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Detailed structure of a Pb-doped $Bi_2Sr_2CuO_6$ superconductor

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The crystal structure of $(Bi_{1.82}Pb_{0.18})$ $(Sr_{1.84}Pb_{0.16})$ CuO_6 was determined from single-crystal intensity data measured on a four-circle diffractometer. The structure is orthorhombic, space group *Cccm* (No. 66); the lattice parameters: $a=5.392(3)$ Å, $b=24.603(5)$ Å, $c=5.300(3)$ Å, $V=703.2$ (5) Å^3 (the space group can be denoted as *Amaa* by a cyclic transformation of the cell constants). The R value was 0.048 for 418 unique reflections with $I>3.00\ \sigma(I)$. One of the O atoms bonded to Bi ions is disordered at two sites with a half occupancy and $B_{eq}=3.6(6)$ Å^2; although the thermal parameter is not so large as that reported by Torardi *et al.* [Phys. Rev. B **38**, 225 (1988)], the disorder suggests that the crystal has a lower symmetry. The valence state of the Cu ion in the present compound was evaluated to be trivalent based on the Cu-O distances [Asbrink and Norrby, Acta Crystallogr. B **26**, 8 (1970)] and the valence of Bi was estimated in comparison with that in other compounds. The O(3) sublattice dynamics in these types of superconductors is discussed based on the structural investigations. [S0163-1829(98)05629-X]

I. INTRODUCTION

The discovery by Bednorz and Müller of high- T_c superconductivity in the Ba-La-Cu-O system[1] led to the subsequent discovery by Wu *et al.* of high-temperature superconductivity in the Y-Ba-Cu-O (YBCO) system.[2] Many high-temperature superconducting oxides have been prepared with elemental substitutions in these systems. Fundamentally, such oxides contain cations such as Cu atoms (a critical element for the occurrence of superconductivity), an alkaline earth, and a rare earth or yttrium atoms. Moreover, since superconducting materials with T_c of 85 or 105 K in a Bi-Sr-Ca-Cu-O compound (2212 system) were discovered by Maeda *et al.*,[3] many studies have been carried out by elemental substitutions in order to increase T_c and improve other superconducting properties of this system. The crystal structures of the YBCO system were analyzed by previous workers[4–8] in order to investigate the conduction mechanism in the superconducting state. It is very interesting that the substitution of trivalent rare-earth atoms for Y in $YBa_2Cu_3O_7$ has little effect on the superconductivity and relatively little changes are observed in the cell constants for Pr, Sm, Eu, Gd, Dy, Ho, Er, and Tm substitutions,[7,8] in spite of the different structure types of their sesquioxides like Sm_2O_3 and Dy_2O_3. In the 2212 system, superconductors are the Bi-based high-T_c materials with the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ ($n=1$, 2, or 3) where all Cu atoms lie in CuO_2 planes.[9] The crystal structures in this system were investigated energetically and systematically by Tarascon *et al.*[10–13] and some workers[14] using single crystals. Tarascon *et al.*[9] concluded that the transition temperature is independent of the average copper valency, determined to be 2.15 ± 0.3 for $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ with $n=1$, 2, and 3, though the crystal structures have not been discussed in detail be-

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TABLE I. Atomic parameters and occupancy for Pb-doped Bi-2201. A sample dimensions are 0.16×0.10×0.01 mm^3. Estimated standard deviations refer to the last digit. $B_{\mathrm{eq}}=(8/3)\pi^2\{U_{11}(aa^*)^2 + U_{22}(bb^*)^2+U_{33}(cc^*)^2 +2U_{12}aa^*bb^* \cos\gamma+2U_{13}aa^*cc^* \cos\beta+2U_{23}bb^*cc^* \cos\alpha\}$.

