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Superconductivity in bulk and thin films of $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ and $Ba_2YCu_3O_{7-\delta}$

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A laser-ablation technique was used to deposit thin films from the bulk oxides $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ and $Ba_2YCu_3O_{7-\delta}$, whose superconductivity properties were investigated by dc resistivity, complex ac susceptibility, and microwave response. The latter technique was employed to establish that the thin films have superconducting regions with properties similar to the bulk materials.

Following the first observation of superconductivity at 30 K in the Ba-La-Cu-O system,[1] the superconducting phase was identified as $La_{1.85}Ba_{0.15}CuO_{4-\delta}$,[2] and T_c's near 40 K were obtained in compounds with Sr substituting for Ba.[3-5] Later, $T_c \simeq 90$ K was observed in the Ba-Y-Cu-O system[6] and the superconducting phase established.[7] These events have led to extraordinary research activity on the properties, structure, etc. of these materials,[8-10] and many reports of which the few just referenced are examples.

There is considerable interest in preparing thin films of these materials both for fundamental research and possible applications. Laser methods for such film preparation are especially attractive, and we report here what we believe to be the first results on partially superconducting thin films produced using a high-power, pulsed, excimer laser operating in the ultraviolet to ablate material off bulk samples of high-T_c superconductors. The superconductivity in the films was established by a novel variant of a microwave technique,[11] and the observed values of T_c are found to correlate well with the values obtained for the bulk samples by ac susceptibility and resistance measurements.

The La-Sr-Cu-O ceramic was prepared by solid state reaction of appropriate amounts of $Ba(OH)_2$, $SrCO_3$, and CuO powder at 1000 °C in air. The composition was examined by a powder x-ray pattern and found to be the phase $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ as suggested by Cava, van Dover, Batlogg, and Rietman.[4] There was a small amount of a second phase which was not identified. A La-Sr-Cu-O ceramic disk ($\simeq$3.8 cm in diameter) was prepared by hydraulic pressing of this powdered compound and firing at 1000 °C in air. The Ba-Y-Cu-O superconducting material was prepared by sintering appropriate amounts of $BaCO_3$, Y_2O_3, and CuO at 900 °C in air. The resulting powder was examined by x-ray diffraction and found to be primarily the $Ba_2YCu_3O_{7-\delta}$ compound, with only a small amount of unidentified second phase present. A Ba-Y-Cu-O ceramic disk ($\simeq$6.2 cm in diameter) was prepared by hydraulic pressing of the powdered Ba-Y-Cu-O compound and firing at 950 °C in air, followed by a slow stepwise cooling to 350 °C. Samples for bulk measurements and for thin-film preparation were cut from these ceramic disks. The superconductivity and superconducting transition temperatures of the bulk La-Sr-Cu-O and Ba-Y-Cu-O samples were established by conventional measurements of dc resistance (four-probe method on bar-shaped specimens 1.2×0.8×8 mm) and ac magnetic susceptibility (made on a $\simeq$100 mg sample from a compacted disk using a Hartshorn-type bridge circuit) as functions of temperature. The La-Sr-Cu-O resistivity was 2.6 mΩ cm at room temperature but exhibited only a broad fall with decreasing temperature down to 15 K without reaching zero resistivity. This latter behavior is probably related to the nonconnectivity of the superconducting regions since a relative Meissner effect in the real part of the magnetic susceptibility was clearly observed at 41.5 K, as seen in Fig. 1. The corresponding relative Meissner effect for Ba-Y-Cu-O (room-temperature resistivity 63 mΩ cm) is shown in Fig. 2, where the onset temperature for superconductivity (94.5 K) correlates well with that obtained by resistivity. The imaginary part of the magnetic susceptibility was also measured and is shown in Figs. 1 and 2 for La-Sr-Cu-O and Ba-Y-Cu-O,

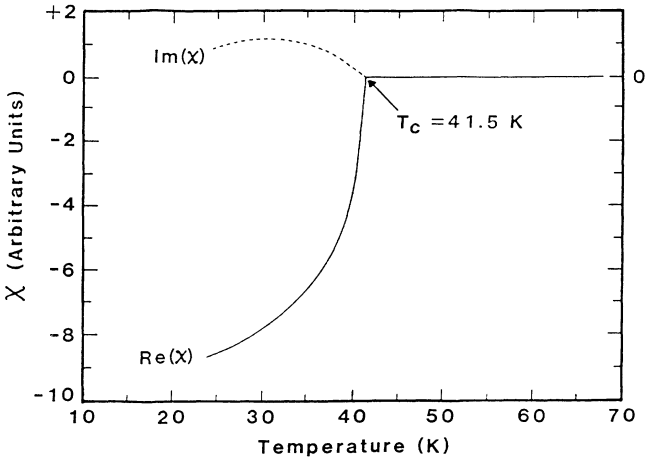

FIG. 1. Real (solid line) and imaginary (dashed line) parts of the alternating field magnetic susceptibility χ as a function of temperature for bulk $La_{1.85}Sr_{0.15}CuO_{4-\delta}$.

