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High-Pressure Synthesis of Homologous Series of High Critical Temperature (T_c) Superconductors

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Under high pressure, a variety of elements can be accommodated at the cation sites in the charge reservoirs of cuprate superconductors. Furthermore, high pressure allows the insertion of higher number of CuO_2 planes (i.e., the insertion period of a charge reservoir becomes variable). Because of these effects, many new high critical temperature (T_c) superconductors have been discovered under high pressure. In this paper, we will survey their structural and superconducting properties. The role of high pressure and its effect on the size mismatch between the charge reservoir and the CuO_2 plane will also be discussed.

Contents

1. Introduction

The key structural unit in high critical temperature (T_c) superconductors is the CuO_2 plane shown in Figure 1. This two-dimensional (2D) plane consists of divalent copper and oxygen ions and has a formal charge of 2−. Although the mechanism of high T_c superconductivity has not yet been fully elucidated, there is a general consensus that this plane plays an essential role in the formation of the Cooper pairs, and therefore, in the appearance of superconductivity itself. Divalent copper ion is a d^9 ion and metallic behavior might be expected for a compound containing such an ion. However, because of a strong electron−electron interaction, the ninth electron tends to be localized on each copper site, resulting in semiconducting or insulating behavior. This phenomenon also happens in the CuO_2 plane, and its ground state is not superconducting but is antiferromagnetic instead. Ten years ago, Bednorz and Müller discovered that superconductivity appears if this plane is doped with holes (or electrons), and the formal valence of the copper ion deviates from 2+.[1] After enormous subsequent studies, researchers reached to the conclusion that there is an optimum doping level for holes (electrons) and that both underdoping and overdoping may deplete superconductivity or even completely suppress it. A high T_c superconductor should, therefore, have at least two structural features; (i) a layered structure based on the CuO_2 plane, and (ii) in addition to the CuO_2 plane, a certain structural block, called a charge reservoir, where a proper number of carriers are created and doped into the CuO_2 plane.

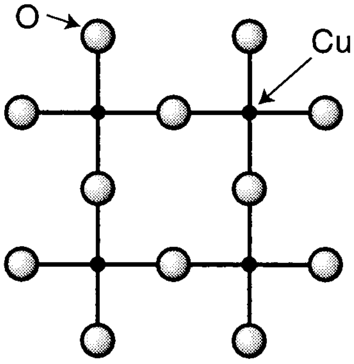

Figure 1. The CuO_2 2D plane.

At the early stage of high-T_c superconductor research, conventional solid-state reaction under ambient pressure was the most important technique for the exploration and synthesis of new materials. However, high-pressure synthesis has been recognized as another powerful technique in these several years because of its various successful achievements. Under high pressure, a wider variety of charge reservoirs can be adjusted to the CuO_2 plane and many new high T_c superconductors can thus be stabilized. In this review, we will survey their structural and superconducting properties and compare them with the ambient-pressure stable phases. Furthermore, the role of high pressure in stabilizing the layered structures will be discussed in connection with the size mismatch between the charge reservoir and the CuO_2 plane.

2. Crystal Structures of High T_c Superconductors

The formal charge of the CuO_2 plane is 2−, and therefore the simplest layered structure based on it is formed by insertion of a divalent cation plane. The so-called "infinite-layer" compound $Sr_xCa_{1-x}CuO_2$ has this type of structure and constitutes the common parent oxide for all high T_c cuprate superconductors. It has a very narrow homogeneity range near $x = 0.15$ under

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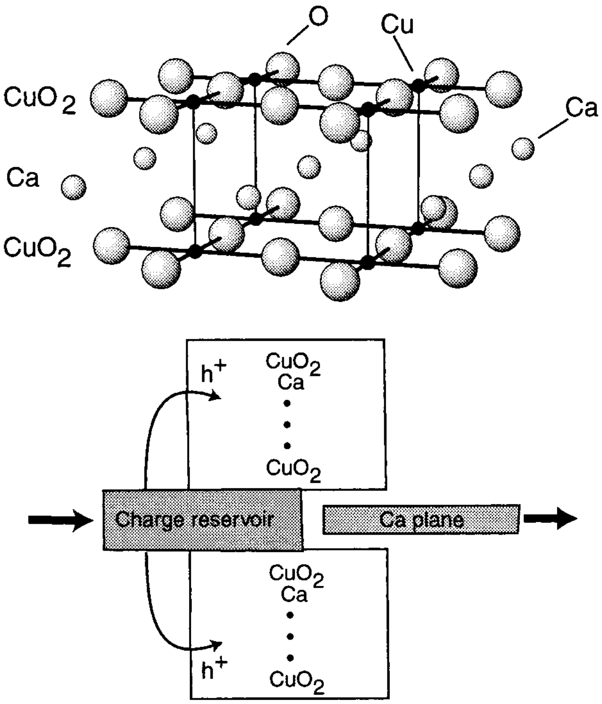

Figure 2. Crystal structure of infinite-layer $CaCuO_2$ and hole-doping mechanism into the CuO_2 plane.

ambient pressure.[2] Under high pressure, however, an entire solid solution can be formed with respect to Sr/Ca.[3] Its structure consists of alternate stacking of the (Sr,Ca) and CuO_2 planes as shown in Figure 2 (drawn for the end member of $CaCuO_2$). This phase itself is not superconducting because copper is divalent and no carriers (neither electrons nor holes) are present. Many studies since the pioneering work by Bednorz and Müller[1] have shown that superconductivity appears in the CuO_2 plane after doping it with carriers up to a certain level.

A simple way to dope carriers into the CuO_2 plane in the infinite-layer compound is through heterovalent metal substitution for Ca/Sr. An *n*-type superconductor with electrons as carriers is formed by partial replacement of Ca/Sr by a trivalent metal such as lanthanum or neodymium.[4,5] This may imply that a *p*-type superconductor with holes as carriers can be formed by monovalent metal (such as sodium) substitution for Sr/Ca. However, attempts to produce such a material have not succeeded thus far. The possibility of the carrier doping seems to relate to the coordination number of the copper atom. In the infinite layer compound, the copper atom is surrounded by four coplanar oxygen atoms and it is empirically known that an increase of the coordination number to five or six is needed for the hole doping.

The hole doping to the CuO_2 plane has been, therefore, achieved through a completely different procedure rather than the simple substitution for Sr/Ca. If every other Ca plane in the infinite-layer $CaCuO_2$ is removed and instead BaO−TlO−BaO triple planes are inserted, we will obtain a compound $TlBa_2CaCu_2O_7$. In this phase, the Cu atom is surrounded by a pyramid of five oxygen atoms (shown in Figure 3) and this is the necessary crystal chemical factor to introduce holes. The triple planes have a formal charge of 1+ per unit formula, assuming trivalent state for thallium, and this value is lower than 2+ of the Ca plane. In other words, the substitution for every other Ca plane results in creation of one hole per unit formula of $TlBa_2CaCu_2O_7$ or 0.5 hole per copper atom. Substitution of every third Ca plane by triple planes yields $TlBa_2Ca_2Cu_3O_9$ (Figure 3), or more generally, substitution for every n^{th} Ca plane yields $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$.[6−13] Structural blocks such as BaO−TlO−BaO supply carriers to the CuO_2 plane (see Figure 2), and the term "charge reservoir" is derived from this role.

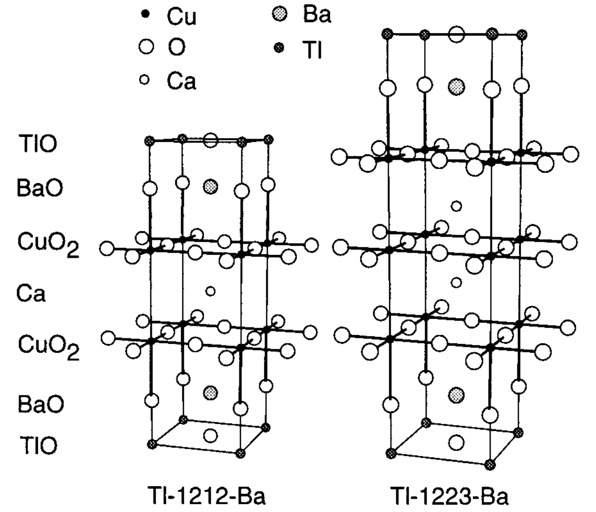

Figure 3. Crystal structures of $TlBa_2CaCu_2O_7$ [Tl-1212-Ba] and $TlBa_2Ca_2Cu_3O_9$ [Tl-1223-Ba].

If one hole is created in a charge reservoir, the average copper valence is expected to decrease, obeying the relation $2 + 1/n$, with increasing *n*-value. There are two types of Cu atoms (pyramidal and square planar coordinated) in the phases with $n > 2$. The hole distribution is not simple, therefore, and the average copper valence may not be an exact measure of the effective carrier concentration. Nevertheless, a systematic decrease of the carrier concentration with *n* has been reported for several systems and the *n*-value seems to be one of the most important factors governing the carrier concentration. In addition, further complications are derived from various kinds of crystal defects which are often introduced into the high T_c superconductors. An average copper valence based on an ideal composition may sometimes be inaccurate because of excess lattice oxygen, oxygen or cation vacancies, mutual substitution of cations, etc.

In this paper, we will discuss five types of charge reservoir blocks whose ideal compositions are AO−MO−AO, AO−MO−MO−AO, AO−MO−AO−MO−AO, and AO−AO. Here, M is a metal that characterizes the charge reservoir and A is an alkaline earth or a rare earth metal. From the AO−MO−AO type block, a homologous series $MA_2Ca_{n-1}Cu_nO_{2n+3}$ is formed, and we will use a simple abbreviation M-12(*n*-1)*n*-A to express it (e.g., Tl-12(*n*-1)*n*-Ba for $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$). The 1, 2, (*n*-1), and *n* imply an atomic ratio of M, A, Ca, and Cu (in the CuO_2 plane). The M and A in the abbreviation specify the constituent elements of the charge reservoir. Following the same nomenclature, M-22(*n*-1)*n*-A and M-23(*n*-1)*n*-A correspond to the AO−MO−MO−AO and AO−MO−AO−MO−AO blocks, respectively. The last block, AO−AO, does not contain the MO

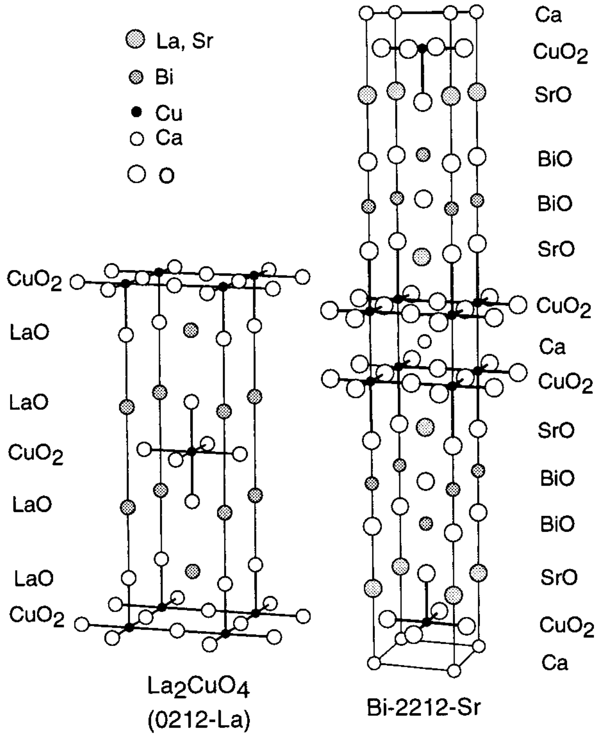

Figure 4. Crystal structures of La_2CuO_4 [0212-La] and Bi-2212-Sr. Although they belong to the orthorhombic system, the quasitetragonal cells are drawn.

plane and we will use the abbreviation 02(*n*-1)*n*-A to express an $A_2Ca_{n-1}Cu_nO_{2n+2}$ series based on such structural unit. The calcium site is often completely or partly replaced by a foreign element such as yttrium or strontium. In such a case, we will add the metal placed at the Ca site to the abbreviation (e.g., M-12(*n*-1)*n*-A-Y or M-12(*n*-1)*n*-A-(Sr,Ca); vide infra). Another case may be the halogen substituting for oxygen in the AO-AO block to yield an $A_2Ca_{n-1}Cu_nO_{2n}X_2$ series, which will be abbreviated as 02(*n*-1)*n*X-A.

