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Crystal structure of stage-2 iodine-intercalated superconducting IBi$_4$Sr$_4$Ca$_2$Cu$_4$O$_x$

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The crystal structure of stage-2 iodine-intercalated superconducting IBi$_4$Sr$_4$Ca$_2$Cu$_2$O$_x$ has been determined by transmission electron microscopy to belong to the space group Bbmb with lattice parameters $a = 5.4$ Å, $b = 5.4$ Å, $c = 68.5$ Å. Iodine intercalates between every other Bi–O bilayer of the superconducting crystal, expanding the distance between the contiguous Bi–O layers by 3.6 Å and altering the atomic stacking across these Bi–O layers from the staggered configuration characteristic of superconducting Bi$_2$Sr$_2$CaCu$_2$O$_x$ to the registered configuration characteristics of stage-1 iodine-intercalated superconducting IBi$_2$Sr$_2$CaCu$_2$O$_x$.

1. Introduction

Recently, a number of stage-1 iodine-intercalated Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ ($n = 1,2,3$) superconductors were discovered, and the superconducting response of these materials was related to the amount of lattice expansion induced along the c-axis due to intercalation [1,2]. Beginning with host superconductors Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ ($n = 1,2,3$), iodine was intercalated at temperatures in the range of 150–200°C for times between 10–15 days. It was found from the temperature dependence of the AC and DC magnetic susceptibility that the stage-1 iodine-intercalated compounds behave as bulk superconductors with 2–10 K lower superconducting transition temperatures than those of the host materials. Both the weight change and energy dispersive X-ray spectroscopy of the stage-1 iodine-intercalated materials yielded a 1:2 ratio of I to Bi, corresponding to the stoichiometric formula IBi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ ($n = 1,2,3$). The crystal structure of the stage-1 iodine-intercalated superconducting IBi$_2$Sr$_2$CaCu$_2$O$_x$ was determined by X-ray diffraction analysis [2] and transmission electron microscopy [3]. The data

showed that iodine atoms intercalate between the Bi–O bilayers, with a corresponding expansion along the c-axis by 3.6 Å for each Bi–O bilayer, and that the intercalated iodine layers were epitaxial with respect to the adjacent Bi–O layers, assuming specific lattice sites. The intercalated iodine atoms also altered the atomic stacking across Bi–O layers from the staggered configuration characteristic of superconducting Bi$_2$Sr$_2$CaCu$_2$O$_x$ to a perfectly registered configuration in IBi$_2$Sr$_2$CaCu$_2$O$_x$. It was also found from the atomic spacings apparent in the high-resolution transmission electron microscope images of IBi$_2$Sr$_2$CaCu$_2$O$_x$ that the iodine layers bond to their neighboring Bi–O layers by van der Waals interactions.

Very recently, a stage-2 iodine-intercalated superconductor was synthesized as the dominant phase in a multi-phase microstructure containing some higher-stage compounds [4]. It was found from the temperature dependence of the AC and DC magnetic susceptibility that the stage-2 iodine-intercalated compound behaves as a bulk superconductor with 5 K higher superconducting transition temperature than that of the stage-1 iodine-intercalated super-

conducting $IBi_2Sr_2CaCu_2O_x$. In order to clarify the sequence of the iodine-intercalation, this detailed study of the crystal structure of $IBi_4Sr_4Ca_2Cu_4O_x$ has been undertaken using transmission electron microscopy.

2. Experimental

A plate-like crystal which dominantly contains the stage-2 iodine-intercalated superconducting $IBi_4Sr_4Ca_2Cu_4O_x$ was prepared by encapsulating iodine and a high-quality single crystal of $Bi_2Sr_2CaCu_2O_x$ in a Pyrex tube under a vacuum of $< 10^{-3}$ Torr. Iodine intercalation was carried out at $300°C$ for 10 days in a uniform-temperature furnace.

A transmission Laue pattern of the iodine-intercalated product was used to orient the crystal for precise cutting into thin wafers, which were subsequently sandwiched between silicon wafers, mechanically thinned and dimpled, then ion-milled to electron transparency. Ion milling was carried out at 77 K using argon ions accelerated at 3 kV through an incidence angle of 10 degrees. Transmission electron microscopy was performed in the Berkeley JEOL© JEM ARM-1000™ operating at 800 kV. Images were Fourier filtered using the image processing program SEMPER [5], and compared with images simulated by the code NCEMSS [6] at the National Center for Electron Microscopy.

