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Correlation between transition temperature, in-plane copper-oxygen bond length, and tilt/buckling of the CuO_2 plane in cuprate superconductors

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Abstract

Correlation among transition temperature, in-plane Cu-O bond length, and tilt / buckling in cuprate superconductors were examined in detail. As for cuprates with a single CuO_2 layer, tilt structure was observed in the region, whose in-plane Cu-O length was 1.906-1.926Å, and that the tilt structure drastically suppressed superconductivity. As for cuprates with double CuO_2 layers, all the compounds had buckling distortion in a CuO_5 pyramid. The degree of distortion was determined only by a kind of cation between the two facing CuO_5 pyramids, that is, calcium or yttrium. A higher transition temperature was obtained for a copper oxide with having larger Cu-O length and smaller buckling degree. A common feature of layered cuprates was the existence of three major classes distinguished by the cations Ba^{2+}, Sr^{2+}, and Ln^{3+} occupying the 9-coordination sites.

1. Introduction

The highest T_c of cuprate superconductors is achieved in structures with flat and square CuO_2 layers and long apical Cu-O bonds[1). In other words, the tilt/buckling of the CuO_2 plane lowers the transition temperature[2-10). This is because the tilt/buckling and shortening of apical Cu-O bonds would localize a hole[11-13).

On the other hand, the Cu-O bond length in the CuO_2 layer also strongly affects its T_c[14). This is because the T_c is strongly correlated with hole concentration; Hole-doping into the CuO_2 plane removes electrons from 2p-3d (x^2-y^2) bonds. Since the in-plane Cu-O bonds have anti-bonding character, hole doping strengthens them. Therefore, hole doping leads to shortening of the in-plane Cu-O bond length.

The DV-$X\alpha$ calculation for a CuO_5 pyramid[15) shows that if a hole is doped to the CuO_5 pyramid, the hole is located almost in the Cu-O (plane) orbital, and that an increase in the Cu-O (apex) length is effective in increasing the hole at the O (apex) more than that in the Cu-O (plane) length or buckling is. However, since these parameters change simultaneously in many cases, the correlation between the transition temperature and structural must be examined together for various high-T_c and non-superconducting layered cuprates.

We focused our attention on the Cu-O (plane) length and flatness of the CuO_2 plane because the two parameters are directly correlated with the bonding state between $Cu_{3d(x^2+y^2)}$ and O_{2p} orbitals, through which superconductivity is induced. The first purpose of this work is to examine in detail the correlation between transition temperature,

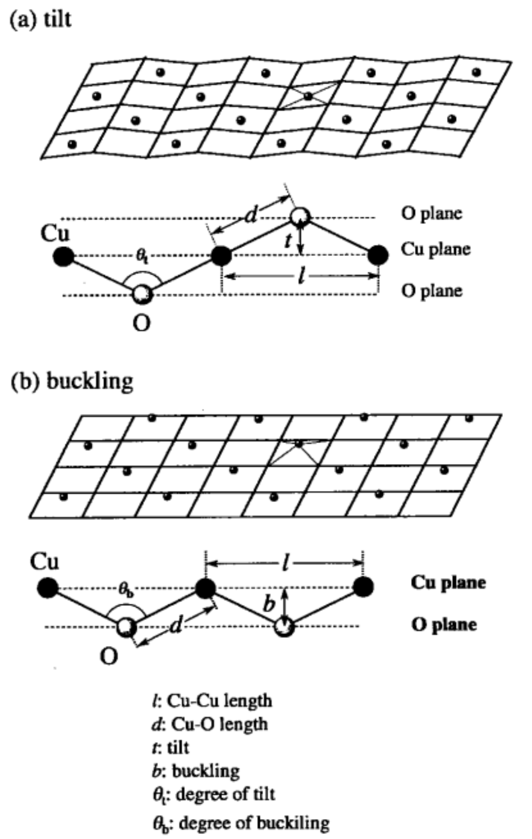

Fig. 1 Models of (a) tilt and (b) buckling in the CuO_2 plane. Orthorhombic or monoclinic distortion of $CuO_{4/2}$ is neglected by averaging.

in-plane copper-oxygen bond length, and the tilt/buckling of the CuO_2 plane for cuprates, and the second to examine the correlation between the transition temperature and the in-plane copper-copper bond length for layered cuprates.

2. Method of analysis

From many references containing both structural and superconducting data measured at room temperature in the air, we picked up reliable data of the in-plane Cu-Cu length (l), Cu-O length (d), tilt (t, θ_t), buckling (b, θ_b), T_c, and electric property of layered cuprates[16-60]. However, several cuprates whose accurate structure is not reported are listed in Table 3 and 4 without values of buckling for them. While the correlation between d and T_c is discussed in Fig. 1-3, that between l and T_c is discussed in Fig. 4, which includes the data of Table 3 & 4.

