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PHYSICAL PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS II

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CRYSTAL STRUCTURES OF HIGH-TEMPERATURE SUPERCONDUCTORS

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I. Introduction

Research on the atomic structures of high-temperature superconductors has played a prominent role in characterizing this new class of materials. Crystallographic studies are critical to understanding the mechanisms of superconductivity, to predicting and synthesizing chemically distinct variants, and to engineering these novel materials into wires, thin films, and other useful forms.

By September of 1989 at least nineteen distinct layered copper-oxide superconductor structure types had been described. Several of these structures exist in more than one space group (the *T* and *O* varieties of 1-2-3, for example), as well as in dozens of compositional variants. More than 500 separate high T_c structures, refined from x-ray, neutron, or electron diffraction data of either polycrystalline or single-crystal samples, have been published since the seminal article of Bednorz and Mueller.[1] Many authors of these crystallographic articles recognized that close ties must exist between the novel atomic structures of copper-oxide superconductors and their superconducting mechanisms. Early attempts to find some simple relation between atomic arrangement and critical temperatures have failed, however, and the crystallographer's role has proven somewhat frustrating as evidence of oxygen nonstoichiometry, modulations, cation disorder, twinning, and other short-range structural phenomena crucial to electronic behavior have appeared in structure after structure. Nevertheless, unique structural aspects shared by all copper-oxide high-temperature superconductors are still widely accepted as a principal consideration in any model of their superconducting behavior.

The principal objective of this review is to collect and tabulate in one place data on the long-range atomic structures of all known high-temperature copper oxide superconductors. Essential structural parameters, including unit-cell dimensions, atomic fractional coordinates, and interatomic bond distances and angles, are given for each of twenty-eight variants of nineteen topologically distinct high-T_c structures (Table 1). There is not room to include all of the hundreds of redundant published refinements, but several different refinements are recorded for each structure (when available), to indicate the range in published values. These reference data, though only part of the complex story of superconductor structures, serve as the starting point for any consideration of superconducting properties and mechanisms.

Table 1. Summary of Cu-O high-temperature superconductor structures.

Structure Number	Composition	Space Group	Abbreviations	Refinements
1a	La_2CuO_4	I4/mmm	214-T	1-37
1b		$P4_2$/ncm		
1c		Bmab	214-O	
1d		Fmmm		
2	Nd_2CuO_4	I4/mmm	214-T'	38-44
3	$(Nd,Ce,Sr)_2CuO_4$	P4/mmm	214-T*	45-47
4a	$YBa_2Cu_3O_6$	P4/mmm	123-T	48-153
4b	$YBa_2Cu_3O_7$	Pmmm	123-O	
5	$YBa_2Cu_4O_8$	Ammm	124	154-159
6	$Y_2Ba_4Cu_7O_{15}$	Ammm	247	160
7	$(Ba,Nd)_2(Nd,Ce)_2Cu_3O_8$	I4/mmm	223	161
8a	$Pb_2YSr_2Cu_3O_8$	P4/mmm	2123	162-165
8b		Cmmm		
9a	$Bi_2Sr_2CuO_6$	Amaa	Bi-2201	166-169
9b		A2/a		
9c		C2		
10a	$Bi_2Sr_2CaCu2O_8$	Fmmm	Bi-2212	170-181
10b		Amaa		
11	$Bi_2Sr_2Ca_2Cu_3O_{10}$	I4/mmm	Bi-2223	none
12a	$Tl_2Ba_2CuO_6$	I4/mmm	Tl-2201	182-187
12b		Fmmm		
13	$Tl_2Ba_2CaCu_2O_8$	I4/mmm	Tl-2212	188-194
14	$Tl_2Ba_2Ca_2Cu_3O_{10}$	I4/mmm	Tl-2223	195-199
15	$Tl_2Ba_2Ca_3Cu_4O_{12}$	I4/mmm	Tl-2234	none
16	$TlBa_2CuO_5$	P4/mmm	Tl-1201	200-204
17	$TlBa_2CaCu_2O_7$	P4/mmm	Tl-1212	205-211
18	$TlBa_2Ca_2Cu_3O_9$	P4/mmm	Tl-1223	212-218
19	$TlBa_2Ca_3Cu_4O_{11}$	P4/mmm	Tl-1234	none

II. The La_2CuO_4 (2-1-4) Structures

Bednorz and Mueller[1] suggested that their "possible" superconducting material in the system La-Ba-Cu-O had the tetragonal K_2NiF_4 structure - a suggestion soon confirmed by Takagi *et al.*[2] Recent research on 2-1-4 compositional variations has revealed two additional distinct topologies, characteristic of Nd_2CuO_4 and $(Nd,Ce,Sr)_2CuO_4$. In each of the three 2-1-4 structures,

Table 2. K_2NiF_4 structures

1A. Tetragonal I4/mmm (D^{17}_{4h})

$a = b \cong 3.8$ Å $c \cong 13.2$ Å $Z = 2$

Atoms	Site	Symmetry	x	y	z
La	4e	4mm	0	0	0.36
Cu	2a	4/mmm	0	0	0
O1	4c	mmm	0	1/2	0
O2	4e	4mm	0	0	0.18

1B. Tetragonal $P4_2$/ncm (D^{16}_{4h})

$a = b \cong 5.4$ Å $c \cong 13.2$ Å $Z = 4$

Atoms	Site	Symmetry	x	y	z
La	8i	m	0.004	=x	0.36
Cu	4d	2/m	0	0	0
O1	4e	mm	1/4	1/4	0.01
O1'	4a	222	3/4	1/4	0
O2	8i	m	-0.02	=x	0.18

1C. Orthorhombic Bmab (D^{18}_{2h})

$a \cong b \cong 5.4$ Å $c \cong 13.2$ Å $Z = 4$

Atoms	Site	Symmetry	x	y	z
La	8f	m	0	0.01	0.36
Cu	4a	2/m	0	0	0
O1	8e	2	1/4	1/4	0
O2	8f	m	0	-0.03	0.18

1D. Orthorhombic Fmmm (D^{23}_{2h})

$a \cong b \cong 5.4$ Å $c \cong 13.2$ Å $Z = 4$

Atoms	Site	Symmetry	x	y	z
La	8i	mm	0	0	0.36
Cu	4a	mmm	0	0	0
O1	8e	2/m	1/4	1/4	0
O2	8i	mm	0	0	0.18

Table 3. Refinements of the K_2NiF_4 structure

#	Composition	T(K)	a(Å)	b(Å)	c(Å)	Space Group	y_{La}	z_{La}	z_{O1}	y_{O2}	z_{O2}	Technique*	Ref
1	La_2CuO_4	10	5.3350(1)	5.4209(1)	13.1068(2)	Bmab	.0095(2)	.3618(1)	0085(1)	-.0426(2)	.1839(1)	NPD	3
2	La_2CuO_4	300	5.3548(4)	5.4006(3)	13.1529(9)	Bmab	.0079(4)	.3610(1)	.0072(2)	-.0333(5)	.1838(2)	NPD	4
3	La_2CuO_4	528	3.812(1)	-	13.219(2)	I4/mmm	0	.3614(1)	0	0	.1839(12)	SXD	5
4	$La_2CuO_{4-\delta}$	300	5.3535(3)	5.4031(3)	13.1441(7)	Bmab	.0074(3)	.3610(1)	.0078(2)	-.0343(3)	.1841(1)	NPD	4
5	$La_2CuO_{4+\delta}$	10	5.3364(2)	5.3955(2)	13.1615(5)	Fmmm	0	.3604(2)	0	0	.1828(4)	NPD	3
6	$La_2CuO4.032$	15	5.350(1)	5.398(3)	13.148(6)	Bmab	.0069(2)	.3611(1)	.0067(1)	-.0349(3)	.1830(1)	SND	6
7	$La_2CuO_{4.032}$	300	5.360(1)	5.393(3)	13.181(6)	Bmab	.0046(2)	.3611(1)	.0051(1)	-.0243(5)	.1829(1)	SND	6
8	$La_2(Cu_{.95}Li_{.05})O_4$	295	5.359(1)	5.363(1)	13.127(2)	Bmab	.0028(2)	.3619(1)	.0032(1)	-.0014(1)	.1827(1)	SND	7
9	$(La_{1.92}Sr_{0.08})CuO_{3.96}$	15	5.3275(6)	5.3780(6)	13.154(2)	Bmab	-.015(4)	.3621(4)	.0108(7)	-.051(2)	.1859(6)	SND	8
10	$(La_{1.92}Sr_{0.08})CuO_{3.96}$	40	5.3296(6)	5.3755(6)	13.157(2)	Bmab	-.010(2)	.3614(1)	.0108(2)	-.027(1)	.1815(3)	SND	8
11	$(La_{1.92}Sr_{0.08})CuO_{3.96}$	100	5.3296(6)	5.3755(6)	13.156(1)	Bmab	-.012(6)	.3610(4)	.0068(5)	-.033(1)	.1813(3)	SND	8
12	$(La_{1.92}Sr_{0.08})CuO_{3.96}$	150	5.3331(6)	5.3741(6)	13.165(2)	Bmab	-.009(6)	.3618(2)	.0052(8)	-.049(2)	.1822(6)	SND	8
13	$(La_{1.92}Sr_{0.08})CuO_{3.96}$	295	3.7866(2)	-	13.1970(8)	I4/mmm	0	.3612(1)	0	0	.1829(2)	SND	8
14	$(La_{1.85}Sr_{.15})CuO_4$	10	5.3240(1)	5.3547(1)	13.1844(1)	Bmab	-.00496(1)	.3607(1)	.0057(1)	-.0255(1)	.1826(1)	NPD	9
15	$(La_{1.85}Sr_{.15})CuO_4$	60	5.3252(1)	5.3546(1)	13.1832(1)	Bmab	-.00496(1)	.3607(1)	.0056(1)	-.0256(1)	.1826(1)	NPD	9
16	$(La_{1.85}Sr_{.15})CuO_4$	295	3.7066(7)	-	13.186(4)	I4/mmm	0	.3609(1)	0	0	.1825(3)	SXD	10
17	$(La_{1.85}Sr_{.15})CuO_4$	300	3.7793(1)	-	13.2260(3)	I4/mmm	0	.3605(1)	0	0	.1824(1)	NPD	9
18	$(La_{1.8}Sr_{0.2})CuO_4$	11	3.7630(1)	-	13.2013(7)	I4/mmm	0	.3609(2)	0	0	.1815(3)	NPD	11
19	$(La_{1.8}Sr_{0.2})CuO_4$	50	3.7632(1)	-	13.2007(7)	I4/mmm	0	.3607(2)	0	0	.1812(3)	NPD	11
20	$(La_{1.8}Sr_{0.2})CuO_4$	200	3.7675(1)	-	13.2220(6)	I4/mmm	0	.3607(2)	0	0	.1824(3)	NPD	11
21	$(La_{1.7}Sr_{0.3})CuO_4$	25	5.356(2)	5.375(2)	13.183(6)	Bmab	.0056(5)	.3610(1)	.0055(5)	-.025(1)	.1826(2)	SND	12
22	$(La_{1.7}Sr_{.16}Pb_{.14})CuO_4$	15	5.359(1)	5.368(1)	13.193(4)	Bmab	.0045(3)	.3611(1)	.0048(3)	-.021(1)	.1827(1)	SND	12
23	$(La_{1.7}Sr_{.16}Pb_{.14})CuO_4$	295	3.799(2)	-	13.338(6)	I4/mmm	0	.3612(1)	0	0	.1824(1)	SND	12
24	$(La_{1.9}Ba_{0.1})CuO_4$	15	5.360(1)	-	13.2356(3)	$P4_2/ncm$	.0042(2)	.3612(1)	.0081(4)	-.0213(3)	.1824(2)	NPD	13
25	$(La_{1.9}Ba_{0.1})CuO_4$	45	5.360(1)	-	13.2379(8)	$P4_2/ncm$	.0039(4)	.3619(4)	.0102(9)	-.0198(6)	.1822(7)	NPD	13
26	$(La1.9Ba_{0.1})CuO4$	45	5.3404(3)	5.3801(3)	13.227(2)	Bmab	.0089(1)	.3590(8)	.0052(10	-.0298(15)	.1829(12)	NPD	13
27	$(La_{1.9}Ba_{0.1})CuO_4$	60	5.3415(5)	5.3805(5)	13.2409(8)	Bmab	.0062(7)	.3608(1)	.0047(4)	-.0313(11)	.1828(2)	NPD	13
28	$(La_{1.9}Ba_{0.1})CuO_4$	91	5.3436(1)	5.3773(1)	13.2386(2)	Bmab	.0056(4)	.3609(1)	.0054(2)	-.0279(5)	.1825(2)	NPD	13
29	$(La_{1.9}Ba_{0.1})CuO_4$	285	3.7931(1)	-	13.2755(2)	I4/mmm	0	.3607(1)	0	0	.1824(1)	NPD	13
30	$(La_{1.85}Ba_{.15})CuO_4$	11	5.3381(11)	5.3500(11)	13.244(2)	Bmab	*	.3610(2)	.0102(10)	-.031(3)	.1818(4)	NPD	13
31	$(La_{1.85}Ba_{.15})CuO_4$	90	5.3349(10)	5.3511(9)	13.243(2)	Bmab	*	.3609(2)	.0097(10)	-.029(3)	.1824(3)	NPD	13
32	$(La_{1.85}Ba_{.15})CuO_4$	293	3.7840(5)	-	13.283(2)	I4/mmm	0	.3606(2)	0	0	.1822(3)	NPD	13
33	$(La_{1.85}Ba_{.15})CuO_4$	295	3.7873(1)	-	13.2883(3)	I4/mmm	0	.3606(1)	0	0	.1828(2)	NPD	14
34	$(La_{1.8}Na_{0.2})CuO_4$	11	5.3239(3)	5.3626(2)	13.1501(9)	Bmab	.0053(5)	.3609(2)	.0055(5)	-.030(1)	.1830(3)	NPD	15
35	$(La_{1.8}Na_{0.2})CuO_4$	295	3.7796(1)	-	13.1871(4)	I4/mmm	0	.3606(2)	0	0	.1830(2)	NPD	15
36	$(La_{1.8}K_{0.2})CuO_4$	295	5.3431(2)	5.3596(3)	13.1933(6)	Bmab	.011(1)	.3610(2)	.0056(5)	-.008(2)	.1831(3)	NPD	15
37	$(La_{1.8}K_{0.2})CuO_4$	295	3.7833(1)	-	13.1918(8)	I4/mmm	0	.3609(2)	0	0	.1830(3)	NPD	15

* NPD= Neutron powder diffraction, SND= Single-crystal Neutron diffraction, SXD= Single-crystal X-ray diffraction

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.

Pure stoichiometric 2-1-4 phases are not found to be superconducting. Substitutions of monovalent, divalent, or tetravalent cations for lanthanum, or deviations from 4.00 oxygens, are required to obtain the superconducting state.

A . *The $La_2CuO_4(T)$ Structure*

The first known high-temperature copper oxide superconductor, $(La_{1.85}Ba_{0.15})CuO_4$, is tetragonal (space group *I4/mmm*) at room temperature. Its structure is identical to that of K_2NiF_4, also referred to as the 2-1-4 or *T* structure (Table 2). Subsequent studies of La_2CuO_4 at different temperatures or with different chemical substitutions have revealed at least three other topologically identical forms with lower symmetry. More than thirty published structure refinements of these phases help to clarify the phase transition behavior of *T*-type compounds (Table 3).

The K_2NiF_4 topology is known for only a fairly narrow range of copper oxide compositions, all of which are based on La_2CuO_4. The lanthanum site can accommodate partial substitution of other rare earth elements, such as Pr, Nd, Eu, or Gd, as well as the alkaline earths Ca, Sr, and Ba, and the alkali metals Na and K. Substitution of a few percent Zn, Ni, or Li for Cu has been demonstrated, and slightly fluorinated varieties are also known.

1. Structure 1A: the *I4/mmm* structure

The aristotype structure with K_2NiF_4 topology displays space group *I4/mmm*, with four atoms in the asymmetric unit and only two variable positional parameters - the *z* coordinates of La and O2 (Figure 1; Table 3). This high-symmetry form is adopted by La_2CuO_4 at temperatures above 500 K (Table 3; refinement 3), and it is stabilized at lower temperatures by the partial substitution of Ba, Sr, K, or Na for La (Table 3; refinements 13, 16-20, 23, 29, 32, 33, 35, and 37).

Each copper in this ideal *T* structure is coordinated to four O1 oxygens in a perfect corner-linked array of square planes, with Cu-O1 distances approximately 1.9 Å(equals *a/2*, where *a is* the tetragonal unit-cell edge; see Table 4). Two additional O2 oxygens lie above and below each copper (Cu-O2 ~ 2.4 Å). (Note that a few authors refer to the oxygens in the Cu-O plane as "O2," and the out-of-plane oxygens as "O1." Data in Tables 3 and 4 have been recast for consistency.)

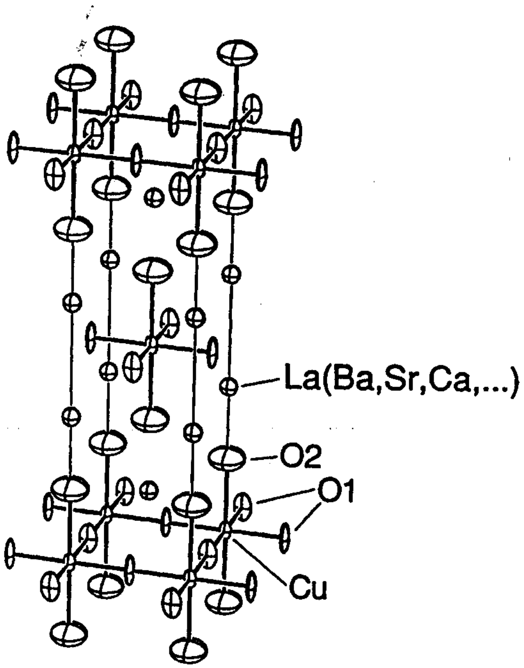

Figure 1. The crystal structure of (La,Ba)$_2$CuO$_4$ in space group *I4/mmm*, from Jorgensen .[16]

The Cu site can be described, and is often illustrated, as an extremely elongated octahedron with *4/mmm* point symmetry, though band theory calculations suggest that Cu-O2 interactions parallel to *c* are minimal. Layers of corner-linked octahedra are topologically identical to those of perovskite, such as LaCuO$_3$. The La$_2$CuO$_4$ structure differs from perovskite in that apical oxygens are not linked to adjacent octahedral layers to form a three-dimensional octahedral array. Furthermore, these adjacent layers are offset by *(a+b)/2* with respect to each other.

Lanthanum is coordinated to nine oxygens: four O1 at 2.6 Å, one O2 at 2.4 Å, and four O2 at 2.7 Å, for a 2.65 Å average La-O distance. Both symmetrically distinct oxygen atoms in the *T* structure are ctahedrally coordinated, as in the true perovskite structure. Each O1 is linked to two Cu at 1.9 and four La at 2.6 Å, while O2 has one distant Cu neighbor at 2.4 Å, one La at 2.4 Å, and four a at 2.7 Å.

All *T*-type superconductors display peak splitting or other evidence of distortion from *I/mmm* symmetry at low temperatures. These distortions, outlined below, appear to play a itical, but as yet unknown, role in high-temperature superconductivity.

2. Structure 1C: the *Bmab* structure

On cooling, many *T*-type compounds with the *I4/mmm* structure undergo a displacive ansition to an orthorhombic (O) form with tilted CuO$_6$ octahedra (Figure 2; this phenomenon

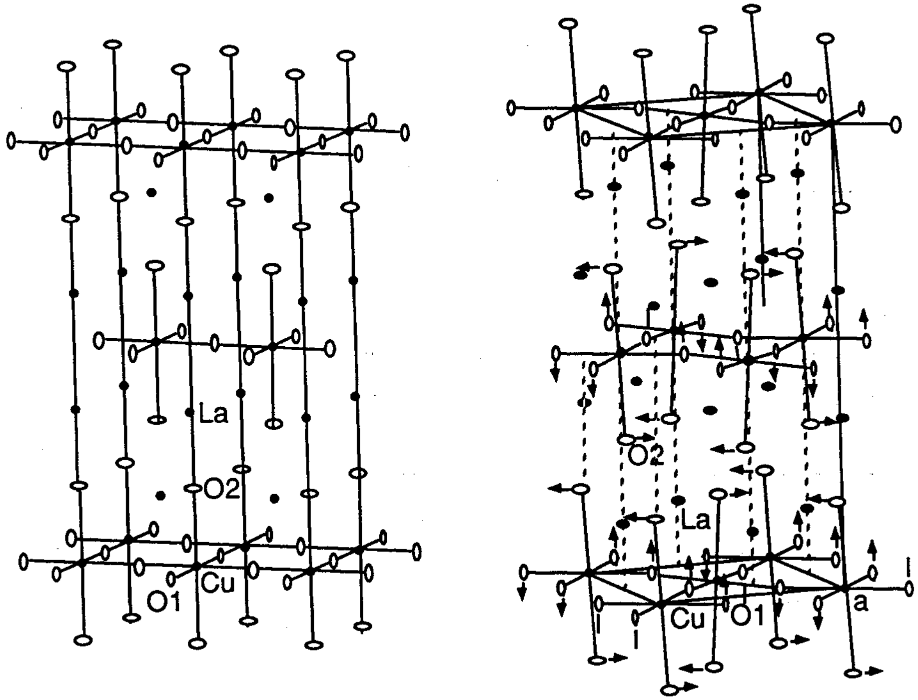

Figure 2. Comparison of the crystal structures of tetragonal (*I4/mmm*; left) and orthorhombic (*Bmab*; right) types of La$_2$CuO$_4$, from Onoda *et al.*[5] Note the octahedral tilts in the orthorhombic form.

is equally well described as a buckled Cu-O sheet). Tilt angles are typically a few degrees, ranging from 1.3° in lithium-substituted lanthanum cuprate (Table 3; refinement 9) to 4.3° in (La$_{1.92}$Sr$_{0.08}$)CuO$_4$ at low temperature (Table 3; refinement 8). Thus, reported Cu-O1-Cu angles range from 177.4° to 171.4°, as opposed to the ideal value of 180°. Most known *T*-type superconductors display this tilted structure at superconducting temperatures (see Table 3; refinements 1, 2, 4, 6-12, 14, 15, 21, 22, 26-28, 30, 31, 34, and 36). One consequence of this tilting is to double the size of the unit cell: tetragonal (110) and (1$\bar{1}$0) become two of the three orthorhombic unit-with K_2NiF_4 structure. See Table 1a for speciment description and reference

#	Cu-O1 [4]	Cu-O2 [2]	La-O1 [4]	La-O2 [1]	La-O2 [4]	Average La-O
17	1.8896(1)	2.4124(5)	2.6409(3)	2.3557(1)	2.732(1)	2.650
16	1.898(1)	2.406(4)	2.639(1)	2.354(4)	2.745(1)	2.654
20	1.884(1)	2.412(4)	2.635(2)	2.357(5)	2.724(1)	2.644
35	1.890(1)	2.414(3)	2.634(1)	2.345(4)	2.735(1)	2.647
37	1.892(1)	2.414(4)	2.636(1)	2.346(5)	2.737(1)	2.648

Table 5. Selected bond distances (Å) and angles ( ) for orthorhombic (Bmab) compounds with the K_2NiF_4 topology. See Table 1a for specimen description and reference.

