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Explanation for the temperature dependence of plasma frequencies in $SrTiO_3$ using mixed-polaron theory

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A theory of mixed polarons is used to interpret the published experimental results of Gervais *et al.* on temperature-dependent plasma frequencies in Nb-doped $SrTiO_3$. For given polaron masses before mixing, the appropriate average mixed-polaron mass at any temperature T depends on two quantities, δ and b, which are measures of the separation between the bottoms of large and nearly small polaron bands before mixing and of a mixing matrix element; δ and b are assumed to have arbitrary linear dependences on T, probably related to a T dependence of the bare mass, and a term quadratic in T is included in δ, determined from the T dependence of large-polaron binding energies. Including a constraint on the ratio $\delta/|b|$ at low T from known masses from specific-heat data, satisfactory agreement is obtained with masses determined from plasma frequencies. This gives further support for the theory of mixed polarons in $SrTiO_3$ in addition to that already published. [S0163-1829(96)01125-3]

I. INTRODUCTION

There are many reasons for thinking that polarons in $SrTiO_3$ are of an unusual type. The first is that, whereas optical properties are similar to those of small polarons,[1] experimentally determined effective masses[2,3] are closer to those of large polarons. The next is that there is evidence from data on magnetic-field penetration depths and from curves of superconducting T_c versus carrier concentration in Zr-doped $SrTiO_3$,[4] that effective masses increase very rapidly with Zr concentration, by amounts of the order of 20% for each atomic percent Zr substitution for Ti.[5] A third reason is the temperature dependence of effective masses determined by thermoelectric-power measurements,[3] density-of-states masses increasing from about 6 m_e to 16 m_e between 77 and 300 K. A fourth unusual property is that plasma frequencies decrease as the temperature rises, by a factor of between 4 and 6 between 77 and 1000 K.[6] The first three of these four unusual properties have already been explained in some detail by a theory of mixed polarons,[7–10] in which the lowest energy state of current carriers is a superposition of comparable amounts of large[11] and nearly small polarons.[12] The first property arises because the transport mass of mixed polarons is to a first approximation determined by a weighted average of the reciprocal masses of the two types of polaron, and so is dominated by the lighter component, whereas, for photon energies above a few tenths of an eV, the optical properties are dominated by transitions involving the heavier (small-polaron like) component of either the initial or final state or both.[8,9] The second unusual property, viz., the extreme sensitivity of the effective mass to small additions of Zr can be explained in terms of small changes in the bare mass bringing about significant changes in the proportions of the two types of polaron in the mixed-polaron wave functions, and hence large changes in carrier masses.[7–9] The third property, the temperature dependence of the density-of-states mass, arises because the proportion of nearly small polaron states in carrier wave functions increases as the temperature rises.[10] The fourth property, the decrease of plasma frequencies as the temperature rises, has a qualitatively similar explanation to the third. However, several new factors have to be taken into account to interpret the data: (i) the relevant average mass for determining plasma frequencies is different from the density-of-states mass, (ii) some experimental data is at sufficiently high temperatures that partial occupation of the upper mixed-polaron band should not be ignored, and (iii) modifications of the theory by use of Fermi-Dirac statistics is required for some of the specimens at the lowest temperatures studied. This last factor should strictly have been allowed for in the low-temperature calculations reported in Ref. 10. However, since the Fermi levels in the specimens on which the measurements were performed correspond to temperatures at which the calculated masses do not differ much from those calculated at low temperatures in our theory, in which departures from Boltzmann statistics were ignored, we think that errors due to this omission were small.

The observed temperature-dependent plasma frequencies are explained quantitatively by the mixed-polaron model in the present paper. A brief description of the calculations required to determine plasma frequencies in mixed-polaron theory is given in Sec. II, and results from fitting the data are presented and discussed in Secs. III and IV. Readers wishing more details of the calculations described briefly in Sec. II may request a copy of a longer version of the manuscript from the authors.

II. CALCULATION OF PLASMA FREQUENCIES IN MIXED-POLARON THEORY

We shall be concerned with the samples studied in Ref. 6 for which the conduction bands have less than 1% occupation by current carriers, and so we make the approximation that the energies $E_{w\mathbf{k}}$ and $E_{n\mathbf{k}}$ of pure large and nearly small polarons of wave vector **k** depend quadratically on the magnitude of **k** measured from the nearest band minimum. This will be a good approximation at low temperatures. At high temperatures occupation of states with large wave vectors will be non-negligible. However we shall give arguments later stating why we think that the quadratic approximation will not cause large errors in our estimates of masses in $SrTiO_3$.