Some of crystal structure data came from neutron powder diffraction (NPD), while others came from X-ray powder diffraction (XPD) because of lack of NPD data. The data refined by XPD/NPD are marked in the tables. Standard deviation of l estimated by NPD Rietveld refinement, XPD Rietveld refinement and minimum square method is around ±0.0002Å and ±0.002Å, and ±0.005Å, respectively. Thus, the l, d, t, and b values listed in tables 1-4 include some error in the three decimal places.

The data of cuprates that we picked up are those of optimally doped superconductors and typical non-superconducting layered cuprates.

Definition of the in-plane Cu-Cu length (l), Cu-O length (d) and tilt (θ_t, t) or buckling (θ_b, b) is displayed in Fig. 1. The values d and l were calculated by averaging a- and b-axis length, thus neglecting orthorhombic or monoclinic distortion of the $CuO_{4/2}$.

For complicated layered cuprates such as Bi(Pb) 2223 or Tl2223 that has a modulated structure, several data reported by different groups are referenced[41-58].

To elucidate the whole correlation between the in-plane Cu-Cu length (l) and T_c, we also collected the data of more than two hundred specimens of over-, optimum-, and under-doped superconductors and of non-superconducting layered cuprates. It is to be noted that the parameter l instead of d is used in Fig. 6, because the position of the oxygen site for some cuprates is not determined in detail. The estimated maximum difference between d and $l/2$ is about 0.02Å, which does not affect the total trend so much.

3. Results and discussion

3-1 A single CuO_2 layer

The layered cuprates with a single CuO_2 layer ($n=1$) consist of so-called 1201 and 2201 phases. In table 1, l, d, t, θ_t, and T_c are listed.

The (In, Sc) Ba_2CuO_y compound with the longest Cu-O length has double perovskite struc-

Table 1 Correlation among in-plane Cu-Cu length, *l*, Cu-O length, *d*, degree of tilt, *t* & θ_t, transition temperature T_c of layered cuprates with a single CuO_2 layer ($n=1$).

Layered cuprate	l (Å)	d (Å)	t (Å)	θ_t (deg)	T_c (K)	Method[a]	Ref.
$InBa_2CuO_y$[b]	4.182	2.090	0	180	–	XPD	16)
$ScBa_2CuO_y$[b]	4.130	2.065	0	180	–	XPD[d]	17)
$HgBa_2CuO_y$	3.875	1.938	0	180	98	NPD	18)
$Tl_2Ba_2CuO_y$	3.864	1.932	0	180	95	NPD	19)
$(Hg_{0.7}Cr_{0.3})Sr_2CuO_y$	3.846	1.923	0	180	58	XPD	20)
$Ga(Sr_{1.1}La_{0.9})CuO_y$	3.839	1.922	0.0950	174.3	–	XPD	21)
$Ga(Sr_{1.1}Nd_{0.9})CuO_y$	3.837	1.923	0.1330	172.1	–	XPD	22)
$(Tl,Pb)_{0.5}(CO_3)_{0.5}Sr_2CuO_y$	3.820	1.920	0.1916[c]	168.5[c]	70	XPD	23)
La_2CuO_4	3.807	1.906	0.0950	174.3	–	NPD	24)
$Pb_2Cu(SrLa)_2CuO_6$	3.792	1.896	0	180	32	XPD	25)
$(Hg_{0.7}Mo_{0.3})Sr_2CuO_y$	3.788	1.894	0	180	60	NPD	20)
$(LaBa)_2CuO_4$	3.787	1.894	0	180	38	NPD	26)
$(Pb_{0.6}Cu_{0.5})SrLaCuO_y$	3.787	1.894	0	180	25	XPD	27)
$(LaSr)_2CuO_4$	3.779	1.890	0	180	33	NPD	28)
$(Pb_{0.5}Cu_{0.5})SrLaCuO_y$	3.777	1.899	0	180	33	XPD[d]	29)
$(Pb_{0.5}Cu_{0.5})SrLaCuO_y$	3.773	1.887	0	180	37	XPD[d]	30)
$(Pb_{0.5}Cu_{0.5})Sr_{1.1}La_{0.9}CuO_y$	3.769	1.885	0	180	31.5	XPD[d]	31)

