Possible Pairing without Superconductivity at Low Carrier Concentrations in Bulk and Thin-Film Superconducting Semiconductors

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Simultaneous equations for the BCS parameter Δ and for the Fermi energy in the BCS state are studied at low carrier concentrations in bulk and thin-film superconducting semiconductors at $T=0$ for large cutoff energies, and solutions are plotted in the form of universal curves. For electron-electron attraction greater than some critical value in bulk material or for any attractive interaction in very thin films, the pair-binding energy tends to a constant limit for low n, and pairing without superconductivity is expected in some temperature range. Solutions of simultaneous equations for T_c as obtained by formal application of the BCS theory, and for the Fermi energy at T_c, are also obtained in bulk material; but it is shown that at low carrier concentrations the temperature T_p at which pairing takes place is given by $T_p=2T_c$, while it is thought that superconductivity will not set in until a lower temperature, of the order of the Bose-Einstein condensation temperature of the pairs, is reached. By combining the above theory with a previously published model for superconductivity in Zr-doped $SrTiO_3$, predictions for this material in the region of low carrier concentrations are made.

I. INTRODUCTION

DURING the course of an investigation[1] of a model to explain published experimental results[2] on superconductivity in Zr-doped $SrTiO_3$ at carrier concentrations above about 4.10^{18} cm^{-3}, an unusual phenomenon was noticed. The model for strongly Zr-doped specimens indicated that, if the carrier concentration n were reduced below 10^{18} cm^{-3}, superconducting transition temperatures T_c would increase steadily until effects associated with T_c becoming comparable with the Fermi energy would have to be considered. Under such circumstances, shifts in the Fermi level due to temperature changes and to the formation of the superconducting state have to be included in the theory. Assuming a density of states rising as (energy)$^{1/2}$, as expected for parabolic bands, and a constant attraction between electrons within a phonon energy $\hbar\omega_c$ of the bottom of the band, the simultaneous BCS[3] equations for T_c and for the Fermi energy $-\zeta$ at T_c were discussed in the low-concentration limit previously.[1] It was found that, if the pairing attraction were greater than some critical value V_c, then the Fermi level went below the bottom of the band at T_c for low carrier concentrations, and that T_c decreased very slowly as n decreased in this region. The possibility that T_c in this limit represented a pairing temperature rather than a superconducting transition temperature was discussed. However, in this limit, where an independent pair model might be expected to give a fair representation of the actual situation, the finite-temperature BCS equation, which involves cooperative effects with the energy gap decreasing as some pairs are split up into single particles, is particularly suspect. On the other hand, since the concept of pairing is quite physical, the zero-temperature BCS equation is thought to have physical significance.

In this paper, for an (energy)$^{1/2}$ density-of-states rise, solutions of the simultaneous equations for the BCS parameter Δ and for the Fermi energy $-\zeta$ in the BCS state at $T=0$ are found by numerical methods for all carrier concentrations in the form of universal curves, under the condition that the cutoff energy $\hbar\omega_c$ is large compared with all other energies occurring in the problem. For interactions greater than the critical strength, we find that ζ tends to a limiting finite value in the low-concentration limit, and the pair-binding energy E_p in this limit satisfies $E_p=2\zeta$. Similarly, universal curves for the transition temperature T_c are obtained and are compared with the Bose-Einstein condensation temperature for the pairs T_B. However, by taking the binding energy per pair for strong coupling in the low-concentration limit at $T=0$ and by using chemical-equilibrium theory, it is shown that the temperature T_p at which pairing becomes important is related to T_c of the BCS equations by $T_p=2T_c$, i.e., $2T_c$ is a more significant quantity than T_c.

In bulk material, with an (energy)$^{1/2}$ density of states, it is necessary for V to be greater than some critical value in order to obtain interesting effects at low carrier concentrations. This may be compared with results for critical strengths for square-well potentials required for binding in three dimensions.[4] However, for very thin films of superconducting semiconductors, because of quantization of the motion in the direction of the thickness of the film, it is possible to form effectively

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[1] D. M. Eagles, Phys. Rev. **178**, 668 (1969).
[2] J. K. Hulm, C. K. Jones, R. C. Miller, and T. Y. Tien, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966*, edited by M. P. Malkov (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967), Vol. IIA, pp. 86–114.
[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957). The authors are hereafter referred to as BCS.
[4] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955).

two-dimensional systems[5,6] with densities of states independent of energy. Solutions of simultaneous equations for the BCS parameter Δ and for the Fermi energy $-\zeta$ in the BCS state under these circumstances can be obtained in simple analytic form for all carrier concentrations, provided only that the phonon energy $\hbar\omega_c$ is large compared with all other energies in the problem. For a constant density of states, the quantity ζ tends to a finite value in the low-concentration limit for any attractive interaction, and, as in bulk, in this limit the pair-binding energy E_p is 2ζ.

To illustrate the results, they are applied to the model for superconductivity in Zr-doped $SrTiO_3$ mentioned earlier,[1] and regions of temperature and concentration where pairing without superconductivity might be expected are indicated. Ways in which nonsuperconducting pairing would show in experiments are discussed.

In Sec. II, the bulk BCS equations are treated; Sec. III deals with the effectively two-dimensional case; and in Sec. IV the results are applied to the model for Zr-doped $SrTiO_3$. A short discussion of the results is given in Sec. V, and conclusions are stated in Sec. VI.

