

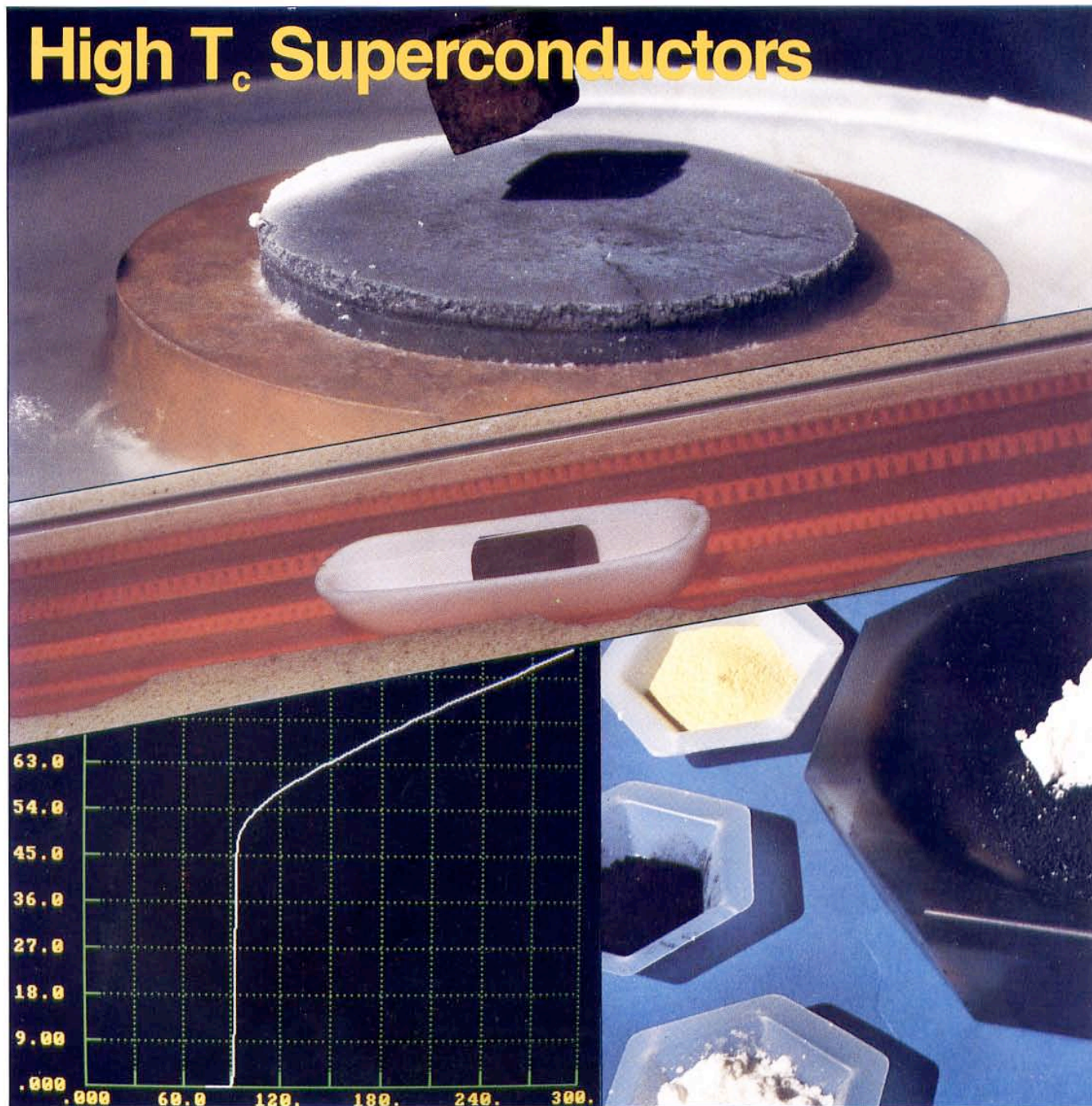
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High T_c Superconductors



Structure of High T_c Oxide Superconductors

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Introduction

Our understanding of the superconducting mechanism in the newly discovered oxide superconductors is closely connected with a detailed knowledge of the structural properties displayed by these materials. Moreover, it is important to explore possible connections between structural and superconducting properties and to establish general structural principles which can guide our search for new compounds.

