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Crystal structure of a new high-T_c $TlBa_2Ca_3Cu_4O_{11}$ superconductor by high-resolution electron microscopy

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The crystal structure of a new high-T_c $TlBa_2Ca_3Cu_4O_{11}$ (1:2:3:4) superconductor was studied by a high-resolution electron microscopic measurement. The electron diffraction patterns give a simple tetragonal lattice with the lattice constants of $a=b=3.9$ Å and $c=19$ Å. The lattice image viewed along [010] showed clearly the single Tl-O layer alternating with four Cu-O sheets. The A-site layers of Ba or Ca atoms also alternate with the B-site layers of Tl or Cu atoms as in the layered perovskite compound ABO_x. Since oxygen sites in the Ca layer are vacant, the structure is one of the oxygen-deficient perovskite. This phase has a new space group of $P4/mmm$ different from the previous cuprate oxide superconductors and it has a large new superconductor family of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ ($n=1,2,3,4,5,\ldots$).

A new $Tl_1Ba_2Ca_3Cu_4O_{11}$ (1:2:3:4) superconductor with a high-T_c of 122.1 K has been discovered[1] in the Tl-Ba-Ca-Cu-O system.[2] An x-ray diffraction (XRD) measurement for the new 1:2:3:4 powder phase revealed a tetragonal structure with a lattice constant of $a=b=3.85$ Å and $c=19.1$ Å.[1] The exact lattice structure is still an open question.

In this work the electron diffraction patterns and the lattice images were observed by high-resolution transmission electron microscope (TEM) measurements for the refinement of the lattice structure. We revealed the lattice structure and space group of the new cuprate-oxide superconductor with a single Tl-O layer and four CuO layers for the first time.

The samples of 1:2:3:4 phase were prepared by firing the pellets of mixed powders of Tl_2O_3, CaO, BaO_2, and $BaCu_3O_4$ with a nominal composition of $Tl_4Ba_2Ca_3Cu_4O_{15}$ at 890 °C for about 20 min in a flowing oxygen gas. The firing time was controlled by monitoring the weight of evaporated Tl_2O_3. This preparation process was more controllable than another preparation process with a furnace cooling after 10 min firing.[1] The sample was confirmed to be an almost single phase of tetragonal 1:2:3:4 phase by x-ray powder diffraction analysis except for a trace of $BaCuO_2$ and 2:2:2:3 phases. The composition of the samples was determined by an electron probe microanalysis and inductively coupled plasma spectrometer. The oxygen content was measured by an inert-gas fusion nondispersive ir method. The T_c (50% drop point of the resistance transition) of the sample was 121.9 K and the zero resistance point was 120.0 K.

Electron microscope observations were performed on a JEM 2000 EX at 200 kV. The microscope has a point resolution of 2.1 Å. The sample was crushed in an agate mortar. The sample cleaves easily on a preferred c plane, since the sample is a layered compound. Almost all the particles have a preferred c plane. The preferred orientation of the sheets was convenient for the observation along [001], but it made difficult the observation along [010] due to a small opportunity to find the b plane. The dimension of observed sample crystallites was about 2 μm.

Figure 1 shows the electron diffraction pattern (inserted in upper and right part) and the lattice image viewed along [001]. The electron diffraction pattern gives a simple tetragonal structure with the lattice constant of $a=b=3.9$ Å, because every ($hk0$) spot is observed and any extinction rule is not observed. The lattice constant is consistent with $a=b=3.85$ Å from the XRD measurement.[1]

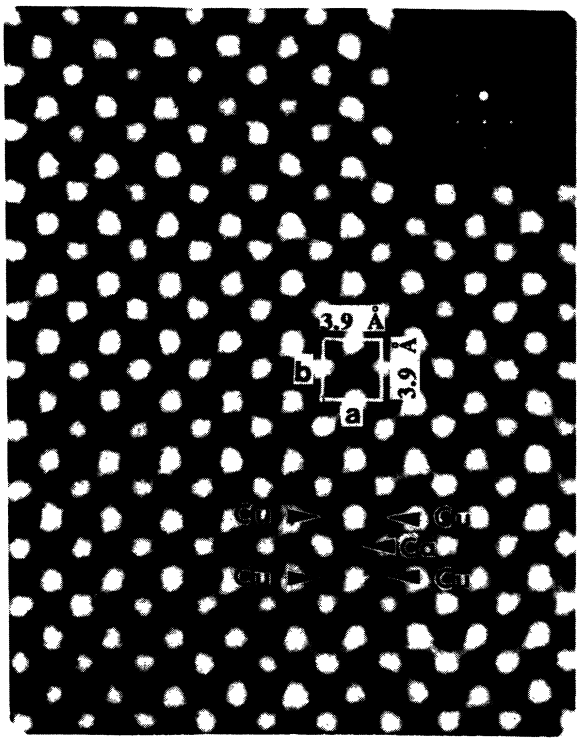

FIG. 1. The electron diffraction pattern and the lattice image of the [001] zone of a $TlBa_2Ca_3Cu_4O_{11}$ crystal, which gives a simple square lattice of $a=b=3.9$ Å.

