Predicted Transition Temperatures of Very Thin Films and Whiskers of Superconducting Semiconductors—Application to $SrTiO_3$

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Approximate solutions of the BCS energy-gap equation with constant kernel are found for superconducting semiconductors at carrier concentrations such that the distance of the Fermi level above the bottom of the band is less than or of the order of the relevant phonon energy. Results of Tavger and Demikhovskii for the energy gap in effectively two-dimensional films are generalized to all values of the Fermi energy, and approximate gaps for effectively one-dimensional whiskers are calculated. Screening by free carriers in quasi-one- and two-dimensional systems is studied by the Lindhard method; the results lend some support to the hypothesis that in many-valleyed semiconductors the interaction strength between electrons will not be greatly altered by production in suitably oriented thin-film or whisker form. With the usual BCS relation between transition temperature and energy gap, and using a simple model with an interaction which is equal to a constant for electrons within a phonon energy 0.099 eV of the Fermi level and zero otherwise, an effective interaction strength V as a function of carrier concentration in bulk $SrTiO_3$ is deduced from published experimental results on concentration dependence of transition temperature in this material. Hence, assuming a localized interaction of the same strength occurs in effectively two-dimensional films or one-dimensional whiskers, which assumption implies, respectively, effective interactions V_2 and V_1 given by $V_2=\frac{3}{2}V$ and $V_1=(\frac{3}{2})^2V$, transition temperatures for films and whiskers are predicted as a function of carrier concentration for several different thicknesses. Transition temperatures higher than those of any known superconductor are predicted on this model for (111) films of 7 and 14 Å thicknesses, and for [111] whiskers of $(7\text{ Å})^2$, $(14\text{ Å})^2$, and $(21\text{ Å})^2$ cross sections, but at such small thicknesses the model can be expected to give only indications of trends.

1. INTRODUCTION

IN the last few years quite a lot of attention has been given by theoreticians to proposals for obtaining superconductivity at higher temperatures than those at which it is normally observed.[1–8] The BCS theory of superconductivity[9] predicts transition temperatures T_c such that $kT_c\simeq 1.14\hbar\omega\exp\{-1/N(0)V\}$, where ω is the frequency of the excitations mediating an attraction between electrons (usually ω is a phonon frequency), $N(0)$ is the density of states per unit energy at the Fermi level, and V measures the strength of the electron-electron attraction. Thus, within the framework of the usual theory, proposals for increasing transition temperatures may be classified into three types: (1) those which suggest an increase of energy of the excitations mediating the attraction, particularly suggestions involving interaction via electronic excitations[1–3]; (2) proposals for increasing the density of states[4,5] $N(0)$; (3) proposals for increasing the interaction V.[6–8] Proposals of the first type, particularly that of Little,[1] have received the most attention and are probably of most interest for obtaining very high transition temperatures. However, to obtain moderate increases in T_c, proposals coming under categories (2) and (3) may be easier to bring to realization. In this paper we discuss in some detail a proposal, first put forward by Tavger and Demikhovskii,[4] for increasing the density of states at the Fermi level in superconducting semiconductors, by making them in very thin film form. This increase in density of states comes about because, at low carrier concentrations n and thicknesses d, all electrons are in the lowest state with respect to motion perpendicular to the film, and so we have an effectively two-dimensional system. The density of states versus energy for parabolic bands is flat in two dimensions as opposed to rising as $(\text{energy})^{1/2}$ in three dimensions. Thus, for small n, the effective density of states is considerably increased, and the increase turns out to be proportional to the reciprocal of the thickness of the film.

In addition to this density-of-states effect, for a localized δ-function interaction of a given strength it can be shown[10] that the effective interaction between electrons in the same quantum level with respect to motion perpendicular to the film is increased by a factor $\frac{3}{2}$. Hence if the basic interaction is localized, and

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[1] W. A. Little, Phys. Rev. **134**, A1416 (1964).

[2] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **47**, 2318 (1964) [English transl.: Soviet Phys.—JETP **20**, 1549 (1965)].

[3] B. T. Geilikman, Usp. Fiz. Nauk. **88**, 327 (1966) [English transl.: Soviet Phys.—Usp. **9**, 142 (1966)].

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

[5] H. Fröhlich and C. Terreaux, Proc. Phys. Soc. (London) **86**, 233 (1965).

[6] W. Silvert, Physics **2**, 153 (1966).

[7] R. H. Parmenter, Phys. Rev. **116**, 1390 (1959); **140**, A1952 (1965).

[8] D. M. Eagles, Phys. Letters **20**, 591 (1966).

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

[10] A. Paskin and A. D. Singh, Phys. Rev. **140**, A1965 (1965).

does not change much on going to thin-film form, then considerable increases in T_c could occur both because of the enhanced density of states and because of the increase in effective interaction strength.

In very thin, effectively one-dimensional whiskers, where the density of states is proportional to $(\text{energy})^{-1/2}$, and the effective interaction strength for a given localized interaction is increased by a factor 9/4, we expect even greater enhancements of transition temperatures.

Since the increase in density of states is greatest at low carrier concentrations, it turns out that in the region of most interest, the distance of the Fermi level at absolute zero above the bottom of the band will be smaller than, or of the order of, the relevant phonon energy. The usual solution of the BCS gap equation is not valid under such conditions, and in Sec. 2 approximate solutions to it are found for simple bands for all ranges of ϵ_F in one-, two-, and three-dimensional systems, subject to the condition that the half-gap Δ is small compared with ϵ_F. In Sec. 3 a study of screening by free electrons in effectively one- and two-dimensional systems is made by the Lindhard method[11]; the results of this study lend some support to the hypothesis that in suitably oriented films or whiskers of many-valleyed superconducting semiconductors, the interaction strength may not be greatly altered from its value in bulk material. In Sec. 4, using the usual relation between energy gap and transition temperature, published experimental results[12] on T_c versus carrier concentration in $SrTiO_3$ are used, together with the results of Sec. 2, to calculate an effective interaction as a function of carrier concentration in bulk $SrTiO_3$ for a simple model in which the electron-electron interaction is assumed constant within a longitudinal optical phonon energy of the Fermi level, and zero otherwise. For a given localized interaction, it is then shown how the effective interaction increases by factors $\frac{3}{2}$ and $(\frac{3}{2})^2$ for films and whiskers, respectively. Thus, using the interaction strength for bulk $SrTiO_3$ and multiplying it by these factors, transition temperatures for films and whiskers are predicted as a function of carrier concentration for three different thicknesses. Some shortcomings of the simple model are discussed in Sec. 5, and conclusions are stated in Sec. 6.

