# Optical Evidence of an Electronic Contribution to the Pairing Interaction in Superconducting $Tl_2Ba_2Ca_2Cu_3O_{10}$

M. J. Holcomb,*,† J. P. Collman,* and W. A. Little†

*Departments of Chemistry and Physics, Stanford University, Stanford, California 94305*

(Received 20 May 1994)

We report the results of a study of the temperature-dependent thermal difference reflectance spectra of $Tl_2Ba_2Ca_2Cu_3O_{10}$. At temperatures below $T_c$, a feature emerges in the spectra with an integrated amplitude that scales as $\Delta_0^2(T)$, where $\Delta_0(T)$ is the temperature-dependent superconducting gap. The temperature dependence and location of this feature can be described by an Eliashberg model with a coupling function that includes both an electron-phonon interaction *and* an interaction located at $\sim 1.6$ eV. We find remarkably good agreement between theory and experiment based upon this description of the superconducting state.

PACS numbers: 74.25.Gz, 74.20.Mn, 74.72.Fq

The most fundamental problem of high-$T_c$ superconductivity is the determination of the mechanism responsible for the high critical temperatures observed in the cuprate superconductors. If the superconducting state of the cuprates can be described by Eliashberg theory then the problem is one of the precise experimental determination of the energy dependence of the electron-boson coupling function which mediates the pairing of the electrons. Other theoretical models can be expected to contain analogous information on the pairing mechanism. This information is usually obtained by a measurement of the conductance vs voltage of a normal/insulator/superconductor ($N/I/S$) tunnel junction [1]. Such studies have enjoyed much success in conventional low-temperature superconductors, but there has been little success with the cuprates [2]. Though the magnitude of the superconducting gap edge [3], $\Delta(\Delta(\omega = 0), T \approx 0) \equiv \Delta_0$, has been determined with limited accuracy [4], it is the small variations in the tunneling conductance at energies well above the gap edge that contain information on the nature of the pairing interaction [1]. These data are inconclusive and have not revealed the nature of the pairing interaction in the cuprates to date.

The energy dependence of the electron-boson coupling function can also be obtained from the optical properties of a superconductor [5–8]. The transmittance, or reflectance, of a superconductor is a measure of both a superconducting joint density of states function and a joint coherence factor function which results from the coherent nature of the superconducting state [6,9]. In principle, by measuring the changes in the reflectance, or transmittance, of a material when it becomes superconducting it is possible to calculate the electron-boson coupling function responsible for the superconductivity, using the same inversion techniques that have been used so effectively in tunneling experiments [10]. Like $N/I/S$ tunneling, this approach has a long history in the study of conventional low-temperature superconductors [11–19], but because of the inferior signal-to-noise ratios in these measurements as compared to tunneling measurements and the numerical complexity of the inversion process [17], no rigorous inversion of optical data has been attempted. More recently, significant changes in the optical properties of the cuprate superconductors have been measured over a wide range of energies as the materials enter the superconducting state [20–26]. In most of these studies, an approximate optical gap $2\Delta_0$ has been determined, but again, no rigorous inversion of the optical data has been attempted. Like tunneling measurements, the important information on the detailed nature of the pairing interaction lies in the small variation of the optical properties of the superconductor at energies well above $2\Delta_0$. The difficulty with this measurement is that the changes in the optical properties of the material are of order $[\Delta(\omega)/\omega]^2$, where $\Delta(\omega)$ is the complex energy dependent superconducting gap function [27]. In a standard reflectance measurement these changes may be as small as 0.01% of the total reflectance and thus will be hidden in the experimental linewidth.

