

## Microwave response of $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ crystals: Evidence for a multicomponent order parameter

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New features are reported in precision measurements of the complex microwave conductivity of high-quality  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  crystals grown in  $\text{BaZrO}_3$  crucibles. A *third* peak in the normal conductivity,  $\sigma_1(T)$ , at around 80 K, and enhanced pair conductivity  $\sigma_2(T)$  below  $\sim 65$  K are observed. The data are inconsistent with a *single* order parameter, and instead are indicative of multicomponent superconductivity. Overall, these results point to the presence of multiple pairing interactions in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  and also provide a natural explanation to account for the low-temperature 35-K conductivity peak observed in all  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  crystals. [S0163-1829(97)52322-8]

The mechanism for superconductivity and the nature of the superconducting state in the cuprates continue to be prime issues that are being debated.<sup>1</sup> Microwave measurements have yielded important information on the nature of the pairing, the quasiparticle density of states, and scattering in the cuprate superconductors.<sup>2-4</sup> Surface impedance of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  (YBCO) single crystals in the past have consistently shown two features: A linear penetration depth [ $\lambda(T) \propto T$ ] over a limited low  $T$  range, and the presence of a bump in the surface resistance  $R_s(T)$  which results in a peak in the normal conductivity  $\sigma_1(T)$  at  $\sim 35$  K, well below the superconducting  $T_c \sim 93$  K.<sup>2,5</sup> The former behavior has been attributed to *d*-wave order-parameter symmetry or, in general, the presence of nodes in the gap. A rapidly decreasing quasiparticle scattering rate below  $T_c$  has been proposed to account for the latter feature.<sup>5,6</sup> There is a general consensus that the experimental results can be explained in the framework of a single *d*-wave order parameter with inclusion of effects due to strong coupling, scattering with strong temperature dependence, and fluctuation.<sup>5,7</sup>

In this paper, we present results on the microwave response of high-quality  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  single crystals grown by a new method that avoids crucible corrosion. We measure the temperature-dependent surface impedance  $Z_s = R_s + iX_s$  and penetration depth  $\lambda (= X_s / \mu_0 \omega)$  from which we extract the complex conductivity  $\sigma_s = \sigma_1 - i\sigma_2$ . The two features mentioned above,  $\lambda(T) \propto T$  at low  $T$  and the 35-K peak in  $\sigma_1$ , are still present in these crystals. However, in addition, a new peak in  $\sigma_1(T)$  at  $\sim 80$  K and a distinct increase in  $\sigma_2(T)$  below  $\sim 65$  K are observed. A single *d*-wave order parameter is insufficient to describe the new data, and instead we show that an analysis in terms of two-component superconductivity is necessary.

The single crystals (typically  $1.3 \times 1.3 \times 0.1$  mm<sup>3</sup> in size) used in this work were of very high quality grown from  $\text{BaZrO}_3$  crucibles (BZO).<sup>8</sup> This growth method leads to crystals with extremely clean surfaces and exceptional purity exceeding 99.995% (Ref. 9), in contrast to crystals grown in other crucibles which have final reported purities of 99.5–99.95%.<sup>10,11</sup> As shown in this paper, this difference in

purity appears to play a significant role in the microwave properties. Standard oxygen annealing procedures were followed to obtain optimally doped crystals with oxygen stoichiometry around  $\text{O}_{6.95}$ .<sup>12</sup> The crystals have  $T_c = 93.4$  K, and very sharp transitions in  $R_s(T)$  and superconducting quantum interference device (SQUID) magnetic susceptibility measurements. Crystals grown by this method also have unique physical properties due to their exceptional purity, as revealed in other experiments.<sup>13,14</sup> Unlike the case in earlier crystals, the vortex lattice was imaged for the first time in YBCO with a low-temperature scanning tunneling microscope.<sup>13</sup> Specific heat measurements indicated extremely sharp jumps at  $T_c$ .<sup>14</sup>

Three crystals of optimally doped  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  grown in BZO crucibles (hereafter called YBCO/BZO) were measured. In addition, measurements on a  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  crystal (of comparable dimensions) grown in the commonly used yttria-stabilized zirconia (YSZ) crucible (hereafter called YBCO/YSZ) are also presented for comparison.