We present here a survey of the structures of the recently discovered oxide superconductors. The common feature of these structures (with the exception of cubic $Ba_{1-x}K_xBiO_{3-y}$) is the presence of one or more planes of copper atoms with four strongly bonded oxygen atom neighbors in a square planar arrangement at a distance of approximately 1.90 Å ("CuO₂ planes"). In some structures these planes occur in groups, with the individual planes inside a group being separated by one Y or Ca layer and the groups being intercalated by a variable number of LaO, BaO, CuO, TiO and/or BiO layers. (The intercalated CuO layer is crystallographically distinct from the "CuO₂ plane"). A natural model for superconductivity which arises from these structures is that the conductivity occurs predominantly in the CuO₂ planes, while the other (intercalated) layers provide in some fashion carriers and/or the coupling mechanism necessary for the superconductivity.

Cubic ($Ba_{1-x}K_x$)BiO_{3-y}

Although the $Ba_{1-x}K_xBiO_{3-y}$ system is the most recently discovered, it has the simplest structure and a moderately "low" T_c (~30 K). Its simple cubic perovskite structure was determined using powder x-ray diffraction¹ and confirmed by powder neutron diffraction and Rietveld refinement.² The structure

consists of a perovskite cube with Ba or K on the corners, Bi in the center, and oxygens in the faces, as shown in Figure 1. Being a truly cubic system, it cannot be described as a layered compound. The superconducting phase and structure is present for $x > 0.25$ with the highest T_c occurring for compositions close to a structural phase transition into a nonsuperconducting phase at $x \sim 0.25$.

It is important to highlight a major structural feature of this superconductor by comparing it with the long-known $BaPb_{1-x}Bi_xO_3$ compound ($T_c \sim 13$ K).³ Under the generally believed assumption that the conductivity occurs in the strongly bonded three-dimensional Bi-O sublattice, the doping of the Bi site is more detrimental to superconductivity (i.e., lower T_c) than the doping in the Ba site. The nonmetallic parent compound common to both structures, $BaBiO_3$, can be made metallic (and superconducting) by doping with Pb on the Bi site or K on the Ba site. The K-doped compound, $Ba_{1-x}K_xBiO_3$, where the Bi-O sublattice remains intact, has a substantially higher T_c .

"Single-Layered" $La_{2-x}R_xCuO_4$ ($R = Ba, Sr, Ca$)

The discovery of superconductivity near 30 K in $La_{2-x}Ba_xCuO_4$ by Bednorz and Müller was the beginning of the unprecedented activity in this field.⁴ The structure of this compound is identical to that of the undoped orthorhombic La_2CuO_4 structure or its high-temperature tetragonal polymorph. It can be described either as a stacking of perovskite cubes or as a layered compound. For the rest of this article, it is convenient and more consistent with the electronic properties to discuss its structure as a layered superconductor.

The structure of the superconducting

compositions was first studied by x-ray and neutron diffraction.^{5,6} It consists of one plane of Cu atoms with four strongly bonded oxygen neighbors in a square-planar arrangement at a distance of 1.89 Å, and two additional weakly bonded oxygen neighbors above and below the Cu atom at a distance of 2.43 Å, as shown in Figure 2. If one considers the weakly bonded oxygen atoms to be associated with La rather than with Cu (consistent with calculations of the electronic structure), the layered nature of the structure is clearer. The square-planar CuO₂ planes are intercalated by two LaO layers (or, equivalently, a corrugated double LaO layer). Successive CuO₂ planes are displaced from one another by 1/2 of the unit cell along the tetragonal [110] direction, resulting in a doubling of the unit cell along the c axis.

