Theory of Transitions from Large to Nearly-Small Polarons, with Application to Zr-Doped Superconducting $SrTiO_3$

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Expressions for the matrix elements of the Hamiltonian and overlap integrals between large-polaron and nearly-small-polaron states are given in terms of various large- and nearly-small-polaron parameters. The dependence of the mass of the ground state on the bare-electron mass in a region of transition between large- and nearly-small-polaron states is found. Parameters of the theory are evaluated using the continuum-polarization model of electron-phonon interactions. Modifications due to anisotropy and the presence of many longitudinal polar modes of lattice vibration are discussed briefly. Making use of a recent analysis by Reik of free-carrier optical-absorption results in $SrTiO_3$ using small-polaron theory, it is shown that the rate of mass rise deducible from superconductivity data on Zr-doped $SrTiO_3$ can be explained by the theory if the bare transverse mass m_{bt} is taken to be $m_{bt} \simeq 0.6 m_e$, where m_e is the free-electron mass, and if small-polaron binding energies are assumed to be larger by a factor of about 1.4 than their values in the continuum-polarization model. The dependence on Zr concentration of the ratio of phonon-induced to Coulomb intervalley electron-electron interactions deducible from the superconductivity data is discussed within the framework of the model.

I. INTRODUCTION

FOR electrons in interaction with acoustical phonons in semiconductors or insulators, Toyozawa[1] predicted that, when the interaction becomes greater than a certain critical strength, then the lowest state of the system of electron plus acoustical phonons suddenly changes from that of an almost-free electron to a state where the electron mass becomes nearly infinite, i.e., to a self-trapped state. For electrons interacting with optical phonons, Landau[2] introduced the concept of a self-trapped electron; and later work of Tjablikov,[3] Sewell,[4] Yamashita and Kurosawa,[5] Holstein,[6] and others[7–17] on small-polaron theory may perhaps be regarded as an elaboration of this concept. However, in large-polaron theory,[18,19] where the whole effect of the periodic potential of the rigid lattice is assumed to be to give the electron a bare effective mass different from the free-electron mass, work by Feynman[20] appeared to indicate that, for optical phonons, it was probable that a smooth variation of polaron parameters should be obtained as the interaction with the phonons passes from the weak- to the strong-coupling regime. This smooth variation was not established, however, when the effect of the periodic potential of the crystal lattice was taken into account in detail. In 1966, during work[21] on a slight modification of small-polaron theory (designated nearly-small-polaron theory), indications appeared that it was possible for the conditions of validity of weak-coupling large-polaron theory and of adiabatic nearly-small-polaron theory to hold simultaneously, and hence the lowest-energy state could undergo a sharp transition in its properties when parameters such as pressure or temperature were varied. A possible candidate for such a transition was shown to be $SrTiO_3$.

In a recent paper,[22] it was shown that an interpretation of published experimental results[23] on the superconducting transition temperature as a function of carrier concentration, and on magnetic field penetration depth in Zr-doped $SrTiO_3$, led to the conclusion that large increases in the conduction-electron effective mass were taking place as Zr ions replaced Ti, and that it was probable that such increases are associated with a

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crossing of levels associated with small and large masses as Zr is added. In this paper, it is shown that these results can be satisfactorily explained if it is assumed that the small- and large-mass states are large- and nearly-small-polaron states, respectively. Since the two types of polaron state are not orthogonal, and also have nonzero matrix elements of the Hamiltonian between them, the transition is not completely sudden, but has a width on the scale of bare-electron masses, depending on the magnitude of these matrix elements and overlap integrals. It is found that the width of the transition on this scale can be explained by the model, provided that some increases in small-polaron parameters above their values calculated in a continuum-polarization model are assumed. To explain the *position* of the transition on the bare-mass scale with the same departures from the continuum-polarization model, some additional terms in the nearly-small-polaron binding energy, not included in previous small-polaron theories, have to be postulated.

In Sec. II, overlap integrals and matrix elements of the Hamiltonian between large-polaron and adiabatic nearly-small-polaron states are obtained in terms of various sums of products of mode displacements associated with the phonons and of electron-phonon-interaction parameters. Explicit expressions for those of such sums which involve large-polaron parameters are found, using the continuum-polarization model of electron-phonon interactions. Expressions for the quantities involving adiabatic nearly small-polaron parameters only were found previously in Ref. 21.

In Sec. III, the dependence of the polaron mass on the bare mass in the transition region is given in terms of (i) matrix elements of the Hamiltonian and overlap integrals between the polaron states; (ii) changes in electron-energy overlap integrals J; and (iii) three masses m_w, m_n, and m_{wn}, which are the mass at the transition point of the pure large-polaron state, that of the nearly-small-polaron state, and an overlap mass, respectively.

In Sec. IV, the theory of the Secs. II and III is applied to Zr-doped $SrTiO_3$. First, some slight modifications are made in the theory to attempt to take into account anisotropy effects and the presence of many longitudinal polar modes of lattice vibration.[24,25] For large polarons, use is made of some recent work of Kahn[26] on anisotropy in the perturbation-theory, weak-coupling limit. Secondly, assuming that the bare masses increase by the same percentage as the Zr concentration, the bare masses and the required increase of parameters of small-polaron theory over their values in the continuum-polarization model are adjusted to give as good fits as possible to the masses in Zr-doped $SrTiO_3$ deduced from the superconductivity data, and to give agreement with nearly-small-polaron bandwidth reduction factors deducible from some work of Reik[14] on interpretation of free-carrier optical absorption[27] in $SrTiO_3$ using small-polaron theory. The bare transverse mass required to fit the data is consistent with results on an average bare mass obtained from electroreflectance results,[28] but is smaller than the value $m_{bt}=0.96m_e$ deducible from observed masses using large-polaron theory only.[26] Thirdly, an increase in the ratio of the strength of the phonon-induced to the Coulomb interaction with increasing Zr content in the model, needed to explain the superconductivity results, is interpreted as indicating that the carrier-intervalley matrix element for nearly-small polarons is larger by a factor of 1.35 than that for large polarons.

A discussion is given in Sec. V, and conclusions are stated in Sec. VI.

II. MATRIX ELEMENTS BETWEEN LARGE- AND NEARLY-SMALL-POLARON STATES

In this section, state vectors in a simple tight-binding model for weak-coupling large polarons and adiabatic nearly small polarons are written down. These two types of states are then orthogonalized for any given wave vector, and expressions for the matrix elements of the Hamiltonian between these orthogonalized states are obtained.

For simplicity, only one longitudinal polar branch of the phonon spectrum is considered, and the Hamiltonian H for one conduction-band electron in interaction with this branch is written in the usual form

$$H=H^e+H^{e-\mathrm{ph}}+H^{\mathrm{ph}}, \tag{1}$$

where H^e denotes the one-electron Hamiltonian for the rigid lattice, $H^{e-\mathrm{ph}}$ denotes the electron-phonon interaction (assumed to be linear in the phonon coordinates), and H^{ph} denotes the phonon Hamiltonian. More explicitly, we write

$$H^e=-(\hbar^2/2m_e)\nabla^2+V(\mathbf{r}), \tag{2}$$

where m_e is the free-electron mass and $V(\mathbf{r})$ is the periodic potential associated with the rigid lattice at the position $\mathbf{r}$ of the electron;

$$H^{e-\mathrm{ph}}=\sum_{\mathbf{w}} V_{\mathbf{w}}(b_{-\mathbf{w}}{}^{\dagger}+b_{\mathbf{w}})s_{\mathbf{w}}(\mathbf{r})e^{i\mathbf{w}\cdot\mathbf{r}}, \tag{3}$$

where $b_{\mathbf{w}}{}^{\dagger}$ and $b_{\mathbf{w}}$ denote the creation and annihilation operators for the phonon of wave vector $\mathbf{w}$ and angular frequency $\omega_{\mathbf{w}}$, and $s_{\mathbf{w}}(\mathbf{r})$ is a periodic function of $\mathbf{r}$ normalized to unity over unit volume, and

$$H^{\mathrm{ph}}=\sum_{\mathbf{w}} (b_{\mathbf{w}}{}^{\dagger}b_{\mathbf{w}}+\tfrac{1}{2})\hbar\omega_{\mathbf{w}}. \tag{4}$$

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If the continuum-polarization model of electron-phonon interactions is used,[18] then

$$s_{\mathbf{w}}(\mathbf{r})=1, \tag{5a}$$

and, for only one longitudinal branch of the spectrum,

$$V_{\mathbf{w}}=\pm\frac{ie}{w}\left[2\pi\left(\frac{1}{\epsilon_h}-\frac{1}{\epsilon_s}\right)\frac{\hbar\omega_{\mathbf{w}}}{V_0}\right]^{1/2}, \tag{5b}$$

where ϵ_h and ϵ_s denote the high-frequency and static dielectric constants of the material, and V_0 denotes the volume of the crystal. In much of what follows we shall not assume that (5b) holds for short-wavelength phonons, but we shall retain the assumption (5a) about $s_{\mathbf{w}}(\mathbf{r})$ throughout.

