Thermodynamic and other properties of a high-T_c excitonic superconductor

F. Marsiglio and J. P. Carbotte
Physics Department, McMaster University, Hamilton, Ontario, Canada L8S 4M1
(Received 22 June 1987)

We have calculated the isotope effect, the thermodynamics, and the gap (Δ_0) to critical temperature (T_c) ratio for an excitonic superconductor. We consider the possibility that some contribution to the pairing interaction is due to the electron-phonon interaction. As the amount of electron-phonon contribution is increased from zero, the thermodynamic ratios start deviating from Bardeen-Cooper-Schrieffer behavior, but in the opposite direction from conventional strong-coupling superconductors. The isotope effect increases very slowly from zero and $2\Delta_0/k_BT_c$ remains close to 3.54 for a significant range of phonon coupling strength.

The mechanism responsible for the high-temperature (T_c) superconductivity observed in the oxides is a subject of great current interest.[1-5] Strong evidence against the conventional electron-phonon mechanism, which has been so successful in relating the properties of the most well-studied superconductors[6-13] except for the heavy-fermion and perhaps the organic superconductors, is the recent observation of no isotope effect in $Ba_2YCu_3O_7$ and $Ba_2EuCu_3O_7$.[14] This favors a purely electronic mechanism. Other evidence against a conventional mechanism is the recent confirmation from optical absorption measurements that the gap-to-critical-temperature dimensionless ratio $2\Delta_0/k_BT_c$ is not very much larger than the BCS value of 3.54 in both $La_{1.85}Sr_{0.15}CuO_4$ (Ref. 15) and in $YBa_2Cu_3O_{7-\delta}$.[16] Theoretical calculations based on the electron-phonon spectral density calculated by Weber,[1] which assumes a pure phonon mechanism for the superconductivity of the 36 K superconductor $La_{1.85}Sr_{0.15}CuO_4$, give $2\Delta_0/k_BT_c=5.3$ (Ref. 17) which disagrees with the far-infrared measurements. Having said this, it is important to realize that several tunneling measurements[18-21] in this same compound give much larger values of $2\Delta_0/k_BT_c$ than does the infrared. At present there is, however, large differences between the tunneling results obtained by the various groups, and one group[19] finds a range of gaps with highest value no more than 4.5 which would favor a modest average value of the ratio $2\Delta_0/k_BT_c$. The situation for $YBa_2Cu_3O_{7-\delta}$ is not as well studied, but preliminary theoretical estimates[22] based on the assumption that its phonons can be characterized by the same average Allen-Dynes[13] frequency ω_{1n} as for La-Sr-Cu-O, give a value of $2\Delta_0/k_BT_c$ near 7. Even higher values are obtained should there be some softening over the La-Sr-Cu-O case. These results are in sharp disagreement with the far infrared and suggest strongly that a new mechanism is involved. An exciton exchange[23] mechanism with frequencies around one eV would explain the infrared data and the isotope effect. On the other hand, it may well be that the phonons[1,2,23] also play some role and we want to address here the question of thermodynamics and other properties when both phonons and excitons contribute to the superconductivity.

It is not a primary aim here to give a detailed description of the nature of the excitons that might be present in the high-T_c oxides. Varma, Schmitt-Rink, and Abrahams[5] have recently studied this problem and suggest that a charge-transfer mechanism may be operative in these ionic metals and estimate a characteristic energy of about $\frac{1}{2}$ eV. Recently optical-absorption measurements[24] have revealed the existence of electronic excitations in $YBa_2Cu_3O_{7-\delta}$, with $T_c=96$ K, around 0.4 eV. Also, preliminary results[24] indicate that these excitations are greatly suppressed as the oxygen content is reduced and T_c is rapidly depressed towards zero.