3. Results and discussion

Figure 1 shows a high-resolution transmission electron microscope image of the iodine-intercalated compound with the incident electron beam along the [110] direction. Iodine atoms intercalate between every other Bi–O bilayer; however, a number of stacking faults marked S3 or S4, and amorphous pockets marked (P) are observed in the image. These defects are found consistently throughout all regions of the specimens. Less frequently, iodine atoms are found to periodically intercalate between every third Bi–O bilayer in some areas of the sample. The intensities of the diffraction peaks with indices of 00*l* in the X-ray diffraction patterns of the stage-2 iodine-intercalated superconductor were much weaker
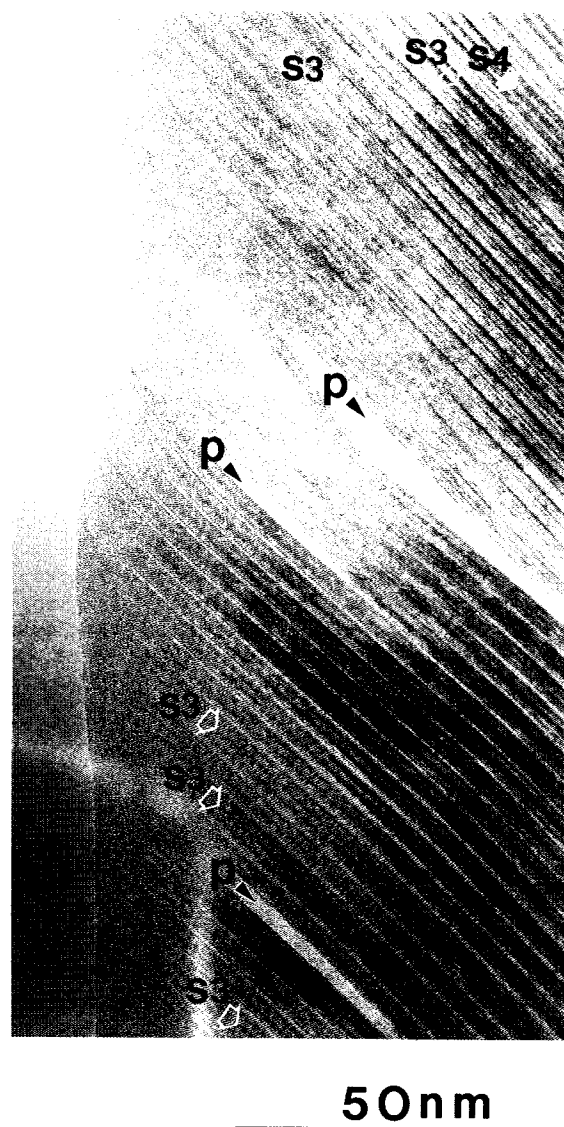

50nm

Fig. 1. Phase contrast high-resolution electron microscope image of the stage-2 iodine-intercalated superconductor. Note that stacking faults (S3, S4) and amorphous pockets (P) are observed in relatively small volume fraction.