In weak- and intermediate-coupling large-polaron theory,[18] it is assumed that the lattice polarization follows the instantaneous position of the electron. Now, if a tight-binding model is used, the state vector $|W\mathbf{k}\rangle$ for a weak-coupling large-polaron state of wave vector $\mathbf{k}$ may be written[29]

$$|W\mathbf{k}\rangle=N_0^{-1/2}\sum_{\mathbf{R}}e^{i\mathbf{k}\cdot\mathbf{R}}\prod_{\mathbf{w}}N_{w\mathbf{k},\mathbf{w}}\times(1-p_{\mathbf{k},\mathbf{w}}b_{\mathbf{w}}^{\dagger}e^{-i\mathbf{w}\cdot\mathbf{R}})c^{\dagger}(\mathbf{R})|0\rangle. \tag{6}$$

Here N_0 denotes the number of unit cells in the crystal, the sum is over all lattice points $\mathbf{R}$, the product is over all phonon wave vectors $\mathbf{w}$, the ket $|0\rangle$ denotes the vacuum state, $c^{\dagger}(\mathbf{R})$ denotes the creation operator for a Wannier function localized at site $\mathbf{R}$, the quantities $p_{\mathbf{k},\mathbf{w}}$ are coefficients determined variationally, and $N_{w\mathbf{k},\mathbf{w}}$ is a normalization factor given by

$$N_{w\mathbf{k},\mathbf{w}}=(1+|p_{\mathbf{k},\mathbf{w}}|^2)^{-1/2}. \tag{7}$$

If the coupling is sufficiently weak for perturbation theory to be used, then

$$p_{\mathbf{k},\mathbf{w}}=V_{\mathbf{w}}^*/\{\hbar\omega_{\mathbf{w}}+(\hbar^2/2m_b)[(\mathbf{k}-\mathbf{w})^2-k^2]\}, \tag{8}$$

where m_b denotes the bare mass of the electron, i.e., the effective mass for the rigid lattice. For slightly stronger coupling, m_b should be replaced by the polaron mass m_p in the denominator. When dispersion of phonon frequencies is neglected, $m_p\simeq m_b(1+\frac{1}{6}\alpha)$, with the polaron coupling constant α defined by[18]

$$\alpha=\tfrac{1}{2}(e^2/r_p\hbar\omega)(1/\epsilon_h-1/\epsilon_s), \tag{9}$$

where $r_p=(\hbar/2m_b\omega)^{1/2}$ denotes the polaron radius. When explicit expressions for $p_{\mathbf{k},\mathbf{w}}$ are used in what follows, we shall ignore the correction which would be obtained by replacing m_b with m_p in the denominator of (8). Since to do this gives the result $m_p=m_b(1-\frac{1}{6}\alpha)^{-1}\simeq m_b(1+\frac{1}{6}\alpha)$, it is probably a good approximation for many purposes if α is small.

[29] Use, e.g., Eqs. (4.26) and (4.23) of Ref. 18, and then specialize to a tight-binding model.

In small-polaron theory one takes as basic building blocks states such that an electron is localized on one lattice site, and is surrounded by the polarization appropriate to such localization. Then, at low temperatures in pure crystals, one may build up running-wave linear combinations of such states to form very narrow energy bands. The narrowing arises because of the small overlap between vibrational wave functions for neighboring sites. In nearly-small-polaron theory, for the basic states the electron is not assumed to be completely localized on one lattice site, but is allowed to spread slightly to its neighbors.[21] This spreading reduces the polarization around the electron. This increases the overlap between vibrational wave functions for neighboring sites, and so reduces the mass somewhat from small-polaron values. Typical nearly-small-polaron masses may range from about 10 to 1000 times the bare-electron mass.

For a nearly-small-polaron state $|N\mathbf{k}\rangle$ of wave vector $\mathbf{k}$, provided that no localized modes of lattice vibration form around the polaron, we may use Eqs. (2.12), (2.31), (2.32), (4.3), and (4.4) of Ref. 21 to find

$$|N\mathbf{k}\rangle=N_0^{-1/2}\sum_{\mathbf{R}'}e^{i\mathbf{k}\cdot\mathbf{R}'}\prod_{\mathbf{w}}N_{n\mathbf{w}}[1-f_{\mathbf{w}}(\mathbf{R}')b_{\mathbf{w}}^{\dagger}]\times[ac^{\dagger}(\mathbf{R}')+\sum_{\mathbf{G}}b(\mathbf{G})c^{\dagger}(\mathbf{R}'+\mathbf{G})]|0\rangle. \tag{10}$$

Here the sum is over all lattice vectors $\mathbf{R}'$;

$$a=[1-z(J/F)^2]^{1/2}, \tag{11}$$

where z denotes the number of nearest-neighbor lattice sites, and

$$b=J/F, \tag{12}$$

where J is an electronic-energy overlap integral. This integral is assumed not to depend strongly on lattice displacements, and can thus be defined as

$$J=-\int\phi(\mathbf{r}-\mathbf{R})H^e\phi(\mathbf{r}-\mathbf{R}-\mathbf{G})d^3r, \tag{13}$$

where the ϕ's are the Wannier functions (assumed to be real) centered on neighboring sites $\mathbf{R}$ and $\mathbf{R}+\mathbf{G}$. The energy F is equal to 4 times the high-temperature hopping activation energy which would occur if the polarons were small rather than nearly small, and is defined by

$$F=2(B_0-C_0), \tag{14}$$

where, from Eqs. (5.11), (5.7), and (2.28) of Ref. 21,

$$B_0=\sum_{\mathbf{w}}\frac{|V_{\mathbf{w}}|^2}{\hbar\omega_{\mathbf{w}}}, \tag{15}$$

and

$$C_0=\sum_{\mathbf{w}}\frac{|V_{\mathbf{w}}|^2}{\hbar\omega_{\mathbf{w}}}e^{-i\mathbf{w}\cdot\mathbf{G}}. \tag{16}$$

Here again the summation is over all wave vectors $\mathbf{w}$. The quantities $f_{\mathbf{w}}(\mathbf{R}')$ in (10) denote mode displacements when the polaron is centered at $\mathbf{R}'$, and are given by

$$f_{\mathbf{w}}(\mathbf{R}')=d_{\mathbf{w}}e^{-i\mathbf{w}\cdot\mathbf{R}'}. \tag{17}$$

If we specialize to the case where electronic overlaps are independent of lattice coordinates and where anharmonic interactions can be ignored, then from Eqs. (2.24), (5.6), and (5.7) of Ref. 21 (noting a difference in sign convention for $V_{\mathbf{w}}$ in the present paper from that used there), we can show that

$$d_{\mathbf{w}}=\frac{V_{\mathbf{w}}^*}{\hbar\omega_{\mathbf{w}}}[1-(J/F)^2\sum_{\mathbf{G}}(1-e^{-i\mathbf{w}\cdot\mathbf{G}})]. \tag{18}$$

Finally, in (10), $N_{n\mathbf{w}}$ is a normalization factor satisfying

$$N_{n\mathbf{w}}=(1+|d_{\mathbf{w}}|^2)^{-1/2}. \tag{19}$$

The first term in the brackets in (18) represents the small-polaron result, and the second term represents a correction due to wave-function spreading. We shall see later that, for $SrTiO_3$, an average overlap energy J is of the order of 0.3 eV, while $F\simeq 1.4$ eV (taking into account increases of small-polaron quantities above their values calculated in the continuum-polarization model). Thus, with six neighbors, the correction terms can be large for short-wavelength phonons.

With the state vectors (6) and (10), we are now in a position to evaluate overlap integrals and diagonal and nondiagonal matrix elements of the Hamiltonian between large- and nearly-small-polaron states. We shall present results for these quantities only for the special case $\mathbf{k}=0$, since we shall be primarily interested in fairly low wave vectors—of the order of the Fermi wave vector, which reaches less than $\frac{1}{10}$ of the way to the edge of the zone for carrier concentrations less than about 10^{20} cm^{-3}.

First, the direct overlap integral I between such states can be shown to satisfy

$$I\equiv\langle W\mathbf{0}|N\mathbf{0}\rangle=e^{-(P+D)/2}(e^Xa+e^Yzb), \tag{20}$$

where P, D, X, and Y are defined by

$$P=\sum_{\mathbf{w}}|p_{\mathbf{w}}|^2, \tag{21a}$$

$$D=\sum_{\mathbf{w}}|d_{\mathbf{w}}|^2, \tag{21b}$$

$$X=\sum_{\mathbf{w}}p_{\mathbf{w}}^*d_{\mathbf{w}}, \tag{21c}$$

and

$$Y=\sum_{\mathbf{w}}p_{\mathbf{w}}^*d_{\mathbf{w}}e^{i\mathbf{w}\cdot\mathbf{G}}, \tag{21d}$$

where we have written $p_{0\mathbf{w}}=p_{\mathbf{w}}$. The quantities P and D thus represent the sums of squares of mode displacements associated with large and nearly-small polarons, while X and Y are sums of products and of modified products of such displacements, respectively.