With these approximations, expressions for the energies $E_{g\mathbf{k}}$ and $E_{e\mathbf{k}}$ of the ground and excited mixed-polaron bands at wave vector **k** can be found in Ref. 10. They were used in that reference to calculate the temperature dependence of the average mass appropriate for thermoelectric-power measurements. Here we use expressions for $E_{g\mathbf{k}}$ and $E_{e\mathbf{k}}$ to calculate a different average mass appearing in an expression for the plasma frequency. From a derivation of an expression for the plasma frequency given in Ref. 13 we can deduce that, for bands with variable mass,

$$\omega_p=(4\pi ne^2/m^*\epsilon_h)^{1/2}, \tag{1}$$

where n is the carrier concentration, ϵ_h is the high-frequency dielectric constant, and

$$m^*=1/\mathrm{Av}(1/m). \tag{2}$$

Here $\mathrm{Av}(1/m)$ is an average of the reciprocal mass, proportional to the magnitude of the second derivative of the energy with respect to the component of the wave vector in a particular direction, weighted by the Boltzmann distribution function or the Fermi-Dirac function according to whether we are above or below the degeneracy temperature. To calculate the mass at a given wave vector we find the average of the radial component of $\nabla^2E_{i\mathbf{k}}$ $(i=g,e)$ in spherical-polar coordinates, and convert to an average of the second derivative in a particular direction by multiplying by (1/3), the average of $\cos^2\theta$ over polar angles.

We calculate thermal averages using both Boltzmann and Fermi-Dirac statistics. For Fermi-Dirac statistics we need to calculate the Fermi energy for a given carrier concentration by integrating the density of states over energy with Fermi-Dirac occupation probabilities. In order to find the limits of integration we use expressions for $E_{i\mathbf{k}}$ at $k=0$ and $k=k_m$, where k_m is the maximum magnitude of the wave vector, approximated by use of a spherical Brillouin zone of the correct volume.

Parameters in the theory, which may be temperature dependent, are m_w and m_n, the masses in the wide (large-polaron) and narrow (nearly small-polaron) bands before mixing, δ, a measure of the difference in energy between the bottoms of the nearly small-polaron and large-polaron bands in units of the phonon energy $\hbar\omega$, and $b=2U/\hbar\omega$, where U is the matrix element of the Hamiltonian between orthogonalized large and nearly small-polaron states.

Up until this point our theory would be applicable to mixtures of any two bands with different masses, whether polaronic or not. However, from now on we will start to introduce formulas specific to polaron theory. For m_w we make use of expressions for the ratio of m_w to the bare mass m_b valid to second order in the coupling constant α (Ref. 14) at $T=0$. There is a temperature dependence of m_w which arises because of nonparabolicity of the bands in large-polaron theory.[14] We neglect this temperature dependence, as in Ref. 10, because it would be inconsistent with the rest of our assumptions to include it.

We have to consider what to assume for the temperature dependence of the other parameters in the problem, i.e., δ, b, and m_n. The particular assumptions we shall make are not generally valid, but may be appropriate for $SrTiO_3$ as we shall discuss below.

III. APPLICATION TO $SrTiO_3$

Form of temperature dependence of parameters assumed. Reasons were given in Ref. 9 for thinking that there may be a slight linear temperature dependence of the bare mass in $SrTiO_3$. This is related to thermal expansion, but, for indirect electronic transfer integrals via oxygen, as discussed in Sec. 3.2 of Ref. 9, it is not obvious whether masses will increase or decrease as temperature rises. We shall assume that

$$m_b=m_{b0}(1-\gamma t), \tag{3}$$

where

$$t=k_BT/\hbar\omega, \tag{4}$$

and γ may be positive or negative. This temperature dependence of m_b will cause a linear temperature dependence of δ, and may give rise to a linear temperature dependence of b. There is also a quadratic temperature dependence of δ because of the temperature dependence of the large-polaron binding energy, for which we use an expression correct to first order in the polaron-coupling constant, α.[14] For the usual type of nearly small polarons with a high saddle point on the adiabatic potential surface between adjacent minima in lattice-vibrational coordinate space, there will also be temperature-dependent terms due to factors of the form $\exp[-(1/2)S(2\overline{n}+1)]$ appearing in polaron bandwidths, where $\overline{n}$ is the phonon occupation number and $(1/2)S$ is an exponent for the bandwidth reduction at $T=0$.[7,12] Similar expressions with different exponents should occur for b. However, as noted in Ref. 10, the saddle point in $SrTiO_3$ is not much higher than the minima, and it is probable that the temperature dependence of the bandwidths for the narrow band will be much smaller than given by the high-saddle-point case, and we shall assume that the same is true for any contributions to b depending exponentially on $\overline{n}$. Thus we shall assume simple temperature dependences of δ and b of the form

$$\delta=\delta_0+\delta_1t-(9\alpha/32)t^2, \tag{5}$$

$$b=b_0+b_1t, \tag{6}$$

and ignore any temperature dependence of m_n. The coefficient δ_1 in Eq. (5) will be related to γ in Eq. (3) by

$$\delta_1=(zJ/\hbar\omega)\gamma, \tag{7}$$

where z is the number of near neighbors, and J is the electronic energy-transfer integral. A linear temperature dependence of m_b may also give rise to a linear temperature de-

TABLE I. Masses deduced from plasma frequencies obtained from Dr. F. Gervais or taken (for 1.5% Nb doping) from Fig. 12 of Ref. 6.