We present three more examples of high T_c superconductors $(La,A)_2CuO_4$ (A = Ca, Sr, Ba), $YBa_2Cu_3O_7$, and $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$. If every Ca plane in $CaCuO_2$ is substituted by double LaO−LaO planes, we obtain the well-known compound La_2CuO_4 (Figure 4). Because the LaO−LaO double planes have a formal charge of 2+ (which is the same as that of the Ca plane), no carriers are created through this substitution and La_2CuO_4 has semiconducting behavior. However, after the substitution, the copper coordination changes from square planar to octahedral and hole introduction becomes possible through partial substitution of an alkaline earth metal for lanthanum. The $(La,Ba)_2CuO_4$ belongs to this class of compounds and was found to be superconducting as early as 1986.[1] This system sometimes has different designations; for examples, La-system, 214, K_2NiF_4-type, etc., but is described as 0201-(La,Ba) in this paper because more general 02(*n*-1)*n*-type phases appear under high pressure. It should be noted that for La_2CuO_4 stacking of planes of LaO−LaO−CuO_2 repeats twice within the *c*-axis length. This double sequence is derived from the presence of a glide plane between the LaO planes, and in general, a double (single) sequence is expected if a charge reservoir includes an even (odd) number of planes. In other words, the number of molecules in a unit cell is two (z = 2) or one (z = 1) for even or odd number of planes, respectively. In La_2CuO_4, however, z is actually four because of its distortion to the orthorhombic system.

In $YBa_2Cu_3O_7$, which is the first superconductor discovered with a T_c above the liquid nitrogen temperature,[14] the charge reservoir consists of triple BaO−CuO−BaO planes. If every other Ca plane in the infinite layer oxide is substituted by these triple planes, we would obtain a hypothetical phase $CuBa_2CaCu_2O_7$ [Cu-1212-Ba]. Further replacement of a Y plane for the Ca plane yields $YBa_2Cu_3O_7$, and one hole per molecule is created through these replacements. According to the aforementioned nomenclature, this $YBa_2Cu_3O_7$ phase can be expressed as Cu-1212-Ba-Y (Y is added to show the presence of the Y plane instead of the Ca one). The last example is $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ [Bi-22(*n*-1)*n*-Sr], which includes composite planes of SrO−BiO−BiO−SrO as the charge reservoir (Figure 4).[15−20] Assuming trivalent bismuth, the composite planes have a formal charge of 2+ and no holes are created. In this series of phases, excess oxygen in the BiO plane is believed to play an essential role for the creation of holes. Indeed, the phases have highly complicated modulated structures that are caused by inclusion of excess oxygen into the BiO plane.[21] Similar 22(*n*-1)*n* phases exist for M = Tl. Therefore, thallium can form two different homologous series, Tl-12(*n*-1)*n*-Ba and Tl-22(*n*-1)*n*-Ba.[6−13,22−25]

Thus far, hundreds of high T_c superconductors have been discovered under ambient pressure and they can be classified taking into account the different characteristics of their charge reservoirs. However, there is a strict restriction on the insertion interval of a charge reservoir (the *n*-value); that is, most of the superconductors prepared under ambient pressure have *n*-values less than three. Exceptions are seen in only four cases: Bi-22(*n*-1)*n*-Sr ($n \leq 3$), Tl-12(*n*-1)*n*-Ba ($n \leq 5$), Tl-22(*n*-1)*n*-Ba ($n \leq 4$), and Hg-12(*n*-1)*n*-Ba ($n \leq 4$) with BaO−HgO_δ−BaO charge reservoir.[26,27] It is worth noting that T_c values >100 K are only observed in these homologous series.

3. Homologous Series of Superconductors Stable under High Pressure

In Table 1 are listed homologous series of superconductors prepared under high pressure. It is clear from this table that high pressure stabilizes higher order phases with large *n* values for a variety of charge reservoirs. Moreover, most of the high-pressure stable series contain members whose T_cs are >100 K. In-plane size mismatch between the CuO_2 plane and the charge reservoir seems to be a key factor governing the energetics of the layered structures of high T_c superconductors. High pressure is expected to greatly affect the energetics because different structural blocks have different compressibilities. In connection with this concept, several high-pressure stable series are discussed later in further detail.

High-pressure syntheses of oxide superconductors are usually conducted at pressures up to 8 GPa and temperatures up to 1400 °C. Piston cylinder, Bridgman anvil, belt, multi-anvil apparatus, etc. may be used to generate such high-pressure/high-temperature conditions. In particular, belt and multi-anvil devices are often used in high-T_c-related synthesis research. The

Table 1. Superconducting Transition Temperatures (in K) of Homologous Series of Superconductors Prepared under High Pressure

homologous series	1	2	3	4	5	6
(Cu,C)-12(*n*-1)*n*-Ba			67	117		
(Cu,C)-12(*n*-1)-Sr		92			70	
(Cu,C)-23(*n*-1)*n*-Ba			91	113	90	
(Cu,S)-12(*n*-1)*n*-Sr			100∼60 ($n = 3∼7$)			
(Cu,P)-12(*n*-1)*n*-Sr-(Ca,Y)			112∼80 ($n = 3∼6$)			
(Cu,Ge)-12(*n*-1)*n*-Sr-(Ca,Y)			90	89		78
(Cu,Cr)-12(*n*-1)*n*-Sr	0	81	103	71	65	32
(C,B)-12(*n*-1)*n*-Sr	50	105	115			
(C,B)-12(*n*-1)-Ba			120			
B-12(*n*-1)*n*-Sr			75	110	85	71
Al-12(*n*-1)*n*-Sr			78	110	83	
Ga-12(*n*-1)*n*-Sr		0	70	107		
C-12(*n*-1)*n*-Ca		47				
Pb-12(*n*-1)*n*-Sr		≈70	122			
Hg-12(*n*-1)*n*-Ba	92[a]	126[a]	135[a]	126[a]	112	106
Hg-22(*n*-1)*n*-Ba-(Ca,Y)		45				
(Hg,Tl)-22(*n*-1)*n*-Ba		100[a]	120	115	92	
02(*n*-1)*n*-Sr	0	70	109	83		
02(*n*-1)*n*F-Sr	46[a]	99	111	≈40	≈40	
02(*n*-1)*n*Cl-Sr		80	≈46			

[a] The phase can be prepared under ambient pressure.

reader is referred elsewhere[28] for more detailed descriptions of high-pressure-generating techniques. In the high-pressure processing of a high T_c material, the starting mixture is usually sealed into a gold capsule that offers a completely closed environment. To control the oxygen pressure during the processing, a proper oxidizer such as Ag_2O, $KClO_4$, SrO_2, BaO_2, etc. may be added into the mixture.

3.1. Oxycarbonate Superconductors. In 1992, the oxycarbonate compound $(Cu,C)(Sr,Ba)_2CuO_5$ [(Cu,C)-1201-(Sr,Ba)] was reported to become superconducting.[29] This phase is stable under ambient pressure and has as a charge reservoir the block (Ba,Sr)O−(Cu,C)O−(Ba,Sr)O. The carbon atom forms a CO_3 oxyacid group in the structure. Soon after the discovery, it was found that carbon can partially replace various metals in superconductors, such as copper in the charge reservoir of Cu-1212-type phases,[30] bismuth in Bi-22(*n*-1)*n*-Sr,[31] thallium in Tl-12(*n*-1)*n*-(Sr,Ba),[32] mercury in Hg-12-(*n*-1)*n*-Ba,[33,34] etc. Now, oxycarbonates are recognized as one of the largest families of superconductors.

The high-pressure technique allowed an even wider variety of oxycarbonates to be discovered. The $(Cu,C)Ba_2Ca_{n-1}Cu_nO_{2n+3}$ [(Cu,C)-12(*n*-1)*n*-Ba, $n = 3, 4$] and $(Cu,C)_2Ba_3Ca_{n-1}Cu_nO_{2n+5}$ [(Cu,C)-23(*n*-1)*n*-Ba, $n = 3, 4, 5$] series of superconductors are typical examples of high-pressure stable oxycarbonates.[35−38] The former series has BaO−(Cu,C)O−BaO as a charge reservoir. The partial occupation of copper in the middle plane is crucial for hole doping because BaO−CO−BaO has formal charge of 2+ and no holes are thus created. For both (Cu,C)-1223-Ba and (Cu,C)-1234-Ba, electron microscope observations showed superlattices of $a_s = 2a$, $b_s = b$, $c_s = 2c$ with respect to simple tetragonal lattices.[35,38] These results are due to ordering of copper and carbon in the (Cu,C) plane; they are placed as Cu−C−Cu−C... along the *a*-axis resulting in the double periodicity of 2a. In an adjacent (Cu,C) plane, the phase of the Cu−C sequence is different as in C−Cu−C−Cu..., causing double periodicity along the *c*-axis (Figure 5). The composition of the charge reservoir is, therefore, $BaO-(Cu_{0.5}C_{0.5})O-BaO$ and it creates one hole per unit formula. A powder neutron study carried out for (Cu,C)-1234-Ba is consistent with the structural model of Figure 5.[39]

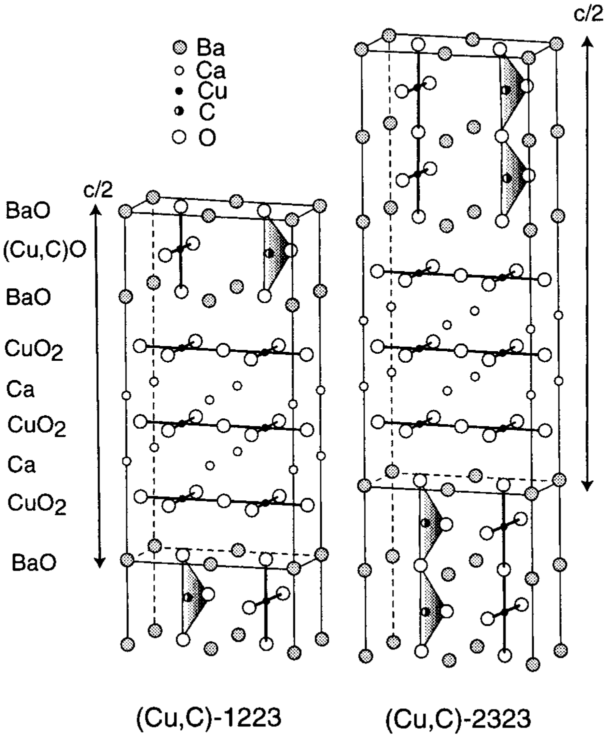

Figure 5. Crystal structures of (Cu,C)-1223-Ba and (Cu,C)-2323-Ba.