The highest T_c in this family of compounds ($T_c \approx 37$ K for $R = Sr$) occurs for compositions near $x = 0.15$. The substitution of the divalent R cation for trivalent La introduces carriers into the conduction band associated with the CuO₂ planes. At this composition, the structure is tetragonal, $I4/mmm$ at room temperature with two formula units per unit cell. However, at low temperature the structure is orthorhombic (identical to undoped La_2CuO_4), with cell edges given approximately by $\sqrt{2}a \times \sqrt{2}a \times c$, where a and c are the tetragonal lattice parameters, resulting from a coordi-

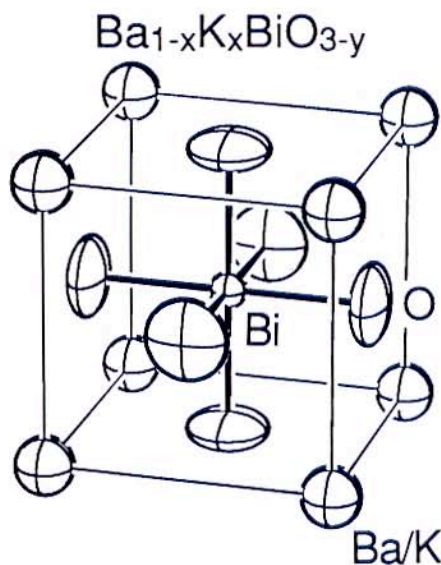


Figure 1. Structure of the cubic ($Ba_{1-x}K_x$)BiO_{3-y} compound.

nated, nearly rigid, tilting of the CuO_6 octahedra.⁷

"Double-Layered" $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$: The 1-2-3 Compound

The most extensively studied high T_c oxide superconductor is the family $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ ($R = \text{Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu}$), which is commonly denoted as the "1-2-3" compound. This system has been studied in detail because it presents a great richness in structure, the possibility of a large number of substitutions with varied effects on the superconductivity, a high T_c (>90 K) and, perhaps more importantly, because a single phase superconducting compound can be made reliably and reproducibly.

The structure of the 1-2-3 compound was determined by a rapid succession of experiments by different groups using x-ray powder, x-ray single-crystal and neutron diffraction.⁸ The most striking structural feature, the ordering of the oxygen vacancies giving rise to one-dimensional Cu-O "chains," was first observed by neutron powder diffraction.⁹ The structure consists of two dimpled CuO_2 planes separated by a Y layer which contains no oxygen and intercalated with two BaO and one CuO layers (containing Cu-O chains) as shown in Figure 3. Note that two distinct crystallographic sites are present for the Cu—one in the CuO_2 planes and one in the intercalated Cu-O chain-containing layer. The presence of the ordered oxygen vacancies gives rise to an orthorhombic symmetry, Pmmm, because of the existence of the Cu-O chains (Cu1, O1 in Figure 3).

A formal oxidation state calculation (assuming a valency of +3 for Y, +2 for Ba, +2 for Cu, and -2 for O) requires an oxygen stoichiometry of 6.5. Therefore, the presence of the oxygens in the chain site, producing a total oxygen stoichiometry near 7, implies that in this case the carriers are provided by the excess oxygen. It is also possible to change the number of carriers in the system by doping on the metal ion sites. Generally, metal ions that do not change the formal oxidation states and preserve the structure have a pronounced effect on the superconductivity only if they substitute in the CuO_2 plane and a small effect if they substitute in other sites.¹⁰ This is true, unexpectedly, even for substitutions of magnetic ions, which undergo long-range ordering, (Dy, Er, Ho) in the Y site.¹¹ A notable exception is the substitution of Pr in the Y site, which gradually

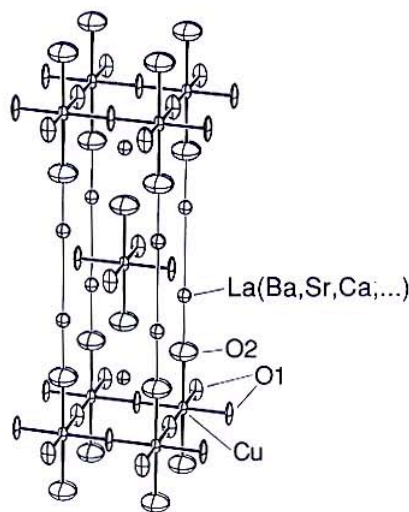


Figure 2. Structure of the "single-layered" $\text{La}_{2-x}\text{R}_x\text{CuO}_4$ compound.