#	Cu-O1[4]	Cu-O2[2]	Cu-O1-Cu	La-O1 [2]	La-O1 [2]	La-O2 [1]	La-O2 [1]	La-O2 [2]	La-O2[1]	Average La-O
6	1.9022(3)	2.46(2)	174.5	2.5923(8)	2.6812(8)	2.352(1)	2.537(2)	2.7417(3)	2.986(2)	2.565
14	1.8893(1)	2.411(1)	175.4(2)	2.595(2)	2.6731(1)	2.3545(1)	2.5784(1)	2.7250(1)	2.897(2)	2.646
15	1.8894(1)	2.411(1)	175.4(2)	2.597(2)	2.6726(1)	2.3545(1)	2.5776(1)	2.7253(1)	2.898(1)	2.647
34	1.891(1)	2.411(4)	175.6	2.595(6)	2.667(6)	2.347(5)	2.557(7)	2.727(1)	2.929(1)	2.651
36	1.893(1)	2.416(4)	175.5	2.616(7)	2.658(7)	2.349(5)	2.645(14)	2.734(1)	2.840(14)	2.650

Table 6. The Nd_2CuO_4 (T') structure

Tetragonal I4/mmm (D^{17}_{4h}) Z = 2

a = b = 3.9 Å c = 12.2

Atoms	Site	Symmetry	x	y	z
Ln	4e	4mm	0	0	0.35
Cu	2a	4/mmm	0	0	0
O1	4c	mmm	0	1/2	0
O2	4d	$\bar{4}$m2	0	1/2	1/4

cell axes. These new axes have length $\sqrt{2}a_{tetragonal}$ ~ 5.4 Å)

It is easiest to describe the *I4/mmm* to *Bmab* transition, which occurs at about 500 K in pure La_2CuO_4 and about 100 K in $(La_{1.85}Ba_{0.15})CuO_4$, by maintaining the long tetragonal *c* axis as the orthorhombic *c*. Thus, while the standard setting *(b > a > c)* yields space group *Cmca* for the *O* phase, most authors adopt *Bmab* as the most appropriate space group. (A third equivalent space group, *Abma*, has also been employed in the somewhat confusing *O*-phase literature.)

Four atoms in the *Bmab* structure are topologically identical to those of the *I4/mmm* aristotype of the *T* phase. Five variable atom coordinates (instead of the two for the tetragonal form) are required to describe this subgroup structure, however. The copper atom is still fixed in a centrosymmetric site at the origin, but La and both oxygens have variable *z*, and La and O2 have variable y coordinates as well (Table 2).

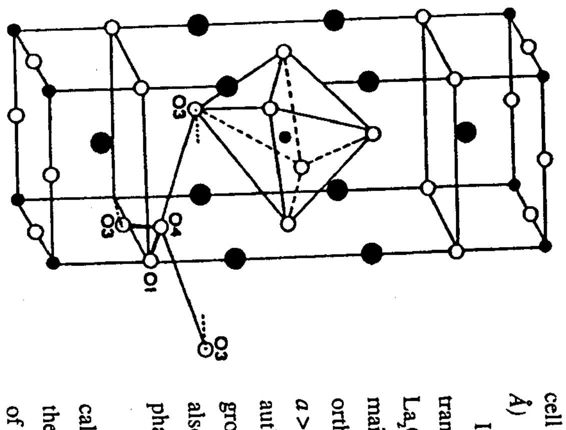

Figure 3. The crystal structure of oxygenated La_2CuO_4, from Chaillout *et al.*[6] Peroxide pairs of O3 and O4, separated by only 1.6 Å, replace single O1 atoms.

Interatomic distances in the *O* form of La_2CuO_4 (Table 5) are similar to those of the higher-temperature structure (Table 4). The most significant difference is in the Cu-O1-Cu angles, which deviate by as much as 8.6° from the ideal 180° of the *I4/mmm* structure.

Chaillout *et al.*[6] reported the structure of an oxygen-enriched sample, $La_2CuO_{4.032}$, with the *Bmab* structure. Their single-crystal neutron diffraction data permitted them to identify sites partially occupied by the excess oxygen. They identify two new oxygen positions: O3 at the general position (0.030, 0.100, 0.182), and O4 at (1/4, 1/4, 0.243). (Note that Chaillout *et al.* use space group *Cmca* and reverse the definitions of O1 and O2, so their reported coordinates and distances must be recast accordingly.) It appears from these oxygen occupancy and position data that the excess oxygens occur as peroxide O3 and O4 pairs, replacing a single O2, with a 1.64

O-O distance. The positions of O3 and O4, and the corresponding distortion of the Cu tahedron, are illustrated in Figure 3.

3. Structure IB: the *P4₂/ncm* structure

Axe *et al.*[13] (see also Table 3; refinements 24 and 25) recognized a distinct low-temperature riant of the *T* structure on the basis of peak splitting of neutron powder diffraction data on $a_{1.9}Ba_{0.1})CuO_4$ below 50 K. They identified this new form as "tetragonal or almost tetragonal with probable symmetry *P4₂/ncm*," which bears a subgroup relationship to *I4/mmm* (Table 2; ucture IB). Axe and coworkers noted that this low-temperature phase can be modeled as "a herent superposition of two orthorhombic (i.e., *Pbcn)* twin-related structures." Tilting angles : similar to that of the *O* form, but tilts alternate about *b* and *a,* as opposed to the repeated *b* is tilts of the *Bmab* structure.

The *P4₂/ncm* structure has been reported only in two refinements - those for $(La_{1.9}$ $_{0.1})CuO_4$ at 45 and 15 K (Table 3; refinements 24 and 25). The same authors did not observe s variant in $(La_{1.85}BaO_{0.15})CuO_4$ at 11 K, and low-temperature studies of the pure lanthanum prate by others have not revealed such a phase. While several other workers have reported anges in neutron diffraction peak profiles of 2-1-4 powders at low temperature,[3,11,15,16] the posed *P4₂/ncm* structure has not been confirmed as of this writing.

4. Structure ID: the *Fmmm* structure

La_2CuO_4 is normally not a superconductor at any temperature, but annealing in an oxygen vironment (especially high-pressure O_2) produces samples that are partially superconducting ibout 35 K. Powder neutron diffraction study of these samples at 10 K by Jorgensen *et al.*[3] (see ble 3, refinement 5) revealed the coexistence of two nearly identical orthorhombic phases. st of their samples consisted of near-stoichiometric La_2CuO_4 with the *Bmab* structure. perconductivity was associated with the second, oxygen-enriched phase, $La_2CuO_{4+\delta}$ ($\delta \leq$ 3). Jorgensen *et al.* proposed a face-centered orthorhombic structure (space group *Fmmm*), ed on two-phase Rietveld refinement of the powder data.

A significant feature of the *Fmmm* refinement is the large thermal parameter of O2 - a nomenon probably resulting from positional disorder of the excess oxygen, as shown by aillout *et al.*[6]The authors proposed that excess oxygens are present as dumbbell-shaped oxide pairs of oxygens substituted for single O2 atoms. The result would be to maintain the topology of the Cu-O plane, while increasing the total oxygen content to more than 4.00 per formula unit and increasing the coordination of some lanthanum atoms from nine to ten.

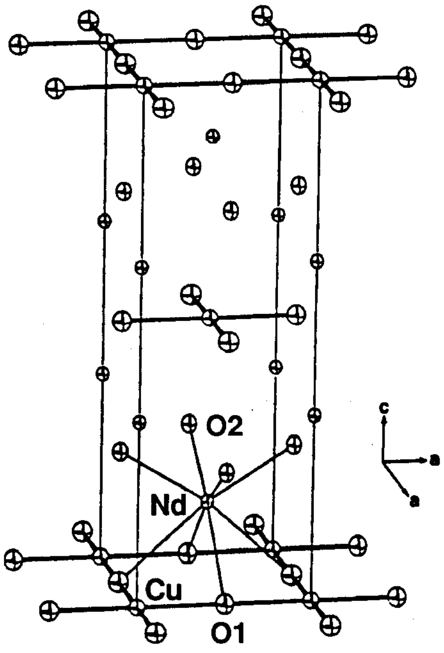

Figure 4. The crystal structure of Nd_2CuO_4, from Izumi *et al.*[22]

5. A Possible Monoclinic Structure

Moss *et al.*[17] observed broadening of neutron diffraction peaks from $(La_{1.8}Ba_{0.2})CuO_4$ at room temperature, and peak splitting at temperatures near 10 K. They interpreted these effects as evidence for the existence of two distinct tetragonal or pseudo-tetragonal phases at room temperature, with a possible reversible transition from tetragonal to a monoclinic distorted form at low temperature for one of the phases. While structural details were not resolved, it is evident that *T*-type compounds can display complex phase separation and displacive transformation behavior near the superconducting transition temperature.

6. Summary: K_2NiF_4-type structures

The 2-1-4 compounds with the deceptively simple *T*-type topology display exceedingly complex behavior. Oxygen nonstoichiometry leads to phase separation in both pure and alkali- or alkaline earth-substituted lanthanum cuprate. These materials also undergo a complex series of perovskite-like octahedral tilt transitions from the *I4/mmm* aristotype to lower symmetry tetragonal, orthorhombic, and perhaps monoclinic forms. Even though these compounds do not possess the highest known critical temperatures, they will continue to provide clues to the origins of superconductivity in layered copper oxides.

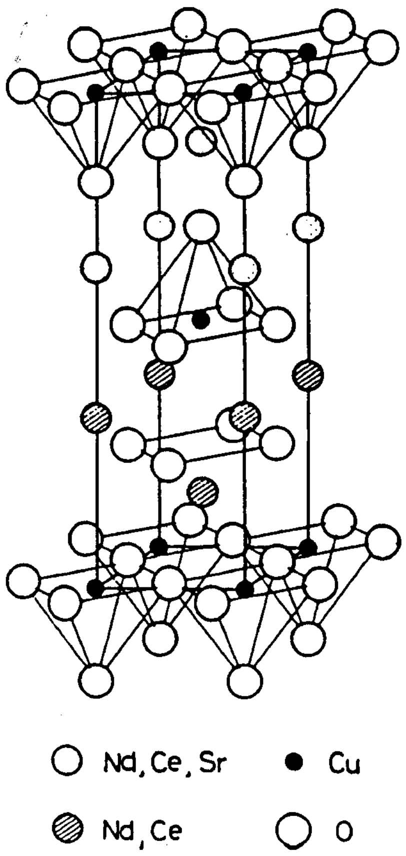

Figure 5. The crystal structure of (Nd,Ce,Sr)$_2$CuO$_4$, from Sawa *et al.*[26]

B. The Nd_2CuO_4 *(T') Structure*

Tokura *et al.*[18] synthesized a new superconductor, Ce-doped Nd_2CuO_4, with an onset critical temperature of about 25 K. This material is the first electron superconductor, with excess negative charge per unit cell. Nd_2CuO_4 and other rare earth element 2-1-4 compounds with large-site cations smaller than lanthanum adopt a tetragonal structure similar to, but topologically distinct from, K_2NiF_4 (Table 6). This structure, also referred to as the *T'* form, is tetragonal *I4/mmm* with Nd, Cu, and O1 in sites identical to those of the *T* phase (Figure 4; Table 7). In the *T'* structure, however, O2 shifts from the apical (0,0,.18) position to the fixed 4d position: (0,1/2,1/4). Unit-cell dimensions of Nd_2CuO_4 and its isomorphs reflect this oxygen shift: the tetragonal *a* axis is about 4% longer, while *c* is almost 8% shorter than in La_2CuO_4.

The slight shift in O2 location alters both Cu and Nd coordination compared to the *T* structure (Figure 4; Table 7). Copper becomes strictly square-planar coordinated, with four Cu-O1 bonds of about 1.9 Å; there are no apical oxygens. The Nd atoms bond to eight oxygens (four O1 at 2.7 Å and four O2 at 2.3 Å), compared to nine oxygens for larger lanthanum in the *T* structure. The choice of *T* versus *T'* structures results, in fact, primarily from this difference in lanthanide atom size.

Recent published refinements of *T'* structures, based on neutron powder diffraction data, include end-member Nd_2CuO_4 and Pr_2CuO_4, as well as the superconducting compound

Table 7. The Nd_2CuO_4 (T') structure: Unit-cell dimensions, refined cation coordinate, and selected bond distances (Å)

#	Composition	T (K)	a (Å)	c(Å)	z_{La}	dCu-O1 [4]	dCu-O1 [4]	dLa-O2 [4]	Ref.
38	Nd_2CuO_4	11	3.9385(1)	12.1465(3)	.3515(1)	1.969(1)	2.675(2)	2.320(2)	19
39	Nd_2CuO_{4-y}	295	3.9438(2)	12.1549(5)	.3513(1)	1.972(1)	2.675(1)	2.325(1)	20
40	Pr_2CuO4	15	3.9550(1)	12.1772(3)	.3517(1)	1.978(1)	2.676(1)	2.328(1)	21
41	Pr_2CuO4	298	3.9615(1)	12.2140(5)	.3512(2)	1.981(1)	2.685(1)	2.337(2)	21
42	Pr_2CuO4	298	3.9625(1)	12.2335(3)	.3515(2)	1.981(1)	2.687(1)	2.339(2)	19
43	$(Nd_{1.845}Ce_{.155})CuO_4$ superconducting	295	3.9469(2)	12.0776(5)	.3525(2)	1.973(1)	2.659(1)	2.330(2)	22
44	$(Nd_{1.845}Ce_{.155})CuO_4$ nonsuperconducting	295	3.9462(2)	12.0764(5)	.3524(2)	1.973(1)	2.659(1)	2.330(2)	22

Table 8. The $(Nd,Sr)_2CuO_4$ (T') structure

Tetragonal P4/mmm (D^7_{4h})

a = b = 3.9 Å c = 12.5 Z = 2

Atoms	Site	Symmetry	x	y	z
(Sr,Ln)	2c	4mm	1/4	1/4	0.39
(Nd,Sm)	2c	4mm	1/4	1/4	0.10
Cu	2c	4mm	3/4	3/4	0.25
O1	4f	mm	3/4	1/4	0.24
O2	2c	4mm	3/4	3/4	0.43
O3	2a	$\bar{4}2m$	3/4	1/4	0

Table 9. The T* structure: Unit cell parameters and refined parameters

#	Composition	T(K)	a(Å)	c(Å)	$Z_{Sr,Ce,La}$	$Z_{Nd,Sm}$	Z_{Cu}	Z_{O1}	Z_{O2}	ref.
45	$(Nd_{1.32}Sr_{.41}Ce_{.27})CuO_4$	295	3.8564(3)	12.4846(9)	.3893(3)	.1035(3)	.2510(3)	.2378(3)	.4291(6)	25
46	$(Nd_{1.32}Sr_{.41}Ce_{.27})CuO_{4-y}$	295	3.8554(2)	12.4747(6)	.3894(2)	.1037(2)	.2508(2)	.2372(2)	.4278(4)	25
47	$(Sm_{1.0}La_{.75}Sr_{.25})CuO_{3.95}$	295	3.8588(2)	12.5725(7)	.390(2)	.106(1)	.244(4)	.243(11)	.422(8)	26

Selected distances (Å) and Cu-O-Cu angle (°)

#	Cu-O1 [4]	Cu-O2 [1]	Nd-01 [4]	Nd-O3 [4]	Sr-O1 [4]	Sr-O2[1]	Sr-O2 [1]	Sr-O2 [2]	Sr-O2 [1]	Cu-O1-Cu
45	1.935(1)	2.24(1)	2.555(3)	2.321(2)	2.701(3)	2.281(9)	2.53(2)	2.783(3)	3.02(3)	170.2(3)
46	1.935(1)	2.22(1)	2.548(2)	2.321(1)	2.705(2)	2.294(7)	2.53(3)	2.779(3)	3.01(2)	169.8(2)

$(Nd_{1.845}Ce_{0.155})CuO_4$. All reported structures (Table 7; refinements 38-44) have the aristotype *I4/mmm* structure. Copper-oxygen layer buckling of the type observed in the *I4/mmm* to *Bmab* transition of *T*-type compounds, though not reported for *T'*-type phases, is possible, and might be observed as more low-temperature refinements of these novel electron superconductors are obtained.

C. The (Nd,Ce,Sr)$_2$CuO$_4$(T) Structure*

Research on substitutions of Sr, Ce, and other atoms for the rare earth element in Nd_2CuO_4-type compounds led to the discovery of a new 2-1-4 structure that incorporates aspects of both the *T* and *T'* topologies (Table 8). The compound $(Nd_{1.32}Sr_{0.41}Ce_{0.27})CuO_{4-y}$ was reported by Akimitsu *et al.*,[23] and the structure was determined shortly thereafter by Takayama-Muromachi *et al.*,[24] who called the new phase the *T** type (Figure 5, Table 9).

As in both the *T* and *T'* structures, *T** has square-plane coordinated copper in Cu-O1 sheets, with larger cations (Nd, Ce, Sr) above and below. On one side of the Cu-O1 layer, the rare earth atom and oxygen adopt the *T*-type configuration: the oxygen (O2) is apical to the copper square plane, and the lanthanide coordination is ninefold. On the other side of the Cu-O plane, however, the cation and oxygen topology is identical to the *T'* form. The oxygen (O3) is not apical, and the large site coordination is eightfold. The *T** structure can thus be viewed as a hybrid of the *T* and *T'* types (Figure 6). Unit-cell dimensions of the *T** structure reflect this intermediate character: both *a* and *c* axes are averages of the *T* and *T'* values.

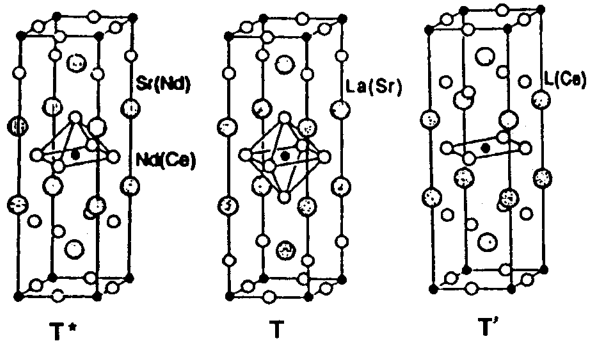

Figure 6. Comparison of the *T*, *T'* , and *T** structures, from Tokura *et al.*[26]

Differing configurations above and below the copper-oxygen layers destroy the Cu centrosymmetry; the *T** structure is tetragonal (space group *P4/nmm*), with copper in a five-coordinated square pyramid of site symmetry *4mm*. Four short Cu-O1 distances in the plane are approximately 1.94 Å, while the fifth O2 apical oxygen is about 2.2 Å above the plane. Eight oxygens around the Nd *T* - like site (*4mm* site symmetry) include four Nd-O1 at 2.6 Å and four Nd-O3 at 2.3 Å. The nine oxygens in the other (*T*-like) large site include four M-O1 bonds of 2.7 Å, and five M-O2 bonds that range from 2.3 to 2.8 Å (Table 9). As expected, larger cations, such as Sr and La, tend to concentrate in the nine-coordinated site, while Nd and Sm occupy the smaller, eight-coordinated position.

No low-temperature refinements of T*-type phases have been reported as of this writing. Lower symmetry variants with buckled Cu-O1 sheets may thus occur near the superconducting transition.

III. YBa$_2$Cu$_3$0$_{6+\delta}$ and Related Structures

The discovery by Wu *et al.*[27] of a superconductor with critical temperature above the technical and psychological 77 K barrier triggered a flurry of crystallographic research unprecedented in the history of materials science.[28] From the almost immediate recognition of their seemingly simple perovskite-like structures to the subsequent revelations of remarkable complexity in their long- and short-range order, 1-2-3 and related structures have commanded the attention of scores of crystallographers. This section is devoted to a description of the long-range ordered structures of the tetragonal and orthorhombic varieties of 1-2-3, as well as the closely related 1-2-4, 2-4-7, mixed 1-2-3/2-1-4, and 2123 structure types.

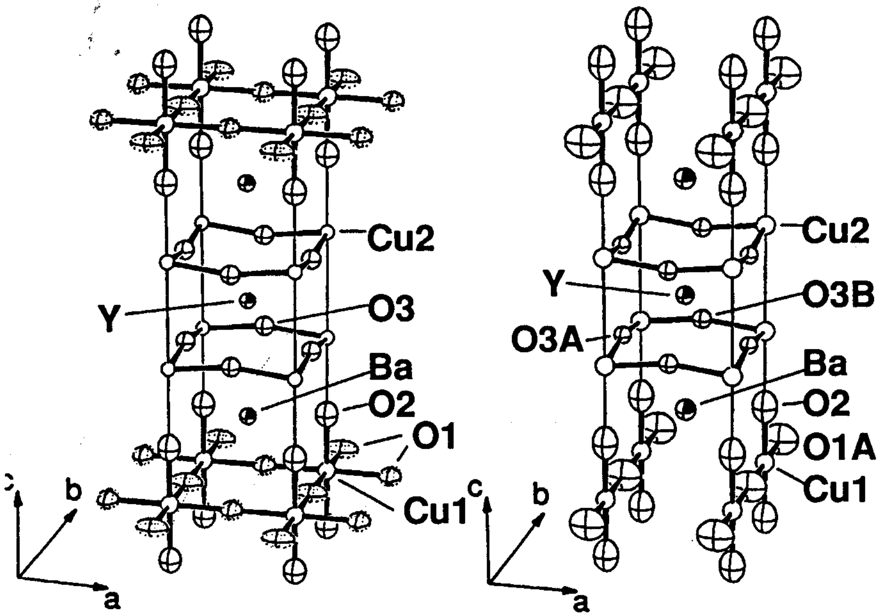

Figure 7. Comparison of the tetragonal (left) and orthorhombic (right) forms of $YBa_2Cu_3O_{6+\delta}$, from Jorgensen.[16] The *c* axes are vertical and *a* axes horizontal.

A. $YBa_2Cu_3O_{6+\delta}$(1-2-3) Structures

Within a month of the announcement of superconductivity in the Y-Ba-Cu-O system,[27] t least a dozen research groups had reported preliminary structural details based on x-ray and lectron diffraction.[29-32] Two-and-a-half years later 50 laboratories around the world have ontributed more than 100 crystallographic research articles. In that relatively brief time at least 00 different three-dimensional structure refinements of Y-Ba-Cu-O superconductors and their somorphs have been published. It is beyond the scope of this review to catalog all of these ontributions. The 106 selected refinements summarized in the following section provide a ross-section of this growing and often redundant literature.

All of the research groups who examined the $YBa_2Cu_3O_{6+\delta}$ structure in late February and arly March of 1987 recognized almost immediately that the structure was based on a simple unit ell, composed of a stack of three perovskite-like cubes.[33] The nearly ideal 1 x 1 x 3 dimensions

(3.9 x 3.9 x 11.7 Å), coupled with the "1-2-3" cation stoichiometry, suggested an ordered metal arrangement with copper filling all the octahedral "B" cube corner sites, and a regular sequence ...Ba-Y-Ba/Ba-Y-Ba... in the large "A" sites.[33] Anion positions, however, were not fully resolved with x-ray experiments. An ideal triple-cell perovskite has nine oxygens per unit cell, but 1-2-3 has only six to seven oxygens. Twinning, anion disorder, and possible coexistence of tetragonal and orthorhombic structures precluded precise determination of oxygen positions in any of the early x-ray structure studies. It was not until the first neutron powder diffraction studies[34-38] that details of oxygen positions were resolved with certainty.

Two principal varieties of 1-2-3 have been recognized, following initial confusion over the correct crystal system (Table 10). Several workers recognized that 1-2-3 crystallizes as tetragonal at high temperature, but converts by oxygen ordering to an orthorhombic form on cooling.[32,39,40] Rapidly cooled 1-2-3, with small domain size, can thus appear tetragonal in single-crystal x-ray studies. The most precise structure determinations have therefore, relied on Rietveld refinement of neutron powder diffraction data.