While there is, at present, no formal derivation of the changes that are needed to the Eliashberg equations so as to include in a rigorous way the excitons, we propose to follow the work of Allender, Bray, and Bardeen.[23] These authors argue that, to a first approximation, it is sufficient to add to the usual electron-phonon spectral density another contribution at higher frequencies which represents the exchange of excitons. Worries about the lack of a Migdal theorem[5] in the exciton case are certainly justified.[25,26] However, they go beyond the scope of this work, which can be thought of as semiphenomenological in that the exciton part of the Eliashberg kernels will be modeled, leaving the question of its calculation from fundamentals to others.

In this work the total spectral density $\alpha_T^2F(\omega)$ describing both phonons and exciton exchange will be taken as the sum of two δ functions at frequencies $\omega_{ph}=8$ meV and $\omega_{ex}=500$ meV with weight $\frac{1}{2}\lambda_{ph}\omega_{ph}$ and $\frac{1}{2}\lambda_{ex}\omega_{ex}$, respectively. Here $\lambda_{ph}(\lambda_{ex})$ is the electron-phonon (electron-exciton) electronic mass renormalization. Thus we have

$$\alpha_T^2F(\omega)=\tfrac{1}{2}\lambda_{ph}\omega_{ph}\delta(\omega-\omega_{ph})+\tfrac{1}{2}\lambda_{ex}\omega_{ex}\delta(\omega-\omega_{ex}) ,$$

which enters the kernel in the Eliashberg equations[7-11] for the Matsubara pairing energy $\tilde{\Delta}(i\omega_n)$ and renormalized frequencies $\tilde{\omega}(i\omega_n)$ with $i\omega_n=i\pi T(2n-1)$, $n=0, \pm1, \pm2, \ldots$. Finally, the Coulomb pseudopotential describing the repulsive part of the electron-electron interaction will be arbitrarily fixed at $\mu^*=0.1$.

Using the linearized version of the Eliashberg equations[7-12] valid near the critical temperature T_c we can fix the ratio of λ_{ex} to the total $\lambda_{tot}=\lambda_{ex}+\lambda_{ph}$ by requiring that T_c be equal to 96 K. Results are then presented as a function of the only remaining parameter $\lambda_{ex}/\lambda_{tot}$.

We start with the isotope effect shown in Fig. 1 (left-hand scale). By definition $\beta \equiv |d\ln T_c/d\ln M|$, where M is the mass of the ions involved. In the case of compounds such as La-Sr-Cu-O and Y-Ba-Cu-O the situation is much more complex than the one which we have just described, since partial isotope effects can be defined for each component element.[27] In the isotope effect measurements previously mentioned only the oxygen ^{16}O is replaced by the higher-mass isotope ^{18}O leaving the other elements unchanged.[14] Here we neglect these complications and consider only changing the average mass by a constant percentage so as to keep things simple. Figure 1 shows that β as a function of $\lambda_{ex}/\lambda_{tot}$ remains near zero for a large range below the pure exciton case which is the limit $\lambda_{ex}/\lambda_{tot}=1$. Even when $\lambda_{ph}=1$, β is still small at value 0.054. At $\lambda_{ph}=3.75$, which is already larger than the values of λ_{ph} observed in conventional superconductors, β is still only 0.17. Thus, even when there is considerable weight given to the phonon contribution in λ_{tot}, the isotope effect remains small in our model. Of course, in the limit of no exciton, i.e., pure electron-phonon coupling ($\lambda_{ex}/\lambda_{tot}=0$), β is very near $\frac{1}{2}$. The very small deviation from $\frac{1}{2}$ is due entirely to the presence of μ^*.

