

## LETTERS TO THE EDITOR

### A Comparative Study of Superconducting $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$ \*

L. GANAPATHI, A. K. GANGULI, R. A. MOHAN RAM,  
AND C. N. R. RAO†

*Solid State and Structural Chemistry Unit, Indian Institute of Science,  
Bangalore 560 012, India*

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Based on X-ray diffraction and electron microscopy it is shown that oxides of the general formula  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  become tetragonal when  $\delta$  deviates slightly from 0. This tetragonal structure is similar to that of  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$ , with a cubic perovskite subcell and triple periodicity. Electron micrographs of these tetragonal oxides show  $90^\circ$  microdomains. Orthorhombic  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with high  $T_c$  ( $\sim 77$  K) is found only when  $\delta \approx 0$ ; this sample is subject to formation of twins. Fluorine substitution seems to favor superconductivity. © 1988 Academic Press, Inc.

High-temperature superconductivity in  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  created considerable interest since these tetragonal phases supposedly did not contain one-dimensional Cu-O chains (1, 2). Recent neutron diffraction studies (3) have, however, shown that  $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14+\delta}$  has a structure similar to that of tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , with partial substitution of La on Ba sites. Segre *et al.* (4) have suggested that members of the  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  system are disordered isomorphs of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  containing Cu-O chains. In these 336 oxides, both the O1 and O5 sites are partially occupied and the superconducting transition temperature increases with the degree

of orthorhombicity. We have been studying oxides of the type  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  for some time and it is on this basis that we identified  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  as the  $x = 1$  member of the  $\text{Y}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  system (5). We have generally found members of the  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  system to possess a tetragonal structure, with relatively low superconducting onset temperatures ( $\sim 50$  K). Our preliminary studies on orthorhombic  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  showed extreme sensitivity of the properties of this oxide system to oxygen stoichiometry. We have therefore investigated the structure and properties of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in some detail along with those of some members of the  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  system.

Samples of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  were prepared by heating appropriate mixtures of  $\text{La}_2\text{O}_3$  (preheated

\* Contribution No. 504 from the Solid State and Structural Chemistry Unit.

† To whom all correspondence should be addressed.

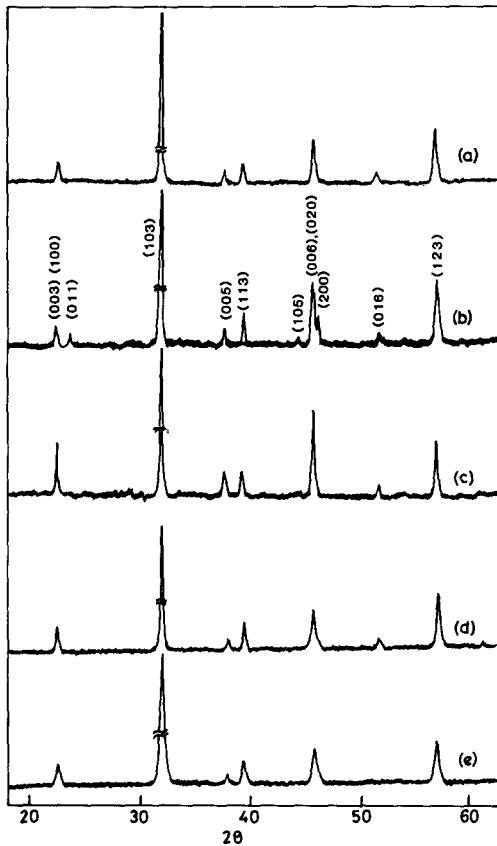


FIG. 1. X-ray diffraction patterns of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . (a)  $\delta = -0.3$ ; (b)  $\delta = -0.05$ ; (c)  $\delta = 0.3$ . Diffraction patterns of  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  for  $x = 0.0$  (d) and  $x = 0.5$  (e) are shown for the purpose of comparison. The  $\delta$  values of samples (d) and (e) were 0.9 and 0.4, respectively.

at 1200 K),  $\text{BaCO}_3$ , or  $\text{BaO}_2$  and  $\text{CuO}$  at 1220 K for 2 days with intermittent grinding. Finally the samples were annealed in oxygen at temperatures between 500 and 950 K for about 24 hr. Orthorhombic  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \approx 0$ ) was generally obtained when the samples were annealed in oxygen at 775 K for 20 hr. The samples obtained were always single-phase compounds without significant amounts of impurities, such as  $\text{BaCuO}_2$ , as determined by X-ray diffraction. All the samples prepared were subjected to careful X-ray and electron diffrac-

tion studies as well as to thermogravimetric analysis. High-resolution electron microscopy was carried out on some of the samples. Electrical resistivity measurements were made on pressed pellets by the four-probe method.

