

## Measurement of the superconducting energy gap in La-Ba-Cu oxide and La-Sr-Cu oxide

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We report on far-infrared (FIR) reflectivity measurements on sintered pressed powder samples of La-Ba-Cu oxide and La-Sr-Cu oxide. The best samples show fairly sharp transitions to zero measurable resistance with a transition midpoint of 28 K for the Ba alloy and 36 K for the Sr alloy. The FIR measurements reveal an energy gap below  $T_c$  with, depending on the measurement criterion used, values of  $2\Delta/k_B T_c$  of 1.3–1.95 for La-Ba-Cu oxide and 1.6–2.7 for La-Sr-Cu oxide, which are lower than expected for a BCS superconductor.

Recently, Bednorz and Müller<sup>1</sup> have observed an apparent superconducting transition in La-Ba-Cu oxide, with the resistive transition beginning at very high temperatures,  $T = 30$  K. The subsequent verification of this transition by Takagi and co-workers,<sup>2,3</sup> through both resistance and magnetic susceptibility measurements, and the identification of the superconducting phase as  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  has resulted in widespread interest in the properties of this material, and of related La-Cu oxides. Here we report on far-infrared reflectivity measurements for sintered powder samples of La-Ba-Cu oxide and La-Sr-Cu oxide. We have found both of these materials to exhibit resistive transitions typical of somewhat inhomogeneous superconductors, with the barium-doped oxide having a resistive transition midpoint at 28 K and the Sr compound at 36 K. In both these materials we have observed, for the first time, direct evidence for the existence of an energy gap in the far-infrared (FIR) absorptivity. Although the inhomogeneities of the sample clearly affected the FIR measurements, the values of these energy gaps are quite consistent with those expected for BCS superconductors.

The samples were prepared using the method outlined by Takagi *et al.*<sup>2</sup> Powders of  $\text{La}_2\text{O}_3$ ,  $\text{ACuO}_3$ , and  $\text{CuO}$ , where  $A$  is either Ba or Sr, were ground and mixed together in the appropriate anion proportions to yield the desired stoichiometry of the reacted compound. The mixed powder was then pressed into a pellet and fired in air at  $1100^\circ\text{C}$  for 20 h. The result was a sintered pellet with a fairly smooth surface that was well suited for far-infrared reflectivity measurements. As the  $\text{La}_{2(1-x)}\text{A}_{2x}\text{CuO}_4$  compound has been identified as the phase most likely responsible for the superconducting transition, the majority of the samples that we have prepared have had this approximate stoichiometry. To date, our best far-infrared results have been obtained with  $x = 0.03$  and with the La:Cu ratio of the starting mixture being approximately 2.5:1, somewhat higher than the ideal 2:1 value. Scanning electron microscopy (SEM) and electron microprobe observations reveal that the surface of the sample has considerable texture and inhomogeneities. Figure 1 is a backscattered electron SEM image obtained from a La-Ba-Cu sample. As can be seen the surface has voids, which show up as

dark spots in the micrograph, of up to  $100\ \mu\text{m}$  in extent. Also seen are light areas which are nonconducting and are Cu and Ba poor, as determined from the microprobe analysis. The gray, conducting areas in the micrograph are regions of the sample with the desired stoichiometry. It has been possible to produce samples with a considerably smaller amount of insulating material than shown here, but these have not displayed as sharp a resistive transition. X-ray powder diffraction of the samples whose infrared behavior is discussed below shows the phase of the sample to be predominantly of the  $\text{K}_2\text{NiO}_4$  type, but some small amount of another, unidentified phase is also present. Higher-resolution scanning electron microscope studies of the conducting material reveal that the surface consists of a relatively well-ordered array of circularlike crystalline grains of approximately  $5\ \mu\text{m}$  diameter with



FIG. 1. A backscattered electron scanning electron micrograph of the surface of a La-Ba-Cu oxide sample. The dark areas are voids in the surface, the light areas are Cu- and Ba-poor regions which are insulating, and the gray areas are conducting with an approximate average La:Ba:Cu composition of 2:0.03:1. The scale bar is  $100\ \mu\text{m}$  long.

pronounced and relatively thick grain boundaries of the order of 50–100 nm thick.

