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HIGH TEMPERATURE SUPERCONDUCTORS

1.1. Background

The solid state physics and materials science communities were entirely unprepared for the Sept. 1986 publication by J. G. Bednorz and K. A. Müller[1] of the discovery of percolative superconductivity near 30 K in a polycrystalline sample in the La-Ba-Cu-O system.[2]

Following the 1911 discovery of superconductivity in mercury at 4.1 K by H. Kamerlingh Onnes[3] there had been steady progress in finding materials with increasing transition temperatures up to Nb_3Ge with $T_c = 23.3$ K, reported in 1973 and 1974 by Gavaler[4] and Testardi *et al.*[5] Although Bernd Matthias and his colleagues[6,7] had achieved early success with additional compounds in the cubic A-15 structure, nothing had been found to surpass Nb_3Ge.

1.1.1. Search and discovery

Sleight *et al.*[8] had found superconductivity at 13 K in the mixed valence oxide $Ba(Pb_{1-x}Bi_x)O_3$, which crystallizes in the perovskite structure. This work undoubtedly caught the attention of Bednorz and Müller, who had devoted much of their scientific careers to research on structural and ferroelectric phase transitions in oxide insulators, many of which

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[1] J. G. Bednorz and K. A. Müller, "Possible high T_c superconductivity in the Ba-La-Cu-O system," *Z. Phys. B* **64**, 189 (1986).

[2] T. H. Geballe and J. K. Hulm, *Science 239*, 367 (1988).

[3] H. K. Onnes, *Commun. Phys. Lab. Univ. Leiden* **120b**, 3 (1911).

[4] J. R. Gavaler, *Appl. Phys. Lett.* **23**, 480 (1973).

[5] L. R. Testardi, J. H. Wernick and W. A. Royer, *Solid. State Commun.* **15**, 1 (1974).

[6] B. T. Matthias, J. K. Hulm and E. J. Kunzler, "The road to superconducting materials," *Physics Today* **34**, 34 (January 1981).

[7] A. M. Clogston, T. H. Geballe and J. K. Hulm, "Bernd T. Matthias," *Physics Today* **34**, 84 (January 1981).

[8] A. W. Sleight, J. L. Gillson and P. E. Bierstedt, *Solid State Commun.* **17**, 27 (1975).

were perovskites.[9] Although Bednorz had participated in a study of Nb-doped $SrTiO_3$[10] and Müller had worked on percolative superconductivity in granular aluminum,[11,12] neither was known to be deeply engaged in research on superconductivity. What had stimulated Müller's interest was the suggestion[13] by H. Thomas at the Erice International School in Summer 1983 that the Jahn-Teller effect[14] might lead to polaron-induced high-temperature superconductivity in transition-metal oxides.[15]

In late Summer 1983 Müller engaged Bednorz[16] in a study of mixed perovskites of composition $La(Ni_{1-x}Al_x)O_3$. Although these materials gave some evidence of a Jahn-Teller effect, there was no indication of a drop in resistivity that might signal a superconducting transition. After two years of part-time effort with no indication of superconductivity, it was decided to shift to copper oxides of mixed valence. Raveau's group at the University of Caen had been actively studying the crystal chemistry of such materials for possible use in catalysis.[17] The mixed perovskite $La_4BaCu_5O_{5(3-y)}$ appeared promising and Bednorz initiated a program of preparation of the system $(La_{5-x}Ba_x)Cu_5O_{5(3-y)}$. Whereas Michel *et al.*[12] had sintered mixed oxides at 1000 °C to achieve solid state reaction, Bednorz was accustomed to precipitate the more finely divided oxalates from solution[18] and was able to sinter at the lower temperature of 900 °C.

A sharp drop in the resistivity of the compound with nominal Ba fraction $x = 0.75$ was observed below 30 K, suggesting the presence of a superconducting phase transition and leading Bednorz and Müller to submit a manuscript[1] to *Zeitschrift für Physik* with the cautious title "Possible High T_c Superconductivity in the Ba-La-Cu-O System."

1.1.2. Confirmation

Bednorz and Müller did not have long to wait for confirmation following publication of their results in *Zeitschrift für Physik* . On November 28, 1986 the Japanese newspaper *Asahi Shinbun*, whose *International Satellite Edition* is received in Zürich, reported that Professor S. Tanaka at the University of Tokyo had observed bulk diamagnetism around 30 K in the Ba-La-Cu-O system, confirming the presence of superconductivity in this system. Further confirmation came at the Fall 1986 meeting of the Materials Research Society where C. W. Chu announced that his group at the University of Houston had reproduced the results of Bednorz and Müller. At the same meeting Dr. K. Kitazawa presented an informal report of the activities of Tanaka's group, of which he was a member.[19,20]

1.1.3. Extension

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[9] W. H. H. Gränicher, "K. Alex Müller and J. Georg Bednorz as graduate students at ETH Zürich," *Ferroelectrics* **89**, iii (1989).

[10] G. Binnig, A. Baratoff, H. E. Hoenig and J. G. Bednorz, *Phys. Rev. Lett.* **45**, 1352 (1980).

[11] K. A. Müller, M. Pomerantz, C. M. Knoedler and D. Abraham, *Phys. Rev. Lett.* **45**, 832 (1980).