In Fig. 1 we present the X-ray diffraction patterns of a few members of the  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $-0.7 < \delta < 0.5$ ) system.  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \approx 0.0$ ) clearly shows the orthorhombic structure ( $a = 3.906 \text{ \AA}$ ,  $b = 3.936 \text{ \AA}$ , and  $c = 11.83 \text{ \AA}$ ) as seen from the distinct appearance of the (006) and (200) reflections. These orthorhombic samples, however, do not show the (102) and (012) reflections as in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Electron diffraction patterns (Fig. 2) of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \approx 0.0$ ) also show evidence of orthorhombicity. As the stoichiometry of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  deviates from  $\delta \approx 0$  on either side, the structure becomes tetragonal, as shown by the X-ray diffraction patterns (Fig. 1).

The X-ray diffraction patterns of members of the  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  (Fig. 1) are readily indexed on a tetragonal cell based on a cubic perovskite subcell of  $\sim 3.92 \text{ \AA}$ , with triple periodicity along the  $c$  axis. The tetragonal structure of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with  $|\delta| \geq 0.1$  is quite similar to that of  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$ , with the lattice parameters in the range  $a = 3.922\text{--}3.932 \text{ \AA}$  and  $c = 11.78\text{--}11.81 \text{ \AA}$ . It is noteworthy that  $\text{LaBa}_2\text{Cu}_3\text{O}_{6.7}$  has a tetragonal structure, unlike the corresponding  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  which has the orthorhombic structure up to  $\delta = 0.6$ . The  $a$  parameter of the tetragonal  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples is larger than that of orthorhombic  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \approx 0$ ), while the  $c$  parameter is smaller. The X-ray unit cell parameters of the  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  samples studied by us are listed in Table I.

The tetragonal structures of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \neq 0$ ) were also established on the basis of electron diffraction studies (Fig. 2) which show the  $3.92 \times 3.92\text{-\AA}$  structure perpendicular to the  $c$  axis. Electron dif-

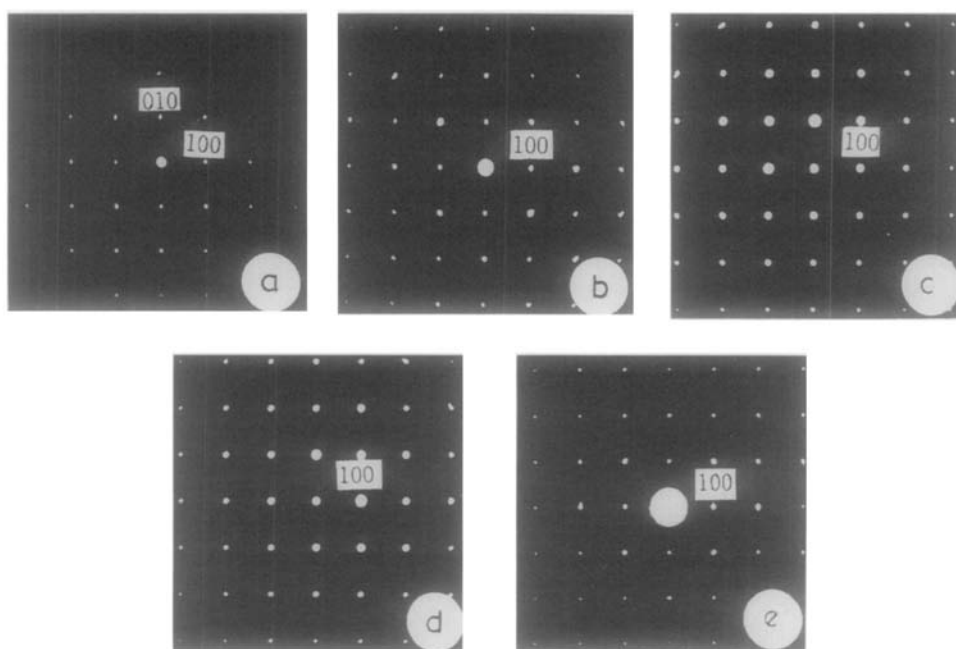


FIG. 2. Electron diffraction patterns of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  taken along [001] zone axis: (a)  $\delta = -0.05$ , orthorhombic phase; (b)  $\delta = 0.30$ , tetragonal phase; (c)  $\delta = -0.3$ , tetragonal phase. Electron diffraction patterns of tetragonal  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  are also shown: (d)  $x = 0.0$ ,  $\delta = 0.5$ , and (e)  $x = 0.5$ ,  $\delta = 0.4$ .

