# Thermodynamics in very strong coupling: A possible model for the high- $T_c$  oxides

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(Received 26 May 1987)

We have calculated the thermodynamic properties of an isotropic electron-phonon superconductor in the very-strong-coupling regime which results when the critical temperature  $(T_c)$  is on the order of a typical phonon energy. In this limit  $2\Delta_0/k_BT_c$ , with  $\Delta_0$  the gap edge, is much larger than the Bardeen-Cooper-Schrieffer (BCS) value of 3.54 while at the same time the other dimensionless thermodynamic indices would indicate weak coupling. In fact  $\Delta C(T_c) / \gamma(0) T_c$ , with  $\Delta C(T_c)$  the specific-heat jump and  $\gamma(0)$  the Sommerfeld constant, can be less than 1.43 and the ratio  $\gamma(0)T_c^2/H_c^2(0)$ , with  $H_c(0)$  the zero-temperature thermodynamic critical magnetic field, greater than 0.168. Also the critical-field deviation function is negative definite and smaller than in BCS. All these results are in striking contrast to the usual modest strong-coupling corrections that apply in conventional superconductors and, except for  $2\Delta_0/k_B T_c$ , are in the opposite direction.

# I. INTRODUCTION

The Eliashberg equations, with the underlying premise that it is the electron-phonon interaction which is the mechanism responsible for superconductivity, have been extremely successful in describing the superconductivity of all well-studied conventional superconductors.<sup>1-10</sup> In this class we include all known superconductors, except for the heavy-fermion systems and the recently discovered oxides with very high values of the critical temperature  $T_c$ .

When good-quality tunneling junctions are fabricated out of conventional superconductors, an image of the phonon spectrum, or more precisely, the weighted electronphonon spectral density, is observed<sup>2</sup> in the currentvoltage  $I-V$  characteristics, provided  $T_c$  is not too small. The phonon structure at a given phonon energy  $(\omega)$  measured from the energy-gap edge  $\Delta_0$ , can be used to obtain the spectral density  $\alpha^2 F(\omega)$ . If the superconductor-oxide interface is sharp, it is possible to invert the  $I-V$  characteristics and obtain, through the Eliashberg equations, a unique value for  $\alpha^2 F(\omega)$  as well as for the Coulomb repulsion pseudopotential  $(\mu^*)$ . The inversion technique pioneered by McMillan and Rowell<sup>2</sup> is unambiguous in such cases and employs the  $I-V$  data only up to the phonon maximum  $\omega_D$  plus  $\Delta_0$ .

A very severe check on the consistency of the above procedure is that, in Pb for example, when the measured  $\alpha^2 F(\omega)$  is introduced into the Eliashberg equations they are found to reproduce well the observed I-V structure in the multiple phonon region beyond  $\omega_D + \Delta_0$ , although these data have, in no way, been used in the inversion process.<sup>2</sup>

In certain systems, such as some transition metals and 415 compounds, it has not always been possible to produce good-quality junctions. In some cases there is a small degraded metallic layer between the pure superconductor and the oxide layer. When this is the case a theory small degraded metallic layer between the pure superconductor and the oxide layer. When this is the case a theory<br>of the proximity effect<sup>3,11–13</sup> has been developed, which allows inversion of the data anyway, although the procedure now introduces a proximity parameter that is to be determined from a fit to the data. While this is clearly a less satisfactory procedure involving a fit parameter, it nevertheless gives reasonable values of  $\alpha^2 F(\omega)$ .

A second important test of the validity of the Eliashberg theory for conventional superconductivity is that the hermodynamic<sup>4-10</sup> and other properties such as the ratio of twice the gap  $\Delta_0$  to  $T_c$  (Ref. 14) can be predicted from the measured  $\alpha^2 F(\omega)$ . The results of finite temperature Eliashberg calculations of superconducting properties, are found to be in very good agreement with the experimental data.<sup>4-10</sup> In general, these data do not conform to Bardeen-Cooper-Schrieffer (BCS) theory, which applies only in the weak coupling limit for which  $T_c$  divided by a ypical phonon energy, say  $\omega_{1n}$  (to be defined later), is very much smaller than  $1.^{10,14}$  When this is not so, significant corrections are observed which can usually be described, semiquantitatively, by corrections of the form  $(T_c/\omega_{1n})^2 \ln[\alpha(\omega_{1n}/T_c)]$  (Refs. 10 and 14) to the corresponding BCS predictions. Here  $\alpha$  is some appropriate constant determined through a fit to full numerical solutions.