[a] XPD; X-ray powder diffraction, NPD; Neutron powder diffraction
[b] Oxygen occupancy of in-plane oxygen site is about 27%
[c] Buckling distortion (*b*)
[d] From X-ray powder diffraction, but not refined by Rietveld analysis

ture[17]. The fact that l of (In, Sc) Ba_2CuO_y compound is much longer than that of the other cuprate compounds is explained by the existence of an oxygen vacancy in the CuO_2 plane, leading to be an insulator. The $HgBa_2CuO_y$ is characteristic of having a flat CuO_2 plane and the highest T_c of 98K among the $n=1$ superconductors with a single CuO_2 layer[18]. The $Tl_2Ba_2CuO_y$ (Tl2201) is characteristic of having a flat CuO_2 plane and the second highest T_c of 95K among the $n=1$ superconductors[19]. The structure of $Bi_2Sr_2CuO_y$ (Bi2201) is homologous to that of the Tl2201 except for having a modulated structure along the *b*-axis. In cooperation with the modulation, the CuO_2 plane is tilted. The electric property of the Bi2201 is known to be semiconducting or superconducting blow 10K. The CuO_2 plane of Ga $(Sr_{1.1}La_{0.9})$ CuO_y and Ga $(Sr_{1.1}Nd_{0.9})$ CuOy is tilted and there exists an oxygen vacancy in a GaO plane[21, 22]. The structure of the La_2CuO_4, $(La,Ba)_2CuO_4$ and $(La,Sr)_2CuO_4$ are K_2NiF_4 type. While the structure of semiconducting La_2CuO_4 is characteristic of having a tilted CuO_2 plane, the structure of superconducting $(La,Ba)_2CuO_4$ and $(La,Sr)_2CuO_4$ is characteristic of having a flat CuO_2 plane. Both of the $Pb_2Cu(Sr,La)_2CuO_6$ and (Pb,Cu) $SrLaCuO_y$ have a flat CuO_2 plane. Their d values are located in the range of 1.885-1.894Å, and their T_c's are in the range of 28-37K.

In Fig. 2, the shape of CuO_2 plane, T_c and electric property are plotted against the length of Cu-O in the CuO_2 plane (d). When d is smaller than 1.896Å or larger than 1.923Å, no tilt is observed. On the other hand, when the d ranges between 1.906-1.922Å, tilt of the CuO_2 plane is