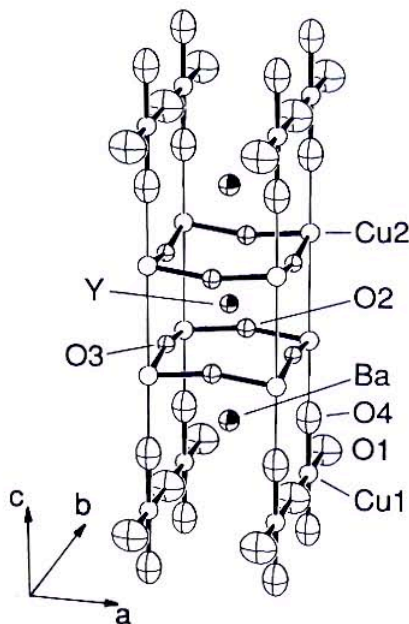


Figure 3. Structure of the "double-layered" $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ "1-2-3" compound.

depresses the superconductivity to zero transition temperature when ~60% of Y is substituted by Pr.¹²

Changes in oxygen stoichiometry have been found to strongly affect super-

conductivity in the 1-2-3 systems.¹³ In $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, as oxygen is removed from the chains, some of the remaining oxygen atoms move to sites between the chains, eventually resulting in a transition to a disordered tetragonal structure.¹⁴ T_c drops with decreasing oxygen content and reaches zero near the orthorhombic-to-tetragonal transition which corresponds to a composition near $\text{YBa}_2\text{Cu}_3\text{O}_{6.4}$.^{15,16}

The common conclusion drawn from experiments where T_c in the 1-2-3 system has been modified by metal-site substitution or changes in oxygen stoichiometry is that the superconductivity depends on the degree of charge transfer from the intercalating layers, which act as "reservoirs" of charge, to the conducting CuO_2 planes.¹⁶⁻¹⁸ However, a variety of studies suggest that the existence of one-dimensional Cu-O chains (perhaps only locally ordered in the structures with average tetragonal symmetry) may also play an important role in the superconductivity.^{13,19-20}

"Multi-Layered" Tl-Ca-Ba-Cu-O and Bi-Ca-Sr-Cu-O

The superconducting compounds in the Tl-Ca-Ba-Cu-O and Bi-Ca-Sr-Cu-O systems form a hierarchy of structures which differ in the number of CuO_2 planes and the number of intercalating layers as shown in Figure 4. The structures consist of $n = 1, 2, 3, \dots$ CuO_2 planes with the Cu-O distance decreasing with increasing n (1.933-1.925 Å in Tl, and ~1.90 Å in Bi). The individual CuO_2 layers are separated by Ca layers which contain no oxygen (analogous to the Y layer in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$) and the groups of layers are intercalated by two BaO layers (or SrO layers in the Bi series) and $m = 1, 2, \dots$ TlO (or BiO) layers. When two TlO or BiO layers are present, the adjacent layers are displaced by 1/2 of the Tl-Tl spacing in the [1,1,0] direction, leading to a doubling of the unit cell. The generic chemical formula is, therefore, $\text{Tl}_m\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+m+2}$ or $\text{Bi}_m\text{Ca}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+m+2}$. The individual compounds are, thus, denoted as the 1021, 1122, 1223, 2021, 2122, 2223, etc. structures according to the order of metal atoms in the order indicated by the general formulas.

Determination of these structures has been complicated because many samples contain mixtures of the various phases. Even microscopic single crystals often contain syntactic intergrowths (i.e., stacking errors along the c axis) of more than one phase.^{21,22} Thus, even

though many general structural features of these compounds were established by powder x-ray and electron diffraction and high-resolution electron microscope lattice imaging,²³⁻²⁴ the precise determination of the structures has been a tedious process involving careful searches for single-phase single crystals from which the structures could be determined by x-ray diffraction. In the Bi series, single-crystal x-ray refinements have been done for the 2021²¹ and 2122 compounds.²⁵⁻²⁶ In the Tl series, which is easier to synthesize, single-crystal x-ray refinements have been done for the 1122,²² 2021,²⁷ 2122,²⁸ and 2223²⁹ structures. The Bi 2122³⁰ and Tl 2021,³¹ 2122,³²⁻³³ and 2223³³ structures have also been studied by neutron powder diffraction.