fraction patterns of tetragonal  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  ( $x = 0$  and  $x = 0.50$ ) presented in Fig. 2 also show the  $3.92 \times 3.92\text{-\AA}$  structure

TABLE I  
X-RAY UNIT CELL PARAMETERS OF  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$   
AND  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$

	$a$ (Å)	$c$ (Å)
$\delta$ in $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$		
0.45	3.932	11.79
-0.03 <sup>a</sup>	3.908	11.81
-0.05 <sup>a</sup>	3.906	11.83
-0.20	3.932	11.79
-0.30	3.937	11.80
-0.40	3.937	11.81
-0.55	3.922	11.78
-0.70	3.923	11.79
$x$ and $\delta$ in $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$		
0.0, 0.5	3.925	11.76
0.5, 0.4	3.926	11.78
0.75, 0.6	3.932	11.78

<sup>a</sup> Orthorhombic,  $b = 3.936\text{--}3.943$ .

perpendicular to the  $c$  axis. Furthermore, two-dimensional electron micrographs of  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  (Fig. 3) show evidence for  $90^\circ$  microdomains indicating that the tetragonal superstructure arises from the presence of the cubic-perovskite subcell. This feature was especially noted in crystals of  $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.9}$  which showed extensive microdomains in a large number of crystals studied. Crystals of  $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.5}$  showed less propensity for such microdomains compared to  $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.9}$ , indicating that excess oxygen tends to make the system more nearly pseudocubic. Microdomains of the type shown in Fig. 3 were also found in the electron micrographs of oxygen excess  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The perovskite subcell reflections ( $0k3l$ ) are brighter in the [100] electron diffraction patterns of most crystals indicating that La and Ba are randomly distributed. The tetragonal structure of  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  found by us is simi-

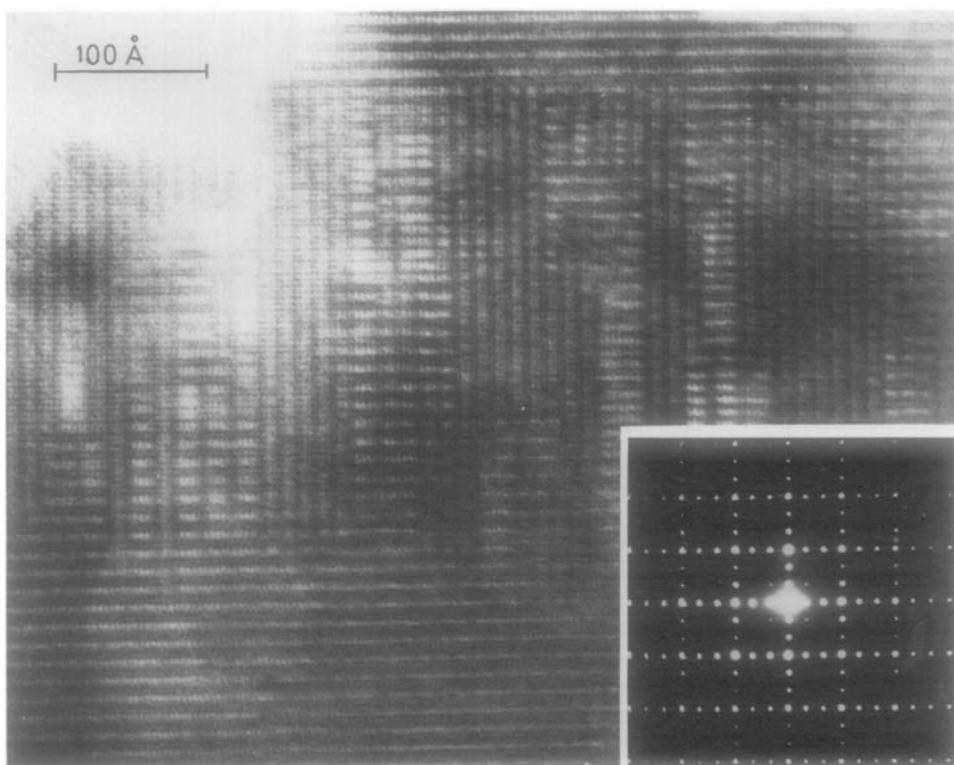


FIG. 3. HREM image of  $\text{La}_{2.5}\text{Ba}_{3.5}\text{Cu}_6\text{O}_{14.4}$  showing  $90^\circ$  microdomains. The inset shows the corresponding electron diffraction pattern.