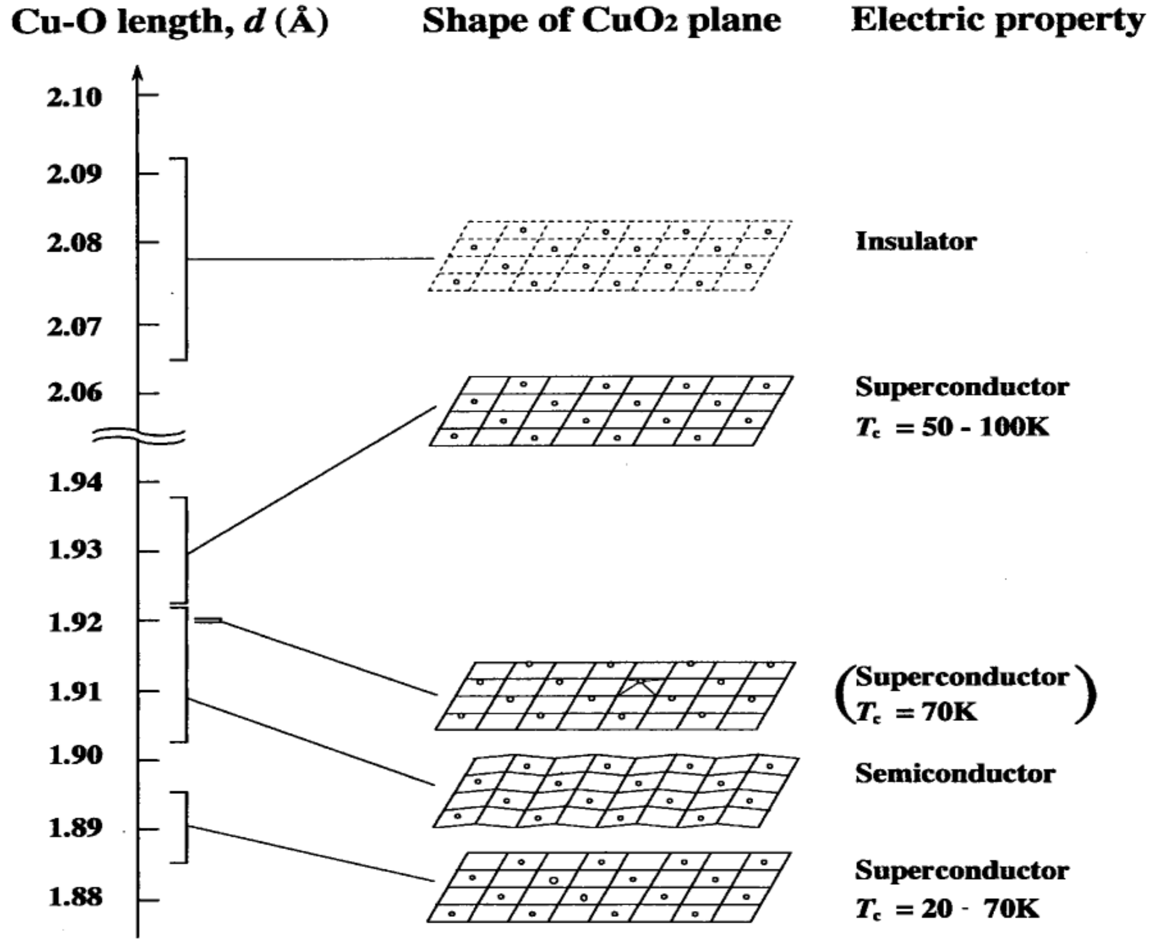

Fig. 2　Correlation between Cu-O length, *d*, shape of CuO_2 plane, and T_c of compounds with a CuO_6 octahedra (n = 1). Shape of CuO_2 plane is determined by Cu-O length, *d*.

shown.

Here we discuss the tilt region. It has already been reported that the tilt distortion stabilizes the CuO_6 octahedron. Using an atom-atom pair potential, including the Coulomb potential, short-range repulsion, and van der Waals terms, Piveteau et al. analyzed cohesive energy E_c of La_2CuO_4 both in its tetragonal and orthorhombic phases[61]. As a result, Landau expansion of the total energy with respect to the order parameters was obtained numerically and the importance of the coupling between the tilt and the movements of the lanthanum atoms to stabilize the distorted phase was emphasized. This large distortion will stabilize the CuO_6 octahedron. Since the CuO_6 octahedron is originally symmetric, it will be distorted as to split the energy level and to decrease the total electron energy.

From these results, we believe that the tilt distortion comes from the instability of (4+2) coordination of a CuO_6 octahedron. This tendency is irrespective of a kind of the rare/alkali earth ion (Ln, Sr, and Ba) occupying the 9-coordination sites (associated with a CuO_2 layer having apical oxygen atoms).

On discussing the distortion of the cuprates with a single CuO_2 layer, the $(Tl,Pb)_{0.5}(CO_3)_{0.5}Sr_2CuO_y$ compound plays a unique role. As shown in Fig. 3, although it has a CuO_6 octahedron, it is heavily distorted; It has a buckling distortion in the CuO_2 plane, which has never been observed in the CuO_6 octahedral compounds else, and the two Cu-O (apex) lengths are 6% different each other. The large distortion will stabilize the CuO_6

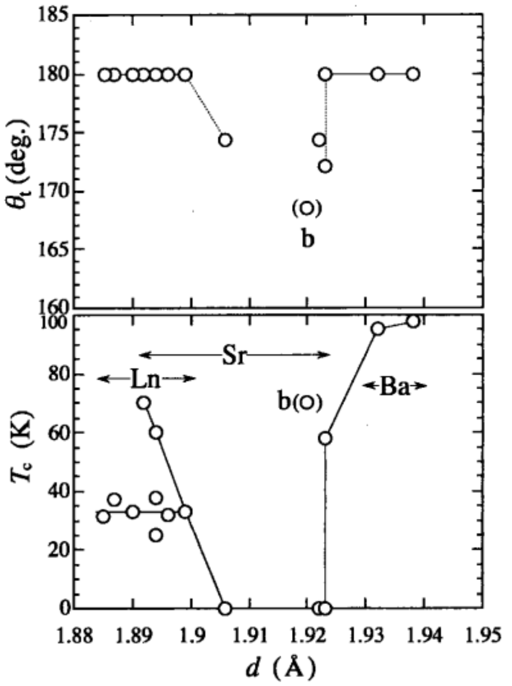

Fig. 3 Correlation between Cu-O length d, tilt/buckling angle θ_t or θ_b, and T_c. Only one point (b) of $(Tl,Pb)_{0.5}(CO_3)_{0.5}Sr_2CuO_6$ shows buckling. Tilt clearly suppresses superconductivity.

octahedron in cooperation with the Jahn-Teller distortion.

