $\mathcal{E}_n$, $\mathcal{E}_{n'}$ and E_F, respectively,

$$c = k_L/k_L{}^F, \quad \delta = (\mathcal{E}_{n'} - \mathcal{E}_n)/E_F, \quad \text{and} \quad \beta = q/2k_F{}^L.$$

[46] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 334 (1963).

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The intravalley kernel in Eq. (III.2) contains the intravalley Coulomb interaction alone and can be evaluated using Eq. (II.5) and Eq. (II.13) with a dynamic dielectric function $\epsilon(\beta,\delta)$ which includes the screening arising from the presence of the Δ_1 valleys. The resulting intravalley kernel is

$$K_C^{\rm ra}(c,\delta)=\frac{e^2}{2\pi\hbar^2 k_F{}^L\epsilon_0}\left\{\frac{4m_L{}^{5/2}}{4m_L{}^{3/2}+6m_\Delta{}^{3/2}}\left[\frac{1}{(\delta+c^2)^{1/2}}\int_{(1/2)|c-(\delta+c^2)^{1/2}|}^{(1/2)|c+(\delta+c^2)^{1/2}|}\frac{\epsilon_1(\beta,\delta)}{\epsilon_1{}^2(\beta,\delta)+\epsilon_2{}^2(\beta,\delta)}\frac{d\beta}{\beta}\right]\right.$$
$$\left.+\frac{6m_\Delta{}^2m_L{}^{1/2}}{4m_L{}^{3/2}+6m_\Delta{}^{3/2}}\left[\frac{1}{(\delta+c^2)^{1/2}}\int_{(1/2x)|c-(\delta+c^2)^{1/2}|}^{(1/2x)|c+(\delta+c^2)^{1/2}|}\frac{\epsilon_1(\beta,\delta)}{\epsilon_1{}^2(\beta,\delta)+\epsilon_2{}^2(\beta,\delta)}\frac{d\beta}{\beta}\right]\right\},\quad\text{(III.3)}$$

where $x=k_L/k_\Delta=(m_L/m_\Delta)^{1/2}$ and $\epsilon(\beta,\delta)$ is the dynamic dielectric function for the Ge-Si alloy.

The above intravalley Coulomb kernel is smaller in the Ge-Si alloy for a given carrier concentration than in Ge. This occurs because the larger density of electron states causes more screening in this situation than in Ge as discussed above.

The intervalley kernel of Eq. (III.2) contains contributions arising from intervalley phonon scattering between different L_1 valleys, between different Δ_1 valleys, and between the L_1 and Δ_1 valleys. To calculate these contributions, the degeneracy factor α of the phonons involved must be determined.

The first of the above three types of scattering is described in Sec. II, and the intervalley phonons in this example are the doubly degenerate X_1 phonons or $\alpha=2$. There exist two types of intervalley scattering between two Δ_1 valleys; the scattering can be along the cubic axis and off the cubic axis. The Δ_1 valleys have their minima at approximately 85% of the way to the Brillouin zone edge going from Γ to X. The intervalley scattering between Δ_1 valleys along the cubic axis will, therefore, involve an Umklapp process. The phonon involved is a Δ_1 phonon[45] which is singly degenerate, $\alpha=1$. The intervalley process between Δ_1 valleys off the cubic axis uses a singly degenerate Σ_1 phonon.[45]

Although a complete analysis of the selection rules which exist for intervalley scattering between Δ_1 and L_1 valleys has not been made, there is one phonon involved and it must be nondegenerate, consequently, the degeneracy factor is $\alpha=1$.

Even though each of the above intervalley processes involves different coupling constants, we expect them to be not very different among themselves and approximately equal to the Ge intervalley (L_1 to L_1) coupling constant. We have, therefore, assumed an average intervalley deformation potential ξ and have expressed all of the above intervalley phonon processes in terms of ξ. The constant ξ is then treated as a parameter.

Following Sec. II, we choose a Bardeen-Pines interaction with a q-independent electron-phonon matrix element and an Einstein distribution for the intervalley phonons of frequency $\omega_0=\omega_{X_1}$. The above assumptions lead to the following form for the intervalley phonon kernel:

$$K_{\rm ph}{}^{\rm er}(c,\delta)=\left(\frac{\hbar^2\Omega}{MN}\right)\left(\frac{ck_L{}^{F3}}{8\pi^2E_F{}^3}\right)\frac{f(x)\xi^2q_0{}^2}{\delta_0{}^2}\frac{1}{1-(\delta/\delta_0)^2},$$

where

$$f(x)=\frac{12x^6+24x^3+15}{2x^3+3}\quad\text{and}\quad\delta_0=\frac{\omega_0}{E_F}.\quad\text{(III.4)}$$