We have recently developed an optical technique of sufficient sensitivity to observe such effects. The technique measures the difference in the reflectivity of a sample at two temperatures as a function of photon energy and uses digital averaging and thermal cycling to minimize the effects of $1/f$ noise. The details of the operation and performance of this thermal difference (TD) spectrometer have been described elsewhere [28]. We have been able to observe temperature induced changes in the relative reflectance as small as 0.005% reliably and reproducibly and can do so over a temperature range of 80 to 340 K. We have used it to study the temperature-dependent TD spectra of a thin film $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223) sample at photon energies of 0.3 to 5.3 eV. The data are collected by first measuring the difference in the sample's reflectance at $T + 5$ K and $T - 5$ K and then dividing this quantity by the average value of the reflectance at $T$. Details of the sample preparation and characterization have been described previously [29]. The $T_c$ of the Tl-2223 sample was measured to be $\sim 120$ K.

In Fig. 1 we plot the TD spectrum of Tl-2223 collected at 300 K from 0.3 to 5.3 eV. The spectrum is dominated

 0031-9007/94/73(17)/2360(4)$06.00 

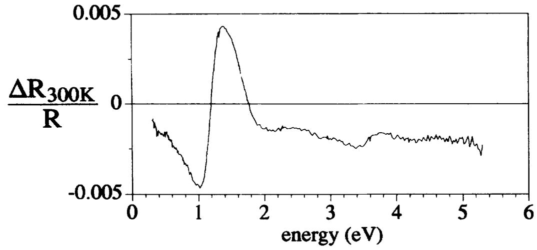


FIG. 1. The thermal difference (TD) reflectance spectrum of $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223) at 300 K from 0.3 to 5.3 eV. The spectrum was collected by measuring the difference in the reflectance of the sample at $T + \Delta T$ and $T - \Delta T$ and dividing by the average value of the reflectance at both of these temperatures. $\Delta T = 5$ K in all of these experiments.

by a derivativelike structure centered at about 1.25 eV, which results from temperature induced changes in the scattering rate and the plasma frequency of the material. The screened plasma energy [30] is approximately the energy of the *most negative point* of the large derivative structure in the TD spectrum [31]. This lies at about 1.1 eV in agreement with the room temperature reflectance and ellipsometric measurements of Bozovic *et al.* [32]. In Fig. 2(a) we plot the TD spectra of the same sample at 195, 175, 155, and 135 K from 0.3 to 3.0 eV. The structure in these spectra has the same form as the 300 K spectrum. We observe that the amplitude of the structure in the TD spectra decreases regularly as the temperature is lowered to 135 K. In Fig. 2(b) we plot the TD spectra at 135, 125, 115, 105, and 95 K. As the temperature is lowered below the $T_c$ of the sample ($\sim$120 K) a new structure emerges in the TD spectra. The amplitude is a maximum at 115 K and gradually decreases with decreasing temperature. The amplitude of the thermal difference spectra varies approximately linearly with temperature *above* $T_c$. This allows us to subtract the extrapolated normal state thermal difference response from the spectra collected *below* $T_c$. In Fig. 2(c) we plot the resulting difference spectra at 145, 125, 115, 105, and 95 K after subtracting from each of the spectra the spectrum collected at 135 K multiplied by a factor $T/135$ to correct for the linear temperature-dependent amplitude of the normal state thermal difference spectrum. For temperatures above 135 K, where no excursion into the superconducting state occurs, this difference signal lies approximately at zero over the entire energy range, while at temperatures below 125 K, a significant structure emerges in the spectra.

Since the normal state thermal difference response of the material has been removed in the subtraction, the data in Fig. 2(c) represent the normalized difference in the reflectance of the material taken between $T + 5$ and $T - 5$ K due to the onset of superconductivity. By then adding these data collected at 10 K intervals we obtain spectra that correspond to the *total* change in the reflectance of the material due to the onset of superconductivity at 120 K. This is equivalent to a numerical integration of the normalized thermal derivative spectra in Fig. 2(c) over temperature from 135 K down to $T$. We then take the absolute value of the integral over energy, of these *temperature-integrated* spectra, as a measure of the total strength of the emerging structure with temperature. This procedure is shown graphically as the inset in Fig. 3, where the area of the shaded region is taken as a measure of the strength of the structure which emerges at temperatures below the sample's critical temperature. These data are plotted as filled circles in Fig. 3 and fitted to the functional forms of $\Delta_0(T)$ and $\Delta_0^2(T)$, where $\Delta_0(T)$ represents the temperature dependence of the superconducting gap edge in the weak