lar to that described by Sishen *et al.* (6) and differs from that of Er-Rakho *et al.* (7) where the  $a$  parameter is nearly  $\sqrt{2}$  times larger than those for the known tetragonal and orthorhombic oxides related to  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . It is curious that  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system has such a great tendency to have oxygen in excess of 7 per formula unit, unlike  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Our observation of the oxygen excess in several of the  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples formed by us (Table I) would be valid even if there were some undetected  $\text{BaCuO}_2$  in the samples.

The structure of orthorhombic  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta = 0$ ) corresponds to that of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and would therefore contain one-dimensional Cu-O chains (8, 9). Deviation from this stoichiometry ( $|\delta| \geq 0.1$ ) probably populates the O5 sites along the  $a$  axis or/

and depletes the O1 sites along the  $b$  axis, giving rise to the tetragonal structure. The structure of tetragonal  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  would be based on that of orthorhombic  $\text{LaBa}_2\text{Cu}_3\text{O}_7$  where the O5 sites become more predominantly populated (9). It is because of this structural similarity that we encounter high-temperature superconductivity and orthorhombicity in the  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  system only when  $x = 1.0$  and  $\delta \approx 0$ .

$\text{LaBa}_2\text{Cu}_3\text{O}_{7.05}$  prepared by us exhibited superconductivity with onset around 95 K and zero-resistance at 77 K. The  $T_c$  however drops drastically even when  $|\delta| \geq 0.1$ , at which compositions the structure also becomes tetragonal (Fig. 4). All the tetragonal  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  oxides studied in this laboratory show  $T_c$  well below 50 K,

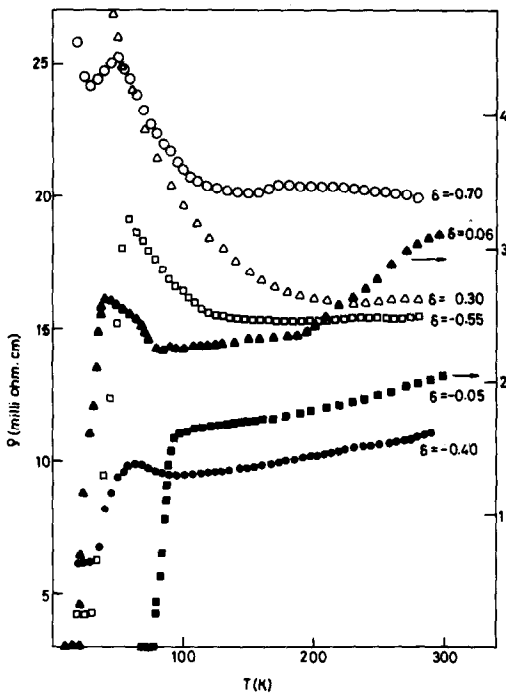


FIG. 4. Electrical resistivity data of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

and any high-temperature superconductivity in such compositions may well be due to the presence of the stoichiometric ( $\delta \approx 0$ )

123 phase (10). The present study establishes that the orthorhombic structure is essential for high- $T_c$  superconductivity.

Orthorhombic  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \approx 0.0$ ) shows the presence of twins in the electron micrographs (Fig. 5), just as orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  does (11, 12). The twins are only found when  $\delta = 0$ . We have not encountered twinning in the tetragonal members of  $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$  or  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Twins form in the orthorhombic structure, which, in turn, is dependent on the presence of Cu-O chains along the  $b$  axis.

We have prepared a number of compositions of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  wherein  $\text{BaCO}_3$  in the starting composition was partly substituted by  $\text{BaF}_2$ . Even in the presence of fluorine, the structure of these oxides becomes tetragonal whenever  $|\delta| \geq 0.1$ . The orthorhombic structure was found only in  $\text{LaBa}_2\text{Cu}_3\text{O}_{7.09}$  prepared in the presence of 0.1  $\text{BaF}_2$ . This sample showed onset of superconductivity at 90 K, with zero-resistance at 55 K. A corresponding sample of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7.10}$  prepared without  $\text{BaF}_2$  has a tetragonal structure and does not exhibit