A third check on Eliashberg theory, which is worth mention, is the first-principle calculations of  $\alpha^2 F(\omega)$ which have now been performed in many cases.<sup>15-20</sup> When these are compared with the tunneling derived  $\alpha^2 F(\omega)$ , a remarkable amount of agreement is usually found as to the shape and absolute values, leaving little doubt about the validity of the underlying concepts. These remarkable achievements rest, of course, on Migdal's theorem which states that, for an electronphonon system, vertex corrections are small and of the order of the square root of the electron to the ion mass ratio. All other diagrams in the perturbation theory are incorporated into the Eliashberg equations.

The initial observation by Bednorz and Müller<sup>21</sup> of superconductivity with onset near 30 K in the Ba-La-Cu-0 system lead directly, and in a remarkably short time, to the discovery of superconductivity above 90 K in Y-Ba-Cu-O.<sup>22-24</sup> The striking difference in the scale of  $T_c$  for these materials, when compared with the conventional case for which  $T_c \le 23$  K, immediately raises doubt about the electron-phonon interaction as the operative mechanism in these systems. Indeed many diferent suggestions

of possible alternate mechanisms have already been put forward<sup>25-28</sup> although as yet none have been conclusively demonstrated. At present, it is fair to say that no consensus exists and that the question of mechanism remains open.

For the case of  $La<sub>1.85</sub>Sr<sub>0.15</sub>CuO<sub>4</sub>$  there exists a detailed state-of-the-art calculation from band-structure results of the electron-phonon spectral density  $\alpha^2 F(\omega)$  by Weber.<sup>29</sup> The calculations indicate that this system is near the boundary of stability for the crystal structure because of a very large electron-phonon interaction. In fact, Weber finds this interaction to be sufficiently large to explain the observed high critical temperature value of 36 K. In addition, Schossmann, Marsiglio, and Carbotte<sup>30</sup> have calculated from Weber's  $\alpha^2 F(\omega)$  data the thermodynamic properties of  $La<sub>1.85</sub>Sr<sub>0.15</sub>CuO<sub>4</sub>$  and have compared the resultant theoretical results with experiment. While the comparison is not conclusive, due to a large extent to uncertainties in present experimental results, an electronphonon mechanism is not as consistent with the data as in conventional superconductors, but is not ruled out although some other mechanism may be making an additional contribution to the pairing potential. While no isotope effect is observed in Y-Ba-Cu-O with  $T_c = 96$  K, and its electron-phonon interaction would need to be three times larger than in  $La<sub>1.85</sub>Sr<sub>0.15</sub>CuO<sub>4</sub>$ , which is likely to be inconsistent with lattice stability, it is nevertheless interesting to consider the limit of a very large electronphonon interaction.

In this paper we calculate the thermodynamic properties of a model electron-phonon superconductor with  $T_c$  =96 K in the very-strong-coupling regime  $(T_c/\omega_{1n} \sim 1)$ and perhaps even larger). We do not address, however, the question of the stability of the crystal structure lattice for the large values of electron-phonon spectral density that are needed. Instead, we calculate the expected thermodynamic properties in the hope that they will be quite diferent from those predicted for conventional systems. The observation (or lack thereof) of the distinctive pattern characterizing this limit could then be taken as important evidence in favor (or against) this mechanism. We note that no expansion based on BCS results with corrections in powers of  $T_c/\omega_{1n}$ , which describes conventional superconductors well with  $T_c/\omega_{1n} \lesssim 0.2$  (Refs. 10 and 14), is now possible and we will proceed numerically. In Sec. II we give some necessary theoretical details while our results appear in Sec. III. Section IV is a short conclusion.