2. ENERGY GAP AT LOW CARRIER CONCENTRATIONS IN ONE-, TWO-, AND THREE-DIMENSIONAL SYSTEMS

In this section we present approximate solutions of the BCS energy-gap equation[9] in one-, two-, and three-dimensional systems, for an interaction between electrons which is constant for energies within a phonon energy $\hbar\omega$ of the Fermi level and zero otherwise, at carrier concentrations such that the distance of the Fermi level above the bottom of the band satisfies $\epsilon_F \lesssim \hbar\omega$, but subject to the limitation that the half energy gap Δ satisfies $\Delta \ll \epsilon_F$.

Under conditions of constant V, the gap equation can be written in the form

$$1 = \sum_{\mathrm{k}} \frac{V}{2(\epsilon_{\mathrm{k}}^2+\Delta^2)^{1/2}} = \tfrac{1}{2} V \int_{\epsilon_0}^{\hbar\omega} \frac{N(\epsilon)\,d\epsilon}{(\epsilon^2+\Delta^2)^{1/2}}. \quad (1)$$

Here ϵ_{k} is the energy of an electron of wave vector $\mathbf{k}$, measured from the Fermi level ϵ_F, $\epsilon_0 = \max\{-\hbar\omega, -\epsilon_F\}$, the summation is over all states of one spin for which $\epsilon_{\mathrm{k}} < \hbar\omega$, and $N(\epsilon)$ denotes the density of states per unit energy. We solve this integral equation by separating out a region of integration within an energy $c\epsilon_F$ of the Fermi level, where $c \ll 1$ but $c\epsilon_F \gg \Delta$. In this region we put $N(\epsilon) \simeq N(0)$, while outside it we put $(\epsilon^2+\Delta^2)^{1/2} \simeq \epsilon$. Then, assuming that in one dimension $N(\epsilon) \propto (\epsilon+\epsilon_F)^{-1/2}$, and in three dimensions $N(\epsilon) \propto (\epsilon+\epsilon_F)^{1/2}$, we find the following expressions for the half-gap Δ in one and three dimensions:

$$\Delta \simeq 8\epsilon_F \exp\{-1/N(0)V\} \times \left\{\frac{(1+p)^{1/2}-1}{(1+p)^{1/2}+1}\right\}^{1/2} e^S, \qquad \epsilon_F < \hbar\omega$$

$$\times \left\{\frac{(1+p)^{1/2}-1}{(1+p)^{1/2}+1}\right\}^{1/2} \left\{\frac{1-(1-p)^{1/2}}{1+(1-p)^{1/2}}\right\}^{1/2} e^S, \qquad \epsilon_F > \hbar\omega, \quad (2)$$

where $p = (\hbar\omega/\epsilon_F)$, and $S = S' = 0$ in one dimension, while in three dimensions $S = [(1+p)^{1/2} - 2]$ and $S' = [(1+p)^{1/2} + (1-p)^{1/2} - 2]$. The second expression in (2) reduces to the usual one when $\epsilon_F \gg \hbar\omega$.

In two dimensions $N(\epsilon)$ is independent of energy, and we find the usual BCS expression if $\epsilon_F > \hbar\omega$, but obtain

$$\Delta \simeq 2\epsilon_F^{1/2}(\hbar\omega)^{1/2} \exp\{-1/N(0)V\}, \quad \text{if } \Delta \ll \epsilon_F < \hbar\omega(2-\mathrm{D}), \quad (3)$$

while in this case we can also solve in the unrealistic opposite limit of $\Delta \gg \epsilon_F$ to find

$$\Delta \simeq 2\hbar\omega \exp\{-2/N(0)V\}, \qquad \epsilon_F \ll \Delta < \hbar\omega(2-\mathrm{D}). \quad (4)$$

The expression (4) was given by Tavger and Demikhovskii[4] for the limit $\epsilon_F \ll \hbar\omega$.

In one and three dimensions we have not obtained expressions for Δ when it is not small compared with ϵ_F; however, it seems safe to say that the expressions (2) will be right in order of magnitude, but should overestimate the gap somewhat.

The BCS integral equation for the transition temperature T_c is similar to Eq. (1) except that

$$[N(\epsilon)\,d\epsilon/(\epsilon^2+\Delta^2)^{1/2}]$$

[11] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fiz. Medd. **28**, No. 8 (1954).

[12] J. F. Schooley, W. R. Hosler, E. Ambler, J. H. Becker, M. L. Cohen, and C. S. Koonce, Phys. Rev. Letters **14**, 305 (1965).

is replaced by

$$[N(\epsilon)\epsilon^{-1}\tanh(\epsilon/2kT_c)d\epsilon]$$

under the integrand. The integral in this equation may be approximated in the same way as that for Δ by dividing the region of integration into the same three parts, and approximating $\tanh(\epsilon/2kT_c)$ by unity in the outer parts. In this way we can show that the usual relationship $kT_c=0.57\Delta$ holds for all values of ϵ_F, provided only that $\Delta\ll\epsilon_F$ is satisfied.