The high-precision microwave measurements were carried out in a 10 GHz Nb cavity using a ‘‘hot finger’’ technique.<sup>15</sup> This method has been extensively validated for precision measurements of the surface impedance in cuprate<sup>3</sup> and other superconductors. All measurements reported in this paper were carried out with the microwave field  $H_{\text{rf}} \parallel \hat{c}$  so that currents flow predominantly in the *ab* planes. Any influence due to *c*-axis properties<sup>4</sup> or finite-size effects are minimal as the results obtained on three samples with slightly different dimensions and varying edge geometries were identical.

The  $T$  dependence of  $\lambda(T)$  of YBCO/BZO and YBCO/YSZ crystals are shown in Fig. 1. The data for the new high-purity YBCO/BZO crystals clearly reveal a new feature—a bump or plateau in the vicinity of 60–80 K, which, to our knowledge, has not been reported in any previous  $\lambda(T)$  data for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  crystals. A plateau in  $\lambda(T)$  similar to that observed here has been reported in films and was attributed there to a two-gap behavior.<sup>16</sup>

The surface resistance  $R_s(T)$  is also displayed in Fig. 1 as a function of  $T/T_c$ . At low temperatures all samples showed

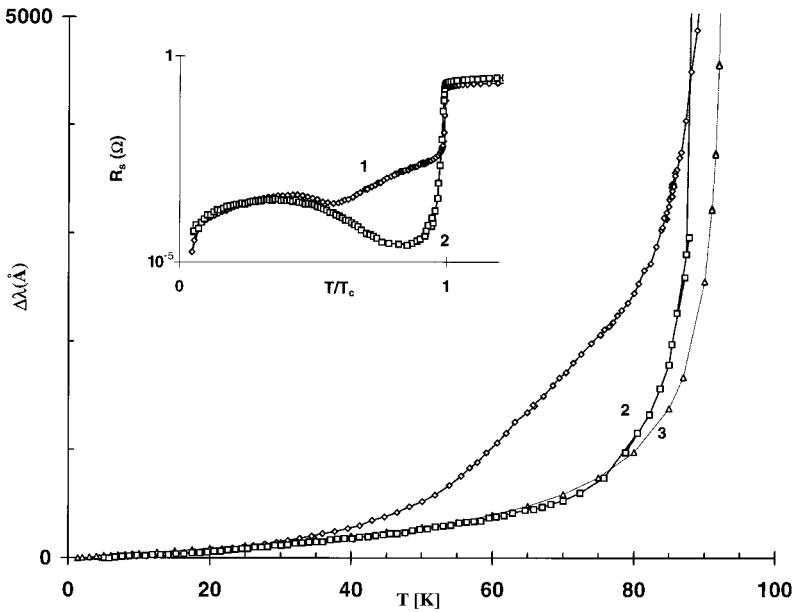


FIG. 1.  $\lambda(T)$  vs  $T$  for YBCO/BZO (curve 1) and YBCO/YSZ (curve 2) crystals. Data from Ref. 2 are also shown for comparison (curve 3). Inset shows  $R_s(T)$  vs  $T/T_c$  of YBCO/BZO and YBCO/YSZ.

the nonmonotonic behavior in  $R_s$  that is well known and the low-temperature values are comparable to that seen previously.<sup>5,6</sup> However, at intermediate temperatures, a new feature is seen—a shoulder in  $R_s$  in the YBCO/BZO sample which is completely absent in the YBCO/YSZ sample. We emphasize that the data for YBCO/YSZ are representative of that reported in literature.<sup>5,2,17</sup>