The lattice image of Fig. 1 consists of a common face-centered square net of 3.9 Å×3.9 Å enclosed with a white line. The image can be interpreted as a projected charge density of the crystal atoms. The squarelike dark spots corresponds to the *A*-site atoms of Ba and Ca or the *B*-site atoms of Tl and Cu. These atoms are aligned along the *c* axis. It is difficult to distinguish which spot is *A* or *B*. The light spots alternating with the dark spots correspond to the oxygen atoms because of the small electron scattering factor of the light oxygen element.

Figure 2 shows the electron diffraction pattern (in upper and right part) and the lattice image viewed along [010]. The electron diffraction pattern of the [010] zone also gives a simple tetragonal structure with a lattice constant of $a=3.9$ Å and $c=19$ Å, because every $(h0l)$ spot is observed and any extinction rule is not observed. The lattice constants are consistent with $a=3.85$ Å and $c=19.1$ Å from the XRD measurement.[1] A modulation with a period of (006) along the $(00l)$ direction is obviously observed, which corresponds to the lattice parameter of 3.2 Å.

The lattice image of Fig. 2 shows the periodic light and dark bands along the *c* axis. The period of a collinear dark spot lines separated by a wide light band is 19 Å. The light band corresponds the light atoms of Cu and Ca, and the dark band to heavy atoms of Tl and Ba. Three collinear thick dark lines in the dark band along the *a* axis are attributed to the single Tl layer and double Ba layers on the both sides of the Tl layer. Seven collinear dark lines in the light band are attributed to the four Cu layers and three Ca layers alternating with each other. The image of the Ca atom is smaller than that of the Cu atom because of the lack of *d* electrons in the Ca atom. All the dark collinear lines along the *a* axis are assigned to all component atoms, as shown in Fig. 2.

The distance between Tl layers is 19 Å, which is consistent with the result of $c=19.1$ Å from the XRD measurement. The distance between the collinear dark spot lines in the dark band is larger than that in the light band. This indicates that the space between Tl and Ba layers is larger than that between Cu and Ca layers. The average space between the Cu layers in the lattice image corresponds to 3.2 Å, which is equal to the distance evaluated from the (006) periodic modulation in the $(h0l)$ diffraction pattern. Then the space between the Tl and Cu layers is estimated as 4.75 Å. Each of the component atoms are aligned along the *a* axis and they have a common distance 3.9 Å along the *a* axis, which is consistent with the lattice constant of $a=3.85$ Å. The rectangular square enclosed with a white line in the Fig. 2 corresponds to the unit cell.

There are two kinds of light spots. One is bright spots between each component atoms except Ca, another is dim

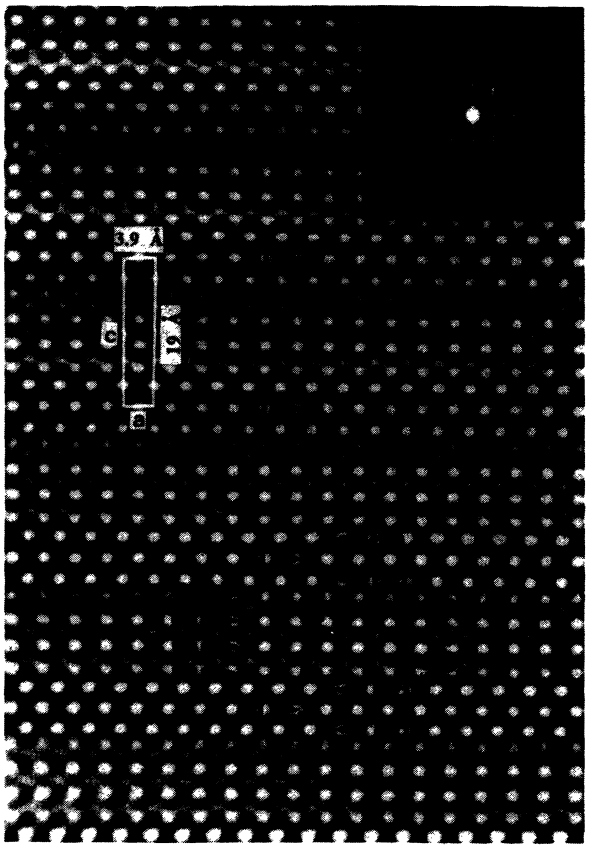

FIG. 2. The electron diffraction pattern and the lattice image of the [010] zone of a $TlBa_2Ca_3Cu_4O_{11}$ crystal, which gives a simple tetragonal lattice with lattice constants of $a=3.9$ Å and $c=19$ Å. Each component atom is observed.