Next, we focus our attention on T_c's. As shown in Fig. 3, the highest T_c was correlated with the kind of the rare/alkali earth ion. The highest T_c's of n=1 cuprates with having a CuO_6 octahedron surrounded by Ln^{3+}, Sr^{2+}, and Ba^{2+}, were 40, 70, and 100K, respectively.

On the other hand, tilt of the CuO_6 octahedron drastically suppressed superconductivity. Suppression of superconductivity by tilt of the CuO_6 octahedron was reported by many groups[2-7]. Tight-binding band theory predicts that the tilt of the CuO_6 octahedron brings in a small band splitting at the Brillouin zone boundary[11]. Consequently, suppression of superconductivity by tilt is probably caused by localization of holes.

3-2 Double CuO_2 layers

$YBa_2Cu_3O_y$ (YBCO or 1-2-3) allows a certain modification of its structure through variation of the coupling between copper-oxygen chain layers. In particular, compounds with two chains $YBa_2Cu_4O_8$ (1-2-4) or $Y_2Ba_4Cu_7O_{15}$ (2-4-7), and the $Pb_2Cu(Y,Ca)Sr_2Cu_3O_y$ (3212) have been synthesized via modification of a layer of Cu-O chains into more complicated structure Pb_2CuO_2. $Bi_2(Sr,Ca)_3Cu_2O_8$ and $Tl_2Ba_2CaCu_2O_8$ have analogous structure, which is named 2212 structure. All of them consist of stacking a block and double CuO_2 layers. Compounds $TlBa_2CaCu_2O_y$, and $HgBa_2CaCu_2O_y$ lie on another series of structure called 1212, which has a single (MO) block layer (M=Hg and Tl). In table 2, l, b, θ_b and T_c of cuprates with double CuO_2 layers are listed. Otherwise n=1 layered cuprates, bumpy distortion of the double CuO_2 layers is only buckling. Further, while some CuO_6 octahedra have a flat CuO_2 sheet, all CuO_5 pyramids have buckling distortion. Universal buckling of the CuO_5 pyramid comes from asymmetry of the pyramid, which is suggested by the fact that the $Cu_{x^2+y^2}$ orbital is bonded with the O_{2p} orbital of surrounding oxygen atoms in the CuO_6 octahedron. Its bonding direction is towards the apex of the octahedron around the Cu. If one oxygen atom of the octahedron is removed, the other oxygen atoms surrounding the Cu moves so as to compensate it, resulting in formation of buckling CuO_5 pyramid.

Fig.4 plots θ_b against l. While θ_b of cuprates with yttrium between the double CuO_2 layer ranges from 164° to 167°, that with calcium ranges from 174° to 179°. On the other hand, the degree of buckling is not influenced by d. Since d is strongly correlated with the kind of cation occupying the 9-coordination sites, it is concluded that θ_b is determined only by the kind of ion between the double CuO_2 layers, irrespective of the in-plane Cu-O length. The difference in bonding angle by the kind cation may be explained by Coulomb attractive force between the cation and oxygen in the CuO_2 plane.

In Fig. 4, T_c is plotted against d, clearly indicating that as d becomes larger and θ_b smaller,

Table 2 Correlation between in-plane Cu-Cu length, *l*, Cu-O length, *d*, degree of buckling, *b* & θ_b, transition temperature T_c of high-T_c superconductors with double CuO_2 layers（*n*=2）.

Layered cuprate	*l* (Å)	*d*(Å)	*t* (Å)	θ_t (deg)	T_c(K)	Method[a]	Ref.
$Y_2Ba_4Cu_7O_{15}$	3.860	1.944	0.2288	166.5	95	XPD	32)
$HgBa_2CaCu_2O_y$	3.858	1.929	0.0165	179.0	127	XPD	33)
$TlBa_2CaCu_2O_y$	3.857	1.929	0.0574	176.6	103	XPD	34)
$YBa_2Cu_4O_8$	3.857	1.943	0.2397	165.8	80	NPD	35)
$YBa_2Cu_3O_y$	3.855	1.946	0.2669	164.2	92	NPD	36)
$Tl_2Ba_2CaCu_2O_8$	3.855	1.928	0.0264	178.4	118	XPD	37)
$Pb_2Sr_2YCu_3O_y$	3.825	1.926	0.2265	166.5	70	XPD	38)
$(La,Sr)_2CaCu_2O_6$	3.821	1.913	0.0882	174.7	58	NPD	39)
$Bi_2(Sr,Ca)_3Cu_2O_y$	3.816	1.909	0.0521	176.9	80	NPD	40)
$(Mo_{0.33}Cu_{0.67})Sr_2YCu_2O_y$	3.815	1.922	0.2318	166.1	37	XPD	15)