These features are best studied in terms of the complex conductivity  $\sigma_s = \sigma_1 - i\sigma_2 = i\mu_0\omega/(R_s + iX_s)^2$ . The pair conductivity  $\sigma_2$  vs  $T$  is shown in Fig. 2, and is a measure of the superfluid density  $n_s(T)$ , since  $\sigma_2 = n_s(T)e^2/m\omega = 1/[\mu_0\omega\lambda^2(T)]$ . Although only changes  $\Delta\lambda(T) \equiv \lambda(T) - \lambda(4.2 \text{ K})$  and correspondingly  $\Delta X_s = \mu_0\omega\Delta\lambda$  are measured in the experiment, the absolute value of  $X_s$  and hence  $\lambda$  are obtained by assuming the normal-state  $R_n = X_n$  at and slightly above  $T_c$ . This procedure yields a consistent value of  $\lambda(0) \approx 1000 \text{ \AA}$  for all the YBCO/BZO crystals and a value of  $\lambda(0) \approx 1400 \text{ \AA}$  for the YBCO/YSZ crystal. The  $\sigma_2(T)$  data indicate an additional onset of pair conductivity below around 60–70 K, never observed in previous crystals reported to data as is evident from the comparison with the plot for the YBCO/YSZ crystal. Also, the pair conductivity  $\sigma_2(T)$  rises to a higher value in the BZO grown crystals compared with the YSZ grown crystals. All the YBCO/BZO crystals showed this feature in the data. While the accuracy of  $\Delta\lambda \sim 1 \text{ \AA}$ , the uncertainty in  $\lambda(0)$  is much larger, perhaps of order 100–300  $\text{\AA}$ . Nevertheless, the results are consistent with a lower  $\lambda(0)$  and hence enhanced pair conductivity in the YBCO/BZO crystals compared with the YBCO/YSZ crystals.

The resultant plot of the normal conductivity  $\sigma_1(T)$  is shown in Fig. 3. The low-temperature peak at around 35 K (labeled A) is observed in several previous measurements on crystals.<sup>5,6</sup> Note that very near  $T_c$  a sharp peak (labeled C) is also present (see insets to Fig. 3) in all YBCO/BZO and YBCO/YSZ samples and which is often attributed to fluctuations.<sup>17</sup> The sharpness of these peaks in the YBCO/BZO crystals attests to the high quality of these crystals. The most striking feature is a new (*third*) conductivity peak (labeled B) clearly visible in the YBCO/BZO data centered at

approximately 80 K ( $\sim 0.9T_c$ ), which has not to our knowledge been reported previously in microwave measurements.

It is clear that the YBCO/BZO crystals reveal *two new important features* in the data: (i) the additional enhancement of pair conductivity  $\sigma_2$  with an onset around 60–70 K, indicative of enhanced pairing below this temperature, and (ii) the *third* normal conductivity peak at around 80 K ( $\sim 0.9T_c$ ) in  $\sigma_1(T)$ . The former was observed in all the YBCO/BZO crystals, while the 80 K peak in  $\sigma_1$  is more sensitive to sample details, particularly the normal-state scat-

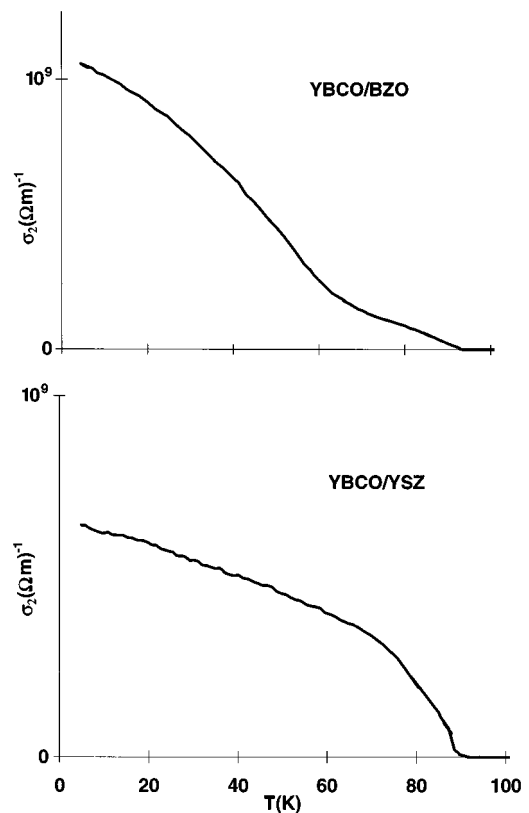


FIG. 2. Pair conductivity  $\sigma_2(T)$  of YBCO/BZO (top) and YBCO/YSZ (bottom).