The study of the superconducting properties of these compounds has been hampered by the same problems with mixed-phase samples and intergrowths. One intriguing proposal has been that the transition temperature is determined by the number of CuO_2 planes in a unit.³⁴ However, it should be noted that interatomic spacings are also changing with the number of CuO_2 planes, and that questions about the details of oxygen ordering, which may affect T_c , are not yet resolved.

Although there appears to be agreement about the general structural features of the Bi and Tl superconductors, as illustrated in Figure 4, several more detailed questions remain unanswered. It is not clear whether the carriers required for superconductivity occur naturally in these compounds or whether a structural defect is required. Various structural studies have given evidence for cation substitution, e.g., Ca/Sr substitution in the Bi structures or Tl/Ca substitution in the Tl structures. The existence of oxygen or metal-site vacancies has also been proposed. Another puzzling question has been the role of static displacements of the Tl(Bi) and O atoms in the Tl(Bi)O layers. Unusually large Debye-Waller factors for these atoms, observed in every structural refinement, suggest that such displacements must exist. Some x-ray and neutron studies in which an attempt has been made to address this question have given information about the direction and magnitude of these displacements and suggest that they may occur in order to allow a more stable Tl(Bi) local configuration. A recent neutron diffraction radial-distribution-function study of local

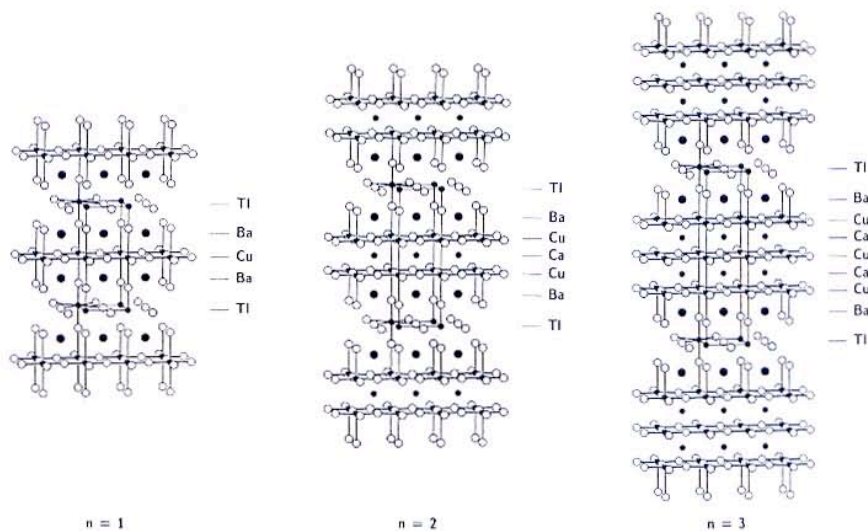


Figure 4a. Structure of the "multilayered" $\text{Tl}_m\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+m+2}$ or $\text{Bi}_m\text{Ca}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+m+2}$ compounds, for $m = 1$.