[12] M. Pomerantz and K. A. Müller, *Physica* **107B**, 325 (1981).

[13] K.-H.. Höck, H. Nickisch and H. Thomas, *Helv. Phys. Acta* **56**, 237 (1983).

[14] C. Kittel, *Introduction to Solid State Physics, Sixth Edition* (Wiley, New York, 1986) p. 409.

[15] K. A. Müller and J. G. Bednorz, *Science* **237**, 1133 (1987).

[16] J. G. Bednorz and K. A. Müller, Nobel Lecture, *Rev. Mod. Phys.* **60**, 585 (1988).

[17] C. Michel, L. Er-Rakho and B. Raveau, *Mater. Res. Bull.* **20**, 667 (1985).

[18] J. G. Bednorz, K. A. Müller, H. Arend and H. Gränicher, *Mater. Res. Bull.* **18**, 181 (1983).

[19] H. S. Takagi, S. Uchida, K. Kitazawa and S. Tanaka, *Jpn. J. Appl. Phys.* **26**, L123 (1987).

[20] S. Uchida, H. Takagi, K. Kitazawa and S. Tanaka, *Jpn. J. Appl. Phys.* **26**, L151 (1987).

By placing their sample of La-Ba-Cu-O under hydrostatic pressure, C. W. Chu *et al.*[21,22] were able to increase the onset temperature from 35 K to over 50 K. Bednorz, Müller and Takashige performed studies[23] in which La was partially replaced by Sr or Ca rather than by Ba. With Sr substitution the transition could be raised to around 40 K at ambient pressure while with Ca the transition temperature could not be raised above 22 K.

Researchers were startled to find that replacing La by the smaller Y raises the onset temperature above the temperature of liquid N_2 to 92 K.[24,25] Superconductivity above 100 K was obtained in the Bi-Sr-Ca-Cu-O system.[26] More recently, Sheng and Herman[27,28] discovered superconductivity near 120 K in the Tl-Ba-Ca-Cu-O system and Parkin *et al.* in a closely related system have obtained a transition to superconductivity at the current record temperature of 125 K.[29]

J. Georg Bednorz and K. Alex Müller were awarded the 1987 Nobel Prize in Physics on 8 December 1987, less than two years after their discovery of high-temperature superconductivity.

1.2. Structure

Much of the systematic work of Bednorz and Müller and their colleagues at the IBM Rüschlikon Laboratory anticipated approaches that would continue to be essential to the analysis of the high-temperature superconductors and to the study of their physical properties. In this section we discuss three approaches that have been found particularly useful: structure analysis, crystal chemistry and the observation of microstructure.

1.2.1. Systems

Structure determination has played a central role in characterizing the high-temperature superconductors. Materials prepared by solid state reaction are commonly a mixture of phases, only some of which become superconducting. Crystallographic studies are crucial to understanding the mechanisms of superconductivity and to the development of improved superconducting materials.[30]

Bednorz and Müller[1] obtained x-ray powder diffractograms of their sintered material and were able to distinguish three phases:

i. The dominant phase was a layer-type perovskite that appeared to have the K_2NiF_4 structure with lattice constants a = 3.79 Å and c = 13.21 Å. This phase turned out to be the superconductor $La_{2-x}Ba_xCuO_4$ and its structure was confirmed by Tyagi *et al.*[16]

ii. A second phase appeared to be the oxygen-deficient perovskite $(La_{1-x}\,Ba_x)$ CuO_{3-y} with the $LaNiO_3$ structure. This phase is not superconducting.

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[21] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao and Z. J. Huang, *Science* **235**, 567 (1987).

[22] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang and Y. Q. Wang, *Phys. Rev. Lett.* **58**, 405 (1987).

[23] J. G. Bednorz, K. A. Müller and M. Takashige, *Science* **236**, 73 (1987).

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

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

[26] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, *Jpn. J. Appl. Phys.* **27**, L209 (1988).

[27] Z. Z. Sheng and A. M. Hermann, *Nature* **332**, 55 (1988).

[28] Z. Z. Sheng and A. M. Hermann, *Nature* **332**, 138 (1988).

[29] S. S. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, R. Beyers and S. La Placa, *Phys. Rev. Lett.* **61**, 750 (1988).

[30] R. J. Cava, "Superconductors beyond 1-2-3," *Scientific American* **263**, 42 (August 1990).

iii. A third phase was stable up to sintering temperatures of 1000 °C with a volume fraction in excess of 30 % . At higher temperatures this phase reacted to form the oxygen-deficient perovskite obtained by Michel *et al.*[14] Chemical analysis suggested the identification of this third phase with unreacted common CuO. Later preparations halved the amount of Cu, eliminating this phase but retaining the other two phases. Single-crystal precession measurements[31] later confirmed the identification of these phases.

Hazen[32,33] has collected and tabulated data on the atomic structures of all known high-temperature copper oxide superconductors. The twenty-nine variants of twenty topologically distinct structures are given in Table 1. Values of T_c are taken in part from the compilation of Junod.[34] The most obvious common structural theme that unites the known layered copper oxide high-temperature superconductors are the corner-linked square-plane coordinated coppers together with oxygen nonstoichiometry in layers that interleave the CuO_2 sheets. In structures with more than one consecutive CuO_2 sheet, divalent or trivalent cations in eight coordination are always found to act as spacers.