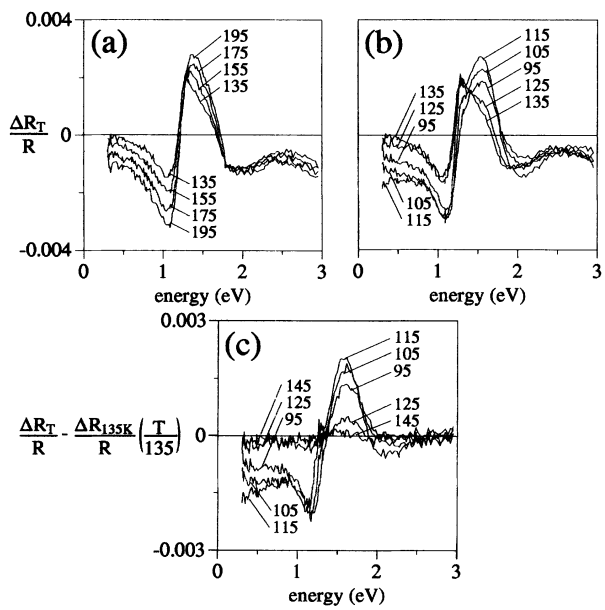


FIG. 2. The temperature-dependent TD reflectance spectra of Tl-2223. (a) The normal state TD spectra at 195, 175, 155, and 135 K. (b) TD spectra of Tl-2223 at 135, 125, 115, 105, and 95 K. The $T_c$ of this sample is approximately 120 K. (c) The TD spectra of Tl-2223 after subtracting the temperature-dependent normal state response from the data.

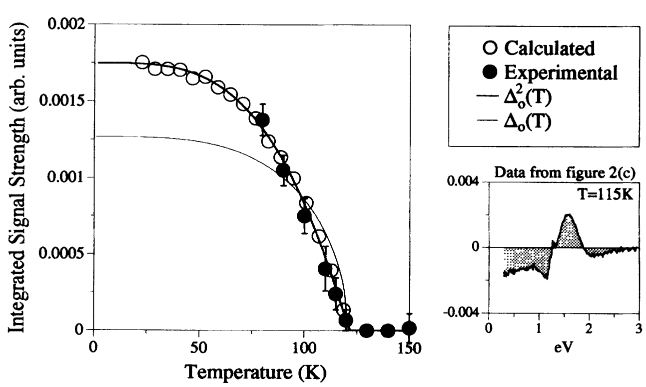


FIG. 3. Amplitude of the normalized, temperature integrated TD spectra from 150 to 80 K, ● experimental, ○ theoretical, with $T_c \sim 120$ K. The shaded area of spectrum in the inset, taken from Fig. 2(c), represents the total change of the sample's reflectance when the material becomes superconducting.

coupling limit [33]. Remarkably good agreement is found with a temperature variation proportional to $\Delta_0^2(T)$, but not with $\Delta_0(T)$.

It is convenient to express these data as the ratio of the reflectivities of the material in the superconducting and normal state $R_S/R_N$. It can be shown that the TD data collected at $T = 115$ K, with the normal state thermal difference response removed [Fig. 2(c)], are directly related to $R_S/R_N$ of the sample at $T = 110$ K. In Fig. 4(a) we plot the resulting $R_S/R_N$ of the Tl-2223 at 110 K.

The structure in the TD spectra is the result of the temperature variation of the complex dielectric function of the material. In metals, this temperature variation is determined by temperature induced changes of both the electron density and scattering rate [31]. Structural studies of a number of the cuprate superconductors indicate that, though there are subtle structural changes in the material's unit cell at temperatures in the neighborhood of $T_c$ ($\pm 20$ K), there are no discontinuous changes in the volume of the unit cell *at* $T_c$ [34–38]. This is confirmed by our measurements of the energy of the plasma frequency, which remained virtually unchanged with temperature. Thus, we interpret our data as resulting from changes in the scattering rate which arise from the growth of $\Delta(\omega)$ at $T < T_c$. This is equivalent to the strong coupling extension of Mattis-Bardeen theory [39] first developed by Nam [5,12].