Atom	x/a	y/b	z/c	B_{eq}	Occupancy
Bi	0.2682(1)	0.06340(4)	0.0000	1.90(2)	0.93
Pb	0.2682(1)	0.06340(4)	0.0000	1.90(2)	0.07
Sr	0.2473(3)	0.1776(1)	0.5000	2.80(5)	0.92(2)
Pb	0.2473(3)	0.1776(1)	0.5000	2.80(5)	0.08
Cu	0.7500	0.2500	0.5000	2.04(8)	1
O(1)	0.5000	0.2512(6)	0.7500	2.7(4)	1
O(2)	0.227(3)	0.144(1)	0.0000	4.2(5)	1
O(3)	0.347(5)	0.070(1)	0.394(5)	3.6(6)	1

cause of a poor structure determination. Generally, it is known that in $\mathrm{Bi_2Sr_2CuO}_y$ (hereafter denoted 2201), the higher the Pb content, the smaller the incommensurate modulation in the structure. Single crystals of Pb doped 2201 were synthesized by Chong *et al.*[15] with very small incommensurate modulation.

In order to determine the valences of Bi and Cu cations from accurate M-O (M=Bi and Cu) distances in these superconductors, a detailed crystal structure analysis of Pb-doped 2201 was made using the single-crystal x-ray-diffraction method. We present its crystal structure in detail and comment on the valences of cations in this system together with those in the Ta analog and other related compounds in the discussion section.

II. STRUCTURE ANALYSES

A single crystal having approximate dimensions of 0.16×0.10×0.01 mm^3 was selected for the x-ray-diffraction study. All measurements were made on a Rigaku AFC5R diffractometer with a graphite monochromated Mo $K\alpha$ radiation.

The data were collected using the $\omega/2\theta$ scan technique to a maximum 2θ value of 60°. The scan speed was 8.0°/min in ω. The weak reflections were rescanned to attain $I>50.0\sigma(I)$ (maximum of four scans). Of 3888 $h\pm k\pm l$ reflections measured, 573 were unique (R_{int}=0.082). The equivalent reflections were merged. Four standard reflections monitored every 150 reflections showed no significant fluctuation. The lattice parameters corresponding to a C-centered orthorhombic cell were determined by a least-squares fitting using the setting angles of 25 carefully centered reflections in the range of $32.86<2\theta<34.81°$ with the Bond method:[16] a=5.392(3) Å, b=24.603(5) Å, c=5.300(3) Å, and V=703.2(5) Å^3. On the basis of systematic absences ($h+k=2n$ for hkl, $l=2n$ for $0kl$ and $l=2n$ for $h0l$ reflections), the space group was determined to be *Cccm* or *Ccc2*. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.16 to 1.00, because the correction could not succeed in the analytical method due to the very thin sample. The data were corrected for Lorentz and polarization effects.

The structure adopting the space group *Cccm* was solved by the Patterson method.[17] The occupation probabilities in the Bi and Sr sites are included in the refinement. All atoms were refined anisotropically. A correction for secondary extinction[18] was applied (coefficient=5.57200E-08). The final cycle of full matrix least-squares refinement was based on 418 observed reflections $[I>3.00\sigma(I)]$ and 39 variable parameters and converged to R=0.048 and Rw=0.077. The largest parameter shift was 0.26 times its standard deviation [for the space group $Ccc2$, R=0.043 and Rw=0.064 for 700 observed reflections ($I>3.00\sigma(I)$) (R_{int}=0.082)]. The maximum and minimum peaks on the final difference Fourier maps were 4.69 and −4.89 e/Å^3, respectively. Neutral atomic scattering factors were taken from Cromer and Waber.[19] Anomalous dispersion effects were included in the F calculation; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[20] The values used for the mass attenuation coefficients are those of Creagh and Hubbel.[21]

III. RESULTS AND DISCUSSION

The coordinates, temperature factors, and site occupancies are listed in Table I. The doped Pb ions are distributed in both Bi and Sr sites. The position of O(3) was obtained from a difference Fourier map. The O(3) atom is statistically distributed at two equivalent sites. The anisotropic temperature factors (Table II) of the metal atoms (Bi, Sr, and Cu) have very large U_{33} components along the c axis in a space group of *Cccm*; this direction for the large component in the temperature factors is different from that of Bi-2212 reported by Sunshine *et al.*[14] The appearance on the incommensurate structure might be related to the direction of the large components in the anisotropic temperature factors of metals. The bond distances are given in Table III and those adopting the space group $Ccc2$ are also given for a comparison.