The structures of the high-temperature copper oxide superconductors are closely related to that of the mineral perovskite $CaTiO_3$ shown in Fig. 1. At the center of the cubic cell is the ion Ti^{4+} surrounded by an octahedron of O^{2-} ions. At the corners are Ca^{2+} ions. This and subsequent figures are scaled to the covalent radii given in Table 2.

Alternatively, perovskite may be regarded as a layered structure in which TiO_2 planes alternate with CaO planes as shown in Fig. 2. Designating these planar structures as 1A and 2A, the structure of perovskite may be represented by the stacking sequence

$$[2A\ (CaO),\ 1A\ (TiO_2)],\ [2A\ (CaO),\ 1A\ (TiO_2)],\ [2A\ (CaO),\ 1A\ (TiO_2)],\ \textit{etc.}$$

La-Cu-O and related structures

The structure of La_2CuO_4 is shown in Fig. 3. In each of the three 2-1-4 structures listed in Table 1, layers of copper in square-plane coordination with oxygen are separated by layers of cations in eight or nine coordination. All three structures have the same cation arrangement, but they differ in the positions of oxygen atoms above and below the Cu-O planes. The structures 1b, 1c and 1d are topologically identical to the 1a structure but have lower symmetry.

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[31] J. G. Bednorz, M. Takashige and K. A. Müller, *Mater., Res. Bull.* **22**, 819 (1987).

[32] R. M. Hazen, "Crystal structures of high-temperature superconductors," in *Physical Properties of High Temperature Superconductors II*, ed. D. M. Ginsberg (World Scientific, Singapore, 1990) ch. 3.

[33] R. M. Hazen, *The Breakthrough: The Race for the Superconductor*, (Summit Books, New York, 1988) is a personal account of the determination of the 123 structure together with an account of the discovery of this compound.

[34] A. Junod, "Specific heat of high temperature superconductors: a review," in *Physical Properties of High Temperature Superconductors II*, ed. D. M. Ginsberg (World Scientific, Singapore, 1990) ch. 2.

Table 1. Copper oxide high-temperature superconducting structures.

Number	Composition	Space Group	Abbreviation	T_c
1a	La_2CuO_4	I4/mmm	214-T	22-37 K
1b		$P4_2/ncm$		
1c		Bmab		
1d		Fmmm		
2	Nd_2CuO_4	I4/mmm	214-T'	25 K
3	$(Nd, Ce, Sr)_2CuO_4$	P4/mmm	214-T*	
4	$(La, Sr)_2CaCu_2O_6$		2126	60 K
5a	$YBa_2Cu_3O_6$	P4/mmm	123-T	
5b	$YBa_2Cu_3O_7$	Pmmm	123-O	92 K
6	$YBa_2Cu_4O_8$	Ammm	124	80 K
7	$Y_2Ba_4Cu_7O_{15}$	Ammm	247	40 K
8	$(Ba, Nd)_2(Nd, Ce)_2Cu_3O_8$	I4/mmm	223	≈ 40 K
9a	$Pb_2YSr_2Cu_3O_8$	P4/mmm	2123	≈ 70 K
9b		Cmmm		
10a	$Bi_2Sr_2CuO_6$	Amaa	Bi-2201	12 K
10b		A2/a		
10c		C2		
11a	$Bi_2Sr_2CaCu_2O_8$	Fmmm	Bi-2212	90 K
11b		Amaa		
12	$Bi_2Sr_2Ca_2Cu_3O_{10}$	I4/mmm	Bi-2223	110 K
13a	$Tl_2Ba_2CuO_6$	I4/mmm	Tl-2201	11 K
13b		Fmmm		
14	$Tl_2Ba_2CaCu_2O_8$	I4/mmm	Tl-2212	110 K
15	$Tl_2Ba_2Ca_2Cu_3O_{10}$	I4/mmm	Tl-2223	121 K
16	$Tl_2Ba_2Ca_3Cu_4O_{12}$	I4/mmm	Tl-2234	
17	$TlBa_2CuO_5$	P4/mmm	Tl-1201	
18	$TlBa_2CaCu_2O_7$	P4/mmm	Tl-1212	90 K
19	$TlBa_2Ca_2Cu_3O_9$	P4/mmm	Tl-1223	110 K
20	$TlBa_2Ca_3Cu_4O_{11}$	P4/mmm	Tl-1234	122 K

The compound Nd_2CuO_4 is the first electron high-temperature superconductor with excess negative charge per unit cell. The substitution of Ce and Sr for Nd leads to a new 2-1-4 structure that incorporates aspects of the T and T' topologies.

The compound $(La, Sr)_2CaCu_2O_6$ shown in Fig. 4 is the least complex of all the structures with double layers of copper oxide pyramids common to the compounds with highest T_c. Superconductivity in this structure, first reported[35] for $La_2SrCu_2O_6$ and $La_2CaCu_2O_6$ has been achieved by Cava *et al.*[36] The highest transition temperature observed is 60 K at the composition $La_{1.6}Sr_{0.4}CaCu_2O_6$.