The (Cu,C)-1234-Ba phase has T_c of 117 K, which is one of the highest values among oxycarbonate superconductors. Moreover, it showed an extremely high critical current density (J_c) after irradiation by neutrons.[40,41] This remarkable property seems to relate to its less anisotropic electronic structure derived from the partial occupation of copper in the charge reservoir.[40,41]

In the other series of superconductors, (Cu,C)-23(*n*-1)*n*-Ba, the charge reservoir consists of BaO−(Cu,C)O−BaO−(Cu,C)O−BaO composite planes; it includes two (Cu,C)O planes between three BaO planes. According to high-resolution transmission electron microscopy (HRTEM) images, the copper and carbon atoms are arranged as Cu−C−Cu−C−, giving double periodicity along the *a*-axis and the composition of $(Cu_{0.5}C_{0.5})O$ as well as in 12(*n*-1)*n*.[36,37] Two (Cu,C) planes within a charge reservoir have the same phase with respect to the Cu−C sequence, making pairs of Cu−Cu and C−C along the *c*-axis (Figure 5). In an adjacent charge reservoir, the Cu−C sequence is out-of-phase in $n = 3$, with a superlattice of $a_s = 2a$, $b_s = b$, $c_s = 2c$, whereas it is in-phase for $n = 4, 5$, with superlattices of $a_s = 2a$, $b_s = b$, $c_s = c$. The composite planes based on the $(Cu_{0.5}C_{0.5})O$ composition cannot create holes as in SrO−BiO−BiO−SrO. Although the detailed hole doping mechanism is not yet well known for this series of phases, it seems to relate to a certain kind of defect, such as excess oxygen or deviation of Cu/C ratio from unity in the (Cu,C) plane.

The (Cu,C)-23(*n*-1)*n*-Ba series include three BaO planes in the charge reservoir and such a structural unit is unusual in high T_c superconductors. Every barium atom is bound to at least one CO_3 group according to the structural model in Figure 5, and this seems to be a key factor for stabilizing the barium-rich charge reservoir.

Replacement for barium in the aforementioned oxycarbonate phases with strontium was tried under high pressure and $(Cu,C)Sr_2Ca_{n-1}Cu_nO_{2n+3}$ [(Cu,C)-12(n-1)-n-Sr] compounds corresponding to (Cu,C)-12(n-1)n-Ba were found.[42,43] However, only two discrete members with $n = 2, 5$ have been prepared thus far.[42,43] Although the reason for this is not clear yet, high-pressure synthesis experiments indicated that the $n = 3$ and $n = 4$ members are not stable but always undergo disproportion to the $n = 2$ and $n = 5$ phases.[43] Another interesting feature of the (Cu,C)-12(n-1)n-Sr series is a different arrangement of Cu−C in the (Cu,C) plane, that is, a four times periodicity along the a-axis was observed for the $n = 2$ phase rather than the 2a one.[42] This superstructure was first explained by a carbon vacancy introduced into every fourth carbon site, implying a composition $C_{1-\delta}Sr_2CaCu_2O_y$ ($\delta \approx 0.25$).[42] However, a subsequent study suggested that this phase has a $(Cu_{0.25}C_{0.75})Sr_2CaCu_2O_7$ composition and the 4a periodicity is due to ordering of Cu and C as C−C−C−Cu... instead.[44] On the other hand, superlattice spots were not observed in the electron diffraction patterns of the $n = 5$ phase, indicating a simple tetragonal structure.[44] This result reveals a random arrangement of Cu and C and the presence of a solid solution with respect to Cu/C in the (Cu,C) plane, although its range has not yet been determined.

Calcium substitution for barium in (Cu,C)-12(n-1)n-Ba was also tried under high pressure and a new oxycarbonate superconductor $CCa_3Cu_2O_{7+\delta}$ was found.[45] This phase is a rare example of a high T_c superconductor that includes only calcium as an A site metal and can be expressed as C-1212-Ca from its converted composition $CCa_2CaCu_2O_{7+\delta}$. Differing from the barium- and strontium-based systems, the charge reservoir of this phase is occupied only by carbon without partial replacement of copper. As already stated, the copper occupation is crucial for the carrier doping. In the C-1212-Ca phase, holes are doped by introduction of excess oxygen into the CO plane.[45]

Partial substitution of boron for carbon in the AO−CO−AO block is also effective for carrier doping because boron is trivalent. This attempt was done successfully under high pressure to obtain (B,C)-based phases, $(B,C)Sr_2Ca_{n-1}Cu_nO_{2n+3}$ [(B,C)-12(n-1)n-Sr, $n = 1, 2, 3$] and $(B,C)Ba_2Ca_2Cu_3O_9$ [(B,C)-1223-Ba].[46,47] All of these phases show superconductivity, in particular, the T_c of (B,C)-1223-Ba increases to 128 K at 8 GPa.[47]

3.2. (Cu,M)-12(n-1)n (M = S, P, Ge, Cr) Series.

Stimulated by the successful preparations of the oxycarbonate superconductors, other oxyacid groups were extensively introduced into the charge reservoir and new oxysulfates were prepared. The oxysulfate family[48] $(Cu,S)Sr_2Ca_{n-1}Cu_nO_{2n+3}$ [(Cu,S)-12(n-1)n-Sr] has as a charge reservoir SrO−(Cu,S)O−SrO, where copper and sulfur are arranged as Cu−S−Cu−S... along the a-axis, resulting in a superlattice cell of $a_s = 2a$, $b_s = b$, $c_s = 2c$ or $c_s = c$ with respect to the tetragonal cell. An adjacent (Cu,S) plane has usually a reversed Cu−S sequence giving $c_s = 2c$, however the $c_s = c$ structure sometimes appears locally or in phases with large n values. Basic structural features of this series are, therefore, very similar to those of (Cu,C)-12(n-1)n-Ba except for the appearance of the $c_s = c$ structure. In an oxysulfate, the sulfur atom is usually hexavalent forming a SO_4 group, which seems to be the case in (Cu,S)-12(n-1)n-Sr. However, we cannot expect hole doping assuming the hexavalent state of sulfur and the composition of $SrO-(Cu_{0.5}S_{0.5})O-SrO$. Holes may originate from excess oxygen, cation vacancies, and/or a deviation of Cu/S ratio from unity in the (Cu,S) plane.

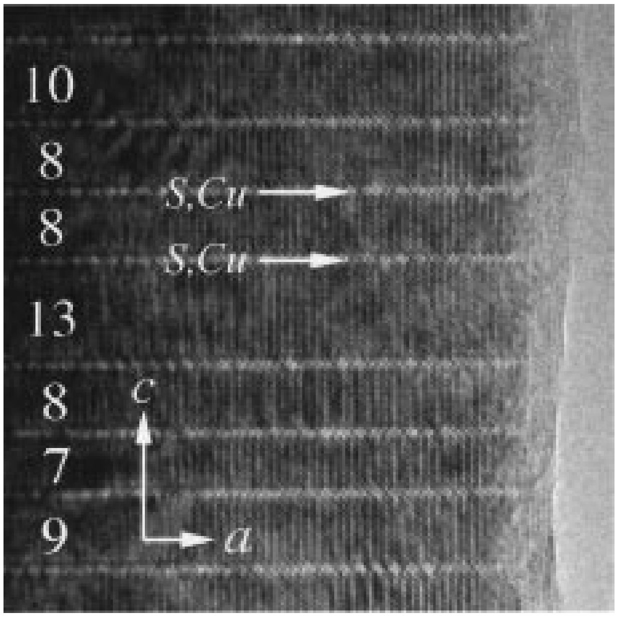

Figure 6. HRTEM image of the (Cu,S)-phase projected along the b-axis.[48] Numbers shown indicate number of the CuO_2 planes. This phase was identified as n = "7" by X-ray diffraction.

The easy insertion of intergrowths of phases with different n-values is worth noting for the oxysulfate family. Although this type of defect is often observed in high T_c superconductors, it is far more pronounced in the oxysulfate family. Figure 6 shows the HRTEM image of an oxysulfate phase projected along the b-axis.[48] This phase was identified by X-ray diffraction as the n = "7" member. However, various phases with n up to 13 can be seen intergrowing randomly in Figure 6. Similar defects were observed in every member from n = "3" to n = "7", and only an averaged n-value can be defined for this series of phases. Superconducting transitions of the oxysulfate phases are generally broad, which may be due to the intergrowth defects.

A series of oxyphosphate superconductors was also prepared under high pressure.[49] The ideal formula for this series is $(Cu,P)Sr_2(Ca,Y)_{n-1}Cu_nO_{2n+3}$ i.e., (Cu,P)-12(n-1)n-Sr-(Ca,Y). The copper and phosphorus atoms in the (Cu,P) plane are arranged as Cu−P−Cu−P... originating an $a_s = 2a$, $b_s = b$, $c_s = 2c$ superlattice. It is difficult to obtain high-quality samples for this series; the high-pressure sample is usually a multiphase mixture including two or more members of the series and impurity phases. This is partly due to easy insertion of intergrowths of phases with various n-values similar to the oxysulfate system. In addition, the phase appearance in the oxyphosphate system seems to highly correlate with the oxygen content and the yttrium content of the starting mixtures. Systematic synthesis experiments for the starting composition of $(Cu_{0.5}P_{0.5})$-$Sr_2(Ca_{1-x}Y_x)_2Cu_3O_y$ (1223 composition) indicated that phases with $n = 4$ and 5 appear in the low y and low x region, whereas the $n = 2$ phase is in the high y and high x region.[49] The $n = 3$ phase is stabilized in a fairly narrow region of the 2D section of y and x. In addition, a higher order phase of $n = 6$ is formed starting from a yttrium-free mixture ($x = 0$). These results suggest that a phase with a small (large) n-value has a high (low) equilibrium oxygen pressure in a synthesis process under high temperature/high pressure. Increase of the initial oxygen content causes high oxygen pressure in the synthesis reaction process, whereas increase of the yttrium content results in the decrease of equilibrium oxygen pressure of a phase through the decrease of the average copper valence. Both processes are effective in stabilizing superconducting phases with small n-values. The relationship between the oxygen pressure and the phase formation will be discussed in further detail later.

In the aforementioned (Cu,M)-based phases with M = C, S, and P, copper and M atoms are always arranged in an ordered way except for (Cu,C)-1245-Sr. This order seems to concern two factors: (i) the large difference between ionic radii of copper and M, and (ii) the strong interaction between an oxyacid group and an alkaline earth atom in the charge reservoir. The ordered arrangement is favorable because (i) it diminishes instability due to the size mismatch through hindering concentration of smaller or larger elements, and (ii) every alkaline earth atom can bond to an oxyacid group.

Under high pressure, a (Cu,M)-type homologous series is also formed for M = Ge whose formula is (Cu,Ge)-$Sr_2(Ca,Y)_{n-1}Cu_nO_{2n+3}$ [(Cu,Ge)-12(n-1)n-Sr-(Ca,Y), n = 3, 4, 6].[50,51] Electron microscope observations showed simple tetragonal lattices without any superstructures for all members of the series indicating a random arrangement of germanium and copper in the (Cu,Ge) plane. Furthermore, the Cu/Ge ratio within the plane seems to deviate from unity; it is close to 0.6/0.4 for $n = 3$, and it is 0.7/0.3 for $n = 4$ and $n = 6$ according to synthesis experiments.[50,51] The germanium atom has a relatively large ionic radius and forms a weak oxyacid when compared with carbon, sulfur, or phosphorus, and these facts seem to relate to the random arrangement of Cu/Ge. In a way similar to (Cu,P)-12(n-1)n-Sr-(Ca,Y), partial yttrium substitution for calcium was required to synthesize the phases with $n = 3$, 4, whereas the $n = 6$ phase was obtained from an yttrium-free mixture. The $n = 5$ phase has not been prepared yet.

Very recently, a new series of Cr-based superconductors $(Cu,Cr)Sr_2Ca_{n-1}Cu_nO_{2n+3+\delta}$ [(Cu,Cr)-12(n-1)n-Sr] were discovered by using the high-pressure synthesis technique.[52] One of the striking features of this series is the wide range of its members synthesized in bulk form ($1 \leq n \leq 9$). HRTEM observations[52] indicated a random distribution between copper and chromium in the (Cu,Cr) plane for the most members of the series, which may be caused by the fact that chromium forms a weak oxyacid. However, very weak superlattice spots were sometimes observed in the electron diffraction patterns of the $n = 4$ phase, which suggests their local and imperfect ordering, (e.g., Cu−Cr−Cu−Cr...).