Next, the expectation value of the Hamiltonian for the large-polaron state is equal to the same quantity for an electron not in interaction with phonons, minus the polaron binding energy $\alpha\hbar\omega$. Thus we have

$$\langle W\mathbf{0}|H|W\mathbf{0}\rangle=U-E_{00}-zJ-\alpha\hbar\omega, \tag{22}$$

where U is the zero-point energy of the lattice vibrations and $-E_{00}$ is the single-site expectation value of H^e, i.e.,

$$E_{00}=-\int\phi(\mathbf{r}-\mathbf{R})H^e\phi(\mathbf{r}-\mathbf{R})d^3r. \tag{23}$$

The energy of the nearly-small-polaron state at $T=0$ can be obtained from Eq. (5.14) of Ref. 21, and, with our assumption that electronic overlaps are not strongly dependent on lattice displacements, can be written

$$\langle N\mathbf{0}|H|N\mathbf{0}\rangle=U_n-E_{00}-B_0-zJ^2/F-zJe^{-S/2}. \tag{24}$$

Here we have allowed for the possibility that the zero-point vibrational energy U_n of the lattice in the presence of the polaron may be modified from its normal value U, the energy F is defined by (14), and S is a parameter associated with the bandwidth reduction by polaron effects. From (3.24), (3.25), (3.28), (3.29), and (5.7) of Ref. 21, S satisfies

$$S=\frac{F}{\hbar\omega}-2z(J/F)^2\frac{2(B_0-C_0)-2(C_0-D_0)}{\hbar\omega}. \tag{25}$$

Here B_0 and C_0 are defined in (15) and (16), and

$$D_0=\frac{1}{z}\sum_{\mathbf{w}}\sum_{\mathbf{G}'}\left(\frac{|V_{\mathbf{w}}|^2}{\hbar\omega_{\mathbf{w}}}e^{-i\mathbf{w}\cdot(\mathbf{G}+\mathbf{G}')}\right). \tag{26}$$

The matrix elements of the Hamiltonian between the large- and nearly small-polaron states require a little more patience to evaluate. Ignoring dispersion of phonon frequencies, i.e., putting $\omega_{\mathbf{w}}=\omega$ for all $\mathbf{w}$, expressions for each of the three terms in the Hamiltonian are as follows. First,

$$\langle W\mathbf{0}|H^e|N\mathbf{0}\rangle=-E_{00}I-e^{-(P+D)/2}(e^Yz Ja+e^Zz^2Jb), \tag{27}$$

where I is the overlap given by (20), P, D, and Y are given by (21), a and b are given by (11) and (12), and Z is defined by

$$Z=\frac{1}{z}\sum_{\mathbf{w}}\sum_{\mathbf{G}'}p_{\mathbf{w}}^*d_{\mathbf{w}}e^{-i\mathbf{w}\cdot(\mathbf{G}+\mathbf{G}')}; \tag{28}$$

secondly,

$$\langle W\mathbf{0}|H^{e-\mathrm{ph}}|N\mathbf{0}\rangle=-e^{-(P+D)/2}\times[e^X(B'+X'\hbar\omega)a+e^Y(C'+X'\hbar\omega)zb], \tag{29}$$

where B', C', and X' are defined by

$$B'=\sum_{\mathbf{w}}d_{\mathbf{w}}V_{\mathbf{w}},$$

$$C'=\sum_{\mathbf{w}}d_{\mathbf{w}}V_{\mathbf{w}}e^{-i\mathbf{w}\cdot\mathbf{G}}, \tag{30}$$

and

$$X'=\sum_{\mathbf{w}}\frac{p_{\mathbf{w}}V_{\mathbf{w}}}{\hbar\omega}, \tag{31}$$

and thirdly,

$$\langle W\mathbf{0}|H^P|N\mathbf{0}\rangle=IU+e^{-(P+D)/2}[e^X Xa+e^Y Yzb]\hbar\omega. \tag{32}$$

Some simplifications can be made in combining (27), (29), and (32) by making use of (18) to relate some of the quantities involved. We find from (21), (18), (15), (16), and (14) that

$$D\hbar\omega=B_0-zJ^2/F, \tag{33}$$

while B' and C' of (30) satisfy

$$B'=B_0-\tfrac{1}{2}(zJ^2/F) \tag{34}$$

and

$$C'=C_0-z(J/F)^2(C_0-D_0). \tag{35}$$

Now the quantity of most interest in the theory of transitions from large to nearly-small polarons is the matrix element U (say) of H between orthogonalized large- and nearly-small-polaron states. From (20), (27), (29), and (32)–(35), it is straightforward to show that, at the transition points where $\langle W\mathbf{0}|H|W\mathbf{0}\rangle=\langle N\mathbf{0}|H|N\mathbf{0}\rangle$, U is given by

$$\begin{aligned}U&\equiv\langle W\mathbf{0}|H|N\mathbf{0}\rangle-\tfrac{1}{2}I[\langle W\mathbf{0}|H|W\mathbf{0}\rangle+\langle N\mathbf{0}|H|N\mathbf{0}\rangle]\\&=\langle W\mathbf{0}|H|N\mathbf{0}\rangle-I\langle N\mathbf{0}|H|N\mathbf{0}\rangle\\&=-e^{Y-(P+D)/2}\{(zJa+e^{Z-Y}z^2Jb)\\&\quad+e^{X-Y}a[-\tfrac{3}{2}(zJ^2/F)+(X'-X)\hbar\omega]\\&\quad+zb[(C'-B_0)+(X'-Y)\hbar\omega-zJ^2/F]\}.\end{aligned} \tag{36}$$

This expression involves rather a lot of parameters. However, those parameters which involve large-polaron mode displacements only can be evaluated to a good approximation by use of the continuum-polarization model. Ignoring effects due to the finite cutoff in phonon wave vectors, we may show, using (5), (8), and the definitions (21), (28), and (31), that

$$2P=X=X'=\alpha, \tag{37}$$

$$Y=\alpha-\frac{2}{\pi}\int_0^\infty\frac{\sin(vG/r_p)dv}{(vG/r_p)(1+v^2)}, \tag{38}$$

and

$$Z=\alpha-\frac{2}{\pi}\frac{1}{z}\sum_{\mathbf{G}'}\int_0^\infty\frac{\sin(v|\mathbf{G}-\mathbf{G}'|/r_p)dv}{(v|\mathbf{G}-\mathbf{G}'|/r_p)(1+v^2)}. \tag{39}$$

Small-polaron parameters may also be evaluated by use of a continuum-polarization model, but, because short-wavelength phonons make the main contribution to these quantities, the model is not expected to give a good approximation for these. For completeness, however, we note that in the model, for a spherical Brillouin zone of radius w_0, we have[30]

$$B_0=(e^2w_0/\pi)(1/\epsilon_h-1/\epsilon_s), \tag{40}$$

$$C_0=B_0[\mathrm{Si}(w_0G)/w_0G], \tag{41}$$

and, for a simple cubic lattice, where $z=6$,

$$D_0=\tfrac{1}{6}B_0\left(1+\frac{4\,\mathrm{Si}(w_0G\sqrt{2})}{w_0G\sqrt{2}}+\mathrm{Si}(2w_0G)\right), \tag{42}$$

where

$$\mathrm{Si}(x)=\int_0^x\frac{\sin t}{t}dt. \tag{43}$$

The cutoff wave vector w_0 is given by $\frac{4}{3}\pi(w_0/2\pi)^3=G^3$ for the simple cubic case.

III. DEPENDENCE OF THE POLARON MASS ON THE BARE MASS IN THE TRANSITION REGION

Let us form orthogonalized states $|W'\mathbf{k}\rangle$ and $|N'\mathbf{k}\rangle$ from the large- and nearly small-polaron states $|W\mathbf{k}\rangle$ and $|N\mathbf{k}\rangle$ for any given wave vector $\mathbf{k}$ by writing

$$|W'\mathbf{k}\rangle=|W\mathbf{k}\rangle-\tfrac{1}{2}I_{\mathbf{k}}^*|N\mathbf{k}\rangle, \tag{44a}$$

and

$$|N'\mathbf{k}\rangle=|N\mathbf{k}\rangle-\tfrac{1}{2}I_{\mathbf{k}}|W\mathbf{k}\rangle, \tag{44b}$$

where $I_{\mathbf{k}}\equiv\langle W\mathbf{k}|N\mathbf{k}\rangle$ is assumed to be small. Terms of order $I_{\mathbf{k}}^2$ will be neglected throughout this section.