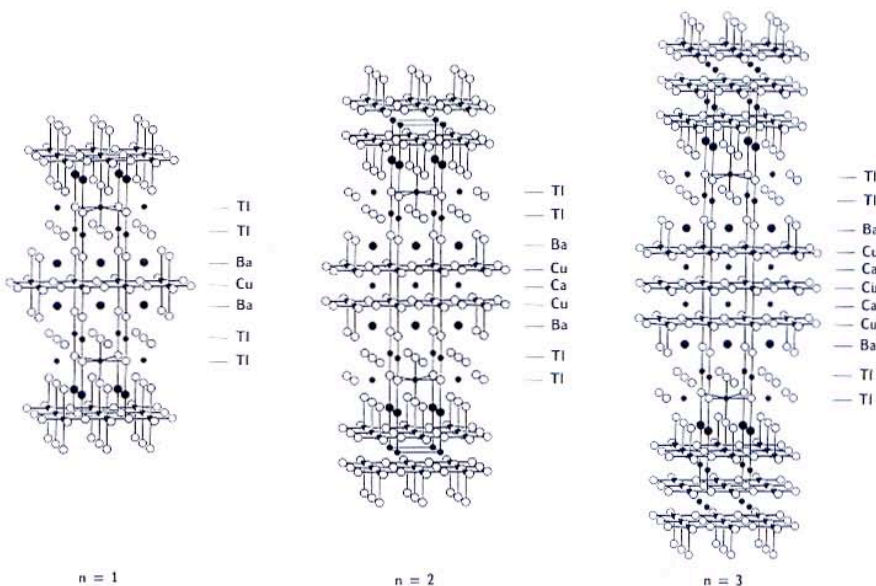


Figure 4b. Structure of the "multilayered" $\text{Tl}_m\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+m+2}$ or $\text{Bi}_m\text{Ca}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+m+2}$ compounds, for $m = 2$.

atom-atom distances in the Tl-2122 system shows that individual Tl-O distances are well defined, even though normal crystallographic studies imply a broad distribution of atom positions.³⁵

These results suggest that strong local ordering, which violates the average symmetry, is present in the intercalating Tl(Bi)O layers of the Tl and Bi systems and raise questions about the existence

of local anisotropic structural features analogous to the one-dimensional chains in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ system.

Conclusions

Structure, metal-site doping, oxygen stoichiometry, and ordering are the important ingredients that determine the superconductivity in ceramic oxides. For the copper-oxide compounds, the structures are formed of units which consist of one or more CuO_2 planes separated by one Y or Ca layer. These groups of planes are intercalated by a variable number of BaO , CuO , TlO or BiO layers. It is thought that the electrical conductivity occurs mainly in the CuO_2 planes and that the intercalated layer provides the carriers and/or the coupling mechanism. The T_c tends to increase with the number of closely spaced CuO_2 planes and is strongly affected by oxygen stoichiometry and metal ion doping in these planes. Doping in other parts of the structure has an effect only if the number of carriers is changed. The role of the oxygen ordering and its influence on the superconductivity has not yet been uniquely determined.

Acknowledgments

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References

1. R.J. Cava, B. Batlogg, J.J. Krajewski, R. Farrow, L.W. Rupp Jr., A.E. White, K. Short, W.F. Peck, and T. Kometani, *Nature* **333** (1988) p. 814.
2. D.G. Hinks, B. Dabrowski, J.D. Jorgensen, A.W. Mitchell, D.R. Richards, S. Pei, and D. Shi, *Nature* **333** (1988) p. 836.
3. See S. Uchida, K. Kitazawa, and S. Tanaka, *Phase Transitions* **8** (1987) p. 95, or B. Batlogg, *Physica B* **126** (1984) p. 275 and the references cited therein.
4. J.G. Bednorz and K.A. Müller, *Z. Phys. B* **64** (1988) p. 189.
5. H. Takagi, S. Uchida, K. Kitazawa, and S.