## II. THEORETICAL EQUATIONS

The Eliashberg equations for the pairing energy  $\tilde{\Delta}(i\omega_n)$ and renormalized frequency  $\tilde{\omega}(i\omega_n)$  in the Matsubara representation are  $4,31,32$ 

$$
\tilde{\Delta}(i\omega_n) = \pi T \sum_m [\lambda(m-n) - \mu^*] \frac{\tilde{\Delta}(i\omega_m)}{[\tilde{\Delta}^2(i\omega_m) + \tilde{\omega}^2(i\omega_m)]^{1/2}}
$$
\n(1)

and

$$
\tilde{\omega}(i\omega_n) = \omega_m + \pi T \sum_m \lambda(m-n) \frac{\tilde{\omega}(i\omega_m)}{[\tilde{\Delta}^2(i\omega_m) + \tilde{\omega}^2(i\omega_m)]^{1/2}},
$$
\n(2)

where  $\mu^*$  is the Coulomb pseudopotential, T the temperature, and  $\lambda (m - n)$  is equal to

$$
\lambda(m-n) = \int \frac{2\Omega a^2 F(\Omega) d\Omega}{\Omega^2 + (\omega_n - \omega_m)^2}
$$
 (3)

with  $i\omega_n = i\pi T(2n - 1)$ ,  $n = 0, \pm 1, \pm 2, \pm 3$ ....

In what follows  $\mu^*$  is taken to be 0.1 and left unchanged in all runs. For the electron-phonon spectral density we wish to use some reasonable model value which is large enough to give a value of  $T_c = 96$  K. While higher values could be used, we believe that 96 K is sufficient to illustrate the main trends associated with the thermodynamics of a superconductor in the very-strong-coupling limit, namely  $T_c/\omega_{1n} \sim 1$ . Here,  $\omega_{1n}$  (in units of meV) is some typical phonon energy, characteristic of the phonon spectrum for the material of interest. While the specific choice of  $\omega_{1n}$  is not essential, it seems reasonable to use the Allen-Dynes<sup>33</sup> parameter

$$
\omega_{1n} = \exp\left(\frac{2}{\lambda} \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} \ln(\omega) d\omega\right) \tag{4}
$$

since it has been used very successfully in works on  $T_c$ (Ref. 33) as well as on the thermodynamics and other properties' '<sup>4</sup> of conventional strong coupling systems with  $T_c/\omega_{1n} \lesssim 0.2$ .

In addition to a knowledge of the solutions of the Eliashberg equations we require an expression for the free-energy difference between normal and superconducting state  $\Delta F$ , which is <sup>4,31</sup>

$$
\Delta F = 2\pi N(0)T \sum_{n>0} \left[ 2\left[ [\tilde{\Delta}^2(i\omega_n) + \tilde{\omega}^2(i\omega_n)]^{1/2} - \tilde{\omega}(i\omega_n) - \frac{1}{2} \frac{\tilde{\Delta}^2(i\omega_n)}{[\tilde{\Delta}^2(i\omega_n) + \tilde{\omega}^2(i\omega_n)]^{1/2}} \right] - [\tilde{\omega}(i\omega_n) - \tilde{\omega}^0(i\omega_n)] \left[ \frac{\tilde{\omega}(i\omega_n)}{[\tilde{\Delta}^2(i\omega_n) + \tilde{\omega}^2(i\omega_n)]^{1/2}} - 1 \right] \right].
$$
 (5)

In Eq.  $(5)$ ,  $N(0)$  is the single-spin electronic density of states at the Fermi surface. It is related to the Sommerfeld constant  $\gamma(0)$ , at zero temperature, through

$$
\gamma(0) = \frac{2}{3} \pi^2 k_B^2 N(0) (1 + \lambda) , \qquad (6)
$$

where  $k_B$  is the Boltzmann constant taken to be 1 in other

parts of this paper, and  $\lambda$  is the electron-phonon mass enhancement.

In the discussion given by Schossmann et al.<sup>30</sup> of the superconducting properties of  $La<sub>1.85</sub>Sr<sub>0.15</sub>CuO<sub>4</sub>$ , which they base on the theoretical electron-phonon spectral density calculated by Weber,  $29$  they point out that, in systems with a very large electron-phonon interaction and large value for  $T_c$ , the normal-state electronic specific heat at  $T_c[C_N(T_c)]$  can be quite different from  $\gamma(0)T_c$  because the Sommerfeld  $\gamma$  is temperature dependent. This was first discussed by Grimvall<sup>34,35</sup> and calculated by others. To present normalized thermodynamic results independent of  $N(0)$ , as is done conventionally, we can divide the appropriate quantities with a factor of  $\gamma(0)$  or  $\gamma(T_c)$  since both are proportional to the electronic density of states. Here we will use  $\gamma(0)$  for several reasons given below.