than those of the pristine host material $Bi_2Sr_2CaCu_2O_x$. Since the periodicity of the iodine-intercalation along the c-axis is irregular, as shown in fig. 1, it is understood why the stage-2 iodine-intercalated superconductor does not yield strong peaks in X-ray diffraction patterns.
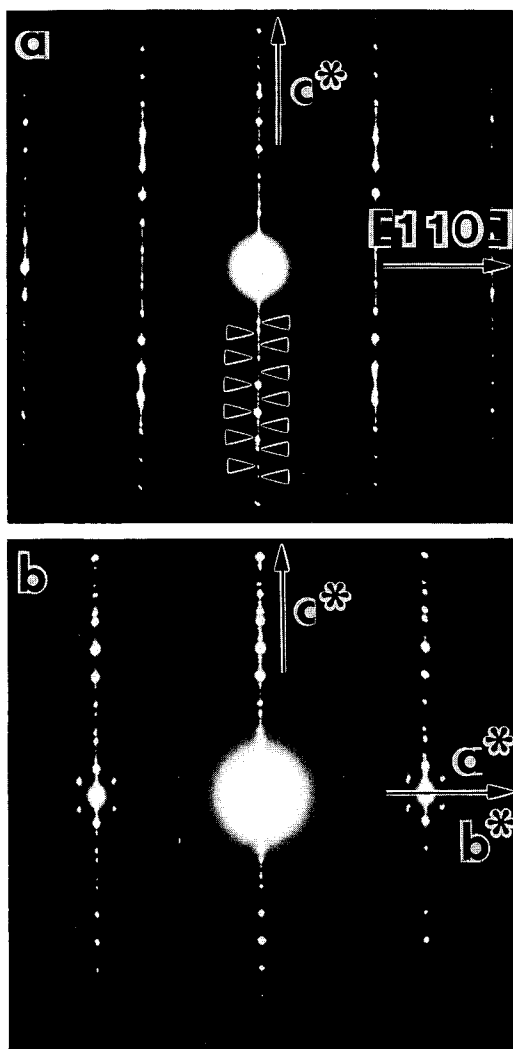
Figure 2 shows selected area electron diffraction

Fig. 2. Selected area electron diffraction patterns from an area near a 90 degree twin boundary in the iodine-intercalated superconductor. (a) $[110]$–c^* plane, (b) a^*–c^* and b^*–c^* planes. The diffraction spots marked by arrows correspond to lattice parameters $a=5.4$ Å, $b=5.4$ Å and $c=68.5$ Å of the stage-2 iodine-intercalated crystal.

patterns from the same area of the stage-2 iodine-intercalated compound in two different zone axes. These diffraction patterns were taken from a specimen area where the stage-2 iodine-intercalated compound was observed to coexist with higher-stage compounds. From fig. 2(b), it is found that the observed area consists of two single crystals with different crystal orientations, which form a 90 degree

twin structure, since both $10l$ primary reflections and satellite spots around $02l$ primary reflections are clearly observed in this reciprocal lattice section. The a-axis of one of the crystals is parallel to the b-axis of the other, while the c-axes of both crystals are also parallel. An identical twin structure has been observed in the host superconducting compound [7]. The $00l$ diffraction spots marked by arrows in fig. 2(a) correspond to the stage-2 iodine-intercalated compound, and the others correspond to the stage-3 iodine-intercalated compound with a c-lattice parameter of 49.4 Å. Lattice parameters of the stage-2 iodine-intercalated compound determined from direct measurements of these patterns are: $a=5.4$ Å, $b=5.4$ Å and $c=68.5$ Å. The a and b axial lengths are identical to those of the pristine host material and the stage-1 iodine-intercalated compound. Conversely, the c parameter is 7.2 Å longer than twice the c parameter (30.65 Å) of the host material [8] and 7.1 Å shorter than 4 times the c parameter (18.9 Å) of the stage-1 iodine-intercalated compound [2,3]. All primary reflections from the stage-2 iodine-intercalated compound are consistently indexed with indices hkl $(h+l=2n)$, $0kl$ $(k=2n, l=2n)$ and $hk0$ $(h=2n, k=2n)$, indicating that the space group of the average crystal structure is Bbmb or Bb2b. These are the same candidate space groups as those belonging to the host material but different from that of the stage-1 iodine-intercalated compound, the latter being Pma2. Satellite spots are also observed in the b^*–c^* reciprocal plane, showing that the structural modulation occurring in the pristine material remains unaltered during stage-2 iodine intercalation, just as is observed in the stage-1 iodine-intercalated superconductor [3].