It is important to realize some important properties of our model. First, to get $T_c=96$ K with a $\mu^*=0.1$ and no phonon contribution $\lambda_{ph}=0$, we need a value of $\lambda_{ex}=0.518$ assuming $\omega_{ex}=0.5$ eV. This is within the range of possible values suggested in the work of Allender, Bray, and Bardeen.[23] Of course, the results of Ref. 23 do not apply directly to the ionic metals considered here since they dealt with slabs of metals alternating with a conventional semiconductor. No estimate of the size of the λ_{ex} is provided in the work of Varma *et al.*[5] based on their idea of an excitonic charge-transfer excitation intrinsic to the oxides. Second, for the pure phonon case we need $\lambda_{ph}=41$, which is completely unrealistic judging by the values that are observed in conventional systems where $\lambda_{ph}\lesssim 3.0$.[10,11] Even if we allow for the fact that the screening is much reduced in the oxides compared with metals, such large values of λ_{ph} seem unlikely. The required value of λ_{ph} could be reduced considerably if the value of ω_{ph} is increased. However, it is only if the coupling is assumed to be predominantly with phonons that have a frequency one order of magnitude greater than those considered here that λ_{ph} can be reduced to near the conventional range. Finally, we note that for $\lambda_{ph}=3.75$, the mass enhancement required for the excitonic excitation is 0.485 compared with the pure excitonic value of 0.518. Thus, even when λ_{ph} takes on realistic values in our model, the excitonic excitations must be almost as large as is required for a pure exciton mechanism.

Results for twice the gap Δ_0 to the critical temperature T_c dimensionless ratio $2\Delta_0/k_BT_c$ vs $\lambda_{ex}/\lambda_{tot}$ are given in Fig. 1 (right-hand scale). We see that the rise in this ratio from a BCS value of 3.54 at $\lambda_{ex}/\lambda_{tot}=1$ (pure excitonic case) is very gradual and that for $\lambda_{ph}=1$ which corresponds to λ_{ex}/λ_T roughly equal to 0.5, it is still no more than 4 and within the range of the present far-infrared measurements. This case is realistic considering the existence of several band-structure calculations indicating a λ_{ph} in the oxides of order 2.5.[1,2] Even accounting for a serious overestimate of λ_{ph} in the existing calculations, it is likely that a significant λ_{ph} exists in the oxides.

It is important to realize that for the realistic case of $\lambda_{ph}=1.0$, the phonons contribute only about 5–8 K to the critical temperature. This can be estimated in two ways. First λ_{ex} can be set equal to zero with the result that $T_c=7.6$ K. Alternatively, λ_{ph} can be set to zero and T_c

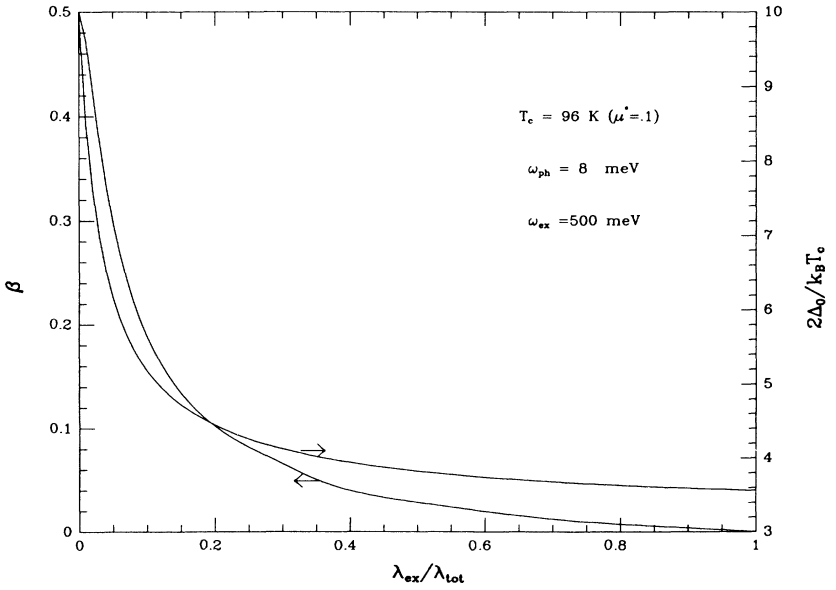

FIG. 1. The isotope effect coefficient $\beta \equiv |d\ln T_c/d\ln M|$ (left-hand scale) with M the average ionic mass in the system as a function of $\lambda_{ex}/\lambda_{tot}$. Here λ_{ex} is the electronic mass enhancement factor for excitonic exchange alone while λ_{tot} is the total. It consists of the sum of the phonon (λ_{ph}) and exciton (λ_{ex}) part. The right-hand scale applies to the ratio of the gap Δ_0 to critical temperature $2\Delta_0/k_BT_c$.

recalculated for a pure exciton mechanism. This gives $T_c = 90.5$ K instead of 96 K for the combined mechanism. While the phonons do not have a strong influence on T_c in this instance, they are sufficient to change $2\Delta_0/k_BT_c$ from the weak-coupling value of 3.54 to a modest strong-coupling value of 4.0, or more.

