

STRUCTURAL RELATIONSHIPS IN HIGH TEMPERATURE SUPERCONDUCTORS*

Ivan K. Schuller, C. U. Segre,** D. G. Hinks, J. D. Jorgensen, L. Soderholm,
M. Beno, and K. Zhang**

CONF-8707109--2

DE88 002924

September 1987

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Submitted for Proceedings of the Adriatico Research Conference on High Temperature Superconductors, July 6-8, Trieste, Italy, World Scientific Publishing Co. (1987).

*Work supported by the U.S. Department of Energy, BES-Materials and Chemical Sciences, under Contract #W-31-109-ENG-38.

**Permanent address: Dept. of Physics, Illinois Institute of Technology, Chicago, IL 60616, USA.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

Structural Relationships in High Temperature Superconductors

Ivan K. Schuller, C.U.Segre[†], D.G. Hinks, J.D. Jorgensen,
L. Soderholm, M. Beno and K. Zhang[†]

Argonne National Laboratory, Argonne, IL, 60439, USA

Proceedings of the Adriatico Research Conference on
High Temperature Superconductors
July 6-8, 1987, Trieste ITALY
World Scientific Publishing Co. (1987)

The submitted manuscript has been authored
by a contractor of the U. S. Government
under contract No. W-31-109-ENG-38.
Accordingly, the U. S. Government retains a
nonexclusive, royalty-free license to publish
or reproduce the published form of this
contribution, or allow others to do so, for
U. S. Government purposes.

Structural Relationships In High Temperature Superconductors

Ivan K. Schuller, C.U.Segre[†], D.G. Hinks, J.D. Jorgensen,
L. Soderholm, M. Beno and K. Zhang[†]

Argonne National Laboratory, Argonne, IL, 60439, USA

The recent discovery of two types of metallic copper oxide compounds which are superconducting to above 90K has renewed interest in the search for new high temperature superconducting materials. It is significant that both classes of compounds, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are intimately related to the extensively studied perovskite family. Both compounds contain highly oxidized, covalently bonded Cu-O sublattices, however, they differ in geometry. In this paper we discuss the relationship of these features to the superconducting properties.

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$

Superconductivity above 30K was first discovered in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ with the K_2NiF_4 tetragonal structure¹⁻⁴. Subsequent work revealed that T_c could be raised to 37K by replacement of Ba by Sr⁵. The undoped La_2CuO_4 compound, which forms in an orthorhombically distorted variant of the K_2NiF_4 structure is non-metallic at low temperatures and shows no superconductivity. Recently it has been shown that in the stoichiometric material, the Cu ions order antiferromagnetically⁶⁻⁸. There are also reports that this compound can be made superconducting by special post-synthesis procedures⁹, however the superconductivity might not be bulk and the reason for its existence is not yet understood. As Sr is substituted for La, superconductivity appears with T_c increasing until $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-y}$. The basic structure of tetragonal $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$ (M=Sr, Ba) is shown in Figure 1¹⁰, however, at low temperatures there is evidence for a slight orthorhombic distortion¹¹. This distortion has little effect on the structural properties we will be discussing below. The most prominent feature in this structure is the presence of two-dimensional (2D) Cu-O planes with short (1.888 Å) distances within the plane. The Cu atoms are octahedrally coordinated with two relatively distant oxygen atoms above and below the planes (2.416 Å). All of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ compounds have very low carrier concentrations^{12,13}, consistent with

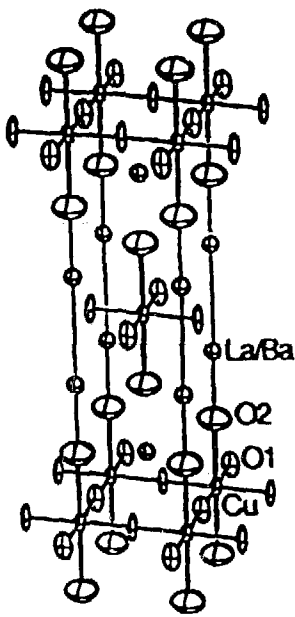


Figure 1. The structure of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$. The Sr-substituted compound has the same structure (ref. 10).

each Sr atom producing a single hole. From a chemical standpoint, the addition of Sr can be considered as increasing the formal oxidation state of the copper. Assuming O^{-2} , La^{+3} and Sr^{+2} , and a composition of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ for the compound with the maximum T_c , the calculated formal charge state of Cu is +2.15. Partial substitution for the Cu atoms in this structure rapidly depresses T_c to 0K within a few percent, while magnetic rare earth substitution for La leads to a slow decrease in T_c [14]. Full substitution of rare earth ions is not possible in this compound because of a structural phase transition which completely destroys superconductivity [15].