The quantities required for a determination of the lowest-energy linear combination $|G\mathbf{k}\rangle=c_{\mathbf{k}}|W'\mathbf{k}\rangle+d_{\mathbf{k}}|N'\mathbf{k}\rangle$ in the transition region, which we write as

$$|G\mathbf{k}\rangle=c_{\mathbf{k}}|W'\mathbf{k}\rangle+d_{\mathbf{k}}|N'\mathbf{k}\rangle, \tag{45}$$

are the energies $E_{w\mathbf{k}}'\simeq E_{w\mathbf{k}}$ and $E_{n\mathbf{k}}'\simeq E_{n\mathbf{k}}$ of $|W'\mathbf{k}\rangle$ and $|N'\mathbf{k}\rangle$, and the matrix element $U_{\mathbf{k}}$ defined by

$$\begin{aligned}U_{\mathbf{k}}&\equiv\langle W'\mathbf{k}|H|N'\mathbf{k}\rangle\\&=\langle W\mathbf{k}|H|N\mathbf{k}\rangle-\tfrac{1}{2}I_{\mathbf{k}}(E_{w\mathbf{k}}+E_{n\mathbf{k}}).\end{aligned} \tag{46}$$

Introducing a quantity $r_{\mathbf{k}}$ defined as

$$r_{\mathbf{k}}\equiv(E_{w\mathbf{k}}'-E_{n\mathbf{k}}')/|2U_{\mathbf{k}}|\simeq(E_{w\mathbf{k}}-E_{n\mathbf{k}})/|2U_{\mathbf{k}}|, \tag{47}$$

we can show, by diagonalization of the 2×2 matrix of the Hamiltonian associated with $|W'\rangle$ and $|N'\rangle$, that the coefficients $c_{\mathbf{k}}$ and $d_{\mathbf{k}}$ of (45) are given by

$$c_{\mathbf{k}}=2^{-1/2}[1-r_{\mathbf{k}}/(r_{\mathbf{k}}^2+1)^{1/2}]^{1/2} \tag{48a}$$

and

$$d_{\mathbf{k}}=2^{-1/2}[1+r_{\mathbf{k}}/(r_{\mathbf{k}}^2+1)^{1/2}]^{1/2}. \tag{48b}$$

When terms of second order in overlap integrals and energies are neglected, the mass associated with the bottom of the band formed from states such as $|G\mathbf{k}\rangle$ can be shown to satisfy

$$\begin{aligned}\frac{1}{m}=\frac{c_{\mathbf{0}}^2}{m_w}+\frac{d_{\mathbf{0}}^2}{m_n}+\frac{2c_{\mathbf{0}}d_{\mathbf{0}}}{m_{wn}}+\hbar^{-2}\left(\frac{d^2c_{\mathbf{k}}^2}{dk^2}\right)_{\mathbf{k}=0}(E_{w\mathbf{0}}-E_{n\mathbf{0}})\\+\hbar^{-2}\left(\frac{d^2}{dk^2}(2c_{\mathbf{k}}d_{\mathbf{k}})\right)_{\mathbf{k}=0}U_{\mathbf{0}}.\end{aligned} \tag{49}$$

Here m_{wn} is a mixing mass given by

$$m_{wn}=\hbar^2/(2J_{wn}G^2), \tag{50}$$

[30] See Eqs. (5.11) and (5.12) of Ref. 21.

where G is the lattice constant and J_{wn} is a mixing overlap energy satisfying

$$2zJ_{wn}=U_{\mathbf{k}_c}-U_0, \tag{51}$$

$\mathbf{k}_c$ denoting the wave vector associated with the top of the band.

For small wave vectors we can write

$$E_{w\mathbf{k}}-E_{n\mathbf{k}}\simeq(E_{w0}-E_{n0})(1+Ak^2/r_0), \tag{52}$$

where

$$A\equiv(\hbar^2/2m_w-\hbar^2/2m_n)/|U_0|. \tag{53}$$

Also, we expect that

$$U_{\mathbf{k}}=U_0(1+A'k^2), \tag{54}$$

where A' is a constant which satisfies $|A'k^2|\lesssim 1$ for all k. Since we are interested in cases where $E_{w0}-E_{n0}$ is small, then for large $\mathbf{k}$ the second term in (52), being of magnitude of the order of the bandwidth of the wide band, will be much larger than the first. Thus it is probable that

$$A/r_0\gg A'. \tag{55}$$

Hence, from (47), (52), (54), and (55) we deduce that

$$r_{\mathbf{k}}\simeq r_0+Ak^2, \tag{56}$$

and, using (48), that

$$\begin{aligned}-\hbar^{-2}\left(\frac{d^2c^2}{dk^2}\right)_{\mathbf{k}=0}(E_{w0}-E_{n0})&=\hbar^{-2}\left(\frac{d^2}{dk^2}(2c_{\mathbf{k}}d_{\mathbf{k}})\right)_{\mathbf{k}=0}U_0\\&=\left(\frac{1}{2m_w}-\frac{1}{2m_n}\right)\frac{r_0}{(1+r_0^2)^{3/2}}.\end{aligned} \tag{57}$$

Thus the last two terms in (49) cancel, and we are left with

$$1/m=c_0^2/m_w+d_0^2/m_n+2c_0d_0/m_{wn}. \tag{58}$$

From standard intermediate-coupling polaron theory[18] we have

$$m_w\simeq m_b(1+\tfrac{1}{6}\alpha), \tag{59}$$

where m_b is the bare mass and α is the coupling constant given by (9), while nearly-small-polaron theory[21] gives

$$m_n=m_be^{S/2}, \tag{60}$$

with S given by (25).

To obtain the mixing mass m_{wn}, we have to evaluate matrix elements of the Hamiltonian between wide- and narrow-band states of nonzero wave vector. We took a wave vector $\mathbf{k}_c=(\pi/G,\pi/G,\pi/G)$ at the corner of the zone for a simple cubic lattice, where G is the lattice constant, and found that the term proportional to zJa in (27) changed sign, and so did the terms involving b in (29) and (32), while the other terms in $\langle W\mathbf{k}_c|H|N\mathbf{k}_c\rangle$ remained the same as in $\langle W\mathbf{0}|H|N\mathbf{0}\rangle$.

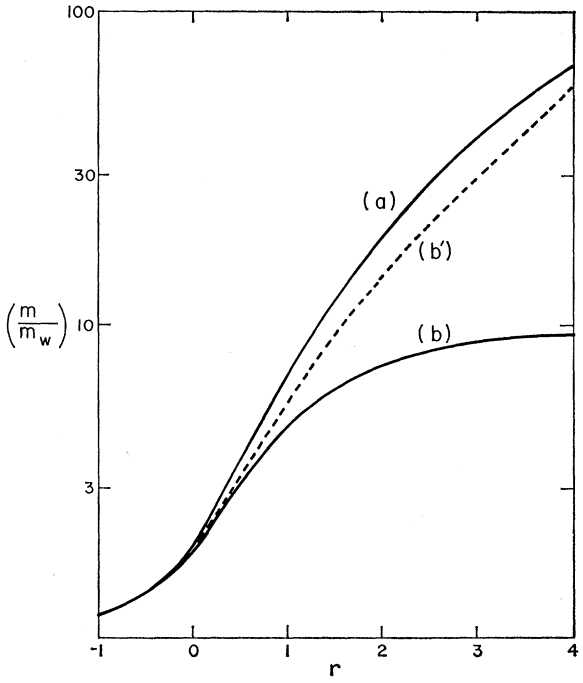

FIG. 1. Mass of the lowest-energy state for a transition between a state of low mass m_w to a state of high mass m_n as a function of the parameter r, defined as the difference in energy between low- and high-mass states divided by twice the magnitude of the matrix element of the Hamiltonian between them. Curve (a) is for the case when the high mass m_n and the mixing mass m_{wn} are infinite, and curve (b) is for the ratios $m_n/m_w=10.2$ and $m_{wn}/m_w=-47$. The values for curve (b) are appropriate for a transition between large- and nearly-small-polaron states in $SrTiO_3$. The dashed curve (b') includes corrections due to the expected dependence of m_n on bare mass for Zr-doped $SrTiO_3$.

In the expression for $I_{\mathbf{k}_c}$, the overlap integral for a wave vector at the corner of the zone, we find that the first term in (20) remains the same as for $\mathbf{k}=\mathbf{0}$, but the second changes sign. Hence, assuming $E_{w0}\simeq E_{n0}$, and using (27), (29), (32), (20), (22), (24), (46), (50), and (51), we can show that

$$\begin{aligned}m_b/m_{wn}&=e^{Y-(D+P)/2}\{a+F^{-1}[(X'-Y)\hbar\omega+C'-zJ-\alpha\hbar\omega]\\&\quad-\tfrac{1}{2}(ae^{X-Y}-zb)(m_b/m_w+m_b/m_n)\}.\end{aligned} \tag{61}$$

Plots of m against r are shown in Fig. 1 for two cases: (a) with $m_w=m_{wn}=\infty$ and (b) with $m_n/m_w=10.2$ and $m_{wn}/m_w=-47$. The figures for case (b) will be shown in Sec. IV to be suitable for a transition from a large- to a nearly-small-polaron state in $SrTiO_3$. Also shown on the figure as a dashed curve (b') is the expected modification of case (b) for Zr-doped $SrTiO_3$ when the increase of the nearly-small-polaron mass with increasing bare mass is included. For $SrTiO_3$ we should interpret r as involving quantities at the wave vector corresponding to the minimum in energy of the conduction band, rather than at zero wave vector.