TABLE II. Anisotropic temperature factors for the atoms of Pb-doped Bi-2201. The general temperature factor expression: $\exp\{-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl)\}$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	0.0145(4)	0.0187(5)	0.0390(5)	−0.0008(4)	0	0
Sr	0.0088(8)	0.033(1)	0.064(2)	−0.0017(7)	0	0
Cu	0.003(2)	0.022(2)	0.0522(3)	0.000(1)	0	0
O(1)	0.008(8)	0.038(10)	0.06(1)	0	−0.004(8)	0
O(2)	0.018(9)	0.03(1)	0.11(2)	−0.003(7)	0	0
O(3)	0.02(1)	0.07(2)	0.05(1)	−0.02(1)	−0.004(10)	0.02(1)

TABLE III. Interatomic distances (Å) in Pb-doped Bi-2201. Cu-O(1): 1.722 for *Ccc*2is unreasonable short distance. Therefore, space-group *Cccm* is selected for the compound.

Bond type	*Cccm* Interatomic distance (Å)
Cu-O(1)	1.8905(6)(×4)
Cu-O(2)	2.6011(254)(×2)
Bi-O(2)	2.003(254)(×1)
Bi-O(3)	2.1358(244)(×2)
Bi-O(3)	2.1541(244)(×2)
Bi-O(3)	3.2457(244)(×2)
Bi-O(3)	3.3547(302)(×2)
Bi-O(3)	3.3708(245)(×2)
Sr-O(1)	2.5697(107)(×2)
Sr-O(1)	2.6252(109)(×2)
Sr-O(2)	2.6846(173)(×1)
Sr-O(2)	2.7752(76)(×2)
Sr-O(3)	2.7623(301)(×2)
Sr-O(2)	2.9504(171)(×1)
	*Ccc*2
Cu-O(1)	2.070(17)(×2)
Cu-O(1)	1.722(18)(×2)
Cu-O(2)	2.595(13)(×2)

The structure of the Bi-2201 compound is generally well known to have similarities to the perovskite-type K_2NiF_4 structure and also has a striking resemblance to $Sr_3Ti_2O_7$ (tetragonal, $I4/mmm$, $a=3.90$ Å, $c=20.38$ Å) which may be considered to have an intermediate structure between Sr_2TiO_4 (K_2NiF_4 type) and $SrTiO_3$ (perovskite).[22] In the substitution of Bi (III) or Ca(II) for Sr and Cu (II) for Ti (IV) sites in the Sr_2TiO_4 structure, Müller-Buschbaum *et al.* and Boivin *et al.* have proposed structure models for Sr_2CuO_3,[23] $CaCu_2O_3$,[24] and Bi_2CuO_4[25] based on their x-ray intensity data. It was considered that copper ions exist in the divalent oxidation state in these compounds which possess a single sheet of corner-sharing CuO_4 units. The 2201 compound could not be considered as a derivative mixed from compounds, for example, such as Sr_2CuO_4 and Bi_2CuO_4. The average Cu-O distances in these sheets are given in Table IV along with those of other oxide superconductors. It is generally believed that the oxygen polyhedra around the Cu (II) ion in the compounds are mainly elongated octahedra with two ligands on the long axis and four on the short axes due to the Jahn-Teller effect.[26] The equatorial (denoted as R_S) and axial (denoted as R_L) Cu-O bond distances in Tl-2201 (Ref. 27) (Nonzero values of the thermal factors β_{12} and β_{13} of the Bi atom in the Bi-2201 compound was reported by Torardi *et al.*,[27] but they should be zero from the symmetry requirement.) are not different from those of Cu (II) O;[28] the orientation of polyhedra around the Cu (II) ion in Pb-doped Bi-2201 is very similar to that of Tl-2201. The tetragonal elongation of the coordination sphere around the Cu (II) cation shows the consequence of a strong Jahn-Teller effect in the compounds.[26]

The R_L values in both Bi-2201 and -2212 systems is reduced significantly (Table IV); according to Bersuker,[26] the R_L distances fall within a range between 2.5 and 3.0 Å, and $R_S=1.92$ Å in the large number of the compounds including Cu (II) atom. A square pyramidal polyhedron around the Cu atom is characteristic in the superconducting compounds and the pyramid clusters are stabilized by the crystal environment. Therefore, it is a reasonable consideration judging from both R_S and R_L bond distances in the 2201 and 2212 compounds that the valence of Cu ion in the pyramid is trivalent.