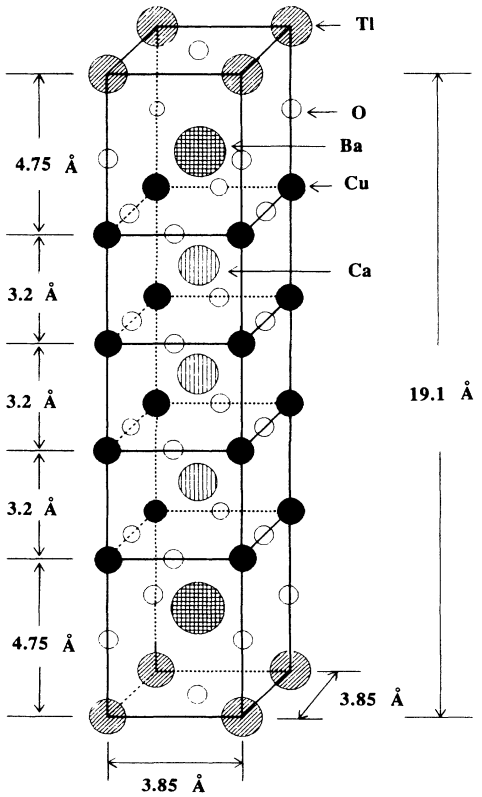

FIG. 3. The lattice structure of a $TlBa_2Ca_3Cu_4O_{11}$ crystal with a space group of $P4/mmm$ and with lattice constants of $a=b=3.85$ Å and $c=19.1$ Å.

spots between Ca atoms. The bright spots correspond to the oxygen atoms which are located around each atom. The dim spots are attributed to the oxygen vacancies in the Ca layer. Since the space of oxygen vacancy is much smaller than that of the oxygen atom and oxygen is a light element with large ion radius, the image of the vacancy becomes smaller and darker than that of the oxygen atom.

From these results, we can derive the simple tetragonal lattice structure of the 1:2:3:4 phase as shown in Fig. 3. The unit cell consists of fivefold simple tetragonal subcells. Threefold subcells in the middle part are composed of Cu and Ca atoms, in which each c parameter is 3.2 Å. The c parameter (marked with c_1) is consistent with the distance of 3.2 Å which corresponds to the distance for periodic (006) modulation in the $(h0l)$ diffraction pattern. The value is nearly equal to 3.17 Å of the distance between Cu and Cu layers in the $Tl_2Ba_2CaCu_2O_8$ compound.[3] Then the oxygen atoms are thought to be eliminated in the Ca layers between the Cu layers of this 1:2:3:4 phase too. Thus the 1:2:3:4 phase is one of oxygen deficient layered perovskite. On the other hand, both top and bottom tetragonal subcells are composed of Tl, Ba, and Cu atoms, in which the c parameter is estimated as 4.75 Å. This c parameter (marked with c_2) is almost the same as 4.72 Å of the distance between Tl and Cu layers in the $Tl_2Ba_2CaCu_2O_8$ compound.[3] From the lattice image of Fig. 2 we can evaluate the distances between the Tl and Ba layers and between the Ba and Cu layers as 2.75 Å and 2.0 Å, respectively.

The oxygen content of the 1:2:3:4 phase is also evaluated as $2n+3=11$ from the lattice structure. The oxygen content is near the observed value of 11.5 ± 1 from an inert-gas fusion and nondispersive ir method.[1]

The primitive tetragonal lattice of Fig. 3 has the four hold symmetry around the c axis and two hold symmetry around a and b axes and the mirror symmetry for each (001), (010), and (001) plane. Then the space group of the 1:2:3:4 phase is $P4/mmm$. The space group is the same as that of tetragonal $YBa_2Cu_3O_6$.[4]

The observed c lattice parameter is consistent with the c-axis rule of $c=6.3+3.2n=19.1$ (Å) $(n=4)$ for the single Tl-O layer compound $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$. This c-axis rule can be derived from the c_1 and c_2 lattice parameters as $c=2c_2+(n-1)c_1$. The rule is different from the c-axis rule of $c/2=8.2+3.2n$ for the double Tl-O layer compound $(Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4})_2$.[3,5]

Other new superconductors of $n=1$, 2, 3, and 5 of this family $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ have been prepared and their lattice constants well followed the c-axis rule of $c=6.3+3.2n$ for the single Tl-O layer compound. They have shown experimentally the c lattice constants of 9.4 Å for $n=1$, 12.6 Å for $n=2$, 15.9 Å for $n=3$, and 22.3 Å for $n=5$.