The energy difference E_w-E_n between the two types

of polaron state may be obtained from (22) and (24) as

$$E_w-E_n=-\alpha\hbar\omega+(U-U_n)+B_0+zJ^2/F -zJ(1-e^{-S/2}). \quad (62)$$

Here $\alpha\hbar\omega$ is the large-polaron binding energy, and the remaining terms represent the nearly-small-polaron binding energy. The quantity $U-U_n$ is the decrease in zero-point energy of the lattice vibrations due to the presence of the polaron.

If we suppose that the bare mass is increased by a small fraction ϵ from its value at the transition point, then the overlap integral is decreased from its critical value J_c to $J_c(1-\epsilon)$. Remembering that $\alpha\propto J^{-1/2}$, we find from (62) and the expression (25) for S that

$$E_w-E_n\simeq\epsilon\Big[zJ_c(1-e^{-S/2}) +zJ_ce^{-S/2}\frac{2zJ_c^2}{F\hbar\omega}\Big(1-\frac{2(C_0-D_0)}{F}\Big) -\tfrac{1}{2}\alpha_c\hbar\omega-2\frac{zJ_c^2}{F}\Big], \quad (63)$$

where α_c denotes the critical value of α. In deriving (63), for want of better knowledge, we have assumed that the zero-point energy difference $U-U_n$ is not sensitive to small changes in J.

The two positive terms in (63) are the largest, and so E_w-E_n increases with increasing bare mass, as we expect. In Fig. 2, E_w and E_n are shown as functions of the bare transverse mass m_{bt} for values of the parameters appropriate to Zr-doped $SrTiO_3$ (see Sec. IV). Also shown in the figure as dotted lines are the energies E_g of the ground state $|G\rangle=c|W\rangle+d|N\rangle$ and E_e of the excited state $|E\rangle=d|W\rangle-c|N\rangle$ in the transition region. The energy difference ΔE between the ground and excited states in this transition region can be shown to satisfy

$$\Delta E=2|U|(1+r^2)^{1/2}. \quad (64)$$

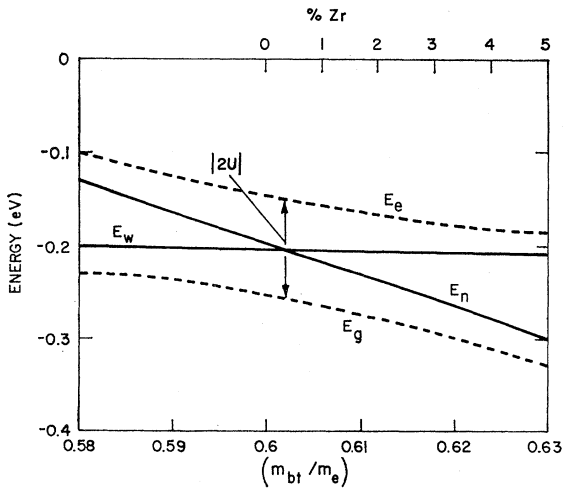

FIG. 2. Plot of the large- and nearly-small-polaron energies E_w and E_n as a function of the bare transverse mass m_{bt} in $SrTiO_3$ in the transition region. Also shown as dashed curves are the energies of the ground and excited mixed states.

IV. APPLICATION TO Zr-DOPED $SrTiO_3$

As mentioned in the Introduction, results on superconductivity[23] in Zr-doped $SrTiO_3$ can be interpreted[22] as implying large conduction-band mass increases as Zr replaces Ti, and these mass increases may be associated with transitions between large- and nearly-small-polaron states as discussed in Secs. II and III. However, before applying the theory of these sections to $SrTiO_3$, we have to modify the theory slightly to take into account effects due to anisotropy of the masses[31,26] and complications due to the presence of many longitudinal polar branches of the phonon spectrum in this material.[32,25] These modifications are considered in Sec. IV A. Then, in Sec. IV B, an interpretation of conduction-band masses deduced[22] from superconductivity data[23] is given in terms of the theory of polaron transitions, use being made of some results due to Reik[14] on interpretation of free-carrier absorption results in $SrTiO_3$, on the basis of small-polaron theory. In Sec. IV C an attempt is made, also on the basis of the theory of polaron transitions, to interpret the dependence of the density-of-states interaction product of superconductivity theory on Zr concentration.

A. Effects of Anisotropy and of Many Modes

The effects of anisotropy in nearly small-polaron theory in $SrTiO_3$ will be treated in a very simple way.

Above 108°K, $SrTiO_3$ has a cubic perovskite structure,[33] i.e., it consists of five simple-cubic sublattices, one each of Ti and Sr and three of O. The unit cell is a cube with a titanium ion at the center, oxygens at the centers of the faces, and strontiums at the corners. Below 108°K there is a slight distortion to a tetragonal structure,[33] but this distortion is sufficiently small to be ignored for many purposes. If the distortion is ignored, the side of the cell[34] at 1°K is 3.899 Å. The conduction band of the material[35,31] is thought to consist of ellipsoids at the edges of the zone in [100] directions, with[31] longitudinal masses four times as large as transverse masses, and an average mass m per ellipsoid given by $m=2.5m_e$. The wave functions are composed

[31] H. P. R. Frederikse, W. R. Hosler, and W. R. Thurber, J. Phys. Soc. Japan Suppl. **21**, 32 (1966); H. P. R. Frederikse, W. R. Hosler, W. R. Thurber, J. Babiskin, and P. G. Siebenmann. Phys. Rev. **158**, 775 (1967); H. P. R. Frederikse and G. A. Candela, *ibid.* **147**, 583 (1966).

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

[33] R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963).

[34] F. T. Lytle, J. Appl. Phys. **35**, 2212 (1964).

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

mainly of Ti-ion orbitals, and bandwidths are determined by indirect overlaps via oxygen ions.[35] We shall ignore complications due to the existence of indirect overlaps. Also, as far as nearly-small-polaron theory is concerned, noting that each Ti ion has six nearest neighbors, we shall suppose that all effects of anisotropy may be treated by making the replacements

$$\begin{aligned} zJ &\rightarrow 4J_t+2J_l, \\ zJ^2 &\rightarrow 4J_t^2+2J_l^2 \end{aligned} \tag{65}$$

whenever these expressions occur in the theory of Secs. II and III. The quantities J_t and J_l are effective overlap energies, related to the bare transverse and longitudinal masses m_{bt} and m_{bl} by $J_{t(l)}=\hbar^2/(2m_{bt(l)}G^2)$, where G is the lattice constant.

The procedure (65) appears to be justifiable for all quantities except those involving the parameters D_0 of (26) or Z of (28). These parameters should be replaced by quantities depending slightly on the direction of the lattice vector $\mathbf{G}$ in a more sophisticated theory. However, at least as far as its effect on the parameter S is concerned (S is related to the polaron mass m_n by $m_n=m_be^{S/2}$, where m_b is the bare mass), the term involving C_0-D_0 in (25) represents a small correction, and so neglect of small anisotropies in D_0 should not be too serious. Thus we shall assume that the ratio m_n/m_b is independent of direction.

Effects of anisotropy on weak-coupling large-polaron theory have been considered by Kahn.[26] With an anisotropy constant K defined as the ratio of longitudinal to transverse mass, it is found that, for $SrTiO_3$, to fit the observed masses by weak-coupling large-polaron theory requires a bare transverse mass $m_{bt}\simeq 0.96m_e$ and a bare-mass anisotropy, which we call K_b, given by $K_b=4.9$. In our theory, since we are supposing that part of the increase in observed mass over the bare mass is due to the presence of some admixture of nearly-small-polaron state to the ground state, we shall need smaller bare masses to fit the observed masses. Since, in weak-coupling large-polaron theory, the mass corrections due to polaron effects are proportional to the square root of the bare mass, we shall make the approximation that the anisotropy differences between the bare and large-polaron masses ΔK (say) satisfy $\Delta K \propto m_{bt}^{1/2}$. Further, we shall suppose to a first approximation that the ground-state mass given by (58) is approximately equal to c^2/m_w. Thus, the anisotropy of the large-polaron masses will be equal to the observed anisotropy of 4. Hence, using Kahn's results that $K_b=4.9$ when $m_{bt}=0.96m_e$, we shall assume

$$K_b=4+0.9(m_{bt}/0.96)^{1/2}. \tag{66}$$

We shall also make use of Kahn's result for the large-polaron binding energy E_{wb}, which we write as

$$E_{wb}=\alpha_e\hbar\omega(m_{bl}/m_e)^{1/2}(K_b-1)^{-1/2} \times\sin^{-1}[(K_b-1)/K_b]^{1/2}, \tag{67}$$

where α_e is the polaron coupling constant which would exist if the bare-electron mass were equal to the free-electron mass, and m_b is the bare longitudinal mass. We shall define an effective polaron coupling constant α by $\alpha=E_{wb}/\hbar\omega$.