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

The current confirmed record-holder for T_c (~90K) is $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, which was discovered as a minority phase in attempts to raise the T_c of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ by replacing La with Y [16]. Subsequently, the single phase composition was found to be $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [17-19] with the orthorhombic structure shown in Figure 2 [20]. This structure is composed of dimered 2D Cu-O planes and one-dimensional (1D) Cu-O chains separated by fairly large distances. The Cu-O bond lengths are 1.928 Å and 1.962 Å within the 2D planes and 1.943 Å along the 1D chains. Furthermore, the Cu1-O4 distance above and below the chains is quite short (1.850 Å). Various neutron diffraction studies find the exact composition to be $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$, corresponding to a formal charge state of +2.23 for Cu [20-23]. At high temperatures, this compound undergoes a phase transition to a tetragonal structure (Figure 3) [24,25]. In-situ

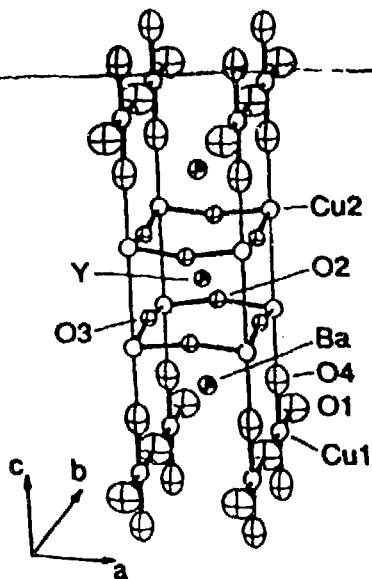


Figure 2. The orthorhombic structure of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (ref. 20).

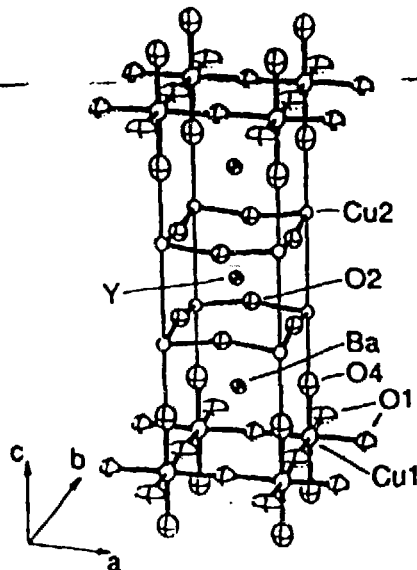


Figure 3. The high-temperature, non-superconducting tetragonal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (ref. 26).

neutron diffraction shows that as the temperature is increased, the oxygens in the 1D chains disorder into the formerly vacant positions along the a-axis^{26]}. Figure 4 shows the site occupation of oxygen in the basal plane as a function of temperature under 100% O_2 . At 750°C, site occupations become equal and the compound becomes tetragonal. The total oxygen stoichiometry of this compound depends on temperature and oxygen partial

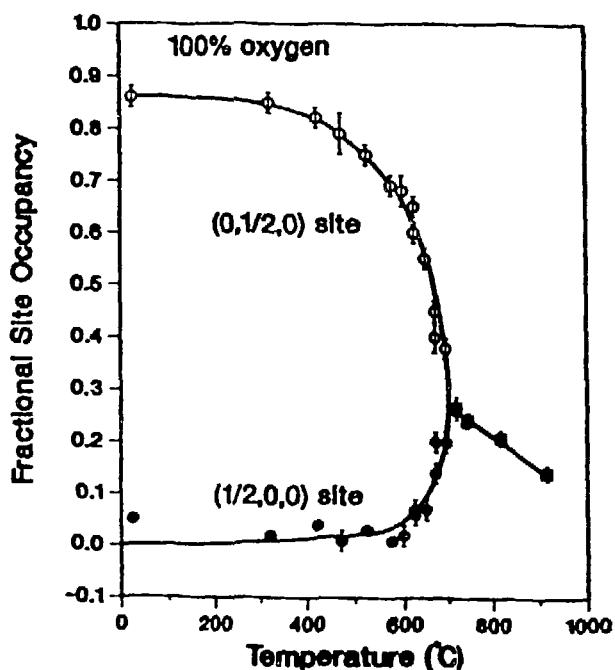


Figure 4. Oxygen site occupancy as a function of temperature in the basal plane of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ under 100% oxygen (ref. 26).

pressure as shown in Figure 5. The temperature at which the structural phase transition occurs is indicated by the vertical lines and is found to correspond to an oxygen content of 6.5, independent of oxygen partial pressure. It should be noted that this stoichiometry corresponds to a formal charge state of +2.00 for Cu. Studies of quenched samples have shown that T_c decreases monotonically to zero at the phase transition²⁷.