II. LOW-CARRIER-CONCENTRATION REGION IN BULK MATERIAL

Let us consider a semiconductor with a density of states $N(\eta)$ at an energy η above the bottom of the band, with an attractive interaction V between all electrons within an energy η_c of the band edge. Let the Fermi energy in the BCS state at $T=0$ be ϵ_{Fs}, and suppose that $\eta_c=\hbar\omega_c+\max(0,\epsilon_{Fs})$, where $\hbar\omega_c$ is some phonon energy. For convenience for treating the very-low-carrier-concentration region we will write $\epsilon_{Fs}=-\zeta$.

With this notation, and by use of ϵ to denote one-electron energies measured from the BCS-state Fermi level, simultaneous equations[7] for Δ and ζ at $T=0$ for a carrier concentration n are

$$1=\tfrac{1}{2}V\int_{\zeta}^{\zeta+\eta_c}\frac{N(\epsilon-\zeta)d\epsilon}{(\epsilon^2+\Delta^2)^{1/2}} \tag{1}$$

and

$$nV_0=2\int_{\zeta}^{\zeta+\eta_c}N(\epsilon-\zeta)\left[\frac{1}{2}\left(1-\frac{\epsilon}{(\epsilon^2+\Delta^2)^{1/2}}\right)\right]d\epsilon, \tag{2}$$

where V_0 denotes the volume of the material.

For bulk material at small energies, one can normally suppose that $N(\eta)=D\eta^{1/2}$, where $D=(V_0/4\pi^2)(2m_d/\hbar^2)^{3/2}$, m_d being the density-of-states effective mass. Then, if $\hbar\omega_c\gg|\zeta|$ and $(\hbar\omega_c/\Delta)^{1/2}\gg1$, Eqs. (1) and (2) reduce to

$$1\simeq DV\Delta^{1/2}[P(\lambda)+(\hbar\omega_c/\Delta)^{1/2}] \tag{3}$$

and

$$nV_0=4D\Delta^{3/2}Q(\lambda), \tag{4}$$

where P and Q are defined by

$$P(\lambda)\equiv\int_0^{\infty}dx\left(\frac{x^2-[1+(x^2+\lambda)^2]^{1/2}}{[1+(x^2+\lambda)^2]^{1/2}}\right) \tag{5}$$

and

$$Q(\lambda)\equiv\int_0^{\infty}x^2dx\left[\frac{1}{2}\left(1-\frac{x^2+\lambda}{[1+(x^2+\lambda)^2]^{1/2}}\right)\right]. \tag{6}$$

Here $x=[(\epsilon-\zeta)/\Delta]^{1/2}$, $\lambda=\zeta/\Delta$, and the upper limit of the first integral can be taken as infinite because of the assumed inequalities.

Introducing a quantity A defined by

$$A\equiv1-[DV(\hbar\omega_c)^{1/2}]^{-1}, \tag{7}$$

we see from (3) that $(\Delta/\hbar\omega_c)A^{-2}=[P(\lambda)]^{-2}$, and using the relation $\epsilon_{Fn0}=(3nV_0/4D)^{2/3}$ between nV_0/D and the Fermi energy ϵ_{Fn0} that would exist in the normal state at $T=0$, we may deduce from (2) and (3) that $(\epsilon_{Fn0}/\hbar\omega_c)^{-2}=[3Q(\lambda)]^{-2/3}[P(\lambda)]^{-2}$. By evaluating $P(\lambda)$ and $Q(\lambda)$ numerically, we thus find $(\Delta/\hbar\omega_c)A^{-2}$ as a function of $(\epsilon_{Fn0}/\hbar\omega_c)A^{-2}$. Two branches of this function arise, one for $A<0$ and the other for $A>0$. The two branches are shown in Fig. 1 on a log-log plot. The values of the

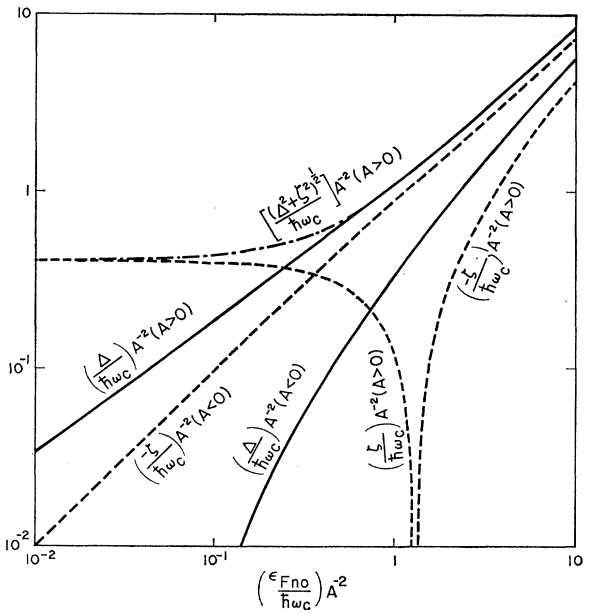

FIG. 1. Universal plots of BCS half-gap parameter Δ and Fermi energy $-\zeta$ in the BCS state at $T=0$, as a function of the Fermi energy ϵ_{Fn0} which would exist in the normal state if it persisted to zero temperature. The parameter A is defined as $A\equiv1-1/DV(\hbar\omega_c)^{1/2}$, where D is related to the density of states at energy η by $N(\eta)=D\eta^{1/2}$, and V and $\hbar\omega_c$ are the BCS interaction parameter and cutoff energy, respectively. It is assumed that $\hbar\omega_c\gg\Delta$, and that $(\hbar\omega_c/|\zeta|)^{1/2}\gg1$.