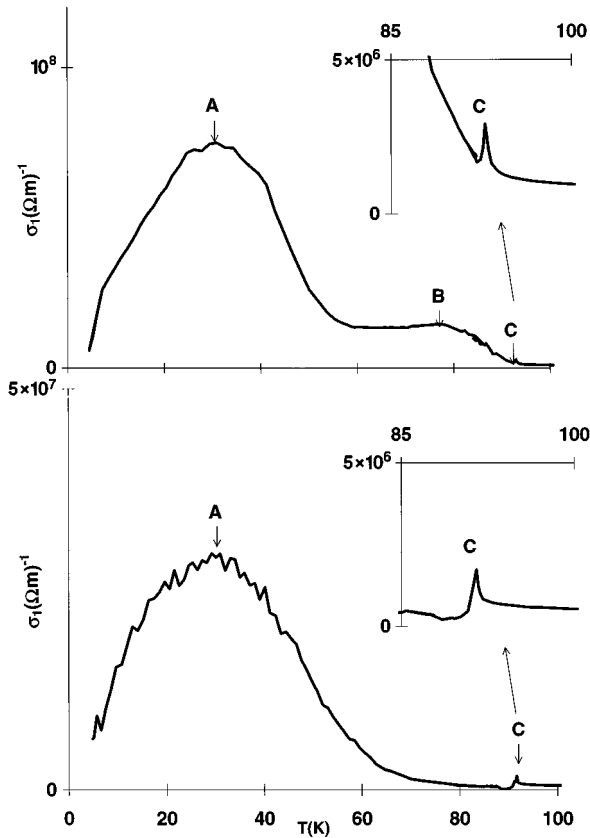


FIG. 3.  $\sigma_1(T)$  of YBCO/BZO (top) and YBCO/YSZ (bottom). The sharp peaks *C* present in both cases are shown in insets. Note the appearance of a new peak *B* in YBCO/BZO.

tering, and was lower in one of the samples which had the highest  $R_n$ . (Details of results on the other  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  and also on specially oxygenated  $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$  crystals will be published elsewhere.)

The data of Fig. 1 for the new YBCO/BZO samples are difficult to describe using a single order parameter below  $T_c$ . This is evident from the curve for  $\lambda^{-2}(T)$  obtained from a weak-coupling *d*-wave calculation shown in Fig. 4.

In the ‘‘hydrodynamic’’ limit,  $\sigma_{1s,d}(T) = n_{qp}(T)e^2\tau(T)/m$ . A single peak in  $\sigma_1(T)$  can arise from a combination of increasing  $\tau$  and decreasing  $n_{qp}$  as  $T$  is lowered. Except for detailed dependences on  $T$ , this peak should occur for an *s*- or *d*-wave superconductor and even in a two-fluid model. (The BCS coherence peak for an *s*-wave superconductor is masked by this effect.) In order to describe the conductivity data in earlier  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  crystals<sup>5,18</sup> in the framework of a *d*-wave model, one needs a dramatic drop in the scattering rate below  $T_c$ . However, any model using a single gap or order parameter (*s*- or *d*-wave) will only lead to a single conductivity peak, in disagreement with the present data.

Instead it is necessary to consider a two-component system to understand the new data. The new feature in the  $\sigma_2(T)$  data suggests that there is additional pairing of carriers below approximately 60–70 K. The essential features of the data can be well described by a simple model of two superconducting components with  $T_{cA} = 65$  K and  $T_{cB} = 93$  K. We have calculated the total conductivity  $\sigma_s \equiv \sigma_1 - i\sigma_2 = (\sigma_{1A} + \sigma_{1B}) - i(\sigma_{2A} + \sigma_{2B})$ . For ease of calculation we used *s*-wave order parameters for both the *A* and *B* compo-