For a many-valleyed semiconductor with ν valleys each containing particles of mass m, the densities of states $N_1(0)$ and $N_2(0)$ for the lowest set of quantum states with respect to motion perpendicular to the thickness for whiskers of cross section d^2 and films of thickness d are given by

$$N_1(0)=(\nu/2\pi)(2m/\hbar^2)^{1/2}(v_0/d^2)\epsilon_F^{-1/2} \quad \text{(whiskers)}, \quad (5)$$

and

$$N_2(0)=(\nu/4\pi)(2m/\hbar^2)(v_0/d) \quad \text{(films)}, \quad (6)$$

where v_0 denotes the volume. In bulk material the density of states $N_3(0)$ satisfies

$$N_3(0)=(\nu/4\pi^2)(2m/\hbar^2)^{3/2}v_0\epsilon_F^{1/2}. \quad (7)$$

For a carrier concentration n, the Fermi energies ϵ_{F1}, ϵ_{F2}, and ϵ_{F3} for the same three cases satisfy

$$\epsilon_{F1}=(\hbar^2/2m)(\tfrac{1}{2}\pi n\nu^{-1}d^2)^2 \quad \text{(whiskers)}, \quad (8)$$

$$\epsilon_{F2}=(\hbar^2/2m)(2\pi n\nu^{-1}d) \quad \text{(films)}, \quad (9)$$

and

$$\epsilon_{F3}=(\hbar^2/2m)(3\pi^2 n\nu^{-1})^{2/3} \quad \text{(bulk)}. \quad (10)$$

By substituting from (5) to (10) into (2) and (3) we may see that, if V were independent of n, then in whiskers Δ would go through a maximum as a function of n [when $N(0)V\simeq\frac{1}{2}$], whereas in films and bulk material it would increase monotonically with n.

Assuming boundary conditions such that wave functions vanish at the surfaces of whiskers and films, the difference in energy $\Delta\epsilon$ between the lowest and next lowest states with respect to motion perpendicular to the specimen in square whiskers of side d or films of thickness d satisfies $\Delta\epsilon=(\hbar^2/2m)(3\pi^2/d^2)$. Thus using (8) and (9), the maximum carrier concentrations n_{m1} and n_{m2} at which all particles are in the lowest state with respect to motion perpendicular to the specimen are given by

$$n_{m1}=(2\nu\sqrt{3}/d^3) \quad \text{(whiskers)},$$

and

$$n_{m2}=(\tfrac{3}{2}\nu\pi/d^3) \quad \text{(films)}. \quad (11)$$

Interactions between electrons, e.g., the Coulomb repulsion, may modify these conditions somewhat, since such interactions tend to mix up states of different kinetic energy. Perturbations mixing two states of different energies normally tend to increase their energy separation, and so on this basis interactions might be expected to split the lowest level off further from the next level. Thus, the actual maximum concentrations for which all carriers are in the lowest state with respect to motion in the direction of the thickness would be somewhat larger than those given by (11). Presumably, this effect will become significant when an average Coulomb repulsion energy per electron becomes comparable with the separation between levels, i.e., when

$$\{e^2k_n/\varepsilon(k_n,0)\}\sim(\hbar^2/2m)(3\pi^2/d^2), \quad (12)$$

where $k_n=n^{1/3}$, and $\varepsilon(k_n, 0)$ is the static dielectric constant for this wave vector.

3. SCREENING IN ONE- AND TWO-DIMENSIONAL SYSTEMS

In order to estimate changes of electron-electron interactions due to production of material in whisker or film form, it is necessary to have information about the dielectric function of materials in such forms. Although the thin whiskers and films being discussed in this paper are not truly one or two dimensional, there is no freedom of motion for electrons moving perpendicular to the film or whiskers, and so as far as interaction between electrons is concerned we are only interested in the dielectric function $\varepsilon(\mathbf{k}, \omega)$ for wave vectors along the line of the whisker or in the plane of the film. Also, provided that the thickness d is large compared with the screening length, we expect that edge effects will be unimportant. Thus, it is relevant to calculate the dielectric function for a gas of infinite plane charges or infinite line charges. In this section, we study the static dielectric function $\varepsilon(\mathbf{k}, 0)$ for such systems by the Lindhard method,[11] which essentially contains only the first term in an expansion in powers of $(1/k_F r_B')$, where k_F is the Fermi wave vector, and r_B' is an effective Bohr radius for the system, given by $r_B'=(\varepsilon_\infty\hbar^2/me^2)$, where m is the electron effective mass and ε_∞ the high-frequency dielectric constant of the system. The method is thus limited in validity to a high-concentration region. However, since, at least in three dimensions, a study of screening at low carrier concentrations appears to be rather difficult,[13] this is probably the best that can be done without a lot of effort, and it is helpful for seeing the sort of changes which come about as the number of dimensions is changed.

Lindhard's method[11,14] consists of a calculation by first-order perturbation theory of the polarization

[13] See J. Hubbard [Proc. Roy. Soc. (London) **243**, 336 (1958)], and L. Kleinman [Phys. Rev. **160**, 585 (1967)], for some discussion of improvements on the Lindhard dielectric function.

[14] A brief summary of the Lindhard method and its application to nondegenerate semiconductors is given in S. Doniach, Proc. Phys. Soc. (London) **78**, 849 (1959).

induced in a statistical distribution of electrons by a self-consistent potential of running wave form, and use of Poisson's equation to relate the induced displacement of charge to the dielectric constant. Writing the total dielectric function ε as $\varepsilon=\varepsilon_\infty+\varepsilon_{ph}+\varepsilon_c$, where ε_∞ is the high-frequency dielectric constant, ε_{ph} the contribution from the ionic displacements, and ε_c the part due to the free carriers, for wave vectors along the line of a whisker, in the plane of a film, or in any direction in bulk material, the method gives, for a semiconductor with a simple band containing electrons of mass m, that

$$\varepsilon_c(\mathbf{k},\omega)=\left(\frac{8\pi me^2}{\hbar^2k^2v_0}\right)\times\sum_t f(\epsilon_t)\{[k^2+2\mathbf{k}\cdot\mathbf{k}_t+(2m/\hbar)(-\omega-i\gamma_t/\hbar)]^{-1}+[k^2-2\mathbf{k}\cdot\mathbf{k}_t+(2m/\hbar)(\omega+i\gamma_t/\hbar)]^{-1}\}. \quad (13)$$

