Effective Masses in Zr-Doped Superconducting Ceramic SrTiO$_3$

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An analysis is made of published experimental results on superconducting transition temperature as a function of carrier concentration and on magnetic field penetration depths in Zr-doped ceramic SrTiO$_3$. From the penetration-depth results it is deduced that the ratio of effective masses m_3 and m_1 for 3% and 1% of Ti ions replaced by Zr satisfies $(m_3/m_1) \simeq 1.48$ if Zr ions are the main scattering centers. Using a model involving screened electron-electron interaction via intervalley phonons of energy 0.0497 eV modified by intervalley Coulomb repulsion and by intravalley effects, it is shown that the transition-temperature data can be fitted fairly well with mass changes of the above magnitude, provided that the ratio of phonon-induced to Coulomb intervalley interactions is postulated to increase by about 5% for each percent of Zr doping. It is argued that the large mass increases may imply that a crossing of levels associated with small and large mass states is taking place as Zr is added. The possibility of superconductivity at very low carrier concentrations in specimens with 3% Zr content is discussed.

I. INTRODUCTION

EXPERIMENTS of Hulm, Jones, Miller, and Tien[1] (to be referred to as HJMT) on superconducting ceramic SrTiO$_3$ with some Zr replacing Ti show two features of particular interest. Firstly, the carrier concentration n_m at which the transition temperature T_c reaches its maximum shifts to lower values with increasing Zr concentration; the concentrations n_{m0}, n_{m1}, and n_{m2} at the T_c maximum for 0, 1, and 2% Zr additions are $n_{m0} = 7 \times 10^{19}$ cm^{-3}, $n_{m1} = 3.5 \times 10^{19}$ cm^{-3}, and $n_{m2} = 1.3 \times 10^{19}$ cm^{-3}. Secondly, the magnetic field penetration depth λ increases with Zr doping, rising (for a fixed carrier concentration $n = 10^{19}$ cm^{-3}) from 16 μ for 1% Zr to 52 μ for 3% Zr. Both these effects can be explained in terms of a large increase in electron effective mass m with increasing Zr content. The penetration-depth results arise because, in dirty London superconductors, a dependence $\lambda \propto (mN_s^{1/2}/n^{1/3}T_c^{1/2})$, where N_s denotes the concentration of scattering centers, can be shown to be plausible; the connection between the shift in the T_c maximum and increasing mass arises from the fact that, for a given carrier concentration, free-carrier screening is proportional to the mass. In this paper, we give arguments which indicate that the increase in mass is most probably by a factor of about 1.7 as 3% Zr replaces Ti, and show that such increases point to the likelihood that a transition between a small and a very large mass state is taking place as Zr is added. In a following paper, we shall discuss whether the transition concerned could be between large and nearly small polaron states.[2,3]

In Sec. II the mass increases deducible from the penetration-depth results are discussed. In Sec. III it is shown that such large mass increases will not occur in the simplest tight-binding model that we can construct. In Sec. IV a model to explain the transition-temperature data is developed. It is shown that a fair fit to the experimental results can be obtained using the mass changes deducible from the penetration-depth analysis, provided that some increase in the ratio of strengths of phonon-induced to Coulomb intervalley interaction is allowed as Zr replaces Ti. In the model used, the transition temperature in 3% Zr-doped specimens continues to rise as the carrier concentration is decreased, until effects associated with kT_c becoming comparable with the Fermi energy cause a levelling. A solution of the BCS equation in the low concentration limit is presented and shows a very gradual fall of T_c with decreasing concentration in this region. Some discussion is given in Sec. V, and conclusions are stated in Sec. VI.

II. PENETRATION-DEPTH ANALYSIS

Penetration depths λ are large in superconducting semiconductors[1,4] because of the small carrier concentrations. The coherence lengths in pure materials, however, are comparable with those of superconducting metals, since, in the expression $\xi_0 = (0.18\hbar v_F/kT_c)$, small Fermi velocities v_F are compensated by small T_c's. Thus $\lambda \gg \xi_0$, and expressions for London superconductors are applicable. Mobilities for the ceramic SrTi$_{1-y}$Zr$_y$O$_3$ specimens used by HJMT are not known, but it is probable that the mean free paths are short. Thus the penetration depth should be given by the dirty-limit formula[5]

$$\lambda = (mc^2/4\pi ne^2)^{1/2}(\xi_0/l)^{1/2}. \qquad (1)$$

Now $l = v_F\tau$, where τ is the scattering time and v_F is the Fermi velocity, and $\xi_0 \propto v_F/T_c$. Thus $\xi_0/l \propto \tau^{-1}T_c^{-1}$. Furthermore, it is probable that the scattering rate

[1] J. K. Hulm, C. K. Jones, R. C. Miller, and T. Y. Tien, in *Proceedings of the Tenth International Conference on Low-Temperature Physics* (VINITI, Moscow, 1967), Vol. IIA, pp. 86–114.
[2] D. M. Eagles, Phys. Rev. 145, 645 (1966).
[3] D. M. Eagles (to be published).
[4] J. F. Schooley and W. R. Thurber, J. Phys. Soc. Japan Suppl. 21, 639 (1966).
[5] See, e.g., P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966), pp. 24–26.

$1/\tau \propto N(0)N_s$, where $N(0)$ denotes the density of states per unit energy at the Fermi level, and N_s denotes the concentration of scattering centers. Since $N(0) \propto mn^{1/3}$, we deduce that $\xi_0/l \propto N_s mn^{1/3}/T_c$, and hence, using (1), that

$$\lambda \propto mN_s^{1/2}n^{-1/3}T_c^{-1/2}. \tag{2}$$

By plotting the diamagnetic susceptibility in Zr-doped specimens as a function of the product of the average grain size of the ceramic specimens with the square root of the carrier density, and using an analysis assuming spherical grains, HJMT[1] show that the penetration depths λ_1 and λ_3 for 1 and 3% Zr-doped specimens at $n = 10^{19}$ cm⁻³ satisfy $\lambda_1 = 16 \mu$ and $\lambda_3 = 52 \mu$. Although the absolute magnitudes of the penetration depths deduced in this way may not be very accurate because of uncertainties about grain-size distributions, it seems probable that the ratio $\lambda_3/\lambda_1 = 3.25$ may be reliable. The transition temperatures at this concentration are given by $T_{c1} = 0.24°$K and $T_{c3} = 0.15°$K. Thus using (2) we deduce that the ratio of the masses m_3 and m_1, for 3 and 1% Zr additions, satisfies

$$m_3/m_1 = 2.57(N_{s1}/N_{s3})^{1/2}, \tag{3}$$

where N_{sq} denotes the concentration of scatterers for $q\%$ Zr. Since the Zr concentration is quite high, it is probable that Zr ions are the main scatterers. Hence $N_{s1}/N_{s3} = \frac{1}{3}$, and so

$$m_3/m_1 = 1.48. \tag{4}$$

III. BARE MASS IN A SIMPLE TIGHT-BINDING MODEL

In Sec. II we showed from penetration-depth analysis that a change of Zr content from 1 to 3% in SrTi₁₋ᵧZrᵧO₃ most probably gives rise to carrier mass changes by a factor of 1.48. In this section we show, in the simplest tight-binding model that we can construct, involving direct overlaps and no degeneracy of wave functions, that it is difficult to see how the electron mass for the rigid lattice can change proportionally more than the fraction of Zr impurities.

