

Superconductivity above 90 K in the Square-Planar Compound System $ABa_2Cu_3O_{6+x}$ with $A = Y, La, Nd, Sm, Eu, Gd, Ho, Er,$ and Lu

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We have found superconductivity in the 90-K range in $ABa_2Cu_3O_{6+x}$ with $A = La, Nd, Sm, Eu, Gd, Ho, Er,$ and Lu in addition to Y . The results suggest that the unique square-planar Cu atoms, each surrounded by four or six oxygen atoms, are crucial to the superconductivity of oxides in general. In particular, the high T_c of $ABa_2Cu_3O_{6+x}$ is attributed mainly to the quasi two-dimensional assembly of the CuO_2 - Ba - CuO_{2+x} - Ba - CuO_2 layers sandwiched between two A layers, with particular emphasis in the CuO_{2+x} layers. Higher- T_c oxides are predicted for compounds with bigger assemblies of CuO_2 layers coupled by Ba layers.

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Superconductivity above 30 K was first reported¹ in the mixed-phase La - Ba - Cu - O compound system. Subsequent studies attributed^{1,2} the superconductivity observed in this and other related compounds to the single layeredlike K_2NiF_4 structural phase. With the steady improvements in sample conditions and the application of pressure, the superconducting transition temperature has been raised to above 40 K at ambient pressure^{3,4} and 57 K under pressure,⁵ and the transition width has been reduced³ to 1.4 K. Recently, superconductivity starting at 98 K with a zero-resistance state at 94 K was discovered^{6,7} in the mixed-phase Y - Ba - Cu - O system with nominal compositions represented by $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$. Later, superconductivity near 90 K with a zero-resistance state at ~ 70 K was also reported⁸ in the mixed-phase $Lu_{1.8}Ba_{0.2}CuO_4$ compounds. Preliminary examinations showed⁹ that the Y - Ba - Cu - O compounds are different from those with the K_2NiF_4 structure. Recently, the two phases in the Y - Ba - Cu - O compound system were separated and identified¹⁰: tetragonal $YBa_2Cu_3O_{6+x}$ (black) and orthorhombic Y_2BaCuO_5 (green). Magnetic measurements on the Y - Ba - Cu - O compounds showed¹¹ that the black phase is responsible for the high-temperature superconductivity detected. Indeed, single-phase $YBa_2Cu_3O_{6+x}$ samples exhibiting 100% ac diamagnetic shift $\Delta\chi$ were obtained.¹¹ This is consistent with the most recent reports from other laboratories.¹²

To determine the role of Y and of different structures, e.g., K_2NiF_4 and $YBa_2Cu_3O_{6+x}$ planes, in high-temperature superconductivity, we have synthesized and examined the $ABa_2Cu_3O_{6+x}$ compound systems with $A = La, Nd, Sm, Eu, Gd, Ho, Er,$ and Lu , in addition to Y . They all were found to be superconducting with an onset temperature between 90 and 98 K and a zero-resistance state between 70 and 94 K. This shows that the trivalent A atoms, even if they are magnetic, do not affect the superconductivity in this class of compounds. Superconductivity must then be associated with the

CuO_2 - Ba - CuO_{2+x} - Ba - CuO_2 plane assembly sandwiched between the A layers. The significance of the interplane coupling or screening within the layer assembly is especially evident from the enhancement of the superconducting transition from ~ 30 K in the K_2NiF_4 structure^{1,2} to ~ 90 K in the $ABa_2Cu_3O_{6+x}$ structure in the La - Ba - Cu - O system observed in this study. Bigger layer assembly is predicted for higher- T_c superconducting oxides.

All samples with the $ABa_2Cu_3O_{6+x}$ structure and $A = Y, La, Nd, Sm, Eu, Gd, Ho, Er,$ and Lu were synthesized by the solid-state reaction of appropriate amounts of sesqui-oxides of $La, Nd, Sm, Eu, Gd, Ho, Er,$ and $Lu, BaCO_3,$ and CuO in a fashion similar to that previously described.⁵ Structural analyses were carried out with a Rigaku D-MAX x-ray powder diffractometer. Samples of dimensions ~ 1 mm \times 0.5 mm \times 4 mm were cut from the sintered cylinders. A standard four-lead technique was employed for the resistance (R) measurements, and a Linear Research ac inductance bridge was used for the magnetic susceptibility (χ) determinations. The temperature was measured by use of an $Au \pm 0.07\%$ Fe-Chromel or Chromel-Alumel thermocouple above 30 K and a Ge thermometer below.