Preliminary electron microprobe analysis of these surfaces has shown that there is a strong variation in the density of the Ba or Sr component as one moves from the surface into an individual grain. In particular, we find that deep inside the grain the composition of the material is close to that of the starting material. But as the surface is approached the Ba or Sr composition increases dramatically. For example, for a Ba sample with a nominal value of  $x = 0.03$ , when the microprobe energy is such that only the first 1  $\mu\text{m}$  or so of material from the surface is being probed we find that here  $x = 0.05$ . Low-energy microprobe line scans also indicate a high proportion of Ba or Sr at the grain boundaries. X-ray photoemission spectroscopy (XPS) measurements have confirmed the existence of a strong composition gradient, in that surface XPS scans typically indicate a Ba or Sr concentration in the first 5–10 nm of the surface of  $x = 0.3$  or greater, even though the bulk concentration is again only  $x = 0.03$ . If superconductivity is only present for a limited range of  $x$ , then this composition variation could result in an admixture of superconducting and normal regions, within each individual grain. Of course, the grain boundaries are quite likely to be nonsuperconducting, even if they are conducting and not insulating or semiconductor Josephson tunnel barriers.

Resistive transitions of a Ba and of a Sr sintered pellet sample are shown in Fig. 2. Above  $T_c$  both samples had an effective bulk dc resistivity of approximately 5 m $\Omega$  cm, which represented a resistivity drop from 300 K of about a factor of 3. The Ba sample shows a fairly sharp transition, with a midpoint at approximately 28 K, while the Sr sample has a slightly broader transition with a midpoint at about 36 K. The breadth of the transition can of course be readily attributed to a mixture of superconducting and normal regions with the coupling between the superconducting regions being due to the Josephson effect which

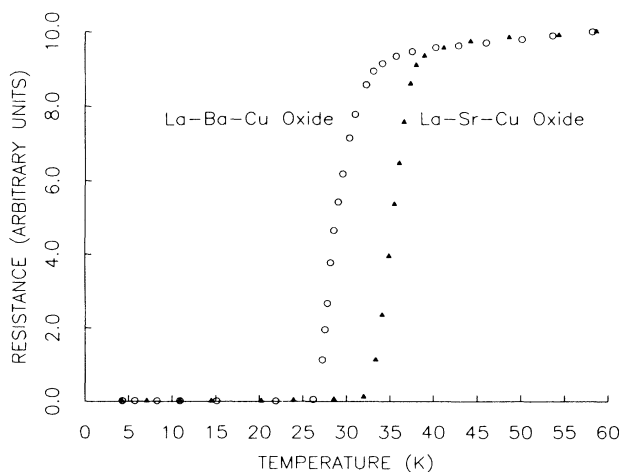


FIG. 2. The resistive transition of a La-Ba-Cu oxide and of a La-Sr-Cu oxide sintered powder sample. The starting material was prepared in a 1:0.03:0.4 ratio. These are the same samples used in the FIR measurements. At 50 K both samples had a resistivity of approximately 4 m $\Omega$  cm.

grows in strength as  $T$  drops below  $T_c$ . The normal region could be due to the aforementioned composition variation within the individual grains and/or at the grain boundary. These same samples were used in the far-infrared reflectivity studies which we will now discuss.

A two-bounce reflectivity measurement has been used to determine the absorptivity in the frequency interval from 10 to 150  $\text{cm}^{-1}$ . The experiment makes use of a Michelson interferometer coupled by brass light pipes to a cryostat containing a He<sup>3</sup>-cooled bolometer detector. The sample assembly is positioned in this cryostat 30 cm above the detector chamber so that the sample temperature can be varied between 4.2 and 40 K without significantly changing the bolometer sensitivity. The sintered samples are clamped at two right angle bends in a compact brass light pipe assembly which can be rotated out of the radiation path and replaced with its neighbor, an identical assembly which holds two mirrors for reference.

Since these thick samples are opaque, the ratio of the intensity reflected by the sample  $I_m$  to that of the reference  $I_r$  gives

$$I_m/I_r = \langle R_m \rangle^2 / \langle R_r \rangle^2, \quad (1)$$

where  $\langle \rangle$  indicates the average over the angular spread around the 45° angle of incidence direction. When both polarizations and the angular spread of the beam are counted, a good approximation for the normal-incidence absorptivity is<sup>4</sup>

$$A_m = 0.95[1 - (I_m/I_r)^{1/2}], \quad (2)$$

where we can set  $R_r = 1$  in this frequency region because of the low conductivity of the sample.