In summary, the high-resolution electron microscopic measurement gave the simple tetragonal diffraction patterns and the layered perovskite lattice images with lattice constants of $a=b=3.9$ Å and $c=19$ Å. The lattice is one of the oxygen-deficient layered-perovskite structure with single Tl-O layer alternating with four Cu-O layers following the c-axis rule of $c=6.3+3.2n$ (Å). The results gives a new space group of $P4/mmm$ different from the previous oxide superconductors. The phase has a large superconductor family of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ $(n=1,2,3,4,5,\ldots)$.

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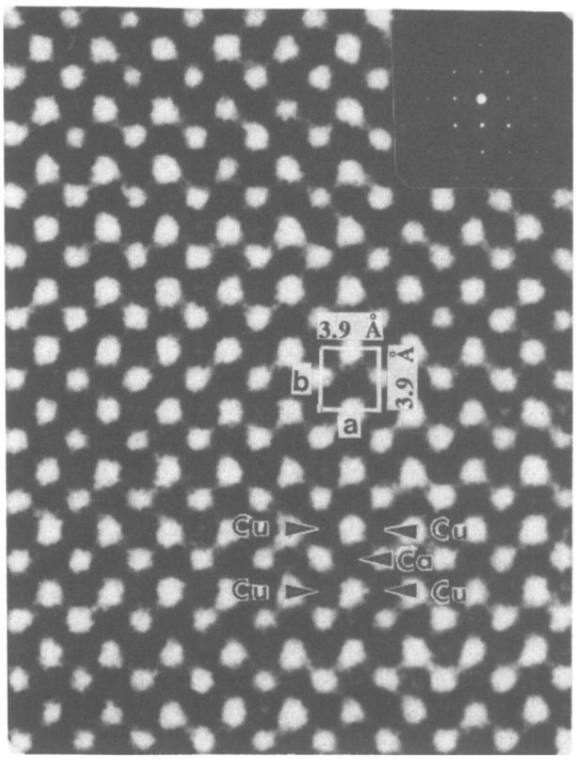

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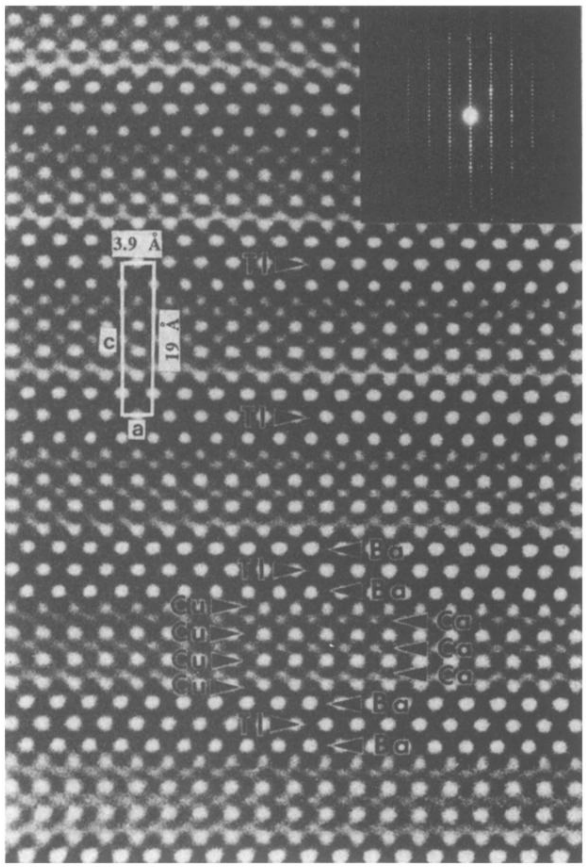

FIG. 2. The electron diffraction pattern and the lattice image of the [010] zone of a $TlBa_2Ca_3Cu_4O_{11}$ crystal, which gives a simple tetragonal lattice with lattice constants of $a = 3.9$ Å and $c = 19$ Å. Each component atom is observed.