1. Structure 4A: the *P4/mmm* structure, $YBa_2Cu_3O_{6+\delta}$

Essential features of the tetragonal 1-2-3 structure are illustrated in Figure 7. All oxygen atoms assume perovskite-like anion positions, halfway between copper atoms along cube edges. There are no oxygens at the level of Y, but O2 oxygens at the level of Ba and O3 oxygens at the level of Cu2 are fully occupied, accounting for six oxygens per unit cell. The resulting structural slab, consisting of layers $BaO/CuO_2/Y/CuO_2/BaO$ (the 1-2-2 module), recurs in many of the high-temperature superconductors. These structures differ primarily in the additional atom layers that link 1-2-2 modules. Nonsuperconducting $YBa_2Cu_3O_6$ (Table 11; refinements 48-51), for example, has a single interleaved Cu1 with no oxygen between each pair of adjacent 1-2-2 slabs. Copper thus adopts an unusual linear two coordination with two Cu1-O2 bonds at 1.80 Å (Table 12). This topology, coupled with charge balance considerations, suggests that the Cu1 site contains Cu $^{1+}$ ions, as found in delafossite.[50] Y^{3+} is in 8-fold cube coordination, with eight equivalent Y-O3 bonds at 2.40 Å, while 8-coordinated Ba^{2+} has four Ba-O2 at 2.7 Å, and four Ba-O3 at 2.8 Å, for a 2.75 Å average Ba-O distance. These Y^{3+}-O and Ba^{2+}-O distances are typical of those found in other oxides.

Planes of Cu2 and O3, similar to the Cu^{2+}-O planes found in 2-1-4 compounds, are important features of 1-2-3 compounds. Each Cu2 has four nearest neighbor O3 oxygens at about

TABLE 10. The $YBa_2Cu_3O_{7-\delta}$ (1–2–3) structures.

4A. Tetragonal P4/mmm ($D^7{}_{4h}$)

a = b ≅3.9 Å c ≅ 11.8 Å Z = 1

Atoms	Site	Symmetry	x	y	z
Y	1d	4/mmm	1/2	1/2	1/2
Ba	2h	4mm	1/2	1/2	0.19
Cu1	1a	4/mmm	0	0	0
Cu2	2g	4mm	0	0	0.36
O1*	2f	mmm	0	1/2	0
O2	2g	4mm		0	0.15
O3	4i	mm	0	1/2	0.38

*occupancy 01 << 1.0

4B. Orthorhombic Pmmm (D^14h)

a ≅ b ≅ 3.9 Å c ≅ 11.8 Å Z = 1

Atoms	Site	Symmetry	x	y	z
Y	1h	mmm	1/2	1/2	1/2
Ba	2t	mm	1/2	1/2	0.19
Cu1	1a	mmm	0	0	0
Cu2	2q	mm	0	0	0.36
O1A†	1b	mmm	1/2	0	0
O1B†	1e	mmm	0	1/2	0
O2	2q	mm	0	0	0.16
O3A	2r	mm	0	1/2	0.38
O3B	2s	mm	1/2	0	0.38

†occupancies 01A >> O1B << 1.0

Table 11. Refinements of tetragonal 1-2-3 phases in the Y-Ba-Cu-O system

#	Composition	T(K)	a=b(Å)	c (Å)	Z_{Ba}	Z_{Cu2}	Z_{O2}	Z_{O3}	Occupancy O1	Technique*	Ref.
48	$YBa_2Cu_3O_6$	295	3.8594(5)	11.814(4)	.1946(1)	.3611(2)	.1524(13)	.3798(8)	~0	SXD	41
49	$YBa_2Cu_3O_6$	295	3.8570(1)	11.8194(3)	.1952(2)	.3607(1)	.1518(2)	.3791(1)	.014(2)	NPD	42
50	$YBa_2Cu_3O_6$	295	3.8519(1)	11.8037(4)	.1952(4)	.3605(3)	.1518(4)	.3794(2)	~0	NPD	38
51	$YBa_2Cu_3O_6$	295	3.863(2)	11.830(4)	.1934(1)	.3604(2)	.1533(13)	.3793(6)	~0	SXD	43
52	$YBa_2Cu_3O_{6.18}$	49	3.8533(2)	11.7631(7)	.1944(3)	.3602(3)	.1537(4)	.3785(2)	0.09	NPD	44
53	$YBa_2Cu_3O_{6\ 09}$	295	3.8600(1)	11.8168(2)	.1946(2)	.3611(1)	.1524(3)	.3795(1)	.10(1)	NPD	45
54	$YBa_2Cu_3O_{6.28}$	295	3.8621(1)	11.7961(2)	.1935(2)	.3607(1)	.1527(2)	.3789(1)	.39(2)	NPD	45
55	$YBa_2Cu_3O_{6.32}$	295	3.8571(3)	11.775(1)	.1933(7)	.3591(6)	.1557(8)	.3797(5)	.16(2)	NPD	36
56	$YBa_2Cu_3O_{6\ 34}$	295	3.8617(1)	11.7799(2)	.1929(2)	.3600(2)	.1529(2)	.3790(1)	.32(3)	NPD	45
57	$YBa2Cu3O_{6.4}$	8	3.8516(2)	11.7304(1)	.1942(3)	.3597(3)	.1529(4)	.3785(2)	.43(3)	NPD	46
58	$YBa2Cu3O_{6\ 4}$	296	3.8592(2)	11.7811(9)	.1930(3)	.3598(2)	.1525(4)	.3797(2)	.33(2)	NPD	46
59	$YBa_2Cu_3O_{6.34}$	750	3.8823(5)	11.826(2)	.1908(11)	.3592(10)	.1538(15)	.3799(7)	.33(3)	NPD	47
60	$YBa_2Cu_{2.9}O_{6.4}$	295	3.8640(4)	11.755(3)	.1927(2)	.3608(3)	.1538(18)	.3789(9)	0.2	SXD	48
61	$Y_{0.9}Ba_{2.1}Cu_3O_6$	295	3.8715(6)	11.738(2)	.1921(1)	.3605(2)	.154(1)	.3794(7)	•	SXD	49

*SXD = Single-crystal x-ray diffraction; NPD = Neutron powder diffraction

Table 12. Selected interatomic distances (Å) and Cu2-O3-Cu2 angle ( ) for tetragonal 1-2-3

#	Ba-O1[4]	Ba-O2[4]	Ba-O3[4]	MeanBa-O	Y-O3[8]	Cu1-O1[4]	Cu1-O2[2]	Cu2-O3[4]	Cu2-O2[1]	Cu2-O3-Cu
48	-	2.774(4)	2.918(8)	2.846	2.396(6)	-	1.801(15)	1.942(2)	2.466(13)	167
49	-	2.7751(5)	2.905(1)	2.828	2.4004(8)	-	1.795(2)	1.9406(3)	2.469(2)	167.2
50	-	2772(2)	2.905(4)	2.838	2.395(1)	-	1.792(5)	1.939(1)	2.463(4)	166.8
51	-	2.773(3)	2.927(6)	2.850	2.402(4)	-	1.81(2)	1.944(1)	2.45(2)	166.8
52	2.990(3)	2.767(1)	2.899(4)	2.833	2.399(2)	1.927	1.808(5)	1.939(1)	2.430(6)	167.2
55	2.983(7)	2.763(2)	2.922(8)	2.843	2.393(3)	1.929	1.833(9)	1.944(1)	2.395(11)	166.7
57	2.983(3)	2.766(1)	2.896(3)	2.861	2.396(2)	1.926	1.794(5)	1.939(1)	2.426(6)	166.9
58	2.982(2)	2.770(1)	2.926(3)	2.875	2.394(1)	1.93	1.797(5)	1.944(1)	2.442(5)	166.1
60	2.977(2)	2.770(3)	2.920(8)	2.889	2.400(6)	1.932	1.808(21)	1.944(1)	2.434(21)	167.4
61	-	2.775(3)	2.929(7)	2.852	2.399(6)	-	1.804(16)	1.948(1)	2.428(16)	166.9

1.94 Å, as well as a fifth weakly-bonded apical O2 at 2.45 Å. Each O3 is displaced along *c* towards Y, so Cu2-O3 layers are buckled, as in orthorhombic 2-1-4. The Cu2-O3-Cu2 angle in YBa$_2$Cu$_3$O$_6$ is approximately 167° (Table 12).

Both O2 and O3 oxygens are in distorted octahedral coordination. The O2 coordination group includes one short Cu1-O2 bonds of only 1.8 Å and a long Cu2-O2 bond of 2.45 Å. Thus, there is little coupling between the Cu2-O layers and Cu1 in the YBa$_2$Cu$_3$O$_6$ structure. Oxygen content in tetragonal YBa$_2$Cu$_3$O$_6$ may exceed six per unit cell (Table 11), depending on temperature and annealing conditions. Excess oxygens enter the O1 position at (0,1/2,0), which can hold up to two oxygens per unit cell. The O1 position is thus typically about 1/4 occupied in the Y-Ba-Cu-O phase at room temperature (Table 11; refinements 52-61). An important consequence of greater O1 occupancy is increased average valence of the Cu1.

The advantages of neutron powder diffraction over single-crystal x-ray diffraction in studying these crystals are evident from uncertainties in oxygen coordination (Table 11) and cation-oxygen distances (Table 12). Uncertainties from x-ray refinements (refinements 48, 51, 60, 61) average five times greater than those of neutron diffraction studies. Nevertheless, all 14 refinements recorded in Table 11 show similar results.

2. Structure 4B: the *Pmmm* structure, YBa$_2$Cu$_3$O$_{6+\delta}$

The orthorhombic 1-2-3 structure is topologically almost identical to the tetragonal form (Figure 7). The *a* and *b* axes generally differ by less than 2%, giving a pseudotetragonal unit cell (typically 3.82 x 3.88 x 11.65 Å). Different authors use different axial conventions: in this review $a < b < c$, so data in Tables 13 and 14 have been recast accordingly.

The four cations (Y, Ba, Cu1, and Cu2) as well as O2 are in positions identical to those of the tetragonal form, yielding the identical 1-2-2 structural module. Tetragonal O3 at (0, 1/2, .38) splits into two fully occupied oxygens - O3A at (0, 1/2, .38) and O3B at (1/2, 0, .38) - in the orthorhombic form. Similarly, the partially occupied tetragonal O1 splits into O1A at (0, 1/2, 0) and O1B at (1/2, 0, 0). Note that oxygen site nomenclature differs widely for 1-2-3 compounds. At least eight different designations of the five symmetrically distinct oxygen atoms are used by authors cited in Table 13. This review adopts the mineralogical convention, with *Pmmm* subgroup atom names dictated by the *P4/mmm* supergroup definitions. Thus, tetragonal O3 becomes orthorhombic O3A + O3B, and structural comparisons between the two forms are more readily made.

Table 13. Orthorhombic 1-2-3 phases in the Y-Ba-Cu-O system

#	Composition	T(K)	a(Å)	b(Å)	c(Å)	Z_{Ba}	Z_{Cu2}	Z_{O2}	Z_{O3A}	Z_{O3B}	Occupancy O1A	Occupancy O1B	Tech	ref.
62	$YBa_2Cu_3O_{7.1}$	71	3.8753(10)	3.8095(10)	11.624(5)	.1841(8)	.3537(9)	.1598(8)	.3790(9)	.3772(9)	.88(4)	.25(4)	NPD	51
63	$YBa_2Cu_3O_{7.1}$	124	2.8729(10)	3.8088(10)	11.634(5)	.1840(5)	.3541(9)	.1591(8)	.3775(9)	.3776(8)	.96(4)	.10(3)	NPD	51
64	$YBa_2Cu_3O_{7.1}$	295	3.8774(10)	3.8132(10)	11.653(12)	.1854(9)	.3557(7)	.1574(9)	.3771(13)	.3804(13)	1.00(3)	.10(3)	NPD	52
65	$YBa_2Cu_3O_7$	5	3.8128(1)	3.8806(2)	11.6303(5)	.1826(5)	.3542(3)	.1595(4)	.3773(4)	.3769(5)	1	•	NPD	35
66	$YBa_2Cu_3O_7$	30	3.8124(2)	3.8807(2)	11.6303(5)	.1830(3)	.3543(2)	.1592(3)	.3764(3)	.3773(4)	1	•	NPD	35
67	$YBa_2Cu_3O_7$	75	3.8131(1)	3.8806(2)	11.6329(5)	.1827(5)	.3547(3)	.1590(5)	.3771(5)	.3773(5)	1	•	NPD	35
68	$YBa_2Cu_3O_7$	120	3.8141(1)	3.8812(2)	11.6395(5)	.1827(5)	.3545(3)	.1588(4)	.3775(4)	.3770(5)	1	•	NPD	35
69	$YBa_2Cu_3O_7$	200	3.8164(2)	3.8824(2)	11.6546(5)	.1841(3)	.3547(2)	.1587(3)	.3768(3)	.3776(3)	1	•	NPD	35
70	$YBa_2Cu_3O_7$	300	3.8206(1)	3.8851(1)	11.6757(4)	.1841(4)	.3549(3)	.1581(4)	.3779(4)	.3777(5)	1	•	NPD	35
71	$YBa_2Cu_3O_7$	10.	3.8126(1)	3.8804(1)	11.6333(3)	.1837(2)	.3546(1)	.1593(2)	.3780(2)	.3772(2)	1	•	NPD	37
72	$YBa_2Cu_3O_7$	296	3.8198(1)	3.8849(1)	11.6762(3)	.1839(2)	.3547(1)	.1581(2)	.3779(2)	.3776(2)	1	•	NPD	37
73	$YBa_2Cu_3O_7$	298	3.827(1)	3.893(1)	11.699(2)	.1850(2)	.3565(5)	.1566(23)	.3776(21)	.3765(21)	1	•	SXD	53
74	$YBa_2Cu_3O_7$	298	3.8172(1)	3.8822(1)	11.6707(4)	.1839(3)	.3546(2)	.1589(3)	.3783(3)	.3780(3)	.96(2)	.04(1)	NPD	54
75	$YBa_2Cu_3O_{6.96}$	8	3.8127(2)	3.8786(3)	11.6311(10)	.1853(4)	.3559(2)	.1586(3)	.3786(4)	.3776(4)	.82(2)	•	NPD	46
76	$YBa_2Cu_3O_{6.96}$	120	3.8134(3)	3.8784(3)	11.6409(11)	.1854(4)	.3553(2)	.1579(4)	.3778(5)	.3773(4)	.94(3)	•	NPD	46
77	$YBa_2Cu_3O_{6.96}$	296	3.8240(2)	3.8879(2)	11.6901(8)	.1854(3)	.3557(2)	.1582(3)	.3775(3)	.3786(3)	.96(1)	•	NPD	46
78	$YBa_2Cu_3O_{6.93}$	296	3.8227(1)	3.8872(1)	11.6802(2)	.1843(2)	.3556(1)	.1590(2)	.3779(2)	.3790(2)	.90(1)	.03(1)	NPD	45
79	$YBa_2Cu_3O_{6.89}$	42	3.8122(3)	3.8800(3)	11.6264(9)	.1845(4)	.3536(2)	.1595(3)	.3773(4)	.3779(4)	.84(2)	.05(1)	NPD	55
80	$YBa_2Cu_3O_{6.84}$	20	3.8148(9)	3.8794(9)	11.6492(25)	.1855(3)	.3558(2)	.1584(3)	.3778(3)	.3779(3)	.84(1)	•	SXD	56
81	$YBa_2Cu_3O_{6.8}$	10	3.1674(1)	3.8804(1)	11.6520(3)	.1854(2)	.3559(1)	.1585(2)	.3777(2)	.3778(3)	.85(1)	•	NPD	37
82	$YBa_2Cu_3O_{6.8}$	296	3.8198(1)	3.8864(1)	11.6945(4)	.1866(5)	.3562(3)	.1576(3)	.3790(4)	.3774(3)	.79(1)	•	NPD	37
83	$YBa_2Cu_3O_{6.74}$	295	3.818(1)	3.889(1)	11.669(5)	.186(1)	.355(1)	.156(1)	.376(2)	.380(2)	.91(3)	•	NPD	57
84	$YBa_2Cu3O6_{.73}$	295	3.8275(1)	3:8875(1)	11.7063(2)	.1871(2)	.3569(1)	.1572(2)	.3788(2)	.3780(2)	.74(1)	.03(1)	SND	45
85	$YBa_2Cu_3O_{6.7}$	40	3.8273(5)	3.8773(5)	11.6548(13)	.1865(4)	.3557(3)	.1577(4)	.3780(2)	.3780(2)	.77(2)	•	SND	58
86	$YBa_2Cu_3O_{6.7}$	100	3.8308(5)	3.8803(5)	11.6669(13)	.1868(5)	.3555(3)	.1577(5)	.3783(2)	.3783(2)	.76(2)	•	NPD	58
87	$YBa_2Cu_3O_{6.66}$	295	3.8336(2)	3.8844(3)	11.7126(10)	.1888(3)	.3572(2)	.1572(3)	.3782(4)	.3769(5)	.71(2)	•	NPD	46
88	$YBa_2Cu_3O_{6.60}$	295	3.8349(1)	3.8851(1)	11.7279(2)	.1879(2)	.3578(1)	.1561(2)	.3786(2)	.3779(2)	.69(1)	.04(1)	NPD	45
89	$YBa_2Cu_3O_{6.55}$	295	3.8362(1)	3.8808(1)	11.7286(2)	.1892(2)	.3579(1)	.1559(2)	.3787(2)	.3784(2)	.56(1)	.04(1)	NPD	45
90	$YBa_2Cu_3O_{6.5}$	295	3.8468(1)	3.8747(1)	11.7468(5)	.1917(2)	.3598(2)	.1528(3)	.3788(4)	.3787(4)	0.5	•	NPD	59
91	$YBa_2Cu_3O_{6.48}$	295	3.8415(1)	3.8778(1)	11.7470(2)	.1896(2)	.3587(2)	.1553(2)	.3787(3)	.3778(3)	.56(2)	.06(1)	NPD	45
92	$YBa_2Cu_3O_{6.45}$	295	3.8433(1)	3.8764(1)	11.7512(2)	.1904(2)	.3588(1)	.1547(2)	.3785(3)	.3787(3)	.45(2)	.04(1)	NPD	45
93	$YBa_2Cu_3O_{6.41}$	295	3.8468(1)	3.9736(1)	11.7601(2)	.1905(2)	.3592(1)	.1543(2)	.3791(3)	.3779(3)	.48(2)	.08(1)	NPD	45
94	$YBa_2Cu_3O_{6.38}$	295	3.8510(1)	3.8700(1)	11.7711(2)	.1915(2)	.3596(1)	.1536(2)	.3794(4)	.3778(4)	.38(2)	.12(2)	NPD	45

Both Y^{3+} and Cu^{2+} coordinations of orthorhombic 1-2-3 are almost identical to those of the tetragonal structure. Y is eight-coordinated by a distorted cube of O3A and O3B, with average Y-O distance 2.40 Å, the same as in the tetragonal form. Cu2-O3A and Cu2-O3B bonds form sheets of square-planar Cu-O with about 1.94 Å distances, and a fifth apical O2 at 2.3 Å. Typical Cu2-O3A-Cu2 and Cu2-O3B-Cu2 angles are close to 165° (Table 14). Slabs of Y sandwiched between two Cu2-O3A/B layers in orthorhombic 1-2-3 are thus topologically identical to the tetragonal form .

The most significant difference between the tetragonal and orthorhombic forms of $YBa_2Cu_3O_{6+\delta}$ occurs at the OlA/B positions between adjacent 1-2-2 slabs (Figure 7). In the tetragonal structure these sites are symmetrically equivalent and must be equally occupied. In the orthorhombic structure, however, oxygen concentrates in OlA, halfway along the *b*-axis, so *b* is slightly longer than *a*. In ideal $YBa_2Cu_3O_7$, therefore, OlA is fully occupied while OlB is empty, leading to distinctive CuO_3 chains oriented parallel to the *b* axis.

Each OlA oxygen is linked to two Cul atoms at about 1.94 Å, and four Ba atoms at 2.9 Å. If OlA is fully occupied then Ba^{2+} becomes 10 coordinated, and Cul square-plane coordinated, as shown in Figure 7. Charge balance, furthermore, suggests that the four Cul sites must contain Cu^{3+} ions in their oxygenated form. The O2 oxygens have one shorter Cul-O2 bond of 1.85 Å and one longer Cu2-O2 bond of 2.3 Å. Thus, the O2 atom in orthorhombic 1-2-3 is more equidistant between Cul and Cu2 than in the tetragonal form, which suggests that interaction between Cu2-O planes and Cul-O chains is enhanced in the orthorhombic structures. OlA/B content of orthorhombic 1-2-3 varies significantly depending on conditions of synthesis. Under high oxygen pressure the structure may actually accommodate more than seven oxygens (Table 13; refinements 62-64). Under other annealing conditions 1-2-3 incorporates fewer than seven oxygens.[60] Changing OlA occupancy has relatively minor effect on structural parameters. In general, lower oxygen content leads to a longer *c* axis, as Cu2-O2 bond distances parallel to *c* increase.

Several low-temperature refinements of 1-2-3 (Table 13; refinements 52, 57, 79-81, 85) reveal structural details at superconducting temperatures. No obvious differences between these data and those at room temperature, other than slightly shorter bond distances, are observed.

Table 14. Selected interatomic distances (Å) for orthorhombic 1-2-3 compounds in the Y-Ba-Cu-O system

#	Ba-O1A[2]	Ba-O2[4]	Ba-O3A[2]	Ba-O3B[2]	Average Ba-O	Y-O3A[4]	Y-O3B[4]	Average Y-O	Cu1-O1A[2]	Cu1O2[2]	Cu1-O3A[2]	Cu2-O3B[2]	Cu2-O2[1]	Cu2-O3A-Cu2	Cu2-O3B-Cu2
64	2.882	2.739	2.937	2.987	2.857	2.385	2.388	2.387	1.939	1.834	1.928	1.955	2.311	162.3	164.3
65	2.854(4)	2.733(1)	2.957(6)	2.982(6)	2.852	2.384(4)	2.409(3)	2.396	1.940	1.855(5)	1.925(1)	1.958(1)	2.264(6)	163.6	163.7
66	2.857(3)	2.734(1)	2.957(4)	2.971(4)	2.851	2.381(2)	2.415(2)	2.398	1.940	1.851(4)	1.923(1)	1.959(1)	2.269(4)	165.1	163.1
67	2.855(4)	2.734(1)	2.960(6)	2.979(6)	2.852	2.382(4)	2.411(3)	2.396	1.940	1.850(5)	1.921(1)	1.958(1)	2.276(7)	163.9	164.2
68	2.856(4)	2.735(1)	2.958(6)	2.984(6)	2.854	2.385(3)	2.408(3)	2.396	1.941	1.848(5)	1.926(1)	1.958(1)	2.278(6)	164.9	164.0
69	2.871(3)	2.738(1)	2.954(4)	2.969(4)	2.854	2.382(2)	2.414(2)	2.398	1.941	1.849(3)	1.926(1)	1.959(1)	2.284(4)	164.7	164.2
70	2.876(4)	2.741(1)	2.959(6)	2.982(5)	2.860	2.385(3)	2.409(3)	2.397	1.942	1.846(5)	1.929(1)	1.961(1)	2.298(6)	164.0	164.3
71	2.866(2)	2.7346(4)	2.949(2)	2.979(2)	2.858	2.382(1)	2.403(1)	2.393	1.940	1.853(2)	1.9296(4)	1.9578(4)	2.272(3)	164.9	164.1
72	2.874(2)	2.7408(4)	2.960(2)	2.984(2)	2.855	2.386(1)	2.409(1)	2.398	1.943	1.846(2)	1.9299(4)	1.9607(4)	2.295(3)	164.2	164.1
73	2.891(2)	2.750(3)	2.948(19)	2.980(19)	2.863	2.399(15)	2.418(15)	2.409	1.947	1.834(27)	1.929(3)	1.961(3)	2.234(3)	165.3	166.3
74	2.871(3)	2.738(1)	2.962(4)	2.986(4)	2.859	2.382(2)	2.406(2)	2.394	1.941	1.853(3)	1.928(1)	1.960(1)	2.285(4)	163.6	164.0
75	2.878(3)	2.737(1)	2.947(5)	2.960(5)	2.852	2.372(3)	2.406(3)	2.389	1.939	1.845(4)	1.923(1)	1.957(1)	2.294(5)	164.9	164.5
76	2.880(3)	2.738(1)	2.941(6)	2.959(5)	2.851	2.379(3)	2.408(3)	2.394	1.938	1.838(4)	1.924(1)	1.957(1)	2.298(5)	164.7	164.7
77	2.890(2)	2.745(1)	2.949(4)	2.980(4)	2.862	2.389(2)	2.407(2)	2.398	1.944	1.849(3)	1.931(1)	1.961(1)	2.308(4)	164.0	165.1
79	2.869(3)	2.735(1)	2.943(5)	2.970(5)	2.85	2.381(2)	2.404(3)	2.393	1.940	1.854(4)	1.927(1)	1.959(1)	2.257(5)	163.9	163.0
81	2.883(2)	2.7396(4)	2.944(2)	2.964(2)	2.854	2.381(1)	2.407(3)	2.394	1.940	1.847(2)	1.9255(4)	1.9568(4)	2.298(3)	165.0	164.8
82	2.901(4)	2.7470(8)	2.938(6)	2.972(3)	2.861	2.389(2)	2.403(3)	2.396	1.943	1.843(3)	1.9305(6)	1.9585(8)	2.323(4)	164.2	165.2
83	2.91(2)	2.74(4)	2.94(6)	•	•	2.38(2)	2.40(2)	2.39	1.945	1.83(2)	1.94(6)	1.96(6)	2.33(4)	165.2	163.0
85	2.897(4)	2.745(1)	2.941(5)	2.957(4)	2.857	2.385(2)	2.405(2)	2.395	1.939	1.840(5)	1.956(1)	1.931(1)	2.307(6)	165.0	162.1
86	2.901(4)	2.747(1)	2.943(5)	2.959(5)	2.859	2.384(2)	2.404(2)	2.394	1.940	1.840(6)	1.958(1)	1.933(1)	2.308(7)	164.9	164.4

3. Compositional Variants of YBa$_2$Cu$_3$O$_{6+\delta}$

Numerous compositional variants of 1-2-3 have been synthesized. This extensive and somewhat contradictory literature has been summarized by Beyers and Shaw,[60] who review structural aspects of these substitutions. The following section summarizes some of these results and tabulates refined structural parameters of 1-2-3 isomorphs.

a) Cation substitutions for copper

Partial substitutions of transition metals Fe, Co, Ni, Zn, and Ga, as well as Mg, Al, and a variety of other elements[60] have been recorded (Table 15). In all cases T_c is suppressed, and complete substitution of copper has not been achieved.