The powder x-ray diffraction patterns showed that all samples except $A = Lu$ possess the single tetragonal $YBa_2Cu_3O_{6+x}$ structure, although for a couple of cases orthorhombic symmetry¹² was also detected. The results show that the difference in the structural symmetries reported^{10,12} for the Y - Ba - Cu - O system may be caused by the oxygen content and the slight difference in composition. As will be evident later, the structural symmetry in this class of oxides apparently does not have a large effect on the superconductivity. The lattice parameters are given in Table I. In addition to the orthorhombic $YBa_2Cu_3O_6$ structure, the $A = Lu$ compound exhibits other phases, which, we believe, can be eliminated by proper heat treatments. Sample-preparation parameters were found¹³ to affect the electronic and magnetic prop-

TABLE I. Lattice parameters and critical temperatures of samples with $ABa_2Cu_3O_{6+x}$ structure.

| A | T_{c0} (K) | T_{c1} (K) | T_{dl} (K) | a (Å) | b (Å) | c (Å) |
|-------------------|--------------|--------------|--------------|---------|---------|---------|
| Y ^{a,b} | 98 | 94 | 100 | 3.86 | 3.86 | 11.71 |
| La ^c | 91 | 75 | 99 | 3.95 | 3.95 | 11.79 |
| Nd ^c | 91 | 70 | 93 | 3.89 | 3.89 | 11.73 |
| Sm ^c | 94 | 82 | 135 | 3.88 | 3.88 | 11.73 |
| Eu ^c | 94 | 88 | 160 | 3.86 | 3.86 | 11.74 |
| Gd ^c | 95 | 92 | 135 | 3.89 | 3.89 | 11.73 |
| Ho ^c | 93 | 88 | 130 | 3.89 | 3.89 | 11.52 |
| Er ^c | 94 | 87 | 120 | 3.83 | 3.85 | 11.65 |
| Lu ^{c,d} | 91 | 85 | 120 | 3.83 | 3.87 | 11.73 |

^aReference 6.

^cPresent work.

^bReference 10.

^dReference 8.

erties of this class of compounds drastically. Furthermore, they are closely coupled to one another, i.e., the reaction time, the reaction temperature, the quenching rate, the reaction atmosphere, and the compositions are all interrelated. For instance, all these compounds can be made insulating, partially superconducting, or completely superconducting by our varying the reaction atmosphere and the quenching rate while keeping the compositions unchanged. In particular, the La-Ba-Cu-O system can even be made magnetic.⁷ In spite of this wide range of variation of electrical properties, the samples showed only very slight differences in their x-ray diffraction patterns, strongly suggesting that oxygen content plays an important role in the superconductivity of oxides. In fact, we found that the formation conditions for superconducting $ABa_2Cu_3O_{6+x}$ for different A 's are different. Details of the physical chemistry for compound synthesis will be published elsewhere.¹⁴

All samples studied show rather sharp R drops with an onset temperature T_{c0} between 90 and 98 K, a zero- R -state temperature T_{c1} between 70 and 94 K, and a deviation from linear temperature dependence of R at temper-

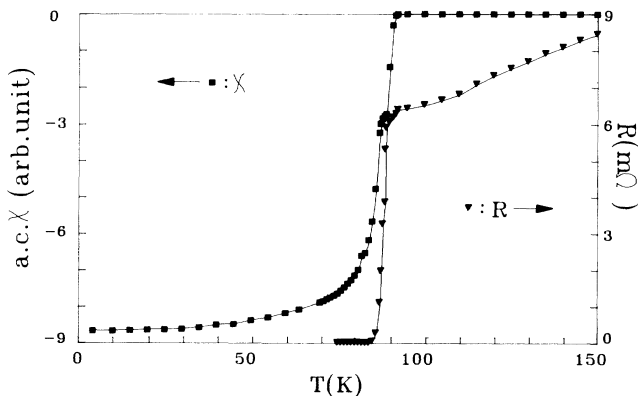


FIG. 1. R - T and χ - T for A =Gd.

ature T_{dl} between 93 and 160 K. Whether T_{dl} represents the beginning of superconductivity is yet to be determined. All relevant data are given in Table I, and the typical temperature dependence of R is displayed in Fig. 1 for A =Gd. All samples except for A =Lu show a (97-100)% ac diamagnetic shift at 4.2 K, which is represented also in Fig. 1 for A =Gd. It is, therefore, evident that the sample starts to superconduct at ~ 90 K, consistent with the R measurements, and that the whole sample becomes superconducting at lower temperatures. It should be noted that the ac diamagnetic shift represents only the upper limit of the superconducting volume fraction of the samples, since it arises from not only the Meissner effect but also the ac-shielding effect.