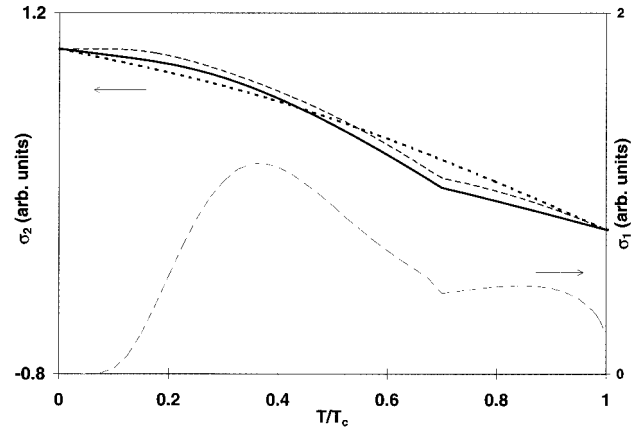


FIG. 4. Calculations of  $\sigma_1(T)$  and  $\sigma_2(T)$  using the two-component model assuming two *s*-wave order parameters (long dashed lines). For  $\sigma_2(T)$ , the case for a more realistic situation of an *s* + *d* symmetry is also shown (solid line). The short dashed line represents the calculations for a single weak-coupling *d*-wave order parameter.

nents to calculate the conductivities using Mattis-Bardeen expressions. In the case of  $\sigma_2$ , calculations assuming *s* and *d* which are closer to the realistic case are also presented. Gap values of  $\Delta_A(0)/kT_{cA} = 1.5$  and  $\Delta_B(0)/kT_{cB} = 2.8$  were used. For  $\sigma_1$ , temperature-dependent scattering times  $\tau_{A,B} = \tau_{0A,B}/[1 + (T/T_{A,B}^*)^4]$ , with  $\tau_{0A}/\tau_{0B} = 2$ ,  $T_A^* = 37$  K,  $T_B^* = 83$  K were assumed. The calculations reproduce the essential features of the data, viz., the onset of pairing around 60 K observed in  $\sigma_2(T)$ , and the two peaks in  $\sigma_1(T)$ , as shown in Fig. 4. Although we have used two decoupled components in the above model for illustrative purposes, a small attractive coupling between the two components is probably essential. It is easy to show in the framework of Ginzburg-Landau theory<sup>19</sup> that such coupling does not change the results much, and the essential features of the data are retained in more elaborate models.

The microwave measurements do not directly yield the symmetry of the order parameter in the *A* and *B* components, except as can be inferred from the temperature dependence of the data. The fact that  $\lambda(T)$  is linear at low temperatures would indicate that pairing in component *A* could be *d*-wave like, exhibiting nodes in the gap. Several theories have suggested the strong possibility of a mixed *s* + *d* state in the presence of orthorhombic distortion as is the case in YBCO,<sup>20,21</sup> and detailed BCS calculations, such as those in Ref. 20 of coupled *s*-*d* mixtures, do yield penetration depth [ $\lambda^{-2}(T)$  vs  $T$ ] curves similar to the present  $\sigma_2(T)$  data.

It is tempting to assign the two superconducting components *A* and *B* with the associated condensates residing on Cu-O planes and chains, respectively, in the YBCO system. However, such an interpretation might be inappropriate given the facts that the crystals are twinned and microwaves probe a length scale spanning several hundred unit cells. Instead the two sets of condensates may originate from different types of pairing associated with different regions of the Fermi surface. Such a scenario based on band structure taking into account the chain-plane coupling in YBCO and eventually leading to two types of pairing interactions has been proposed.<sup>21</sup>

Our results resolve an important issue regarding the origin of the conductivity peak at 35 K. While in previous cases it was necessary to invoke a precipitous drop in the scattering rate to account for its location, it is natural from Figs. 2 and 3 to *associate the low  $T$  (35-K) peak with the  $A$  ( $T_{cA} \approx 60$  K) component and not the  $B$  ( $T_{cB} \approx 93$  K) component.* The location at 35 K ( $\sim 0.5T_{cA}$ ) is now reasonable for a conductivity peak associated with onset of pairing at  $T_{cA}$ . This implies that the type- $A$  condensate is present in the YBCO/YSZ samples also but has a weaker, almost gapless, temperature dependence. We therefore believe that the same mechanisms were operating in earlier samples also but are clearly distinguished in the new YBCO/BZO crystals.