[5] B. A. Tavger and V. Ya. Demhikovskii, Zh. Eksperim. i Teor. Fiz. **48**, 748 (1965) [English transl.: Soviet Phys.—JETP **21**, 494 (1965)].

[6] D. M. Eagles, Phys. Rev. **164**, 489 (1967).

[7] Equations of this type were considered by J. Labbé, J. Barisic, and J. Friedel [Phys. Rev. Letters **19**, 1039 (1967)] for a density of states proportional to (energy)$^{-1/2}$, thought by these authors to be suitable for the strong-coupling superconductors V_3Si and Nb_3Sn.

Fermi energy in the BCS state can also be obtained in universal form, and a reduced value of $|\zeta|$ is plotted in Fig. 1 as well. For the $A>0$ branch of the curve, corresponding to interactions $V>V_c$, where V_c is defined by

$$DV_c(\hbar\omega_c)^{1/2}=1, \tag{8}$$

we notice that at low carrier concentrations the Fermi energy changes sign and passes beneath the bottom of the band. Thus, only the tail of the BCS distribution is present. The lowest single-particle excitation energy is not equal to Δ under these circumstances but from a simple viewpoint might be thought to be $(\Delta^2+\zeta^2)^{1/2}$, and so this energy is also plotted on Fig. 1. For $A>0$, it can be shown that, in the low-concentration limit, ζ satisfies

$$\zeta/\hbar\omega_c=(2/\pi)^2A^2, \tag{9}$$

and that the binding energy per pair E_p is given by

$$E_p=2\zeta. \tag{10}$$

The latter result can be obtained by more general arguments.[8]

Simultaneous equations for the BCS transition temperature T_c and for the Fermi energy $-\zeta$ at T_c can be discussed in a similar way, although the physical significance of these equations in the low-concentration limit is not clear. It is straightforward to show that results for $2kT_c$ under the conditions $\hbar\omega_c\gg|\zeta|$ and $(\hbar\omega_c/2kT_c)^{1/2}\gg1$ are formally similar to those for Δ, if we make the transformations

$$\Delta\rightarrow 2kT_c, \quad P(\lambda)\rightarrow R(\mu), \quad Q(\lambda)\rightarrow S(\mu), \tag{11}$$

where $\mu=\zeta/2kT_c$, and R and S are defined by

$$R(\mu)\equiv\int_0^\infty\left(\frac{y^2th(y^2+\mu)-(y^2+\mu)}{y^2+\mu}\right)dy \tag{12}$$

and

$$S(\mu)\equiv\int_0^\infty\frac{y^2dy}{1+e^{[2(y^2+\mu)]}}. \tag{13}$$

Thus, by numerical methods, universal curves for T_c can be obtained in the same way as those for Δ, and these are shown in Fig. 2. As before, we have two branches, according to whether A is positive or negative, i.e., whether V is greater or less than its critical value given by (8). A very slow fall of T_c with decreasing n occurs on the upper branch.

Since the diameter of the pairs will become smaller than the mean distance between them in the low-concentration region for the upper curve, it seems that superconductivity will be limited to temperatures below a temperature of the order of the Bose-Einstein condensation temperature of the pairs, T_B. Using standard expressions,[8] T_B can be shown to satisfy

$$kT_B=0.22\epsilon_{Fn0}, \tag{14}$$

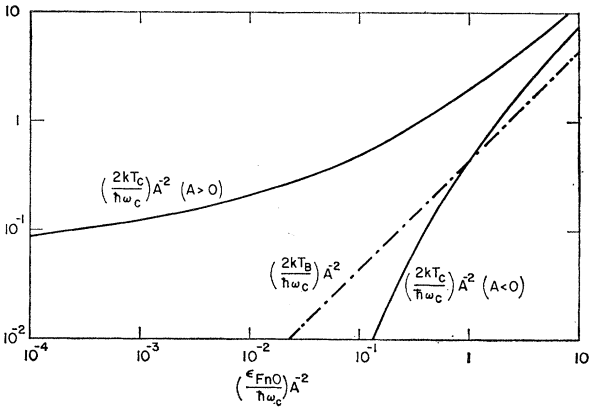

FIG. 2. Universal plots of the BCS transition temperature T_c and of the Bose-Einstein condensation temperature T_B of pairs as functions of zero-temperature normal-state Fermi energy ϵ_{Fn0}, under conditions $\hbar\omega_c\gg2kT_c$ and $(\hbar\omega_c/2kT_c)^{1/2}\gg1$. For definitions, see the caption to Fig. 1.

where $\epsilon_{Fn0}=(\hbar^2/2m_d)(3\pi^2n)^{2/3}$ is the Fermi energy for single particles which would exist in the normal state at $T=0$, if this state persisted to zero temperature. Here m_d denotes the density-of-states mass for single particles. The quantity kT_B is also plotted in Fig. 2. It falls below T_c throughout the upper branch of the curve and also on parts of the lower branch.