The observation of superconductivity with an almost constant T_{c0} in $ABa_2Cu_3O_{6+x}$ for A =Y, La, Nd, Sm, Eu, Gd, Ho, Er, and Lu in the present study and in previous investigations^{6,8} clearly demonstrates that the superconductivity in this class of compounds is not sensitive to A . This is particularly true in view of the wide range of the magnetic properties of the A atoms in the compounds. The present results, therefore, strongly suggest that superconductivity in $ABa_2Cu_3O_{6+x}$ must be associated with the CuO_2 -Ba- CuO_{2+x} -Ba- CuO_2 plane assembly sandwiched by two layers of A atoms, as represented schematically in Fig. 2 for A =La. These layer assemblies of ~ 8 -Å thickness may be considered to be disrupted by the A layers only along the c axis, and thus they may retain their quasi two-dimensional characteristics. It is also possible that the two CuO_2 layers in the assembly provide shielding for the CuO_{2+x} layers from the A layers. For this situation, superconductivity will then be confined only to the CuO_{2+x} layers within the layer assembly mentioned. In the K_2NiF_4 structure of the La-

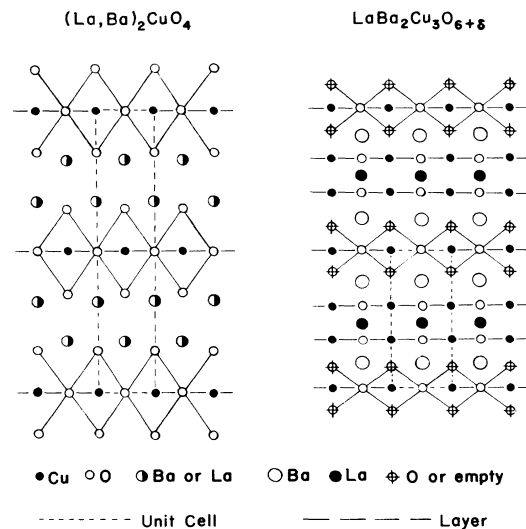


FIG. 2. Schematic representation of the structures of $(La_{0.9}Ba_{0.1})_2CuO_{4-x}$ and $LaBa_2Cu_3O_{6+x}$.

Ba-Cu-O system, as shown also in Fig. 2, only individual square planes of Cu atoms with coordination six exist, with a different stacking sequence. They are disrupted along the c axis by the disordered La-Ba layers. The x-ray diffraction patterns for the two structural La-Ba-Cu-O compounds are shown in Fig. 3 for comparison. The difference between the two structures clearly is responsible for the threefold difference in T_c . It may be accidental that the number ratio of CuO_2 planes in the two structures is also ~ 3 . A higher T_c may hence be obtainable by structures with more than three CuO_2 layers sandwiched between two A layers.

It has been shown¹⁵ that it is extremely difficult to achieve a T_c above 40 K based on the conventional electron-phonon interaction. A superconducting mechanism of electronic nature appears to be needed. Because of the presence of defects in these high- T_c oxides, local deformations must be important. Two general situations to achieve enhanced superconductivity that make use of the local-field effect can be summarized as follows: The excitations and the charge carriers are in different or the same spatial regions. For the former, an enhanced superconducting interaction occurs between electrons via the virtual exchange of excitons across the interfaces^{5,16} which may arise from intergrowths, or homojunctions between different phases, or in one phase, concentration fluctuations or layered structure. The large diamagnetic signal observed for these superconducting compounds rules out the possibility of interfaces between different structural phases. For the second case, where excitons coexist with the charge carriers in the same spatial region, enhanced superconductivity has been proposed through plasmons,¹⁷ charge-transfer excitations,¹⁵ spin fluctuations,¹⁸ or resonating valence bonds.¹⁹ The two-dimensional acoustic plasmons have been shown¹⁷ to give rise to a high T_c . The second type of excitation appears

to be consistent with charge fluctuations between $\text{Cu}^{++}\text{O}^{--}$ and Cu^+O^- in the CuO_{2+x} planes. The rest are compatible with the subtle correlation between superconductivity and magnetism in these compounds.^{7,20} For instance, Curie-Weiss behavior above T_c with a negative Curie temperature was apparent²⁰ in the Y-Ba-Cu-O system, suggesting the existence of a frustrated antiferromagnetic interaction. The variation of the compound system from insulating to superconducting by the change of only the heat treatment of the compounds makes the last model particularly appealing. At present, experiments have yet to be devised to differentiate the above models.

In conclusion, we have demonstrated that superconductivity above 90 K in $\text{ABa}_2\text{Cu}_3\text{O}_{6+x}$ is associated with the CuO_2 -Ba-CuO_{2+x}-Ba-CuO₂ plane assembly interrupted by A layers only along the c axis. At the same time, superconductivity can also be confined to the CuO_{2+x} layers while the CuO_2 layers provide the shielding from the A layers. The ordering of A and Ba atoms may also play a role in the high T_c . Compounds with more CuO_2 layers coupled by more Ba atoms may offer an avenue to even higher T_c . To account for the high T_c , one, perhaps, needs excitations of electronic nature.