The transition metals from iron to zinc have received the greatest attention, though many details of their structural behavior remain in dispute. Nickel and zinc (Table 15; refinements 106, 108, 109) substitute as divalent cations for Cu2 in the Cu-O planes. The critical temperature is rapidly suppressed by these two cations, presumably by disruption of the superconducting structure. Substitution of Ni and Zn do not affect the orthorhombic distortion of 1-2-3.

Cobalt and aluminum (Table 15; refinements 101-105, 110-111), on the other hand, are trivalent and substitute for Cul. Substitution of Co and Al, and presumably of Ga^{3+} and Fe^{3+} as well, draws more oxygen into O1 sites and stabilizes a disordered oxygen arrangement. At room temperature, therefore, some superconducting varieties of R^{3+} substituted 1-2-3 are tetragonal. While the transition temperature is lowered somewhat (e.g., to about 60 K in YBa$_2$FeCu$_2$O$_{6+\delta}$), all of Cul can be replaced by Fe or Co without destroying superconductivity.

Iron primarily enters the Cul site, but the character of Fe-Mossbauer spectra changes demonstrably depending on the oxygen fugacity of synthesis and annealing. The complex case of iron has led to a somewhat confused literature. The most oxidized samples (e.g., Table 15; refinements 98-100) seem to contain iron exclusively in Cul sites. Oxygen content exceeding 7 and tetragonal symmetry are observed for samples with more than about 15% substitution. Under more reducing conditions, however, iron may also enter Cu2 (refinements 251, 252, 259). Because of the similarity in size and scattering power of Fe and Cu it is difficult to distinguish site occupancy information from diffraction data.

Table 15. 1-2-3 compounds with partial substitution into Y-Ba-Cu-O system

#	Composition	T(K)	Sym	a(Å)	b(Å)	c(Å)	Z_{Ba}	Z_{Cu2}	Z_{O2}	$Z_{O3/3A}$	Z_{O3B}	Occupancy O1/1A	Occupancy O1B	Tech	ref.
95	$YBa_2(Cu_{.985}Fe_{.015})_3O_{6.71}$	295	O	3.8564(2)	3.8682(2)	11.6540(6)	.1854(2)	.3562(4)	.151(2)	.369(4)	.384(3)	.71(7)	•	XPD	61
96	$YBa_2(Cu_{.95}Fe_{.05})_3O_{6.91}$	295	O	3.8688(3)	3.8716(3)	11.6336(6)	.1860(2)	.3578(4)	.157(2)	.365(7)	.396(7)	.91(8)	•	XPD	61
97	$YBa_2(Cu_{.90}Fe_{.10})_3O_{6.96}$	295	O	3.8704(6)	3.8692(6)	11.6294(6)	.1836(2)	.3562(4)	.159(2)	.398(6)	.360(6)	.96(6)	•	XPD	61
98	$YBa_2(Cu_{.90}Fe_{.10})_3O_{7.15}$	295	O	3.8655(15)	—	11.674(5)	.1863(3)	.3565(2)	.1576(5)	.3781(3)	—	•	—	NPD	62
99	$YBa_2(Cu_{.83}Fe_{.17})_3O_{7.00}$	295	T	3.8791(15)	—	11.721(6)	.1886(1)	.3589(3)	.1528(19)	.3776(9)	—	•	—	SXD	63
100	$YBa_2(Cu_{.83}Fe_{.17})_3O_{7.23}$	10	T	3.8505(15)	—	11.576(5)	.1849(4)	.3562(2)	.1588(4)	.3781(3)	—	•	—	NPD	62
101	$YBa_2(Cu_{.9}Co_{1})_3O_{6.81}$	295	T	3.8752(2)	—	11.6851(9)	.1875(7)	.3595(7)	.1564(8)	.3779(5)	—	.41(1)	—	NPD	64
102	$YBa_2(Cu_{.89}Co_{.11})_3O_{7.06}$	295	T	3.8689(1)	—	11.6594(2)	.1867(2)	.3579(1)	.1562(2)	.3783(1)	—	.54(6)	—	NPD	65
103	$YBa_2(Cu_{.72}Co_{.28})_3O_{7.32}$	295	T	3.8879(8)	—	11.636(3)	.1870(4)	.3595(3)	.1568(5)	.3772(3)	—	.76(2)	—	NPD	66
104	$YBa_2(Cu_{.67}Co_{.33})_3O_{7.16}$	295	T	3.8847(1)	—	11.6391(1)	.1858(10)	.3621(7)	.1583(9)	.3800(5)	—	.58(3)	—	NPD	67
105	$YBa_2(Cu_{.67}Co_{.33})_3O_{7.25}$	295	T	3.8905(8)	—	11.674(4)	.1880(1)	.3590(3)	.1574(18)	.3779(9)	—	•	—	SXD	63
106	$YBa_2(Cu_{.93}Ni_{.07})_3O_{6.85}$	295	O	3.8226(2)	3.8788(3)	11.631(1)	.1847(10)	.3554(6)	.1607(8)	.3823(11)	.3734(10)	.88(4)	•	NPD	67
107	$YBa_2(Cu_{.94}Mg_{.06})_3O_7$	295	O	3.827(2)	3.882(2)	11.670(6)	.1813(9)	.3590(8)	.1656(8)	.3753(19)	.3779(19)	.72(6)	.16(5)	NPD	68
108	$YBa_2(Cu_{.93}Zn_{.07})_3O_{6.94}$	295	O	3.8214(2)	3.8920(2)	11.6829(7)	.1840(3)	.3543(2)	.1591(2)	.3787(3)	.3784(3)	.91(1)	.03(1)	NPD	69
109	$YBa_2(Cu_{.9}Zn_{.1})_3O_{6.75}$	295	O	3.8430(4)	3.8870(4)	11.662(2)	.1818(14)	.3583(8)	.1603(10)	.3828(16)	.3727(15)	.86(3)	•	NPD	67
110	$YBa_2(Cu_{.93}Al_{.07})_3O_{6.4}$	295	T	3.8637(2)	—	11.7231(7)	.1902(1)	.3587(2)	.155(1)	.3797(7)	—	.21(3)	—	SXD	70
111	$YBa_2(Cu_{.93}Al_{.07})_3O_{6.5}$	295	T	3.8789(4)	—	11.494(1)	.1851(1)	.3521(2)	.156(3)	.373(1)	—	•	—	SXD	70
112	$YBa_2Cu_3O_{6.94}H_{0.2}$	295	O	3.850(2)	3.911(2)	11.778(5)	.1858	.3560	.1585	.3763	.3801	.70(4)	.24(4)	NPD	71

b) A-site substitutions

All of the lanthanide elements except Ce and Tb - the two members of the series that readily form +4 ions - can substitute fully in the 1-2-3 structure (Table 16). Furthermore, with the exception of Pr, which also has a propensity for the 4+ state, these lanthanide substitutions have little effect on T_c.

The only appreciable structure effect of rare-earth element substitutions are associated with the slightly differing sizes of these R^{3+} ions. Plots of cell edges, unit-cell volume, or R^{3+}-O distance versus element reveal trends consistent with well established rare-earth element crystal chemistry (Tables 17 and 18). Other distances, such as Ba-O, Cu-O, and metal-metal separations, are unaffected.

A number of authors have studied partial substitutions of rare-earth elements for Ba in the systems $(La_{1+x}Ba_{1-x})Cu_3O_{6+\delta}$[72-78] and $(Nd_{1+x}Ba_{1-x})Cu_3O_{6+\delta}$.[81-83] Some of their work was an effort to reexamine the phase $La_3Ba_3Cu_6O_{14}$ (the "3-3-6" phase), originally described in 1981 by Er-Rakho *et al.*[94] Raveau *et al.* described this structure as a 5.3 x 5.3 x 11.7 Å perovskite-like phase with cation and anion ordering. Subsequent studies,[75-78] however, have demonstrated that 3-3-6 has disordered Ba and La in the 1-2-3 Ba position, and is thus a true 1-2-3 isomorph.

Partial substitution of La or Nd for Ba (Table 16; refinements 116-125, 127-129) causes a significant depression of T_c as well as a gradual transition from orthorhombic to tetragonal symmetry. Details of these structural and physical changes are reported by Newsam *et al.*[75] and Takita *et al.*[81] In summary, substitution of R^{3+} for Ba^{2+} shortens *c* and corresponding Cu-O2 distances, with little effect on dimensions in the *a-b* plane (Tables 17 and 18).

B. The $YBa_2Cu_4O_8$ (1-2-4) Structure

The discovery of 1-2-3 initiated a rush of phase equilibria studies, particularly in chemical systems related to Y-Ba-Cu-O. This activity has led to the synthesis of four new superconducting rare-earth cuprates, each with a close structural relationship to 1-2-3. The first of these new phases was described by Marsh *et al.*,[95] who prepared a new 80 K superconductor as a distinct thin-film phase during studies of the Y-Ba-Cu-O system. This compound, distinguished by its 3.9 x 3.9 x 27.2 Å unit cell, was not available to Marsh and coworkers in bulk form. They were able to deduce its structure, however, by thin-film diffraction analysis of the material, coupled with its similarity to the 1-2-3 dimensions (Tables 19 and 20; refinement 154).

Table 16. Refinements of 1-2-3 compounds with Y replaced by REE

#	Composition	T(K)	Sym	a(Å)	b(Å)	c(Å)	Z_{Ba}	Z_{Cu2}	Z_{O2}	$Z_{O2/3A}$	Z_{O3B}	Occupancy O1/1A	Occupancy O1B	Technique*	Ref.
113	$LaBa_2Cu_3O_{6.92}$	295	O	3.8938(4)	3.9374(4)	11.8156(1)	.1842(2)	.3461(1)	.1580(2)	.3666(3)	.3659(3)	.71(1)	.11(1)	NPD	72
114	$LaBa_2Cu_3O_{6.7}$	295	T	3.895	-	11.727	.1846(5)	.3521(3)	.1720(4)	.3840(5)	-	.325	-	SXD	73
115	$LaBa_2Cu_3O_{6.4}$	295	T	3.9257(1)	-	11.832(1)	.1878(5)	.348(1)	.148(7)	.368(3)	-	.86(4)	.2(1)	XPD	74
116	$LaE_{1.125}Ba_{1.875}Cu_3O_{7.21}$	295	O	3.9147(5)	3.9325(5)	11.782(1)	.1846(4)	.3468(3)	.1546(5)	.3630(14)	.3707(16)	.59(7)	.56(7)	NPD	75
117	$La_{1.25}Ba_{1.75}Cu_3O_{7.16}$	295	O	3.9136(7)	3.9244(7)	11.743(1)	.1841(4)	.3469(3)	.1546(5)	.3671(15)	.3654(15)	.43(7)	.40(6)	NPD	75
118	$La_{1.375}Ba_{1.625}Cu_3O_{7.14}$	295	T	3.9143(2)	-	11.718(1)	.1838(4)	.3469(3)	.1543(6)	.3662(3)	-	.57(2)	-	NPD	75
119	$La_{1.5}Ba_{1.5}Cu_3O_{7.2}$	295	T	3.9112(2)	-	11.701(1)	.1810(4)	.3460(2)	.1573(6)	.3656(3)	-	.60(2)	-	NPD	75
120	$La_{1.5}Ba_{1.5}Cu_3O_{7.35}$	295	T	3.9150(1)	-	11,6929(6)	.1790(2)	.3463(1)	.1583(3)	.3542(2)	-	.33(12)	-	NPD	76
121	$La_{1.5}Ba_{1.5}Cu_{2.94}O_{6.94}$	295	T	3.9108(1)	-	11.7070(4)	.1806(5)	.346(1)	.156(7)	.368(3)	-	.6(1)	-	XPD	77
122	$La1.5Ba_{1.5}Cu_3O_{7.3}$	295	T	3.9106(2)	-	11.7150(9)	.1814(4)	.3465(3)	.1562(6)	.3657(3)	-	.65(1)	-	NPD	76
123	$PrBa_2Cu_3O_7$	295	T	3.905(2)	-	11.660(10)	.1840(3)	.3507(8)	.157(5)	.371(4)	-	1.0(2)	-	SXD	79
124	$PrBa_2Cu_3O_{6.87}$	295	O	3.864(2)	3.923(2)	11.717(6)	.1820(10)	.3497(9)	.1584(12)	.3686(23)	.3750(21)	.72(5)	.25(5)	NPD	80
125	$NdBa_2Cu_3O_7$	295	O	3.8590(1)	3.9112(2)	11.7412(6)	.1812(6)	.348(1)	.160(7)	.368(6)	.372(5)	.93(10)	.07(10	XPD	81
126	$NdBa_2Cu_3O_{7.18}$	295	O	3.8446(3)	3.8923(5)	11.680(1)	.1819(9)	.3472(7)	.1576(8)	.3668(20)	.3733(17)	.86(5)	.29(5)	NPD	82
127	$Nd_{1.1}Ba_{1.9}Cu_3O_7$	295	O	3.8613(1)	3.9087(2)	11.7311(6)	.1817(5)	.350(1)	.162(6)	.374(5)	.374(5)	.88(8)	.12(6)	XPD	81
128	$Nd_{1.2}Ba_{1.8}Cu_3O_7$	295	T	3.8919(3)	-	11.6811(9)	.1842(5)	.3605(4)	.1566(6)	.3702(3)	-	.49(2)	-	NPD	83
129	$Nd_{1.4}Ba_{1.6}Cu_3O_7$	295	F	3.8822(1)	-	11.6357(4)	.1814(5)	.351(1)	.166(5)	.370(3)	-	.62(8)	-	XPD	81
130	$SmBa_2Cu_3O_{6.6}$	295	T	3.891(1)	3.894(1)	11.660(1)	.1853(2)	.2554(4)	.158(3)	.374(4)	-	.8(2)	-	SXD	79
131	$SmBa_2Cu_3O_7$	295	O	3.8458(1)	3.9033(1)	11.7272(3)	.1817(4)	.350(1)	.162(5)	.372(4)	.374(4)	.9(1)	.1(1)	XPD	84
132	$Sm_{1.15}Ba_{1.85}Cu_3O_7$	295	O	3.8550(1)	3.8897(2)	11.6869(5)	.1826(4)	.351(1)	.162(5)	.374(5)	.376(5)	.8(1)	.2(1)	XPD	84
133	$EuBa_2Cu_3O_{6.4}$	295	T	3.869(2)	3.879(3)	11.693(6)	.1847(3)	.3530(8)	.159(5)	.374(4)	-	.4(2)	-	SXD	79
134	$EuBa_2Cu_3O_7$	295	O	3.8384(2)	3.8973(3)	11.7069(8)	.1818(8)	.361(2)	.158(11)	.376(8)	.365(8)	.8(2)	.2(2)	XPD	85
135	$GdBa_2Cu_3O_{6.7}$	295	T	3.854(2)	3.896(2)	11.701(7)	.1855(2)	.3646(4)	.151(2)	.377(2)	-	.7(2)	-	SXD	79
136	$GdBa_2Cu_3O_7$	295	O	3.8350(2)	3.8947(2)	11.6992(6)	.1820(8)	.350(2)	.161(10)	.372(8)	.366(8)	.8(2)	.2(2)	XPD	85
137	$GdBa_2Cu_3O_{7-\delta}$	295	O	3.850(1)	3.885(2)	11.759(3)	.1866(1)	.3557(3)	.1563(17)	.3757(14)	.3744(14)	-	-	SXD	86
138	$DyBa_2Cu_3O_{6.35}$	295	T	3.8675(9)	-	11.811(3)	.1830(1)	.3599(2)	.1546(9)	.3786(6)	-	-	-	SXD	87
139	$DyBa_2Cu_3O_{6.7}$	295	T	3.830(3)	3.885(3)	11.709(3)	.1864(2)	.3564(3)	.157(2)	.378(2)	-	.7(2)	-	SXD	79
140	$DyBa_2Cu_3O_7$	295	O	3.8246(1)	3.8865(1)	11.6857(3)	.1830(4)	.3528(9)	.153(5)	.384(4)	.372(4)	.9(1)	.1(1)	XPD	88
141	$HoBa_2Cu_3O_6$	295	T	3.8650(1)	-	11.824(4)	.1931(1)	.3602(2)	.1542(9)	.3791(6)	-	-	-	SXD	87
142	$HoBa_2Cu_3O_{6.8}$	295	T	3.844(1)	3.881(1)	11.840(2)	.1858(2)	.3577(4)	.158(3)	.378(2)	-	.4(2)	-	SXD	79
143	$HoBa_2Cu_3O_{6.98}$	295	O	3.8205(3)	3.8851(3)	11.682(1)	.1843(3)	.3545(2)	.1584(3)	.3775(3)	.3784(3)	.88(2)	.07(1)	NPD	88
144	$ErBa_2Cu_3O_{6.11}$	20	T	3.846(2)	-	11.792(8)	.1951(4)	.3610(3)	.1532(4)	.3797(3)	-	.11(2)	-	NPD	90
145	$ErBa_2Cu_3O_{6.34}$	20	O	3.844(1)	3.851(1)	11.760(5)	.1935(3)	.3609(3)	.1538(4)	.3828(6)	.3792(2)	.34(2)	-	NPD	90
146	$ErBa_2Cu_3O_{6.53}$	20	O	3.823(1)	3.865(1)	11.694(5)	.1899(3)	.3584(3)	.1550(4)	.3802(5)	.3770(3)	.53(2)	-	NPD	90
147	$ErBa_2Cu_3O_{6.87}$	20	O	3.812(1)	3.877(1)	11.650(5)	.1852(4)	.3565(2)	.1584(3)	.3785(4)	.3789(4)	.87(2)	-	NPD	90
148	$ErBa_2Cu_3O_{6.95}$	41	O	3.8044(2)	3.8737(2)	11.6194(7)	.1845(3)	.3546(2)	.1600(3)	.3784(3)	.3793(3)	.88(1)	.05(1)	NPD	91
149	$ErBa_2Cu_3O_{6.95}$	295	O	3.8127(3)	3.8785(3)	11.6656(9)	.1852(3)	.3544(2)	.1591(3)	.3784(3)	.3793(3)	.87(1)	.08(1)	NPD	91
150	$ErBa_2Cu_3O_{7.0}$	20	O	3.803(1)	3.873(1)	11.620(4)	.1838(3)	.3552(2)	.1586(4)	.3779(3)	.3790(3)	.02(2)	-	NPD	90
151	$TmBa_2Cu_3O_{6.5}$	295	T	3.829(3)	3.860(3)	11.715(2)	.1892(1)	.3593(2)	.155(2)	.380(1)	-	.5(1)	-	SXD	79
152	$TmBa_2Cu_3O_7$	215	O	3.8087(1)	3.8746(2)	11.6655(6)	.1832(7)	.354(2)	.156(8)	.372(6)	.379(6)	.9(1)	.1(1)	XPD	92
153	$YbBa_2Cu_3O_7$	295	O	3.8018(2)	3.8710(2)	11.6576(5)	.1834(6)	.354(1)	.157(7)	.370(7)	.374(7)	.9(1)	.1(1)	XPD	93

* NPD– NEUTRON POWDER DIFFRACTION; SXD and XPD– SINGLE-CRYSTAL AND POWDER X-RAY DIFFRACTION, RESPECTIVELY.