In Fig. 2 (left-hand scale) we show results for the specific-heat jump at T_c $[\Delta C(T_c)]$ normalized to its normal-state value of $\gamma(0)T_c$ with $\gamma(0)$ the zero temperature Sommerfeld constant. Our results are striking and quite unexpected from the naive extrapolation to the present case, of the known results for phonon superconductors. In this well-studied case $\Delta C(T_c)/\gamma(0)T_c$ increases (as ω_{1n} is lowered) to values much larger than its weak-coupling BCS value of 1.43. The BCS value applies only to the limit when the characteristic phonon energy ω_{1n} is much larger than T_c. In our case, however, ω_{1n} and T_c are of the same order, and Marsiglio, Akis, and Carbotte[22] have found that in this very strong-coupling regime a pure phonon superconductor can have a jump which is much less than the BCS value.[22] Here we have the same effect even though the high T_c is not due to the electron-phonon interaction but rather to the exciton. Specifically, for $\lambda_{ph}=1$, $\Delta C(T_c)/\gamma(0)T_c$ is now less than 1. It is clear that any estimate of the Sommerfeld $\gamma(0)$ based on the measured value of $\Delta C(T_c)$ and a BCS relation $\Delta C(T_c)/\gamma(0)T_c = 1.43$ will underestimate $\gamma(0)$.

Similar results hold for the other dimensionless ratio $\gamma(0)T_c^2/H_c^2(0)$, with $H_c(0)$ the zero temperature thermodynamic critical magnetic field. This is displayed in Fig. 2 (right-hand scale) where we see that $\gamma(0)T_c^2/H_c^2(0)$ becomes *larger* than the BCS value of 0.169 as we add phonons to the pure excitonic superconductor. This is opposite to the observation in conventional strong-coupling materials[11] for which this ratio is seen to decrease. Again we stress that for the usual case T_c/ω_{1n} is small, of the order or less than 0.25, while in the present case T_c/ω_{1n} is of order 1, i.e., the critical temperature has reached a value which is of the same magnitude as a typical phonon energy. In this regime old intuitions do not hold.

In summary, we have calculated the thermodynamic properties of an excitonic superconductor with high T_c including as well a variable amount of electron-phonon interaction which adds on to the exciton part. The important ratio of twice the gap Δ_0 to the critical temperature was also considered along with the average isotope effect in a model for which all the masses are changed by the same percentage amount. For the pure excitonic case all dimensionless ratios take on their BCS value and the isotope effect is zero. As some phonons are included, the isotope effect and $2\Delta_0/k_BT_c$ are found to increase slightly but very slowly. In terms of the parameter $\lambda_{ex}/\lambda_{tot}$ where λ_{ex} is the excitonic contribution to the total (λ_{tot}) electron mass renormalization, we find that for a $\lambda_{ex}/\lambda_{tot}=0.35$, the necessary value of λ_{ph} is 1.0 (possibly a conservative value for the oxides) while $2\Delta_0/k_BT_c \cong 4.0$ and the isotope effect coefficient $\beta=0.054$ is still very small. At the same time, the jump at T_c in the specific heat normalized to its normal-state value, has dropped to a value below 1. This result was not at all expected and is opposite from what is observed for conventional strong-coupling superconductivity in which the jump is always greater than its BCS limit of 1.43. A similar situation is found to hold for $\gamma(0)T_c^2/H_c^2(0)$, which becomes greater than 0.2 for the same parameters as described above. This is greater than the BCS value of 0.169, whereas it is always smaller in the case of conventional strong couplers. These unusual results are due to the fact that even for modest values of λ_{ph}