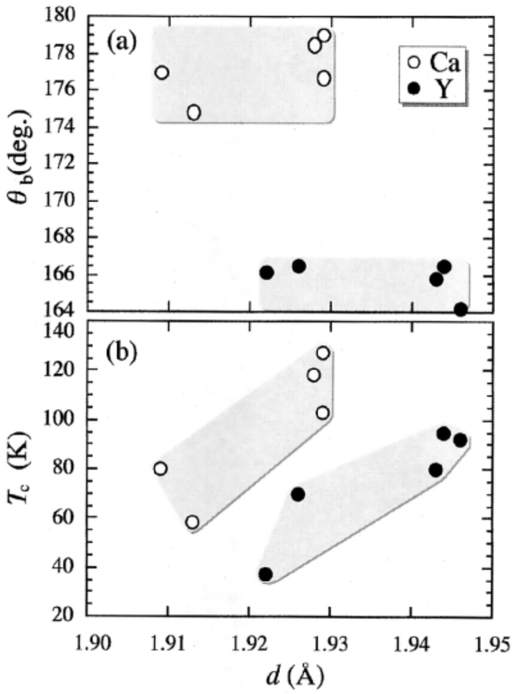

Fig. 4 Correlation between Cu-O length, *d*, buckling angle, θ_b,, and T_c of the compounds with two CuO_5 pyramids (*n*=2). Buckling angle is primarily determined by the species of cation, Y or Ca, between two CuO_2 planes.

T_c becomes higher. Slope of T_c vs. *d*（$\Delta T_c/\Delta d$）is 1500-3000 K/Å. The decrease in T_c by buckling is explained by the change in electronic structure[14]．

3-3 Triple and quadruple CuO_2 layers（*n*=3 and 4）

Layered cuprates with triple and tetra CuO_2 layers are all on the homologous series of $A_2B_2Ca_{n-1}Cu_nO_{2n+4}$ or $AB_2Ca_{n+1}Cu_nO_{2n+3}$, where A=Bi, Tl, Hg, and B=Sr, Ba. These compounds have triple or tetra CuO_2 layers. The layers are separated by an（AO）or $(AO)_2$ block layer. The CuO_2 layers are composed of two CuO_5 pyramids and one（*n*=3）or two（*n*=4）CuO_4 sheets.

In table 3, *l*, *d*, *b*, θ_b and T_c of cuprates with triple and tetra CuO_2 layers are listed. Similar to *n*=2 compounds, bumpy distortion of the CuO_5 pyramid is only buckling. The central planar CuO_2 plane is reported to be flat in every case.

However, because of lack of accurate crystallographic data, correlations among *l*, *d*, *b*, θ_b and T_c have not been known yet.

3-4 Common feature of layered cuprates（*n*=1-4）

In Fig.5, Tc's of various kind of cuprate superconductors are plotted against the Cu-Cu length in the CuO_2 plane, *l*. In addition to the data listed in table 1-3 represented by circles, recent data listed in table 4, those after Whangbo et al.[14]，and ours of Bi-based superconductors are

Table 3 Correlation between in-plane Cu-Cu length, *l*, Cu-O length, *d*, degree of buckling, *b* & θ_b transition temperature, T_c of high-T_c superconductors with three CuO_2 layers and more ($3 \leqq n \leqq 4$).

Layered cuprate	l (Å)	d(Å)	t (Å)	θ_t (deg)	T_c(K)	Method[a]	Ref.
$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_y$	3.818	–	–	–	107	XPD[a]	41)
$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_y$	3.822	–	–	–	111	XPD[a]	42)
$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_y$	3.822	–	–	–	111	XPD[a]	43)
$Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_{10.5}$	3.822	–	–	–	111	XPD[a]	44)
$Bi_{1.84}Pb_{0.34}Sr_{1.91}Ca_{2.03}Cu_{3.06}O_y$	3.822	–	–	–	111	XPD[a]	45)
$Bi_{1.68}Pb_{0.32}Sr_{1.75}Ca_{1.75}Cu_{2.85}O_y$	3.826	–	–	–	108	XPD[a]	46)
$Bi_{1.84}Pb_{0.34}Sr_{1.91}Ca_{2.03}Cu_{3.06}O_y$	3.818	–	–	–	107	XPD[a]	47)
$TlBa_2Ca_2Cu_3O_{8.5}$	3.847	(1.924)	(0)	(180)	112	XPD[a]	48)
$TlBa_2Ca_2Cu_3O_{9+y}$	3.843	1.922	0.0317	178.1	123	XPD	49)
$Tl_2Ba_2Ca_2Cu_3O_{10+x}$	3.818	–	–	–	102	XPD[a]	50)
$Tl_2Ba_2Ca_2Cu_3O_{10}$	3.848	1.926	0.0818	175.1	116	XPD	51)
$Tl_2Ba_2Ca_2Cu_3O_{10.5}$	3.850	–	–	–	114	XPD[a]	52)
$Tl_2Ba_2Ca_2Cu_3O_{10}$	3.849	1.925	0.0285	178.3	125	XPD	53)
$Tl_2Ba_2Ca_2Cu_3O_{8.41}$	3.818	–	–	–	133	XPD[a]	54)
$TlBa_2Ca_3Cu_4O_{10.5}$	3.848	(1.924)	(0)	–	112	XPD[a]	55)
$TlBa_2Ca_3Cu_4O_{11}$	3.850	(1.925)	(0)	–	112	XPD[a]	56)
$Tl_2Ba_2Ca_3Cu_4O_{12}$	3.852	–	–	–	104	XPD[a]	57)
$Tl_2Ba_2Ca_3Cu_4O_{12}$	3.850	(1.925)	(0)	–	112	XPD[a]	58)