6. J.D. Jorgensen, H.B. Schüttler, D.G. Hinks, D.W. Capone II, K. Zhang, M.B. Brodsky, and D.J. Scalapino, *Phys. Rev. Lett.* **58** (1987) p. 1024.
7. R.M. Flemming, B. Batlogg, R.J. Cava, and E.A. Rietman, *Phys. Rev. B* **35** (1987) p. 7191.
8. See J.D. Jorgensen, *Jpn. J. Appl. Phys.* **26** (Supplement 26-3) (1987) p. 2017 for a review of the relevant literature.
9. M.A. Beno, L. Soderholm, D.W. Capone II, D.G. Hinks, J.D. Jorgensen, J.D. Grace, I.K. Schuller, C.U. Segre, and K. Zhang, *Appl. Phys. Lett.* **51** (1987) p. 57; J.E. Greedan, A. O'Reilly, and D.V. Stanger, *Phys. Rev. B* **35** (1987) p. 8770; J.J. Capponi, C. Chaillout, A.W. Hewat, P. Lejay, M. Tholence, and R. Tournier, *Europhys. Lett.* **3** (1987) p. 1301.
10. G. Xiao, M.Z. Cieplak, D. Musser, A. Garvin, F.H. Strietz, C.L. Chien, J.J. Rhyne, and J.A. Gotaas, *Nature* **332** (1988) p. 238.
11. B.D. Dunlap, M. Slaski, D.G. Hinks, L. Soderholm, M.A. Beno, K. Zhang, C.U. Segre, G.W. Crabtree, W.K. Kwok, S.K. Malik, I.K. Schuller, J.D. Jorgensen, and Z. Sungalia, *J. Magn. Magn. Mater.* **68** (1987) p. L139; J.W. Lynn, W.H. Li, Q. Li, H.C. Ku, H.D. Yang, and R.N. Shelton, *Phys. Rev. B* **36** (1987) p. 2374.
12. L. Soderholm, K. Zhang, D.G. Hinks, M.A. Beno, J.D. Jorgensen, C.U. Segre, and I.K. Schuller, *Nature* **328** (1987) p. 604.
13. I.K. Schuller, D.G. Hinks, M.A. Beno, D.W. Capone II, L. Soderholm, J.P. Locquet, Y. Bruynseraede, C.U. Segre, and K. Zhang, *Solid State Commun.* **63** (1987) p. 385.
14. J.D. Jorgensen, M.A. Beno, D.G. Hinks, L. Soderholm, K.J. Volin, R.L. Hitterman, J.D. Grace, I.K. Schuller, C.U. Segre, K. Zhang, and M.S. Kleefisch, *Phys. Rev. B* **36** (1987) p. 3608.
15. D.C. Johnston, A.J. Jacobsen, J.M. Newsam, J.T. Lewandowski, D.P. Goshorn, D. Xie, and W.B. Yelon, in *Chemistry of High-Temperature Superconductors*, edited by D.L. Nelson, M.S. Whittingham, and T.F. George (American Chemical Society, Washington, DC, 1987) p. 136; R.J. Cava, B. Batlogg, C.H. Chen, E.A. Rietman, S.M. Zahurak, and D. Werder, *Phys. Rev. B* **36** (1987) p. 5719; J.D. Jorgensen, B.W. Veal, W.K. Kwok, G.W. Crabtree, A. Umezawa, L.J. Nowicki, and A.P. Paulikas, *Phys. Rev. B* **36** (1987) p. 5731; E. Takayama-Muromachi, Y. Uchida, M. Ishii, T. Tanaka, and K. Kato, *Jpn. J. Appl. Phys.* **26** (1987) p. L1156; J.D. Jorgensen, H. Shaked, D.G. Hinks, B. Dabrowski, B.W. Veal, A.P. Paulikas, L.J. Nowicki, G.W. Crabtree, W.K. Kwok, L.H. Nunez, and H. Claus, *Physica C* **153-155** (1988) p. 578.
16. R.J. Cava et al., *Physica C* **153-155** (1988) p. 560.
17. Y. Tokura, J.B. Torrance, T.C. Huang, and A.I. Nazzari, *Phys. Rev. B* **38** (1988) p. 7156.
18. J.D. Jorgensen, D.G. Hinks, H. Shaked, B. Dabrowski, B.W. Veal, A.P. Paulikas, L.J. Nowicki, G.W. Crabtree, W.K. Kwok, A. Umezawa, L.H. Nunez, and B.D. Dunlap, *Physica B* (in press).
19. C.U. Segre, B. Dabrowski, D.G. Hinks, K. Zhang, J.D. Jorgensen, M.A. Beno, and