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[35] N. Nguyen, L. Er-Rakho, C. Michel, J. Choisnet and B. Raveau, *Mater. Res. Bull.* **15**, 891 (1980).

[36] R. J. Cava, B. Batlogg, R. B. van Dover, J. J. Krajewski, J. V. Waszczak, R. M. Fleming, W. F. Peck Jr., L. W. Rupp Jr., P. Marsh, A. C. W. P. James and L. F. Schneemeyer, *Nature* **345**, 602 (1990).

Table 2. Covalent radii.

atom	radius, nm.	atom	radius, nm.	atom	radius, nm
O	0.073	Y	0.162	Ba	0.198
Cu	0.117	La	0.169	Ln	0.156-0.169
Ti	0.132	Ca	0.174		

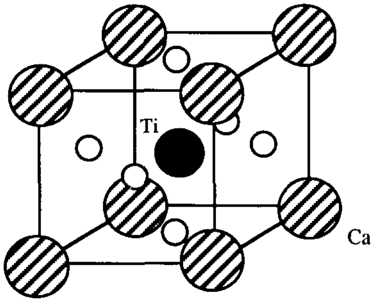
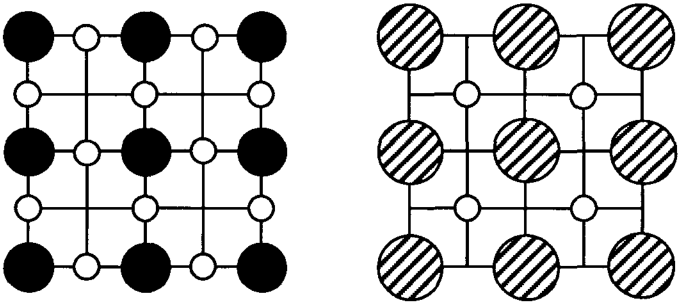


Figure 1. The mineral perovskite $CaTiO_3$. Ti is at the body center, O at the face centers and Ca at the corners.



1A (TiO_2) plane

2A (CaO) plane

Figure 2. Planes of the mineral perovskite $CaTiO_3$

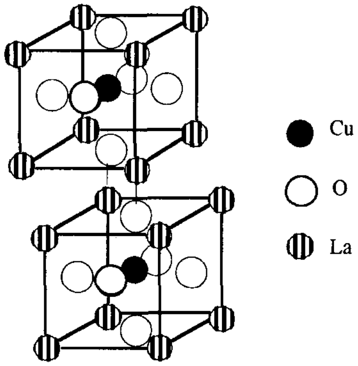


Figure 3. The crystal structure of La_2CuO_4.

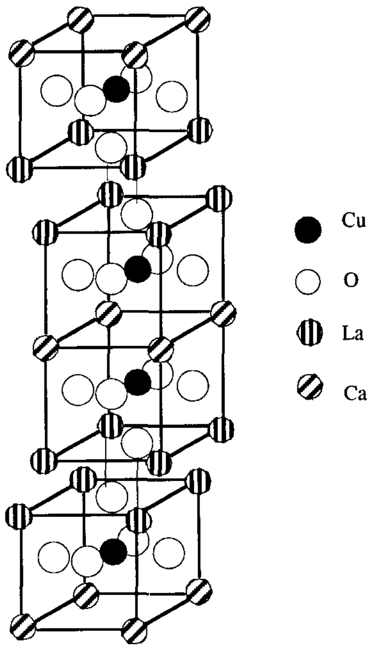
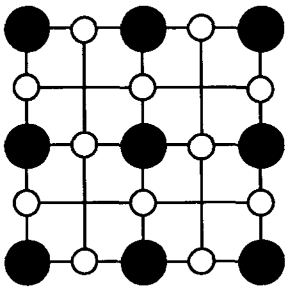
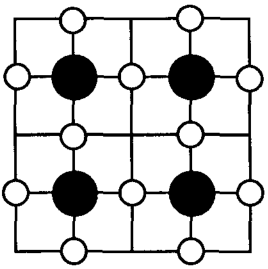


Figure 4. The crystal structure of $La_2CaCu_2O_6$. This structure is related to that of La_2CuO_4 shown in Fig. 3 by replacing the layer of octahedra by a double layer of pyramids.

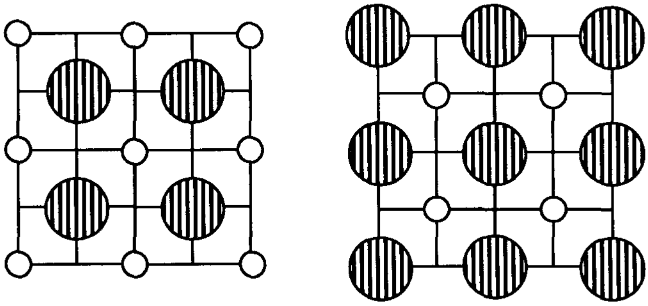


1A (CuO_2) plane



1B (CuO_2) plane

Figure 5. The two CuO_2 planes, displaced along a face diagonal



2A (LnO) plane

2B (LnO) plane

Figure 6. The two lanthanide LnO planes, displaced along a face diagonal.

The 2-1-4 and related structures may be developed from the perovskite planes shown in Fig. 2 with the addition of planes shifted by half a face diagonal as shown in Fig. 5 for the CuO_2 planes, which have the same configuration as the perovskite TiO_2 planes and in Fig.