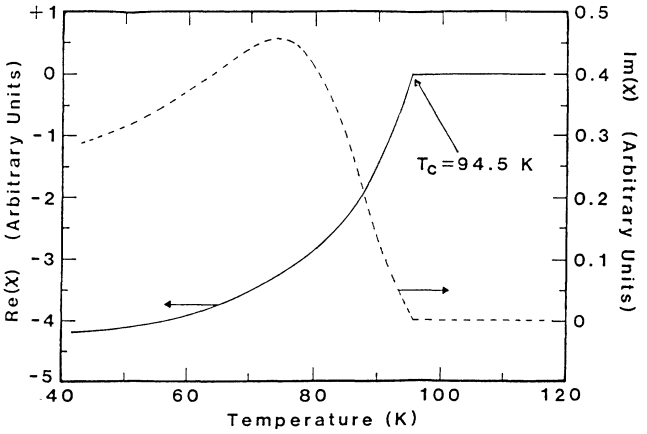

FIG. 2. Real (solid line) and imaginary (dashed line) parts of the alternating field magnetic susceptibility χ as a function of temperature for bulk $Ba_2YCu_3O_{7-\delta}$.

respectively. Below T_c this quantity is due to energy dissipation in portions of the samples which are not superconducting but which do have a low enough resistivity to carry a significant amount of current. Such regions appear to be present in both samples.

The thin films were prepared by laser ablation in vacuum using a pulsed excimer laser operating at 193 nm. The laser beam was focused onto the disk of source material, prepared as described above, by a spherical fused silica lens. Films resulted from part of the material ablated from the source disk depositing on a receiving substrate of fused silica which was placed in front of and oriented at 30° with respect to the source disk. The films discussed here were formed either by irradiation of a single spot on the source material for 30–100 s using a pulse rate of 10 Hz, with an average energy per pulse in the range 120–170 mJ, or by stepwise rastering the irradiation spot across the bulk sample during the same irradiation time. The area of the deposited films was approximately 1 cm^2, and the film thickness varied considerably across this area, being about 2 μm in the center of the deposit and thinning out considerably on going to the edges of the sample. Samples used in the measurements were approximately 2×5 mm in size and were cut, silica substrate and all, from the center of the films. They were used as prepared except for being exposed to and measured in air following removal from the preparation cell.

The presence of superconducting regions in these thin-films samples was established by a novel variant of methods based on observing the change in microwave loss during a superconductive transition.[11] Microwave methods are applicable even though our films are inhomogeneous with nonconductive regions and thus did not show either a superconducting transition or significant room temperature conductivity in dc resistance measurements. Our method, which utilizes a conventional homodyne-type electron-spin-resonance (ESR) spectrometer operating at X band (ca. 9.1 GHz), is based on observing that part of the change in microwave loss which is produced by application of a small ac magnetic field (≤ 5 Oe). This is readily accomplished by the ESR spectrometer's standard operating mode which phase detects the microwave power reflected from the cavity at the ac field modulation frequency. The ac field is superimposed on a dc magnetic field, which can be varied over a wide range and thus permits observations of dc magnetic field effects, but is always large enough that the combined ac+dc field never changes sign because this would complicate the phase detection process. The advantages of this method over other microwave methods are ease of implementation using commercial ESR apparatus, high sensitivity stemming from the noise reduction by narrow-band amplification and phase-sensitive detection, and selectivity arising from the fact that only those changes in sample resistivity which are magnetic field dependent will be observed. These last conditions are just the characteristics of a superconducting transition.

A test application of this method to the conventional superconductor niobium shows an absorption-peak-like signal (Fig. 3) as the sample temperature is varied through the superconducting transition at 9.3 K. Although the details of the mechanism leading to this response remain to be investigated, the response seems reasonable given, first, that the sample resistance and thus the reflected microwave power is changing rapidly from one relatively constant value to another at T_c, and, second, that increasing the external magnetic field lowers T_c. Thus, near T_c a change in magnetic field acts much like a change in sample temperature and the magnetic field modulation is thus equivalent to a temperature modulation. Consequently, the spectrometer response at the modulation frequency is proportional to the derivative of the sample resistivity with respect to temperature, which for the steplike change in resistance at T_c is a peak at T_c.