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Note added.—After the submission of our manuscript, we became aware that similar work on Gd-Ba-Cu-O was carried out by Fisk *et al.*²¹ at Los Alamos National Laboratory.

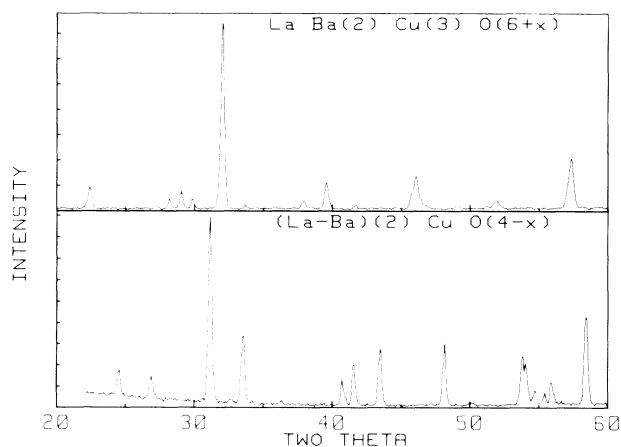


FIG. 3. X-ray diffraction patterns for $(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_{4-x}$ and $\text{LaBa}_2\text{Cu}_3\text{O}_{6+x}$.

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¹J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).

²H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, *Jpn. J. Appl. Phys. Lett.* (to be published).

³R. J. Cava, B. Batlogg, R. B. Van Dover, and E. A. Rietman, *Phys. Rev. Lett.* **58**, 408 (1987).

⁴Z. X. Zhao, L. Q. Chen, C. G. Cu, Y. Z. Huang, J. X. Liu, G. H. Chen, S. L. Li, S. Q. Guo, and Y. Y. He, to be published.

⁵C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, *Phys. Rev. Lett.* **58**, 405 (1987); C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, and Z. J. Huang, *Science* **235**, 567 (1987); P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and C. W. Chu, to be published.

⁶M. K. Wu, J. R. Ashburn, C. T. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.* **58**, 908 (1987).

⁷C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, J. Bechtold, D. Campbell, M. K. Wu, J. Ashburn,

and C. Y. Huang, to be published.

⁸A. R. Moodenbaugh, M. Suenaga, T. Assano, R. N. Shelton, H. C. Ku, R. W. McMallum, and P. Klavine, this issue [Phys. Rev. Lett. **58**, 1885 (1987)].

⁹P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y. Q. Wang, K. Forster, J. Vassiliou, C. W. Chu, M. K. Wu, J. R. Ashburn, and C. T. Torng, Phys. Rev. Lett. **58**, 911 (1987).

¹⁰R. M. Hazen, L. W. Finger, R. L. Angel, C. T. Prewitt, N. L. Ross, H. K. Mao, C. G. Hadjidakos, P. H. Hor, R. L. Meng, and C. W. Chu, Phys. Rev. B (to be published).

¹¹P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, J. Bechtold, K. Forster, C. W. Chu, H. K. Mao, R. M. Hazen, L. W. Finger, R. L. Angel, and N. L. Ross, unpublished.

¹²R. J. Cava, B. Batlogg, R. B. Van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987). P. M. Grant, R. B. Beyers, E. M. Engler, G. Lim, S. S. P. Parkin, M. L. Ramirez, V. Y. Lee, A. Nazzal, J. E. Vazquez, and R. J. Savoy, Phys. Rev. B (to be published).

¹³D. Gubser, R. A. Hein, S. H. Lawrence, M. S. Osofsky, D. J. Schrodt, L. E. Toth, and S. A. Wolf, Phys. Rev. B **35**, 5350 (1987).

¹⁴R. L. Meng, P. H. Hor, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, to be published.

¹⁵C. M. Varma, S. Schmitt-Rink, and E. Abrahams, to be published, and references therein.

¹⁶J. Bardeen, in *Superconductivity in d- and f-Band Metals*, edited by D. Douglas (Plenum, New York, 1976), p. 1; M. L. Cohen and S. G. Louie, *ibid.*, p. 7; C. S. Ting, D. Y. Xing, and W. Y. Lai, to be published.

¹⁷V. Kresin, to be published; J. Ruvalds, to be published.

¹⁸See, for example, A. J. Leggett and J. C. Wheatley, Rev. Mod. Phys. **41**, 331 (1975).

¹⁹P. W. Anderson, Science **235**, 1196 (1987).

²⁰P. H. Hor, R. L. Meng, C. W. Chu, C. Y. Huang, E. Zirngiebl, and J. D. Thompson, to be published.

²¹Z. Fisk, J. D. Thompson, E. Zirngiebl, J. L. Smith, and S.-W. Cheong, Solid State Commun. (to be published).