As mentioned in the Introduction, the physical significance of the BCS transition-temperature equation at low carrier concentrations is in serious doubt, but since the concept of pairing is physical, the zero-temperature BCS equation is thought to have some physical validity. Thus, in the limit when the diameter of pairs is small compared with the mean distance between pairs, it seems that the best way to find the temperature T_p at which pairing becomes significant is to use the chemical theory of equilibrium between pairs and single particles,[8,9] with the binding energy per pair given by (10), (9), and (7).

If n_s and n_p denote the concentrations of single particles and pairs at a temperature T, and $n=n_s+2n_p$, by use of this type of theory we can show, for equilibrium between pairs of spin 0 and single particles of spin $\frac{1}{2}$, that

$$n_s^2+n_sB(T)-nB(T)=0, \tag{15}$$

where

$$B(T)\equiv\tfrac{1}{4}(m_dkT/\hbar^2\pi)^{3/2}e^{-E_p/kT}. \tag{16}$$

The equation for n_s differs slightly from an equation in Blatt's book[8] for a similar problem, because of our inclusion of two different spin states for the single particles.

The equation for the temperature T_c from a formal solution of the BCS equations in the low-concentration limit may be written in the form

$$\tfrac{1}{4}(2m_dkT_c/\pi\hbar^2)^{3/2}e^{-\zeta/kT_c}=n. \tag{17}$$

[8] J. M. Blatt, *Theory of Superconductivity* (Academic Press Inc., New York, 1964).

[9] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Co., New York, 1939).

Hence, since $E_p=2\zeta$, the quantity $B(T)$ in (16) is equal to n when $T=2T_c$, and so

$$n_s/n=\tfrac{1}{2}(\sqrt{5}-1). \tag{18}$$

Thus the temperature T_p at which pairing becomes significant in this limit satisfies

$$T_p=2T_c, \tag{19}$$

where T_c is the temperature obtained from a formal solution of the BCS equations plotted in Fig. 2.

III. VERY THIN FILMS

For films with plane-parallel surfaces, only discrete values of electron wave vector in the direction of the film thickness are possible. This limitation on wave vectors causes the density of states to rise in a series of steps instead of in a smooth (energy)$^{1/2}$ curve, and leads to oscillations in the superconducting transition temperature.[10,11] For semiconductors, for thicknesses less than some critical value d_m, it is possible to have all carriers in the lowest quantum state with respect to motion in the direction of the thickness at low temperatures, and hence to have an effectively two-dimensional system with a density of states independent of energy.[5,6] For a semiconductor with ν valleys, a carrier concentration n, and boundary conditions such that wave functions vanish at the surface, d_m is given by

$$d_m=(\tfrac{3}{2}\nu\pi/n)^{1/3}. \tag{20}$$

However, if the cutoff energy $\hbar\omega_c$ for superconductivity is large, in order to apply a model with a constant density of states it also will be necessary for d to satisfy $d<d_c$, where

$$(\hbar^2/2m)3\pi^2/d_c^2=\hbar\omega_c. \tag{21}$$

Using standard expressions for the bulk Fermi energy ϵ_F, we deduce from (20) and (21) that

$$d_c/d_m=(\epsilon_F/\hbar\omega_c)^{1/2}(3\pi^2)^{1/6}. \tag{22}$$

For effectively two-dimensional systems, the density of states is proportional to the reciprocal of the thickness, and consequently large increases in the density of states at the Fermi level are possible for sufficiently small thicknesses. Also, for a given local value of the electron-electron interaction, it turns out that, for electrons in one quantum level, because of better fitting of wave functions, the effective V in the BCS theory is increased by a factor of 1.5 over that for electrons in different quantum levels.[11] Thus, if the local value of interactions is assumed to stay the same on passing to thin films, the combination of the density-of-states effect with the factor of 1.5 on effective V can give rise to large predicted increases in thin-film superconducting transition temperatures.[6] However, since screening at low frequencies is likely to be proportional to the density of states, at high carrier concentrations the assumption that the local value of interactions will remain unchanged on passing to thin-film form is misleading, and so, for $SrTiO_3$, the best that can be done is to choose a thickness giving a density of states corresponding to that in bulk at the maximum in transition temperature. One will then be left with the factor of 1.5 on V, insofar as interactions are local.

On the other hand, at very low carrier concentrations, the frequency range in which screening is significant is so small that the unscreened interaction should dominate, and the full force of densities-of-states increases in thin films should be felt. In this concentration region, however, shifts of the Fermi level in the BCS state have to be taken in to account, and thus simultaneous equations for the Fermi level ϵ_{Fs} and for the parameter Δ in the BCS state have to be considered, just as they must be for the bulk for strong interactions and low carrier concentrations.

For a density of states equal to a constant N, say, it is simple to solve Eqs. (1) and (2) analytically for all carrier concentrations, provided, as before, that the cutoff energy $\hbar\omega_c$ is large compared with all other energies in the problem. We put $\epsilon_{Fs}=-\zeta$ as before, and for convenience introduce a dimensionless carrier concentration y defined by

$$y\equiv(\epsilon_{Fn0}/\hbar\omega_c)e^{2/NV}, \tag{23}$$

where ϵ_{Fn0}, the Fermi energy which would exist if the normal state persisted to $T=0$, is proportional to the carrier concentration for an effectively two-dimensional system. Then the results obtained for Δ and ζ when $\hbar\omega_c\gg\zeta$, Δ and $\hbar\omega_c>\epsilon_{Fn0}$ are

$$(\Delta/\hbar\omega_c)e^{2/NV}=2y^{1/2} \tag{24}$$

and

$$(\zeta/\hbar\omega_c)e^{2/NV}=1-y. \tag{25}$$

In the low-concentration limit, the binding energy per pair E_p satisfies

$$E_p=2\zeta=2\hbar\omega_c e^{-2/NV}, \tag{26}$$

and this tends to a limit independent of carrier concentration for any attractive interaction. There is a factor of 2 in the exponent in (26) not present in the expression for Δ at more usual carrier concentrations, but because of the possibility of large densities-of-states enhancements and the domination of unscreened interactions, this factor of 2 does not necessarily stop pair-binding energies from becoming large.