The microwave response of a very small (≤ 1 mg) sample of bulk La-Sr-Cu-O, shown in Fig. 4(a), is a peak at 36 K which is in good agreement with T_c determined from the Meissner effect, given the known inhomogeneity of this sample. Figure 4(b) shows the corresponding microwave response for a La-Sr-Cu-O thin film prepared by

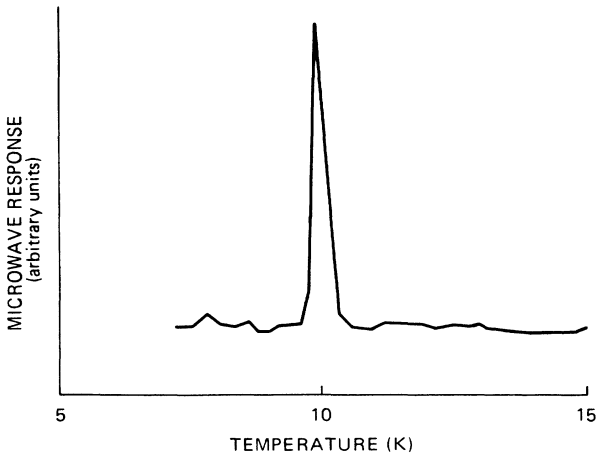

FIG. 3. Microwave signal vs temperature for a bulk sample of niobium.

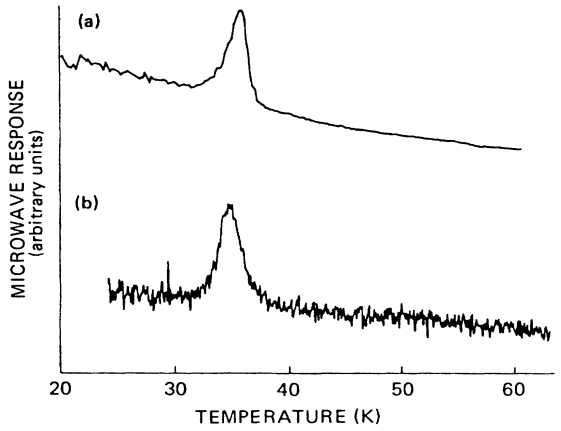

FIG. 4. Microwave signal vs temperature for $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ in (a) bulk and (b) thin film.

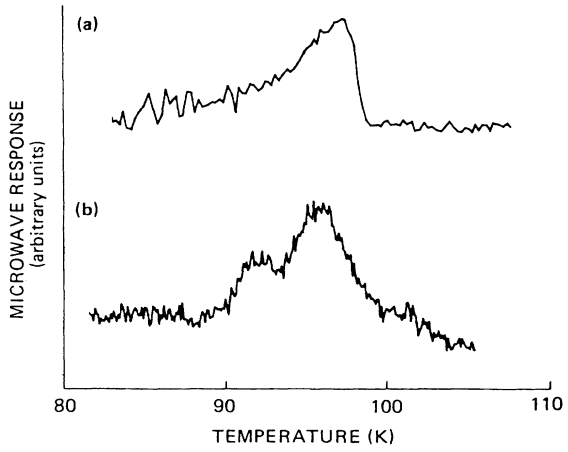

FIG. 5. Microwave signal vs temperature for $Ba_2YCu_3O_{7-\delta}$ in (a) bulk and (b) thin film.

laser ablation. It contains a peak at the same temperature which strongly supports the existence of superconducting regions in the film. Figure 5 shows the corresponding results for Ba-Y-Cu-O in the bulk and thin-film forms. Again, the peak at 95 K for the bulk sample is in good agreement with the resistivity and Meissner effect determinations of T_c in this material. The double peak in the thin-film sample is indicative of two superconductive phases with slightly different values of T_c.

In summary, thin films of $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ and $Ba_2YCu_3O_{7-\delta}$, prepared by laser ablation from the corresponding bulk materials, contain superconducting regions. Although the present films are inhomogeneous, the fact that they are prepared by a relatively simple method without subsequent heat treatment, which could be inconvenient in some applications, is an encouraging step in the preparation of superconducting thin films. Further work, aimed at improving the homogeneity of the films, is in progress.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2] H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L123 (1987).
[3] C. W. Chu, P. H. Hor, R. L. Mong, L. Gao, Z. J. Huang, and Y. O. Wang, Phys. Rev. Lett. **38**, 405 (1987).
[4] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).
[5] J. M. Tarascon, L. H. Green, W. R. Mckinnon, G. W. Hull, and T. H. Geballe, Science **235**, 1373 (1987).
[6] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, A. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).
[7] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and C. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).
[8] A. R. Moodenbaugh, M. Suenaga, T. Asano, R. N. Shelton, H. C. Ku, R. W. McCallum, and P. Klavins, Phys. Rev. Lett. **58**, 1885 (1987).
[9] D. W. Murphy, S. Sunshine, R. B. van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schneemeyer, Phys. Rev. Lett. **58**, 1888 (1987).
[10] P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987).
[11] J. I. Gittleman, S. Bozowski, and B. Rosenblum, Phys. Rev. **161**, 398 (1967); J. I. Gittleman and B. Rosenblum, J. Appl. Phys. **39**, 2617 (1968).