Figure 3 shows a magnified version (a) of the high-resolution transmission electron micrograph (a) and a corresponding processed image (b) of the stage-2 iodine-intercalated compound. The box in fig. 3(b) shows a unit cell. It is clearly observed in the figures that iodine atoms marked (I) intercalate between every other Bi–O bilayer. As in the host material, the basic building blocks of Bi, Sr, Ca, Cu and oxygen are staggered by half of the a axial length across the Bi–O bilayer wherever no iodine intercalation occurs. When iodine does intercalate between Bi–O bilayers, it pulls the basic building blocks back into registry, as is observed in the stage-1 iodine-intercalated
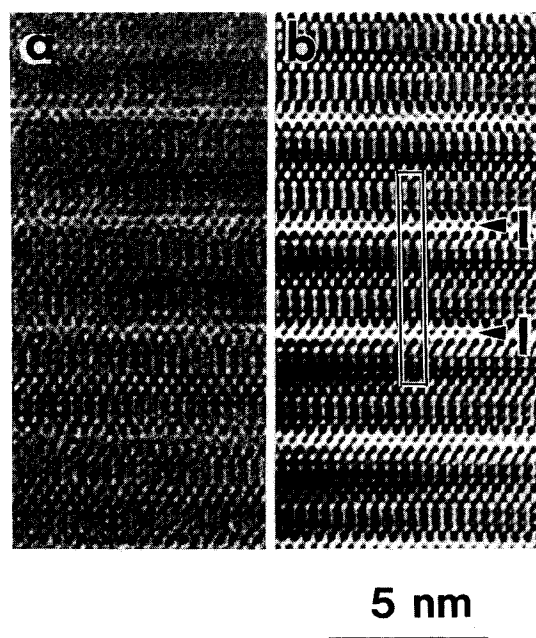
5 nm

Fig. 3. Phase contrast high-resolution electron microscope image (a) and corresponding processed image (b) of the stage-2 iodine-intercalated superconducting $IBi_4Sr_4Ca_2Cu_4O_x$ with the incident electron beam along the [110] direction. The box shows the unit cell, which includes two iodine layers and four basic building blocks of Bi, Sr, Cu, Ca and oxygen atoms. Compare with fig. 7(b).

compound. Consequently, the c lattice parameter of the stage-2 iodine-intercalated compound is much longer than that of either the host material or the stage-1 iodine-intercalated compound. Figure 4(a) shows a "diffraction pattern" generated by Fourier transformation of fig. 3(a) and (in 4(b)) an electron diffraction pattern simulated using the atomic positions in table 1, and assuming the lattice parameters and space group for the stage-2 iodine-intercalated crystal reported above. Both of these diffraction patterns are consistent with fig. 2(a). Figure 5 shows a through-focus series of original high-resolution transmission electron micrographs (a, b, c), the corresponding processed images (d, e, f) and simulated images (g, h, i) with a [110] incident beam direction through a 4 nm-thick sample. Table 1 summarizes the atomic positions within the stage-2 iodine-intercalated crystal used during image simulation. Note that there is good agreement between experimental and simulated images for all
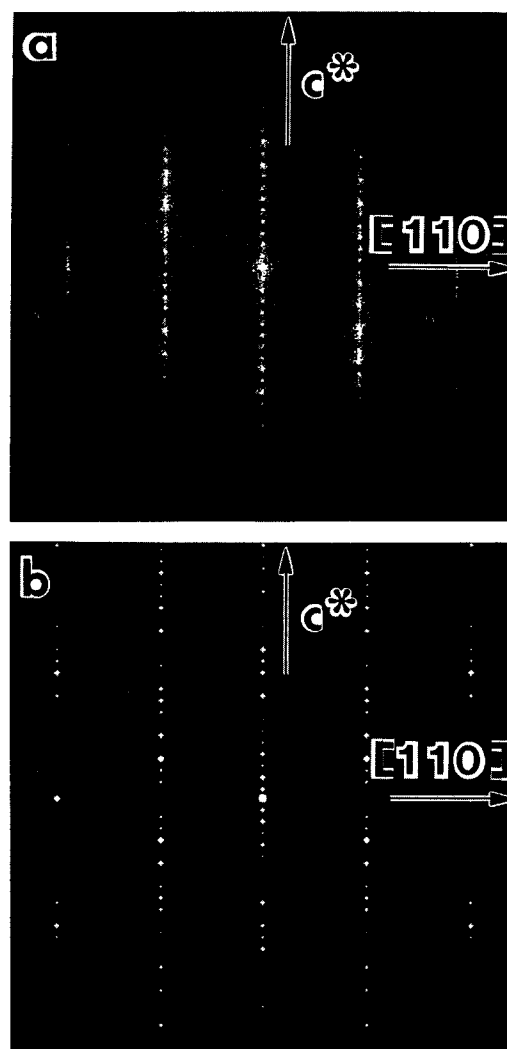