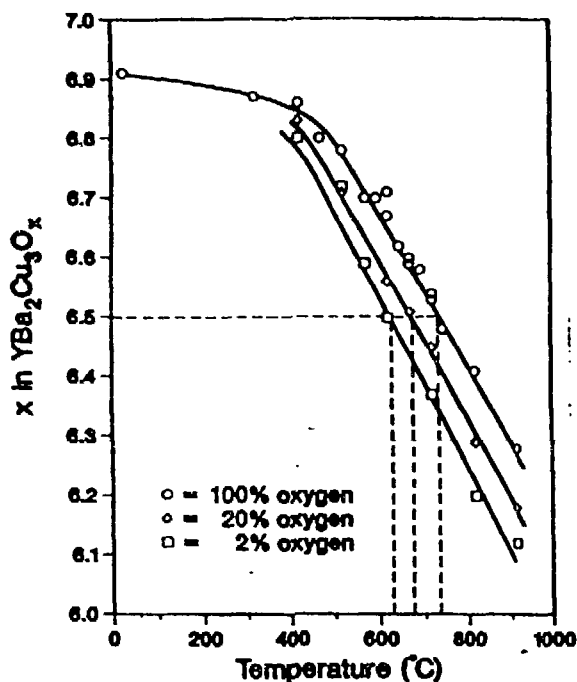


Figure 5. Total oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_x$ as a function of temperature for varying partial pressures of oxygen. The vertical dashed lines mark the temperature of the orthorhombic-to-tetragonal phase transition (ref. 26).

Substitution of Y by trivalent rare earth elements does not affect T_c despite the rare earth magnetic moments being introduced into the structure^{28,29}. Of the three rare earths which have stable tetravalent states (Ce, Pr and Tb), only Pr can be substituted for Y in this compound³⁰. Figure 6 shows the temperature dependent relative resistivity for various concentrations of Pr in $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. If Pr enters as a tetravalent ion, the observed transition from metallic to semiconducting behavior could be understood as a reduction of the formal charge state of Cu to below +2.00.

Structural Considerations and Superconductivity

The origin of superconductivity in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ compounds is clearly in the 2D Cu-O planes, while there is some question as to whether the 1D chains or the nearly 2D planes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are more important for superconductivity. It is surprising that the addition of 1D chains more than doubles the superconducting transition temperature. Some insight can be gained by considering the results of magnetic rare earth substitution into both these structures. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, the magnetic ion lies adjacent to the planes carrying the superconductivity (see Figure 1, La/Ba positions) and depresses T_c . On the other hand, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure is quite insensitive to

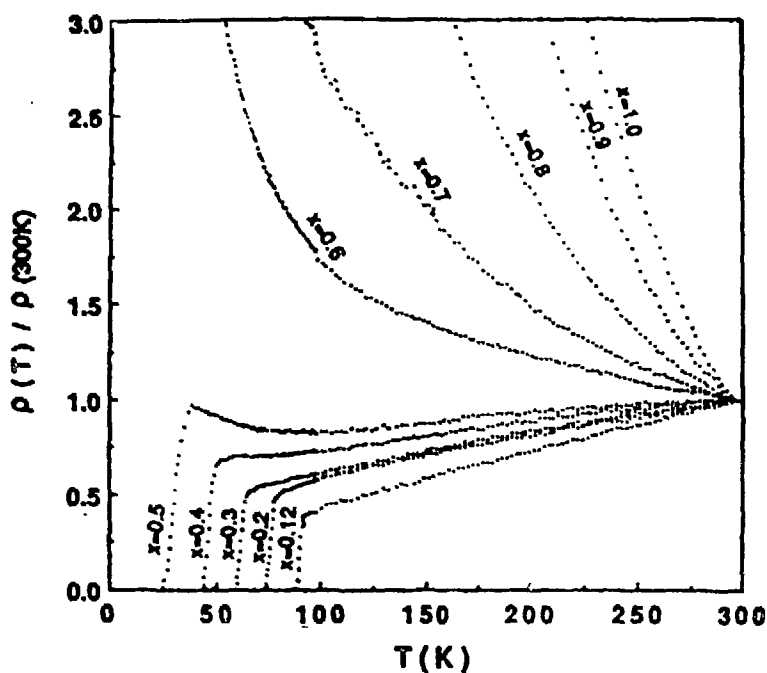


Figure 6. Relative resistivity as a function of temperature for compounds in the series $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (ref. 30).