The frequency dependence of the absorptivity of La-Sr-Cu oxide at two temperatures is shown in Fig. 3(a). Each curve stems from an average of two to four numerator ( $I_m$ ) and denominator ( $I_r$ ) runs at a resolution of about 4  $\text{cm}^{-1}$ , and each curve represents the results over a different frequency interval. The solid lines correspond to  $T = 4.2$  K and the dashed lines to  $T = 40$  K. Measurements over the same frequency region on La-Ba-Cu oxide are shown in Fig. 3(b) but now the solid lines correspond to  $T = 6$  K and the dashed ones to  $T = 29$  K. All of these curves have similar shapes: nearly independent of frequency at low frequency and then increasing monotonically with a hint of saturation beginning at the largest frequencies.

The blackbody loading of the detector can be kept fairly constant when the temperature dependence of the absorptivity ( $\Delta A = A_N - A_S$ ) is measured for a single sample and these results are shown for La-Sr-Cu oxide and La-Ba-Cu oxide in Figs. 4(a) and 4(b), respectively. The two temperatures are 4.2 and 40 K in Fig. 4(a) and 6 and 29 K in Fig. 4(b). These data bring out more clearly that the temperature dependence of the absorptivity is confined to the far-infrared spectral region. Other intermediate temperature FIR measurements indicate that with increasing temperature  $\Delta A$  grows rapidly near  $T_c$  and that no further change is observed in  $\Delta A$  for temperatures greater than  $T_c$ .

The absorptivity change is clearly related to the dc resis-

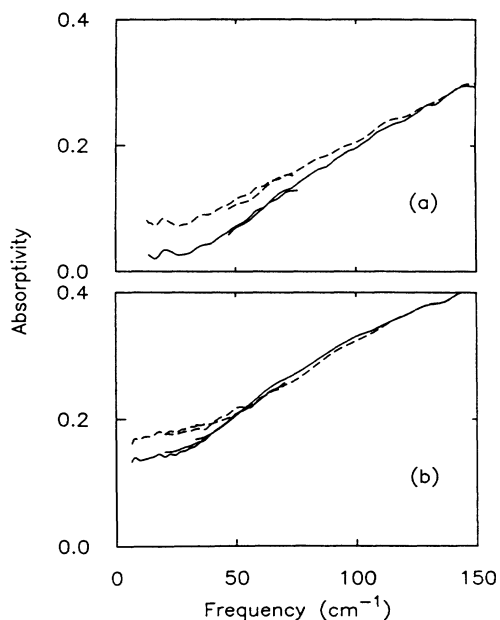


FIG. 3. Absorptivity vs frequency of sintered powder samples. (a) La-Sr-Cu oxide. (b) La-Ba-Cu oxide. The solid curves are taken at temperatures below the superconducting transition [4.2 K in (a) and 6 K in (b)], while the dashed curves are taken above  $T_c$  [40 K in (a) and 29 K in (b)]. The resolution is approximately 4% of the maximum frequency of each curve.

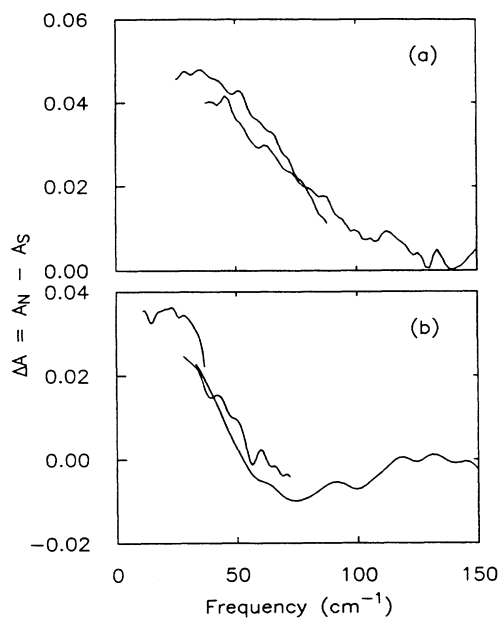


FIG. 4. Change in absorptivity between the normal state and the superconducting state vs frequency. (a) La-Sr-Cu oxide. (b) La-Ba-Cu oxide.  $\Delta A = A_N - A_S$  is obtained without moving the sample between the two temperatures given in Fig. 3 so that the sample surface structure is unchanged. The gap extends almost twice as far in (a) as in (b), with the midpoints at 75 and 42  $\text{cm}^{-1}$ , respectively.