0.3% Nb, 4% Ca			0.6% Nb			0.9% Nb			1.5% Nb		
T(K)	ω_p (cm^{-1})	m^*/m_e	T(K)	ω_p (cm^{-1})	m^*/m_e	T(K)	ω_p (cm^{-1})	m^*/m_e	T(K)	ω_p (cm^{-1})	m^*/m_e
			90	515	6.6	90	980	2.7	81	944	4.9
300	235	15.9	300	305	18.8	300	515	9.9	161	756	7.7
630	125	56.2	398	255	26.9	450	350	21.4	241	700	8.9
820	110	72.6	500	185	51.0	600	250	41.9	299	633	10.9
1020	90	108.4	599	165	64.1	796	185	76.5	425	500	17.5
			744	157	70.8	1005	150	116.4	563	400	27.3
			888	140	89.1				793	300	48.5

pendence of b, but the coefficient could be difficult to calculate. The value of m_n is taken from Ref. 10 to be $m_n=116m_e$.

Masses inferred from plasma frequencies. Using $\epsilon_h=5.2$ (Ref. 15) and $a=3.90$ Å ,[16] from numerical values for some data points on plasma frequencies in Nb-doped $SrTiO_3$ (see Fig. 12 of Ref. 6) provided by Gervais, and for some additional points obtained from Fig. 12 of Ref. 6, we deduce the masses at various temperatures and Nb concentrations shown in Table I. Masses typically increase by factors between 10 and 28 between 90 and 800 K, a phenomenon unique to $SrTiO_3$ as far as we know at this time.

Determination of parameters by data fitting and use of a constraint from known densities-of-states masses at low T. Analysis[9] of infrared-absorption data in reduced $SrTiO_3$ using mixed-polaron theory[8] and a many-valley model for the conduction band[17] led to a bare mass $m_b=1.21m_e$ in each valley, and earlier work gave a weighted longitudinal optical-phonon energy of 0.09 eV, and a polaron coupling constant $\alpha=2.34(m_b/m_e)^{1/2}$. The analysis of infrared absorption also gave values of the parameters δ and b at two temperatures. However, if we use values deduced from this analysis to infer δ_0, δ_1, b_0, and b_1 in Eqs. (5) and (6), we find that the average mass defined in Eq. (2) does not rise sufficiently rapidly with temperature to fit the data of Ref. 6. Since more assumptions go into the theory of infrared absorption by mixed polarons[8] than into the theory used here for mixed-polaron masses, and also there may be a difference between reduced and Nb-doped samples, we think it reasonable to treat some parameters as adjustable. To have variable parameters and to use Fermi-Dirac statistics too would give rather an involved data-fitting problem. However, if we use Boltzmann statistics and confine ourselves to temperatures for which this is a fair approximation, then we can determine some parameters from data fitting. We have four parameters, δ_0, δ_1, b_0, and b_1, but the number of adjustable parameters is reduced to three by use of a constraint from densities-of-states masses at low temperatures deduced from specific-heat data interpreted by mixed-polaron theory.[10] Using the expression for densities-of-states mass m_d at low temperatures for a three-valley model of the conduction band given in Ref. 10, and $m_d=(5.3\pm0.3)m_e$ determined[10] from specific-heat data,[2] we deduce that

$$\delta_0/|b_0|=0.61\pm0.2. \tag{8}$$

We use the most probable value of 0.61 as our constraint, and we then have three independent parameters to vary, which we choose to be δ_1, b_0, and b_1. Since the masses deduced from plasma frequencies differ appreciably for the different specimens, we cannot hope to fit all the data accurately with one set of parameters. However, the masses for the 0.6 and 0.9% Nb specimens are not drastically different, and we concentrate on a combined fit to 11 data points at 300 K and above for these two specimens. Gervais informs us[20] that experimental uncertainties for plasma frequencies can be as high as 10–20%, with uncertainties increasing as the damping increases. However, we do not have sufficiently detailed information to be able to take into account variations in fractional uncertainties in our weighting function property. We weight assuming a constant fractional experimental error in plasma frequencies or masses. The parameters for the best fit to the combined 0.6 and 0.9% data are