Here v_0 denotes the volume of the specimen, $f(\epsilon_t)$ is the occupation number of the electronic state of energy ϵ_t, γ_t is the imaginary part of the energy of the excited state concerned, and the summation is over all states t. If energies are measured from the Fermi surface, than, at $T=0$, $f(\epsilon_t)$ is a step function at the origin. Replacing the summations by integrations according to the prescriptions

$$\sum_t f(\epsilon_t)\rightarrow(v_0n/2k_F)\int_{-k_F}^{k_F}dk_t \qquad \text{(whiskers)},$$

and

$$\sum_t f(\epsilon_t)\rightarrow(v_0n/\pi k_F^2)\int_0^{k_F}k_tdk_t\int_0^{2\pi}d\theta \qquad \text{(films)},$$

where θ denotes the angle between $\mathbf{k}_t$ and $\mathbf{k}$, and specializing to the case $\omega=\gamma_t=0$ and zero temperature, we find that for whiskers

$$\varepsilon_{c1}(\mathbf{k},0)=\frac{4\pi me^2n}{\hbar^2k^2k_F^2}\left[\frac{k_F}{k}\ln\left|\frac{k+2k_F}{k-2k_F}\right|\right], \quad (14)$$

and for films

$$\varepsilon_{c2}(\mathbf{k},0)=\frac{8\pi me^2n}{\hbar^2k^2k_F^2}\times\begin{bmatrix}1, & k<2k_F\\ \{1-(1-4k_F^2/k^2)^{1/2}\}, & k>2k_F\end{bmatrix}. \quad (15)$$

These results may be compared with that for bulk material,

$$\varepsilon_{c3}(\mathbf{k},0)=\frac{12\pi me^2n}{\hbar^2k^2k_F^2}\times\left[\frac{1}{2}+\frac{k_F}{2k}\left\{1-\left(\frac{k}{2k_F}\right)^2\right\}\ln\left|\frac{k+2k_F}{k-2k_F}\right|\right]. \quad (16)$$

At small wave vectors the terms inside the square brackets are all equal to unity. Since for small n, according to Eqs. (8)–(10), the quantity (n/k_F^2) is larger in whiskers and films than in bulk material, then we deduce from (14)–(16) that screening at small wave vectors in films and whiskers is considerably *increased* over that in bulk for any given concentration of carriers. However, we should note that the results (14) and (15), obtained under neglect of edge effects, should be modified for very small k such that $kd\lesssim1$ (see end of this section) in such a way as to reduce the screening in this wave-vector range from that given by (14) and (15).

For many-valleyed semiconductors at wave vectors $\mathbf{k}$ sufficiently small that intervalley transitions are not possible, Eqs. (14)–(16) will remain valid, with n as the total carrier concentration, but m as the mass and k_F the radius of the Fermi sphere in any one valley. For large $\mathbf{k}$, additional terms due to intervalley processes might come in in general. However, in many cases, e.g., $SrTiO_3$, the periodic parts of the wave functions at the bottom of each valley are orthgonal to each other, and so intervalley contributions to ε should be small. We shall ignore them in what follows.

For large $\mathbf{k}$ the expressions in brackets in Eqs. (14)–(16) reduce to $(4k_F^2/k^2)$, $(2k_F^2/k^2)$, and $(\frac{4}{3}k_F^2/k^2)$, respectively, i.e., the screening at a given large wave vector is the same for a given carrier concentration in any number of dimensions. Nonparabolicity of the bands and contributions due to transitions to higher bands may become important at large $\mathbf{k}$, and so the results for ε_c may not be very accurate in this region. However, they do show that for a given carrier concentration, screening at large wave vectors will not be greatly changed from that in the bulk material. Thus, for many-valleyed semiconductors, at concentrations such that k_F in any valley is small compared with the intervalley wave vector k_v, it should be a fair approximation to neglect effects due to change of screening on passing from bulk to whisker or film form.

The conclusions of this section for films and whiskers thick compared with a screening length are somewhat different from those of Stern[15] and Kuper,[16] who consider smaller thicknesses.

Stern[15] calculates the susceptibility and dielectric constant associated with electrons confined to a plane, with the plane imbedded in a three-dimensional medium. In the static limit his results for the susceptibility in the plane reduce to $(1/4\pi)$ times the right-hand side of Eq. (15) of this paper, but the relation between dielectric constant and susceptibility becomes modified in the system discussed by him, and the carrier contribution to the dielectric constant becomes proportional to $1/k$ instead of $1/k^2$ in the long-wave-

[15] F. Stern, Phys. Rev. Letters **18**, 546 (1967).
[16] C. G. Kuper, Phys. Rev. **150**, 189 (1966).

length limit. This modification should be taken into account in the case considered in this paper for wave vectors such that $k \lesssim 1/d$, but for wave vectors such that $kd \gg 1$ the usual susceptibility–dielectric-constant relation should hold, and thus Eqs. (14) and (15) will be valid.

Kuper[16] studies a one-dimensional system of dimensions comparable with the screening length, by assuming that the electrostatic potential Φ obeys an equation $\nabla^2\Phi = K^2\Phi$ inside a cylinder of radius a, where $1/K$ is the Thomas-Fermi screening length for a free-electron gas, and that $\nabla^2\Phi = 0$ outside the cylinder; solutions for Φ are found which join smoothly between the two regions. If $Ka \gg 1$, interactions between electrons in the cylinder are screened as in the bulk material, whereas in the opposite limit $Ka \ll 1$ there is negligible screening. Kuper's study thus shows the transition between the limiting cases for a simple model, but ignores the problem of first calculating the correct susceptibility function within the material.