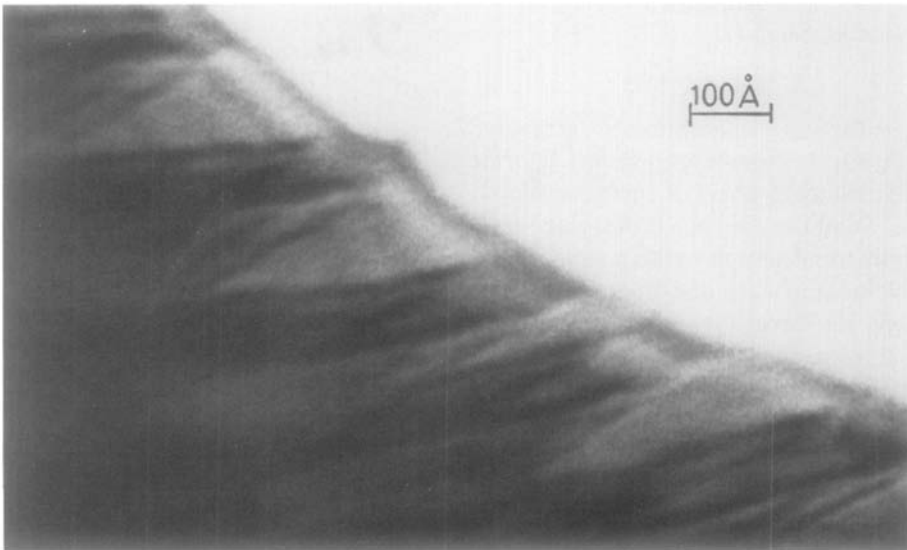


FIG. 5. Electron micrograph showing twins in orthorhombic  $\text{LaBa}_2\text{Cu}_3\text{O}_{7.05}$ .

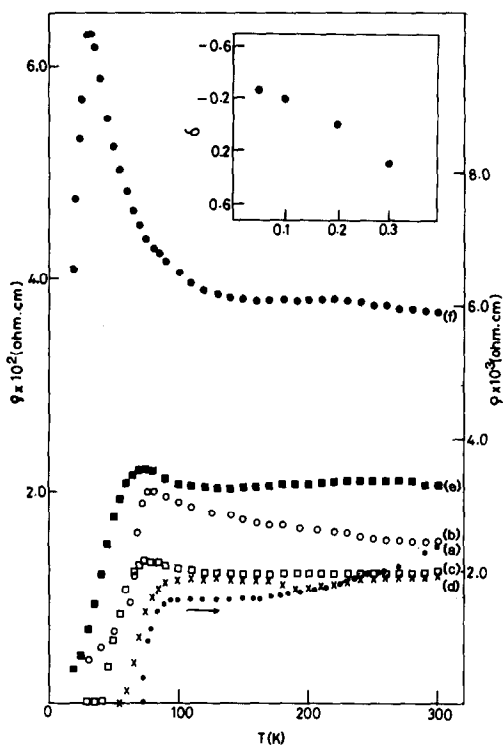


Fig. 6. Resistivity vs temperature plots for (a)  $\text{LaBa}_2\text{Cu}_3\text{O}_{7.05}$ , (b)  $\text{LaBa}_2\text{Cu}_3\text{O}_{7.25}$  (0.05  $\text{BaF}_2$ ), (c)  $\text{LaBa}_2\text{Cu}_3\text{O}_{7.20}$  (0.1  $\text{BaF}_2$ ), (d)  $\text{LaBa}_2\text{Cu}_3\text{O}_{7.09}$  (0.1  $\text{BaF}_2$ ), (e)  $\text{LaBa}_2\text{Cu}_3\text{O}_{7.10}$  (0.2  $\text{BaF}_2$ ), and (f)  $\text{LaBa}_2\text{Cu}_3\text{O}_{6.73}$  (0.3  $\text{BaF}_2$ ). Inset shows variation of  $\delta$  in  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with the nominal number of moles of  $\text{BaF}_2$  (per mole of the oxide) taken initially.

superconductivity. Samples of tetragonal  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  containing some fluorine show evidence for onset of superconductivity (Fig. 6); in the absence of fluorine, however, tetragonal samples with a similar oxygen stoichiometry are nonsuperconducting. Although we have not quantitatively estimated how much fluorine has entered the oxygen site in  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , we find that the oxygen content in the samples decreases with the  $\text{BaF}_2$  content, as deter-

mined by TGA (see inset of Fig. 6). This suggests partial incorporation of fluorine on oxygen sites.

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