Table 17. Selected interatomic distances (Å) and Cu2-O3-Cu2 angle (°) for tetragonal 1-2-3

#	Ba-01[4]	Ba-02[4]	Ba-03[4]	Mean Ba-O	Y-03[8]	Cu1-01[4]	Cu1-02[2]	Cu2-03[4]	Cu2-02[1]	Cu2-03-Cu2
99	2.74(4)	2.775(3)	2.944(8)	2.860	2.413(6)	1.966(11)	1.791(2)	1.952(1)	2.42(2)	167.1
103	2.72(1)	2.772(1)	2.946(3)	2.859	2.413(3)	1.969(3)	1.824(5)	1.955(1)	2.359(6)	167.0
105	2.74(3)	2.774(3)	2.950(8)	2.862	2.412(6)	1.970(7)	1.84(2)	1.958(1)	2.35(2)	167.1
114	2.912	2.758	3.051	2.905	2.37	2.017	1.947	1.985	2.112	151.1*
115	2.965(4)	2.82(1)	2.90(3)	2.895	2.51(2)	1.963	1.75(7)	1.977(4)	2.37(7)	165.8
118	2.911(3)	2.789(1)	2.897(4)	2.857	2.508(2)	1.957	1.808(7)	1.970(1)	2.257(7)	166.8
119	2.882(3)	2.779(1)	2.914(4)	2.854	2.510(2)	1.956	1.840(7)	1.969(1)	2.208(7)	166.3
120	2.865(2)	2.779(1)	2.919(3)	2.849	2.521(1)	1.958	1.851(4)	1.969(1)	2.199(4)	174.5
121	2.880(4)	2.777(7)	2.94(3)	2.869	2.49(2)	1.955	1.86(9)	1.973(5)	2.19(9)	164.2
122	2.888(3)	2.781(3)	2.913(6)	2.857	2.510(2)	1.955	1.830(7)	1.968(1)	2.229(6)	166.8
138	2.990(1)	2.772(2)	2.923(5)	2.846	2.407(4)	1.934	1.825(11)	1.946(1)	2.426(11)	167.0
141	-	2.771(2)	2.928(5)	2.850	2.403(4)	-	1.824(11)	1.945(1)	2.435(11)	167.0

Table 18. Selected interatomic distances (Å) and angles (°) for 1-2-3 compounds

#	Ba-01A[2]	Ba-02[4]	Ba-03A[2]	Ba-03B[2]	Average Y-O	Y-O3B[4]	Y-O3B[4]	Average Y-O	Cu1-O1A[2]	Cu1-O2[2]	Cu2-03A[2]	Cu2-O3B[2]	Cu2-02[1]	Cu2-03A-Cu2	Cu2-03B-Cu2
106	2.876(2)	2.743(1)	2.968(4)	2.994(4)	2.865	2.381(2)	2.407(2)	2.394	1.946	1.858(3)	1.966(1)	1.932(1)	2.281(4)	163.1	163.2
107	2.853	2.732	2.964	3.005	2.857	2.404	2.408	2.406	1.941	1.933	1.950	1.926	2.257	168.7	166.5
116	2.927(3)	2.797(1)	2.94(1)	2.89(1)	2.867	2.48(1)	2.54(1)	2.51	1.966	1.821(6)	1.986(3)	1.967(2)	2.265(6)	168.7	163.4
117	2.916(3)	2.793(1)	2.89(1)	2.91(1)	2.862	2.52(1)	2.51(1)	2.51	1.962	1.816(6)	1.974(2)	1.971(2)	2.258(7)	166.0	167.1
124	2.878(9)	2.767(2)	2.93(2)	2.99(2)	2.866	2.46(2)	2.45(2)	2.46	1.962	1.856(14)	1.976(4)	1.955(4)	2.242(18)	166.0	162.5
126	2.865(8)	2.750(2)	2.89(3)	2.96(2)	2.851	2.47(1)	2.45(1)	2.46	1.946	1.841(9)	1.959(3)	1.946(4)	2.216(17)	166.2	162.2
137	2.94	2.764	2.926	2.924	2.864	2.421	2.440	2.431	1.943	1.838	1.957	1.942	2.344	165.9	166.4
143	2.878(3)	2.740(1)	2.957(4)	2.985(4)	2.860	2.387(2)	2.407(2)	2.397	1.943	1.862(3)	1.961(1)	1.931(1)	2.279(4)	164.0	163.4
148	2.866(2)	2.730(1)	2.949(4)	2.979(3)	2.851	2.369(2)	2.391(2)	2.38	1.937	1.859(3)	1.957(1)	1.924(1)	2.262(4)	163.4	162.9
149	2.881(3)	2.736(1)	2.952(4)	2.981(4)	2.856	2.376(2)	2.387(2)	2.387	1.939	1.856(3)	1.959(1)	1.928(1)	2.279(4)	163.3	162.7

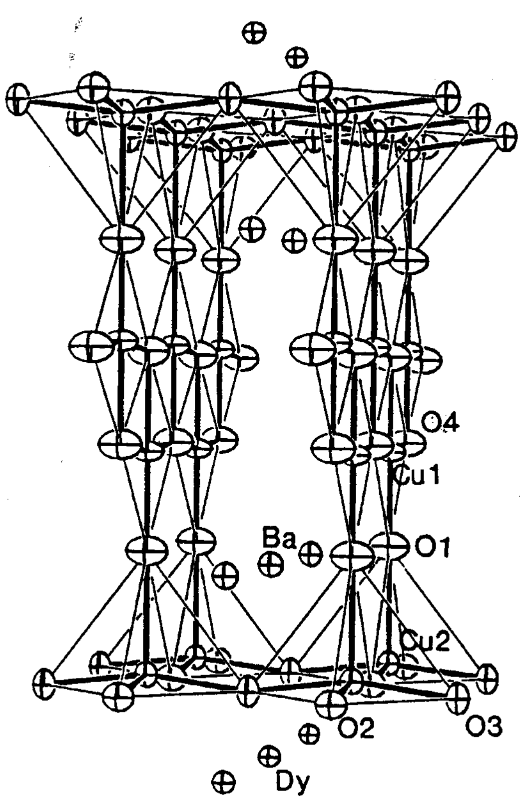

Figure 8. The crystal structure of $DyBa_2Cu_4O_8$, from Hazen, Finger, and Morris.[98]

Marsh *et al.* proposed a structure nearly identical to orthorhombic 1-2-3, but with an extra copper plus oxygen in the Cu-O strip (Figure 8). They suggested a structural formula of $YBa_2Cu_4O_8$, and thus the abbreviation "1-2-4." Each 1-2-4 unit is 13.6 Å along *c*, but the extra Cu-O strip causes an offset which doubles the long axis to 27.2 Å.

The structure proposed by Marsh *et al.* was confirmed by single-crystal studies [97,98] on material synthesized under high oxygen pressure.[96,99] Morris *et al.*[99] produced eight additional members of the 1-2-4 series $RBa_2Cu_4O_8$ (R = Nd, Sm, Eu, Gd, Dy, Ho, Er, and Tm), several of which have been examined by single-crystal x-ray techniques.

Much of the 1-2-4 structure is topologically identical to 1-2-3 (Figure 8). Two Cu2-O2/3 layers of square-plane coordinated copper sandwich an eight-coordinated rare-earth atom. Typical Cu2-O2/3 and Y-O distances (about 1.94 and 2.40 Å, respectively; Table 21) are identical in 1-2-3 and 1-2-4. Above and below this Cu-Y-Cu slab are perovskite-like Ba-O1 layers, with ten-coordinated Ba (average Ba-O distance about 2.87 Å, compared to 2.86 Å in 1-2-3). These atoms comprise the previously described 1-2-2 slab, also found in 1-2-3.

TABLE 19. The $YBa_2Cu_4O_8$ (1-2-4) structure.

Orthorhombic Ammm (D^{19}_{2h}) Z = 2

a ≈ b ≈ 3.9 Å c ≈ 27.2

Atoms	Site	Symmetry	x	y	z
Y	2c	mmm	1/2	1/2	0
Ba	4j	mm	1/2	1/2	0.13
Cu1	4i	mm	0	0	0.21
Cu2	4i	mm	0	0	0.06
O1	4i	mm	0	0	0.15
O2	4j	mm	1/2	0	0.05
O3	4i	mm	0	1/2	0.05
O4	4i	mm	0	1/2	0.22

Each Cu2-O2/3 square plane is capped by a weakly bonded fifth oxygen (Cu2-O1 = 2.29 Å). These capping O1 oxygens border Cu1-O1/4 strips parallel to (100). To this point the descriptions of 1-2-3 and 1-2-4 are identical, but unlike the corner-sharing single chains of orthorhombic 1-2-3, the unique 1-2-4 copper-oxygen strips consist of edge-sharing square planes with twice as many oxygen and copper atoms. The average Cu1-O1/4 distance is 1.89 Å, similar to Cu1-O1 distances in 1-2-3. The Cu1, O1, and O4 atoms are constrained to lie in the *x* = 0 plane, so the strip feature is flat. Short O4-O4 edges (2.58 Å) compared to O1-O4 unshared edges (2.77 Å), however, gemerate significant deviations from ideal square coordination of copper. The O4-Cu1-O4 angle is between 170 and 172° instead of the ideal 180°.

Oxygen coordination in the Cu-O strips is an important difference between the 1-2-3 and 1-2-4 structures. In 1-2-3, O1 is two-coordinated, leading to large observed thermal vibrations and significant oxygen diffusion and disorder, as evidenced by the modest temperature of the orthorhombic-to-tetragonal ordering transition.[39,40] In 1-2-4, however, O1 and O4 are three coordinated, causing much smaller thermal vibrations and a more constrained oxygen stoichiometry. Oxygen contents of 1-2-4 superconductors appear to remain close to 8 per formula unit, and it seems unlikely that a tetragonal variant with disordered oxygens would be stable.

Table 20. Refinements of the $YBa_2Cu_4O_8$ structure at 295K

#	Composition	a(Å)	b(Å)	c(Å)	z_{Ba}	z_{Cu1}	z_{Cu2}	z_{O1}	z_{O2}	z_{O3}	z_{O4}	Tech	ref.
154	$YBa_2Cu_4O_8$	3.86(1)	3.86(1)	27.24(6)	.1347(5)	.2135(8)	.0621(8)	.147(3)	.049(4)	.057(3)	.216(3)	SXD	95
155	$YBa_2Cu_4O_8$	3.8415(3)	3.8707(3)	27.240(2)	.1356(1)	.2127(1)	.0614(1)	.1454(1)	.0524(1)	.0528(1)	.2187(1)	NPD	96
156	$YBa_2Cu_4O_8$	3.8454(8)	3.876(1)	27.263(50	.13483(1)	.21298(1)	.06153(1)	.14545(5)	.05228(8)	.05236(5)	.21801(6)	SXD	97
157	$DyBa_2Cu_4O_8$	3.8463(3)	3.8726(3)	27.237(2)	.13496(3)	.21312(5)	.06180(6)	.1458(3)	.0526(3)	.0532(3)	.2186(3)	SXD	98
158	$ErBa_2Cu_4O_8$	3.8300(8)	3.8618(7)	27.195(1)	.13464(3)	.21296(5)	.06103(7)	.1457(3)	.0516(3)	.0519(3)	.2187(3)	SXD	99
159	$EuBa_2Cu_4O_8$	3.8581(7)	3.8786(8)	27.249(1)	.13546(3)	.21315(5)	.06273(6)	.1448(3)	.0541(3)	.0539(3)	.2181(3)	SXD	99

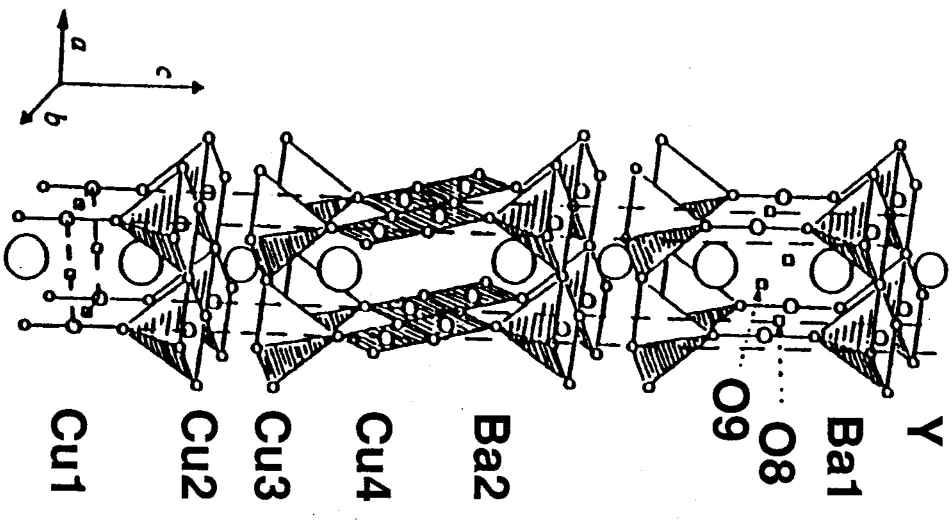

Figure 9. The crystal structure of $Y_2Ba_4Cu_7O_{15}$, from Bordet *et al.*[100]

Table 21. Selected interatomic distances (Å) and angles (°) for $YBa_2Cu_4O_8$ structure

#	Cu-O1[1]	Cu1-O4[2]	Cu1-O4[1]	Cu1-O4-Cu1	Cu2-O1[1]	Cu2-O2[2]	Cu2-O3[2]	Cu2-O2-Cu2	Cu2-O3-Cu2
154	1.82(6)	1.93(2)	1.92(7)	176	2.30(6)	1.961(7)	1.935(6)	159	172
155	1.833(4)	1.943(4)	1.869(4)	170.2	2.288(4)	1.936(4)	1.950(4)	165.3	165.9
156	1.841(1)	1.9430(1)	1.881(2)	171.8	2.288(1)	1.9392(2)	1.9543(2)	166.5	166.6
157	1.834(9)	1.942(1)	1.860(9)	171.2(5)	2.287(10)	1.939(1)	1.951(1)	165.2(5)	166.2(5)
158	1.831(8)	1.936(1)	1.860(8)	170.8(4)	2.301(9)	1.934(1)	1.945(1)	164.7(5)	165.3(5)
159	1.862(8)	1.944(1)	1.873(8)	172.0(5)	2.237(8)	1.943(1)	1.945(1)	166.1(5)	165.8(5)

Table 21. (continued)

#	Y-O2[4]	Y-O3[4]	mean Y-O	Ba-O1[4]	Ba-O2[2]	Ba-O3[2]	Ba-O4[2]	mean Ba-O
154	2.35(5)	2.48(5)	2.415	2.748(7)	3.02(7)	2.87(6)	2.93(5)	2.86
155	2.405(2)	2.399(2)	2.402	2.740(3)	2.981(3)	2.962(3)	2.969(3)	2.878
156	2.406(1)	2.3947(8)	2.400	2.7354(1)	2.970(1)	2.958(1)	2.973(1)	2.874
157	2.409(5)	2.407(5)	2.408	2.745(1)	2.963(7)	2.943(6)	2.981(7)	2.876
158	2.385(5)	2.380(5)	2.383	2.736(1)	2.971(7)	2.956(7)	2.982(7)	2.876
159	2.436(5)	2.424(5)	2.43	2.747(1)	2.946(6)	2.943(7)	2.966(6)	2.870

Table 22. The $Y_2Ba_4Cu_7O_{15}$(2-4-7) structure

Orthorhombic Pmmm ($D^{19}{}_{2h}$)

a = 3.851 (1) Å b = 3.869 (1) Å c = 50.29 (2) Å Z = 2

Atoms	Site	Symmetry	x	y	z	Occupancy
Ba1	4j	mm	1/2	1/2	.04310(3)	1
Ba2	4j	mm	1/2	1/2	.18797(2)	1
Y	2a	mmm	0	0	.11545(4)	1
Cu1	4i	mm	0	0	0	1
Cu2	4l	mm	0	0	.08293(5)	1
Cu3	4i	mm	0	0	.14831(5)	1
Cu4	4i	mm	0	0	.23012(5)	1
O1	4i	mm	0	0	.0353(8)	1
O2	4j	mm	1/2	0	.0871(3)	1
O3	4j	mm	0	1/2	.0865(3)	1
O4	4j	mm	1/2	0	.1430(3)	1
O5	4j	mm	0	1/2	.1432(3)	1
O6	4i	mm	0	0	.1937(2)	1
O7	4j	mm	0	1/2	.2328(3)	1
O8	2b	mmm	0	1/2	0	0.10(7)
O9	2d	mmm	1/2	0	0	0.20(7)

Data from Bordet *et al* (100; refinement 160).

Table 23. Selected interatomic distances (Å) and angles (°) for $Y_2Ba_4Cu_7O_{15}$

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Angle (°)
Ba1-O1[4]	2.757(6)	Cu1-O1[2]	1.78(4)	O1-Cu1-O1	180
Ba1-O2[2]	2.94(1)	Cu2-O1[1]	2.39(4)		
Ba1-O3[2]	2.91(1)	Cu2-O2[2]	1.937(2)	Cu2-O2-Cu2	167.3
Mean Ba1-O	2.84	Cu2-O3[2]	1.942(1)	Cu2-O3-Cu2	169.1
Ba2-O4[2]	2.98(1)				
Ba2-O5[2]	2.96(1)	Cu3-O4[2]	1.944(2)	Cu3-O4-Cu3	164.0
Ba2-O6[4]	2.744(1)	Cu3-O5[2]	1.951(2)	Cu3-O5-Cu3	164.6
Ba2-O7[2]	2.96(1)	Cu3-O6[1]	2.28(1)		
Mean Ba2-O	2.88				
		Cu4-O6[1]	1.83(1)		
Y-O2[2]	2.402(9)	Cu4-O7[1]	1.87(1)	Cu4-O7-Cu4	171.8
Y-O3[2]	2.415(9)	Cu4-O7[2]	1.939(1)		
Y-O4[2]	2.379(9)				
Y-O5[2]	2.378(9)				
Mean Y-O	2.394				

Data based on Bordet *et al* (100; refinement 160).

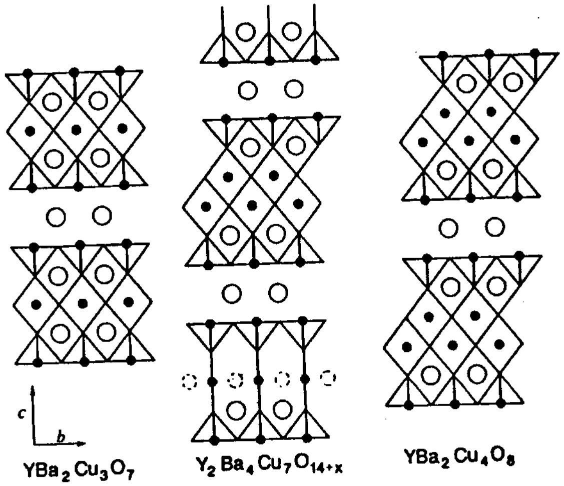

Figure 10. Schematic comparison of the 1-2-3, 1-2-4, and 2-4-7 structures, from Bordet *et al.* [100]

C. The $Y_2Ba_4Cu_7O_{15}$ (2-4-7) Structure

Bordet *et al.*[100] discovered a new superconductor (T_c = 40 K) during pressure-temperature-composition studies of phase relations in the Y-Ba-Cu-O system. The elongated unit cell, 3.85 x 3.87 x 50.3 Å, suggested a mixed-layer structure related to 1-2-3 and 1-2-4. This suspicion was confirmed by single-crystal x-ray diffraction, which revealed an alternating layering of 1-2-3 and 1-2-4 units in an *A*-centered orthorhombic cell (Figure 9; Tables 22 and 23), and a structural formula $Y_2Ba_4Cu_7O_{15}$ (or "2-4-7").

The single published crystal structure analysis of yttrium 2-4-7[100] displays distances and angles nearly identical to those of isolated 1-2-3 and 1-2-4 layers. The close relationship between these three structure types is illustrated schematically in Figure 10. This behavior is typical of mixed-layer materials, such as clays and other layer silicates.

Morris *et al.*,[101] who synthesized six variants of the $R_2Ba_4Cu_7O_{15}$ structure (*R* = Y, Eu, Gd, Dy, Ho, Er), noted that basal plane areas are larger, and orthorhombic distortions smaller, than in the corresponding 1-2-3 and 1-2-4 compounds. They propose that these differences are a consequence of differing oxygen content of 2-4-7 relative to the other two phases.

D. The (Ba, Nd)$_2$ (Nd, Ce)$_2$ Cu$_3$O$_{8+\delta}$ Structure

Sawa *et al.*[102] identified a series of new superconductors (maximum critical temperature about 40 K) with a tetragonal 3.875 x 3.875 x 28.60 Å unit cell. Izumi *et al.*[103] describe the structure of $(Ba_{0.633}Nd_{0.367})_2(Nd_{0.675}Ce_{0.325})_2Cu_3O_{8+\delta}$, which is part of the new family of superconduc-

Table 24. The $(Ba,Nd)_2(Nd,Ce)_2Cu_3O_{8+\delta}$ (2-2-3) structure

Tetragonal I4/mmm (D^{17}_{4h})

a = 3.8747 (4) Å   b = 28.599 (3) Å   Z = 2

Atoms	Site	Symmetry	x	y	z	Occupancy
(Ba,Nd)	4e	4mm	0	0	0.4244(2)	1
(Nd,Ce)	4e	4mm	0	0	0.2956(1)	1
Cu1	8h	mm	0.053(2)	=x	0	1/4
Cu2	4e	4mm	0	0	0.1418(1)	1
O1	16l	m	0.060(7)	0.440(8)	0	0.114(5)
O2	16m	m	0.054(5)	=x	0.0639(2)	1/4
O3	8g	mm	0	1/2	0.3525(1)	1
O4	4d	$\bar{4}$m2	0	1/2	1/4	1

Data from Izumi et al (102; refinement 161) based on neutron powder diffraction data. The reported composition is $(Ba_{.633}Nd_{.367})_2(Nd_{.675}Ce_{.325})_2Cu_3O_{8.91}$.

Table 25. Selected interatomic distances (Å) and angles of $(Ba_{.633}Nd_{.367})_2(Nd_{.675}Ce_{.325})_2Cu_3O_{8.91}$, based on refinement 161 by Izumu *et al.*[103]

Atoms	Distance	Atoms	Distance/Angle
(Ba,Nd)-O2[4/4]	2.466(28)	Cu1-O2[2]	1.826
(Ba,Nd)-O2[4/4]	3.056(28)	O2-Cu1-O2	180
(Ba,Nd)-O3[8/4]	2.777(3)		
(Ba,Nd)-O3[4]	2.825(4)	Cu2-O3[4]	1.9443(4)
Mean (Ba,Nd)-O	2.797	Cu2-O2[4/4]	2.248(9)
		Cu2-O3-Cu2	170.2
(Nd,Ce)-O3[4]	2.529(3)		
(Nd,Ce)-O4[4]	2.336(2)		
Mean (Nd,Ce)-O	2.433		

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tors with the general formula $(Ba_{1-x}Ln_x)_2(Ln_{1-y}Ce_y)_2Cu_3O_{8+\delta}$ (Ln = Nd, Sm. Eu, and Gd). The structure is derived by alternate stacking of tetragonal 1-2-3 layers and Nd atoms in coordination like that of Nd_2CuO_4 (Tables 24 and 25; Figure 11).

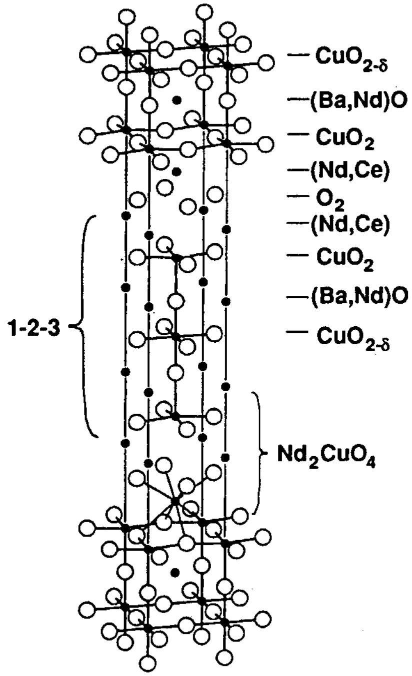


Figure 11. The crystal structure of $(Ba,Nd)_2(Nd,Ce)_2Cu_3O_8$, from Izumi *et al.*[103] Slabs of 1-2-3-type and Nd_2CuO_4-structure are noted.

In $(Ba_{0.633}Nd_{0.367})_2(Nd_{0.675}Ce_{0.325})_2Cu_3O_{8+\delta}$, Ba and Nd occupy the 1-2-3-1ike Ba sites, yielding slabs with approximate composition $(Ba,Nd)_2Cu_30_{6+\delta}$, identical in structure to the Ba-Cu-O portion of tetragonal $YBa_2Cu_30_{6+\delta}$. Cu2 is in square pyramid coordination with four planar Cu2-O3 bonds (1.944 Å) and one apical Cu2-O2 bond (2.25 Å), while two coordinated CuI is approximately 1.83 Å from O2 in linear coordination. Oxygen occupancy in the CuI plane (termed O1 by Izumi *et al.*) is only 0.11, similar to that of many tetragonal 1-2-3 compounds (see Table 11). The (Ba,Nd) site is eight coordinated with a 2.8 Å average distance to oxygen. A double layer of eight-coordinated (Nd,Ce) links these 1-2-3-1ike slabs.

Structural slabs encompassing two adjacent Cu2-O3 layers and the (Nd,Ce) sites are topologically identical to the Nd_2CuO_4 structure (compare Figures 4 and 11). Each (Nd,Ce) is eight coordinated, with four 2.34 and four 2.53 Å bonds.

E. The $Pb_2ASr_2Cu_30_{8+\delta}$ (2-1-2-3) Structure

Cava *et al.*[106] described a new family of near-70 K superconductors with the general formula $Pb_2ASr_2Cu_3O_{8+\delta}$ (*A* = Y, rare earths, Ca, Sr). This "2-1-2-3" structure, as determined by Cava *et al.*, bears a close relationship to that of tetragonal $YBa_2Cu_3O_6$ (Tables 26-28; Figure 12).