Although the intervalley Coulomb kernel can be neglected in the case of Ge, in the alloy, because of the larger density of states, it can contribute a larger repulsive interaction. Using Eqs. (II.2) and (II.5) this kernel becomes

$$K_C{}^{\rm er}(c,\delta)=\frac{e^2}{2\pi\hbar^2}\left[\frac{6m_L}{k_F{}^L}\left(\frac{1+2x^3}{2+3x^3}\right)\frac{1}{(\delta+c^2)^{1/2}}\int_{(1/2)|c-(\delta+c^2)^{1/2}|}^{(1/2)|c+(\delta+c^2)^{1/2}|}\frac{\epsilon_1(\beta+\beta_0,\delta)}{\epsilon_0'[\epsilon_1{}^2(\beta+\beta_0,\delta)+\epsilon_2{}^2(\beta+\beta_0,\delta)]}\frac{\beta d\beta}{(\beta+\beta_0)^2}\right.$$
$$\left.+\frac{3}{x}\left(\frac{4+5x^3}{2+3x^3}\right)\frac{1}{(\delta+c^2)^{1/2}}\int_{(1/2x)|c-(\delta+c^2)|^{1/2}}^{(1/2x)|c+(\delta+c^2)^{1/2}|}\frac{\epsilon_1(\beta+\beta_0,\delta)}{\epsilon_0'[\epsilon_1{}^2(\beta+\beta_0,\delta)+\epsilon_2{}^2(\beta+\beta_0,\delta)]}\frac{\beta d\beta}{(\beta+\beta_0)^2}\right],\quad\text{(III.5)}$$

where ϵ_0' is again the reduced static dielectric constant arising from the fact that we are dealing only with short range correlations. The dielectric function $\epsilon(\beta,\delta)$ is the dynamic dielectric function described in Sec. II with $\epsilon_0\rightarrow\epsilon_0'$, and the contribution to the screening of the Δ_1 valleys has to be accounted for.

The intravalley Coulomb, Eq. (III.3), intervalley phonon, Eq. (III.4), and intervalley Coulomb, Eq. (III.5), kernels were evaluated for three different values of n, the carrier concentration. These values were $n=5\times10^{19}$ carriers/cc, $n=10^{20}$ carriers/cc, and $n=5\times10^{20}$ carriers/cc. The intervalley phonon kernel was computed for five values of ξ ($\xi=6$, 7, 8, 9 and 10 eV) for each value of n. The resulting kernels were

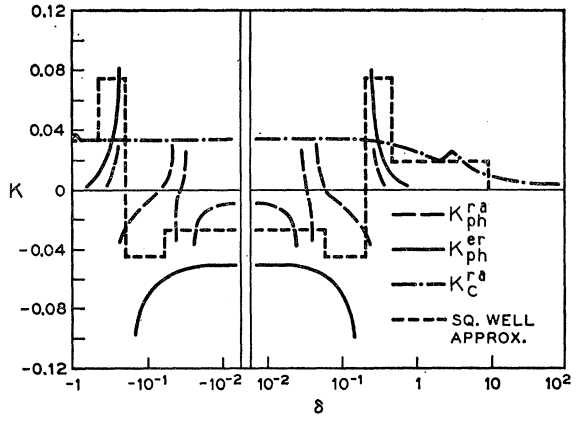

FIG. 5. Intravalley Coulomb and intervalley phonon kernels for the Ge–Si alloy. The square-well approximation to the total kernel is also given.

approximated by a series of square wells. As in the case of Ge, the contribution of the peaks in the intervalley phonon kernel were evaluated by assuming a square well kernel in the region of the peaks. Using this square-well approximation, the contribution of the peaks can be estimated with a maximum error of about 40%. This uncertainty in the contribution of the peaks is equivalent to approximately a 4% change in the coupling constant ξ.

By means of square-well approximations for the kernels, the integral equations, which each have the form of Eq. (III.1), were solved for the superconducting transition temperature. As an example of these kernels, we show in Fig. 5 the kernel for $\xi=8$ eV and $n=10^{20}$ carriers/cc. We have plotted the Coulomb and phonon contributions to the total kernel as a function of δ for $c=1$, and the square-well approximation to the kernel also appears in this figure. The integral equation, Eq. (III.1) has then been solved numerically for the superconducting transition temperature. The transition temperature for the sample kernel in Fig. 5 with $\xi=8$ and $n=10^{20}$ is $T_c=0.16$°K. Although as in the case of Ge, this transition temperature is only to be considered approximate because of the uncertainties in the kernels, it is worth noting that T_c is in a measurable range for a reasonable choice of ξ and n ($\xi=8$ eV, $n=10^{20}$ carriers/cc). We also note that for $n=10^{20}$ carriers/cc the minimum ξ for which the phonon kernel is larger than the Coulomb kernel is $\xi\approx 4.9$ eV.

We have solved in a similar way the integral equation for the other values of ξ and n mentioned above. By interpolating between these values, we have plotted isotherms for three values of the transition temperature T_c: $T_c=0.002$°K, $T_c=0.16$°K, and $T_c=1.5$°K. These isotherms appear in Fig. 6 and indicate that T_c is a strong function of both ξ and n, as is expected, and can vary by orders of magnitude for a 20% change in either of these constants.