We consider a band for which the electronic wave functions for the case of no Zr addition are composed of Bloch-type linear combinations of nondegenerate orthogonalized wave functions ϕ localized on Ti sites, such that the matrix element of the electronic part of the Hamiltonian between ϕ's on neighboring sites is equal to $(-J)$. The difference in energy between the top of the band at $\mathbf{k} = (\pi/a, \pi/a, \pi/a)$, where a is the lattice distance, and the bottom of the band at $\mathbf{k} = 0$, is then $2zJ$, where $z = 6$ is the number of nearest-neighbor sites.

If we now suppose that the Zr replacements produce about the most drastic effects that we can imagine, namely that all conduction electrons are kept off the Zr ions completely, then for a fraction y of Zr ions, the wave function for a state of wave vector $\mathbf{k}$ satisfies

$$\psi_\mathbf{k} = N_0^{-1/2}(1-y)^{-1/2} \sum_\mathbf{R}{}' \exp(i\mathbf{k} \cdot \mathbf{R})\phi(\mathbf{r} - \mathbf{R}). \tag{5}$$

Here N_0 denotes the number of lattice sites, $\sum'$ denotes a summation only over those sites occupied by Ti ions, and $\phi(\mathbf{r} - \mathbf{R})$ is the Wannier function for the site $\mathbf{R}$. Thus if y is small, the number of overlaps for the $\mathbf{k} = 0$ state is decreased by a fraction $1 - 2y$, but the expectation value of the energy is only changed by a fraction $(1 - 2y)/(1 - y) \simeq 1 - y$. Hence, the difference in energy between the top and bottom of the band is decreased by a factor $1 - y$, and the mass is increased by a factor of approximately $1 + y$.

For less extreme cases where there is some probability of an electron being located on a Zr ion, smaller changes in mass would be expected. Thus, in this simple model, it is difficult to see how the electron mass can change proportionally more than the fractional Zr addition, i.e., we expect the mass m_q for a $q\%$ doped specimen to satisfy

$$m_q/m_0 = 1 + \gamma q/100, \tag{6}$$

where $\gamma \leqslant 1$.

One possible way in which large masses could occur in a more complicated model would be by crossing of a small and a large mass state—brought about by Zr additions. In order for the mass increase not to be discontinuous on such a model, mixing of levels would have to occur because of electron-phonon interactions or by other means. Such a pair of small and large mass states of nearly the same energy could perhaps arise in band-structure calculations for some materials, but Kahn and Leyendecker's band-structure calculations[6] for SrTiO₃ show a fairly well isolated state at the [100] conduction-band minimum. An alternative possibility for such a pair of levels, involving large and nearly-small polaron states, will be discussed in a subsequent paper.[3] Use will be made of some work of Reik[7] on interpretation of free-carrier absorption in SrTiO₃ in terms of small polaron theory.

IV. TRANSITION TEMPERATURES IN SrTi₁₋ᵧZrᵧO₃

A. Description of Model

In this section we attempt to interpret superconducting transition temperature versus carrier-concentration results of HJMT[1] in ceramic Zr-doped SrTiO₃. Following Koonce and co-workers,[8] we assume that intervalley phonons of energy 0.0497 eV dominate the attraction, but include some modifications due to the difference between intravalley attraction via optical phonons and intravalley Coulomb repulsion, and due to high-frequency effects. However, in order to avoid too much computational work, a simpler model than that of Ref. 8 is used. We assume a BCS type of model[9]

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

[7] H. G. Reik, Z. Physik **203**, 346 (1967).

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

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

modified for small Fermi energies,[10] with the pairing interaction V constant within an energy $\hbar\omega_c$ of the Fermi level, and take a form for V suitable for screened attraction via intervalley phonons modified in magnitude by screened intervalley Coulomb repulsion and by intravalley effects. The interaction in material without Zr involves two adjustable parameters, one associated with the total strength of the interaction and the other associated with the ratio of the strengths of phonon-induced and Coulomb intervalley interactions. Since, in high-dielectric-constant materials at low frequencies, the intravalley Coulomb repulsion and attraction via optical phonons almost cancel each other, it is necessary to discuss the frequency-dependent interaction in order to deduce the effects of intravalley interactions on the intervalley V. A discussion of such interactions for frequencies below the intervalley phonon frequency ω_c is given in Sec. IV B.

B. Effect of Intravalley Interactions for Frequencies below ω_c

Our basic assumptions about the intravalley interactions are (a) that interaction via acoustic phonons will be of negligible importance because of the high dielectric constant in $SrTiO_3$ at low frequencies,[11] and (b) that interaction via optical phonons is given by the continuum polarization model of electron-phonon interactions[12] as modified by screening[13] and by the presence of several longitudinal polar branches of the mode spectrum.[14]

For a material such as $SrTiO_3$ with three longitudinal polar branches of the phonon spectrum,[15] in the continuum polarization model the unscreened electron-phonon matrix elements V_{ik} for phonons of wave vector k in the ith branch satisfy[14]

$$\frac{2|V_{ik}|^2}{\hbar\omega_i} = \frac{4\pi e^2}{k^2 V_0} f_i^2 \left(\frac{1}{\varepsilon_h} - \frac{1}{\varepsilon_s}\right), \quad (7)$$

where V_0 is the volume, ε_h and ε_s are the high-frequency and static dielectric constants of the material, and

$$f_i^2 = \alpha_i(\hbar\omega_i)^{1/2} / \sum_{i=1}^{3} \alpha_i(\hbar\omega_i)^{1/2}. \quad (8)$$

Here α_i denotes the polaron coupling constant with the ith branch.

Hence, neglecting strong-coupling polaron effects, for an electron energy difference $\hbar\omega$ and wave-vector difference k, the unscreened phonon-induced electron-electron attraction $V_{ik,\omega}{}^u$ is given by

$$V_{ik,\omega}{}^u = \frac{4\pi e^2}{k^2 V_0} f_i^2 \left(\frac{1}{\varepsilon_h} - \frac{1}{\varepsilon_s}\right)\left(\frac{\omega_i^2}{\omega_i^2 - \omega^2}\right). \quad (9)$$

For polarons in an intermediate or strong-coupling regime, we expect that only a fraction g of the total interaction will be due to single-phonon processes, and that the remainder of the interaction due to many-phonon processes will be much less strongly frequency-dependent. However, at least for large polarons, renormalization of electron-phonon matrix elements is not important for small wave vectors, and we shall thus assume that $g=1$.