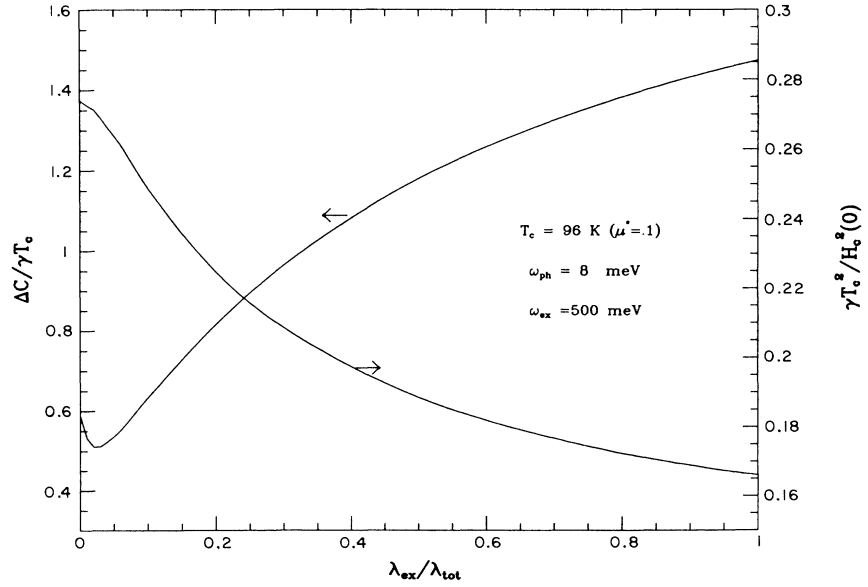

FIG. 2. The dimensionless ratio $[\Delta C(T_c)/\gamma(0)T_c]$ (left-hand scale) of the specific-heat jump at T_c $[\Delta C(T_c)]$ normalized to the normal-state value $\gamma(0)T_c$ with $\gamma(0)$ the Sommerfeld constant. On the horizontal axis is the ratio of the exciton contribution to the electronic mass renormalization (λ_{ex}) to the total $\lambda_{tot}=\lambda_{ex}+\lambda_{ph}$ where λ_{ph} is the phonon part. The right-hand scale applies to the dimensionless ratio $\gamma(0)T_c^2/H_c^2(0)$ where $H_c(0)$ it the zero temperature thermodynamic critical magnetic field.

we have entered the very strong-coupling regime described by Marsiglio *et al.*[22] for the pure electron-phonon case. In this regime $T_c(=96\ \mathrm{K})$ is of the same order as a phonon energy ($\omega_{1n}=8$ meV), and no expansion is possible in powers of T_c/ω_{1n} with BCS theory resulting for $T_c/\omega_{1n}\rightarrow 0$.

To close, we stress once more that, in this paper, we have not directly concerned ourselves with the precise nature of the excitons involved. Rather we have taken them as given since their existence seems to be indicated in experiments. We refer the reader to the work of Varma *et al.*[5] for a possible theoretical model. Also, we have not been directly concerned with modifications to the strong-coupling Eliashberg equations which might be required in a rigorous mathematical treatment of the exciton mechanism for which there is no Migdal theorem. Here, we have simply assumed that, to a first approximation, these complications can all be lumped into a redefinition of the exciton kernel. In our approach, we model this kernel and do not try to calculate it from first principles. This would, in any case, be difficult and quite a distinct problem from the one addressed here. While our description of the exciton exchange mechanism is in some sense crude, it is more sophisticated than the original square-well model for the pairing interaction which was so successfully employed in BCS theory. We plan to study other cases and different physical properties in another publication.

This research was supported in part by the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank our colleagues, D. Bonn, J. Greedan, D. Tanner, T. Timusk, M. Schossmann, and C. Stager for many clarifying conversations.