Fig. 4. (a) Diffraction pattern generated by Fourier transformation of fig. 3(a) and (b) electron diffraction pattern simulated using the atomic positions listed in table 1, lattice parameters $a=5.4$ Å, $b=5.4$ Å, $c=68.5$ Å, and space group Bbmb. Compare with fig. 2(a).

three values of objective lens defocus labeled in the left column (-20 nm, -25 nm and -30 nm). Since the satellite spots are observed in the b^*-c^* reciprocal plane shown in fig. 2(b), all of the atoms in the structure seem to be displaced from their average positions, with the oxygen atoms in the Bi-O layers undergoing the largest displacement. Unfortunately, it is not possible to determine the actual atomic co-

Table 1
Atomic positions for the stage-2 iodine-intercalated supercon-
ductor $IBi_4Sr_4Ca_2Cu_4O_x$ used in image simulations

Atom	Site	x	y	z
I	4e	0.25	0.0	0.250
Bi(1)	8I	0.28	0.5	0.024
Bi(2)	8I	0.22	0.5	0.200
Sr(1)	8I	0.25	0.0	0.063
Sr(2)	8I	0.25	0.0	0.161
Cu(1)	8I	0.25	0.5	0.088
Cu(2)	8I	0.25	0.5	0.136
Ca	8I	0.25	0.0	0.112
O(1)	8I	0.22	0.0	0.024
O(2)	8I	0.28	0.0	0.200
O(3)	8I	0.25	0.5	0.054
O(4)	8I	0.25	0.5	0.170
O(5)	8h	0.0	0.25	0.088
O(6)	8h	0.5	0.25	0.088
O(7)	8h	0.0	0.25	0.136
O(8)	8h	0.5	0.25	0.136

ordinates of the oxygen atoms in the Bi–O layers be-
cause of their smaller electron scattering coefficients
relative to those of the adjacent heavy atoms. There-
fore, the atomic coordinates of those oxygen atoms
were fixed at the center of the adjacent four Bi atoms
in the image simulations used in the present study.

Figure 6 depicts the crystal structure of the stage-
2 iodine-intercalated superconductor
$IBi_4Sr_4Ca_2Cu_4O_x$ that best fits the experimental im-
ages, while fig. 7 compares this structure of the stage-
2 iodine-intercalated crystal with those of pristine
$Bi_2Sr_2CaCu_2O_x$ and the stage-1 iodine intercalated
crystal $IBi_2Sr_2CaCu_2O_x$. The intercalated supercon-
ductors have the same basic building blocks of Bi, Sr,
Cu, Ca and oxygen as the host crystal, with one Ca
layer, two Cu–O layers and two Sr–O layers sand-
wiched between double Bi–O layers. During inter-
calation, iodine atoms are inserted between every
other Bi–O bilayer in the stage-2 iodine-intercalated
crystal and between every Bi–O bilayer in the stage-
1 iodine-intercalated crystal. In the host crystal, the
basic building blocks are staggered by half of the a
axial length (fig. 7(a)), while in the stage-1 iodine-
intercalated crystal, they are in registry (fig. 7(c)).
In the stage-2 iodine-intercalated crystal, (fig. 7(b)),
these building blocks are again staggered by half of
the a axial length across the Bi–O bilayer whenever
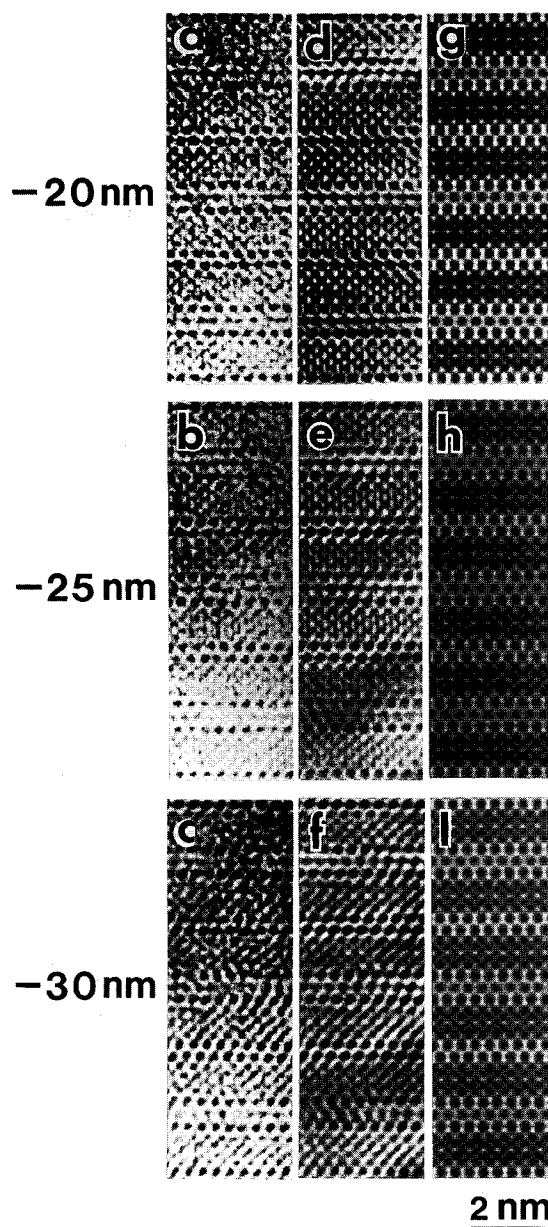there are no iodine atoms present, but remain in re-