For the case of only one longitudinal branch of the spectrum of frequency ω, it has been shown[13] that, if the effect of screening is to divide (9) by $[\varepsilon_{el}(k,\omega)/\varepsilon_h]^2$, where $\varepsilon_{el}(k,\omega) = \varepsilon_h + \varepsilon_c(k,\omega)$ denotes the total, high-frequency plus free-carrier, electronic contribution to the dielectric constant at wave vector k and frequency ω, and to change ω_i^2 in the denominator on the right to its renormalized value $\bar\omega_i^2$, given by

$$\frac{\bar\omega_i^2(k,\omega)}{\omega_i^2} = \frac{\varepsilon_h}{\varepsilon_s} + \frac{\varepsilon_h}{\varepsilon_{el}(k,\omega)} - \frac{\varepsilon_h^2}{\varepsilon_s \varepsilon_{el}(k,\omega)}, \quad (10)$$

then the phonon-induced attraction can be written in the alternative form

$$V_{k,\omega} = \frac{4\pi e^2}{k^2 V_0} \frac{\pi_{ph}}{\varepsilon_{el}(\varepsilon_{el} + \pi_{ph})}, \quad (11)$$

where π_{ph} denotes the polarizability associated with the phonons, which is equal to $(\varepsilon_s - \varepsilon_h)$ in the zero-frequency limit.

For the case of three modes, the condition $\varepsilon(k,\omega_l) = 0$ determining the longitudinal-mode frequencies, where ε denotes the total dielectric constant, becomes a quartic equation[16] for ω_l^2 at small k. However, we shall be interested primarily in cases for which the carrier concentration is sufficiently small that the plasma frequency ω_p is screened by the static dielectric constant,[17] and is thus very low. In this case, the Fermi energy ϵ_F will be greater than $\hbar\omega_p$ for high-dielectric-constant materials, and, for ω such that $\hbar\omega > \epsilon_b$, where ϵ_b is some energy of the order of ϵ_F, carrier contributions

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

[11] Models in which intravalley acoustic phonons dominate the attraction have been considered by J. Appel, Phys. Rev. Letters 17, 1045 (1966), and Bull. Am. Phys. Soc. 13, 426 (1968). In these papers a form of electron interaction with those phonons similar to that normally used for metals is assumed. However, in view of the large dielectric constant due to lattice polarization in SrTiO₃, and also because of other differences from metals, this assumption does not appear to be justified.

[12] H. Fröhlich, Advan. Phys. 3, 325 (1954); in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1963).

[13] M. L. Cohen and C. S. Koonce, J. Phys. Soc. Japan Suppl. 21, 633 (1966).

[14] D. M. Eagles, J. Phys. Chem. Solids 25, 1243 (1964).

[15] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. 126, 1710 (1962).

[16] A. S. Barker, Jr., in *Proceedings of the International Colloquim on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1966), p. 452.

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

to the dielectric constant will be small, and thus screening of electron-electron interactions and renormalization of phonon frequencies will be negligible.

In SrTiO$_3$ it turns out that $f_1{}^2$ is negligible,[18] and so for frequencies small compared with ω_2 and ω_3, we see from (9) that the unscreened phonon-induced attraction and the Coulomb repulsion $(4\pi e^2/k^2\varepsilon_h V_0)$ almost exactly cancel. This cancellation is not expected to be altered by the screening. Hence, if $\epsilon_b \sim \epsilon_F \ll \hbar\omega_2$, we can ignore the intravalley interaction for $\hbar\omega < \epsilon_b$, and for $\hbar\omega > \epsilon_b$ can take the unscreened attraction via the ith mode in the form (9). Since the polaron coupling constant is largest for the highest frequency mode[18] in SrTiO$_3$, the biggest contribution to the intervalley interaction comes from this mode.

Now if, in a BCS-like theory, we take the half-energy-gap Δ to be a function only of the energy ϵ measured from the Fermi level, and take an intervalley interaction equal to a constant V_e within an energy $\hbar\omega_c$ of the Fermi level, and assume that the gap is zero beyond $\hbar\omega_c$, then the gap equation at $T=0$ can be written in the form

$$\Delta(\epsilon_1) = \frac{1}{Z'}\left[\frac{1}{2}V_e \int_{\epsilon_0}^{\hbar\omega_c} \frac{N(\epsilon)\Delta(\epsilon)d\epsilon}{(\epsilon^2+\Delta^2)^{1/2}}\right.$$
$$\left. +\frac{1}{2}\int_{\epsilon_b+\epsilon_1}^{\hbar\omega_c} \frac{V_a(\epsilon_1,\epsilon)N(\epsilon)\Delta(\epsilon)d\epsilon}{\epsilon}\right]. \quad (12)$$

Here we use $N(\epsilon)$ to denote the one-spin density of states per unit energy, including normal-state renormalization effects, $\epsilon_0 = \max(-\epsilon_F, -\hbar\omega_c)$, $\epsilon_b \sim \epsilon_F$ is the energy introduced above, and Z' is a renormalization parameter, which we assume is independent of ϵ_1 and ϵ. Since we have chosen to write our equation in terms of the dressed rather than the bare density of states, it appears that Z' should be related to the renormalization parameter Z more commonly used [8,19,20] by

$$Z'=Z^2. \quad (13)$$

The approximation $[\epsilon^2+\Delta^2(\epsilon)]^{1/2} \simeq \epsilon$ has been made in the second term of the right-hand side of (12), since we expect $\Delta \ll \epsilon_b$. The quantity $V_a(\epsilon_1,\epsilon)$ denotes the intravalley interaction between electrons of energies ϵ_1 and ϵ averaged over directions, and from (9) and the arguments above, satisfies, for SrTiO$_3$,

$$V_a(\epsilon_1,\epsilon) = \frac{4\pi e^2}{\varepsilon_h V_0}\left\{f_2{}^2\Big/\left[1-\left(\frac{\epsilon-\epsilon_1}{\hbar\omega_2}\right)^2\right]\right.$$
$$\left. +f_3{}^2\Big/\left[1-\left(\frac{\epsilon-\epsilon_1}{\hbar\omega_3}\right)^2\right]-1\right\}\,\mathrm{Av}\left[\frac{1}{|\mathbf{k}_{\epsilon_1}-\mathbf{k}_\epsilon|^2}\right], \quad (14)$$

where the average is over directions of wave vectors on the two constant energy surfaces ϵ and ϵ_1. If $\epsilon_1=0$ and $\epsilon > \epsilon_b > \epsilon_F$, then

$$\mathrm{Av}[|\mathbf{k}_{\epsilon_1}-\mathbf{k}_\epsilon|^{-2}] = \nu^{-1}(\hbar^2/2m)\epsilon^{-1}[1+O(\epsilon_F/\epsilon)]. \quad (15)$$

Here ν denotes the number of conduction-band valleys, and m denotes the average mass in each valley. The density of states $N(\epsilon)$ satisfies

$$N(\epsilon) = \frac{V_0\nu}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}(\epsilon+\epsilon_F)^{1/2}$$
$$= \frac{V_0\nu}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}\left[1+O\left(\frac{\epsilon_F}{\epsilon}\right)\right]. \quad (16)$$

Let us now make the further simplifying assumption that $\Delta(\epsilon)$ is independent of ϵ. Then, as far as the determination of $\Delta(0)$ is concerned, the effect of the last term on the right-hand side of (12) is to require the replacement

$$N(0)V_e \to N(0)V_e/(1-I) \quad (17)$$

in the expression for the gap, where

$$I = \frac{1}{2Z'}\int_{\epsilon_b}^{\hbar\omega_c} \frac{V_a(0,\epsilon)N(\epsilon)d\epsilon}{\epsilon}. \quad (18)$$

Since $V_a(0,\epsilon)$ is largest when $\epsilon \sim \hbar\omega_2$ or $\epsilon \sim \hbar\omega_3$, then from (15) and (16), to a first approximation $V_a(0,\epsilon)$ and $N(\epsilon)$ are independent of carrier concentration. The renormalization parameter may vary by a few percent over the concentration range of interest, but we shall ignore this variation. Thus, to this approximation, the effect of intravalley interactions is merely to multiply the intervalley interaction by a constant factor.