We follow Nam [12] and assume a Drude-like [30,40] form for the normal state optical conductivity and express the scattering time in the superconducting state, $\tau_S$, as a function of both the normal state scattering time $\tau_N$ and an integral involving $\Delta(\omega)$. This integral [6] consists of both a joint density of states function and a function which results from case II coherence factors appropriate for electromagnetic absorption [9]. The normal state reflectivity at energy $\omega$ can be modeled by taking the normal state scattering rate $1/\tau_N$ equal to $0.6\omega$ [40] and using the values obtained by Bozovic *et al.* [32] on Tl-2223 for the bare plasma frequency ($\sim 2.6$ eV) and the high frequency dielectric constant ($\sim 4.5$). The change in the mass renormalization is small for energies between 0.3 and 5.3 eV and is neglected. These parameters yield

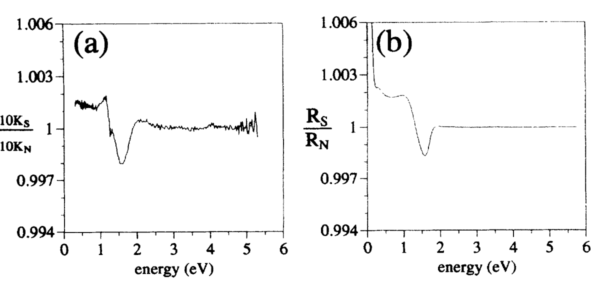


FIG. 4. (a) The $R_S/R_N$ of Tl-2223 at 110 K from 0.3 to 5.3 eV obtained with the TD spectrometer. (b) The calculated $R_S/R_N$ of an Eliashberg superconductor with a coupling function which consists of both an electron-phonon component *and* an interaction centered at 1.6 eV.

a normal state Drude-like reflectivity which is closely similar to that observed. To calculate the reflectivity in the superconducting state, we *guess* a trial electron-boson coupling function and solve the Eliashberg integral equations to obtain $\Delta(\omega)$. We then solve for $\tau_S$, calculate the reflectivity of the material in the superconducting state, and compare it with the observed data. Changes are then made to the trial function until agreement is obtained. In these calculations, the real and imaginary parts of $\Delta(\omega)$ are related by causality. We find they must be calculated to four decimal places in order to satisfy the sum rules with the appropriate accuracy necessary to calculate the structure in the reflectance ratio.

Our calculations reveal that the measured structure near 1.5 eV in Fig. 4(a) cannot be obtained if the electron pairing is mediated by phonons alone, assuming the phonon energies are less than 100 meV. This result is consistent with the fact that, even in the classic experiments [11,13] and calculations [12] of the optical response of lead, the real part of the optical conductivity in the superconducting state approaches that of the normal state at energies approximately 5 times the energies of the phonons that mediate the pairing. Thus, *irrespective* of the strength of the electron-phonon coupling in Tl-2223, our results cannot be explained in terms of a model that only involves phonons of energy less than 100 meV. The electron-phonon coupling function, and the resulting structure in $\Delta(\omega)$, is too low in energy to alter the reflectance of the material in the superconducting state in the near-infrared and visible region of the spectrum.

Reasonable agreement between the calculations and our data is obtained by adding to the electron-phonon coupling function an additional coupling interaction centered at approximately 1.6 eV, with a half-width of 100 meV. This is shown in Fig. 4(b). Details of the specific form of the electron-boson interaction and the procedures used in the calculations will be given in a later paper.

The temperature dependence of the structure in the reflectance spectra can also be calculated, assuming a critical temperature of 120 K and a weak coupling temperature dependence for $\Delta(\omega)$ [33]. The results are shown in Fig. 3, where the open circles represent the *calculated* temperature-dependent amplitude of the thermal difference optical structure based upon the existence of the additional electron interaction at 1.6 eV. Again, remarkable agreement between experiment and theory is found, for the amplitude of the calculated structure clearly fits the functional form of the weak coupling $\Delta_0^2(T)$.