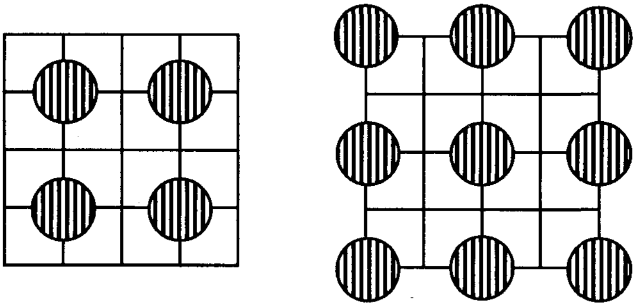
6 for the lanthanide LnO planes, which have the same configuration as the perovskite CaO planes.

In terms of these structures, La_2CuO_4 may be represented by the six layers

[2A (LaO), 1A (CuO_2), 2A (LaO)|2B (LaO), 1B (CuO_2), 2B (LaO)], *etc.*

Nd-Cu-O and related structures

$Nd_{2-x}Ce_xCuO_4$ is the model single CuO_2-layer n-type superconductor as $La_{2-x}Sr_xCuO_4$ is the model CuO_2-layer p-type superconductor. To indicate the structure of $Nd_{2-x}Ce_xCuO_4$ it is necessary to introduce three more planar structures. The first two are the lanthanide planes shown in Fig. 7 and obtained from Fig. 6 by removing all the oxygen.



2A (Ln) planes 2B (Ln) planes

Figure 7. Lanthanide (Ln) planes formed by removing all the oxygen from LnO planes

The third structure is that of the oxygens in the CuO_2 planes shown in Fig. 8 and obtained from Fig. 5 by removing all the copper.

With these additional layers, the structure of $Nd_{2-x}Ce_xCuO_4$ is represented by the eight layers

[2A (Nd), 1A (CuO_2), 2A (Nd), 1 (O_2)| 2B (Nd), 1B (CuO_2), 2B (Nd), 1 (O_2)], *etc.*

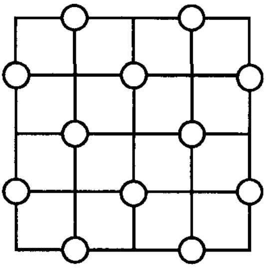


Figure 8. 1(O_2) planes. The oxygens in this plane are in the same position as in the CuO_2 planes.

Y-Ba-Cu-O and related structures

The discovery by Wu *et al.*[21] of the superconductor $YBa_2Cu_3O_{7-d}$ with a transition temperature of 92 K has stimulated a massive amount of crystallographic research. The structure is based on a simple unit cell composed of a stack of three perovskite-like cubes shown in Fig. 9. It was not, however, until the first neutron powder diffraction studies that the details of the oxygen positions were resolved with certainty. The 123 structure crystallizes as tetragonal at high temperature, but converts by oxygen ordering to an orthorhombic form on cooling. Orthorhombic 123 with small domain size may appear tetragonal in single-crystal x-ray studies. The most precise structure determinations have relied on Rietveld refinement of neutron powder diffraction data. Compositional variants of the 123 structure have been summarized by Beyers and Shaw.[37]

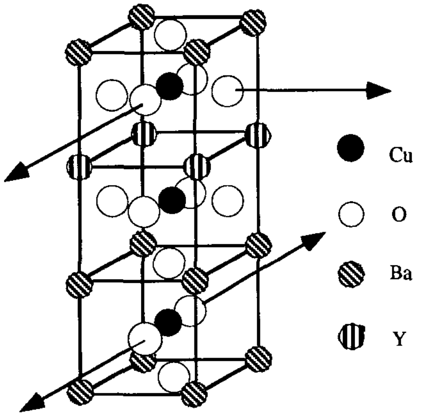


Figure 9. The crystal structure of $YBa_2Cu_3O_7$ showing the one-dimensional Cu-O chains and the two-dimensional pyramidal planes. This structure is derived from the structure of $La_2CaCu_2O_6$ by adding the Cu-O chains and shifting the pyramidal planes to align their apices.

Morris *et al.*[38] have produced eight members with the 1-2-4 structure, and six variants of the 247 structure,[39] with both groups topologically equivalent to 123.

Cava *et al.*[40] have described a new family of near-70K superconductors with a 2-1-2-3 structure that bears a close relationship to the tetragonal 1-2-3 structure.

In order to represent the structure of $YBa_2Cu_3O_7$, two additional planar structures are required. In Fig. 10 are represented the CuO chain structures obtained from Fig. 5 by removing half the oxygens.

The structure of $YBa_2Cu_3O_7$ is represented by the six layers

[2A (BaO), 1A (CuO_2), 2A (Y), 1A (CuO_2), 2A (BaO), 1A (CuO)], *etc.*

Bi-Sr-Ca-Cu-O structures

Michel et al. reported the first of a series of modular layer structures in which the copper and oxygen form in sheets typical of all the high-temperature superconductors spaced by

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[37] R. Beyers and T. M. Shaw, "The Structure of $YBa_2Cu_3O_{7-\delta}$ and its Derivatives," in *Solid State Physics*, Volume 42, eds. H. Ehrenreich and D. Trunbull (Academic, Boston, 1989) p 135.