$$\delta_1=-2.15, \quad b_0=2.05, \quad b_1=0.38, \tag{9}$$

with an average percentage error for masses for these points of 27%. We note that δ becomes negative at the highest temperatures at which measurements were made, i.e., the bottom of the nearly small polaron band falls below that of the large-polaron band. From the value of δ_1 obtained by fitting the combined data for 0.6 and 0.9% Nb, we deduce from Eq. (7) that $\gamma=-0.16$, i.e., about a 1.6% increase in bare mass per 100 K, which is consistent with a $(1\pm2)\%$ per 100 K inferred in Ref. 9. The values of δ and b deduced from the fitting parameters plus use of Eq. (8) are 0.814 and 2.13 at 200 K, and 0.5 and 2.17 at 330 K. These are not very close to the values deduced from infrared absorption on reduced $SrTiO_3$, viz., 0.323 and 1.06 at 200 K, and 0.446 and 1.41 at 330 K. Whether the difference is due to the extra approximations made in analyzing the infrared absorption giving unreliable values of parameters, to the differences between reduced and Nb-doped $SrTiO_3$, or due to other causes, is not clear.

The masses obtained by the fits and the percentage differences of these from the experimentally determined masses are shown in Table II. We also compared theoretical and experimental masses for 0.9% Nb doping at lower temperatures than used in the fit, with theoretical values obtained by use of the same parameters as in Table II, but with inclusion of Fermi-Dirac statistics too. The difference between theory and experiment below 300 K is small with both types of

TABLE II. Theoretical and experimental masses obtained by fitting combined data for 0.6 and 0.9% Nb doping at 300 K and above.

% Nb	T(K)	δ	b	m_w/m_e	m_{th}	m^*/m_e	% difference
0.6	300	0.575	2.16	2.04	11.6	18.8	−38
	398	0.327	2.20	2.07	26.3	26.9	−2
	500	0.053	2.24	2.11	43.9	51.0	−14
	599	−0.227	2.27	2.14	57.9	64.1	−10
	744	−0.664	2.33	2.20	70.9	70.8	0
	888	−1.129	2.38	2.25	77.8	89.1	−13
0.9	300	0.575	2.16	2.04	11.6	9.9	17
	450	0.189	2.22	2.09	35.4	21.4	66
	600	−0.230	2.27	2.14	58.0	41.9	39
	796	−0.828	2.35	2.22	73.9	76.5	−3
	1005	−1.532	2.42	2.29	81.0	116.4	−30

statistics (rms discrepancy 6% with Boltzmann statistics and 9% with Fermi-Dirac statistics between 276 and 92 K). Fermi-Dirac statistics increases the theoretical masses by between 3 and 5% in this temperature range.

IV. APPROXIMATION OF USING PARABOLIC BANDS

Since, at some of the temperatures considered, occupation of states with large wave vectors is appreciable, it might be thought that the approximation of assuming a parabolic dispersion relation may produce serious errors. However, we have some reasons for thinking that the errors may be small. First we note that the appreciable nonparabolicity of the wide band occurring in, e.g., a tight-binding band-structure calculation, does not occur until wide-band energies are reached at which the mixing into the lower mixed-polaron band is small. Second, we note that in Ref. 10 we gave reasons for thinking that a ''nearly free-polaron'' approach was appropriate for calculating the mass and band structure of the nearly small polarons in $SrTiO_3$. Hence we should not expect much nonparabolicity for this band except very close to the edge of the Brillouin zone. The fact that we obtain fair agreement with experiment assuming parabolic dispersion relations for the bands before mixing when we treat three parameters as adjustable lends some support to this viewpoint.

V. CONCLUSIONS

A satisfactory fit to the temperature-dependent masses determined from plasma frequencies in Nb-doped $SrTiO_3$ has been obtained by the same type of theory of mixed polarons used to explain dependence of masses on Zr concentration, infrared absorption, and temperature-dependent masses determined from thermoelectric-power data. This gives further support for the validity of this type of theory for $SrTiO_3$. However, values of parameters required to fit the data are somewhat different than those obtained by fitting infrared data at two temperatures.

Whether average masses increase or decrease as a function of temperature can depend on how much mixing there is between the two types of polaron and also on the concentration of polarons. In $Pr_2NiO_{4.22}$ it has recently been inferred from fitting infrared data with a theory involving two types of polarons but negligible mixing that plasma frequencies increase as temperature rises.[18] We find it surprising that, as far as we know, no other material has yet been found with a plasma frequency which decreases as the temperature rises, as ranges of coupling constant for which two types of polaron state can exist are not particularly small,[19] and if two types of state are possible we would have thought that to have an appreciable mixing between them would not be that uncommon. Studies of alloys of $SrTiO_3$ with other similar materials might shed some light on this problem.

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