The expressions for reduced Δ, $|\zeta|$, and $(\Delta^2+\zeta^2)^{1/2}$ are plotted as a function of the reduced carrier concentration y in Fig. 3. Plotted in this form, the results are very similar to those for the upper curves for bulk material shown in Fig. 1. As in bulk, for low carrier concentrations the diameter of pairs will become small compared with the distance between pairs, and so there should

[10] J. M. Blatt and C. J. Thompson, Phys. Rev. Letters **10**, 332 (1963).
[11] A. Paskin and A. D. Singh, Phys. Rev. **140**, A1965 (1965).

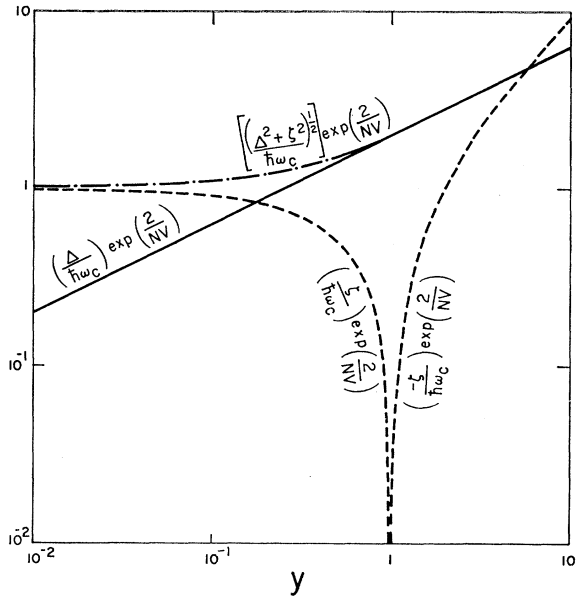

FIG. 3. Universal plots of BCS half-gap parameter Δ and Fermi energy $-\zeta$ in the BCS state at $T=0$, as a function of reduced carrier concentration y defined by Eq. (23), for an effectively two-dimensional system with a density of states N independent of energy. It is assumed that the cutoff energy $\hbar\omega_c$ is larger than all other energies occurring in the problem.

exist regions of pairing without superconductivity. In two-dimensional films, however, this phenomenon should occur for any attractive interaction, i.e., it is not necessary for V to be larger than a critical value as in bulk.

Since a Bose gas does not undergo a condensation in two dimensions, it is not clear whether there will be superconductivity or even quasisuperconductivity (i.e., greatly enhanced conductivity) at low carrier concentrations at any temperature for thin films. However, it seems probable that something unusual will occur when temperatures such that $kT\sim\frac{1}{4}\epsilon_{F2}$ are reached, where we use ϵ_{F2} to denote the Fermi energy for the film (note that $\epsilon_{F2}\propto n$ for a two-dimensional system), and we bring in the factor of $\frac{1}{4}$ to reduce to a Fermi energy for $\frac{1}{2}n$ hypothetical fermions of mass equal to twice the single-carrier mass.

IV. APPLICATION TO Zr-DOPED $SrTiO_3$

A. Bulk Materials

The model for Zr-doped $SrTiO_3$ discussed in the Introduction[1] made use of an expression[6] for transition temperatures in a BCS-like model for semiconductors with Fermi energies ϵ_F smaller than cutoff energies $\hbar\omega_c$, but with $kT_c\ll\epsilon_F$. For a density of states rising as (energy)$^{1/2}$, this expression is

$$kT_c=0.614\epsilon_F\left(\frac{(1+p)^{1/2}-1}{(1+p)^{1/2}+1}\right)^{1/2}\times\exp\left((1+p)^{1/2}-\frac{1}{[N(0)V]_{\rm eff}}\right), \quad (27)$$

where $p=\hbar\omega_c/\epsilon_F>1$, and $[N(0)V]_{\rm eff}$ is an effective density-of-states interaction product including effects of renormalization. The cutoff energy $\hbar\omega_c$ was taken as $\hbar\omega_c=0.0497$ eV, following Koonce *et al.*,[12] and the form chosen for $[N(0)V]_{\rm eff}$ was

$$[N(0)V]_{\rm eff}=A_q\left(\frac{B_qM_qN^{1/3}}{(1+2EM_qN^{1/3})^2}-\frac{EM_qN^{1/3}}{1+2EM_qN^{1/3}}\right). \quad (28)$$