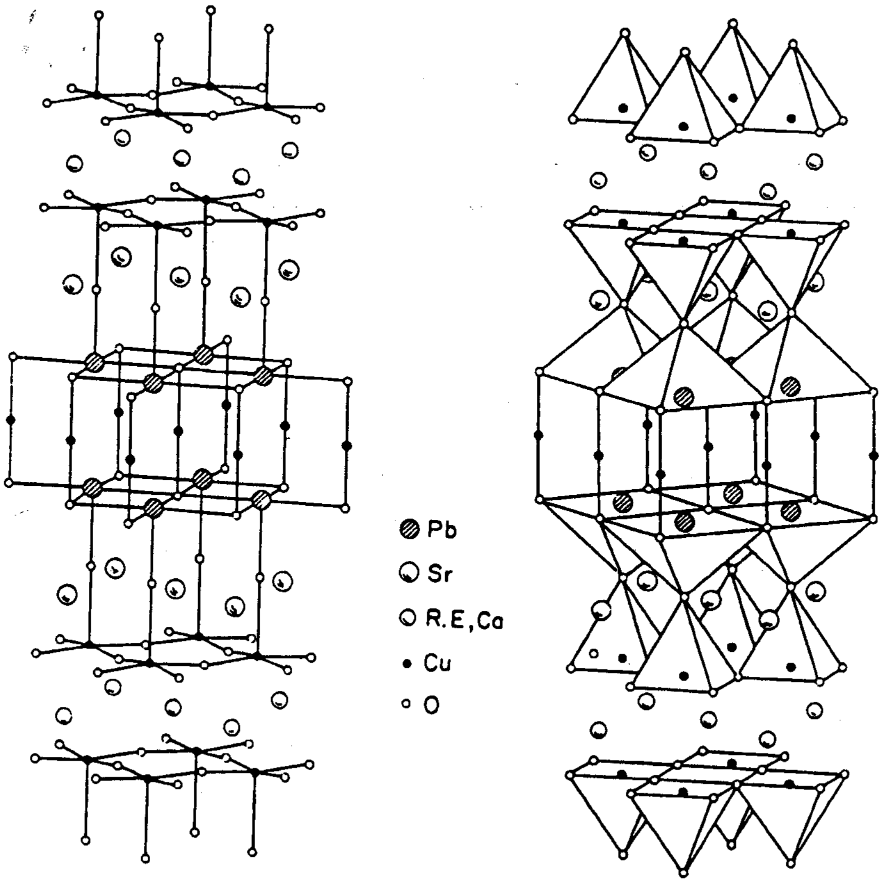


Figure 12. Two views of the crystal structure of $Pb_2YSr_2Cu_3O_8$, from Cava *et al.*[106]

The familiar central structural 1-2-2 slab occurs in both 1-2-3 and 2-1-2-3, with Sr and rare earths substituting for Ba and Y of 1-2-3. The $ASr_2Cu_2O_6$ modules are linked in $Pb_2YBa_2Cu_3O_8$ by two PbO layers added on either side of the two-coordinated Cu, giving unique Pb_2CuO_2 modules (Figure 12).

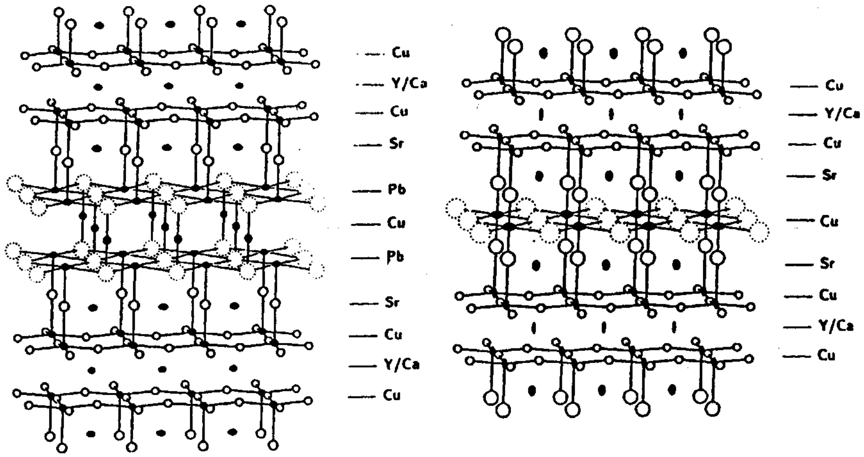


Figure 13. Comparison of the crystal structures of $Pb_2(Y,Ca)Sr_2Cu_3O_8$ (left) and $(Y,Ca)Sr_2Cu_3O_7$ (right), which has the 1-2-3 structure, from Subramanian *et al.*[104]

Each Pb atom is five-coordinated by a distorted square plane of four O3 and an apical O2. These Pb square pyramids share edges to form infinite (001) sheets that contrast with the corner-sharing sheets of Cu square pyramids. The coordination chemistry of *A*, Sr, and Cu is identical in the two structures, and the only significant difference is the intercalation of the two PbO layers (Figure 13).

Two variants of the 2-1-2-3 structure have been described. The original Bell Laboratory material[106] was described as orthorhombic (*Cmmm*), with a 5.40 x 5.43 x 15.8 Å unit cell. In this space group, however, the origin of the orthorhombic distortion is not obvious. Subsequent electron microscopy by that group[108,109] suggests that oxygen ordering in the Pb-O plane may cause violations of *C*-centering. These deviations are minor, and all refinements of orthorhombic 2-1-2-3 have used *Cmmm*.

Subramanian *et al.*[104] and Capponi *et al.*,[110] on the other hand, report tetragonal symmetry (*P4/mmm*) in some samples. Capponi *et al.* describe the lattice parameters of $Pb_2(Y_{1-x}Ca_x)Sr_2Cu_3O_{8+\delta}$ which is orthorhombic for material oxidized at 450°C and slow cooled, but tetragonal for material oxidized at 500°C and rapidly quenched. This behavior also suggests that oxygen ordering is responsible for deviations from tetragonal symmetry.

TABLE 26. The $Pb_2YSr_2Cu_3O_8$ (2-1-2-3) structures.

8A. Tetragonal P4/mmm ($D^1{}_{4h}$)

a = b ≈ 3.8 Å   c ≈ 15.8 Å   Z = 2

Atoms	Site	Symmetry	x	y	z
Pb	2h	4mm	1/2	1/2	0.39
Sr	2g	4mm	0	0	0.22
Y	1a	4/mmm	0	0	0
Cu1	2h	4mm	1/2	1/2	0.11
Cu2	1b	4/mmm	0	0	1/2
O1	4i	mm	0	1/2	0.10
O2	2h	4mm	1/2	1/2	0.25
O3*	2g	4mm	0	0	0.38

*O3 may be modeled as a split atom at site 8s at (.12,0,.38).

8B. Orthorhombic Cmmm ($D^{19}{}_{2h}$)

a ≈ b ≈ 5.4 Å   c ≈ 15.7 Å   Z = 2

Atoms	Site	Symmetry	x	y	z
Pb	4l	mm	1/2	0	0.39
Sr	4k	mm	0	0	0.22
Y	2a	mmm	0	0	0
Cu1	4l	mm	1/2	0	0.11
Cu2	2d	mmm	0	0	1/2
O1	8m	m	1/4	1/4	0.10
O2	4l	mm	1/2	0	0.25
O3	4k*	mm	0	0	0.38

*O3 may be modeled as a split atom at site 16r at (.08,-.08,.39).

Table 27. Refinements of the $Pb_2YSr_2Cu_3O_8$ structure

#	Composition	Symmetry	a(Å)	b(Å)	c(Å)	Z_{Pb}	Z_{Sr}	Z_{Cu1}	Z_{O1}	Z_{O2}	Z_{O3}	Tech	ref.
62	$Pb_2(Y_{.75}Ca_{.25})Sr_2Cu_3O_8$	P4/mmm	3.813(2)	—	15.76(1)	.3874(1)	.2206(3)	.1070(4)	.096(1)	.249(2)	.384(3)	SXD	104
63	$Pb_2YSr_2Cu_3O_8$	Cmmm	5.3933(2)	5.4311(2)	15.7334(6)	.3883(2)	.2207(2)	.1062(2)	.0918(2)	.2514(3)	.3849(4)	NPD	105
64	$Pb_2Nd_{.76}Sr_{2.24}Cu_3O_8$	Cmmm	5.435(1)	5.463(1)	15.817(3)	.38858(4)	.22184(9)	.11074(13)	.0995(5)	.2546(8)	.384(3)	XPD	106
65	$Pb_2(Nd_{.76}Sr_{.24})(Sr_{.94}Nd_{.06})_2Cu_3O_8$	Cmmm	5.437(3)	5.472(2)	15.797(7)	.38859(5)	.2217(2)	.1103(2)	.0985(8)	.257(1)	.389(2)	SXD	107

Table 28. Selected interatomic distances for $PbYSr_2Cu_3O_8$ structure

#	Cu-O1[4]	Cu1-O2[1]	Cu2-O3[2]	Y-O1[8]	Sr-O1[4]	Sr-O2[2]	Sr-O2[2]	Sr-O3[1]	mean Sr-O
162	1.915(2)	2.23(4)	1.89(4)	2.43(1)	2.74(1)	2.732(6)	2.732(6)	2.61(4)	2.72
163	1.9268(5)	2.285(5)	1.876(7)	2.398(2)	2.788(3)	2.740(1)	2.758(1)	2.629(8)	2.753
165	1.937(1)	2.31(2)	1.84(3)	2.478(8)	2.74(2)	2.744(4)	2.791(4)	2.71(4)	2.756

Table 28. (continued)

#	Pb-O2[1]	Pb-O3[1]	Pb-O3[1]	Pb-O3[1]	Pb-O3[1]	mean Pb-O	Cu1-O1-Cu1
162	2.19(4)	2.40(3)	2.40(3)	3.0+	3.0+	2.6	169.6
163	2.153(5)	2.332(7)	2.455(8)	2.999(7)	3.128(6)	2.613	166.3
165	2.08(2)	2.35(4)	2.36(4)	3.15(4)	3.17(4)	2.62	169.0(8)

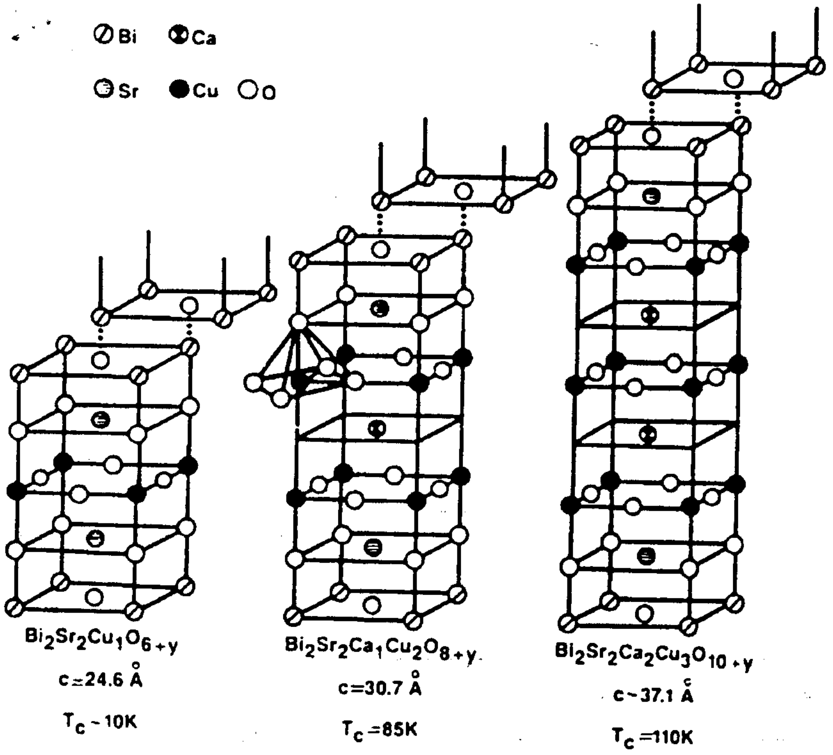


Figure 14. The crystal structures of $Bi_2Sr_2Ca_{(n-1)}Cu_nO_{(2n+1)}$ (n = 1,2,3), from Tarascon *et al.*[115]

IV. $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+6}$ Structures

The discovery by Michel *et al.*[111] of 20 K superconductivity in the Bi-Sr-Cu-O system evoked little immediate response compared to the higher temperature Y-Ba-Cu-O system. Yet this modest beginning led to the first 100 K superconductors in the closely related Bi-Sr-Ca-Cu-O system.[112] The Michel *et al.* superconductor (Tables 29 and 30; Figure 14) is the first of a series of modular layered structures in which copper and oxygen in sheets typical of all the high-temperature superconductors are spaced by alkaline earth cations, and interleaved with Bi_2O_2 layers. Though the basic topology is simple, these structures are always complicated by

Table 29. The $Bi_2Sr_2CuO_6$ (2-2-0-1) structures

9A. Orthorhombic Cmmm (D^{20}_{2h})

a ≈ b ≈ 5.4 Å c ≈ 24.4 Å Z = 4

			Torardi *et al*[113]*			Imai *et al*[114]†		
Atoms	Site	Symmetry	x	y	z	x	y	z
Bi	8l	m	0	.2758(5)	.0660(2)	0	.2745(6)	.0671(2)
Sr	8l	m	1/2	.2479(9)	.1790(4)	1/2	.2467(12)	.1810(4)
Cu	4e	2/m	1/2	3/4	1/4	1/2	3/4	1/4
O1	8g	2	3/4	1/2	.246(2)	3/4	1/2	.242(2)
O2	8l	m	0	.226(12)	.145(4)	0	.194	.145
O3	8l	m	1/2	.334(15)	.064(5)	1/2	.250	.022

*Refinement 166 of $Bi_2Sr_2CuO_6$by Torardi *et al* (113), based on single crystal x-ray diffraction data. a=5.361(2) b=5.370(1) c=24.369(6)

†Refinement 166 of $Bi_2Sr_2CuO_6$by Torardi *et al* (113), based on single crystal x-ray diffraction data a=5.376(1) b=5.383(1) c=24.384(7)

Table 29. (continued)

9B. Monoclinic A2/a (C^6_{2h})

a ≈ b ≈ 5.4 Å   c ≈ 24.3 Å   Z = 4
β ≈ 90°

				Gao *et al* (118)*	
Atoms	Site	Symmetry	x	y	z
Bi	8f	1	.0027(10)	.2726(4)	.0668(2)
Sr,Ca	8f	1	.4991(15)	.2455(9)	.1805(4)
Cu	4c	$\bar{1}$	0	1/4	1/4
O1	8f	1	.756(12)	.499(7)	.241(2)
O2	8f	1	.521(12)	.788(11)	.148(4)
O3	8f	1	.615(14)	.313(16)	.094(3)

*Refinement 168 of $Bi_2(Sr_{.54}Ca_{.32}Bi_{.14})_2CuO_6$ by Gao et al (118) based on single-crystal x-ray dirffraction data.
a=5.362(2) b=5.362(1) c=24.30(1) b=89.93(4)

9C. Monoclinic C2 (C^3_2)

a = 26.856(7) Å
b = 5.380(1) Å
c = 26.908(8) Å
β = 113.55(2)°
Z = 20

Refinement 169 of $Bi_2Sr_2CuO_{5.8}$ by Onoda and Sato (119) based on single-crystal x-ray diffraction data.
The authors propose an average superstructure model with 54 atoms in the asymmetric unit.

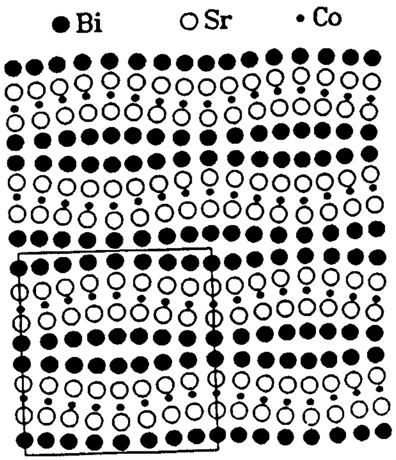


Figure 15. Projection on (010) of the modulated Bi_2Sr_2CuO6 structure, from Tarascon *et al.*[116]

incommensurate modulations, oxygen nonstoichiometry, cation disorder, layer stacking faults, and other nonperiodic behavior. Three principal structures (Figure 14) have been described, and are reviewed below.

A. The $Bi_2Sr_2CuO_6$ (2-2-0-1) Structure

The $Bi_2Sr_2CuO_6$, or "2-2-0-1" structure, consists of corner-linked planes of Cu square coordinated by O1 (Cu-Ol = 1.9 Å), sandwiched between two Sr-O2 layers. The O2 oxygens lie immediately above and below each oxygen (Cu-O2 = 2.6 Å), thus forming an extremely elongated CuO_6 octahedron. Strontium has nine nearest oxygens with an average Sr-O distance about 2.7 Å.

Flanking the Sr-Cu-Sr module are Bi_2O_2 bilayers in which bismuth adopts a very distorted octahedral coordination. Four Bi-O3 bonds near the (001) plane range from 2.2 to 2.9 Å(Table 30), while the Bi-O2 bond linking Bi to the Sr-O2 layer is much shorter (about 2.0 Å). In contrast, the sixth

Table 30. Selected interatomic distances (Å) and angles (°) for $Bi_2Sr_2CuO_6$, refinements 166 and 167

Atoms	Torardi *et al.* 113	Imai *et al.* 114	Atoms	Torardi *et al.*	Imai *et al.*
Bi-O2[1]	1.97(11)	1.95	Sr-O1[2]	2.53(3)	2.42(3)
Bi-O3[1]	2.10(9)	2.18	Sr-O1[2]	2.64(3)	2.67(4)
Bi-O3[1]	3.21(11)	2.78	Sr-O2[1]	2.68(7)	2.53
Bi-O3[2]	2.70(1)	2.91	Sr-O2[2]	2.81(3)	2.84
Bi-O3[1]	3.28(9)	3.03	Sr-O2[1]	2.95(7)	3.14
			Sr-O3[1]	2.87(11)	≥3.0
Mean Bi-O	2.66	2.63	Mean Sr-O	2.72	2.70
Cu-O1[4]	1.900(2)	1.912(6)	Cu-O1-Cu	174.1	168.3
Cu-O2[2]	2.58(11)	2.58			

TABLE 31. The $Bi_2Sr_2CaCu_2O_8$ (2-2-1-2) structures.

10A. Orthorhombic Fmmm (D^{23}_{2h})

a ≈ b ≈ 5.4 Å c ≈ 30.9 A Z = 4

Atoms	Site	Symmetry	x	y	z
Bi	8i	mm	0	0	0.20
Sr	8i	mm	0	1/2	0.11
Ca	4b	mmm	0	1/2	0
Cu	8i	mm	0	0	0.05
O1	16j	2	1/4	1/4	0.05
O2	8i	mm	0	1/2	0.20
O3	8i	mm	0	0	0.13

10B. Orthorhombic Amaa (D^{20}_{2h})

a ≈ b ≈ 5.4 Å c ≈ 30.9 Å Z = 4

Atoms	Site	Symmetry	x	y	z
Bi	8l*	m	1/2	0.23	0.05
Sr	8l	m	0	0.25	0.14
Ca	4e	2/m	0	1/4	1/4
Cu	8l	m	1/2	0.25	0.20
O1	8h	2	1/4	0	0.19
O2	8h	2	1/4	1/2	0.20
O3	8l*	m	1/2	0.31	0.12
O4	8l*	m	0	0.20	0.05

*Atoms Bi, O3 and O4 can be modeled as split atoms in site 16m.

Table 32. Refinemnts of the $Bi_2Sr_2CaCu_2O_8$ structure in space group Fmmm

#	Composition	a(Å)	b(Å)	c(Å)	z_{Bi}	z_{Sr}	z_{Cu}	z_{O1}	z_{O2}	z_{O3}	Tech	ref.
170	$Bi_2Sr_2CaCu_2O_8$	5.411(2)	5.418(2)	30.89(2)	.2026(2)	.1099(2)	.0557(2)	.0553(2)	.2052(5)	.1414(3)	NPD	121
171	$Bi_2Sr_2CaCu2O_8$	5.362(6)	5.443(6)	30.77(2)	.2019(4)	.1083(4)	.0528(5)	.0657(5)	.2038(13)	.1544(12)	NPD	122
172	$Bi_{1.5}Sr_{2.5}CaCu_2O_8$	5.350(7)	5.411(7)	30.36(3)	.1960(6)	.1174(7)	.0557(8)	.0540(5)	.1935(17)	.1300(10)	NPD	123
173	$Bi_{1.8}Sr_{1.2}Ca_{1.2}Cu_{2.2}O_8$	5.39(8)	5.39(8)	30.725(9)	.195(9)	.108(10)	.055(9)	.047(9)	.179(15)	.145(3)	NPD	124
174	$Bi_{2.2}Sr_2Ca_{.8}Cu_2O_8$	5.414(2)	5.418(2)	30.89(1)	.1989(2)	.1091(4)	.0543(7)	.051(3)	.198(4)	.120(5)	SXD	125

Table 33. Selected distances (Å) and angles (°) of the Fmmm $Bi_2Sr_2CaCu_2O_8$ structure

#	Bi-O2[2]	Bi-O2[2]	Bi-O2[1]	Bi-O3[1]	mean Bi-O	Sr-O1[4]	Sr-O3[2]	Sr-O3[2]	Sr-O2[1]	mean Sr-O	Ca-O1[8]	Cu-O1[4]	Cu-O3[1]	Cu-O1-Cu
121	2.707	2.710	2.850	1.890	2.596	2.550	2.875	2.875	2.942	2.739	2.566	1.914	2.645	179.3
122	2.722	2.682	2.902	1.462	2.529	2.320	3.068	3.030	2.932	2.712	2.781	1.951	3.126	156.4
123	2.707	2.676	3.355	2.004	2.688	2.706	2.732	2.702	2.310	2.667	2.511	1.903	2.256	176.8

Table 34. Refinements of the $Bi_2Sr_2CaCu_2O_8$ structure in space group Amaa

#	Composition	a(Å)	b(Å)	c(Å)	Y_{Bi}	Z_{Bi}	Y_{Sr}	Z_{Sr}	Y_{Cu}	Z_{Cu}	Z_{O1}
175	$Bi_2SrCa_2Cu_2O_8$	5.409(5)	5.356(5)	30.37(2)	.241(5)	.0556(8)	.222(6)	.1295(6)	.261(5)	.2006(5)	.1869(8)
176	$Bi_2Sr_2CaCu_2O_8$	5.423(5)	5.376(5)	30.72(1)	.238(4)	.0537(5)	.250(5)	.1422(8)	.250(5)	.1983(4)	.1801(7)
177	$Bi_{2.06}Sr_{1.7}Ca_{1.24}Cu_2O_8$	5.390(1)	5.395(1)	30.65(1)	.2270(5)	.0525(1)	.254(2)	.1405(2)	.249(2)	.1966(3)	.190(1)
178	$Bi_2SrCaCu_2O_8$	5.408(1)	5.413(1)	30.371(5)	.2285(5)	.0522(1)	.2537(10)	.1409(2)	.2498(13)	.1967(3)	.195(2)
179	$Bi_2Sr_{2.33}Ca_{.67}Cu_2O_8$	5.399(2)	5.414(1)	30.90(2)	.2278(5)	.0523(1)	.2523(12)	.1408(3)	.2501(15)	.1974(3)	.201(2)
180	$Bi_2Sr_{2.4}Ca_{.6}Cu_2O_8$	5.467(3)	5.441(1)	30.434(5)	.2294(3)	.0504(1)	.2531(8)	.1379(2)	.2493(9)	.1960(2)	.1947(9)
181	$Bi_2Sr_{1.5}Y_{.5}CaCu_2O_8$	5.386(6)	5.403(6)	30.37(2)	.256(5)	.0478(5)	.208(4)	.1285(6)	.263(4)	.1978(6)	.196(1)

Table 34. (continued)

#	Z_{O3}	Y_{O4}	Z_{O4}	Tech	ref.
175	.1354(7)	.127(5)	.0589(5)	NPD	126
176	.120(1)	.126(7)	.056(1)	NPD	126
177	.117(2)	.25	.017	SXD	122
178	.122(2)	.15(2)	.053(4)	SXD	127
179	—	—	—	SXD	128
180	.117(1)	.163(8)	.055(2)	SXD	129
181	.1289(10)	.190(4)	.0574(4)	NPD	126

Table 35. Selected distances (Å) and angles (°) of the Amaa $Bi_2Sr_2CaCu_2O_8$ structure

#	Bi-O3[1]	Bi-O4[1]	Bi-O4[2]	Bi-O4[2]	Bi-O4[2]	mean Bi-O	Cu-O1[2]	Cu-O2[2]	Cu-O3[1]	Cu-O1-Cu	Cu-O2-Cu
126	2.439	2.191	2.378	3.097	3.299	2.772	1.987	1.873	1.988	155	169
126	2.159	2.251	2.404	3.073	3.260	2.701	1.988	1.936	2.481	148	162
122	2.04	2.13	2.79	2.91	3.02	2.70	1.915(8)	1.921(9)	2.460	168	167
129	2.03(3)	2.1(1)	—	—	—	—	1.927(3)	1.953(6)	2.44(3)	178	161
126	2.466	2.123	2.442	3.131	3.266	2.783	1.956	1.902	2.094	176	157

Table 35. (continued)

#	Sr-O1[2]	Sr-O2[2]	Sr-O3[2]	Sr-O3[2]	Sr-O3[1]	mean Sr-O	Ca-O1[4]	Ca-O2[4]	mean Ca-O
126	2.661	2.319	2.712	2.954	3.070	2.707	2.270	2.315	2.306
126	2.236	2.719	2.865	2.791	3.387	2.734	2.296	2.873	2.572
122	2.45(3)	2.71(3)	2.450	2.810	3.140	2.649	2.65(3)	2.37(3)	2.510
129	2.60(2)	2.83(2)	2.47(4)	2.72(4)	2.62(5)	2.702	2.56(2)	2.34(2)	2.450
126	2.920	2.246	2.694	3.052	3.082	2.767	2.248	2.513	2.381

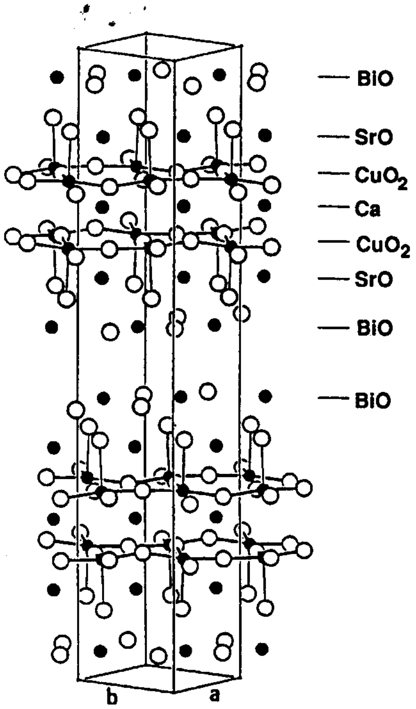


Figure 16. The crystal structure of $Bi_2Sr_2CaCu_2O_8$, from Torardi *et al.* [129]

Bi-O3 bond, which joins adjacent sheets in the Bi_2O_2 bilayer, is longer than 3 Å. This long and weak Bi-O3 bond parallel to the *c* axis results in very weak interlayer bonding and mica-like mechanical behavior in all the Bi superconductors.