When  $T_c$  is large  $C_N(T_c) \equiv \gamma(T_c) T_c$  is superimposed and strongly coupled to a large phonon contribution which cannot easily be subtracted out. It is in fact necessary to use indirect methods to experimentally extract information on the Sommerfeld constant. One method is to measure the slope of the critical magnetic field at  $T_c$  and exploit a known theoretical relation between the slope and  $\gamma(0)$ . This gives no information on  $\gamma(T_c)$  so that it is more natural to use  $\gamma(0)$ . This quantity is also simpler and much more familiar than is  $\gamma(T)$ .

### III. RESULTS

We must now make some choice of  $\alpha^2 F(\omega)$ . As we are interested only in model results that illustrate the kind of thermodynamics that can be expected in the very-strongcoupling regime, this choice is perhaps not critical. Still it seems reasonable to use a spectral density that may be reasonably characteristic of the high- $T_c$  oxides. The only known spectral density for this class of materials is the theoretical estimate of Weber<sup>29</sup> in the case of  $La<sub>1.85</sub>$ - $Sr<sub>0.15</sub>CuO<sub>4</sub>$  which gives a  $T<sub>c</sub>$  of 36 K. To get a value of  $T_c$  =96 K characteristic of Y-Ba-Cu-O from Weber's spectral density, which we now denote by  $\alpha^2 F^0(\omega)$ , we can multiply it by some factor  $B$  (of order 3) or we could soften the phonon spectrum by some constant amount  $b$  or use a combination of both. This leads us to consider a model  $\alpha^2 F(\omega)$  of the form

$$
\alpha^2 F(\omega) \equiv B \alpha^2 F^0(b\omega) \tag{7}
$$

with  $B$  and  $b$  constants.<sup>37</sup>

From Eq. (4), which defines the characteristic phonon energy  $\omega_{1n}$ , it is clear that the scaling factor B in Eq. (7) does not change this quantity and also that  $b$  does with

$$
\omega_{1n} = \omega_{1n}^0/b \tag{8}
$$

It is clear that, in this way, we can change the ratio  $T_c/\omega_{1n}$  at will in the model of Eq. (7) keeping  $T_c = 96$  K. Thus we can describe with this single  $\alpha^2 F^0(\omega)$ , the weak  $(T_c/\omega_{1n} \ll 1)$ , the conventional strong coupling  $(T_c/\omega_{1n})$  $\lesssim$  0.2), and the very strong coupling  $(T_c/\omega_{1n} \sim 1)$  regimes.

Before presenting results we stress that, while we are using a model  $\alpha^2 F(\omega)$  which has deliberately been chosen with Y-Ba-Cu-0 and its observed critical temperature in mind, we cannot expect the model to provide quantitative predictions for this oxide. In fact, the electron-phonon interaction may be only in part responsible for its high  $T_c$ . What we want to do is explore the predictions that result from Eliashberg theory in the very-strong-coupling

limit—when  $T_c$  is of the same order as the typical phonon energy  $\omega_{1n}$ .

Results for the specific-heat jump at  $T_c$ ,  $\Delta C(T_c)$ , normalized to  $\gamma(0)T_c$ , are given in Fig. 1 (solid line). Note that, in the limit  $T_c/\omega_{1n} \to 0$ ,  $\Delta C(T_c)/\gamma(0) T_c$  goes to the BCS number 1.43. As  $T_c/\omega_{1n}$  is increased the value of  $\Delta C(T_c) / \gamma(0) T_c$  is seen to rise until  $T_c/\omega_{1n}$  -0.2. This is the region which is relevant for conventional superconductors which, on the whole, fall on a curve<sup>10</sup>

$$
\frac{\Delta C(T_c)}{\gamma(0)T_c} = 1.43[1 + 53(T_c/\omega_{1n})^2 \ln(\omega_{1n}/3T_c)] \quad . \quad (9)
$$

We now see that formula (9) breaks down completely at higher values of  $T_c/\omega_{1n}$  since  $\Delta C(T_c)/\gamma(0)T_c$  is observed to have a maximum and then to decrease as  $T_c/\omega_{1n}$ increases further. It is very important to realize that, for very large values of  $T_c/\omega_{1n}$ , the curve falls well below BCS which is a surprising result. It is an important result because the predicted behavior is clearly differentiable from BCS behavior. Any new mechanism which involves the exchange of excitations of energy much larger than  $T_c$ would, in a first approximation, give results similar to BCS.