Using the expressions (14)–(16) and (18), we can show that I satisfies

$$I = \frac{1}{Z'}\frac{1}{4\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2}\left(\frac{e^2}{\varepsilon_h}\right)\sum_{i=2,3}(\hbar\omega_i)^{-1/2}f_i{}^2 S_i, \quad (19)$$

where

$$S_i \simeq \left[\ln\left|\frac{1+c_i}{1-c_i}\right| - 2\tan^{-1}c_i\right], \quad (20)$$

with $c_i = (\omega_c/\omega_i)^{1/2}$. In deriving (20) we have ignored a small contribution to S_i of similar type arising from the lower limit of the integral.

C. Figures for SrTiO$_3$

In SrTiO$_3$ the longitudinal polar-mode energies satisfy[18] $\hbar\omega_1=0.021$ eV, $\hbar\omega_2=0.058$ eV, and $\hbar\omega_3=0.099$ eV, while the polaron coupling constants α_i at 85°K are in the ratio $\alpha_1:\alpha_2:\alpha_3 = 0.007:0.56:1.83$. Hence, from (8), $f_1{}^2=0.00$, $f_2{}^2=0.19$, and $f_3{}^2=0.81$. Further[15] $\varepsilon_h=5.2$, and,[21] at 0.3°K, $\varepsilon_s=2.25\times10^4$.

[18] A. S. Barker, Jr., Phys. Rev. 145, 391 (1966).
[19] W. L. McMillan, Phys. Rev. 167, 331 (1968).
[20] C. S. Koonce and M. L. Cohen, Phys. Rev. (to be published).
[21] E. Sawaguchi, A. Kikuchi, and Y. Kodera, J. Phys. Soc. Japan 17, 1666 (1962).

According to Koonce *et al.*,[8] intervalley phonons of energy 0.0497 eV dominate the attraction, i.e., ω_c in (12) and (18) satisfies $\hbar\omega_c = 0.0497$ eV. Assuming three conduction-band minima at the zone edge in [100] directions,[6,22] low-temperature specific-heat measurements[23] yield an average mass per valley of 2.5 m_e. This value is in approximate agreement with the masses determined by other methods,[22,24] and will be used in subsequent calculations.

Thus from (20) we deduce that $S_2 \simeq 1.76$ and $S_3 \simeq 0.537$, and from (19), that, if Δ were independent of ϵ, I would be given by $I \simeq (0.49/Z')$. If anisotropy effects were included in the estimate of I, it would be increased somewhat, because different averages of the longitudinal and transverse masses would arise in (15) and (16). Nonparabolicity of the bands could introduce further complications. Also, we should note that dispersion of the phonon spectrum, lifetime effects, and the reduction of the band gap near the cutoff frequency will all tend to reduce the effect of the resonance associated with the closeness of ω_2 and ω_c, and hence to decrease I.

At a typical concentration $n = 10^{19}$ cm^{-3}, the Fermi energy ϵ_F in SrTiO$_3$ is equal to 3.2×10^{-3} eV, and so $\epsilon_F/\hbar\omega_c$ is small. Thus, over most of the values of n of interest, the concentration-dependent part of I should be small in pure SrTiO$_3$, and even smaller in Zr-doped specimens. Hence, we will assume that intravalley interactions merely multiply the intervalley $N(0)V$ by a factor which is independent of n, but may increase with increasing Zr concentration. In view of the many approximations made in our estimate of the absolute magnitude of the intravalley interactions, and also because of the unknown dependence of the renormalization parameter on Zr concentration, we shall not make use of the formula (19) to determine the mass dependence, but instead will absorb dependence of I on Zr content within a parameter A_q, which will be introduced in an empirical way to include effects of (i) renormalization, (ii) intravalley interactions below ω_c, (iii) frequency dependence of the intervalley screening, and (iv) high-frequency interactions. We shall assume that (A_q/m_q^2) varies linearly with q.

D. Expressions for the Transition Temperature

Having dealt with the intravalley interactions for frequencies below ω_c, we now give a simplified treatment of intervalley interactions to deduce an effective $N(0)V$ to introduce into the expression for the superconducting transition temperature T_c for a BCS-like model[9] for materials such that the Fermi energy ϵ_F is less than the cutoff energy $\hbar\omega_c$ for the interaction.[10]

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

[23] E. Ambler, J. H. Colwell, W. R. Hosler, and J. F. Schooley, Phys. Rev. **148**, 280 (1966).

[24] H. P. R. Frederikse and G. A. Candela, Phys. Rev. **147**, 583 (1966).

We assume that the intervalley interactions are due to the difference between screened attraction via intravalley phonons of energy $\hbar\omega_c = 0.0497$ eV, and screened Coulomb repulsion.[8] For a ν-valleyed semiconductor with a carrier concentration n, the unscreened intervalley Coulomb repulsion $V_{cu}^{(er)}$ satisfies

$$N(0)V_{cu}^{(er)} = \left(\frac{\nu-1}{\nu}\right)\left(\frac{e^2}{\pi\varepsilon_h^{(er)}k_i^2}\right)\left(\frac{2m_d}{\hbar^2}\right)(3\pi^2 n)^{1/3}, \quad (21)$$

where m_d is the density-of-states mass, ε_h is the high-frequency intervalley dielectric constant, and k_i is the magnitude of the intervalley wave vector. Using the expression for intervalley screening given in Ref. 8, we see that the carrier contribution ε_c to the intervalley dielectric constant at low frequencies is proportional to $mn^{1/3}$, and may be written in the form

$$\varepsilon_c = 2\varepsilon_h^{(er)}N(0)V_{cu}^{(er)}. \quad (22)$$

For convenience we introduce dimensionless carrier concentrations N and masses M defined by

$$N \equiv n/(10^{19} \text{ cm}^{-3}) \quad (23)$$

and

$$M \equiv m/m_e, \quad (24)$$

where m_e is free-electron mass; we also define an effective interaction $[N(0)V]_{eff}$ by

$$[N(0)V]_{eff} \equiv N(0)V/Z^2, \quad (25)$$

which we assume is given by

$$[N(0)V]_{eff} = A_q\left[\frac{B_q M_q N^{1/3}}{(1+2EM_q N^{1/3})^2} - \frac{EM_q N^{1/3}}{(1+2EM_q N^{1/3})}\right]. \quad (26)$$

Here M_q denotes the dimensionless mass for $q\%$ Zr doping, $EM_q N^{1/3}$ is the unscreened intervalley Coulomb interaction given by (21), B_q gives a measure of the unscreened intervalley phonon-induced interactions, and A_q is a composite parameter supposed to include effects of renormalization, intravalley interactions, frequency dependence of intervalley screening, and of high-frequency Coulomb repulsion. The denominator in the square bracket of (26) describes the effects of low-frequency intravalley screening; the denominator is squared for the phonon term since the screening comes in twice, once for each vertex. Using (21), (23), and (24), with[8] $\varepsilon_h^{(er)} = 2$, $\nu = 3$, and $k_i = 1.139 \times 10^8$ cm^{-1}, we find $E = 0.0429$.