The topology of the 2-2-0-1 structure is well established, but details of symmetry and supercells are somewhat confused. The body-centered pseudo-tetragonal unit cell, illustrated in Figure 14, is approximately 3.9 x 3.9 x 24.4 Å, but this aristotype is not observed in synthetic crystals. Orthorhombic distortion leads to an *A*-centered 5.4 x 5.4 x 24.4 Å (Table 29; structure 9A), which was employed in several refinements by Torardi *et al.*[113] and Imai *et al.*[114] Gao *et al.*[117] propose a monoclinic variant with *A2/m* symmetry with the same pseudo-tetragonal unit cell (Table 29; structure 9B).

Models of 5 x 5 x 24 Å orthorhombic or monoclinic structures are always complicated by a modulation, which produces a superstructure of approximately 5*b* (Figure 15). This modulation is difficult to handle with conventional diffraction techniques. If the modulation is ignored, then thermal parameters are large and oxygen positions are poorly constrained. Note, for example, the considerable discrepancies in reported O2 and O3 oxygen coordinates and Bi-O interatomic distances in Tables 30 and 31. Alternatively, Onoda and Sato[118] attempted a complete refinement of a commensurate modulated structure in monoclinic (*C2*) symmetry (Table 29; structure 9C). Their model, which includes 54 atoms in the asymmetric unit, provides a better fit to diffraction data, but it obscures the topological simplicity of the 2-2-0-1 structure.

B. The $Bi_2Sr_2CaCu_2O_8$ (2-2-1-2) Structure

Superconductivity above 100 K was first observed in the Bi-Sr-Ca-Cu-O system,[112] and the new phase was quickly identified as $Bi_2Sr_2CaCu_2O_{8+\delta}$, or "2-2-1-2." Hazen *et al.*[119] determined the *A*-centered orthorhombic unit subcell as 5.41 x 5.44 x 30.78 Å, they recognized the close structural and compositional relationship to Michel *et al.'s*[112] 2-2-O-1 phase, and they proposed that these compounds form a series of structures closely related to "Aurivillius phases".[120]

The 2-2-1-2 structure (Tables 31-35; Figures 14, 16) is simply related to that of 2-2-0-1. The Cu-O sheets in 2-2-0-1 are replaced by CuO_2/Ca/CuO_2 sandwiches in 2-2-1-2. Calcium adopts eight coordination, similar to the Y environment in 1-2-3. There are no oxygens at this level, so copper atoms have only five nearest neighbors in square pyramidal coordination, rather than the elongated octahedral coordination of 2-2-0-1. The structural slab containing SrO/CuO_2/Ca/CuO_2/SrO is topologically identical to the $YBa_2Cu_2O_6$ 1-2-2 module portion of the 1-2-3 structure.

Structural details of 2-2-1-2 are greatly complicated by stacking faults, modulations, and oxygen and cation disorder, as well as the tendency of crystallites to bend or otherwise deform.

TABLE 36. The $Bi_2Sr_2Ca_2Cu_3O_{10}$ (2-2-2-3) structure.

Pseudotetragonal I4/mmm (D^{17}_{4h})

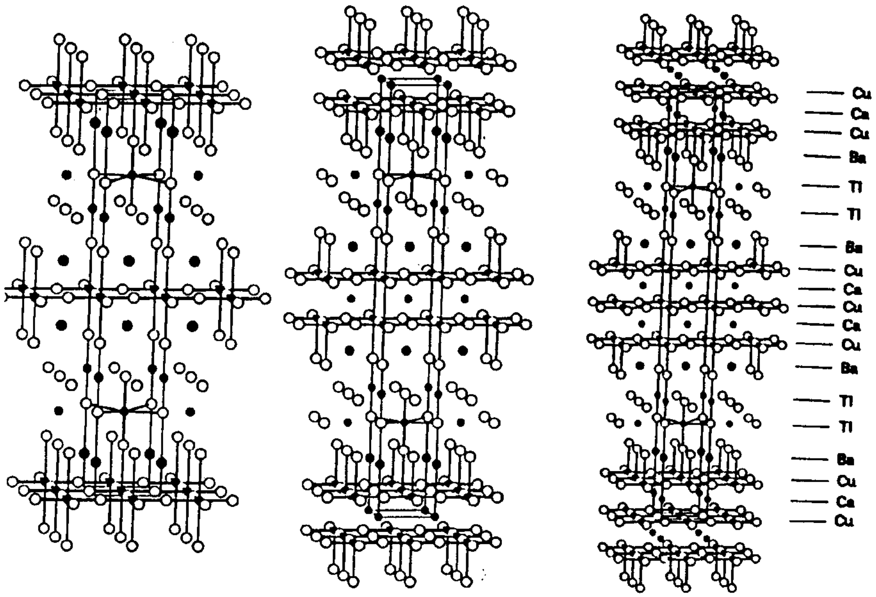
a ≈ b ≈ 3.8 Å Z = 2
c ≈ 37.1 Å

Atoms	Site	Symmetry	x	y	z
Bi	4e	4mm	0	0	0.21
Sr	4e	4mm	1/2	1/2	0.16
Ca	4e	4mm	1/2	1/2	0.05
Cu1	2a	4/mmm	0	0	0
Cu2	4e	4mm	0	0	0.11
O1	4c	mmm	0	1/2	0
O2	8g	mm	0	1/2	0.11
O3	4e	4mm	0	0	0.16
O4	4e	4mm	1/2	1/2	0.21

This phase has been identified by transmission electron microscopy and mixed-phase x-ray powder diffraction. The probable symmetry is orthorhombic, though no complete structure refinements have been published.

ıe structure is pseudo-tetragonal *(I4/mmm)* 3.9 x 3.9 x 30.8 Å, and some workers have tempted refinements in that aristotype space group.[130,131] The true symmetry, however, is no eater than pseudo-orthorhombic, approximating *Fmmm*, with a 5.4 x 5.4 x 30.8 Å unit cell 'able 31, structure I0A; Table 32, refinements 170-174).

ore precise refinements of this pseudo-orthorhombic structure are obtained with space group *naa*, which incorporates two symmetrically distinct oxygens at the level of copper (Table 31, ructure I0B; Table 34, refinements 175-181). Other researchers have employed space groups *cb*[132] and *A2aa* [133] in an effort to describe this intractable structure. None of these models is adequate, however, because of a strong incommensurate modulation parallel to (010), similar to that illustrated in Figure 15 for the 2-2-0-1 structure. This modulation results in large apparent thermal motion in any subcell refinement, and oxygen positions are poorly constrained, particularly in the Bi_2O_2 layers.



$Tl_2Ba_2CuO_6$ $Tl_2Ba_2CaCu_2O_8$ $Tl_2Ba_2Ca_2Cu_3O_{10}$

igure 17. Crystal structures of $T1_2Ba_2Ca_{(n-1)}Cu_nO_{(2n+4)}$ (*n* = 1,2,3), from Torardi *et al.*[146] The structures differ in the number of Cu-O layers, which are interleaved by Ca.

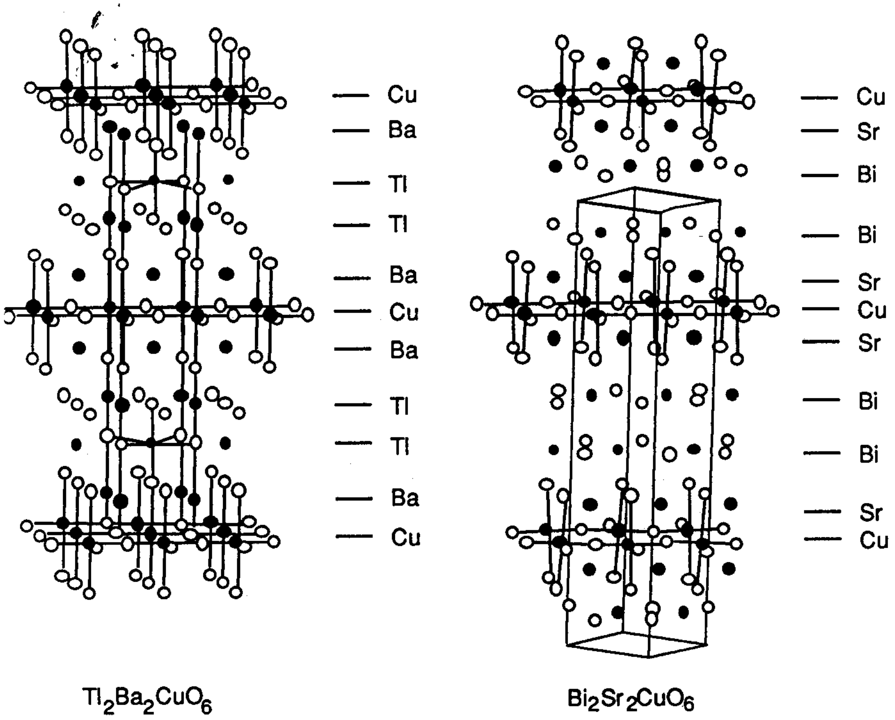
C. The $Bi_2Sr_2Ca_2Cu_3O_{10}$(2-2-2-3) Structure

Transmission electron microscopy and powder diffraction experiments reveal the presence of a pseudotetragonal 3.9 x 3.9 x 37 Å-phase in the Bi-Sr-Ca-Cu-O system. This phase has approximate stoichiometry $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ ("2-2-2-3"), and is the *n* = 3 member of the homologous series $Bi_2Sr_2Ca_{(n-1)}Cu_nO_{(2n+4+\delta)}$. Pure 2-2-2-3 material is difficult to synthesize and a complete structure refinement has not been reported. The topology of the structure is obvious by comparison with 2-2-0-1 and 2-2-1-2, however (Figure 14; Table 36). Additional CuO_2 and Ca layers are inserted within the CuO_2/Ca/CuO_2 sandwich of 2-2-1-2, yielding a CuO_2/Ca/CuO_2/Ca/CuO_2 club sandwich. The outer Cu2 atoms are in the square pyramid coordination found in 1-2-3 and 2-2-1-2, while Cul atoms are in ideal square-plane coordination (Figure 14). The aristotype structure suggested in Table 36 represents only an average topology. Structural details are undoubtedly complicated by modulations and nonperiodic effects characteristic of the other Bi-Sr-Ca-Cu-O superconductors, and the true symmetry is no higher than orthorhombic.

The homologous series of bismuth compounds, $Bi_2Sr_2Ca_{(n-1)}Cu_nO_{(2n+4+\delta)}$ (*n* = 1,2,3) suggests the possible existence of other structures with more copper layers. With the exception of isolated structural slabs observed by high-resolution electron microscopy, phases with *n* = 4 ($Bi_2Sr_2Ca_3Cu_4O_{12}$, "2-2-3-4") and greater have not been prepared in the bismuth system. Recent discovery of 4- and 5-copper layer stacks in closely related thallium superconducting systems has provided an opportunity to study the properties of such structures.

V. $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ Structures

Sheng and Hermann[134,135] discovered superconductivity near 120 K in the Tl-Ba-Ca-Cu-O system. These samples were sent to Hazen *et al.*,[136] who had just completed identification of the bismuth 2-2-1-2 phase.[119] The structures of the bismuth and thallium superconductors proved strikingly similar, and three new superconducting phases - $T1_2Ba_2CuO_6+_\delta$, $T1_2Ba_2CaCu_2O_{8+\delta}$, and $T1_2Ba_2Ca_2Cu_3O(_{10+\delta})$ - were quickly identified in the Tl-Ba-Ca-CuO system. These three phases



igure 18. Comparison of the crystal structures of $Bi_2Sr_2CuO_6$ and $T1_2Ba_2CuO_6$, from Torardi *et al.*[113] The structures differ in the oxygen coordination of Bi versus T1.

orm part of a homologous series $T1_2Ba_2Ca_{(n-1)}Cu_nO_{(2n+4+\delta)}$, which is identical in form, and perhaps opology, to the bismuth series.

The structures of these thallium-based superconductors were elucidated by Subramanian t al.,[142,146] who describe the $n = 1, 2$, and 3 varieties, and show their close topological relationship o the bismuth structures (Tables 37-45; Figures 17 and 18). Structural modules with copper and lkaline earth cations are interleaved by $T1_2O_2$ layers in the same sequence as in the Bi phases. he most significant difference between these two structural groups is the difference between i_2O_2 and $T1_2O_2$ layers. Thallium adopts a flattened octahedral coordination: four Tl-O bonds

TABLE 37. The $Tl_2Ba_2CuO_6$ (2-2-0-1) structures.

12A. Tetragonal I4/mmm (D^{17}_{4h})

$a \approx b \approx 3.9$ Å $Z = 2$
$c \approx 23.2$ Å

Atoms	Site	Symmetry	x	y	z
Tl	4e	4mm	1/2	1/2	0.20
Ba	4e	4mm	0	0	0.08
Cu	2b	4/mmm	1/2	1/2	0
O1	4c	mmm	0	1/2	0
O2	4e	4mm	1/2	1/2	0.12
O3*	4e	4mm	1/2	1/2	0.29

*O3 can be modeled as a split atom on site 16n at (.60,1/2,.29).

12B. Orthorhombic Fmmm (D^{23}_{2h})

$a \approx b \approx 5.5$ Å $Z = 4$
$c \approx 23.2$ Å

Atoms	Site	Symmetry	x	y	z
Tl	8i	mm	0	0	0.20
Ba	8i	mm	1/2	0	0.08
Cu	4a	mmm	0	0	0
O1	8e	2/m	1/4	3/4	0
O2	8i	mm	0	0	0.12
O3	8i	mm	0	0	0.29
O4†	8f	222	1/4	1/4	1/4

†occupancy of O4 << 1

parallel to (001) average 2.7 Å, while two Tl-O bonds parallel to the *c* axis are about 2.0 Å. These relatively short interlayer bonds provide a strong interlayer link, and thallium superconductors thus do not exhibit a strong layered morphology. In contrast, Bi-O bonds parallel to *c* average more than 3.0 Å, resulting in extremely weak interlayer bonding and the mica-like character of the material. These differences in interlayer bonding result in *c* axes that are about 1.2 Å shorter in thallium compounds compared to the corresponding bismuth phases. For example, the one-

Table 38. Refinements of the $Tl_2Ba_2CuO_{6+\delta}$ structure

#	Composition	T(K)	Sym.	a(Å)	b(Å)	c(Å)	z_{Tl}	z_{Ba}	z_{O2}	z_{O3}	Tech	ref.
182	$Tl_2Ba_2CuO_6$	295	T	3.866(1)	–	23.239(6)	.20265(2)	.08301(3)	.1168(4)	.2889(5)	SXD	113
183	$Tl_2Ba_2CuO_6$	295	T	3.8625(2)	–	23.124(2)	.2025(7)	.0840(8)	–	–	SPD	137
184	$Tl_2Ba_2CuO_6$	295	T	3.8656(3)	–	23.225(2)	.2036(1)	.0833(1)	.1187(13)	.2894(20)	SPD	138
185	$Tl_{1.75}Cd_{.25}Ba_2CuO_6$	293	T	3.851(1)	–	23.313(8)	.2026(1)	.0828(2)	.1170(2)	.2892(2)	NPD	139
186	$Tl_2Ba_2CuO_6$	4	O	5.4604(2)	5.4848(2)	23.2038(6)	.2024(1)	.0828(1)	.1163(1)	.2895(2)	NPD	140
187	$Tl_2Ba_2CuO_6$	295	O	5.4474(3)	5.4948(5)	23.180(2)	.2036(1)	.0838(2)	.120(2)	.289(2)	XPD	138

Table 39. Selected interatomic distances (Å) for $Tl_2Ba_2CuO_6$ and $Tl_2Ba_2Cu_2O_8$ structures

#	Structure	Cu-O1[4]	Cu-O2[2]	Tl-O2[1]	Tl-O3[1]	Tl-O3[2]	Tl-O3[2]	mean Tl-O	Ba-O1 [4]	Ba-O2 [4]	Ba-O3 [1]	mean Ba-O	Ca-O3[8]
182	2201	1.9330(5)	2.714(9)	1.995(9)	2.038(11)	2.496(12)	3.011(15)	2.508	2.731(1)	2.844(2)	2.999(11)	2.811	—
185	2201	1.925(1)	2.728(1)	2.008(6)	2.085(7)	2.362(13)	2.818(11)	2.409	2.726(4)	2.837(2)	3.00(1)	2.806	—
186	2201	1.9349(1)	2.698(3)	2.004(3)	—	—	—	—	2.723(2)	2.844(1)	2.981(6)	2.826	—
188	2212	1.928	2.704(4)	1.983(4)	2.022(7)	2.470(5)	3.027(6)	2.5	—	—	—	—	—
189	2212	1.9277(3)	2.699(10)	1.978(10)	2.031(21)	2.462(22)	3.037(28)	2.498	2.788(4)	2.818(3)	2.864(21)	2.81	2.478(4)
193	2212	1.932(1)	2.69(4)	1.98(4)	1.95(5)	2.737(1)	2.737(1)	2.48	2.70(1)	2.82(1)	2.84(5)	2.81	2.478(11)
194	2212	1.925(1)	2.82(4)	2.09(5)	1.86(6)	2.58(1)	2.87(1)	2.48	3.24(4)	2.72(6)	2.14(6)	2.89	2.50(1)

TABLE 40. $Tl_2Ba_2CaCu_2O_8$ (2-2-1-2) structure.

Tetragonal I4/mmm (D^{17}_{4h})

a = b = 3.9 Å Z = 2
c = 29.4 Å

Atoms	Site	Symmetry	x	y	z
Tl	4e	4mm	1/2	1/2	0.21
Ba	4e	4mm	0	0	0.12
Ca	2a	4/mmm	0	0	0
Cu	4e	4mm	1/2	1/2	0.05
O1	8g	mm	0	1/2	0.05
O2	4e	4mm	1/2	1/2	0.15
O3*	4e	4mm	1/2	1/2	0.28

*O3 can be modeled as a split atom on site 16n at (.60,1/2,.28).

layer 2-2-0-1 thallium superconductor has a 23.2 Å *c* axis, compared to 24.4 Å in the bismuth 2-2-0-1 compound (Table 38; refinements 182-187). The *a* and *b* axes, however, are slightly longer in the thallium superconductors, thus yielding in-plane Cu-O bonds approximately 1.93 Å, compared to 1.90 Å in the typical bismuth superconductor (compare Tables 35 and 39).

Unlike the bismuth superconductors, all of which have modulated structures that only approximate orthorhombic symmetry, the thallium superconductors (with the exception of some nonsuperconducting samples of 2-2-0-1) are close to the ideal tetragonal *I4/mmm* symmetry at room temperature. These structures can thus be described with unit cells approximately 3.9 x 3.9 x (17 + 6.2*n*) Å. In spite of these differences, the aristotype structures of Bi and Tl superconductors are topologically identical (for example, compare Tables 36 and 45).