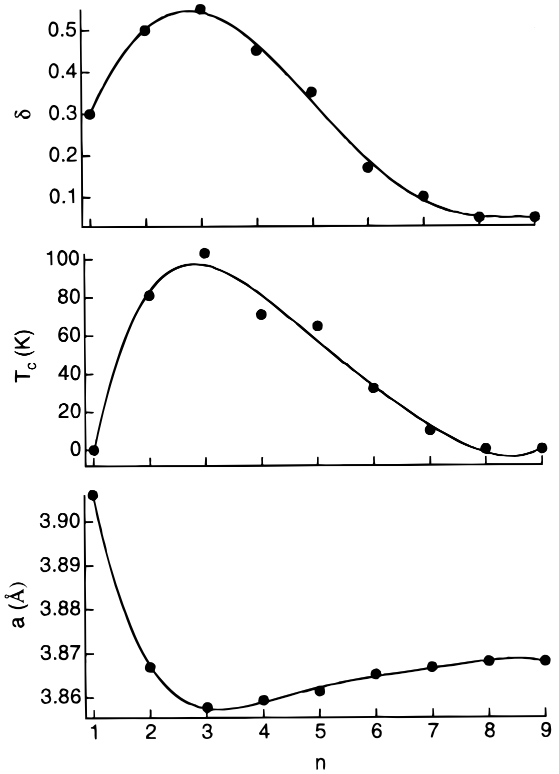

Figure 7. Variation of the a-parameter, T_c and the optimum excess oxygen content δ in starting mixture for (Cu,Cr)-12(n-1)n-Sr.[52]

Chromium has been known as an effective charge reservoir substituent for mercury in the Hg-12(n-1)n-A (A = Sr, Ba) family,[53−55] its oxycarbonate derivatives[56] or thallium for the Tl-12(n-1)n-A family,[57−59] and its oxycarbonates.[60] According to neutron diffraction studies for some of these phases,[59,61,62] chromium adopts tetrahedral coordination, forming a CrO_4 group. This result implies that chromium has a hexavalent state in an oxide superconductor because trivalent chromium prefers strongly octahedral coordination because of its large crystal field stabilization energy in an octahedral site. Chromium in the (Cu,Cr)-12(n-1)n-Sr series appears to be hexavalent as well, and if this is the case, the SrO−$(Cu_{0.5}Cr_{0.5})$O−SrO charge reservoir cannot create holes. According to electron probe microanalysis (EPMA), the Cr content was close to that in the starting mixture (i.e., close to 0.5 in each member of the series[52]), which denies a hole-doping mechanism based on overstoichiometry of copper in the charge reservoir. There are two important defects that concern the hole doping: excess oxygen and copper vacancies in the Cu/Cr site. For (Cu,Cr)-1201-Sr, both defects seem to exist, but the excess oxygen content tends to decrease with n and the cation vacancies in the charge reservoir seem to play a predominant role for the creation of holes.[52]

Each chromium-based phase belongs to the tetragonal system and the c-axis increases linearly with n with a slope of ≈3.2 Å, which reflects the thickness of the CuO_2−Ca composite plane. The variation of the a-parameter is rather unusual, as is shown in Figure 7; it decreases until $n = 3$ and then presents a smooth increase for $n > 3$, showing a correlation with T_c. The first large decrease seems to relate to the excess oxygen because its content also decreases with n.[52] When a relatively small cation is included in a charge reservoir, the *a*-parameter of a homologous series tends to increase with n for two reasons: (i) increasing number of CuO_2 planes that have a larger in-plane size, and (ii) a decrease of the hole concentration with n. The latter is due to the fact that holes are doped into in-plane Cu−O antibonding orbitals, a procedure that strengthens the Cu−O bond. Furthermore, for $n \rightarrow \infty$, the *a*-parameter should approach that of the infinite-layer $CaCuO_2$ (3.8526 Å).[3] As is shown in Figure 7, the *a*-parameter of the chromium system is larger than this value for the entire range of n despite a relatively small ionic radius of the hexavalent chromium. This result may suggest a complex arrangement of chromium, copper, and oxygen in the (Cu,Cr) plane.[59,61,62]

The T_c presents a variation from complete suppression at $n = 1$ via the maximum of 103 K at $n = 3$, then to complete suppression again for $n \geq 8$ (Figure 7). It is believed that this variation reflects the variation of the hole concentration; that is, the system changes from an overdoped region of holes for $n \leq 2$ to an underdoped region for $n \geq 4$ through the optimum point at $n = 3$.[52]

Oxygen pressure is an important processing parameter for phase formation and stabilization in addition to pressure and temperature. If we assume that a constant number of holes is created in the charge reservoir throughout a series of phases and the holes are equally distributed in all CuO_2 planes, the hole concentration per copper atom decreases linearly with n. This variation of the hole concentration (average copper valence) with n suggests that a higher (lower) oxygen pressure is needed to stabilize a lower (higher) n member, as seen in (Cu,P)-12(n-1)n-Sr-(Ca,Y). This relation was also studied in detail for the (Cu,Cr) system.[52] A desired phase with a particular n-value is not obtained only by adjusting cation composition, but a delicate control of the excess oxygen content is also required. In Figure 7, the optimum excess oxygen content δ in the starting mixture of $(Cu_{0.5}Cr_{0.5})Sr_2Ca_{n-1}Cu_nO_{2n+3+\delta}$ is plotted as a function of n. The optimum value by which a single or nearly single phase sample is obtained tends to decrease with increasing n for $n \geq 3$, which is consistent with the aforementioned discussion. Stability ranges with respect to δ are much wider in the $n = 1,2$ phases, and this relates to the apparent decrease of the optimum δ for $n \leq 2$.

3.3. M-12(*n*-1)*n* (M = B, Al, Ga) Series. As already described, boron was used as a substituent for carbon in the charge reservoir to yield a (C,B)-12(n-1)n series of superconductors. High-pressure experiments for a carbon-free system indicated that the complete substitution of boron for carbon was possible and that a series of phases $BSr_2Ca_{n-1}Cu_nO_{2n+3}$ [B-12(n-1)n-Sr] existed.[63−65] Total carbon contents of the samples were determined to check carbon contamination through the starting materials. They included only 0.10∼0.16 wt % carbon which indicated that the carbon content was at most 0.06∼0.10 per molecule.[63−65]

Thus far, four members of series with $n = 3$∼6 have been obtained in nearly monophasic bulk form.[63−65] They are essentially isostructural to the Tl-12(n-1)n-Ba phases. However, the oxygen position in the BO plane may be completely different from that in the TlO plane because boron is expected to adopt triangular or tetrahedral coordination. All these series of phases have simple tetragonal lattices, suggesting that oxygen atoms in the BO plane are more or less disordered in contrast to the gallium-based series of phases (vide infra).

A homologous series similar to B-12(n-1)n-Sr was also discovered for the aluminum-based system. Thus far, $n = 3$, 4, and 5 members of $AlSr_2Ca_{n-1}Cu_nO_{2n+3}$ [Al-12-(n-1)n-Sr] have been prepared in bulk form under high pressure.[66,67] The $n = 4$ member was isolated as a nearly single phase, however, high-quality samples of $n = 5$ were not obtained because of intergrowths of phases with higher n (up to 8).[66] Preparation of a good sample of $n = 3$ phase is also difficult because of the very high oxygen pressure required for the processing. Although the Al-1223-Sr phase was formed from a starting mixture with a large excess oxygen content, the product was a mixture and Al-1223-Sr was not the main phase.[67] Similar to the (Cu,P) system, the partial substitution of yttrium for calcium is quite effective in stabilizing the $n = 3$ phase.[67] A nearly monophasic sample was obtained from a starting mixture of $AlSr_2Ca_{1.9}Y_{0.1}Cu_3O_{9.1}$, which indicated that only 5% of the yttrium substitution brings an immediate result in decreasing equilibrium oxygen pressure of the $n = 3$ phase.

Gallium is located just below aluminum in the periodic table and a superconductor containing it was reported in 1991.[68] Its parent oxide is $GaSr_2YCu_2O_7$ [Ga-1212-Sr-Y] and superconductivity appears after partial substitution of calcium for yttrium.[68,69] The phase is stable under ambient pressure and crystallizes in the orthorhombic system with $a \approx b \approx \sqrt{2}a_p$ ($a > b$) and $c \approx 6c_p$ with respect to the cubic perovskite cell.[68−70] An interesting structural feature of this phase is the presence of GaO_4 tetrahedral chains (Figure 8).[68−70] The chains run along the *b*-axis of the orthorhombic lattice, which corresponds to the diagonal of the cubic cell and is the origin of the orthorhombic distortion.

Although the solubility of calcium is limited to $x \leq 0.3$ in $GaSr_2Y_{1-x}Ca_xCu_2O_7$ under ambient pressure, superconductivity appears at <40 K with the calcium substitution within this range.[68,69] In addition, superconductivity is sometimes observed below 70 K in a multiphase sample with high calcium content,[69] however the 70 K phase had not been identified. Application of the high-pressure technique solved this issue distinctly. Under high pressure, the solubility limit of calcium becomes much higher and the entire solid solution with $0 \leq x \leq 1$ was found to exist.[71] Superconductivity appears in the range $0.2 \leq x \leq 0.8$, and the phase with $x = 0.6$ has the maximum T_c of 49 K and a large enough superconducting volume fraction.[71]

At the first stage, the end member of the solid solution $GaSr_2CaCu_2O_7$ [Ga-1212-Sr] was misidentified as the 70 K phase.[71] However, a subsequent high-pressure study revealed that there exists higher order homologous phases of $GaSr_2Ca_{n-1}Cu_nO_{2n+3}$ [Ga-12(n-1)n-Sr] and its $n = 3$ member is responsible for the 70 K superconductivity.[72] Thus far, members up to $n = 4$ have been prepared.[72] Although the $n = 3$ phase was isolated as a single phase, a good sample has not been obtained yet for the $n = 4$ phase, mainly because of the intensive insertion of intergrowths of phases with $n = 3$ or 5.[73]

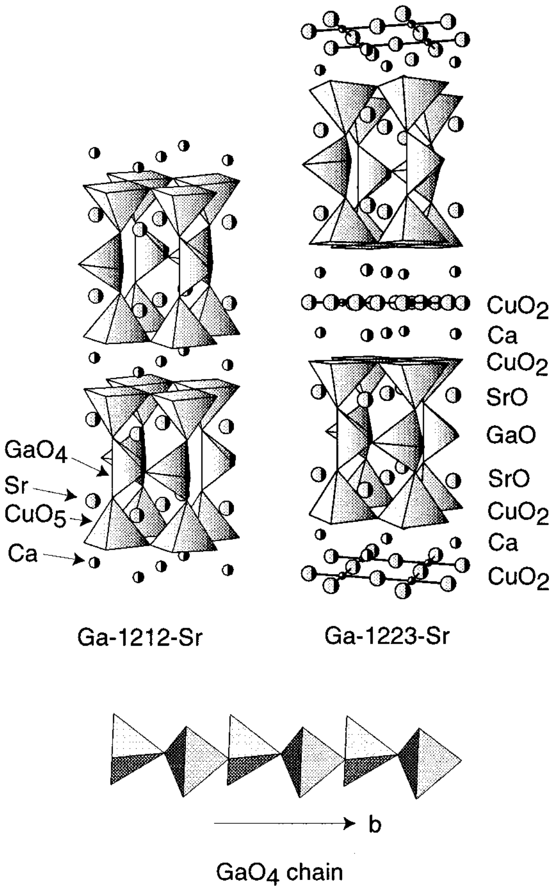

Figure 8. Crystal structures of Ga-1212-Sr and Ga-1223-Sr and the GaO_4 chain.