The quantity given by (26) is now inserted into the expression for the transition temperature T_c for a BCS-like model for materials with Fermi energies ϵ_F such that $\epsilon_F < \hbar\omega_c$, where ω_c is the cutoff for the inter-

action. This expression is[10]

$$kT_c = 4.54\epsilon_F \exp[(1+p)^{1/2}-2]$$
$$\times\{[(1+p)^{1/2}-1]/[(1+p)^{1/2}+1]\}^{1/2}$$
$$\times\exp\{-1/[N(0)V]_{\text{eff}}\}^{-1}, \quad (27)$$

where $p=\hbar\omega_c/\epsilon_F>1$, and we take $\hbar\omega_c=0.0497$ eV. For no Zr doping, the mass m_0 was taken[23] as $m_0=2.50\ m_e$. The parameters A_0 and B_0 were then adjusted to give as good a fit as possible to the experimental results on transition temperature for specimens without Zr; the values obtained were $A_0=1.215$ and $B_0=0.1046$. Since A_q contains a factor $1/Z^2$ and, at least for large Fermi energies,[19] one expects $Z\simeq m/m_b$, where m_b is the bare electron mass, we assumed that a first approximation to A_q might be to take $A_q\propto 1/M_q^2$. We then supposed that departures from this approximation were linear in q, and made use of the value $M_3/M_1=1.48$ determined from penetration-depth results. Thus we took

$$M_0/M_q=1-0.14q, \quad (28)$$

$$A_q=A_0(M_0/M_q)^2(1+qC), \quad (29)$$

and

$$B_q=B_0(1+qD), \quad (30)$$

and varied C and D to give the best fits to the T_c versus n curves for the doped specimens. The values of C and D found in this way were $C=0.264$ and $D=0.050$. Hence, with $M_0=2.50$, $A_0=1.215$, and $B_0=0.1046$, we find from (28)–(30) that $M_1=2.91$, $M_2=3.47$, $M_3=4.31$, $A_1=1.135$, $A_2=0.963$, $A_3=0.733$, $B_1=0.1098$, $B_2=0.1151$, and $B_3=0.1203$.

The theoretical T_c versus n curves with these values of the parameters are shown in Fig. 1. Except at the high-concentration end for the 0- and 1%-Zr curves, the agreement with experiment is quite good. At the high-concentration end our treatment of intravalley
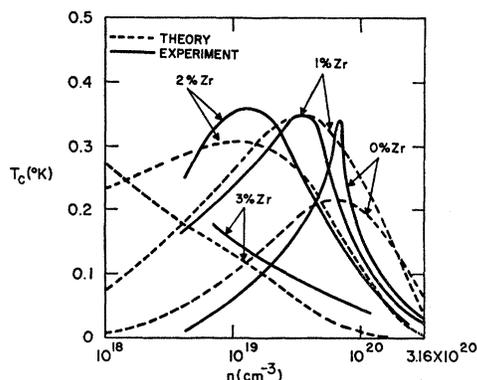

FIG. 1. Comparison of experimental results of Ref. 1 and theoretical curves for transition temperature T_c versus carrier concentration n in ceramic SrTi$_{1-y}$Zr$_y$O$_3$ for various Zr concentrations. The theoretical curves represent predictions for a BCS-like model involving screened interactions via intervalley phonons of energy 0.0497 eV modified by intervalley Coulomb repulsion, by intravalley interactions, and by high-frequency effects. Several adjustable parameters are involved. The model is described in the text.

interactions breaks down for two reasons; firstly because the approximation $\epsilon_F\ll\hbar\omega_c$ made in deriving (17) and (19) is not valid, and secondly because, at these concentrations, longitudinal phonon frequencies start increasing, since this is the region in which the highest-frequency phonon changes into a plasmon.[17] The first of these two effects tends to increase $N(0)V$, but the second tends to decrease it. Rough estimates at $n=3\times10^{20}$ cm^{-3}, using results of Ref. 15 for phonon frequencies, indicate that the second effect predominates, and hence that the theoretical T_c should be lowered as required.

The ratio of phonon-induced to Coulomb intervalley interactions in our model is given by $r=2.44$, whereas one may calculate from the values in the table in Ref. 8 that the corresponding ratio there is $r=2.28$. The fact that the two ratios are not very much different perhaps indicates that our simplified approximation to the model of that reference is not too unrealistic. Our results indicate that the ratio increases by about 5% for each percent Zr addition. A possible reason for this increase will be discussed in a subsequent paper.[3]

E. Importance of High-Frequency Interactions

The parameters A_q of (26) are complex objects with contributions of four main types (i) those due to renormalization factors $1/Z_q^2$; (ii) effects associated with intravalley interactions below ω_c; (iii) effects due to the fact that intervalley screening becomes negligible at frequencies ω such that ω is large compared with $\epsilon_F/\hbar$, and (iv) effects associated with high-frequency intra- and intervalley interactions. For no Zr doping, Koonce et al.[8] estimate that the renormalization parameter $Z_0=1.66-1.75$, depending on carrier concentration. Thus an average $Z_0^2=2.9$, and so $A_0Z_0^2=3.5$, i.e., the combination of effects (ii), (iii), and (iv) above must be large.

In Sec. IV C we estimated that effect (ii) multiplies $N(0)V$ by a factor $R_0=(1-0.49/Z_0^2)^{-1}$ for no Zr doping, i.e., by a factor 1.20 if $Z_0^2=2.9$. For Zr-doped specimens we expect $N(0)V$ to be multiplied by factors R_q satisfying

$$R_q=[1-0.49(M_q/M_0)^{1/2}(1/Z_q)^2]^{-1}. \quad (31)$$

Hence, if $Z_q\propto M_q$, the intravalley effects below ω_c become less important as Zr is added.