Next, we should focus on the coordination around the Bi atom. It is considered that the occurrence of Bi (V) is unlikely in these superconducting compounds.[10] In Bi-2201 and 2212 superconductors, the Bi atom is coordinated to six oxygens in a slightly distorted octahedral arrangement, the Bi-O distances are different from compound to compound, the averaging being 2.66 Å, for Bi-2201, and 2.67 and 2.74 Å for the 2212 compound (Table IV). These values could not be evaluated from the viewpoint of crystallography; actually, it is difficult to distinguish the valence of the Bi atom in the crystal. The average of the five or six short Bi (III)-O distances is generally in a range of 2.32–2.40 Å (Table V).[29,30] However, these values are taken from oxides where the coordination polyhedra are very irregular and the true coordination number is greater than five or six. Cox and Sleight[29] concluded from neutron-diffraction data (Table V) that the occurrence of Bi (III) and Bi (V) results from the Bi-O bond distances (2.28 and 2.12 Å) coordinated octahedrally in Ba_2 Bi (III) Bi (V) O_6 and the shorter average, 2.28 Å of Bi (III)-O distances is due to the covalency of Bi-O bonds; therefore, this covalency favors a low coordination number.

In the present study of the Pb-doped 2201 compound, Bi is coordinated by five oxygens with shorter Bi-O distance of 2.12 and by six O(3) and its equivalents with longer Bi-O bonds (Table III). The shorter value agrees very well with that of Bi (V)-O bonds both expected from Shannon and Prewitt[31] and obtained from some experiments (Table V). Thus, the bonding of Bi can be rationalized on the basis that it is Bi (V). For the space group of *Ccc*2, the shorter Bi-O distance split into two 2.04 and 3.34 Å (the average being 2.71 Å) because of the disordered arrangement of the O(3) atom. It is difficult to evaluate the valence of Bi in such a situation as an unreasonable short Bi-O distance. Therefore, the space group *Cccm* selected for the present compound is more reliable.

In order to elucidate the possibility of our proposed double-well potential for O(3) with the program system PROMETHEUS,[34] another structure analysis of the compound with the different content of Pb was executed using a single-crystal x-ray-diffraction method. The results did not support the Gram-Charlier expansion for O(3), but our model, that is the split atom model.

On the superconducting state, it may be considerable that the structures of these superconductors are partly related closely with that of a sodium chloride (rocksalt type as seen in Fig. 1).

In the crystals of the Bi-2201 compound and Tl analog, Bi or Tl occupies only one site in contrast to two distinct Bi sites in $BaBiO_3$ in which no atom mixing exists. It may be the nature of the Tl-O versus the Bi-O bonding within the double layers that is very important in understanding the ordered structure of the superconducting state at low temperature in the 2201 compounds.

TABLE IV. Crystal data and bond distances for the compounds in the Bi-Sr-Ca-Cu-O system compared with those of some copper (II) oxides.