[1]W. Weber, Phys. Rev. Lett. **58**, 1371 (1987).
[2]W. E. Pickett, H. Krakauer, D. A. Papaconstantopoulos, and L. L. Boyer, Phys. Rev. B **35**, 7252 (1987).
[3]P. W. Anderson, Science **235**, 1196 (1987).
[4]P. Prelovsek, T. M. Rice, and F. C. Zhang, J. Phys. C **20**, L229 (1987).
[5]C. M. Varma, S. Schmitt-Rink, and E. Abrahams (unpublished).
[6]J. P. Carbotte, Sci. Prog. (London) **71**, 329 (1987).
[7]D. Rainer and G. Bergmann, J. Low. Temp. Phys. **14**, 501 (1974).
[8]J. M. Daams and J. P. Carbotte, J. Low Temp. Phys. **43**, 263 (1981).
[9]B. Mitrović, E. Schachinger, and J. P. Carbotte, Phys. Rev. B **29**, 6187 (1984).
[10]B. Mitrović, H. G. Zarate, and J. P. Carbotte, Phys. Rev. B **29**, 184 (1984).
[11]F. Marsiglio and J. P. Carbotte, Phys. Rev. B **33**, 6141 (1986).
[12]P. B. Allen and B. Mitrović, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1981), Vol. 37, p. 1.
[13]P. B. Allen and R. C. Dynes, Phys. Rev. B **12**, 905 (1975).
[14]B. Batlogg, R. J. Cava, A. Jayaraman, R. B. van Dover, G. A. Kourouklis, S. Sunshine, D. W. Murphy, L. W. Rupp, H. S. Chen, A. White, K. T. Short, A. M. Mujsce, and E. A. Reitman, Phys. Rev. Lett. **58**, 2333 (1987).
[15]D. A. Bonn, J. E. Greedan, C. V. Stager, T. Timusk, M. G. Doss, S. L. Herr, K. Kamaras, C. D. Porter, D. B. Tanner, J. M. Tarascon, W. R. McKinnon, and L. H. Greene, Phys. Rev. B **35**, 8843 (1987).
[16]D. A. Bonn, J. E. Greedan, C. V. Stager, T. Timusk, M. Doss, S. Herr, K. Kamaras, and D. A. Tanner, Phys. Rev. Lett. **21**, 2249 (1987).
[17]M. Schossmann, F. Marsiglio, and J. P. Carbotte, this issue, Phys. Rev. B **36**, 3627 (1987).
[18]M. E. Hawley, K. E. Gray, D. W. Capone, and D. G. Hinks, Phys. Rev. B **35**, 7224 (1987).
[19]J. R. Kirtley, C. C. Tsuei, S. I. Park, C. C. Chi, J. Rozen, and M. W. Shafer, Phys. Rev. B **35**, 7216 (1987).
[20]S. Pan, K. W. Ng, A. L. de Lozanne, J. M. Tarascon, and L. H. Greene, Phys. Rev. B **35**, 7220 (1987).
[21]N. Naito, D. T. E. Smith, M. D. Kirk, B. Oli, M. R. Hahn, K. Chai, D. B. Mitzi, J. Z. Sun, D. J. Webb, M. R. Beasley, O. Fischer, T. H. Geballe, R. H. Hammond, A. Kapitutnik, and C. F. Quate, Phys. Rev. B **35**, 7228 (1987).
[22]F. Marsiglio, R. Akis, and J. P. Carbotte (unpublished).
[23]A. Allender, J. Bray, and J. Bardeen, Phys. Rev. B **7**, 1020 (1973).
[24]D. Bonn, D. Tanner, and T. Timusk (private communication).
[25]M. Grabowski and L. J. Sham, Phys. Rev. B **29**, 6132 (1984).
[26]J. C. Inkson and P. W. Anderson, Phys. Rev. B **8**, 4429 (1973).
[27]D. Rainer and F. J. Culetto, Phys. Rev. B **19**, 2540 (1979).