For a two-square-well model[25] with an effective density-of-states interaction product $\lambda(\epsilon,\epsilon')$ satisfying $\lambda(\epsilon,\epsilon')=\lambda$ for $-\epsilon_F<\epsilon<\epsilon_1$, $-\epsilon_F<\epsilon'<\epsilon_1$, and $\lambda(\epsilon,\epsilon')=\lambda_2$ for $\epsilon_1<\epsilon<\epsilon_2$, $-\epsilon_F<\epsilon'<\epsilon_2$ or $\epsilon_1<\epsilon'<\epsilon_2$, $-\epsilon_F<\epsilon<\epsilon_2$, we find that the effect of the λ_2 region is to change the effective interaction from λ_1 to $[\lambda_1+\lambda_2\{[1-\frac{1}{2}\lambda_2\ln(\epsilon_2/\epsilon_1)]^{-1}-1\}]$. We use this result to attempt to estimate the importance of the decrease

[25] N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, A New Method in the Theory of Superconductivity (Academy of Sciences, Moscow, USSR, 1958).

of intervalley screening for frequencies above $\epsilon_F/\hbar$, and of the effect of Coulomb interaction above $\hbar\omega_c$.

Assuming that the screened intervalley interaction $V_s^{(er)}$ changes to the unscreened interaction $V_u^{(er)}$ for frequencies above $b\epsilon_F/\hbar$, where $b\sim1$, and ignoring densities-of-states changes, we see that the decrease of screening may be taken as multiplying the interaction by a factor F_q given by

$$F_q=1+\frac{V_u^{(er)}}{V_s^{(er)}}\times\left[\frac{1}{1-\frac{1}{2}Z_q^{-2}N(0)V_u^{(er)}\ln(\hbar\omega_c/b\epsilon_F)}-1\right].$$
$$(32)$$

The screened interaction is given by the terms in the square brackets in (26) and the unscreened one by the same expression without the energy denominators. At the maximum in the 0% Zr curve, with $N=7$ and $M=2.50$, we find that $N(0)V_u^{(er)}=0.295$ and $N(0)V_s^{(er)}=0.106$, while, with $b=1$, $\hbar\omega_c/\epsilon_F=4.2$, and $\ln(\hbar\omega_c/\epsilon_F)=1.4$. Hence, with $Z_0^2=2.9$, we find $F_0=1.21$. Thus effect (iii) is also not the dominant one contributing to the large value of (A_0/Z_0^2). Both effects (ii) and (iii) may be taken into account by replacing $N(0)V_s^{(er)}$ in the square bracket of (26) by $N(0)V_1$, where

$$V_1=R_qF_qV_s^{(er)}\simeq1.45V_s^{(er)}\qquad(33)$$

for 0%-Zr doping.

Finally, we have to deal with the effect of high-frequency interactions. Let us suppose that these are represented by a constant value of $N(\epsilon)V(\epsilon_1,\epsilon)=-XM_q$ for ϵ between $\hbar\omega_c$ and a cutoff $W_q\propto1/M_q$. Then we may say that we have an effective density-of-states inter-action product $\lambda_1=N(0)V$ below $\hbar\omega_c$, and an interaction $\lambda_2=-\mu_2=-XM_q/Z_q^2$ above $\hbar\omega_c$. Using a two-square-well model again, the effect of μ_2 will be to increase the total interaction by a factor G_q given by

$$G_q=1+\frac{\mu_2}{\lambda_1}\left[1-\frac{1}{1+\frac{1}{2}\mu_2\ln(W_q/\hbar\omega_c)}\right].\qquad(34)$$

Taking W_q as equal to the bandwidth, and using a simple tight-binding model and the observed masses[22-24] at the bottom of the band gives $W_0/\hbar\omega_c=29$, and $\ln(W_q/\hbar\omega_c)=3.4$. For $N=7$ and $M_0=2.5$ we have $N(0)V_s^{(er)}=0.106$, and, hence, from (33), $N(0)V_1=0.15$. We want $N(0)V_1$ to be increased from 0.15 to $0.106\,A_0Z_0^2=0.37$, i.e., by a factor 2.5 by high-frequency effects. This increase will occur if $XM_0=0.75$, i.e., if $XM_0/Z_0^2\simeq0.26$. At $\hbar\omega_c$, intervalley Coulomb inter-actions alone would give $XM_0=0.4$. Intravalley inter-actions are larger in magnitude, but are dominantly attractive and strongly energy-dependent up to the energy 0.099 eV$\simeq2\hbar\omega_c$, and so their effects are difficult to estimate. However, we have demonstrated that there does not seem to be any difficulty in seeing how high-frequency interactions can have effects of the required magnitude. If a smaller cutoff is used for the Coulomb

interaction as is used in Ref. 8, a larger value of XM_0 would be required to provide the required enhancement. On the other hand, we have neglected a probable decrease of the renormalization parameter at high energies, which decrease would tend to pull down the required value of XM_0 again.

We have now shown that the magnitude of $A_0Z_0^2=3.5$ for SrTiO₃ is not implausibly large, the greatest contri-bution to it most probably coming from Coulomb effects above $\hbar\omega_c$. However, if we make the assumption that $Z_q\propto M_q$, we see that our large value of C of (29) would require $A_qZ_q^2$ to increase quite rapidly with Zr doping. Since, at least two of the effects contributing to $A_qZ_q^2$, given by

$$A_qZ_q^2=R_qF_qG_q,\qquad(35)$$

may be seen from (31) and (32) to decrease in impor-tance as Z_q increases, this does not appear to be very probable. Thus it seems more plausible to postulate that Z_q does not rise nearly as rapidly as M_q, and that, in fact, $Z_q^2\propto M_q$ may be a closer approximation to the truth. One possible reason for this type of dependence could be that about half of the mass increase is due to increase in bare mass, while the other half is due to polaron effects. However, the discussion of Sec. III indicates that bare-mass increases of this order of magnitude are not very likely. An alternative hypoth-esis is that the mass increase is entirely due to polaron effects, but that, for polarons in a strong-coupling regime, $Z\propto m/m_b$ is not valid. No theory of renormaliza-tion in a strong-coupling polaron regime appears to be available at present.

F. Possible Superconductivity at Very Low Carrier Concentrations in 3%-Zr-Doped Specimens

An interesting aspect of the model we have used is that T_c for 3%-Zr-doped specimens continues to rise with decreasing carrier concentration until the assump-tion $kT_c\ll\epsilon_F$ made in the derivation[10] of (27) is no longer valid. The continued rise occurs if the variation with carrier concentrations of the $\exp[(1+p)^{1/2}]$ term in (27) dominates over the $\exp[-1/N(0)V]$ term. In order to obtain some feeling for what might happen at very low concentrations,[26] we have obtained an approx-imate solution to the BCS equation in the opposite limit $kT_c\gg\epsilon_{Fn0}$, where ϵ_{Fn0} is the value that would be taken by the Fermi energy at $T=0$ if the normal state persisted to this temperature. As for the derivation of (27), we assumed that the gap function is independent of energy up to the cutoff energy. Denoting the Fermi energy at the transition temperature by $-\zeta$, we have two simultaneous equations to solve for ζ and T_c. If

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[26] Superconductivity for low concentrations of d electrons in a model suitable for certain transition-metal compounds similar to V₃Si has been considered by J. Labbé, S. Barišić, and J. Friedel, Phys. Rev. Letters **19**, 1039 (1967). However, the model used involved a density of states proportional to $(\zeta-\zeta_m)^{-1/2}$, where $(\zeta-\zeta_m)$ denotes the energy above the bottom of the band, instead of the more usual (energy)$^{+1/2}$ dependence assumed here.

the cutoff energy $\hbar\omega_c$ is large compared with ζ, but $\zeta < 2kT_c$, we find, with $p = \hbar\omega_c/\epsilon_{Fn0}$, that

$$\zeta \simeq \left(\frac{2}{\pi}\right)^2 \hbar\omega_c \left\{1 - \frac{1}{p^{1/2}[N(0)V]_{\text{eff}}}\right\}^2,$$

$$\hbar\omega_c \gg \zeta > 2kT_c, \quad (36)$$

provided that $p^{1/2}[N(0)V]_{\text{eff}} > 1$, and that T_c satisfies

$$kT_c = \frac{\zeta}{\ln\left[\frac{1}{4}(2m_d kT_c/\pi\hbar^2)^{3/2}/n\right]}, \quad (37)$$

where m_d is the density-of-states mass. No low-concentration solutions seem to be possible if $p^{1/2}[N(0)V]_{\text{eff}} < 1$.