	Sr_2CuO_3	Bi_2CuO_4	$CaCu_2O_3$	CuO	Tl_2O_3	$Tl_2Ba_2CuO_6$ 2:2:0:1	$Bi_2Sr_2CuO_6$ 2:2:0:1	$(Bi_{1.86}Pb_{0.14})$ $(Sr_{1.84}Pb_{0.16})$ present study	CuO_6	$Bi_{2.2}Sr_2Ca_{0.8}$ $Cu_2O_{8.8}$ 2:2:1:2	$Bi_4(SrCa)_6$ Ca_4O_{16+x} 2:2:1:2
Space group	*Immm*	*P4/ncc*	*Pmmn*	*C 2/c*	*I a3*	*I4/mmm*	*A maa*	*Cccm*	*Ccc2*	*Fmmm*	*I4/mmm*
								(*A maa*)	(*A 2aa*)		
Cell constants (Å)	$a=12.68$	$a=8.510(1)$	$a=9.85$	$a=4.6837(5)$	$a=10.543$	$a=3.866(1)$	$a=5.362(3)$	$a=5.392(3)$	(=5.300)	$a=5.414(2)$	$a=3.814(3)$
	$b=3.91$	$a=5.814(1)$	$b=4.11$	$b=3.4226(5)$		$c=23.239(6)$	$b=5.374(1)$	$b=24.603(5)$	(=5.392)	$b=5.418(2)$	$c=30.52(3)$
	$c=3.48$		$c=3.47$	$c=5.1288(6)$			$c=24.622(6)$	$c=5.300(3)$	(=24.603)	$c=30.89(1)$	
				$\beta=99.54(1)^{O}$							
Average of Cu-O in CuO4 sheet (Rs)	1.95	2.04	1.98	1.956		1.9330(5)	1.900(2)	1.891	1.895	1.92	1.91
Cu-O up (RL)			3.09	2.784(4)		2.714(9)	2.58(11)	2.60(3)	2.59(2)	2.04	2.16
Cu-O down (RL)			3.09	2.784(4)		2.714(9)	2.58(11)	2.60(3)	2.59(2)		
Average of Ca-O			2.35							2.49	2.52
(C.N.[a])			(6)							(8)	(8)
Average of M(II)-O	2.58(Sr-O)					2.81(Ba-O)	2.72(Sr-O)	2.71(Sr-O)	2.71 (Sr-O)	2.68 (Sr-O)	2.68 (Sr-O)
(C.N.[a])	(9)					(9)	(9)	(10)	(9)	(9)	(9)
average of M(III)-O		2.39			2.26 (Tl-O)	2.51 (Tl-O)	2.66 (Bi-O)	2.12 (Bi-O)	2.71 (Bi-O)	2.74 (Bi-O)	2.67 (Bi-O)
		(2.12+0.27)					1.97 3.28		2.04 3.34	2.42 3.17	2.22 2.97
(C.N.[a])		(6)			(6)	(6)	(8)	(5)	(6)	(6)	(6)
Expected[a] Ca-O			2.40							2.52	2.52
(C.N.)			(6)							(8)	(8)
Expected M(II)-O	2.69 (Sr-O)					2.87(Ba-O)	2.69 (Sr-O)	2.72 (Sr-O)	2.69 (Sr-O)	2.69 (Sr-O)	2.69 (Sr-O)
(C.N.)	(9)					(9)	(9)	(10)	(9)	(9)	(9)
Expected M(III)-O		2.42			2.28 (Tl-O)	2.28 (Tl(III)-O)	2.42 (Bi-O)	2.42 (Bi-O)	2.42 (Bi-O)	2.42 (Bi-O)	2.42 (Bi-O)
						2.90 (Tl(I)-O)					
(C.N.)		(6)			(6)	(6)	(6)	(6)	(6)	(6)	(6)
Expected Cu(II)-O	2.02		2.02			2.02	2.02	2.02	2.02	2.02	2.02
R(%)		5.6		3.2	9.0	2.1	13.0	4.8	4.3	17.3	16.0
Reference	23	25	24	28	32	27	27			14	10

[a] Data for coordination number (C.N.) as given by Shannon and Prewitt (Ref. 31).

TABLE V. Bismuth-oxygen coordination and distances in some Bi compounds.

Compound	Total Coord.	Range of Bi-O dist. (Å)	Upper break in dist. (Å)	Inner Coord.	Average Bi-O dist. (Å)	Refs.
$Bi_4Si_3O_{12}$	9	2.15–3.55	2.62	6	2.39	(30)
Bi_2GeO_5	7	2.13–3.18	2.66	6	2.35	(30)
$BiOHCrO_4$ (mono)	9	2.228–3.326	2.579	6	2.376	(30)
$BiOHCrO_4$ (ortho)	9	2.185–3.089	2.678	6	2.382	(30)
$Bi_2O_2SO_4 \cdot H_2O$	10	2.22–3.45	2.57	6	2.38	(30)
		2.10–3.35	2.59	6	2.32	(30)
$BiOHSeO_4 \cdot H_2O$	9	2.19–3.16	2.64	6	2.40	(30)
$Bi_{12}GeO_{20}$	7	2.076–3.170	2.640	6	2.357	(30)
$Ba_2Bi^{3+}Bi^{5+}O_6$	6				2.28	for Bi(III) (29)
$Ba_2Bi^{3+}Bi^{5}+O_6$	6				2.12	for Bi(V) (29)
(BiPb)(Sr Pb)CuO_6	11	2.005–3.371	2.60	5	2.12	This work