Here M_q and N are dimensionless masses and carrier concentrations defined by $M_q\equiv m_q/m_e$ and $N\equiv n/10^{19}$ cm^{-3}, where n is the carrier concentration and m_q is the average mass in one valley for q% Zr-doped specimens. The quantity E gives a measure of the intervalley Coulomb repulsion, and if the intervalley high-frequency dielectric constant for $SrTiO_3$ is taken as equal to 2, then $E=0.0429$. The strength of the unscreened intervalley phonon-induced interactions in q% Zr-doped material is measured by B_q, and A_q is a composite multiplicative parameter supposed to include effects of (i) renormalization, (ii) intravalley interactions below ω_c, (iii) frequency dependence of intervalley screening, and (iv) high-frequency effects. Dependences on q of M_q, A_q, and B_q were taken in the forms

$$M_q^{-1}=M_0^{-1}(1-0.14q), \quad (29)$$

$$A_q=A_0(M_0/M_q)^2(1+qC), \quad (30)$$

and

$$B_q=B_0(1+qD), \quad (31)$$

with $M_0=2.50$. The rate of mass variation given in (29) was obtained from analysis[1,13] of penetration-depth data.[2] In (30) and (31), A_0 and B_0 were obtained by fitting the 0% Zr transition-temperature results as well as possible with the simple model, while C and D were similarly found by fitting results for 1, 2, and 3% Zr doping. Values obtained were $A_0=1.215$, $B_0=0.1046$, $C=0.264$, and $D=0.050$.

Use of this model with Eq. (27) led to predictions that for 3% Zr-doped specimens, T_c would rise steadily as carrier concentration decreased until, for n between 10^{17} and 10^{18} cm^{-3}, effects associated with the failure of the condition $kT_c\ll\epsilon_F$, required for (27) to be valid, had to be considered. Also, for 2% Zr-doped specimens the model predicted that, after a slight fall below 10^{18} cm^{-3}, T_c would rise again as n decreased further, with failure of $kT_c\ll\epsilon_F$ again before n reached 10^{17} cm^{-3}. The universal curves of Fig. 2 can be used to extend the predictions somewhat into the region where $kT_c\sim\epsilon_F$. Also, we can predict pairing temperatures T_p in the very-low-carrier-concentration region, by making use of the result of Sec. II that in this region the temperature

[12] C. S. Koonce, M. L. Cohen, J. F. Schooley, W. R. Hosler, and E. R. Pfeiffer, Phys. Rev. **163**, 380 (1967).

[13] An interpretation of the large mass increases in terms of a transition between different types of polaron state is given in D. M. Eagles, Phys. Rev. **181**, 1278 (1969).

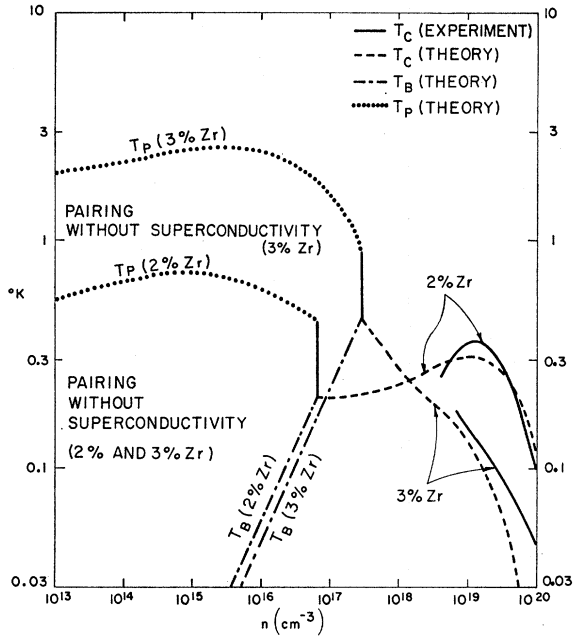

FIG. 4. Extension of predictions of T_c for 2 and 3% Zr-doped $SrTiO_3$ for the model of Ref. 1 to carrier concentrations n below 10^{18} cm^{-3}, and plots of the pairing temperature T_p and the Bose-Einstein condensation temperature T_B of the pairs for the model at low carrier concentrations. Regions where pairing without superconductivity are expected in the model are noted. There is an intermediate carrier-concentration region between about 10^{16} and a few times 10^{17} cm^{-3} where it is not clear at what temperature superconductivity will set in.

T_p at which pairing becomes significant satisfies $T_p = 2T_c$, where T_c represents the formal solution of the BCS equation for the transition temperature.

In Fig. 4 we show on a log-log plot the predictions of the model for 2 and 3% Zr-doped specimens extended into the region below 10^{18} cm^{-3}. The Bose-Einstein condensation temperature of the pairs T_B in the low-carrier-concentration region is also plotted, and regions where pairing without superconductivity is expected are indicated. The limiting values of V at low carrier concentrations for the model are 1.11 and 1.25 times the critical values for 2 and 3% Zr-doped specimens, respectively, and so, using (10), (9), and (7), the pair-binding energies in this limit are given by $E_p/k = 5$°K for 2% Zr doping and $E_p/k = 19$°K for 3% Zr doping. Thus, comparing with Fig. 4, we see that T_p is considerably smaller at all carrier concentrations than the limiting pair-binding energy.

If the linear relations (29)–(31) are assumed to be valid for higher dopings, the model predicts a maximum pairing temperature for 4% Zr-doped specimens of 3.3°K, but that the corresponding temperature for 5% dopings goes down again to 2.6°K.