For our model, from (23), (24), and (26), we find that, in the limit of low concentrations where screening is negligible,

$$p^{1/2}[N(0)V]_{\text{eff}} = 2.47A_q(B_q - E)M_q^{3/2}. \quad (38)$$

Hence, for 3%-Zr doping, with $M_3 = 4.31$, $A_3 = 0.733$, $B_3 = 0.1203$, and $E = 0.429$, the right-hand side of (38) is equal to 1.254. However, screening remains significant over quite a wide range of n, and it is not until $n < 1.5 \times 10^{17}$ cm⁻³ that $p^{1/2}[N(0)V]_{\text{eff}} > 1$.

To illustrate the sort of T_c's we could get at very low n, we consider 3%-Zr-doped material in the limit where screening is negligible, and find the concentrations at which Eqs. (36) and (37) give $T_c = 1$ and 0.8°K. From (36), with $p^{1/2}[N(0)V]_{\text{eff}} = 1.254$, we estimate $\zeta = 0.017\hbar\omega_c$. With $\hbar\omega_c = 0.0497$ eV, this gives $(\zeta/k) \simeq 10°$K. With $m_d = 4.31 \times 3^{2/3}m_e = 8.96m_e$, we deduce from (37) that, if $T_c = 1°$K, then $n = 2 \times 10^{13}$ cm⁻³, while, if $T_c = 0.8°$K, then $n = 10^{12}$ cm⁻³. Thus T_c drops off very slowly as n decreases.

Since the Fermi energy is positive at the transition temperature at high carrier concentrations and negative at low concentrations, at a critical concentration it will pass through zero. We solve for T_c at this concentration, and find

$$kT_c = 0.87\hbar\omega_c \left\{1 - \frac{1}{p^{1/2}[N(0)V]_{\text{eff}}}\right\}^2, \quad \zeta(T_c) = 0. \quad (39)$$

Since, for 3%-Zr-doped SrTiO₃, $p^{1/2}[N(0)V]_{\text{eff}} < 1$ until $n < 1.5 \times 10^{17}$ cm⁻³ in our model, it seems that the critical concentration must be below this value. The degeneracy temperature T_d with $n = 1.5 \times 10^{17}$ cm⁻³ and a density-of-states mass $m_d = 4.31 \times 3^{2/3}m_e = 8.96m_e$ is given by $T_d = 1.3°$K. Thus, at the critical concentration, T_c must be less than 1.3°K. Since the model gives $T_c \simeq 1°$K at $n = 2 \times 10^{13}$ cm⁻³ (or slightly less if screening effects are included), and T_c is increasing with increasing n in this region, it seems that T_c should pass through a maximum for n between about 10^{14} cm⁻³ and 10^{17} cm⁻³ on this model.

Some care is required in making a physical interpretation of the T_c obtained from a formal solution of the BCS equation at low carrier concentrations. Since, for strong interactions, the diameter of a pair will become small compared with $(\frac{1}{2}n)^{-1/3}$ for small n, the pairs may behave like indpendent Bosons in this region. Thus, it seems that the T_ϵ discussed above may represent a temperature at which pairing begins to take place, and that superconductivity will not occur until a lower temperature, of the order of the Bose-Einstein condensation temperature of the pairs, is reached.

V. DISCUSSION

A. Number of Parameters

After the rate of mass increase is fixed from the penetration-depth results, four arbitrary parameters had to be introduced in our model to explain the T_c versus n results for 0%- to 3%-Zr doping. These are (i) A_0, a composite parameter including effects of renormalization, intravalley interactions and high-frequency effects in undoped material, (ii) B_0, measuring the strength of the interaction via intervalley phonons and (iii) C, and (iv) D, measuring the rate of change of these quantities with Zr doping. Since each curve might be considered worth three parameters, except for the short 3%-Zr curve, which is only worth two, the fact that we require only four parameters rather than 11 to explain the results may indicate that our model gives a fair representation of the actual situation. If we allow more arbitrary parameters, e.g., A_q and M_q, or A_q and B_q for each percentage of Zr doping, the fits can be improved somewhat.

B. Concentration Dependence of Factors in A_q

On the whole it seems surprising that the fits we obtain are so good, since we have ignored the carrier-concentration dependence of all four contributions to A_q, viz., (i) the renormalization, (ii) the intravalley interactions below ω_c, (iii) the frequency dependence of the intervalley screening, and (iv) the high-frequency interactions. We discuss these effects below.

(i) The renormalization parameter is expected to increase with decreasing n. According to Ref. 8, Z varies between 1.66 and 1.75 over the observed range of concentrations shown in Ref. 8, and thus Z^2 varies by about 11%. The lowest concentration on the curves HJMT[1] used here are slightly smaller than those shown in Ref. 8, and so the variation of Z could be slightly greater for the case considered here.

(ii) As discussed before, our treatment of intravalley interactions below ω_c breaks down for high n, both because $\epsilon_F/\hbar\omega_c$ is not small, and because phonon frequencies start changing as the plasmon mode changes from being the lowest mode to the highest.[17] This second

effect is thought to be the more important at the high-concentration end of the curve, and could act to pull down the theoretical curves in this region.

(iii) The frequency dependence of the intervalley screening is unimportant at very low concentrations because there is no screening, and is also unimportant at high concentrations when ϵ_F becomes larger than $\hbar\omega_c$. Thus, contribution (iii) should produce maximum effects at some intermediate concentration, and may tend to sharpen to maximum in the T_c versus n curve. Using (33) we estimate that, for 0% Zr, F_q should decrease by about 8% on passing from the maximum in the T_c versus n curve to the lowest value of n on the experimental curve of Fig. 1.

(iv) Our treatment of high-frequency interactions given in Sec. IV E appears to indicate that these come closer to adding a constant amount to $N(0)V$ rather than multiplying it by a constant factor. Since, for undoped material, $N(0)V$ decreases to about 0.7 of its maximum value by the time we get to the lowest concentrations of the experimental curve according to our model, and we have included the high-frequency interactions as a multiplicative factor of about 2.5 on $N(0)V$, one would expect that underestimates of $N(0)V$ must have been made at the low-concentration end by about a factor $(0.7 \times 2.5)/(0.7 + 1.5) = 0.8$. Thus, this effect should compensate for the neglect of the concentration dependence of the renormalization and of the frequency dependence of the intervalley screening.