magnetic rare earth ions whose location is adjacent to the 2D planes but far from the 1D chains (see Figure 2, Y positions). This result seems to indicate that superconductivity may reside in the 1D chains. However, it is also possible that the chains may only serve to stabilize a structure in which two Cu-O 2D planes are much closer together (3.50 Å) than the equally spaced planes in $La_{2-x}Sr_xCuO_{4-y}$ (6.65 Å). The effect of dimensionality on superconductivity in these materials is far from being understood and will require a great deal of additional experimental and theoretical effort.

Superficially, one of the most striking differences in the two compounds is that $La_{2-x}Sr_xCuO_{4-y}$ is basically a solid solution, with La and Sr sharing the same crystallographic sublattice. In contrast, $YBa_2Cu_3O_{7-\delta}$ is a stoichiometric compound with independent Y and Ba sublattices. When one considers the defect nature of these compounds, however, they are electronically quite similar, being low carrier density "doped semiconductors". Both La_2CuO_4 and $YBa_2Cu_3O_{6.5}$, which contain only divalent copper, exhibit semiconducting behavior at low temperatures^{10].} In both these materials, metallic-like behavior and superconductivity occur when the copper is oxidized to greater than a divalent state. In $La_{2-x}Sr_xCuO_{4-y}$ this is accomplished by doping with divalent Sr while in $YBa_2Cu_3O_{7-\delta}$, the same effect is obtained through increasing the oxygen content. Because of the strong covalent nature of the Cu-O sublattices in these materials, it may be inappropriate to consider formal oxidation states of the copper. Indeed, while these compounds are oxidized in a chemical sense, the

holes introduced by doping are delocalized over the entire Cu-O sublattices. In light of this "doped semiconductor" picture, it is not surprising that defects play a major role in determining the electrical, magnetic and superconducting properties of these compounds. A good example is the "unintentionally doped" La_2CuO_4 compound which exhibits a wide range of magnetic and superconducting properties caused by the incorporation of as yet unidentified electrically active defects.

Acknowledgements

This work is supported by Basic Energy Sciences, Divisions of Chemical Sciences and Materials Sciences, under Contract #W-31-109-ENG-38.

[†]Permanent address: Department of Physics, Illinois Institute of Technology, Chicago, IL, 60616, USA.

References

- 1) Bednorz, J.G. and Muller, K.A., *Z. Phys.* **B64**, 189 (1986).
- 2) Uchida, S., Takagi, H., Kitazawa, K. and Tanaka, S., *Jap. J. Appl. Phys. Lett.* **26**, L1 (1987).
- 3) Chu, C.W., Hor, P.H., Meng, R.L., Gao, L., Huang, Z.J. and Wang, Q.Y., *Phys. Rev. Lett.* **58**, 405 (1987).
- 4) Tagaki, H., Uchida, S., Kitazawa, K. and Tanaka, S., *Jap. J. Appl. Phys. Lett.* **26**, L123 (1987).
- 5) Cava, R.J., van Dover, R.B., Batlogg, B. and Rietman, E.A., *Phys. Rev. Lett.* **58**, 405 (1987).
- 6) Vaknin, D., Sinha, S.K., Moncton, D.E., Johnston, D.C., Newson, J., Satinya, C.R. and King Jr., H.E. (preprint).
- 7) Freltoft, T., Remeika, J.P., Moncton, D.E., Cooper, A.S., Fischer, J.E., Harshman, D., Shirane, G., Sinha, S.K., and Vakrin, D. (preprint).
- 8) Mitsuda, S., Shirane, G., Sinha, S.K. and Johnston, D.C. (preprint).
- 9) Grant, P.M., Parkin, S.S.P., Lee, V.Y., Engler, E.M., Ramirez, M.L., Vazquez, J.E., Lim, G., Jacowitz, R.D. and Greene, R.L., *Phys. Rev. Lett.* **58**, 2482 (1987).
- 10) Jorgensen, J.D., Schuttler, H.-B., Hinks, D.G., Capone II, D.W., Zhang, K., Brodsky, M.B. and Scalapino, D.J., *Phys. Rev. Lett.* **58**, 1024 (1987).
- 11) Cava, R.J., Santoro, A., Johnson Jr., D.W. and Rhodes, W.W., *Phys. Rev.* **B35**, 6716 (1987).