Structure analyses of Ga-12(n-1)n-Sr were carried out by electron microscope observations[73,74] and powder neutron diffraction experiments,[75] in particular for the $n = 3$ phase. As shown in Figure 8, the charge reservoir consisting of the GaO_4 chain is common for all members of the series. However, two types of GaO_4 chains (L and R) should be considered due to rotation of the GaO_4 tetrahedra in two different ways. By this additional freedom, superstructures with double periodicity along the direction normal to the chain appear in Ga-12(n-1)n-Sr.[73,74]

The M-12(n-1)n-Sr (M = B, Al, Ga) series of phases are good examples to discuss the correlation between structure, superconductivity, and size of the M metal because boron, aluminum, and gallium are all 3A elements and have similar chemical characteristics. Figure 9 shows the variation of the a-parameter as a function of n for the M-12(n-1)n-Sr series. As already stated, the a-parameter of a homologous series should approach that of infinite layer $CaCuO_2$ (= 3.8526 Å) when n → ∞. The a-parameter of B-12(n-1)n-Sr increases monotonically with increasing n, approaching the value in question. However, the difference in the a-parameters between B-12(n-1)n-Sr and $CaCuO_2$ is quite large when n is small, which reflects a large in-plane size mismatch between the charge reservoir block and the CuO_2 plane. Because boron is one of the smallest constituent elements in high T_c superconductors, the charge reservoir based on it has a small in-plane size. When the constituent element of the charge reservoir becomes larger, as in aluminum and gallium, the difference becomes smaller.

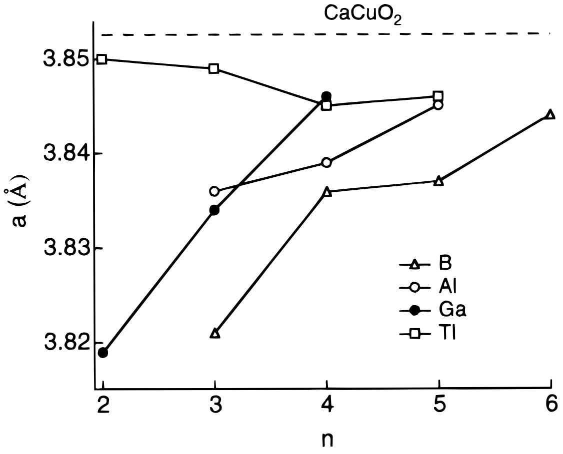

Figure 9. Variation of the a-parameters of M-12(n-1)n-Sr (M = B, Al, Ga)[63-67,71,72] and Tl-12(n-1)n-Ba.[13] The dotted line shows the a-parameter of the infinite-layer phase $CaCuO_2$.[3] The cell parameter of the quasitetragonal system is plotted for the Ga system.

It is worth comparing the aforementioned data with those of the Tl-12(n-1)n-Ba phases. As shown in Figure 9, the a-parameter of Tl-12(n-1)n is almost independent of the n-value and close to that for $CaCuO_2$. This result implies an in-plane size of the BaO−TlO−BaO charge reservoir similar to that of the CuO_2 plane. The phases up to $n = 5$ are stable in the Tl system even under ambient pressure,[6−13] which is consistent with the small size mismatch. The discussion just presented also suggests an important role of high pressure in stabilizing a superconducting phase based on a charge reservoir with a small in-plane size. In such a phase, the charge reservoir block tends to shrink the in-plane dimensions, whereas the CuO_2 plane tends to expand them which causes high strain energy. High-pressure conditions affect this situation because different structural units have different compressibilities. These results suggest strongly that the pressure-induced shrinkage is less pronounced in the charge reservoir than in the CuO_2 plane and that the size mismatch between them tends to decrease under high pressure. On the other hand, most of high T_c superconductors prepared under high pressure are p-type with holes as carriers. The in-plane size of the CuO_2 plane shrinks more or less under high pressure, which is a favorable feature for hole doping into the Cu−O antibonding orbital. This feature may constitute another role of high pressure in the stabilization of p-type superconducting phases.

In tetrahedral coordination, the ionic radius from boron to gallium varies very greatly from 0.11 to 0.47 Å.[76] Corresponding to this, the c-parameter increases linearly with the ionic radius.[63] The expansion along the c-axis is mainly caused by the increase in thickness of the charge reservoir. On the other hand, T_c is almost independent of the M atom (Table 1). This result suggests that thickness of the blocking layer is not an important factor in the determination of T_c and that its role consists only in the creation of holes.[63]

3.4. The 02(*n*-1)*n* Series of Phases. The famous oxide La_2CuO_4 is better described as 0201-La. According to this concept, we can anticipate a more general series of phases of 02(n-1)n-type. The so-called 2126 phase of $La_2ACu_2O_6$ (A = Ca, Sr, Ba)[77] corresponds exactly to the second member of the series. Although

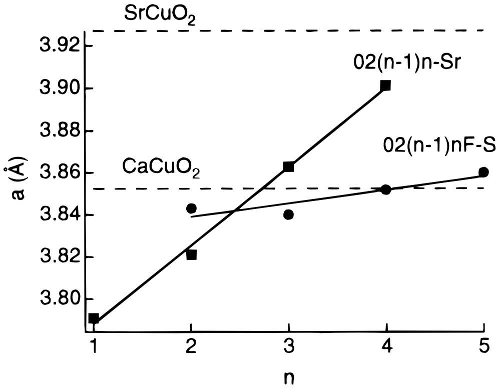

Figure 10. The *a*-parameters of 02(*n*-1)*n*-Sr[84] and 02(*n*-1)F−Sr[93,94] compared with those of infinite-layer $CaCuO_2$ and $SrCuO_2$.[3]

these phases are semiconducting, hole doping is possible by alkaline earth substitution for lanthanum in a similar way to that in La_2CuO_4. The resulting phase $(La,Sr)_2CaCu_2O_6$ [0212-(La,Sr)] shows superconductivity below ~60 K after annealing under high oxygen pressure.[78]

The LaO−LaO block does not create holes because its formal charge is 2+. On the other hand, SrO−SrO double planes can create two holes per unit formula because of its neutral formal charge. An ambient-pressure form of Sr_2CuO_3 includes this type of block.[79] However, this phase is not superconducting because it does not include the CuO_2 plane but instead a one-dimensional (1D) CuO chain plane.[79] Under high pressure, the 02(*n*-1)*n*-type phases based on the SrO−SrO double planes really exist.[80−84] Its first member $Sr_2CuO_{3+\delta}$, has a K_2NiF_4-type lattice and was claimed to be superconducting below 70 K.[82] This system was reinvestigated and positive results were reported for the appearance of superconductivity.[85,86] However, it was found by structure analysis that nearly half of the oxygen sites in the "CuO_2" plane are vacant.[87] This result cast serious questions on the reports that insist on superconductivity, and it was indeed denied by subsequent studies including high-pressure synthesis experiments.[83,84] On the other hand, the $n = 2, 3, 4$ members of $Sr_2Ca_{n-1}Cu_nO_{2n+2}$ [02(*n*-1)*n*-Sr] show superconductivity.[80−84] If the Ca plane of this series is replaced by a SrO plane and the CuO_2 plane by a TiO_2 plane, a typical Ruddlesden−Popper series $Sr_{n+1}Ti_nO_{2n+3}$ is formed. The 02(*n*-1)*n*-Sr may be, therefore, categorized as an oxygen-deficient Ruddlesden−Popper series.

It is quite difficult to obtain a high quality of samples for the 02(*n*-1)*n*-Sr series; the high-pressure product is usually a multiphase mixture and, furthermore, extended insertion of intergrowths of phases with different *n*-values always occurs. Nevertheless, the T_cs of the $n = 2, 3, 4$ phases were specified, as shown in Table 1, by comparison of the superconducting properties of many samples.[84]

Various issues are still open to discussion for the 02(*n*-1)*n*-Sr series of phases because of the poor sample quality. One of these issues is the substantial mixing between strontium and calcium. The 02(*n*-1)*n*-Sr series has tetragonal cells and the *a*-parameter increases linearly with *n* as shown in Figure 10. The slope of the linear line is fairly large and the *a*-parameter exceeds the value of $CaCuO_2$ (3.8526 Å) for $n \geq 3$, approaching that of infinite-layer $SrCuO_2$[3] (3.9269 Å). This result strongly suggests that the calcium sites of the phases are replaced by strontium. The real formula of the series seems, therefore, to be $Sr_2(Sr,Ca)_{n-1}Cu_nO_{2n+2}$ or, more generally, $(Sr,Ca)_2(Sr,Ca)_{n-1}Cu_nO_y$. The fact that 02(*n*-1)*n* phases can be formed in the Ca-free ternary system of Sr−Cu−O[82] is consistent with this suggestion.

Another issue is the oxygen deficiency. Based on the ideal formula of $Sr_2CaCu_2O_6$ for the $n = 2$ member, the average copper valence is 3+, which is highly unlikely. We have to assume the presence of a large amount of oxygen vacancies to decrease the copper valence. As stated before, in the $n = 1$ phase of $Sr_2CuO_{3+\delta}$, oxygen vacancies are mainly concentrated in the "CuO_2" plane.[87] However, this result should not happen in the superconducting phases with $n = 2, 3, 4$ because oxygen vacancies in the CuO_2 plane would suppress superconductivity.

The SrO−SrO double planes create two holes per formula unit. If oxygen in this block is completely replaced by a halogen atom (X = F, Cl, Br), the resulting double planes SrX−SrX have a formal charge of 2+. The halogen-based block is, therefore, expected to behave like the LaO−LaO double planes. This concept was used in 1975 to find $Sr_2CuO_2Cl_2$ [0201Cl-Sr], which is essentially isostructural to La_2CuO_4.[88] Its related phases, $Ca_2CuO_2Cl_2$ [0201Cl-Ca][89] and $Ca_2CuO_2Br_2$ [0201Br-Ca][89], or their higher order phases, $Ca_3Cu_2O_4Cl_2$ [$Ca_2CaCu_2O_4Cl_2$ = 0212Cl-Ca][90,91] and $Ca_3Cu_2O_4Br_2$ [$Ca_2CaCu_2O_4Br_2$ = 0212Br-Ca],[91] were also discovered. However, the hole doping for these phases was not possible under ambient pressure and they did not show superconductivity.

In 1994, an oxyhalide superconductor was prepared for X = F through the reaction of $SrCuO_2$ with F_2 gas at ambient pressure.[92] The phase formed was $Sr_2CuO_2F_{2+\delta}$ and had a La_2CuO_4 (0201)-type structure with an orthorhombic lattice, showing superconductivity below 46 K.[92] The excess fluorine atom, which is probably doped into the SrF plane, is essential for superconductivity because it is the origin of the hole carrier. This superconductor is the $n = 1$ phase of a homologous series of $Sr_2Ca_{n-1}Cu_nO_{2n}F_{2+\delta}$ [02(*n*-1)*n*F-Sr] and higher members with $n = 2-5$ were discovered subsequently using the high-pressure technique.[93,94] Figure 11 shows the crystal structures of the 02(*n*-1)*n*F-Sr phases with $n \leq 3$, where the excess fluorine atom is omitted because of the uncertainty of its exact position. The phases with $n \geq 2$ have simple tetragonal lattices showing no superstructures, which may suggest random distribution of the excess fluorine atoms. Their *a*-parameters are close to that of $CaCuO_2$, as shown in Figure 10, and this proximity may be due to the smaller ionic radius of the fluorine ion than that of the oxygen ion and/or less intensive Ca/Sr mixing.