- I.K. Schuller, *Nature* **329** (1987) p. 227.
20. D.B. Mitzi, P.T. Feffer, J.M. Newsam, D.J. Webb, P. Klavins, A.J. Jacobson, and A. Kapitulnik, *Phys. Rev. B* **38** (1988) p. 6667.
21. S.S.P. Parkin, V.Y. Lee, A.I. Nazzari, R. Savoy, R. Beyers, and S.J. La Placa, *Phys. Rev. Lett.* **61** (1988) p. 750.
22. B. Morosin, D.S. Ginley, P.F. Hlava, M.J. Carr, R.J. Baughman, J.E. Schirber, E.L. Venturini, and J.F. Kwak, *Physica C* **152** (1988) p. 413.
23. R.M. Hazen, L.W. Finger, R.J. Angel, C.T. Prewitt, N.L. Ross, C.G. Hadjidakos, P.J. Heaney, D.R. Veblen, Z.Z. Sheng, A. Eli Ali, and N. Herman, *Phys. Rev. Lett.* **60** (1988) p. 1657.
24. H.W. Zandbergen, Y.K. Huang, M.J.V. Menken, J.N. Li, K. Kadowaki, A.A. Menovski, G. van Tendeloo, and S. Amelinckx, *Nature* **332** (1988) p. 620.
25. M.A. Subramanian, C.C. Torardi, J.C. Calabrese, J. Gopalakrishnan, K.J. Morrissey, T.R. Askew, R.B. Flippen, U. Chowdhry, and A.W. Sleight, *Science* **239** (1988) p. 1015.
26. S.A. Sunshine, T. Siegrist, L.F. Schneemeyer, D.W. Murphy, R.J. Cava, B. Batlogg, R.B. van Dover, R.M. Flemming, S.H. Glarum, S. Nakahara, R. Farrow, J.J. Krajewski, S.M. Zahurak, J.V. Waszczak, J.H. Marshall, P. Marsh, L.W. Rupp Jr., and W.F. Peck, *Phys. Rev. B* **38** (1988) p. 893.
27. C.C. Torardi, M.A. Subramanian, J.C. Calabrese, J. Gopalakrishnan, E.M. McCarron, K.J. Morrissey, T.R. Askew, R.B. Flippen, U. Chowdhry, and A.W. Sleight, *Phys. Rev. B* **38** (1988) p. 225.
28. M.A. Subramanian, J.C. Calabrese, C.C. Torardi, J. Gopalakrishnan, T.R. Askew, R.B. Flippen, K.J. Morrissey, U. Chowdhry, and A.W. Sleight, *Nature* **332** (1988) p. 420.
29. C.C. Torardi, M.A. Subramanian, J.C. Calabrese, J. Gopalakrishnan, K.J. Morrissey, T.R. Askew, R.B. Flippen, U. Chowdhry, and A.W. Sleight, *Science* **240** (1988) p. 631.
30. P. Bordet, J.J. Capponi, C. Chaillout, J. Chenavas, A.W. Hewat, E.A. Hewat, J.L. Hodeau, M. Marezio, J.L. Tholence, and D. Tranqui, *Physica C* **153-155** (1988) p. 623; P. Bordet, J.J. Capponi, C. Chaillout, J. Chenavas, A.W. Hewat, E.A. Hewat, J.L. Hodeau, M. Marezio, J.L. Tholence, and D. Tranqui, *Physica C* **156** (1988) p. 189.
31. A.W. Hewat, P. Bordet, J.J. Capponi, C. Chaillout, J. Chenavas, M. Godinho, E.A. Hewat, J.L. Hodeau, and M. Marezio, *Physica C* **156** (1988) p. 369.
32. A.W. Hewat, E.A. Hewat, J. Brynstad, H.A. Mook, and E.D. Specht, *Physica C* **152** (1988) p. 438.
33. D.E. Cox, C.C. Torardi, M.A. Subramanian, J. Gopalakrishnan, and A.W. Sleight, *Phys. Rev. B* **38** (1988) p. 6624.
34. P. Chu, P.H. Hor, R.L. May, Y.Q. Wang, L. Gao, Z.G. Huang, J. Bechtold, K. Forster, C.W. Chu, *Phys. Rev. Lett.* **58** (1987) p. 1891.
35. W. Dmowski, B.H. Toby, T. Egami, M.A. Subramanian, J. Gopalakrishnan, and A.W. Sleight, *Phys. Rev. Lett.* **61** (1988) p. 2608. □