It is possible that there are microdomains within a single phase, the local structure of which is smaller in size than that of the host structure. Since the size of the domains is too small to grow up as nuclei of a guest crystal and distribute randomly throughout the crystal, their x-ray-diffraction pattern would not show any periodicity corresponding to the Laue symmetry. It is conceivable that the structures of these domains are in a dynamic state. The compositionally distinct domains do not firmly occupy in a portion, but, change the sizes and shapes of the domains in the lattice with the continuous migration; These phenomena may lead to the localization of the cations with different ionization state, for example, Tl (I) and Tl (III) or Bi(III) and Bi (V).

According to Torardi *et al.*,[27] the average of Tl-O bonds is 2.51 Å in Tl-2201. This value is almost the mean between 2.28 and 2.90 Å calculated from the sum of Tl (III)+O-(II) radii, and Tl (I)+O-(II) radii, respectively. The coordination number of Tl (III) in Tl $(III)_2O_3$ is six and the average of Tl (III)-O distances is 2.26 Å (Table IV).[32] This fact suggests that at the electron-ordered temperature the Tl atom in the Tl-double layer has the order of Tl (I) and Tl (III) together with a strong Jahn-Teller effect, in other words, each cluster is formed from Tl (I) O_6 and Tl (III) O_6. At a low temperature, it is considered that they are localized to form an ordered state. As previously mentioned in Bi-2201, there is little of the electron-ordered state of Bi, i.e., it exists mainly as Bi (V) together with also a strong Jahn-Teller effect. This supports the positional disorder of the O(3) atom. The difference of the electron-ordered structure may affect the T_c. Moreover, it is interesting that the average of Ba-O distances 2.81 Å is significantly shorter than the mean Ba (II)-O distances of 2.87 Å in Tl-2201 and that the doped Pb atoms partially occupy the Sr (II) sites in Bi-2201.

The O(3) atom which is bonded to Bi in the Bi-2212 has very large temperature factor at room temperature:[14] $B_{\mathrm{iso}}=18(8)$ Å^2. The shortest Bi-O bond, 2.42 Å (Ref. 14) in Bi-2:2:1:2 or 2.22 Å (Ref. 7) in 2212 are longer than that in this study. The difference between them may be ascribed to the cluster migration, though it is not clear. It is possible that the valence of the Bi atom changes partly from V to III corresponding to the mixed valence of copper. In these charge transfers of the compounds including 2201, the role of the alkaline-earth metals, Sr and Ca, should be investigated, that is, the transfer of electron from Sr to Bi (V) to form Bi (III), or from Ca to Cu etc., as Sienko and Sohn proposed for the role of the alkali metal in sodium vanadium bronze.[33] Such a very complicated ordered state may be considered for these compounds below T_c.

On the basis of the structural data presented we can consider some aspects of the oxygen sublattice dynamics, force constants, and discuss influence of the Pb substitution on them. The negatively charged O(3) ions occupy one of two positions between the positively charged Bi ones. This environment leads to an effective double-well potential, $U(z)=-g_2z^2+g_4z^4$ where g_2 and g_4 are positive parameters, and z is the O(3) ion displacement. The importance of the double-well potential for high-temperature superconductivity was discussed.[35] This potential is characterized by two experimentally measured values: the interwell distance $2d\approx 1.12$ Å and a typical value of the O(3) vibration frequency at one of the potential wells which corresponds to the energy $\hbar\omega=30$ meV.[36] The values of g_2 and g_4 can be estimated on the basis of these two parameters. The interwell distance is evaluated as follows: $d_0=\sqrt{g_2/2g_4}$ with the corresponding second derivative $U''(d_0)=4g_2$ and the vibrational frequency $\omega=2\sqrt{g_2/M}$, where M is the oxygen ion mass. The height of the potential barrier between the minima is equal to $|U(d_0)|=g_2^2/4g_4$. First we can find how the oxygen moves between the potential wells. The tunneling time can be found within the semiclassical approach which yields