[38] D. E. Morris, J. H. Nickel, J. Wei, N. G. Asmar, J. S. Scott, U. M. Scheven, C. T. Hultgren, A. G. Markelz, J. E. Post, P. J. Heaney, D. R. Veblen and R. M. Hazen, *Phys. Rev. B* 39, 7347 (1989).

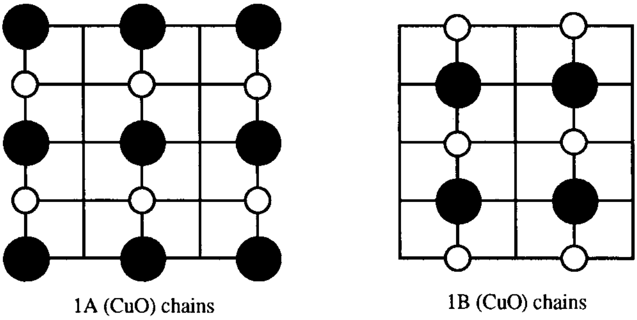
[39] D. E., Morris, N. G. Asmar, J. Wei, J. H. Nickel, R. L. Sid, J. S. Scott and J. E. Post, *Phys. Rev. B* **40**, 11406 (1989).

[40] R. J. Cava, B. Batlogg, J. J. Krajewski, L. W. Rupp, L. F. Schneemeyer, T. Siegrist, R. B. van Dover, P. Marsh, W. F. Peck Jr., P. K. Gallagher, S. H. Glarum, J. H. Marshall, R. C. Farrow, J. V. Waszczak, R. Hull and P. Trevor, *Nature* **336**, 211 (1988).

alkaline-earth cations and interleaved with BiO layers.[41] The simplest structure is that of $Bi_2Sr_2CuO_6$

[2A (BiO), 2B (SrO), 1B (CuO_2), 2B (SrO), 2A (BiO)|

|2B (BiO), 2A (SrO), 1A (CuO_2), 2A (SrO), 2B (BiO)], *etc.*


1A (CuO) chains

1B (CuO) chains

Figure 10. CuO chains formed by the removal of half the oxygen from the CuO_2 planes

The addition of Ca by Maeda *et al.*[23] raised T_c for this system above 100 K. Ca forms multiple layers of CuO_2 separated by Ca. For n CuO_2 layers the formula unit is $Bi_2Sr_2 Ca_{n-1}(CuO_2)_nO_4$. For 2 CuO_2 layers (n = 2) per formula unit the structure is

[2A (BiO), 2B (SrO), 1B (CuO_2), 2B (Ca), 1B (CuO_2), 2B (SrO), 2A (BiO)|

|2B (BiO), 2A (SrO), 1A (CuO_2), 2A (Ca), 1A (CuO_2), 2A (SrO), 2B (BiO)], *etc.*

Tl-Ba-Ca-Cu-O structures

Sheng and Hermann[24,25] discovered superconductivity near 120 K in the Tl-Ba-Ca-Cu-O system. The structures of thallium with three new superconducting phases are strikingly similar to the bismuth superconductors. The compound $Tl_2Ba_2CuO_6$ with the structure

[2B (TlO), 2A (BaO), 1A (CuO_2), 2A (BaO), 2B (TlO)|

|2A (TlO), 2B (BaO), 1B (CuO_2), 2B (BaO), 2A (TlO)], *etc.*

has a transition temperature of 11 K. As with the Bi-compounds, the addition of Ca forms multiple layers of CuO_2 separated by Ca. For n CuO_2 layers the formula unit is $Tl_2Ba_2Ca_{n-1}(CuO_2)_nO_4$. For 2 CuO_2 layers (n = 2) per formula unit, the structure is

[2B (TlO), 2A (BaO), 1A (CuO_2), 2A (Ca), 1A (CuO_2), 2A (BaO), 2B (TlO)|

[2A (Tl(O), 2B (BaO), 1B (CuO_2), 2B (Ca), 1B (CuO_2), 2B (BaO), 2A (TlO)], *etc.*

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[41] C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost and B. Raveau, Z. *Phys. B* **68**, 421 (1987).

Shortly after Sheng and Hermann's work on the Tl-Ba-Ca-Cu-O system, Parkin *et al.*[42,43] reported yet another homologous series of thallium superconductors, which differ from the earlier series in containing only one TlO layer in the unit cell. The compound without Ca

[2A (BaO), 1A (CuO_2), 2A (BaO), 2B (TlO)], *etc.*

is not superconducting. Again, as with the Bi-compounds, the addition of Ca forms multiple layers of CuO_2 separated by Ca. For n CuO_2 layers the formula is $TlBa_2Ca_{n-1}(CuO_2)_nO_3$. For 2 CuO_2 layers (n = 2) the structure is

[2A (BaO), 1A (CuO_2), 2A (Ca), 1A (CuO_2), 2A (BaO), 2B (TlO)], *etc.*

1.2.2. Block layers

Tokura and Arima[44] have introduced the idea of block layers to characterize the functional units that separate CuO_2 planes. For example, $La_{2-x}Sr_xCuO_4$ may be regarded as CuO_2 sheets separated by La_2O_2 layers with the rocksalt structure (the **L**-layer) and written as