With three longitudinal polar modes present as in $SrTiO_3$, experimental results on infrared reflectivity data[32,27] may be used[25] to deduce mode frequencies and polaron coupling constants[24] with each of these modes. In $SrTiO_3$ at 85°K the longitudinal-mode phonon energies $\hbar\omega_i$ and polaron coupling constants α_i are given[25] by $\hbar\omega_1=0.021$ eV, $\hbar\omega_2=0.058$ eV, $\hbar\omega_3=0.099$ eV, $\alpha_1=0.007(m_b/m_e)^{1/2}$, $\alpha_2=0.56(m_b/m_e)^{1/2}$, and $\alpha_3=1.83(m_b/m_e)^{1/2}$. We shall assume that the polaron properties in which we are interested may be obtained by use of a model where all the coupling is considered to be with a single mode whose frequency ω is a weighted average frequency defined by

$$\omega=\sum_i \alpha_i\omega_i/\sum_i \alpha_i, \tag{68}$$

and shall suppose that α_e in the expression (67) for E_{wb} satisfies $\alpha_e=2.40$.

B. Input Data and Calculations to Determine Masses

In Ref. 22, an analysis was made of experimental results[23] on the magnetic field penetration depth and the transition temperature T_c as a function of carrier concentration n in superconducting $SrTiO_3$ with some Ti ions replaced by Zr. A BCS-like model[36] modified for small Fermi energies[37] with a cutoff energy[38,39] of 0.0497 eV was used, with a form of density-of-states interaction product suitable for screened interaction via intervalley phonons modified by intervalley Coulomb repulsion, by intravalley interactions, and by high-frequency Coulomb effects. It was shown that the results for 0–3% Zr addition could be explained if it was assumed that the average carrier effective mass m_q in one valley for q% Zr-doped specimens satisfied

$$2.5/m_q=1-0.14q, \tag{69}$$

and if the ratio of unscreened phonon-induced to Coulomb intervalley interactions increased by about 5% for each percent Zr doping. To fit the results it was also required that a parameter A_q, a complex object

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

[37] D. M. Eagles, Phys. Rev. **164**, 489 (1967). See the discussion section of Ref. 22 for some comments on the parts of this paper which deal specifically with predictions of transition temperatures in films or whiskers.

[38] C. S. Koonce, M. L. Cohen, J. F. Schooley, W. R. Hosler, and E. R. Pfeiffer, Phys. Rev. **163**, 380 (1967). The energy 0.0497 eV was shown in this paper to be that of the intervalley phonons which can cause interactions between conduction-band states at the bottoms of different valleys, if the symmetries of these states and of the phonons are as given in Refs. 35 and 39, respectively. Slight departures from the cubic phase at low temperatures were ignored.

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

containing effects due to renormalization, intravalley interactions, frequency dependence of screening, and high-frequency Coulomb repulsion, should change in such a way that A_q/m_q^2 would increase by 26% for each percent Zr addition. In this subsection, we shall show that the mass changes given by (69) can be explained by polaron theory. The results on the ratio of phonon-induced to Coulomb intervalley interactions will be discussed in Sec. IV C.

Another piece of input data to put in our theory may be obtained from an analysis of infrared free-carrier absorption results by Reik,[14] who shows that the mean number of phonons participating in infrared absorption by small polarons is 5.3. For small polarons, this quantity can be identified with the quantity S of (25), which is related to the polaron mass by (50). We assume that this identification can be made for nearly-small polarons, i.e., we suppose that

$$S=5.3. \tag{70}$$

On the basis of a simple tight-binding model with simple direct overlaps, it can be shown[22] that, if conduction electrons based on the Ti ions keep off substituted Zr ions entirely, then a q% Zr addition will give a q% increase in bare-electron mass. This is likely to represent the most drastic effect of Zr ions, and so it seems safe to say that the bare mass m_q for q% Zr doping satisfies

$$m_{bq}/m_{b0}=1+\gamma q/100, \tag{71}$$

where $\gamma \leqslant 1$. We shall assume that $\gamma=1$ in the remainder of this section.

Our procedure in trying to fit the input data (69) and (70) is as follows. First we assume an arbitrary increase of all small-polaron parameters B_0, C_0, D_0, and F by factors which we denote by $1+Q$ over their values calculated in a continuum-polarization model, and assume arbitrary bare transverse masses m_{bt}. We determine the anisotropy of the bare masses by use of (66), and then use (25), (65), the value $S=5.3$ from (70), and other results of Secs. II and IV A to determine Q as a function of m_{bt}. For a given m_{bt} and corresponding value of Q, we then use (36) and (65), with large-polaron quantities calculated in the continuum-polarization model, to determine the matrix elements U of the Hamiltonian between orthogonalized wide- and narrow-band states. Next, (63) and (71) (with $\gamma=1$) are used to determine the parameter β in the relation

$$r=r_0+\beta q, \tag{72}$$

where r is the parameter defined in (47) (we drop the suffix $\mathbf{k}$ for convenience) and r_0 its value for no Zr addition. Further, r_0 may be determined, for a given bare mass, by (58), (48), (60), (61), (66), (67), and graphical results in Ref. 26 for the dependence of large-polaron masses on anisotropy K, together with the conditions that the observed[31] average mass m_0 in $SrTiO_3$ without Zr satisfies $m_0=2.5m_e$ and the anisotropy $K=4$. Hence, by use of (72) and the results of Sec. III, we can determine the masses m_0, m_1, m_2, and m_3 from our theory [using a value for m_w/m_b averaged over directions in (58)], and we adjust the bare mass until approximately the correct rate of increase of the polaron mass with Zr content is obtained. Besides the values of the lattice constant $G=3.899$ Å, of the mean phonon frequency given by $\hbar\omega=0.089$ eV, and of an effective polaron coupling constant given by $\alpha=E_{wb}/\hbar\omega$, with $\alpha_e=2.40$ in (57) as discussed in Sec. IV A, we shall make use of a value $\epsilon_h=5.2$ for the high-frequency dielectric constant, and will assume that ϵ_s is sufficiently large that ϵ_s^{-1} can be neglected at low temperatures in expressions such as (40) for B_0.

By a procedure such as described above, we find, with $m_{bt}=0.6m_e$, which value implies that $1+Q=1.42$, that we can obtain

$$m_0^{-1}:m_1^{-1}:m_2^{-1}:m_3^{-1}=1:0.85:0.72:0.60,$$

i.e., roughly the required 14% decrease of m_q^{-1} with each percent Zr concentration. With these values of m_{bt} and $1+Q$, with $G=3.899$ Å, and with $\hbar\omega$ and $\alpha=E_{wb}/\hbar\omega$ as given in Sec. IV A, the values of other parameters occurring in the theory are $r_0=-0.06$, $w_0=1.00\times10^8$ cm^{-1}, $K_b=4.7$, $J_t=0.42$ eV, $J_l=0.089$ eV, $E_{wb}=0.20$ eV, $X=X'=2.29$, $Y=1.72$, $Z=1.63$, $P=0.57$, $B_0=1.26$ eV, $C_0=0.57$ eV, $D_0=0.47$ eV, $F=1.37$ eV, $a=0.79$, $D=4.12$, $I=0.14$, $\mathrm{av}(m_w/m_b)=1.38$, $m_n/m_b=14.2$, and $\mathrm{av}(m_{wn}/m_w)=-47$. The prefactor $e^{Y-(P+D)/2}$ of (36) is equal to 0.0516, while the three terms in the postfactor are equal to 3.74, -1.08, and -1.61 eV, respectively, and $|2U|=0.107$ eV. Equation (63) gives $E_w-E_n=1.88\epsilon$ eV, and so β of (72) is given by $\beta=0.18$. The values of $r_q=(E_w-E_n)/|2U|$, c_q^2, d_q^2 (the fractions of large- and nearly-small-polaron states in the ground state), and the mass ratios m_q/m_w and m_q/m_e at q% Zr for $q=0$–3 are shown in Table I. Also shown in the table are the energy differences between the ground and excited states as given by (64). Since $d_0^2=0.47$, we notice that, even for no Zr addition, the nearly-small-polaron state gives an important contribution to the ground state.

TABLE I. Parameters associated with the theory of polaron transitions in $SrTiO_3$ with q% of Ti ions replaced by Zr. Values of most quantities occurring in the theory are given in Sec. IV B.

Quantity	Definition or defining equation	Values for various Zr concentrations			
q	[% Zr]	0	1	2	3
r	(47)	−0.06	0.12	0.30	0.48
c_q^2	(48a)	0.53	0.44	0.36	0.28
d_q^2	(48b)	0.47	0.56	0.64	0.72
m_q/m_w	(58)	1.80	2.11	2.51	2.99
m_q/m_e	(58) and (59)	2.50	2.93	3.49	4.16
ΔE_q (eV)	(64)	0.107	0.108	0.112	0.119
m_q/m_e	Fig. 1(b′)	2.50	2.96	3.59	4.39

The dependence of the mass on r in the transition region is shown in curve (b) of Fig. 1. However, the nearly-small-polaron mass $m_n=m_b e^{S/2}$ is quite sensitive to small changes in the bare mass through changes in the second term of (25) with changing bare mass. Using the figures quoted above, we may write $S=15.4-10(m_{b0}/m_b)^2$, where m_{b0} denotes the bare mass for no Zr doping. The dashed curve (b') indicates the form of mass rise expected when the variation of m_n with m_b is taken into account. We see that large changes occur for large values of r. In the range of particular interest to us, viz., $-0.06\leqslant r\leqslant 0.48$, the effect of the change is to make the variation of reciprocal mass with r closer to linear, as assumed originally. The values of m_q/m_e for $q=0$–3 including these corrections are shown in the last line of Table I. Small further changes due to dependence of m_{wn} on bare mass have not been included. For values shown in the last line of Table I, we have $m_3/m_1=1.48$, as required to fit the penetration depth results.