4. TRANSITION TEMPERATURES IN FILMS AND WHISKERS OF $SrTiO_3$

In the last section, we studied screening on a simple model, and the results indicated that at large wave vectors the screening does not change on passing from bulk material to thin film or whisker form. If specimens of only a few lattice constants thickness are produced, the phonon spectrum and electron-phonon interaction might be expected to be considerably altered from the same quantities in the bulk. However, since short-wavelength phonons are of most importance for electron-electron attraction in many-valleyed semiconductors, this alteration may not be too serious. Further, if instead of production of actual thin films, a thin inversion layer near the surface of a specimen is used to give an effectively two-dimensional system of electrons, then the phonons will still be those of the bulk material. Thus, in thin whiskers or films of many-valleyed semiconductors of orientations such that the energy minima of different valleys do not become shifted relative to each other, it may be a fair approximation to assume that both phonon energies and the local strengths of intervalley electron-phonon and electron-electron interactions take approximately the same values as they have in bulk material.

In this section we make use of published experimental data on carrier concentration dependence of transition temperature in $SrTiO_3$ and the results of Sec. 2 to deduce an effective interaction V as a function of concentration n in bulk material for a simple model in which V is assumed constant within a phonon energy $\hbar\omega = 0.099$ eV of the Fermi level and zero otherwise. (See next paragraph for reasons for this choice of phonon energy.) It is then demonstrated that, for a localized interaction of given strength, the effective interaction strength between electrons in the same quantum level with respect to motion in the direction of the thickness is increased by factors $\frac{3}{2}$ and $\frac{9}{4}$ for films and whiskers, respectively. Thus, assuming a model where the bulk V multiplied by these factors holds for films and whiskers of orientations such that the energies of electrons in different valleys become shifted by the same amount, the results of Sec. 2 are again used to estimate energy gaps and hence transition temperatures of these as a function of carrier concentration and thickness for $SrTiO_3$. Since the valleys in $SrTiO_3$ are thought to be in the [100] directions,[17] the orientations required are (111) films or [111] whiskers of suitable shape. The lattice constant in the [111] direction is equal to $3.9\times\sqrt{3} = 6.8$ Å. For [111] whiskers of equilateral triangular cross section with $[1\bar{1}0]$ sides, the lattice constant in the directions $[11\bar{2}]$ of the perpendicular bisectors of these sides is $3.9\times(\sqrt{6})$, and so the minimum area of the triangle is $(3.9)^2\times(\sqrt{12}) \simeq (7.3)^2$ Å^2. For both films and whiskers it seems sensible to do calculations for d equal to multiples of the basic units of about 7 Å. We have actually made calculations for $d = 7$, 14, and 21 Å. For $d > 21$ Å the separation between the lowest and next lowest level with respect to motion perpendicular to the thickness given by $\Delta\epsilon = (\hbar^2/2m)\cdot(3\pi^2/d^2)$ becomes less than 0.099 eV, and so the model will need modification at such thicknesses.

Group-theoretical analysis to determine the phonons which should dominate intervalley processes can be made[18,19] if one uses Cowley's work[20] on lattice dynamics of $SrTiO_3$ and Kahn and Leyendecker's band-structure calculations,[17] which indicate lowest conduction-band wave functions of symmetry type X_3 at the zone edge in the [001] directions. It is not clear, though, whether selection rules made on this basis will remain intact when polaron effects are included. Our choice of phonon energy corresponds to that of the highest-energy longitudinal optical branch of the spectrum, obtained as 0.099 eV at $\mathbf{k} = 0$ from analysis of infrared reflection data.[21] In Cowley's model IV for $SrTiO_3$, which gives a fair fit to data obtained by neutron spectroscopy on the low-frequency branches at 90°K, this branch is flat on the line OM from the origin to the zone-edge point M in the [110] direction. Thus we expect that the zone-edge phonon energy will be 0.099

[17] A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

[18] For a method of deducing selection rules from results of group theory, see R. J. Elliott and R. Loudon, J. Phys. Chem. Solids **15**, 146 (1960).

[19] Character tables for the irreducible representations of the relevant groups (of type D_{4h}) may be found, e.g., in a review article by G. F. Koster, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. V, p. 173.

[20] R. A. Cowley, Phys. Rev. **134**, A981 (1964).

[21] D. M. Eagles, J. Phys. Chem. Solids **26**, 672 (1965). [The polaron coupling constant for the lowest-frequency mode should be $\alpha_1 \simeq 0.01(m/me)^{1/2}$ and not $\alpha_1 \simeq 0.001(m/me)^{1/2}$ as stated in this note.]

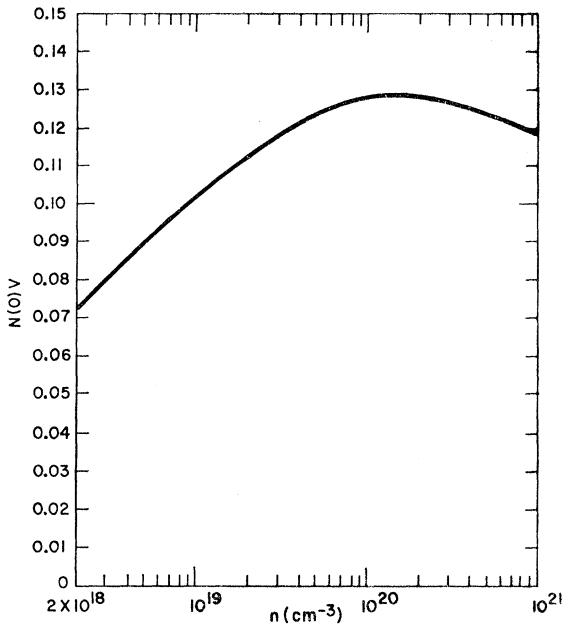

FIG. 1. Plot of $N(0)V$ for bulk $SrTiO_3$ for the simple model described in the text, as deduced from published experimental results (Ref. 12) on transition temperature as a function of carrier concentration n in this material.

eV also. Our only justification for choice of this branch of the spectrum is that it does dominate electron-phonon interactions at long wavelengths, and hence it is plausible that it could be important for intervalley processes too. [*Note added in proof.* However, recently published work[22] on superconducting $SrTiO_3$ makes it appear likely that intervalley phonons of energy 0.0497 eV might have been a more realistic choice.]