L-[CuO_2]-**L**-[CuO_2]-**L**-[CuO_2]-**L**-[CuO_2]-

with **L** = 2A (LaO), 2B (LaO) or 2B (LaO), 2A (LaO). On the other hand, $Nd_{2-x}Ce_xCuO_4$ may be regarded as CuO_2 sheets separated by N_2O_2 layers with the fluorite structure (the **G**-layer) and written as

G-[CuO_2]-**G**-[CuO_2]-**G**-[CuO_2]-**G**-[CuO_2]-

with **G** = 2A (Nd), 1 (O_2), 2B (Nd), or 2B (Nd), 1 (O_2), 2A (Nd).

The block-layers may or may not provide apical oxygens for the CuO_2 planes. For example, the **L**-layers do supply apical oxygens while the **G**-layers do not. The oxygen structure that surrounds the copper (squares, pyramids or octahedra) is determined by the block layers. A second function of the block-layers, doping of the CuO_2 planes, is discussed below.

1.2.3. Structural chemistry

Sleight has discussed the chemistry of the oxide superconductors with reference to the oxidation states of copper.[45] One of the simplest methods of connecting CuO_4 units together forms the infinite sheets that are present in all the copper oxide superconductors with the corner oxygens shared by adjacent copper atoms. High-temperature superconductivity occurs only in oxides where there is high covalency, which is necessary for the formation of bands that support metallic behavior. All the oxide superconductors contain in addition mixed-valent cations, a requirement of the dispropor-tionation mechanisms for superconductivity.

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[42] S. S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, R. Beyers and S. La Placa, *Phys. Rev. Lett.* **61**, 750 (1988).

[43] R. Beyers, S. S. P. Parkin, V. Y. Lee, SA. I. Nazzal, R. Savoy, G. Gorman, T. C. Huang and S. La Placa, *Appl. Phys. Lett.* **53**, 432 (1988).

[44] Y. Tokura and T. Arima, "New classification method for layered copper oxide compounds and its application to design of new high T_c superconductors," *Jpn. J. Appl. Phys.* **29**, 2388 (1990).

[45] A. W. Sleight, *Science* **242**, 1519 (1988).

The structural chemistry of $YBa_2Cu_3O_7$ is best understood[39] by first examining $YBa_2Cu_3O_6$, which has the planar structure

[2A (BaO), 1A (CuO_2), 2A (Y), 1A (CuO_2), 2A (BaO), 1A (Cu)], *etc.*

where the 1A (Cu) planes are the 1A (CuO_2) planes with all the oxygen removed. This compound is an antiferromagnetic insulator. When $YBa_2Cu_3O_6$ is annealed in an oxygen-containing atmosphere, it acquires oxygen to form $YBa_2Cu_3O_7$, which is metallic and superconducting with the planar structure

[2A (BaO), 1A (CuO_2), 2A (Y), 1A (CuO_2), 2A (BaO), 1A (CuO)], *etc.*

Raveau *et al.*[46] and Greene and Bagley[47] have reviewed studies of oxygen nonstoichiometry in connection with the mixed valence of copper. Cava[48] has reviewed the known copper oxide superconductors with particular emphasis on the way in which they fall into structural families.

Tokura and Arima[44] have described the crystal chemistry of the CuO_2-layer compounds in terms of the block-layers that they have identified. An important role of the block-layers is to supply the CuO_2 planes with carriers. As they explain from the viewpoint of ionic crystals, an insulating CuO_2 sheet consists of Cu^{2+} and O^{2-} and hence is charged -2 per formula unit. To maintain charge neutrality, the average charge of the block-layer must be +2 in the insulating compound. The charge of the **L**- and **G**- layers described above is just +2. The substitution of Sr^{2+} for La^{3+} or Ce^{4+} for Nd^{3+} reduces or increases the charge per formula unit in the CuO_2 planes. In $La_{2-x}Sr_xCuO_4$ the charge of the **L**-layer is 2 - x and the effective charge per CuO_2 unit is - 2 + x. In $Nd_{2-x}Ce_xCuO_4$ the charge of the **G**-layer is 2 + x and the charge per formula unit in the CuO_2 planes is - 2 - x. The former process corresponds to hole-doping and the latter to electron-doping. In this way the block-layers control the carrier concentration in the CuO_2 planes.

1.2.4. Microstructure

Microstructure—twin and grain boundaries, second phases, incommensurate modulation, intergrowth defects, *etc.* have profound effects on the physical properties of the high-temperature superconductors. Much of what has been learned through transmission electron microscopy (TEM) on well characterized materials is reviewed by Chen.[49]

Powders and ceramics

Oxygen stoichiometry significantly affects the properties of the high-temperature superconductors. Cava found in the Y-Ba-Cu-O system[50] a plateau in T_c and a minimum

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[46] B. Raveau, C. Michel, M. Hervieu, J. Provost and F. Studer, "Oxygen nonstoichiometry and valence states in superconductive cuprates," in *Earlier and Recent Aspects of Superconductivity*, eds. J. G. Bednorz and K. A. Müller (Springer-Verlag, Berlin, 1990) pp. 66-95.