The $n = 2, 3$ phases of the oxyfluoride series undergo very sharp superconducting transitions with high onset temperatures at 99 and 111 K, respectively.[93] These values are comparable to, or even higher than, the corresponding ones of the 02(*n*-1)*n*-Sr phases (77 K and 109 K, respectively). In the oxyfluoride phases, the apical site around the copper atom is occupied by

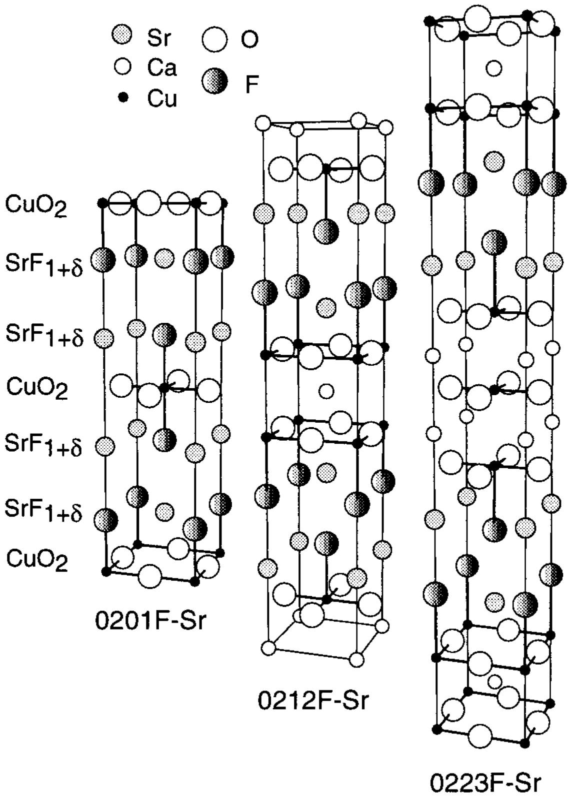

Figure 11. Crystal structures of 02(n-1)nF-Sr ($n = 1, 2, 3$). The quasitetragonal cell is shown for the $n = 1$ phase.

Figure 12. HRTEM image of 0223F-Sr projected along the b-axis.[93] The numbers shown indicate number of the CuO_2 planes.

fluorine. This fact suggests once more that T_c is essentially governed by the CuO_2 plane and its hole concentration. The sharp superconducting transitions in the $n = 2, 3$ phases seem to be caused by less pronounced intergrowth formation in their structure. Figure 12 shows an HRTEM image projected along the b-axis for 0223F-Sr. The SrF−SrF block can be clearly distinguished because of its relatively white contrast, and the stacking of planes is almost perfect except for intergrowth of one $n = 4$ slab.

The hole doping for X = Cl phases also became possible with the high-pressure technique. Because of its relatively large size, the chlorine ion cannot be introduced into an interstitial site. Instead, enough holes are doped by partial substitution of sodium or potassium for calcium or of oxygen for chlorine and this induces superconductivity. Oxychloride superconductors reported so far include $(Ca,Na)_2Ca_{n-1}Cu_nO_{2n}Cl_2$ [02-(n-1)nCl-(Ca,Na)] with $n = 1$[95] or 2,[96] $(Ca,K)_2CuO_2Cl_2$ [0201Cl-(Ca,K)],[97] and $Sr_2Ca_{n-1}Cu_nO_{2n+y}Cl_{2-y}$ [02(n-1)-nCl-Sr], with $n = 2$ or 3.[98] The superconducting transition temperatures for the X = Cl phases are relatively low and transitions are generally broad when compared with the corresponding X = F phases; the highest T_c of ≈80 K was observed for 0212Cl-Sr.[98]

3.5. Hg- and Pb-Phases and Other Phases. In 1993, the mercury-based superconductor $HgBa_2CuO_{4+\delta}$ was discovered using the conventional solid-state reaction in a sealed silica tube.[26] This phase is the $n = 1$ member of the homologous series of $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ [Hg-12(n-1)n-Ba]. Soon after the discovery, $n = 2$ and $n = 3$ members of the series were prepared using the same technique.[27] This series of phases attracted many researchers' attention because their superconducting transition temperatures were extremely high. In particular, the T_c of the $n = 3$ phase $HgBa_2Ca_2Cu_3O_{8+\delta}$, 135 K, is the highest recorded T_c among all superconductors.[27,99] Furthermore, the T_c of Hg-1223-Ba increases drastically with the application of hydrostatic pressure, reaching the value of 164 K at 31 GPa.[100]

Although phases up to $n = 4$ were obtained in bulk form under ambient pressure,[26,27,101,102] the obtained samples are usually multiphase mixtures except for Hg-1201-Ba. The difficulty in preparing a phase pure sample is mainly derived from a low thermal stability of the mercury compounds. Mercuric oxide, HgO, used as a mercury source, is decomposed under ambient pressure near 400 °C. To keep the stoichiometry, precise control of the mercury pressure is indispensable during heat treatment, which is usually done at a temperature much higher than 400 °C. However, such a control is difficult with the silica tube technique.

The high-pressure synthesis technique has been recognized as a satisfactory method to solve the aforementioned problem[99,103−111] because the overall metal and oxygen contents in a sample are kept constant in a high-pressure apparatus even if it contains a volatile element. However, many processing parameters relate to the phase formation, and their optimizations are crucial to prepare high-quality samples even using the high-pressure technique; the parameters to be optimized include pressure, temperature, precursor, oxygen content in the starting mixture, heating period, etc.[99,103−111] Thanks to these efforts, monophasic or nearly monophasic samples have been obtained using the high-pressure technique for members up to $n = 6$. In addition, the formation of $n = 7$, 8 members was confirmed under high pressure, and their lattice parameters were reported.[107]

The Hg-12(n-1)n-Ba phases are essentially isostructural to the corresponding Tl-12(n-1)n-Ba phases except that the oxygen site on the mercury plane is almost vacant. For instance, in Hg-1201-Ba, the occupation

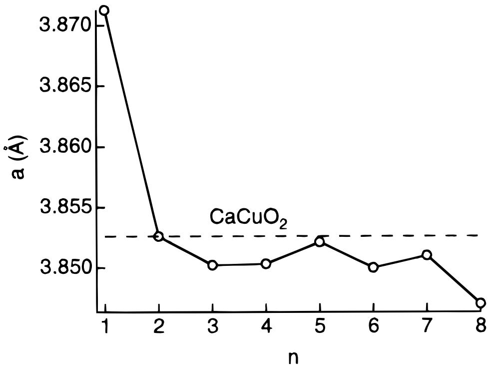

Figure 13. The *a*-parameters of Hg-12(*n*-1)*n*-Ba[106,107] compared with that of infinite-layer $CaCuO_2$.[3]

factor for the site is only ≈0.1 and most of the mercury atoms adopt dumbbell-type linear coordination.[26] Nevertheless, the interstitial oxygen atoms are crucial for superconductivity because they are responsible for 2δ holes per unit formula. The interstitial oxygen atom is present in all the other members of the series and its content (δ) varies, in particular in phases with small *n*-values, depending on the synthesis conditions or postannealing conditions.[109,111]

Figure 13 shows the variation of the *a*-parameter as a function of *n* for Hg-12(*n*-1)*n*-Ba. Because the *a*-parameter is also a function of δ, which depends on the heating process, it has a certain width at each *n*. Nevertheless, it is worth noting that the a-parameters in Figure 13 are, except for $n = 1$, close to that for $CaCuO_2$, as in the Tl system. This result implies that the natural in-plane size of the $BaO-HgO_\delta-BaO$ block is also close to that of the CuO_2 plane, in contrast to the M-12(*n*-1)*n*-Sr (M = B, Al, Ga) systems.

In the early stage of the formation of higher *n* members of the Hg-12(*n*-1)*n*-Ba series, the lower *n* members appear and are converted through intercalation of CuO_2-Ca planes.[99,108] This process is very sluggish and seems to be the rate-determining step. It should be also noted that a relatively lower pressure of ≈2 GPa or even 1 GPa gas pressure is effective[104] for preparation of Hg-12(*n*-1)*n*-Ba and a higher pressure of 4 GPa causes formation of unexpected lower *n* members and impurity phases.[111] On the contrary, high pressure in the range 5∼6 GPa is needed for M-12(*n*-1)*n*-Sr (M = B, Al, Ga). These facts, together with the different variation of the *a*-parameter, suggests that the role of high pressure on the phase formation is somewhat different in the mercury-based system; that is, it appears to concern kinetics rather than thermodynamic energetics. The high pressure condition seems effective so long as it is concerned with offering a completely closed solid-state system where the decomposition of the mercury oxide is hindered, and moreover, the rate-determining process is highly accelerated.

The Hg-12(*n*-1)*n*-Ba series of phases contain a single HgO_δ plane in the charge reservoir. On the other hand, the corresponding series Bi-12(*n*-1)*n*-Sr do not exist, but instead, the Bi-22(*n*-1)*n*-Sr series based on the BiO−BiO double planes appears in the Bi system. In the Tl-based system, both types of series, Tl-12(*n*-1)*n*-Ba and Tl-22(*n*-1)*n*-Ba exist. By analogy to these 22(*n*-1)*n* phases, attempts to prepare Hg-22(*n*-1)*n* series of phases with the double $HgO_\delta-HgO_\delta$ planes were carried out. The high-pressure technique was again effective for such an issue and $Hg_2Ba_2YCu_2O_{8-y}$ [Hg-2212-Ba-Y] was prepared under the high pressure of 1.8 GPa.[112] This phase is essentially isostructural to Bi-2212-Sr (Figure 4), but is insulating because of an insufficient hole concentration. Superconductivity with $T_c \approx 45$ K appeared after partial substitution of calcium for yttrium for the range, $0.3 \leq x \leq 0.5$ in $Hg_2Ba_2Y_{1-x}Ca_x$-Cu_2O_{8-y}.[112] Higher members with the double planes were prepared by a different approach; that is, the mercury was partly substituted by thallium[113] to obtain $(Hg,Tl)_2Ba_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ [(Hg,Tl)-22(*n*-1)*n*-Ba]. Thus far, phases up to $n = 5$ have been synthesized and (Hg,Tl)-2223-Ba shows T_c as high as 120 K after H_2/Ar annealing.[114,115]

Three heavy metals, mercury, thallium, and bismuth, located near by each other in the periodic table, can form a homologous series of superconductors. Lead, which is between thallium and bismuth, therefore appears to be a possible candidate for a charge reservoir metal. Indeed, $Pb_2Sr_2(Y,Ca)Cu_3O_8$ was discovered and showed superconductivity.[116] This phase consists of a complicated charge reservoir of SrO−PbO−Cu−PbO−SrO and an infinite layer block of $CuO_2-(Y,Ca)-CuO_2$ (i.e., $n = 2$).[116] Subsequently, various phases including lead were found under ambient pressure. Examples are (Pb,Sr)-$Sr_2(Y,Ca)Cu_2O_y$,[117] $(Pb,Cu)(Ba,Sr,Ca)_2(Y,Ca)Cu_2O_y$,[118−120] etc. These phases includes two CuO_2 planes per unit formula ($n = 2$).

The high-pressure technique was satisfactorily applied to lead-containing systems to find a homologous series of phases with an ideal formula of $PbSr_2$-$Ca_{n-1}Cu_nO_{2n+3}$ [Pb-12(*n*-1)*n*-Sr].[121−124] Thus far, $n = 2$, 3, 4 members of the series have been isolated, and the highest T_c of 122 K was observed for $n = 3$ after postannealing in argon.[124]

Recently, new superconducting phases were found in the carbon-free Ba−Ca−Cu−O system under high pressure.[125−127] It was claimed that there are at least two superconducting phases with transition temperatures of 126 and 107 K. The 107 K phase was identified by X-ray diffraction and electron microscopy to be $CaBa_2Ca_2Cu_3O_9$ [Ca-1223-Ba].[127] The 126 K phase is unstable against water and carbon dioxide in air and further studies seem to be needed for its distinct identification.

4. Conclusions

Most cuprate superconductors are derived from their "infinite-layer" $CaCuO_2$ parent oxide by replacing the Ca plane with a charge reservoir block. The substitution for every n^{th} Ca plane yields a layered structure including *n* CuO_2 planes in a unit sequence. Carriers created in the charge reservoir block are doped into the CuO_2 plane, resulting in the appearance of superconductivity. Various kinds of charge reservoirs have been found by phase search experiments under ambient pressure. However, except for some systems, ambient-pressure synthesis yields only narrow range ($n < 3$) of members of a homologous series.