We also note in Fig. 6 that for very high concentrations ($n\approx 5\times 10^{20}$) the transition temperature is still in the 0.01°K to the 0.1°K range for an average coupling constant, ξ, 25% less than that expected for Ge.[11] This indicates that at high concentrations of impurities the Ge-Si alloy will very probably show superconducting properties and therefore seems to be a very promising choice for an experimental investigation.

IV. DISCUSSION

Our investigation of Ge and the Ge-Si alloy indicate the important properties required of a semiconductor in which a superconducting transition is expected to occur. These properties can be best illustrated by discussing the band-structure parameters of the semiconductor and considering them adjustable variables which maximize 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 (b) it makes the dielectric screening more complete. The increase in the number of available states is equivalent to effectively increasing the "$N(0)V$" parameter of the BCS theory, mainly through the effect on the kernel of the attractive intervalley processes. The effect of a better screening is twofold: it reduces the repulsive intravalley-Coulomb interaction but at the same time the attractive intravalley-phonon interaction is also reduced. The latter is not very important in our case: the dominant phonon processes are those arising from intervalley scattering, which, because of the large momentum transfer, are essentially unscreened.

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

The density of states and screening of the intra-

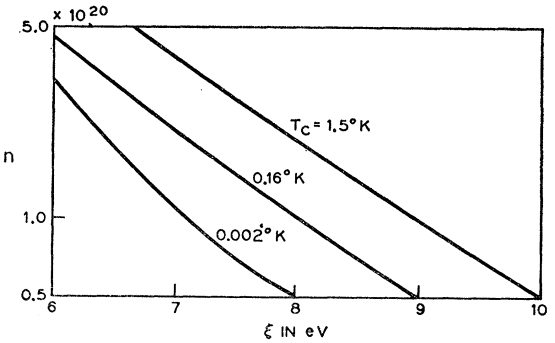

FIG. 6. Approximate isotherms for the superconducting transition temperature T_c of the Ge–Si alloy are drawn as a function of the carrier concentration n and the intervalley coupling constant ξ.

valley Coulomb interaction are also increased by maximizing m^*, the single-valley effective mass, and ϵ_0, the static dielectric constant. Let us incidentally remark that the intervalley Coulomb interaction is also reduced significantly by a large ϵ_0.

Finally, ξ, the intervalley coupling constant and α, the phonon degeneracy factor, should both be as large as possible. The degeneracy factor α can be determined by a group-theoretical analysis of intervalley scattering in the crystal. The coupling constant ξ can be extracted from a measurement of the change of the semiconducting energy gap as a function of temperature. Despite the fact that the value of ξ is difficult to obtain accurately and has not been determined for most materials, the values of the other parameters mentioned can easily be obtained, giving an indication of how promising a choice a semiconductor will be for observing superconductivity.

There are many semiconductors having band structures which are of the many-valley type. Some of these have many-valley valence bands indicating that p-type semiconductors should also be examined. Although the Ge-Si alloy with $\nu=10$ was used in our calculations, semiconductors having $\nu>10$ exist. Semiconductors, insulators, and ferroelectrics with static dielectric constants an order of magnitude larger than that of the Ge-Si alloy and with effective masses larger than the free electron mass also exist (i.e., $SrTiO_3$ and $KTaO_3$). We can therefore expect to find very promising semiconductors for the observance of superconductivity among the large number of semiconductors found in nature. It is expected that most of the materials discussed, if superconducting, will be type II superconductors.

The theory presented in Sec. II and Sec. III should also be applicable to semimetals. The band-structure parameters (treated as variable) which should be maximized are the same as those suggested for semiconductors. Of prime importance is an examination of the size of the masses since these are generally smaller in semimetals than in semiconductors.

In Sec. I we discussed the possible utility of a semiconductor in a superconducting state; in particular, the possibility of independently varying the carrier concentration and band structure was mentioned. The latter can be achieved in a many-valley semiconductor through the use of alloying and uniaxial strain, keeping the carrier concentration fixed. Through the use of alloying and uniaxial strain, the number of degenerate valleys can be changed, and the transition temperature can be studied as a function of this change.

Since intervalley processes are dominant, this change in the number of degenerate valleys would have a strong effect on the superconductivity. In fact, it is expected that a many-valley semiconductor in a superconducting state should exhibit a transition to the normal state if uniaxial strain is applied in such a manner so as to completely decouple the degenerate valleys.

By introducing different concentrations of impurities into a many-valley semiconductor, one could vary the number of carriers with only small changes in the band structure. The transition temperature can then be observed as a function of carrier concentration alone. A higher concentration is expected to yield a higher transition temperature.

Although the above description is qualitative, a more quantitative description of the dependence of the transition temperature on band-structure changes and carrier concentration can be made for specific semiconductors.

It is hoped that our analysis will encourage experimental investigations of many-valley semiconductors for superconductivity,[52] and that, if found, such a semiconductor will prove to be a useful tool for further investigations.

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[52] The possibility of superconductivity in GeTe has been discussed by J. K. Hulm and R. A. Hein. See M. L. Cohen, Rev. Mod. Phys. **36**, 240 (1964).