Fugol *et al.* [26] have studied the optical absorption of two high $T_c$ superconductors at 1.7 and 1.9 eV and found a similar change upon entering the superconducting state. They interpret their data in terms of a model involving transitions to a narrow hole band near the Fermi energy within which a superconducting gap opens yielding a decrease in absorption proportional to $\Delta^2(T)$. Their model, however, predicts an increase in absorption of similar magnitude proportional to $T^2$ at $T > T_c$ which is not observed, nor can it explain the sign reversal of the differential absorption at certain energies as implied in Fig. 2.

Our results strongly suggest that the superconductivity in the Tl-2223 material can be described within the Eliashberg formalism and that the pertinent electron coupling function consists of an electron-phonon interaction *plus* a previously unobserved interaction at approximately 1.6 eV. We estimate the error in the precise location of the high energy coupling function to be $\pm 0.15$ eV because of the uncertainty in the normal state optical properties and the effects of anisotropy on $\Delta(\omega)$ and $\tau_N$.

Having established the energy scale of the interaction believed to be responsible for the high critical temperature of Tl-2223, we may speculate on its microscopic origin. Optical studies of a variety of the cuprate materials all show an optical transition at approximately 1.7 eV [41–44]. This transition has been tentatively designated as a $d^9$-$d^{10}\underline{L}$ charge transfer associated with the extended Cu-O network common to all these materials [43]. Because of the close proximity of this to the energy of the feature we observe, we suggest that it provides the interaction responsible for the high temperature superconductivity. We, thus, *predict* that this interaction will be present at this energy for all the high temperature superconductors that possess the extended Cu-O network, and that the distribution of critical temperatures among these materials is not determined by differences in the energy of this interaction but by the *strength* of the coupling to this high energy interaction.

In conclusion, these experiments suggest that $Tl_2Ba_2Ca_2Cu_3O_{10}$ may be described as an Eliashberg superconductor, albeit one with an unusual normal state. Further, the results indicate that electron-phonon coupling is not solely responsible for the high $T_c$ of the material, and that the most likely origin of the excitation responsible for the high $T_c$ is an electronic transition near $1.6 \pm 0.15$ eV. Future experiments on other high temperature superconductors should confirm or disprove this model.

We are indebted to Dr. Wen Y. Lee of IBM Almaden Research Center, San Jose, for providing thin films of $Tl_2Ba_2Ca_2Cu_3O_{10}$.

*Department of Chemistry.

,†

*

†Department of Physics.