Two variants of the thallium 2-2-0-1 structure have been described.[138] Superconducting 2-2-0-1, prepared by annealing samples in oxygen and then quenching, are tetragonal *I4/mmm* at room temperature (Table 37, structure 12A; Table 38, refinements 182-185). Slow cooling in oxygen, on the other hand, yields nonsuperconducting 2-2-0-1 with a distinct orthorhombic distortion (space group *Fmmm* (Table 37, structure 12B; Table 38, refinements 186). Parise *et*

Table 41. Refinements of the $Tl_2Ba_2CaCu_2O_8$ structure

#	Composition	T(K)	a(Å)	c(Å)	Z_{Tl}	Z_{Ba}	Z_{Cu}	Z_{O1}	Z_{O2}	Z_{O3}	Tech	ref.
188	$Tl_2Ba_2CaCu_2O_8$	293	3.8559(1)	29.4199(1)	.2129(1)	.1201(1)	.0536(1)	.0526(1)	.1455(1)	.2803(2)	NPD	141
189	$Tl_2Ba_2CaCu_2O_8$	295	3.8550(6)	29.318(4)	.21359(2)	.12179(3)	.0540(1)	.0531(2)	.1461(3)	.2815(7)	SPD	142
190	$Tl_2Ba_2CaCu_2O_8$	125	3.843(1)	29.263(9)	.2133(1)	.1212(1)	.0538(1)	.0522(2)	.1456(5)	.280(1)	SPD	143
191	$Tl_2Ba_2CaCu_2O_8$	295	3.851(6)	29.308(4)	.2133(1)	.1213(1)	.0538(1)	.0523(3)	.1458(6)	.280(1)	SPD	143
192	$Tl_2Ba_2CaCu_2O_8$	295	3.8565(4)	29.326(3)	.2137(2)	.1217(2)	.0540(4)	.053(1)	.146(1)	.282(2)	XPD	138
193	$Tl_{1.95}Ba_2Ca_{.85}Cu_{2.18}O_8$	295	3.864(2)	29.18(4)	.2138(1)	.1221(1)	.0539(2)	.0532(6)	.146(1)	.281(2)	SPD	144
194	$TlKBa_2CaCu_2O_8$	295	3.847(4)	29.22(5)	.2198(13)	.1439(15)	.0519(8)	.0546(7)	.148(1)	.283(1)	NPD	145

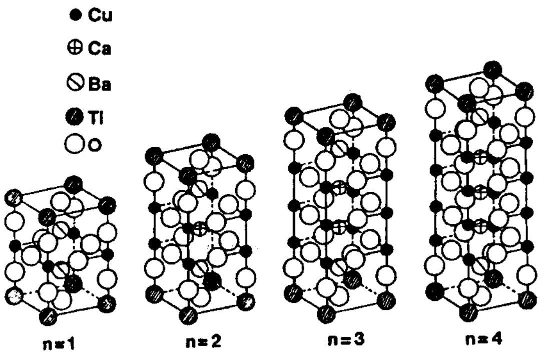
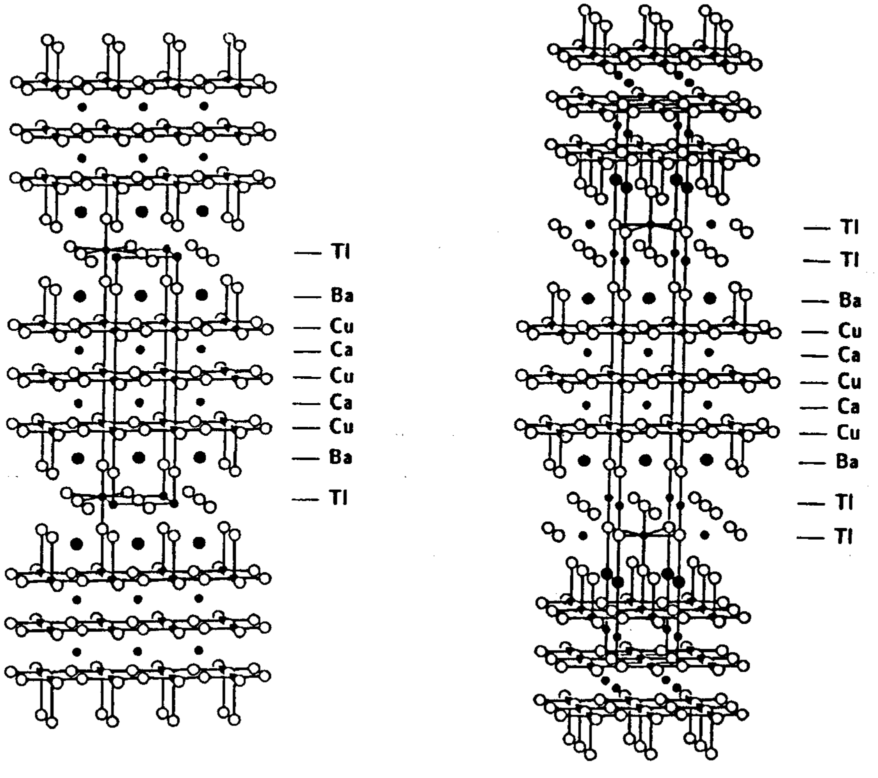


Figure 19. Crystal structures of $TlBa_2Ca_{(n-1)}Cu_nO_{(2n+3)}$ (n = 1,2,3,4), from Haldar *et al.*[161]

al.[140] observed a similar but smaller orthorhombic distortion in superconducting 2-2-0-1 at 4 K. It is possible, therefore, that some 2-2-0-1 compounds adopt the lower symmetry at superconducting temperatures. No atomic sites become symmetrically split in the transition from *I4/mmm* to *Fmmm*, so the transition mechanism is not obvious.

All refinements of thallium 2-2-1-2 and 2-2-2-3 superconductors, including refinements at 125 K for 2-2-1-2 (Table 41; refinement 190) and 13 and 150 K for 2-2-2-3 (Table 43; refinements 196-197), employ *I4/mmm* symmetry. In each case, however, oxygen atoms in special position 4e at the level of thallium (O3 in 2-2-0-1 and 2-2-1-2, but O4 in 2-2-2-3) display extremely large apparent thermal motion in the (001) plane. These oxygens are better modeled as a split atom with 25% occupancy in general position 16n. Oxygen positions, when refined in this way, generally converge at positions approximately 0.4 Å along *a* from the ideal 4e locations. One important consequence of these alternate positions is to distort significantly the square base of the thallium octahedron, giving on average two short (2.2 Å) and two long (3.0 Å) Tl-O bonds in the (001) plane.



$TlBa_2Ca_2Cu_3O_9$

$Tl_2Ba_2Ca_2Cu_3O_{10}$

Figure 20. Comparison of the crystal structures of $TlBa_2Ca_2Cu_3O_9$ (left) with $Tl_2Ba_2Ca_2Cu_3O_{10}$ (right), from Subramanian *et al.*[156]

TABLE 42. $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2-2-2-3) structure.

Tetragonal I4/mmm (D^{17}_{4h})

a = b = 3.9 Å Z = 2
c = 36 Å

Atoms	Site	Symmetry	x	y	z
Tl	4e	4mm	1/2	1/2	0.22
Ba	4e	4mm	0	0	0.14
Ca	4e	4mm	0	0	0.05
Cu	2b	4/mmm	1/2	1/2	0
Cu2	4e	4mm	1/2	1/2	0.09
O1	4c	mmm	1/2	0	0
O2	8g	mm	1/2	0	0.09
O3	4e	4mm	1/2	1/2	0.17
O4*	4e	4mm	1/2	1/2	0.28

*O4 can be modeled as a split atom on site 16n at (.60,1/2,.28).

Several authors have reported observing a $c = 42$ Å phase, corresponding to a thallium 2-2-3-4 superconductor.[162,166] No pure phase samples or structural refinements have been reported, but the topology of such a phase is obvious by extension from the 1-, 2-, and 3-layer compounds (Table 45).

VI. $TlBa_2Ca_{n-1}Cu_nO_{2n+3+\delta}$ Structures

Shortly after Sheng and Hermann's seminal work on the Tl-Ba-Ca-Cu-O system,[134,135] Parkin *et al.*[147] reported on yet another homologous series of thallium superconductors. These compounds, now including the $n = 1$ to 5 members of the series $TlBa_2Ca_{n-1}Cu_nO_{2n+3+\delta}$ differ from the Tl_2 series simply in the number of Tl-O layers. These compounds have thus acquired the abbreviations 1-2-0-1, 1-2-1-2, 1-2-2-3, etc.

Thallium monolayer compounds have single layers of octahedrally-coordinated Tl between the familiar BaO/CuO$_2$/Ca ... /CuO$_2$/BaO modules. Single octahedral layers do not require an offset of adjacent modules so this series is primitive tetragonal, space group *P4/mmm*, with 3.8 x 3.8 x (5.4 + 3.4*n*) Å unit cells (Tables 46-51; Figure 19). Thallium is in a flattened

Table 43. Refinements of the $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ structure.

#	Composition	T(K)	a(Å)	c(Å)	z_{Tl}	z_{Ba}	z_{Ca}	z_{Cu2}	z_{O2}	z_{O3}	z_{O4}	Tech	ref.
195	$Tl_2Ba_2Ca_2Cu_3O_{10}$	295	3.8503(6)	35.88(3)	.2201(1)	.1448(1)	.0463(2)	.0896(2)	.0875(6)	.1588(13)	.2719(14)	SXD	146
196	$Tl_2Ba_2Ca_2Cu_3O_{10}$	13	3.8473(1)	35.630(2)	.2197(1)	.1445(2)	.0454(2)	.0884(1)	.0881(1)	.1650(2)	.2756(3)	NPD	141
197	$Tl_2Ba_2Ca_2Cu_3O_{10}$	150	3.8487(1)	35.662(2)	.2195(1)	.1444(2)	.0454(2)	.0886(1)	.0878(1)	.1650(2)	.2750(2)	NPD	141
198	$Tl_2Ba_2Ca_2Cu_3O_{10}$	295	3.8496(4)	35.638(4)	.2201(1)	.1442(2)	.0439(4)	.0889(3)	.0878(7)	.1643(12)	.2751(17)	XPD	138
199	$Tl_2Ba_2Ca_2Cu_3O_{10}$	295	3.8502(2)	35.572(2)	.2209(5)	.1457(5)	.0466(9)	.0874(10)	.0875	.1588	.2719	XPD	137

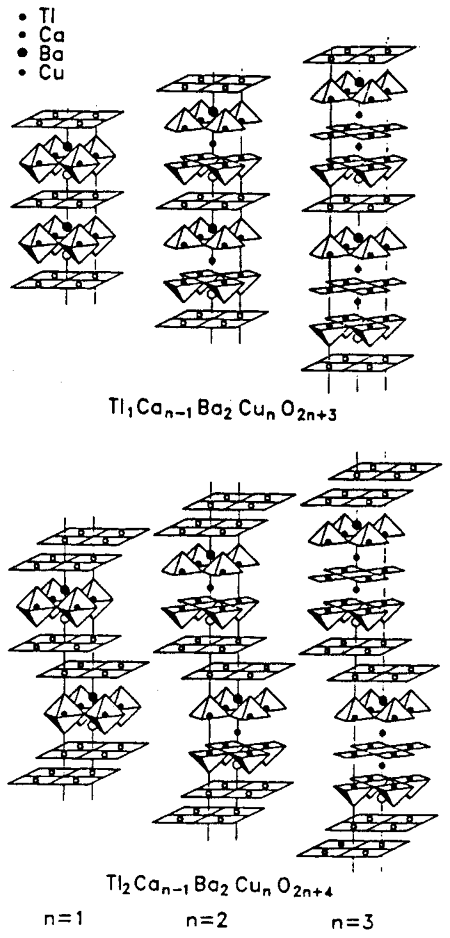


Figure 21. Comparison of crystal structures of 1-, 2-, and 3-copper layer superconductors in the Tl-Ba-Ca-Cu-O system, from Parkin *et al.*[160]

TABLE 44. Selected interatomic distances (Å) and angles for $Tl_2Ba_2Ca_2Cu_3O_{10}$ refinement 195 (Torardi *et al*, 146)

Atoms	Distance(Å)	Atoms	Distance(Å)	Atoms	Angle(°)
Cu1-O1[4]	1.9252(3)	Ba-O2[4]	2.82(2)	Cu1-O1-Cu1	180°
		Ba-O3[4]	2.768(9)	O1-Cu1-O1	90°
Cu2-O2[4]	1.927(1)	Ba-O4[1]	2.99(3)		
Cu2-O3[1]	2.48(5)	mean Ba-O	2.82		
				Cu2-O2-Cu2	175(1)
Tl-O3[1]	2.20(5)	Ca-O1[4]	2.542(5)	O2-Cu2-O2	89.9(1)
Tl-O4[1]	1.92(3)	Ca-O2[4]	2.427(14)	O2-Cu2-O3	92.3(7)
Tl-O4[2]	2.48(3)	mean Ca-O	2.485		
Tl-O4[2]	3.02(4)				
Mean Tl-O	2.54				

TABLE 45. The $Tl_2Ba_2Ca_3Cu_4O_{12+\delta}$ (2-2-3-4) structures.

Tetragonal I4/mmm (D^{17}_{4h})

$a = b \approx 3.9$ Å $Z = 2$
$c \approx 42$ Å

Atoms	Site	Symmetry	x	y	z
Tl	4e	4mm	1/2	1/2	0.236
Ba	4e	4mm	0	0	0.160
Ca1	2a	4/mmm	0	0	0
Ca2	4e	4mm	0	0	0.076
Cu1	4e	4mm	1/2	1/2	0.038
Cu2	4e	4mm	1/2	1/2	0.114
O1	8g	mm	1/2	0	0.038
O2	8g	mm	1/2	0	0.114
O3	4e	4mm	1/2	1/2	0.162
O4	4e	4mm	1/2	1/2	0.280

After Liang *et al* (162).

Table 46. The $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ structures

Tetragonal P4/mmm (D^{14}_h)

$a = b \approx 3.8$ Å $c \approx 5.4+3.4n$ Å $Z = 1$

			16. n=1 (1-2-0-1)			17. n=2 (1-2-1-2)			18. n=3 (1-2-2-3)			19. n=4 (1-2-3-4)		
Atoms	Site	Symmetry	x	y	z	x	y	z	x	y	z	x	y	z
Tl	1a	4/mmm	0	0	0	0	0	0	0	0	0	0	0	0
Ba	2h	4mm	1/2	1/2	0.29	1/2	1/2	0.22	1/2	1/2	0.18	1/2	1/2	0.15
Ca1	1d	4/mmm	-	-	-	1/2	1/2	1/2	-	-	-	1/2	1/2	1/2
Ca2	2h	4mm	-	-	-	-	-	-	1/2	1/2	0.40	1/2	1/2	0.33
Cu1	1b	4/mmm	0	0	1/2	-	-	-	0	0	1/2	-	-	-
Cu2	2g	4mm	-	-	-	0	0	0.36	0	0	0.30	0	0	0.25
Cu1	2g	4mm	-	-	-	-	-	-	-	-	-	0	0	0.42
O1	2e	4mm	0	1/2	1/2	-	-	-	0	1/2	1/2	-	-	-
O1	4i	mm	-	-	-	-	1/2	0.36	-	-	-	0	0	0.42
O2	2g	4mm	0	0	0.21	0	0	0.18	-	-	-	-	-	-
O2	4i	mm	-	-	-	-	-	-	0	1/2	0.30	0	1/2	0.25
O3	1c	4/mmm	1/2	1/2	0	1/2	1/2	0	-	-	-	-	-	-
O3	2g	4mm	-	-	-	-	-	-	0	0	0.13	0	0	0.12
O4	1c	4/mmm	-	-	-	-	-	-	1/2	1/2	0	1/2	1/2	0

TABLE 47. Refinements of the $TlBa_2CuO_5$ structure at 295K by powder x-ray diffraction.

#	Composition	a(Å)	c(Å)	Z_{Ba}	Z_{O2}	ref.
200	$(Tl_{.75}Bi_{.25})Sr_2CuO_5$	3.745(4)	9.002(10)	.29	.21	148
201	$Tl(LaSr)CuO_5$	3.7796(2)	8.8060(7)	.289(1)	.22(1)	149
202	$Tl_{.8}(LaSr)Cu_{1.2}O_5$	3.7731(2)	8.8268(5)	.291(1)	.222(9)	149
203	$Tl_{.6}(LaSr)Cu_{1.4}O_5$	3.7707(3)	8.8528(8)	.290(2)	.20(1)	149
204	$Tl_{.4}(LaSr)Cu_{1.6}O_5$	3.7714(3)	8.8558(9)	.289(2)	.20(1)	149
204A	$Tl_{.7}(LaSr)CuO_5$	3.7743(1)	8.8308(4)	.292(1)	.232(7)	149

Table 48. Selected interatomic distances for $TlBa_2CuO_5$ and $TlBa_2CaCu_2O_7$ structures

#	Structure	Cu-O1[4]	Cu-O2 [2]	Tl-O2 [2]	Tl-O3 [4]	mean Tl-O	Ba-O1 [4]	Ba-O2 [4]	Ba-O3 [1]	mean Ba-O	Ca-O [8]	Cu-O1-Cu
200	1201	1.87	1.89	2.61	2.65	2.64	2.66	2.65	2.61	2.65	–	180
205	1212	1.92	2.45	2.24	2.771	2.55	2.75	2.81	2.69	2.77	2.49	176.2
206	1212	1.929	2.76(2)	2.01(4)	2.727(1)	2.49	2.837(8)	2.825(5)	2.752(2)	2.822	2.470(7)	176.6
207	1212	1.9027	2.443(7)	1.996(7)	2.7	2.47	2.648(4)	2.656(6)	2.764(2)	2.664	2.470(2)	177.5(3)
208	1212	1.9	2.316	2.089	2.69	2.49	2.735	2.680	2.602	2.696	2.447	175.3
209	1212	1.892	2.309	2.097	2.68	2.49	2.719	2.670	2.575	2.681	2.477	173.5
210	1212	1.909	2.411	1.989	2.699	2.462	2.753	2.671	2.531	2.692	2.508	180
211	1212	1.917 (6)	2.304(14)	1.968(14)	2.744	2.485	2.748(3)	2.736(5)	2.560(7)	2.722	2.419(4)	170.6

Table 49. Refinements of the $TlBa_2CaCuO_7$ structure at 295K

#	Composition	a(Å)	c(Å)	Z_{Ba}	Z_{Cu}	Z_{O1}	Z_{O2}	Tech	ref.
205	$TlBa_2CaCu_2O_7$	3.833	12.68	.213(1)	.370(2)	.375(6)	.177(6)	XPD	150
206	$TlBa_2CaCu_2O_7$	3.8566(4)	12.754(2)	.2158(1)	.3745(2)	.3790(8)	.158(1)	SXD	151
207	$(Tl_{.5}Pb_{.5})Sr_2CaCu_2O_7$	3.8023(3)	12.107(1)	.2175(4)	.3663(3)	.3697(3)	.1645(5)	NPD	152
208	$(Tl_{.5}Pb_{.5})Sr_2CaCu_2O_7$	3.7941(2)	12.0813(6)	.2154(3)	.3632(4)	.3721(10)	.1715(20)	XPD	153
209	$(Tl_{.8}Pb_{.2})Sr_2CaCu_2O_7$	3.7805(2)	12.1258(5)	.2124(3)	.3616(5)	.3680(13)	.1713(21)	XPD	153
210	$Tl_{.5}Sr_2(Ca_{.5}Sm_{.5})Cu_2O_7$	3.817	12.054	.210	.365	.365	.165	XPD	154
211	$(Pb_{.71}Cu_{.29})Sr_2(Y_{.73}Cu_{.27})Cu_2O_7$	3.8207(4)	11.826(1)	.2089(1)	.3613(1)	.3746(6)	.1664(12)	SXD	155

Table 50. Refinements of the $TlBa_2Ca_2Cu_3O_9$ structure

#	Composition	a(Å)	c(Å)	Z_{Ba}	Z_{Ca}	Z_{Cu2}	Z_{O2}	Z_{O3}	Tech	ref.
212	$TlBa_2Ca_2Cu_3O_9$	3.853(1)	15.913(4)	.1729(1)	.3953(3)	.2991(2)	.3019(7)	.1277(11)	SXD	156
213	$TlBa_2Ca_2Cu_3O_9$	3.843(2)	15.871(3)	.176	.397	.302	.304	.132	XPD	147
214	$TlBa_2Ca_2Cu_3O_9$	3.8532(9)	15.922(5)	.1720(2)	.3963(4)	.2985(3)	.304(1)	.125(2)	SXD	157
215	$TlBa_2Ca_2Cu_3O_9$	3.848(4)	15.89(1)	.17197(4)	.3961(1)	.2984(1)	.3024(3)	.1258(5)	SXD	158
216	$TlBa_2Ca_2Cu_3O_9$	3.849(2)	15.83(1)	.1738(1)	.3956(2)	.2994(1)	.3025(5)	.1254(9)	SXD(@125K)	143
217	$(Tl_{.5}Pb_{.5})Sr_2Ca_2Cu_3O_9$	3.8206(2)	15.294(1)	.1720(4)	.3840(8)	.2830(6)	.2908(5)	.1266(6)	NPD	152
218	$(Tl_{.55}Pb_{.55}Sr_2Ca_{1.9})Cu_3O_9$	3.808(1)	15.232(7)	.1709(2)	.3928(3)	.2868(2)	.2924(7)	.1311(11	SXD	159

Table 51. Selected interatomic distances for $TlBa_2Ca_2Cu_3O_9$ structures

#	Cu-O1[4]	Cu2-O3[4]	Cu2-O3 [1]	Tl-O3[2]	Tl-O4[2]	Tl-O4[2]	mean Tl-0	Ba-O2 [4]	Ba-O3 [1]	Ba-O4[1]	mean Ba-O	Ca-O1[4]	Ca-O2[4]	mean Ca-O	Cu2-O2-Cu2
212	1.9265(5)	1.9270(6)	2.73(2)	2.06(2)	2.503(4)	2.966(5)	2.51	2.816(9)	2.818(4)	2.751(2)	2.81	2.547(2)	2.433(8)	2.49	177.3(8)
214	1.9266(5)	1.930(8)	2.76(3)	2.007(3)	2.725(7)	2.55	2.486	2.852(9)	2.823(8)	2.738(3)	2.826	2.538(5)	2.411(7)	2.475	174.8
215	1.924	1.925	2.743	2.027	2.496	2.966	2.496	2.828	2.818	2.733	2.813	2.535	2.433	2.484	176.1
217	1.9102(1)	1.9140(7)	2.391(13)	1.97(1)	2.45(4)	2.98(4)	2.47	2.636(6)	2.789(3)	2.631(6)	2.703	2.607(9)	2.383(9)	2.495	172.8(6)
218	1.9040(5)	1.9059(7)	2.37(2)	2.01(2)	2.23	3.19	2.48	2.655(7)	2.760(4)	2.633(1)	2.699	2.509(3)	2.442(7)	2.378	174.9(7)

octahedron with four longer in-plane Tl-O bonds (about 2.7 Å) and two shorter Tl-O bonds parallel to *c* (2.0Å)

Figures 20 and 21 highlight the close similarities between the Tl_2 and Tl_1 superconductors. These figures, furthermore, emphasize the modular layered aspect of copper oxide superconductors.

Several groups have successfully synthesized the 1-2-3-4[161-164,166] and 1-2-4-5[165-167] mem- ers of the Tl_1 series. Ihara *et al.*[163] prepared essentially pure 1-2-3-4 material and published its owder diffraction profile. Ihara *et al.*[164] used high-resolution transmission electron microscopy o document the structure, Haldar *et al.*[161] (Figure 19) illustrate the 4-1ayer variant, and Liang *et l.*[162] calculated trial fractional coordinates, but no three-dimensional structure refinements of his phase had been published as of this writing.

Sugise *et al.*[165] used pure 1-2-3-4 as starting material in the synthesis of relatively pure -2-4-5 by heating, and consequent thallium removal. Gai *et al.* [167] studied "1-2-4-5" samples by igh-resolution transmission electron microscopy and observed numerous stacking faults with ommon slab-like regions of 1-2-3-4 and 1-2-5-6 structure. This behavior underscores the mportance of local, short-range effects in characterizing the structures and interpreting the prop- rties of high-temperature superconductors.

VII. Conclusions

What common structural themes unite the known layered copper-oxygen high-tempera- ure superconductors? The most obvious features are the CuO_2 sheets of corner-linked square- lane coordinated copper and apparent oxygen nonstoichiometry or cation disorder in layers that nterleave the CuO_2 sheets. In structures with more than one consecutive CuO_2 sheet, divalent r trivalent cations in eight coordination always act as spacers.

Within these constraints there are many possible variations. The spacer atoms range from a, Sr, and Ba, to Y and the rare earths. Interleaving slabs include Cu, CuO, Cu_2O_2, $CuPb_2O_2$, n_2O_2, Bi_2O_2, Tl_2O_2, and TlO. One can imagine many additional structures simply by stacking alternating the known modules in different sequences. In addition, layer structures with other, yet undiscovered, modules undoubtedly exist. The principal constraints include approximate odule charge balance and a square lattice approximately 3.9 Å on edge. We can thus anticipate e discovery of dozens of other superconducting compounds, each with the extraordinary ysical properties and great structural beauty characteristic of these remarkable materials.

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THE MICROSTRUCTURE OF HIGH-TEMPERATURE OXIDE SUPERCONDUCTORS

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