We now make use of Eqs. (2), (7), and (10) of Sec. 2, together with published experimental results[12] on transition temperature versus carrier concentration n in bulk $SrTiO_3$, and the relation $kT_c \simeq 0.57\Delta$, to deduce an effective V in our model as a function of n in bulk $SrTiO_3$. A density-of-states mass $m_d = 5m_0$, where m_0 is the free-electron mass is assumed.[23] Thus, with three valleys, an average mass m in each valley is given by $m = 3^{-2/3} \times 5m_0 = 2.4m_0$. The results for $N(0)$ and log V are plotted in Figs. 1 and 2, respectively. We notice that in this model V is decreasing with increasing n even at low carrier concentrations. Since at these concentrations the screening wave vector k_s is considerably smaller than the intervalley phonon wave vector $k_v \simeq 1.1 \times 10^8$ cm^{-1}, this probably indicates that intravalley interactions are having appreciable effects,[24] as has been suggested by Appel.[25]

[22] *Footnote added in proof*: C. S. Koonce, M. L. Cohen, J. F. Schooley, W. R. Hosler, and E. R. Pfeiffer, Phys. Rev. **163**, 380 (1967).

[23] H. P. R. Frederikse, W. R. Hosler, and W. R. Thurber, J. Phys. Soc. Japan Suppl. **21**, 32 (1966).

[24] If we suppose that intervalley phonons of lower energy are dominant, then we find a stronger dependence of V on n at low carrier concentrations.

[25] J. Appel, Phys. Rev. Letters **17**, 1045 (1966).

Now it was demonstrated by Paskin and Singh[10] that, for a localized interaction of given strength, the effective pairing interaction between electrons in the same quantum state with respect to motion perpendicular to the plane of the film is increased by a factor of $\frac{3}{2}$. Mathematically, in our case, with wave functions assumed to vanish at the surface, this increase comes from the fact that

$$(2/d)^2 \int_0^d \int_0^d \sin\left(\frac{\pi n x}{d}\right) \sin\left(\frac{\pi n x'}{d}\right) \delta(x-x') \sin\left(\frac{\pi n' x}{d}\right) \times \sin\left(\frac{\pi n' x'}{d}\right) dx dx' = d^{-1}(1+\tfrac{1}{2}\delta_{nn'}). \quad (17)$$

Here x denotes the coordinate perpendicular to the plane of the film. Hence, if $n=n'$, for given components $\mathbf{k}$ and $\mathbf{k}'$ of wave vector in the plane of the film, we have pairing matrix elements between states $(n\mathbf{k})$, $(n'\mathbf{k}')$ enhanced by a factor $\frac{3}{2}$ over their values when $n \neq n'$. Similarly, we can show that for whiskers we obtain a product of two such enhancement factors, i.e., a factor $(3/2)^2 = (9/4)$.

We now take our values of $V = V(n)$ obtained for bulk material and assume $V_2(n)$ and $V_1(n)$ in films and whiskers satisfy $V_2(n) = (3/2)V(n)$, $V_1(n) = (9/4)V(n)$. Thus, using $kT_c \simeq 0.57\Delta$ and Eqs. (2), (3), (5), (6), (8), and (9) of Sec. 2, we predict approximate BCS transition temperatures as a function of carrier concentration for three different thicknesses d for films and whiskers. The predictions are shown in Figs. 3 and 4. The curve beyond $n = 10^{21}$ cm^{-3} for 7 Å whiskers is based on an extrapolation of the $N(0)V$ curve of Fig. 1. The carrier concentrations at which the model predicts $2kT_c = \epsilon_f$ are shown by the black circles in the figures. Since the derivations of the approximate expressions (2) and (3) were based on the assumption that $\Delta = 1.75\ kT_c \ll \epsilon_f$, the results are not accurate to the left of the black circles, and the curves are shown dotted in this region. However, if $\hbar\omega \gg 2kT_c = \epsilon_f$, the error in using (3) for films is only about 8%. The maximum carrier concentrations n_{m1} and n_{m2} for which all carriers can lie in the lowest state, given by (11) and (12), are greater than 10^{21} cm^{-3} in all cases. From Eq. (12), since the static dielectric con-

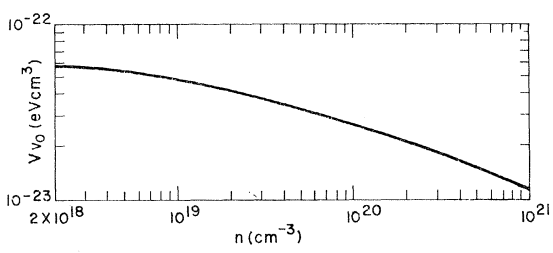

FIG. 2. Plot of log$V$ versus log$n$ in bulk $SrTiO_3$ for the simple model described in the text.

stant in insulating $SiTiO_3$ is over 300 and screening will increase it still further, it appears that for the specimens being considered here, modifications of level separations due to Coulomb repulsion should be negligible.

We should note that most of the dashed part of the curves in Figs. 3 and 4 lie in the region where $N(0)V>0.5$ (e.g., for 7 Å films this inequality is satisfied when $n\lesssim 1.6\times 10^{20}$ cm^{-3}). Certain calculations for metals[26,27] indicate that, when $N(0)V>0.5$, the phonon frequencies become imaginary, and the lattice should become unstable. However, besides other specialized assumptions, these calculations assume that the Fermi energy is large compared with a phonon energy, and thus are not relevant to the cases being considered in this paper. It would be surprising if interaction between phonons and the small concentrations of electrons present in the conduction band in semiconductors could make the lattice become unstable, but study of the required modifications of the instability criterion for small carrier concentrations might be of interest. A further point to note regarding the instability criterion is that the theory is formulated in terms of bare electron energies, phonon frequencies, and electron-phonon interaction parameters. There are indications[28] that their normalized value of $N(0)V$ can be considerably larger than 0.5 without the lattice becoming unstable in many known superconducting materials.

From Figs. 3 and 4 we see that, for film thicknesses of 7 and 14 Å, and for whiskers of cross sections $(7\text{Å})^2$, $(14\text{ Å})^2$, and $(21\text{ Å})^2$, transition temperatures greater than those of any known superconductor are predicted on this model.