[1] W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Vol. 1, p. 561.
[2] J. R. Kirtley, J. Mod. Phys. B **4**, 201 (1990).
[3] D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Vol. 1, p. 449.
[4] N. Miyakawa *et al.*, J. Phys. Soc. Jap. **62**, 2445 (1993).
[5] S. B. Nam, Phys. Rev. **156**, 470 (1967).
[6] W. Shaw and J. C. Swihart, Phys. Rev. Lett. **20**, 1000 (1968).
[7] W. Lee, D. Rainer, and W. Zimmermann, Physica (Amsterdam) **159C**, 535 (1989).
[8] N. E. Bickers *et al.*, Phys. Rev. B **42**, 67 (1990).
[9] M. Tinkham, in *Introduction to Superconductivity* (Krieger, New York, 1980), p. 57.
[10] W. A. Little and J. P. Collman, Proc. Natl. Acad. Sci. U.S.A. **85**, 4596 (1988).
[11] R. E. Glover and M. Tinkham, Phys. Rev. **108**, 243 (1957).
[12] S. B. Nam, Phys. Rev. **156**, 487 (1967).
[13] L. H. Palmer and M. Tinkham, Phys. Rev. **165**, 588 (1968).
[14] R. E. Harris and D. M. Ginsberg, Phys. Rev. **188**, 737 (1969).
[15] R. R. Joyce and P. R. Richards, Phys. Rev. Lett. **24**, 1007 (1970).
[16] P. B. Allen, Phys. Rev. B **3**, 305 (1971).
[17] B. Farnworth and T. Timusk, Phys. Rev. B **10**, 2799 (1974).
[18] B. Farnworth and T. Timusk, Phys. Rev. B **14**, 5119 (1976).
[19] D. Karecki, R. E. Peña, and S. Perkowitz, Phys. Rev. B **25**, 1565 (1982).
[20] P. E. Sulewski *et al.*, Phys. Rev. B **35**, 8829 (1987).
[21] Z. Schlesinger *et al.*, Phys. Rev. Lett. **59**, 1958 (1987).
[22] T. Timusk and D. B. Tanner, Physica (Amsterdam) **169C**, 425 (1990).
[23] Z. Schlesinger *et al.*, Nature (London) **343**, 242 (1990).
[24] Z. Schlesinger *et al.*, Phys. Rev. B **41**, 11 237 (1990).
[25] T. Timusk, C. D. Porter, and D. B. Tanner, Phys. Rev. Lett. **66**, 663 (1991).
[26] I. Fugol *et al.*, Solid State Commun. **86**, 385 (1993).
[27] D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev. **148**, 263 (1966).
[28] M. J. Holcomb, J. P. Collman, and W. A. Little, Rev. Sci. Instrum. **64**, 1867 (1993).
[29] W. Y. Lee, J. Appl. Phys. **70**, 3952 (1991).
[30] I. Bozovic, Phys. Rev. B **42**, 1969 (1990).
[31] M. Cardona, in *Modulation Spectroscopy, Solid State Physics Series*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, New York, 1960).
[32] I. Bozovic *et al.*, Phys. Rev. B **43**, 1169 (1991).
[33] D. J. Scalapino, Y. Wada, and J. C. Swihart, Phys. Rev. Lett. **14**, 102 (1965).
[34] H. You *et al.*, Phys. Rev. B **38**, 9213 (1988).
[35] H. You, U. Welp, and Y. Fang, Phys. Rev. B **43**, 3660 (1991).
[36] M. Okaji *et al.*, Cryogenics **34**, 163 (1994).
[37] S. Huimin *et al.*, Supercond. Sci. Technol. **2**, 52 (1989).
[38] Y. Ono and S. Narita, Jpn. J. Appl. Phys. **31**, L224 (1992).
[39] D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).
[40] Z. Schlesinger *et al.*, Phys. Rev. Lett. **65**, 801 (1990).
[41] M. K. Kelly *et al.*, Phys. Rev. B **40**, 6797 (1989).
[42] D. E. Aspnes and M. K. Kelly, IEEE J. Quantum Electron. **25**, 2378 (1989).
[43] T. Yamamoto *et al.*, Jpn. J. Appl. Phys. **31**, L327 (1992).
[44] S. Uchida, Physica (Amsterdam) **185-189C**, 28 (1991).

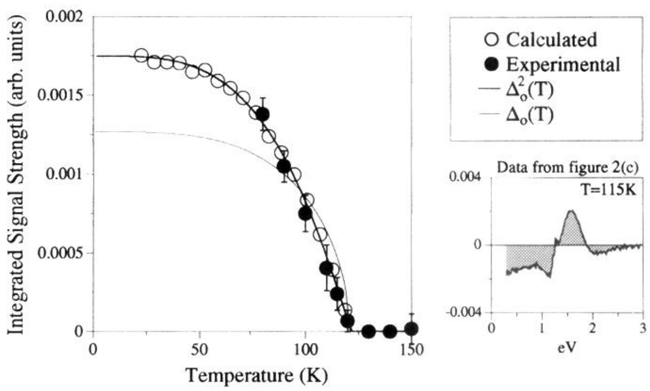


FIG. 3. Amplitude of the normalized, temperature integrated TD spectra from 150 to 80 K, ● experimental, ○ theoretical, with $T_c \sim 120$ K. The shaded area of spectrum in the inset, taken from Fig. 2(c), represents the total change of the sample's reflectance when the material becomes superconducting.