We wish now to make several points with respect to Fig. 1. First, if we had assumed that the phonons in  $La<sub>1.85</sub>Sr<sub>0.15</sub>CuO<sub>4</sub>$  are also characteristic of the higher- $T_c$ oxides and therefore scaled  $\alpha^2 F^0(\omega)$  by a simple multiplicative factor  $B$ , without the introduction of any softening or stiffening, we would find for  $T_c/\omega_{1n}$  a value of 0.6. From Fig. <sup>1</sup> it is clear that this would put us well into the very-strong-coupling limit and the specific-heat ratio would differ markedly from that expected in a conventional strong coupler. In fact, instead of being quite large



FIG. 1. The normalized specific-heat jump  $\Delta C(T_c)/\gamma(0)T_c$ at  $T_c$  plotted vs  $T_c/\omega_{1n}$  where  $\gamma(0)$  is the zero temperature Sommerfeld constant and  $\omega_{1n}$  is a characteristic phonon energy. The solid line was obtained using scaled spectra obtained for Weber's suggested electron-phonon spectral density  $a^2F(\omega)$ , while the dotted curve employs a Pb spectrum. The curves illustrate that qualitatively a trend is very clear as the strongcoupling parameter  $T_c/\omega_{1n}$  increases.

compared to BCS it would be close to 1.43. If, alternatively, we would argue that the critical temperature in Y-Ba-Cu-O is large compared with that for  $La<sub>1.85</sub>$ - $Sr<sub>0.15</sub>CuO<sub>4</sub>$ , mainly because of phonon softening, this would be simulated in our model by a value of the scaling factor b which would be greater than 1 and  $T_c/\omega_{1n}$  would greatly increase. This would push us even further into the very-strong-coupling regime.

If we believed that the actual mechanism for superconductivity is a combination of electron-phonon and some other mechanism, such as excitonic or plasmon exchange, then to a rough first approximation we could use the results of Fig. 1 with a value of characteristic frequency  $\omega_{1n}$ which would be an appropriate weighting of phonon and exciton or plasmon energy. The  $\omega_{1n}$  would presumably be larger than the  $\omega_{1n}$  of  $\alpha^2 F^0(\omega)$  which is  $\sim$  14 meV so that now  $T_c/\omega_{1n}$  would be reduced and we would be pushed towards the more conventional part of the curve in Fig. 1. This last remark is based on the analysis of Allender, Bray, and Bardeen<sup>28</sup> who considered first a joint phonon and exciton mechanism. They formulate their theory in terms of a set of Eliashberg equations but now with an additional piece of the kernel which augments the spectral density at high energies. This describes the exciton part of the interaction and would lead to an effective  $\omega_{1n}^*$  which is increased over its value for phonons alone. We note that for excitons the Eliashberg equations based on Migdal's theorem may well require modifications because of the possible failure of this theorem in this case.

One may well wonder if the results of Fig. <sup>1</sup> are not model dependent. To check on this we have done another complete set of calculations using the  $\alpha^2 F(\omega)$  of Pb. The resulting thermodynamics is given by the dotted curve of Fig. 1. While there are some noticeable differences between solid and dotted curve, the general trend is the same. This indicates that the shape assumed for  $\alpha^2 F(\omega)$ is only of secondary importance. This resulting observation points out, as was stressed by Marsiglio and Carbotte,<sup>38</sup> that  $T_c/\omega_{1n}$  is the important parameter and not the details of  $\alpha^2 F(\omega)$  so that our model results have wide applicability.