XPD[a]: determined by X-ray powder diffraction but not refined by Rietveld analysis

plotted by squares, triangles, and pentagons, respectively. Here, data of over- and under-doped samples are included.

In spite of a drastic increase in the kind of cuprate superconductors after the work by Whangbo et al., the feature that the existence of three major classes of T_c vs. l correlations (represented by solid lines) which are distinguished by the cations Ba^{2+}, Sr^{2+}, and Ln^{3+} occupying the 9-coordination sites represented by green, yellow, and red points, are unchanged. It is also confirmed that each class seems to have an optimum value of l, 3.846, 3.820, and 3.776 Å, respectively. In average, the Ba-class has larger Cu-Cu length than the Sr-class, and the Sr-class has larger Cu-Cu length than the Ln-class. This is because the in-plane Cu-Cu length is primarily governed by the size of the 9-coordination site cation, and the ionic radii of these cations increase in the order $Ln^{3+} < Sr^{2+} < Ba^{2+}$.

Another remarkable feature is wide variation of the Cu-Cu length for the Sr-class. While the tolerance of the Ln- and Ba- class is about 0.05 Å, that of the Sr class is about 0.1 Å. The wide tolerance region of the Sr class made it possible to synthesize various Sr-contained compounds represented by $(M,Cu)Sr_2YCu_2O_y$[15]. Although it is interesting that the Sr-class has about double tolerance of the Cu-Cu length compared with the Ln- and Ba-class, the reason is not so clear. Maybe, stable phases besides the layered cuprate will compete with the layered cuprate phase for the Ba- and Ln- class. For example, it is reported that $(M,Cu)Sr_2YCu_2O_y$ is more stable than $(M,Cu)Ba_2YCu_2O_y$[62].

The feature pointed out by Wangbo et al. telling that the slope of over-doped region of T_c vs. Cu-Cu length of each class overlaps[19], was not