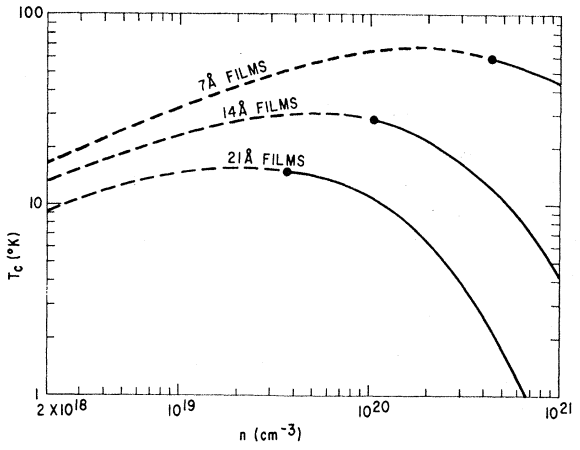

FIG. 3. Predicted superconducting transition temperatures as a function of carrier concentration for (111) films of $SrTiO_3$ of 7, 14, and 21 Å thicknesses in the simple model. The black circles denote the points at which $2kT_c=\epsilon_f$. Results are not accurate to the left of these circles.

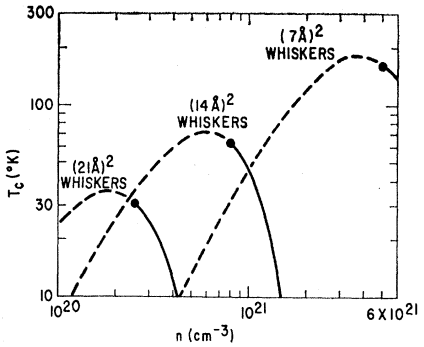

FIG. 4. Predicted transition temperatures as a function of carrier concentration for [111] whiskers of $SrTiO_3$ of $(7\text{ Å})^2$, $(14\text{ Å})^2$, and $(21\text{ Å})^2$ cross section in the simple model. The curves for $n>10^{21}$ cm^{-3} are based on an extrapolation of the $N(0)V$ curve of Fig. 1. The black circles denote the points at which $2kT_c=\epsilon_f$. Results are not accurate to the left of these circles.

5. DISCUSSION

In this section some of the shortcomings of the model used in Sec. 4 are discussed.

The main assumptions of the preceding theory may be listed as follows: (A) Only one type of phonon, of energy $\hbar\omega=0.099$ eV, contributes to the electron-electron interaction. (B) The retarded interaction between electrons is replaced by an instantaneous interaction V, which is assumed independent of electron wave vectors. (C) The electron-electron interaction in films and whiskers has been taken to be localized and of the same strength as in bulk, giving increased effective interactions between electrons in the same level with respect to motion in the direction of the thickness by factors $\frac{3}{2}$ for films and $(\frac{3}{2})^2$ for whiskers. (D) Nonuniformities of film thickness are neglected. (E) If films are deposited on a substrate, properties of the substrate are implicitly assumed in supposing that electrons are localized within the film thickness. (F) Basic problems regarding the existence of superconductivity and validity of the usual type of gap equation (i) in one- and two-dimensional systems and (ii) when the Fermi energy is smaller than the relevant phonon energy, have been ignored.

These points will be discussed in further detail below.

(A) A discussion of the choice of phonon energy was given in the previous section. As pointed out there, the assumption that intervalley phonons of this energy only contribute to the interaction is not quite consistent, in that V deduced from experiment on this assumption decreases with carrier concentration at concentrations too small for intervalley screening effects to be significant. [*Note added in proof.* A recent paper[22] indicates that it is likely that intervalley phonons of energy 0.0497 eV may dominate the interaction, with some contribution from intravalley

[26] A. B. Migdal, Zh. Eksperim. i Teor. Fiz. **34**, 1438 (1958) [English transl.: Soviet Phys.—JETP **7**, 996 (1958)].
[27] J. M. Blatt, *Theory of Superconductivity* (Academic Press Inc., New York, 1964), pp. 199–208.
[28] T. H. Geballe, in Proceedings of Tenth International Conference in Low Temperature Physics, Moscow, 1966 (to be published).

phonons of various energies. If 0.0497 eV phonons are dominant, then, using (2) and (3), it is clear that the ratio of the predicted T_c for films to that shown in Fig. 3 will lie between 0.7 and 1.]

(B) The assumption of an instantaneous interaction independent of electron wave vectors is the same as that of the original BCS theory; since it gives good results for weak-coupling metallic superconductors, it is likely to be good for bulk $SrTiO_3$ where the coupling is weak. However, corrections associated with strong-coupling effects[29] might be expected if a theory including retardation were used for thin films and whiskers, since for these the parameter $N(0)V$ can satisfy $N(0)\gtrsim 1$.