Hence, in general, it looks as if the fair agreement with experiment which we obtain may be in part due to a tendency for opposite errors to cancel. The use of an adjustable ratio of phonon-induced to Coulomb interaction is also a help in compensating for over-simplifications of the theory.

C. Extent of Linear Region

It will be shown in a subsequent paper that, for a transition between small and large mass states, the fraction d^2 of heavy-mass state in the ground state of the system depends on a parameter r defined as $r = (E_w - E_n)/|2U|$, where E_w and E_n are the energies of the small- and large-mass states, and U is the magnitude of the matrix element of the Hamiltonian between them. For small r, the variation is approximately linear in r, and, for Zr-doped $SrTiO_3$, we expect r to vary linearly with Zr content. Thus, the assumptions (28) to (30) of linear variations of $1/M$, A, and B with q are expected to be good in a limited concentration range only. For this reason, we have not made detailed predictions from the model of what may happen at higher Zr concentrations.

D. Alternative Model for T_c

It is possible we may have attached too much weight to the penetration-depth results. If we ignore these

results, the T_c versus n curves can be explained with other rates of mass rise. If we assume that the ratio of phonon-induced to Coulomb intervalley interactions is independent of Zr doping, and treat the masses as adjustable, we find only about 45% mass rise for 3%-Zr doping, instead of about 70% in the present model.

E. Thin Films

Zr-doped $SrTiO_3$ is of interest in connection with size effects in thin films of superconducting semiconductors,[10,27] since the thicknesses required to have a given number of quantum states occupied is proportional to $n^{1/3}$. Thus, for 3%-Zr-doped specimens, size effects may become significant at quite large thicknesses. In connection with the predictions of T_c's in thin films and whiskers in Ref. 10, it should be stated that the assumption made there, that screening does not change as one passes from 3-dimensional systems to effectively 2- or 1-dimensional systems, is not likely to be valid. The assumption was based on the use of a Lindhard model[28] for free electrons at large wave vectors. Since the energy difference between free-electron states for large wave-vector differences is large, while for electrons in different valleys the energy difference can be small, the free-electron results were misleading. It is more realistic to assume that the screening at low frequencies increases by the same amount as the density of states increases. Hence, at high carrier concentrations, much of the increase in T_c predicted in Ref. 10 would disappear. On the other hand, at very low carrier concentrations, not considered in detail in that reference, the frequency range in which there is screening is so small that the unscreened interaction would dominate, and the full effects of the density-of-states increase could be felt. Hence, it is now thought that the low-concentration region in oriented films would be the most promising for obtaining high-temperature effects.

VI. CONCLUSIONS

A model involving electron-electron interactions dominated by screened attraction via 0.0497-eV intervalley phonons has been developed to interpret experimental results on superconducting transition temperature as a function of carrier concentration and on magnetic field penetration depth in Zr-doped ceramic $SrTiO_3$. To fit the data it is required that the reciprocal of the carrier effective mass decreases by about 14% for each percent Zr addition, and that the ratio of the phonon-induced to Coulomb intervalley interactions

[27] B. A. Tavger and V. Ya. Demikhovskii, Zh. Eksperim i Teor. Fiz. 48, 748 (1965) [English transl.: Soviet Phys.—JETP 21, 494 (1965)].
[28] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fyz, Medd. 28, 8 (1954).

increases by about 5% for each percent Zr. It is argued that such mass increases may indicate crossing of a small and a large mass band as Zr is added. The model used predicts superconductivity at very low carrier concentrations in 3% Zr-doped specimens.

Grüneisen Functions for Some Type-I Superconductors

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The thermal expansion of some type-I superconductors (indium, lead, tantalum, and tin) is discussed thermodynamically in terms of Grüneisen functions, which describe the volume dependence of the entropy. The Grüneisen functions for the normal and superconducting states can be taken to differ only in their electronic components, γ^{en} and γ^{es}. Values of γ^{en} obtained from thermal-expansion measurements in the normal state are shown to be more reliable than values obtained from critical-field measurements on superconductors, because the magnetic data are not accurate enough in the limiting low-temperature region determining γ^{en}. The values of γ^{es} for the four metals all appear to be negative, unlike γ^{en}. Theoretical values of γ^{es} calculated using the BCS theory for weak coupling and the similarity principle are consistent with experiment for all the metals except lead. The disagreement for lead is probably due to its particularly strong electron-phonon coupling. According to the theory, the values of γ^{es} depend through $d\ln T_c/d \ln V$ on the volume dependence of the electron-phonon interaction, as well as on properties of the normal state. The experimental evidence for significant changes in lattice properties is discussed; such a change appears to be established for indium but not for lead.

1. INTRODUCTION

SINCE superconductivity occurs only at very low temperatures, the thermal expansion of superconductors is very small. However, experimental techniques developed in the last ten years are sufficiently sensitive to measure such small thermal expansions, and data are now available down to about 2°K for a variety of metals in both the normal and superconducting states. In this paper, we analyze and discuss measurements for some type-I superconductors.

As is usual, we discuss thermal expansion in terms of the thermodynamic *Grüneisen functions* (defined in Sec. 2). These are dimensionless parameters of the order of unity, which are often slowly varying functions of temperature, unlike the thermal expansion itself. A further advantage is that they are related to the strain dependence of the entropy, which is simpler to discuss theoretically than the thermal expansion. The strain dependence of the entropy is in turn a quantity fundamental to the discussion of the strain (and stress) dependence of thermal properties.

Since the normal-to-superconducting transition is fundamentally an electronic effect, we shall be concerned principally with Grüneisen functions for the electronic contribution to the entropy in each state. For the normal state, the electronic Grüneisen function

has been measured by two methods, magnetic and thermal expansion, but these have often given conflicting results. The origin of such discrepancies is discussed in Sec. 3. Numerical values of Grüneisen functions for the superconducting state of indium, lead, tantalum and tin are presented in Sec. 4, and the theoretical interpretation of these results is considered in Sec. 5.

2. GRÜNEISEN FUNCTIONS AND THERMAL EXPANSION

Definition of Grüneisen Functions

The volume coefficient of thermal expansion β can be expressed, using thermodynamic formulas, as[1]

$$\beta = \gamma C_\eta \chi_T / V. \tag{1}$$

Here C_η is the heat capacity at constant strain, χ_T is the isothermal compressibility, and γ is the Grüneisen function defined by

$$\gamma = (1/C_\eta)(\partial S/\partial \ln V)_T. \tag{2}$$

Equation (2) is valid for noncubic as well as cubic solids, provided that the change of volume takes place under isotropic stress.[1] In superconductors and other systems where magnetic effects are important, the quantities in Eqs. (1) and (2) depend on the magnetic conditions

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[1] T. H. K. Barron and R. W. Munn, Phil. Mag. **15**, 101 (1967).