- 12] Shafer, M.W., Penney, T. and Olson, B.L. (preprint).
- 13] Penney, T. Shafer, M.W., Olson, B.L. and Plaskett, T.S. (preprint).
- 14] Soderholm, L., Morss, L., Alp, E.E., Kwok, W.K. and Crabtree, G.W. (preprint).
- 15] Singh, K.K., Ganguly, P., Rao, C.N.R., Mat. Res. Bull. 17, 493 (1982).
- 16] Wu, M.K., Ashburn, J.R., Torng, C.J., Hor, P.H., Meng, R.L., Gao, L., Huang, Z.J., Wang, Y.Q. and Chu, C.W., Phys. Rev. Lett. 58, 908 (1987).
- 17] Hinks, D.G., Soderholm, L., Capone II, D.W., Jorgensen, J.D., Schuller, I.K., Segre, C.U., Zhang, K. and Grace, J.D., Appl. Phys. Lett. 50, 1688 (1987).
- 18] Grant, P.M., Beyers, R.B., Engler, E.M., Lim, G., Parkin, S.S.P., Ramirez, M.L., Lee, V.Y., Nazzari, A., Vasquez, J.E. and Savoy, R.J., Phys. Rev. B35, 7242 (1987).
- 19] Cava, R.J., Batlogg, B., van Dover, R.B., Murphy, D.W., Sunshine, S., Siegriest, T., Remeika, J.P., Rietman, E.A., Zahurak, S. and Espinosa, G.P., Phys. Rev. Lett. 58, 1676 (1987).
- 20] Beno, M.A., Soderholm, L., Capone II, D.W., Hinks, D.G., Jorgensen, J.D., Schuller, I.K., Segre, C.U., Zhang, K. and Grace, J.D., Appl. Phys. Lett. (in press).
- 21] Greedan, J.E., O'Reilly, A. and Stager, C.V. (preprint).
- 22] David, W.I.F., Harrison, W.T.A., Gunn, J.M.F., Moze, O., Soper, A.K., Day, P., Jorgensen, J.D., Beno, M.A., Capone II, D.W., Hinks, D.G., Schuller, I.K., Soderholm, L., Segre, C.U., Zhang, K. and Grace, J.D., Nature (in press).
- 23] Capponi, J.J., Chaillout, C., Hewat, A.W., Lejay, P., Marezio, M., Nguyen, N., Raveau, B., Soubeyroux, J.L., Tholence, J.L. and Tournier, R., Europhysics Lett. (in press).
- 24] Schuller, I.K., Hinks, D.G., Beno, M.A., Capone II, D.W., Soderholm, L., Locquet, J.-P., Bruynseraede, Y., Segre, C.U., and Zhang, K., Solid State Commun. (in press).
- 25] Van Tendeloo, C., Zondbergen, H.W. and Amelinckx, S., Solid State Commun. (in press).
- 26] Jorgensen, J.D., Beno, M.A., Hinks, D.G., Soderholm, L., Volin, K.J., Hitterman, R.L., Grace, J.D., Schuller, I.K., Segre, C.U., Zhang, K. and Kleefisch, M.S. (submitted, Phys. Rev. B).
- 27] van den Berg, J., von der Beek, C.J., Kes, P.H., Nieuwenhuys, G.J., Mydosh, J.A., Zandbergen, H.W., van Berkel, F.P.F., Steens, R. and Ijdo, D.J.W., Europhysics Lett. (submitted).
- 28] Willis, J.O., Fisk, Z., Thompson, J.D., Cheong, S-W., Aikin, R.M., Smith, J.L. and Zimigiebl, E., J. Magn. Magn. Mat. 67, L139 (1987).
- 29] Murphy, D.W., Sunshine, S., van Dover, R.B., Cava, R.J., Batlogg, B., Zahurak, S.M. and Schrieemeyer, L.F., Phys. Rev. Lett. 58, 1888 (1987).
- 30] Soderholm, L., Zhang, K., Hinks, D.G., Beno, M.A., Jorgensen, J.D., Segre, C.U. and Schuller, I.K. (submitted to Nature).