A natural suspicion that arises is whether the data in the new YBCO/BZO crystals arise from inadequate oxygen annealing leading to macroscopic chemical phase separation. It is important to note that the annealing procedures for the YBCO/BZO crystals were exactly the same as for the YBCO/YSZ crystals.<sup>12</sup> An estimate suggests that the data

cannot be explained by macroscopic segregation of an  $O_{6.5}$  60-K phase and an ideal  $O_7$  90-K phase. For  $O_{6.95}$  one would require  $\sim 6-10\%$  of the 60 K phase which cannot, however, account for the relative weights of the two components in our  $\sigma_2(T)$  data. Instead, our data point to a physical mechanism like interlayer coupling rather than to chemical segregation for our results.

In conclusion, measurements of the microwave properties of ultrapure  $YBa_2Cu_3O_{7-\delta}$  crystals reveal new features suggesting the presence of two superconducting components in this compound. Our work provides a possible explanation for the 35-K microwave conductivity peak, and yields insights into the pairing mechanism in the high-temperature superconductors.

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<sup>1</sup>J. R. Kirtley, C. C. Tsuei, and L. S. Yu-Jahnes, *Nature* (London) **373**, 225 (1995).

<sup>2</sup>W. N. Hardy *et al.*, *Phys. Rev. Lett.* **70**, 3999 (1993).

<sup>3</sup>T. Jacobs *et al.*, *Phys. Rev. Lett.* **75**, 4516 (1995).

<sup>4</sup>S. F. Lee *et al.*, *Phys. Rev. Lett.* **77**, 735 (1996).

<sup>5</sup>T. Jacobs *et al.*, *J. Phys. Chem. Solids* **6**, 1945 (1995).

<sup>6</sup>D. A. Bonn, P. Donsajh, R. Liang, and W. N. Hardy, *Phys. Rev. Lett.* **68**, 2390 (1992).

<sup>7</sup>P. J. Hirschfeld, W. O. Putikka, and D. J. Scalapino, *Phys. Rev. B* **50**, 10 250 (1994).

<sup>8</sup>A. Erb, E. Walker, and R. Flükiger, *Physica C* **245**, 245 (1995).

<sup>9</sup>A. Erb, E. Walker, and R. Flükiger, *Physica C* **258**, 9 (1996).

<sup>10</sup>H. Ikuta and D. M. Ginsberg, *J. Supercond.* **9**, 259 (1996).

<sup>11</sup>H. Casalta *et al.*, *Physica C* **258**, 321 (1996).

<sup>12</sup>A. Erb, E. Walker, and R. Flükiger, *Physica C* **259**, 83 (1996).

<sup>13</sup>I. Maggio-Aprile *et al.*, *Phys. Rev. Lett.* **75**, 2754 (1995).

<sup>14</sup>M. Roulin, A. Junod, A. Erb, and E. Walker, *J. Low Temp. Phys.* **105**, 1099 (1996).

<sup>15</sup>S. Sridhar and W. L. Kennedy, *Rev. Sci. Instrum.* **59**, 531 (1988).

<sup>16</sup>N. Klein *et al.*, *Phys. Rev. Lett.* **71**, 3355 (1993).

<sup>17</sup>S. M. Anlage, J. Mao, and J. L. Peng, *Phys. Rev. B* **53**, 2792 (1996).

<sup>18</sup>P. J. Hirschfeld, W. O. Putikka, and D. J. Scalapino, *Phys. Rev. Lett.* **71**, 3705 (1993).

<sup>19</sup>J. Betouras and R. Joynt, *Europhys. Lett.* **31**, 119 (1995).

<sup>20</sup>C. O'Donovan and J. P. Carbotte, *Phys. Rev. B* **52**, 16 208 (1995).

<sup>21</sup>R. Combescot and X. Leynoras, *Phys. Rev. Lett.* **75**, 3732 (1995).