Besides the normalized specific-heat jump at  $T_c$ , the dimensionless ratio  $\gamma(0) T_c^2/H_c^2(0)$  is also often discussed. Here  $H_c(0)$  is the zero-temperature thermodynamic critical field. Results are shown in Fig. 2. The solid line applies, as before, to the La-Sr-Cu-0 base spectrum, while the dotted line is for a Pb base. In this case, the results of the two models are even closer than found for the specific-heat jump. As  $T_c/\omega_{1n} \rightarrow 0$  the value of  $\gamma(0) T_c^2/H_c^2(0) \rightarrow 0.168$  (the BCS value). As  $T_c/\omega_{1n}$  increases the ratio decreases, has a minimum near  $T_c/\omega_{1n} \approx 0.2$  to 0.3, and then starts rising towards values that can be as large as 0.4 for  $T_c/\omega_{1n} = 1.6$ . Again we note that all the conventional superconductors discussed in the work of Marsiglio and Carbotte<sup>10</sup> for instance, fall in the small region before the minimum. Also we stress that in the very-strong-coupling regime, Eliashberg theory predicts a behavior for this ratio which is quite different from what is found in the conventional case. This should serve as a clear signature of a large electron-phonon spectral density.



FIG. 2. Same as for Fig. <sup>1</sup> except that we are plotting  $\gamma(0) T_c^2/H_c^2(0)$  with  $H_c(0)$  the zero-temperature thermodynamic critical field.

In addition to the zero temperature critical magnetic field, we can consider its finite temperature counterpart and introduce the deviation function

$$
D(t) = H_c(T)/H_c(0) - (1 - t^2)
$$
 (10)

In Fig. 3 we show results for the maximum or minimum (or both) value of this function versus  $T_c/\omega_{1n}$ . For values  $\leq 0.2$ , the deviation function is positive definite (the conventional strong coupling regime) but as  $T_c/\omega_{1n}$  is increased beyond this range, the maximum in  $D(t)$  peaks and then begins to drop. Eventually both a maximum and a minimum are present [S shape curve for  $D(t)$ ] and finally there is only a minimum with  $D(t)$  negative definite. Note that in the very-strong-coupling limit, the

0.05 0.00  $-0.05$ 4  $La-Sr-Cu-O$ -0.10  $\mathbf{P} \mathbf{b}$ Cl -0.15  $-0.20\,$   $_{0.0}^{-1}$ I I 0.2 0.4 0.6<br> $T_c/\omega_{\rm in}$ 0.8 1.0  $1.2$ 1.2 1.4

FIG. 3. Same as in Fig. <sup>1</sup> except that we are plotting the maximum or minimum (or both when it is  $S$  shaped) of the critical magnetic field deviation function.



FIG. 4. Same as for Fig. <sup>1</sup> except that we are now plotting  $2\Delta_0/k_B T_c$  with  $\Delta_0$  the gap edge. Note that contrary to the previous three cases, this ratio continues to rise in the very strong coupling regime, thus following the trend established in the strong coupling regime  $(T_c/\omega_{1n} \lesssim 0.2)$ .

minimum of  $D(t)$  can be very much smaller than the BCS value of  $-0.036$ . This is again a definite prediction that could help confirm or rule out the electron-phonon interaction as the mechanism for superconductivity in the high- $T_c$  oxides.

In Fig. 4 we turn to our results for the ratio of the energy gap  $\Delta_0$  to  $T_c$ . To calculate this quantity from our imaginary-frequency Eliashberg solutions we need to perform an analytic continuation to real frequencies. The form an analytic continuation to real frequencies. The technique of Padé approximants is now standard.<sup>11</sup> As reviewed by Scalapino<sup>39</sup> inelastic phonon scattering leads to quasiparticle damping which should reduce both  $\Delta_0$  and  $T_c$ . However, the reduction in  $T_c$  should be larger because of thermal phonons and so  $2\Delta_0/k_B T_c$  is larger than in BCS. Our results show that  $2\Delta_0/k_B T_c$  simply keeps rising as  $T_c/\omega_{1n}$  increases. This was also observed in the work of Carbotte, Marsiglio, and Mitrović.<sup>40</sup> These authors were the first to point out that a maximum value exists for this ratio in Eliashberg theory. Similar curves to our Pb results are to be found in the work of Marsiglio and Carbotte<sup>38</sup> which was directed mainly towards La<sub>1.85</sub>Sr<sub>0.15</sub>CuO<sub>4</sub> so that the range of values for  $T_c/\omega_{1n}$ considered was much more restricted than that considered here.