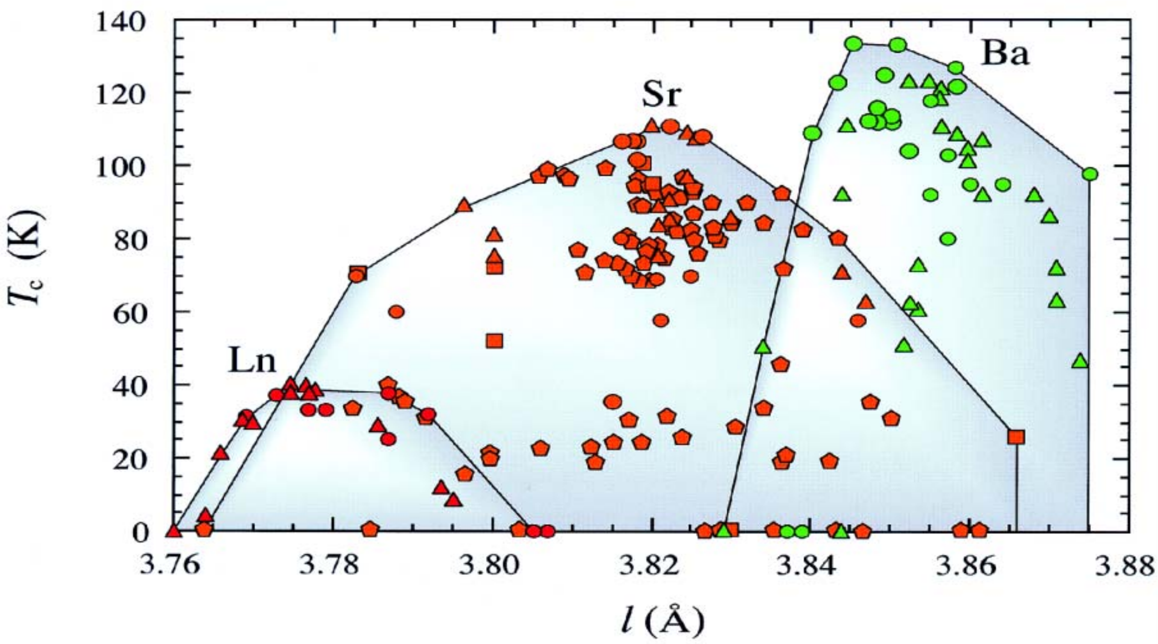

Fig. 5　Correlation between Cu-Cu length, l, shape of CuO_2 plane, and T_c with 1 to 4 CuO_2 layers. Only for this figure, data of under- and over-doped samples together with optimum-doped samples are plotted. Data of new compounds[59,60], those after Whangbo et al.[14], and our data of Bi-based cuprates are represented by triangles, squares, and pentagons, respectively. Three classes distinguished by the cations Ba^{2+}, Sr^{2+}, and Ln^{3+} occupying the 9-coordination sites are displayed in green, yellow, and red points.

Table 4　Correlation between in-plane Cu-Cu length, l, Cu-O length, d, buckling, b, degree of buckling θ_b, transition temperature T_c of various high-T_c superconductors.

Layered cuprate	l (Å)	d (Å)	t (Å)	θ_t (deg)	T_c (K)	Method[a]	Ref.
$Bi_2Sr_2(Sm_{0.75}Ce_{0.25})_2Cu_2O_{10+y}$	3.866	1.938	0.143	171.5	24	XPD	59)
$(Hg_{0.7}Mo_{0.3})Sr_2CuO_y$	3.800	–	–	–	52-72	XPD[a]	60)
$(Hg0.9Re_{0.1})Sr_2CuO_y$	3.783	–	–	–	70	XPD[a]	60)
$(Hg_{0.7}Mo_{0.3})Sr_2(Ca_{0.7}Y_{0.3})Cu_2O_y$	3.821	–	–	–	95-0	XPD[a]	60)
$(Hg_{0.8}Re_{0.2})Sr_2(Ca_{0.7}Y_{0.3})Cu_2O_y$	3.818	–	–	–	100	XPD[a]	60)

XPD[a]: determined by X-ray powder diffraction but not refined by Rietveld analysis

confirmed by our result. Considering that the ratio of itinerant holes in the CuO_2 plane vs. localized holes in the block layer is varied by both the Cu-O bond and the Madelung potential around the Cu-O bond correlated with crystal structure[15], the hole doping level may be different one another even if the Cu-O length is the same. Therefore, it is expected that all slopes of over-doped region of T_c vs. Cu-Cu length of each class may not overlap.

4. Conclusion

As for cuprates with a single CuO_2 layer, a tilt region, where the in-plane Cu-O length was between 1.906-1.923Å, was revealed. Tilt drastically suppressed superconductivity. As for cuprates with double CuO_2 layers, all the compounds had buckling-type distortion in a CuO_5 pyramid. The degree of distortion, θ_b was 164-167° and 174-179° when the kind of cation between the two facing CuO_5 pyramids was calcium and yttrium, respectively. The highest transition temperature of 127K was obtained for $HgBa_2CaCu_2O_y$ with having largest Cu-O length and smallest buckling degree.

As for layered cuprates ($1 \leqq n \leqq 4$), among transition temperatures, in-plane copper oxygen bonds length and tilting/buckling of the CuO_2 plane was examined. A common feature of the layered cuprates was the existence of three major class of Tc vs. Cu-Cu length, which is distinguished by the cations Ba^{2+}, Sr^{2+}, and Ln^{3+} occupying the 9-coordination sites. Another remarkable feature was wide tolerance of the Cu-Cu length for the Sr-class. While the tolerance of the Ln- and Ba-class was about 0.05Å, that of the Sr class was about 0.1Å.

From the results, it is found that tilt/buckling is strongly correlated with in-plane copper oxygen bond length and that T_c's of the cuprate superconductor are correlated with both the in-plane copper-oxygen bond length and the tilt/buckling of the CuO_2 plane. These facts suggest that the T_c is primarily determined by the shape of the copper-oxygen bond.

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