$$\omega\tau_t=\exp\left(\frac{2}{\hbar}\int_{-d}^{d_0}|p(x)|dx\right)=\exp\left(\frac{2d_0^2}{3x_0^2}\right);$$

$$|p(x)|=\sqrt{2M[U(x)-U(d_0)]},$$

where $x_0=\sqrt{\hbar/2M\omega}$ is the zero-point vibrational amplitude. Due to large value $d_0/x_0\approx 10$ the tunneling mechanism is not effective in this case. However, the thermal activation time $\tau_a=\omega^{-1}\exp(|U(d_0)|/T)$ is not larger than 10^{-4} s at $T=100$ K. The ratio $d_0/c\approx 0.1$ corresponds to the first-principles estimation of lattice nonlinearities which yields $d_0/c\sim(m/M)^{1/4}=0.076\ll 1$, where m is the electron mass.[37] Another way to understand the role of nonlinearities is to evaluate the relative shift of the phonon frequency due to

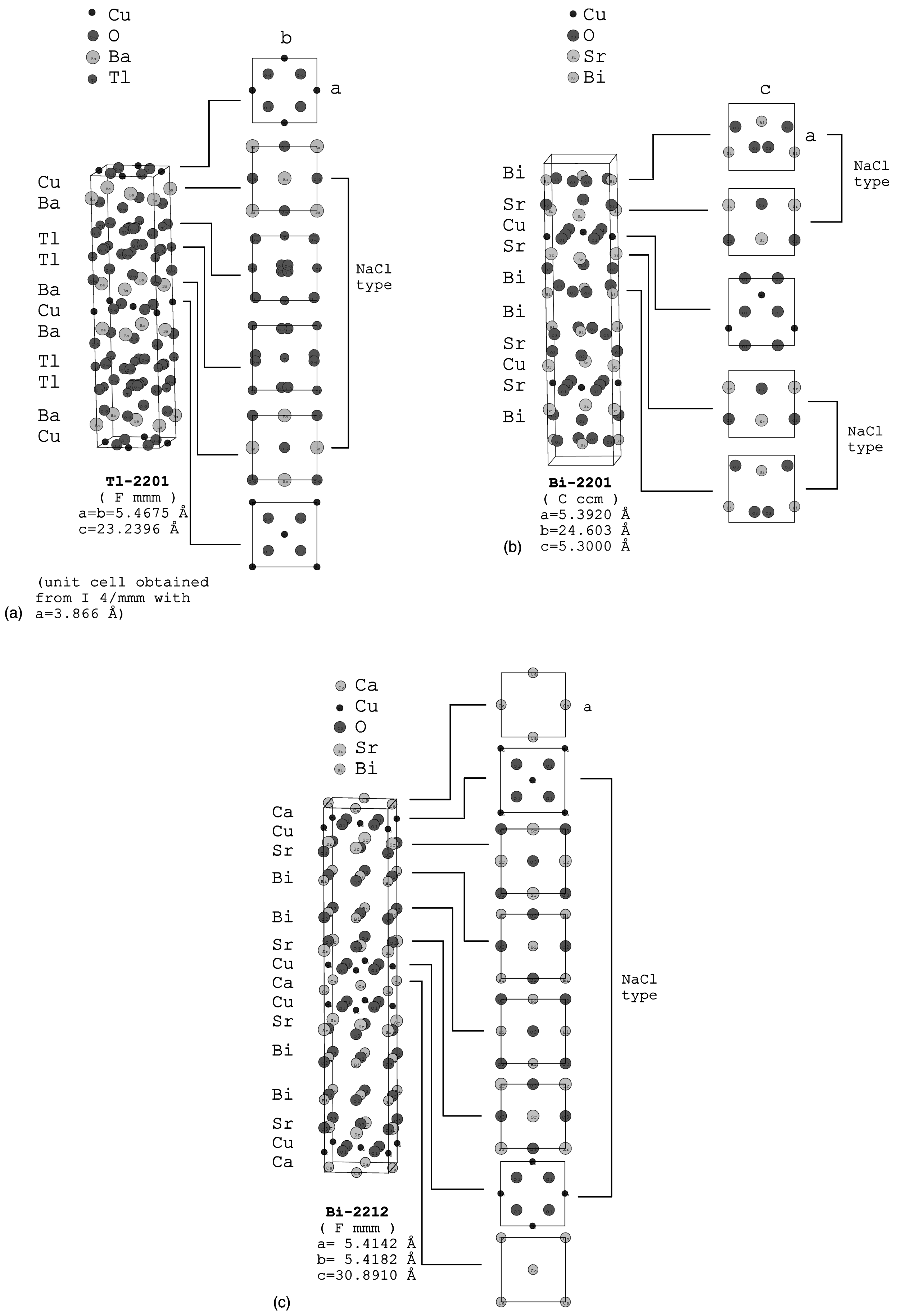

FIG. 1. Crystal structures in Tl- and Bi-2201, and Bi-2212.

nonlinearities: $\Delta\omega_n/\omega = 15x_0^2/4d_0^2 \approx 0.04$. This small value confirms a weak role of nonlinearities for lattice dynamics and superconductivity.

Now we can estimate parameters of the effective potential and compare them to the strength of the Coulomb interaction at BiO(3) planes with the aim to understand what forces are responsible for the lattice dynamics and crystal structure. From experimental estimation we get: $g_2 = M\omega^2/4 \approx 2\times10^4$ erg/cm^2. From consideration of the direct unscreened Coulomb interaction within the BiO(3) planes we obtain the value: $g_{2,C} \approx -2Q_{\rm Bi}Q_{\rm O}/(c/2)^3 \approx 12\times10^4$ erg/cm^2 where $Q_{\rm Bi}$ and $Q_{\rm O}$ are the charges of the corresponding ions. This sharp difference $g_{2,C} \approx 6g_2$shows that Coulomb interaction is considerably screened and covalent (non-Coulomb) interactions play a very important role for these planes.