Under high pressure, higher order phases with large *n*-values can easily be obtained. Furthermore, a wider variety of charge reservoirs can be inserted. In particular, high pressure is quite effective in the stabilization of a homologous series of superconductors based on charge reservoirs with small in-plane sizes, such as SrO−BO−SrO. In such phases, the charge reservoir block tends to shrink the in-plane dimensions whereas the CuO_2 plane tends to expand them resulting in high strain energy. High-pressure conditions affect this situation because different units have different compressibilities. The existence of many high-pressure stable superconductors suggests that pressure shrinkage in the charge reservoir is less pronounced than in the CuO_2 plane and the size mismatch between them tends to decrease with high pressure.

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References

(1) Bednorz, J. G.; Müller, K. A. *Z. Phys. B* **1986**, *64*, 189.
(2) Siegrist, T.; Zahurak, S. M.; Murphy, D. W.; Roth, R. S. *Nature* **1988**, *334*, 231.
(3) Kobayashi, N.; Hiroi, Z.; Takano, M. *J. Solid State Chem.* **1997**, *132*, 274.
(4) Smith, M. G.; Manthiram, A.; Zhou, J.; Goodenough, J. B.; Markert, J. T. *Nature* **1991**, *351*, 549.
(5) Ikeda, N.; Hiroi, Z.; Azuma, M.; Takano, M.; Bando, Y. *Physica C* **1993**, *210*, 367.
(6) Sheng, Z. Z.; Hermann, A. M. *Nature* **1988**, *332*, 55.
(7) Parkin, S. S. P.; Lee, V. Y.; Nazzal, A. I.; Savoy, R.; Huang, T. C.; Gorman, G.; Beyers, R. *Phys. Rev. B* **1988**, *38*, 6531.
(8) Martin, C.; Michel, C.; Maignan, A.; Hervieu, M.; Raveau, B. C. R. *Acad. Sci. Paris* **1988**, *307*, 27.
(9) Parkin, S. S. P.; Lee, V. Y.; Nazzal, A. I.; Savoy, R.; Beyers, R.; La Placa, S. J. *Phys. Rev. Lett.* **1988**, *61*, 750.
(10) Sulpice, A.; Giordanengo, B.; Tournier, R.; Hervieu, M.; Maignan, A.; Martin, C.; Michel, C.; Provost, J. *Physica C* **1988**, *156*, 243.
(11) Hervieu, M.; Maignan, A.; Martin, C.; Michel, C.; Provost, J.; Raveau, B. *J. Solid State Chem.* **1988**, *75*, 212.
(12) Bourgault, D.; Martin, C.; Michel, C.; Hervieu, M.; Provost, J.; Raveau, B. *J. Solid State Chem.* **1989**, *78*, 326.
(13) Syono, Y.; Kikuchi, M.; Nakajima, S.; Suzuki, T.; Oku, T.; Hiraga, K.; Kobayashi, N.; Iwasaki, H.; Muto, Y. *Mater. Res. Soc. Symp. Proc.* **1989**, *156*, 229.
(14) Wu, M. K.; Ashburn, J. R.; Torng, C. J.; Hor, P. H.; Meng, R. L.; Gao, L.; Huang, Z. J.; Wang, Y. Q.; Chu, C. W. *Phys. Rev. Lett.* **1987**, *58*, 908.
(15) Maeda, H.; Tanaka, Y.; Fukutomi, M.; Asano, T. *Jpn. J. Appl. Phys.* **1988**, *27*, L209.
(16) Michel, C.; Hervieu, M.; Borel, M. M.; Grandin, A.; Deslandes, F.; Provost, J.; Raveau, B. *Z. Phys. B* **1987**, *68*, 421.
(17) Takayama-Muromachi, E.; Uchida, Y.; Ono, A.; Izumi, F.; Onoda, M.; Matsui, Y.; Kosuda, K.; Takekawa, S.; Kato, K. *Jpn. J. Appl. Phys.* **1988**, *27*, L365.
(18) Subramanian, M. A.; Torardi, C. C.; Calabrese, J. C.; Gopalakrishnan, J.; Morrissey, K. J.; Askew, T. R.; Flippen, R. B.; Chowdhry, U.; Sleight, A. W. *Science* **1988**, *239*, 1015.
(19) Tarascon, J. M.; Le Page, Y.; Barboux, P.; Bagley, B. G.; Greene, L. H.; Mckinnon, W. R.; Hull, G. W.; Giroud, M.; Hwang, D. M. *Phys. Rev. B* **1988**, *37*, 9382.
(20) Takayama-Muromachi, E.; Uchida, Y.; Matsui, Y.; Onoda, M.; Kato, K. *Jpn. J. Appl. Phys.* **1988**, *27*, L556.
(21) Yamamoto, A.; Onoda, M.; Takayama-Muromachi, E.; Izumi, F.; Ishigaki, T.; Asano, H. *Phys. Rev. B* **1990**, *42*, 4228.
(22) Hazen, R. M.; Finger, L. W.; Angel, R. J.; Prewitt, C. T.; Ross, N. L.; Hadidiacos, C. G.; Heaney, P. J.; Veblen, D. R.; Sheng, Z. Z.; El Ali, A.; Hermann, A. M. *Phys. Rev. Lett.* **1988**, *60*, 1657.
(23) Torardi, C. C.; Subramanian, M. A.; Calabrese, J. C.; Gopalakrishnan, J.; Morrissey, K. J.; Askew, T. R.; Flippen, R. B.; Chowdhry, U.; Sleight, A. W. *Science* **1988**, *240*, 631.
(24) Parkin, S. S. P.; Lee, V. Y.; Engler, E. M.; Nazzal, A. I.; Huang, T. C.; Gorman, G.; Savoy, R.; Beyers, R. *Phys. Rev. Lett.* **1988**, *60*, 2539.
(25) Subramanian, M. A.; Calabrese, J. C.; Torardi, C. C.; Gopalakrishnan, J.; Askew, T. R.; Flippen, R. B.; Morrissey, K. J.; Chowdhry, U.; Sleight, A. W. *Nature* **1988**, *332*, 420.
(26) Putilin, S. N.; Antipov, E. V.; Chmaissem, O.; Marezio, M. *Nature* **1993**, *362*, 226.
(27) Schilling, A.; Cantoni, M.; Guo, J. D.; Ott, H. R. *Nature* **1993**, *363*, 56.
(28) Klement, W., Jr.; Jayaraman, A. In *Progress in Solid State Chemistry*, Vol. 3; Reiss, H., Ed.; Pergamon: Oxford, 1967; pp 289−376.
(29) Kinoshita, K.; Yamada, T. *Nature* **1992**, *357*, 313.
(30) Miyazaki, Y.; Yamane, H.; Ohnishi, N.; Kajitani, T.; Hiraga, K.; Morii, Y.; Funahashi, S.; Hirai, T. *Physica C* **1992**, *198*, 7.
(31) Pelloquin, D.; Caldes, M.; Maignan, A.; Michel, C.; Hervieu, M.; Raveau, B. *Physica C* **1993**, *208*, 121.
(32) Goutenoire, F.; Hervieu, M.; Maignan, A.; Michel, C.; Martin, C.; Raveau, B. *Physica C* **1993**, *210*, 359.
(33) Uehara, M.; Sahoda, S.; Nakata, H.; Akimitsu, J.; Matsui, Y. *Physica C* **1994**, *222*, 27.
(34) Martin, C.; Hervieu, M.; Huve, M.; Michel, C.; Maignan, A.; Van Tendeloo, G.; Raveau, B. *Physica C* **1994**, *222*, 19.
(35) Kawashima, T.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1994**, *224*, 69.
(36) Kawashima, T.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1994**, *227*, 95.
(37) Kawashima, T.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1994**, *233*, 143.
(38) Alario-Franco, M. A.; Bordet, P.; Capponi, J.-J.; Chaillout, C.; Chenavas, J.; Fournier, T.; Marezio, M.; Souletie, B.; Sulpice, A.; Tholence, J.-L.; Colliex, C.; Argoud, R.; Baldonedo, J. L.; Gorius, M. F.; Perroux, M. *Physica C* **1994**, *231*, 103.
(39) Shimakawa, Y.; Jorgensen, J. D.; Hinks, D. G.; Shaked, H.; Hitterman, R. L.; Izumi, F.; Kawashima, T.; Takayama-Muromachi, E.; Kamiyama, T. *Phys. Rev. B* **1994**, *50*, 16008.
(40) Kumakura, H.; Togano, K.; Kawashima, T.; Takayama-Muromachi, E. *Physica C* **1994**, *226*, 222.
(41) Kumakura, H.; Kitaguchi, H.; Togano, K.; Kawashima, T.; Takayama-Muromachi, E.; Okayasu, S.; Kazumata, Y. *IEEE Trans. Appl. Supercond.* **1995**, *5*, 1399.
(42) Yamaura, K.; Hiroi, Z.; Takano, M. *Physica C* **1994**, *229*, 183.
(43) Matveev, A. T.; Matsui, Y.; Takayama-Muromachi, E. *Advances in Superconductivity IX*, Proceedings of the 9th International Symposium on Superconductivity, 1997; p 341.
(44) Zhigadlo, N. D.; Matveev, A. T.; Ishida Y.; Anan, Y.; Matsui, Y.; Takayama-Muromachi, E. *Physica C*, in press.
(45) Matveev, A. T.; Matsui, Y.; Yamaoka, S.; Takayama-Muromachi, E. *Physica C* **1997**, *288*, 185.
(46) Uehara, M.; Uoshima, M.; Ishiyama, S.; Nakata, H.; Akimitsu, J.; Matsui, Y.; Arima, T.; Tokura, Y.; Mori, N. *Physica C* **1994**, *229*, 310.
(47) Sato, M.; Akimitsu, J.; Takahashi, H.; Mori, N. *Physica C* **1996**, *271*, 79.
(48) Takayama-Muromachi, E.; Matsui, Y.; Ramirez-Castellanos, J. *Physica C* **1995**, *252*, 221.
(49) Isobe, M.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1996**, *273*, 72.
(50) Matveev, A. T.; Ramirez-Castellanos, J.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1996**, *262*, 279.
(51) Matveev, A. T.; Ramirez-Castellanos, J.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1997**, *274*, 48.
(52) Loureiro, S. M.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1998**, *302*, 244.
(53) Chmaissem, O.; Sheng, Z. Z. *Physica C* **1995**, *242*, 23.
(54) Maignan, A.; Pelloquin, D.; Malo, S.; Michel, C.; Hervieu, M.; Raveau, B. *Physica C* **1995**, *243*, 233.
(55) Shimoyama, J.; Hahakura, S.; Kitazawa, K.; Yamafuji, K.; Kishio, K. *Physica C* **1994**, *224*, 1.
(56) Pelloquin, D.; Hervieu, M.; Malo, S.; Michel, C.; Maignan, A.; Raveau, B. *Physica C* **1995**, *246*, 1.
(57) Sheng, Z. Z.; Li, Y. F.; Tang, Y. Q.; Chen, Z. Y.; Pederson, D. O. *Solid State Commun.* **1992**, *83*, 205.
(58) Chen, Z. Y.; Sheng, Z. Z.; Tang, Y. Q.; Li, Y. F.; Wang, L. M.; Pederson, D. O. *Appl. Phys. Lett.* **1993**, *62*, 3034.
(59) Michel, C.; Letouze, F.; Martin, C.; Hervieu, M.; Raveau, B. *Physica C* **1996**, *262*, 159.
(60) Maignan, A.; Pelloquin, D.; Malo, S.; Michel, C.; Hervieu, M.; Raveau, B. *Physica C* **1995**, *249*, 220.
(61) Chmaissem, O.; Jorgensen, J. D.; Hinks, D. G.; Storey, B. G.; Dabrowski, B.; Zhang, H.; Marks, L. D. *Physica C* **1997**, *279*, 1.
(62) Chmaissem, O.; Argyriou, D. N.; Hinks, D. G.; Jorgensen, J. D.; Storey, B. G.; Zhang, H.; Marks, L. D.; Wang, Y. Y.; Dravid, V. P.; Dabrowski, B. *Phys. Rev. B* **1995**, *52*, 15636.
(63) Takayama-Muromachi, E.; Matsui, Y.; Kosuda, K. *Physica C* **1995**, *241*, 137.
(64) Kawashima, T.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1995**, *254*, 131.
(65) Kawashima, T.; Matsui, Y.; Takayama-Muromachi, E. Proceedings of the 5th NIRIM International Symposium on Advanced Materials (ISAM′98); NIRIM: Tsukuba, 1998; p 229.