The results of Fig. 4 are in striking contrast to those of Figs. <sup>1</sup> to 3. In the very-strong-coupling regime Eliashberg theory predicts a large  $2\Delta_0/k_B T_c$  of the order of 10 or more<sup>41</sup> while at the same time  $[\Delta C(T_c)]/[\gamma(0)T_c]$  is much smaller than the BCS value of 1.43 and  $[\gamma(0)T_c^2]/[H_c^2(0)]$  much larger than 0.168. Also,  $D(t)$  is

negative definite with <sup>a</sup> minimum value much less than —0.036. These predictions are very different from BCS theory and also from the pattern of behavior predicted and observed in conventional strong coupling systems.

In conclusion, we have studied the thermodynamic properties that result for an electron-phonon superconductor described by Eliashberg theory, in the limit when the critical temperature  $T_c$  is large and of the same order as the characteristic phonon energy  $\omega_{1n}$ . No attempt is made to understand whether or not the electron-phonon spectral densities that we use are consistent with lattice stability. Instead we ask the question, given a spectral density which gives  $T_c$  and  $\omega_{1n}$  of the same order, what will be the values for the various dimensionless thermodynamic indices and, more importantly, how will they differ from those found in conventional strong coupling systems  $(T_c/\omega_{1n} \lesssim 0.2)$ .

For the conventional case the ratio of twice the gap to critical temperature ratio  $2\Delta_0/k_B T_c$ , the specific-heat jump at  $T_c$  divided by the zero-temperature Sommerfeld constant  $\gamma(0)$  multiplied by  $T_c[\Delta C(T_c)/\gamma(0)T_c]$  and the extremum of the critical magnetic field deviation function, all increase with increasing value of  $T_c/\omega_{1n}$  while  $\gamma(0) T_c^2/H_c^2(0)$ , where  $H_c(0)$  is the zero-temperature thermodynamic critical field, decreases. For  $T_c/\omega_{1n} \approx 1$ the situation is strikingly different. The ratio  $2\Delta_0/k_B T_c$ does continue to increase with increasing value of  $T_c/\omega_{1n}$ <br>and can be much larger than the BCS value of 3.54  $(z_1)$ . At the same time  $\Delta C(T_c)/\gamma(0) T_c$  can be smaller than the BCS value of 1.43 and  $\gamma(0)T_c^2/H_c^2(0)$  larger than 0.168. Also, the critical-field deviation function  $D(t)$ can be negative definite with minimum value much less than —0.036. This behavior is quite distinctive and different from the conventional case  $(T_c/\omega_{1n} \lesssim 0.2)$ .

Accurate measurements of the thermodynamic indices in the high- $T_c$  oxides such as Y-Ba-Cu-O offer the possibility, at least in principle, of confirming or rejecting the predictions of a pure electron-phonon mechanism. If, in fact, there is a large electron-phonon interaction in these systems, but at the same time this interaction is aided by some other mechanism such as excitonic or exchange of plasmons, the thermodynamics will be intermediate between the very-strong-coupling limit  $T_c/\omega_{1n} \sim 1$  and the more conventional case  $T_c/\omega_{1n} \leq 0.2$ .

# ACKNOWLEDGMENTS

This research was supported in part by the Natural Sciences and Engineering Research Council of Canada (NSERC). We have benefited from discussions with M. Schossmann.