(C) If our assumption that intervalley phonons dominate the electron-electron interaction via phonons is correct, then this interaction should be localized. Also, the Coulomb repulsion will be localized in a distance of the order of the screening length, and so it should be a fair approximation to take a localized net interaction. Thus, for a given local strength of interaction, we obtain the multiplication factors mentioned for the effective strength of attraction between electrons in a given quantum level. However, the supposition that the local strength of the interaction remains the same in films or whiskers as in the bulk for a given carrier concentration is expected to be the main source of error in predicted transition temperatures. Four points in connection with this may be noted in particular: (1) As mentioned before, unless a "quasi-thin film" is produced by forming an inversion layer at the surface of bulk $SrTiO_3$, the phonon spectrum and electron-phonon interaction strengths may be considerably altered for films or whiskers of a few atomic distances thick. Also, since an appreciable fraction of atoms lie in surface layers at such thicknesses, mean interatomic distances and many other properties may be significantly different from their bulk values for very thin specimens. Further, surface contamination could alter values V under these circumstances. (2) The results of Sec. 3 indicate that, for a given large wave vector, screening should be the same as in the bulk. However, in films or whiskers the intervalley distances do not remain the same as in the bulk. Denoting the wave vector at the edge of the zone in the [100] direction in bulk material by k_m, [$k_m=\pi/3.9=0.8$ Å^{-1}], the intervalley distance in bulk is $k_m\sqrt{2}$, while in (111) films there are two intervalley distances of $k_m\sqrt{2}$ and $k_m(2/3)^{1/2}$. In [111] whiskers all the valleys coincide at the zone-edge point $(k_m/\sqrt{3})$, and so one might think that the dielectric constant at very small wave vectors would become relevant. However, if one is concerned with the screening of interactions with phonons for which different sublattices move in opposite directions, then $\varepsilon(\mathbf{K})$, where $\mathbf{K}$ is a reciprocal lattice vector, should be what is required. Since the smallest reciprocal lattice vector for [111] whiskers is $(2k_m/\sqrt{3})=1.15k_m$, which is not very greatly different from $k_m\sqrt{2}$, our assumptions about screening may not be too bad. (3) The net attractive interaction between electrons in $SrTiO_3$ is composed of a difference between two larger quantities, the attraction via phonons and the Coulomb repulsion. Thus, small relative changes of these contributions could upset the delicate balance between them, and we cannot rule out the possibility that for very thin films or whiskers the net interaction could become repulsive. (4) The effective masses in any valley in $SrTiO_3$ are anisotropic,[23] with longitudinal masses $m_e\simeq 6m_e$, and transverse masses $m_t\simeq 1.5m_e$. The shift in energy of any valley in films of thickness d will be of the order of $(\hbar^2/2m)(\pi/d)^2$, where m denotes the mass perpendicular to the film, since (π/d) is the perpendicular component of the wave vector of the lowest state with respect to motion across the thickness. Thus, for (100) films, two valleys are shifted upwards in energy with respect to the third by amounts of order $(\hbar^2/2m_e)(\pi/d)^2\times[(1/1.5)-(1/6)]\simeq 0.4$ eV for 7 Å films. This shift is sufficiently large to push all carriers into the lowest-energy valley for carrier concentrations of interest. Presumably, there is a smooth change of energy shift for orientations varying from (100) to (111), and so small departures from (111) orientation for these very thin films would be quite serious. Similar arguments will apply to whiskers.

(D) The effects of small nonuniformities of thickness become greatly magnified when thicknesses of the order of 20 Å or less are considered. If a variable-thickness specimen is prepared, one might make a first guess that the density of states and hence transition temperature should be equal to those for a uniform specimen such that the reciprocal of its thickness (or the fourth power thereof for whiskers) equalled the average reciprocal thickness (or the average of the fourth power thereof) of the actual film (or whisker). However, differences of dielectric and other properties from those of the bulk material are likely to be greater for nonuniform specimens, and so an estimate of the transition temperature on this basis could be too optimistic.

(E) If the film of $SrTiO_3$ is deposited on a substrate, then, in order that the electrons in the conduction band of the film should not penetrate into the substrate, we require that the energy of the bottom of the conduction band of the $SrTiO_3$ film should lie at a level inside the band gap of an insulating or semiconducting substrate. This condition should not be difficult to attain, and merely requires that we use a substrate sample of sufficiently small impurity content that the Fermi level lies within the band gap.

[29] Calculations by W. L. McMillan (not yet published) on strong-coupling superconducting metals indicate that the quantity λ corresponding to $N(0)V$ in a theory with retarded interactions has to be replaced approximately by $\{\lambda/(1+\lambda)\}$ when renormalization effects are taken into account.

(F) (i) It has been argued[30,31] that it is impossible to obtain the long-range order required for superconductivity in infinite one- and two-dimensional systems, since fluctuations associated with collective electronic oscillations of the system will destroy this long-range order. However, these arguments need modification in finite systems,[32] and in two dimensions it appears that such fluctuations will not produce serious effects for samples of ordinary sizes.[33] In any case there is a body of opinion which suggests that a transition to some state something like a superconducting state can occur even in infinite one-dimensional systems[34]; presumably the energy gap and transition temperature of such a state, if it exists, will be determined by equations somewhat resembling the BCS equations, which are obtained by use of a reduced Hamiltonian which does not contain the terms on which the existence of collective oscillations depends. Thus, we expect that our calculations will give approximate superconducting transition temperatures for finite films, and approximate transition temperatures to a superconductinglike state for whiskers.

(ii) A second basic problem regarding the theory is that the usual justification of a BCS-like theory based on Green's functions[35] depends on the smallness of the parameter $(\hbar\omega/\epsilon_F)$. However, as the physical concept of particles pairing in an attractive potential does not depend on having a large concentration of particles, it seems probable that other justifications could be found which do not depend on $(\hbar\omega/\epsilon_F)$ being small. At low concentrations, though, the condensation temperature T_B (say) of the pairs may be lower than the pairing temperature, and so in this region, it seems that superconducting transition temperatures will be limited by this condensation temperature, i.e., at concentrations such that our calculated T_c satisfies $kT_c \gtrsim kT_b \sim \epsilon_F$, it seems that our calculations give an estimate of a critical temperature for pairing, but not of the superconducting transition temperature.

Besides the theoretical limitations of our simple model, we should also mention the probable extreme difficulty of production of films or whiskers of $SrTiO_3$ of such small thicknesses. We shall not comment on these problems here.

6. CONCLUSIONS

The transition temperatures of very thin films and whiskers of superconducting $SrTiO_3$ have been calculated on a simple model involving a BCS-like theory with an interaction between electrons constant within a high-frequency longitudinal optical phonon energy of the Fermi level. Transition temperatures greater than those of any known superconductor are predicted on this model for (111) films of 7 and 14 Å thicknesses, and for [111] whiskers of $(7\text{ Å})^2$, $(14\text{ Å})^2$, and $(21\text{ Å})^2$ cross sections. Although the simple model has many shortcomings, the results do appear to indicate that an experimental study of thin films or whiskers of this material would be of great interest.

ACKNOWLEDGMENTS

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