(66) Isobe, M.; Kawashima, T.; Kosuda, K.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1994**, *234*, 120.

(67) Matveev, A. T.; Takayama-Muromachi, E. *Physica C* **1995**, *254*, 26.

(68) Vaughey, J. T.; Thiel, J. P.; Hasty, E. F.; Groenke, D. A.; Stern, C. L.; Poeppelmeier, K. R.; Dabrowski, B.; Hinks, D. G.; Mitchell, A. W. *Chem. Mater.* **1991**, *3*, 935.

(69) Dabrowski, B.; Radaelli, P.; Hinks, D. G.; Mitchell, A. W.; Vaughey, J. T.; Groenke, D. A.; Poeppelmeier, K. R. *Physica C* **1992**, *193*, 63.

(70) Roth, G.; Adelmann, P.; Heger, G.; Knitter, R.; Wolf, Th. *J. Phys. I* **1991**, *1*, 721.

(71) Isobe, M.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1994**, *222*, 310.

(72) Takayama-Muromachi, E.; Isobe, M. *Jpn. J. Appl. Phys.* **1994**, *33*, L1399.

(73) Ramirez-Castellanos, J.; Matsui, Y.; Takayama-Muromachi, E.; Isobe, M. *J. Solid State Chem.* **1996**, *123*, 378.

(74) Ramirez-Castellanos, J.; Matsui, Y.; Takayama-Muromachi, E.; Isobe, M. *Physica C* **1995**, *251*, 279.

(75) Khasanova, N. R.; Izumi, F.; Takayama-Muromachi, E.; Hewat, A. W. *Physica C* **1996**, *263*, 200.

(76) Shannon, R. D. *Acta Crystallogr. A* **1976**, *32*, 751.

(77) Nguyen, N.; Er−Rakho, L.; Michel, C.; Choisnet, J.; Raveau, B. *Mater. Res. Bull.* **1980**, *15*, 891.

(78) Cava, R. J.; Batlogg, B.; Van Dover: R. B.; Krajewski, J. J.; Waszczak, J. V.; Fleming, R. M.; Peck Jr., W. F.; Rupp Jr., L. W.; Marsh, P.; James, A. C. W. P.; Schneemeyer, L. F. *Nature* **1990**, *345*, 602.

(79) Taske, C. L.; Müller-Buschbaum, Hk. *Z. Anorg. Allg. Chem.* **1969**, *371*, 325.

(80) Adachi, S.; Yamauchi, H.; Tanaka, S.; Mori, N. *Physica C* **1993**, *208*, 226.

(81) Adachi, S.; Yamauchi, H.; Tanaka, S.; Mori, N. *Physica C* **1993**, *212*, 164.

(82) Hiroi, Z.; Takano, M.; Azuma, M.; Takeda, Y. *Nature* **1993**, *364*, 315.

(83) Shaked, H.; Shimakawa, Y.; Hunter, B. A.; Hitterman, R. L.; Jorgensen, J. D.; Han, P. D.; Payne, D. A. *Phys. Rev. B* **1995**, *51*, 11784.

(84) Kawashima, T.; Takayama-Muromachi, E. *Physica C* **1996**, *267*, 106.

(85) Laffez, P.; Wu, X. J.; Adachi, S.; Yamauchi, H.; Mori, N. *Physica C* **1994**, *222*, 303.

(86) Han, P. D.; Chang, L.; Payne, D. A. *Physica C* **1994**, *228*, 129.

(87) Shimakawa, Y.; Jorgensen, J. D.; Mitchell, J. F.; Hunter, B. A.; Shaked, H.; Hinks, D. G.; Hitterman, R. L.; Hiroi, Z.; Takano, M. *Physica C* **1994**, *228*, 73.

(88) Grande, B.; Müller-Buschbaum, Hk. *Z. Anorg. Allg. Chem.* **1975**, *417*, 68.

(89) Grande, B.; Müller-Buschbaum, Hk. *Z. Anorg. Allg. Chem.* **1977**, *429*, 88.

(90) Sowa, T.; Hiratani, M.; Miyauchi, K. *J. Solid State Chem.* **1990**, *84*, 178.

(91) Huang, J.; Hoffmann, R.-D.; Sleight, A. W. *Mater. Res. Bull.* **1990**, *25*, 1085.

(92) Al-Mamouri, M.; Edwards, P. P.; Greaves, C.; Slaski, M. *Nature* **1994**, *369*, 382.

(93) Kawashima, T.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1996**, *257*, 313.

(94) Kawashima, T.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1997**, *282−287*, 513.

(95) Hiroi, Z.; Kobayashi, N.; Takano, M. *Nature* **1994**, *371*, 139.

(96) Zenitani, Y.; Inari, K.; Sahoda, S.; Uehara, M.; Akimitsu, J.; Kubota, N.; Ayabe, M. *Physica C* **1995**, *248*, 167.

(97) Tatsuki, T.; Adachi, S.; Itoh, M.; Tamura, T.; Wu, X.-J.; Jin, C.-Q.; Koshizuka, N.; Tanabe, K. *Physica C* **1995**, *255*, 61.

(98) Wu, X.-J.; Jin, C.-Q.; Laffez, P.; Tatsuki, T.; Tamura, T.; Adachi, S.; Yamauchi, H.; Koshizuka, N. *Physica C* **1996**, *258*, 143.

(99) Antipov, E. V.; Loureiro, S. M.; Chaillout, C.; Capponi, J. J.; Bordet, P.; Tholence, J. L.; Putilin, S. N.; Marezio, M. *Physica C* **1993**, *215*, 1.

(100) Gao, L.; Xue, Y. Y.; Chen, F.; Xiong, Q.; Meng. R. L.; Ramirez, D.; Chu, C. W.; Eggert, J. H.; Mao, H. K. *Phys. Rev. B* **1994**, *50*, 4260.

(101) Paranthaman, M.; Chakoumakos, B. C. *J. Solid State Chem.* **1996**, *122*, 221.

(102) Usami, R.; Adachi, S.; Itoh, M.; Tatsuki, T.; Tokiwa-Yamamoto, A.; Tanabe, K. *Physica C* **1996**, *262*, 21.

(103) Hirabayashi, M.; Tokiwa, K.; Tokumoto, M.; Ihara, H. *Jpn. J. Appl. Phys.* **1993**, *32*, L1206.

(104) Morawski, A.; Lada, T.; Paszewin, A.; Karpinski, J.; Conder, K.; Wisniewski, A.; Nabialek, A. *Physica C* **1994**, *235−240*, 921.

(105) Yao, Y. S.; Su, Y. J.; Liu, W.; Liu, Z. X.; Gong, H.; Li. J. W.; Cao, G. H.; Wu, F.; Zhao, Z. X. *Physica C* **1994**, *224*, 91.

(106) Loureiro, S. M.; Antipov, E. V.; Alexandre, E. T.; Kopnin, E.; Gorius, M. F.; Souletie, B.; Perroux, M.; Argoud, R.; Gheorghe, O.; Tholence, J. L.; Capponi, J. J. *Physica C* **1994**, *235−240*, 905.

(107) Scott, B. A.; Suard, E. Y.; Tsuei, C. C.; Mitzi, D. B.; McGuire, T. R.; Chen B.-H.; Walker, D. *Physica C* **1994**, *230*, 239.

(108) Lin, Q. M.; He, Z. H.; Sun, Y. Y.; Gao, L.; Xue, Y. Y.; Chu, C. W. *Physica C* **1995**, *254*, 207.

(109) Capponi, J. J.; Kopnin, E. M.; Loureiro, S. M.; Antipov, E. V.; Gautier, E.; Chaillout, C.; Souletie, B.; Brunner, M.; Tholence, J. L.; Marezio, M. *Physica C* **1996**, *256*, 1.

(110) Loureiro, S. M.; Stott, C.; Philip, L.; Gorius, M. F.; Perroux, M.; Le Floch, S.; Capponi, J. J.; Xenikos, D.; Toulemonde, P.; Tholence, J. L. *Physica C* **1996**, *272*, 94.

(111) Lokshin, K. A.; Kuzemskaya, I. G.; Kulikova, L. F.; Antipov, E. V.; Itskevich, E. S. *Physica C* **1997**, *279*, 11.

(112) Radaelli, P. G.; Marezio, M.; Perroux, M.; De Brion, S.; Tholence, J. L.; Huang, Q.; Santoro, A. *Science* **1994**, *265*, 380.

(113) Bryntse, I. *Physica C* **1994**, *226*, 184.

(114) Tatsuki, T.; Tokiwa-Yamamoto, A.; Tamura, T.; Wu, X.-J.; Moriwaki, Y.; Adachi, S.; Tanabe, K. *Physica C* **1996**, *273*, 65.

(115) Tokiwa-Yamamoto, A.; Tatsuki, T.; Wu, X.-J.; Adachi, S.; Tanabe, K. *Physica C* **1997**, *282−287*, 887.

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

(117) Rouillon, T,; Provost, J.; Hervieu, M.; Groult, D.; Michel, C.; Raveau, B. *Physica C* **1989**, *159*, 201.

(118) Koriyama, S.; Sakuyama, K.; Maeda, T.; Yamauchi, H.; Tanaka, S. *Physica C* **1990**, *166*, 413.

(119) Ono, A.; Uchida, Y. *Jpn. J. Appl. Phys.* **1990**, *29*, L586.

(120) Tokiwa, A.; Nagoshi, M.; Oku, T.; Kobayashi, N.; Kikuchi, M.; Hiraga, K.; Syono, Y. *Physica C* **1990**, *168*, 285.

(121) Yamauchi, H.; Tamura, T.; Wu, X.-J.; Adachi, S.; Tanaka, S. *Jpn. J. Appl. Phys.* **1995**, *34*, L349.

(122) Wu, X.-J.; Tamura, T.; Adachi, S.; Jin, C.-Q.; Tatsuki, T.; Yamauchi, H. *Physica C* **1995**, *247*, 96.

(123) Tamura, T.; Adachi, S.; Wu, X.-J.; Jin, C.-Q.; Tatsuki, T.; Yamauchi, H. *Physica C* **1995**, *249*, 111.

(124) Tamura, T.; Adachi, S.; Wu, X.-J.; Tatsuki, T.; Tanabe, K. *Physica C* **1997**, *277*, 1.

(125) Chu, C. W.; Du, Z. L.; Cao, Y.; Xue, Y. Y.; Sun, Y. Y.; Rusakova, I.; Gao, L. *Philos. Mag. Lett.* **1997**, *75*, 15.

(126) Xue, Y. Y.; Sun, Y. Y.; Rusakova, I.; Ross, D. K.; Du, Z. L.; Wu, N. L.; Cao, Y.; Gao, L.; Hickey, B.; Chu, C. W. *Physica C* **1998**, *294*, 316.

(127) Wu, N. L.; Du, Z. L.; Xue, Y. Y.; Rusakova, I.; Ross, D. K.; Gao, L.; Cao, Y.; Sun, Y. Y.; Chu, C. W.; Hervieu, M.; Raveau, B. submitted for publication in *Physica C*.

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