tivity change but as we now show the low-frequency normal-metal data shown in Figs. 3 and 4 do not agree with the classical skin effect prediction. Since these intermetallic resistivities at low temperature are much larger than copper at room temperature in the far-infrared,  $\omega\tau \ll 1$  and we would expect the absorptivity for normal incidence on a smooth surface to have the simple Hagen-Rubens form

$$A_n = (2\omega/\pi\sigma_0)^{1/2}, \quad (3)$$

in which  $\sigma_0$  is the dc conductivity so  $A_n$  increases as  $\omega^{1/2}$ . No evidence for this frequency dependence is seen in Figs. 3 or 4. Note that in the latter figure  $A_s = 0$  below the gap so the data should follow Eq. (3) at the lowest frequencies and  $\Delta A \propto \omega^{1/2}$ . Clearly they do not. In addition, the magnitude of the absorptivity for both samples is surprisingly large in this region and if intrinsic in nature would imply that the carrier densities are extremely small ( $\sim 10^{18} \text{ cm}^{-3}$ ). A more likely explanation is that the large voids which intercept the flat sample surface shown in the SEM micrograph in Fig. 1 (some comparable in size with the wavelength of the FIR radiation) scatter and/or trap a significant fraction of the radiation so that the frequency-dependent absorptivity obtained by comparing the reflectivity from this textured surface to that from smooth metal mirrors only provides a weak upper bound to the true value for a smooth sample surface. The surface morphology is fixed and plays a less important role during a temperature-dependent study with a particular sample, hence the data shown in Fig. 4 represent our most accurate results.

From the difference in absorptivity for the normal and superconducting regimes in Fig. 4 an estimate of the energy gap can be obtained. For simple BCS superconductors the absorptivity difference<sup>5</sup> is a maximum at the gap energy  $2\Delta$  and decreases to zero at  $\hbar\omega \sim 2.2(2\Delta)$ . Measurements<sup>5</sup> on the strong coupling superconductor Pb show the absorptivity difference to be zero at  $\hbar\omega \sim 1.3(2\Delta)$  with the half height occurring at  $\hbar\omega \sim 1.1(2\Delta)$ . Using the half height criterion we find that at 4.2 K,  $2\Delta = 38 \text{ cm}^{-1} = 4.7 \text{ meV}$  for La-Ba-Cu oxide and  $2\Delta = 67 \text{ cm}^{-1} = 8.3 \text{ meV}$  for La-Sr-Cu oxide. In the case of the barium material this value of  $2\Delta/kT_c = 1.95$  is below what would be expected for a BCS superconductor, even more so for a strong coupling superconductor. The value of  $2\Delta/kT_c = 2.7$  for the Sr sample is closer to the 3.52 BCS value, but still low. Use of the alternative criterion to determine the gap yields still lower values for  $2\Delta/kT_c$  in both cases: 1.3 for La-Ba-Cu oxide and 1.6 for La-Sr-Cu oxide. These results could be indications that, as shown by the electron microprobe and XPS measurements, the materials are far from homogeneous. As is suggested by the width of the resistive transitions, the conducting parts of the samples quite possibly consist of adjacent superconducting and normal regions which, if small enough, would act to reduce the measured energy gap though the proximity effect. We note the fact that the FIR radiation only examines the surface of the material to about a depth of 1  $\mu\text{m}$ , whereas the resistivity measurement examines the highest  $T_c$  path though the bulk of the sample. But we also point out that the mea-

sured FIR absorptivity in both cases does have, at least qualitatively, the expected temperature dependence, and does stop changing with  $T$  at essentially the same  $T_c$  as determined by the resistivity measurements. Thus, this lower than expected energy gap could well be intrinsic.

In summary, samples of La-Ba-Cu oxide and La-Sr-Cu oxide have been prepared which have reasonably sharp, high-temperature resistivity transitions with a transition temperature midpoint of 28 K for the Ba material and 36 K for the Sr material. While the samples are clearly inhomogeneous, FIR reflectivity measurements have directly revealed the existence of a superconducting energy gap with, depending on the measurement criterion used,  $2\Delta/kT_c = 1.3$  or  $1.95$  for La-Ba-Cu oxide and  $1.6$  or  $2.7$  for

La-Sr-Cu oxides. Even the larger of these values are considerably lower than expected for BCS superconductors.

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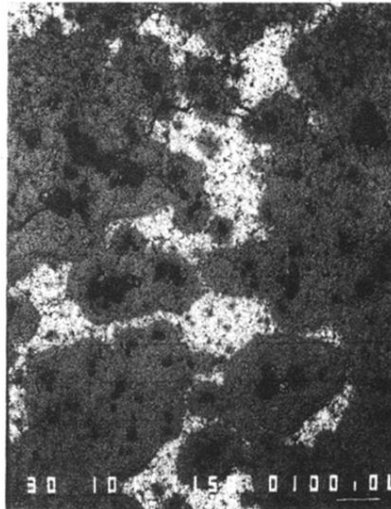


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