[47] L. H. Greene and B. G. Bagley, "Oxygen stoichiometric effects and related atomic substitutions in the high-T_c cuprates," in *Physical Properties of High Temperature Superconductors II*, ed. D. M. Ginsberg (World Scientific, Singapore, 1990) ch. 8.

[48] R. J. Cava, *Science* **247**, 656 (1990).

[49] C. H. Chen, "The microstructure of high-temperature oxide superconductors," in *Physical Properties of High Temperature Superconductors II*, ed. D. M. Ginsberg (World Scientific, Singapore, 1990) ch. 4.

[50] R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak and D. J. Werder, *Nature* **329**, 423 (1987) and *Phys. Rev. B* **36**, 5719 (1987).

in the room temperature resistivity as a function of oxygen concentration. This observation suggested the possibility of oxygen-vacancy ordering, which has since been confirmed by both electron and x-ray diffraction studies.

Defects and second phases concentrate at grain boundaries in sintered ceramic samples, leading to critical current densities as low as 400 A/cm^2. Grain boundaries are predominantly parallel to the (001) basal planes in at least one of the adjacent grains, suggesting that the basal plane may be the fastest growing face.

Crystals

A number of the high-temperature superconductiors undergo a transition from tetragonal to orthorhombic as they are cooled. This transition can be observed in TEM with the nucleation and growth of twin domains as the temperature is reduced.

Studies of the surface layers of oriented single crystals indicate that the orthorhombicity and defect density at the surface may differ significantly from the bulk of the crystal. Single crystals also contain intergrowth defects that result from reduced oxygenation.

Epitaxial films

Significant advances have been made in the preparation of crystalline films, grown epitaxially on suitably oriented insulating crystals. Although these films are not entirely defect free, those defects that are present appear to be well localized.

1.3. Physical Properties

1.3.1. Resistivity

Bednorz and Müller[1] measured dc resistivity with a four-point method that had the advantage of reducing the sensitivity to contact resistance. Gold electrodes were attached to rectangular samples that had been cut from the sintered pellets. Contact to the electrodes was made with indium wires.

Samples with fractional Ba concentration $x < 1$ exhibited a metallic-like resistivity that above 100 K dropped linearly with temperature. With further reduction in temperature the resistivity of samples annealed in air increased somewhat, followed by a precipitous drop in the 30 K region. Annealing in a reducing atmosphere enhanced the resistivity maximum observed below 100 K. Current densities above 0.5 A/cm^2 led to partial suppression of the resistivity maximum.

1.3.2. Magnetic susceptibility

In a second paper,[51] submitted for publication in October 1986, Bednorz, Müller and Takashige measured the magnetic susceptibility of their ceramic samples as a function of temperature. The very considerable importance of magnetic susceptibility is that the development of macroscopic diamagnetism, more than a resistivity drop alone, is required to establish the presence of superconductivity.

Samples were measured in a commercial variable-temperature susceptometer at temperatures down to 4.2 K and in fields up to 5 T. The presence of a transition to superconductivity in $(La_{1-x}Ba_x)CuO_4$ was confirmed. For samples cooled in fields below 0.1 T, bulk diamagnetism appeared at a somewhat lower temperature than did the drop in

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[51] J. G. Bednorz, M. Takashige and K. A. Müller, *Europhys. Lett.* **3**, 379 (1987).

resistivity. Cooling in fields above 1 T suppressed the development of bulk diamagnetism. If, however, the samples were cooled below T_c in zero field and the field was then applied, diamagnetism could be observed in fields above 1 T.[52] The origin of this difference in magnetic behavior has received considerable attention and is considered in Ch. 6.

1.3.3. Surface impedance

Because alternating electric and magnetic fields are largely excluded from conductors, it is useful to characterize the response of conductors in terms of what is called a surface impedance rather than in terms of bulk quantities like resistivity and inductivity. The theoretical background to this approach is discussed in Ch. 3. The approach is particularly useful at radio and microwave frequencies but also of use for magnetic susceptibility measurements at low alternating frequencies.

Blazey *et al.*[53] measured the modulated microwave surface resistance using a commercial electron spin resonance spectrometer and obtained large low-field signals, which were ascribed to the granular structure of their superconducting samples in the La-Cu-O system. This technique has proved useful in the study of intergranular coupling[54,55] further discussed in Ch. 13.

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[52] K. A. Müller, M. Takashige and J. G. Bednorz, *Phys. Rev. Lett.* **58**, 1143 (1987).

[53] K. W. Blazey, K. A. Müller, J. G. Bednorz, W. Berlinger, G. Amoretti, E. Buluggiu, A. Vera and F. Mattacotta, *Phys. Rev.* **36**, 7241 (1987).

[54] K. W. Blazey, "Microwave absorption in granular guperconductors," in *Earlier and Recent Aspects of Superconductivity,* eds. J. G. Bednorz and K. A. Müller (Springer-Verlag, Berlin, 1990) pp. 262-277.

[55] A. M. Portis, "Microwaves and superconductivity: processes in the intergranular medium," in *Earlier and Recent Aspects of Superconductivity,* eds. J. G. Bednorz and K. A. Müller (Springer-Verlag, Berlin, 1990) pp. 278-303.