The rate of rise of polaron mass with Zr addition is quite sensitive to changes in the bare mass, since the exponential term in (36) and some of the terms in (63) are sensitive to small changes of the parameter Q, which in turn varies quite rapidly with changes in the bare mass. To illustrate, if we take $m_{bt}=0.5m_e$, then $1+Q=1.65$ and $m_3/m_0=2.2$, compared with $1+Q=1.42$ and $m_3/m_0=1.7$ with $m_{bt}=0.6m_e$.

The transverse bare mass $m_{bt}=0.6m_e$ may be compared with an estimate by Zook[28] of an average bare mass $m_{ba}=(0.73\pm0.1)m_e$ from electroreflectance data. Since the free-carrier contribution to the refractive index is proportional to m^{-1}, it is probable that $m_{ba}^{-1}=\frac{1}{3}(2m_{bt}^{-1}+m_{bl}^{-1})$. Hence, taking $m_{bl}/m_{bt}=4.7$, we deduce that $m_{bt}=(0.54\pm0.07)m_e$. Thus, the value $m_{bt}=0.6m_e$ lies within the required range.

C. Change of Ratio of Phonon-Induced to Coulomb Intervalley Interactions

As mentioned in Sec. IV B, in order to fit the superconductivity data, an increase of the ratio of phonon-induced to Coulomb intervalley interactions by about 5% for each percent Zr addition was required. In this subsection, we use this rate of increase to deduce the ratio g of the magnitudes of intervalley polaron-phonon matrix elements for nearly-small- and large-polaron states.

For mixed large- and nearly-small-polaron states $|G\rangle=c|W\rangle+d|N\rangle$, as discussed in Sec. III, phonon-induced interactions can take place via either the ground states or the excited states $|E\rangle=d|W\rangle-c|N\rangle$. However, the energy denominators for interactions via the excited states are increased by factors $1+\Delta E_q/\hbar\omega_c$ for carriers of equal energy, where the energy differences ΔE_q, between ground and excited states are given by (64) with $r=r_q$, and are shown in Table I. Thus we expect that the strength V_{pq} of the phonon-induced interaction should satisfy

$$V_{pq}=\frac{2|\langle G_q,0|H|G_q,1\rangle|^2}{\hbar\omega_c}+\frac{2|\langle G_q,0|H|E_q,1\rangle|^2}{\hbar\omega_c+\Delta E_q}, \quad (73)$$

where $\hbar\omega_c$ is the relevant phonon energy, and the numbers 0 and 1 inside the state-vector brackets denote the absence or presence of an intervalley phonon. If the matrix elements of the intervalley electron-phonon interactions are increased by a factor g for nearly small polarons over those for large polarons, and overlap matrix elements are ignored, then we can deduce that

$$V_{pq}\propto c_q^2+g^2d_q^2-c_q^2d_q^2(g-1)^2 \times[1-1/(1+\Delta E_q/\hbar\omega_c)]. \quad (74)$$

We want V_{pq} to increase by about 15% as q changes from 0 to 3. Using values of c_q^2, d_q^2, and ΔE_q from Table I, together with $\hbar\omega_c=0.0497$ eV, we find that this will occur if $g=1.35$, and that the change in V_{pq} is linear to a first approximation.

V. DISCUSSION

We saw in Sec. IV that, by use of the theory of transitions between large- and nearly-small-polaron states, we can explain the rate of rise of carrier mass with Zr concentration in Zr-doped $SrTiO_3$ as determined from analysis[22] of superconductivity data,[23] provided that we assume a bare transverse mass $m_{bt}=0.6m_e$. This value of the mass is consistent with some results of Zook[28] on the bare mass, deduced from electroreflectance results. An increase of small-polaron binding energies by a factor 1.42 above their values calculated in a continuum-polarization model is used in the theory. However, this factor of 1.42 is not introduced as an arbitrary parameter, but is determined, for a given bare mass, from work of Reik[14] on interpretation of infrared absorption results using small-polaron theory. Besides explaining the mass increases, we can also interpret the rate of increase in strength of intervalley phonon-induced interactions with Zr content as implying that polaron-intervalley phonon matrix elements are greater by a factor 1.35 for nearly small polarons than for large polarons.

On the whole it seems that to be able to interpret the rate of mass rise using a bare mass within the range determined from experiment and using no adjustable parameters gives a strong indication that the basic concept of the occurrence of a transition between polaron states in Zr-doped $SrTiO_3$ is correct. If not, there would be no reason, except coincidence, to explain why the rate of rise of mass from such a theory should lie even within an order of magnitude of the observed one. However, there are a number of points arising in connection with the theory which are not fully cleared up. Some of these are discussed in (a)–(d) below.

A. Some Difficulties

(a) The parameter $1+Q=1.42$, the factor by which small-polaron energies are increased above their values calculated on a continuum-polarization model, has not been determined from first principles, but was introduced to ensure consistency with Reik's results.[14] However, the fact that $Q\neq 0$ is not surprising in view of the importance of short-wavelength modes in determining small-polaron properties. We may note that, if we accept an estimate[38] for the intervalley high-frequency dielectric constant $\epsilon_h^{(er)}=2$, then a modified continuum-polarization model with this dielectric constant would give an increase of small-polaron binding energies by a factor

$$\frac{1/\epsilon_h^{(er)}-1/\epsilon_s^{(er)}}{1/\epsilon_h-1/\epsilon_s}\approx\frac{\epsilon_h}{\epsilon_h^{(er)}}=2.6.$$

Since it seems likely that there will be a monotonic decrease of ϵ_h as the wave vector moves from the origin to the edge of the zone, a model involving use of the dielectric constant at whatever wave vector is concerned would give $1<1+Q<2.6$, in agreement with our value $1+Q=1.42$.

In principle, another effect which could produce increases in binding energies for a given interaction strength is a decrease of phonon frequencies around the polaron. If the electron-phonon interaction is written as an interaction parameter multiplied by a mode coordinate measuring atomic displacements as in Ref. 6 (rather than as a factor $V_{\mathbf{w}}$ multiplying creation and annihilation operators for phonons as in this paper), then we find[40] that, with a fixed interaction parameter, energies such as the small-polaron binding energy in the limit of zero overlap B_0, change by a factor of x^{-2} for a frequency change by a factor of x. However, Reik's estimate[14] of the phonon energies significant in absorption by small polarons in $SrTiO_3$ gives $\hbar\omega=0.088$ eV, in fair agreement with our calculated value of $\hbar\omega=0.089$ eV, and so it seems that, at least for the phonons of significance for the optical properties, frequency changes are small.

(b) A second difficulty with the theory is that, according to (62), modified for anisotropy effects according to (65) and (67), with values of the parameters concerned given in Sec. IV B, we find that, to make $E_w=E_n$ at the transition point, we require that the decrease $U-U_n$ in zero-point energy of the lattice vibrations due to the presence of the nearly small polaron has to have the fairly large value of 0.14 eV. In large-polaron theory, there is an increase in binding energy in a strong-coupling theory[41] by an amount ΔE_p satisfying

$$(3\ln 2+\tfrac{3}{4})\hbar\omega<\Delta E_p<(6\ln 2)\hbar\omega, \tag{75}$$

which would be more than enough to explain the discrepancy. We would expect a smaller effect for nearly-small-polaron theory, but how much smaller is difficult to estimate. In view of the approximate agreement of Reik's estimate of phonon energies contributing to optical absorption by small polarons in $SrTiO_3$ with our calculated mean phonon energy, it seems that, to obtain $U-U_n=0.14$ eV, we would have either to invoke a small frequency change in a very large number of modes or to suppose that some modes other than those significant for the optical absorption process have their frequencies shifted significantly. Possibly shifts may occur for some modes with odd parity about the center of the polaron, for which modes only interactions quadratic in the normal coordinates can occur.