- 'J. P. Carbotte, Sci. Prog. Oxford 71, 329 (1987).
- <sup>2</sup>W. L. McMillan and J. M. Rowell, in Superconductivity, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. I, p. 561.
- sE. L. Wolf and G. B. Arnold, Phys. Rep. 91, 31 (1982).
- 4J. M. Daams and J. P. Carbotte, J. Low Temp. Phys. 43, 263 (1981).
- 5B. Mitrovic, E. Schachinger, and J. P. Carobotte, Phys. Rev. B 29, 6187 (1984).
- E. Schachinger, H. G. Zarate, M. Schossmann, and J. P. Carbotte, J. Low Temp. Phys. 63, <sup>1</sup> (1986).
- 7J. M. Daams, J. P. Carbotte, M. Ashraf, and R. Baquero, J. Low Temp. Phys. 55, <sup>1</sup> (1984).
- 8B. Mitrović and J. P. Carbotte, Phys. Rev. B 25, 1244 (1982).
- <sup>9</sup>B. Mitrović and J. P. Carbotte, Phys. Rev. B 33, 591 (1986).
- <sup>10</sup>F. Marsiglio and J. P. Carbotte, Phys. Rev. B 33, 6141 (1986).
- <sup>11</sup>B. Mitrović, H. G. Zarate, and J. P. Carbotte, Phys. Rev. B 29, 184 (1984).
- <sup>12</sup>G. B. Arnold, Phys. Rev. B 18, 1076 (1978).
- <sup>13</sup>G. B. Arnold, J. Zasadzinski, and E. L. Wolf, Phys. Lett. 69A, 136 (1978).
- <sup>14</sup>J. Zasadzinski, W. K. Schubert, E. L. Wolf, and G. B. Arnold, in Superconductivity in d- and f-Band Metals, edited by H. Suhl and M. B. Maple (Academic, New York, 1980), p. 159.
- <sup>15</sup>H. K. Leung, J. P. Carbotte, D. W. Taylor, and C. R. Leavens, Can. J. Phys. 54, 1585 (1976).
- '6P. Tomlinson and J. P. Carbotte, Phys. Rev. B 13, 4738 (1976).
- <sup>17</sup>W. H. Butler, in Ref. 14, p. 443.
- $^{18}F.$  J. Pinski, P. B. Allen, and W. H. Butler, J. Phys. (Paris) Colloq. 39, C6-472 (1978).
- <sup>19</sup>W. Weber, Physica B 126, 217 (1984).
- <sup>20</sup>H. Rietschel, H. Winter, and W. Reichart, Phys. Rev. B 22, 4284 (1980).
- Z'J. G. Bednorz and K. A. Miiller, Z. Phys. 8 64, 189 (1986).
- M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. 58, 908 (1987).
- <sup>23</sup>J. Z. Sun, D. J. Webb, M. Naito, K. Char, M. R. Hahn, J. W.

P. Hsu, A. D. Kent, D. B. Mitzi, B. Oh, M. R. Beasley, T. H. Geballe, R. H. Hammond, and A. Kapitulnik, Phys. Rev. Lett. 58, 1574 (1987).

- $24R$ . J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. 58, 1676 (1987).
- <sup>25</sup>P. W. Anderson, Science 235, 1196 (1987).
- $^{26}$ A. Alexandrov and J. Ranninger, Phys. Rev. B 23, 1796 (1981).
- $27B.$  K. Chakraverty, J. Phys. Lett. 40, L99 (1979); P. Prelovsek, T. M. Rice, and F. C. Zhang (unpublished).
- <sup>28</sup>D. Allender, J. Bray, and J. Bardeen, Phys. Rev. B 7, 1020 (1973).
- Z9W. Weber, Phys. Rev. Lett. 58, 1371 (1987).
- M. Schossmann, F. Marsiglio, and J. P. Carbotte, Phys. Rev. 8 36, 3627 (1987).
- 3<sup>1</sup>D. Rainer and G. Bergmann, J. Low Temp. Phys. 14, 501 (1974).
- <sup>32</sup>P. B. Allen and B. Mitrović, in Theory of Superconducting  $T_c$ , Solid State Physics, Vol. 37, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1982), p. l.
- 33P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).
- s4G. Grimvall, J. Phys. Chem. Solids 29, 1221 (1968).
- <sup>35</sup>G. Grimvall, Phys. Condens. Matter 9, 283 (1969).
- $36V$ . Z. Kresin and G. O. Baitsev, Zh. Eksp. Teor. Fiz. 74, 1886 (1978) [Sov. Phys. JETP 97, 983 (1979)].
- <sup>37</sup>J. M. Coombes and J. P. Carbotte, J. Low Temp. Phys. 63, 431 (1986).
- 38F. Marsiglio and J. P. Carbotte, Solid State Commun. 63, 419 (1987).
- $39D$ . J. Scalapino, in Ref. 2, p. 541.
- <sup>40</sup>J. P. Carbotte, F. Marsiglio, and B. Mitrović, Phys. Rev. B 33, 6135 (1986).
- <sup>41</sup>In the work of Refs. 39, a delta function was used for  $a^2F(\omega)$ and it was not possible for numerical reasons to go to the lowest of frequencies. Since then this has become possible and we find a maximum  $2\Delta_0/k_B T_c \approx 12$  for the case  $\mu^* = 0.0$ occurring in the limit as the delta-function frequency approaches zero.