B. Films

It is not simple to see how to modify the $[N(0)V]_{\text{eff}}$ of (28) to apply to the very thin films. However, the density of states is known, and it is probable that the low-frequency screening is proportional to the density of states. Thus, for a two-dimensional film, it seems that a first approximation to the correct form for $[N(0)V]_{\text{eff}}$ at high carrier concentrations would be to introduce the factor of 1.5 on effective V for local interactions, and then to multiply each term $M_q N^{1/3}$ in (28) by the ratios of the film and bulk densities of states. For a (111) film of $SrTiO_3$ of thickness d, this ratio, which we write as $N_2(0)/N_3(0)$, is given by[6]

$$N_2(0)/N_3(0) = \pi/k_F d, \tag{32}$$

where k_F denotes the Fermi wave vector in bulk material measured from the bottom of any one valley. Neglecting anisotropy in any valley, for a carrier concentration n, k_F is given by $k_F = (3\pi^2 n\nu^{-1})^{1/3}$, where ν denotes the number of valleys ($\nu = 3$ in $SrTiO_3$).

Since expression (28) passes through a maximum at some optimum value of the density of states, it seems that, at high carrier concentrations, in order to maximize the transition temperature we should choose a film thickness corresponding to the optimum density of states. This thickness turns out to be about 35 Å for $SrTiO_3$ without Zr, but rather larger for Zr-doped specimens. In order to estimate the optimum carrier concentration for obtaining high T_c's, we make use of (24), but note that, when $\epsilon_{Fn0} > \hbar\omega_c$, the usual expression $\Delta = 2\hbar\omega_c e^{-1/NV}$ replaces (24). Thus, since $kT_c = 0.57\Delta$ when $\Delta \ll \epsilon_F$, it would appear at first sight to be advantageous to choose a carrier concentration large enough to make $\epsilon_{F2} > \hbar\omega_c$, provided that this is consistent with all the carriers being in the lowest quantum state. However, in the model for $SrTiO_3$ being discussed, the fact that intravalley interactions remain unscreened in the vicinity of $\hbar\omega_c$ is important, and this will not be the case when $\epsilon_{F2} > \hbar\omega_c$. Hence it is probable that the optimum carrier concentration is the largest which is consistent with intravalley screening being insignificant at frequency ω_c. It is expected that the Fermi energy ϵ_{F2} at this carrier concentration is given by $\epsilon_{F2} = b\hbar\omega_c$, where b is slightly less than unity. Assuming optimistically that $b = 1$, and using $\epsilon_{F2} = (\hbar^2/2m)(\frac{2}{3}\pi n d)$ and $m = 2.5m_e$, we find for 35-Å films of $SrTiO_3$ with $\hbar\omega_c = 0.05$ eV that $\epsilon_{F2} = \hbar\omega_c$ when $n = 4.5\times10^{20}$ cm^{-3}. For 35-Å thicknesses, however, the separation ΔE in energy between the lowest and next-lowest energy quantum states, given by $\Delta E = (\hbar^2/2m)3\pi^2/d^2$, satisfies $\Delta E = 0.037$ eV, and so all carriers remain in the lowest state only up to carrier concentrations $n = 3.3\times10^{20}$ cm^{-3}. Values of n slightly below this should maximize transition temperatures. The optimum density-of-states interaction product in our model for bulk $SrTiO_3$ is 0.129, and so, for 35-Å films, the product is expected to be enhanced to $1.5\times0.129 = 0.193$ under our assumptions.

Since $\Delta E < \hbar\omega_c$, we cannot strictly apply the two-dimensional model for 35 Å thicknesses, but it is probably fair to say that the order-of-magnitude increase in T_c over its maximum in bulk should be given by the factor $[\exp(-1/0.193)/\exp(-1/0.129)] \sim 10$, i.e., for

35-Å films with suitable carrier concentrations, $T_c \sim 3°K$. This value is much smaller than temperatures predicted in Ref. 6, because of the unrealistic assumption made there that the local value of interaction remains unchanged on passing to the thin-film form. However, we should note that even the present figure can be regarded only as an order-of-magnitude estimate. The effects of (a) decrease of screening at frequencies above ϵ_F, (b) intravalley interactions, and (c) high-frequency interactions, will all be changed in thin-film form. The high-frequency interactions and intravalley interactions are predominantly nonlocal, and so the multiplicative factor of 1.5 for local interactions may be altered. On the other hand, having bumps in the density of states always gives the possibility of increasing effective $N(0)V$ by putting the bumps at the best places. Decreases of phonon frequencies giving rise to increasing V as in metals should also be considered.[14–16]

Another point worth noting is that the Fermi energy becomes smaller more rapidly in films than in bulk as n decreases, and so effects of decrease of screening at energies above the Fermi energy will be more important. In fact, in the low-concentration limit, with y of Eq. (23) satisfying $y \ll 1$, screening is of no importance. Thus the unscreened interaction dominates, and the full advantage of the densities-of-states increases can be felt. However, because of the factor of 2 in the exponent in (26), it is necessary to go to films of only a few atomic layers thickness in order to obtain large pair-binding energies in this limit. As mentioned in Sec. III, it is not clear whether there will be any transition to a superconducting state at low carrier concentrations in two dimensions, although it is thought that something unusual will happen when $kT \sim \frac{1}{4}\epsilon_{Fn0}$, where ϵ_{Fn0} denotes the normal-state Fermi energy for the film at $T=0$.