With this knowledge we can consider how Pb influences the properties of the Bi-O(3) planes, especially the oxygen disorder there. Pb ions at Bi sites induce asymmetry of the double-well potential. The relative energy shift ΔW of the minima due to the difference of Pb and Bi ions ($\Delta Q = |Q_{\rm Pb} - Q_{\rm Bi}|$) is estimated as $\Delta W = 8\chi|Q_0\Delta Q|d_0/c^2$ where χ is a coefficient which includes both the screening of the Coulomb interaction and the contribution of non-Coulomb forces. The non-Coulomb forces should be changed under the Pb substitution in the same way as the Coulomb ones because the lattice is stable as a result of the equilibrium of the screened Coulomb and non-Coulomb interactions. If $\Delta W > \hbar\omega/2$, which is the case there, the oxygen will be frozen in the lower minima and no tunneling will be possible because of the energy conservation. At the same time, the asymmetry induced by Pb will increase the height of the potential barrier between the wells of the value approximately $\Delta W/2$. This can drastically increase the thermal activation time and prohibit thermal activation from the stable (lower minimum) to the metastable (higher minimum) state. For the same reason, the field of Pb decreases asymmetry of the potential in the vicinity of the stable minimum and leads therefore to an increase of the nonlinearities in the oxygen sublattice dynamics. At the same time, the Pb-Bi asymmetry leads to the opposite change for the metastable O(3) position: it considerably decreases both the activation and tunneling time for the ion motion from the metastable to the stable state. This can lead to changes in the part of the effective electron-electron interaction mediated by excitation of the O(3) motion within the double-well potential. This interaction is strongly retarded because of the large time necessary for the ion to overcome the interwell barrier ($\tau_a \gg 1/\omega$). The Pb substitution can make this interaction less retarded because of the decrease of the relaxation time between the metastable and stable states. At the same time, the Pb substitution leads to a frozen disorder and an increase in the height of the barrier. As a result of these two effects the substitution can diminish the role of this type of indirect carrier-carrier interaction.

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