(c) The conditions of validity of adiabatic nearly small-polaron theory as stated in Ref. 21 are

$$z^{-1}(\tfrac{1}{2}W_r/E_b)^2\ll 1, \tag{76}$$

$$2J>\hbar\tilde{\omega}, \tag{77}$$

and

$$W\ll\hbar\tilde{\omega}, \tag{78}$$

where z is the number of neighbors, W_r is the rigid-lattice bandwidth, E_b is the small-polaron binding energy in the limit when the electronic energy overlap $J=0$, W is the polaron bandwidth, and ω is the mean phonon frequency of phonons contributing to the small-polaron binding. For our model, $z=6$, $\frac{1}{2}W_r=4J_t+2J_l=1.85$ eV, and $E_b(=B_0)=1.26$ eV. Thus, condition (76) is not well satisfied, but at least the left-hand side is less than 1. Since $2J_t>2J_l=0.18$ eV and $\hbar\omega=0.089$ eV, Eq. (77) is valid. The third condition is a requirement for the theory to apply for all wave vectors. Since, for nearly-small polarons in $SrTiO_3$, $W=3.7e^{-2.65}$ eV $=0.26$ eV>0.089 eV, condition (78) is not fulfilled. Thus our theory will not hold for polarons of all wave vectors, but only for those such that the energy is comfortably below 0.089 eV. Since the cutoff of interest for superconductivity[38] is 0.0497 eV, this does not appear to be a major difficulty in the applications of the theory that we have made in this paper.

(d) The model to explain the superconductivity results from which we obtained the raw material to fit by the polaron theory is somewhat oversimplified. The model was discussed in more detail in Ref. 22, and so we shall not repeat this discussion here. The main shortcomings of the theory of that reference was that no detailed explanation was developed for the magnitude of the parameters A_q introduced as multiplicative factors in the effective density-of-states interaction product $[N(0)V]_{\text{eff}}$ for $q\%$ Zr-doped material by

$$[N(0)V]_{\text{eff}}=A_q\lambda_q, \tag{79}$$

[40] See Eq. (46) of the first part of Ref. 6.

[41] G. R. Allcock, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1963), p. 45.

where λ_q denotes the $N(0)V$ due to low-frequency intervalley interactions. In order to explain the way in which A_q varied with Zr concentration on the assumption that the mass increases were due to polaron effects, it looked as if one would have to postulate that the renormalization parameter Z_q of superconductivity theory increased more slowly than linearly with increasing polaron mass. To determine whether this result is plausible when nearly-small polarons are involved would seem to require an attempt at a sophisticated theory of superconductivity including renormalization for polarons in a strong-coupling regime. This is likely to be a very difficult problem. Even for weak coupling, the theory is not simple for small Fermi energies.[42]

B. Predictions of the Theory

As far as present experimental results are concerned, the main achievements of the theory developed here are that (a) it explains the rate of rise of carrier mass in Zr-doped $SrTiO_3$ deduced from the superconductivity data and (b) provides a way of reconciling the facts that free-carrier absorption results are best explained[14] by small-polaron theory, while observed carrier masses[31] are closer to those expected for large polarons. However, there are many other predictions of the theory, especially regarding normal-state properties, which could be tested fairly easily. Some of these are as follows:

(i) The masses shown in Table I, and deducible from Fig. 1 for higher Zr concentrations, could be checked by specific-heat measurements.

(ii) The small-polaron contribution to the free-carrier absorption should increase with increasing Zr content as d^2, where d^2 is given by (48), with numerical values in Table I. This contribution to the absorption should increase in width slightly with increasing Zr concentration, because of the dependence on bare mass of the quantity S of (25), which measures the mean number of phonons participating in the absorption.

(iii) There is some evidence that the carrier effective mass in $SrTiO_3$ may increase with increasing temperature, density-of-states masses determined by thermoelectric power measurements[43] rising from $m_d=6m_e$ at 78°K to $m_d=16m_e$ at room temperature. Thus, it seems that increase of temperature may increase the parameter r of Fig. 1. Hence Fig. 1 could perhaps be used to predict effective masses at other temperatures.

(iv) At least in the temperature range where phonons dominate the scattering, the transport properties of carriers might change sharply with Zr concentration as nearly-small-polaron states become dominant. Except in the hopping regime, whose occurrence has not been established for nearly-small polarons, it is not always simple to distinguish between large- and small-polaron transport, but with careful analysis distinctions can be made.[17]

(v) The results of the present paper could be combined with those of Ref. 22 to predict superconducting transition temperature as a function of carrier concentration for Zr concentrations greater than 3%. Thus measurements of T_c as a function of n in this regime would provide further tests of the theory.

(vi) Application of pressure is likely to decrease the bare mass, and hence to bring the carriers nearer to the large-polaron regime. Thus all the above types of experiment might be done under pressure, and opposite results to those produced by Zr doping would be expected.

Pfeiffer and Schooley[44] have looked at superconducting transition temperature in $SrTiO_3$ under hydrostatic pressure and under uniaxial strain on specimens with a fixed carrier concentration for which T_c's lie near their maximum value, and observe decreases in T_c with applied pressure. At higher carrier concentrations, however, according to the present theory, if pressure decreases the bare mass, we might expect a T_c increase with pressure, since the maximum of the T_c-versus-n curve should shift to higher concentrations.

(vii) The bare mass in any suitable polar material would have to lie within a very limited region in order for a transition between large- and nearly small-polaron states to be observable. However, because of many similarities to $SrTiO_3$, it seems possible that the conduction band of $BaTiO_3$ may lie close to such a transition, and so doping or pressure experiments on this material might show similar effects to those seen in $SrTiO_3$.

VI. CONCLUSIONS

(1) A fairly sharp transition between large- and nearly-small-polaron states as a function of bare mass is possible in certain materials.

(2) The rate of rise of carrier mass with Zr content in Zr-doped $SrTiO_3$ deduced from analysis[22] of experimental results on superconductivity[23] can be explained by the theory of transitions between large- and nearly-small-polaron states developed in this paper. The bare transverse mass $m_{bt}=0.6m_e$ used in this theory lies within the range determined from electroreflectance experiments.[28] For this value of the bare mass, an increase in the parameters of small-polaron theory by a factor of 1.42 over their values calculated using a continuum-polarization model is required in order to give consistency with an analysis of infrared absorption results by Reik[14] using small-polaron theory.

(3) An increase in the ratio of phonon-induced to Coulomb intervalley interactions of about 5% for each percent Zr addition, deducible from the analysis of

[42] C. S. Koonce and M. L. Cohen, Phys. Rev. (to be published).

[43] H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, Phys. Rev. 134, A442 (1964).

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superconductivity data, can be interpreted in terms of the theory of polaron transitions, if it is postulated that polaron-intervalley phonon matrix elements are larger by a factor of 1.35 for nearly small polarons than for large polarons.

(4) Predictions of the theory for the normal state could most easily be tested by specific-heat and free-carrier absorption measurements for a given carrier concentration as a function of Zr concentration or of pressure.

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Stored Energy in Irradiated Sodium Chloride*†

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Irradiated NaCl crystals are heated from room temperature to 400°C, and the energy released is measured by calorimetry. F-center densities range from 3×10^{17} to 1.8×10^{18}/cm^3, which are low enough to be measured directly, rather than inferred, as in some previous work. There are three definite peaks in energy release: centered at 135°, 250°, and 350°. The 250° peak is the largest, and is associated with almost all of the coloring changes. The total stored energy is 12.4 eV per F center, of which 8.4 eV is released in the 250° peak and 2.2 eV is released in the 135° peak. Assignment of thermal energies to specific atomic processes is difficult, because there are so many processes but only three experimental peaks. Evidence is good that the 250° peak is mainly a superposition of two unresolved peaks, of which the lower is due to the annealing of the F-center electrons, and the upper to the annealing of vacancies. We suggest that the 350° peak comes from the annealing of M-center divacancies. We do not have good evidence with which to explain the large amount of energy in the 135° peak. A calcium-doped crystal also releases energy in three peaks centered at these temperatures, but here most of the energy, and all of the bleaching, occur under the lowest-temperature peak.

I. INTRODUCTION

THE results are reported here of measurements of the energy released when irradiated NaCl crystals are gradually heated from room temperature to 400°C. As is shown, the data gives a "spectrum" of stored energy release—i.e., a graph of energy-release rate versus temperature shows several peaks. To some extent these peaks can be correlated with measured changes in optical absorption during heating.

Kobayashi[1] used a differential calorimetric technique, similar to that described by Overhauser,[2] to measure the stored-energy spectrum in proton-irradiated NaCl. The energy-release rate had peaks at three fairly well-defined temperatures, which Kobayashi interpreted in terms of specific processes by noting the correspondence in temperature with peaks in the annealing of optical absorption and with peaks in the electrical resistance of irradiated samples. His samples for the thermal measurements were necessarily so heavily colored, because of limitations in calorimeter sensitivity, that the color-center concentrations could only be inferred by extrapolation from less heavily colored samples. Thus, accurate values of the energy could not be assigned to specific centers.

Zavadovskaya[3] and co-workers also used this technique to measure the rate of release of stored energy in several alkali halides, heavily irradiated at room temperature with γ rays. The color-center concentrations apparently were not measured directly; instead, the energy was related to the radiation dose, which is difficult to translate into defect concentration, since the latter depends in fairly complicated fashion on dose rate, irradiation temperature, and trace impurities.

Phelps and Pearlstein[4] measured the *total* stored energy as a function of color-center concentration, using a heat-of-solution method, in NaCl x irradiated at room temperature. They concluded that the energy associated with the annihilation of one F center is 9.2 ± 0.3 eV, which is close to the energy predicted from a simple model. However, as they point out, the interpretation is ambiguous by as much as 3.6 eV per F

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