V. DISCUSSION

A. Comparison with Single-Pair Problem at $T=0$

In the work of the previous sections, our only attempt at justification of the use of the solutions of the zero-temperature BCS equations was the statement that the concept of pairing is physical and does not depend on having high concentrations of particles. In the low-concentration limit, however, we can do better than simply make assertions, and may compare the BCS equation (for constant Δ)

$$1=\sum_{\mathbf{k}} \frac{V}{2(\Delta^2+\epsilon_{\mathbf{k}}^2)^{1/2}} \tag{33}$$

with the corresponding equation for the energy of a single pair for a similar type of attraction, given in Schrieffer's book on superconductivity,[17] viz.,

$$1=\sum_{\mathbf{k}} \frac{V}{2\epsilon_{\mathbf{k}}-W}, \tag{34}$$

where W is the energy of the pair. In Eq. (33) the zero of energy is the Fermi level in the BCS state, and in (34) we can use the same zero of energy for convenience. Since, for V greater than its critical value, $\Delta \ll \zeta$ in the low-concentration limit, where ζ is the distance of the Fermi level below the bottom of the band, Δ can be ignored in (33). Thus, a solution of (34) with the BCS Fermi level as zero of energy is $W=0$. Hence, if the bottom of the band were chosen as zero of energy, we would have $W=2\zeta$, i.e., the binding energy per pair is 2ζ, as was obtained from the BCS equation. Thus, provided that the retarded nature of interactions does not alter things too much, we appear to be justified in the use of the BCS equation in both the high- and low-concentration limits, which lends credibility to its use in the intermediate case.

B. Fluctuations

Effects of fluctuations in the order parameter can be more serious at low carrier concentrations. To illustrate by one example, a theory of Aslamov and Larkin[18] for conductivity in films above T_c gives a contribution to the conductivity dependent only on $T_c/(T-T_c)d$, where d is the thickness. Since the normal-state conductivity might be expected to decrease with a dependence on n something like $n^{2/3}$, the relative importance of fluctuations may go up roughly as $n^{-2/3}$ as n decreases. However, in regions where Fermi-energy shifts start becoming important, it is expected that a different type of theory for the fluctuation contribution to the conductivity will have to be developed.

C. Ways of Observing Pairing

Although the pairing at low carrier concentrations predicted by the theory does not set in suddenly at the temperature T_p, but occurs gradually over a range of temperature, it should not be difficult to see effects of pairing experimentally. Some ways in which it might show up are: (a) in the temperature dependence of electrical conductivity and specific heat; (b) in the electric field dependence of electrical conductivity (electric fields $\mathcal{E}$ such that $\mathcal{E}r_p \sim E_p$, where r_p is the pair radius, should split up the pairs); (c) in a reduction of spin resonance due to pairing, since electrons of opposite spin should be paired; (d) in unusual magnetic properties at temperatures T and fields H such that $kT \ll \mu H$, where μ is the Bohr magneton (a property of the uncondensed Bose gas in this region[8] is a saturation of the

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diamagnetic moment due to motion of the bosons); and (e) possibly in a weak microwave absorption peak due to splitting up of the pairs.

D. Caution Regarding the Model for Zr-Doped $SrTiO_3$

In the model[1] for Zr-doped $SrTiO_3$, which is considerably oversimplified, the interaction V does not become greater than its critical value until $n \sim 10^{17}$ cm^{-3} or less. This is quite a long extrapolation from the range in which superconductivity has been observed up till now. Thus, it is possible that a more accurate model would not give interactions sufficiently large for pairing to occur in bulk.

Another point to note regarding $SrTiO_3$ is that Appel[19] has shown that it is not implausible that the low-temperature phase transitions[20] in $SrTiO_3$, although only giving a very small noncubic distortion of the lattice, can be of sufficient importance to bring phonons which would not be significant in the cubic phase into the problem. The phonons discussed by Appel are originally low-energy transverse zone-edge phonons in the cubic phase, but become zone-center phonons in the new smaller Brillouin zone below the phase transition. There appear to be some misleading assumptions about the interaction with the polar intravalley modes in Appel's paper, since only the lowest-frequency longitudinal modes are considered, whereas the highest-frequency ones are most important.[21] Nevertheless, the point about the possibility of the new low-energy zone-center transverse modes playing an appreciable role is significant. Inclusion of their effects could lower the effective cutoff frequency in (27), and hence make it more difficult for the condition $V > V_c$ to be attained, where V_c is given by (8). (*Note added in proof.* A further reason for thinking that the model for superconductivity in SrTiO used here may need modification is that recently published experimental results[22] indicate that paramagnetic centers may play a role in the reduction of T_c at high carrier concentrations.)

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VI. CONCLUSIONS

Pairing without superconductivity at low carrier concentrations may be attainable in bulk semiconductors for electron-electron attractions V greater than some critical value V_c, and in very thin films of superconducting semiconductors for any attractive interaction. Under such circumstances, superconductivity is not expected until the Bose-Einstein condensation temperatures of the pairs is reached, and possibly not at all in very thin films. Although there is no sharp temperature at which pairing occurs at low carrier concentrations, observable effects associated with pairing are expected in electrical conductivity as a function of temperature and of electric and magnetic fields, in specific heats, in reduction of spin resonance, and in unusual magnetic properties. Zr-doped $SrTiO_3$ appears to be a promising material in which to look for these effects in bulk.

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