Fig. 5. Through-focus series with objective lens defoci −20 nm
through −30 nm, showing actual phase contrast high-resolution
transmission electron microscope images (a–c), corresponding
processed (Fourier-filtered) images (d–f), and simulated (us-
ing the atomic parameters in table 1) images (g–i). The incident
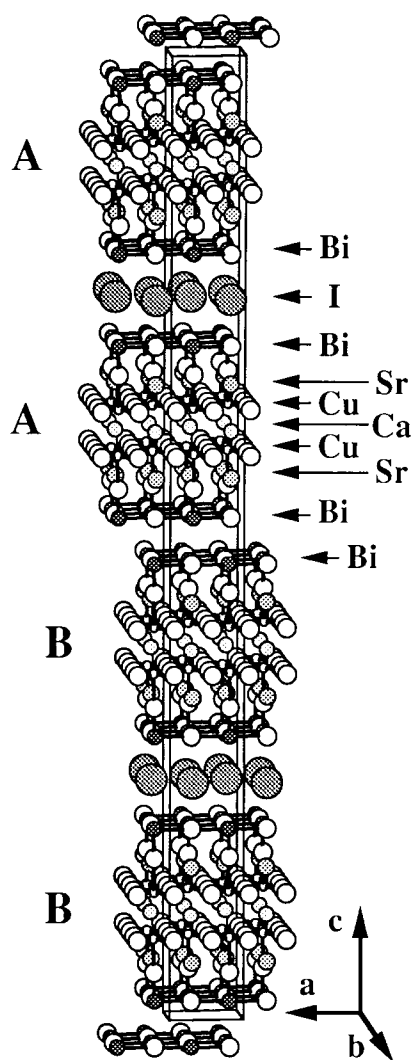electron beam is along the [110] direction, and the specimen
thickness is 4 nm.

Fig. 7. Comparison between the crystal structure of the host superconductor, $Bi_2Sr_2CaCu_2O_x$ (a), the stage-2 iodine-intercalated superconductor, $IBi_4Sr_4Ca_2Cu_4O_x$ (b), and the stage-1 iodine-intercalated superconductor $IBi_2Sr_2CaCu_2O_x$ (c).

Fig. 6. Schematic crystal structure of the stage-2 iodine-intercalated superconducting $IBi_4Sr_4Ca_2Cu4O_x$.

gistry whenever iodine atoms are present.

The actual location of iodine atoms among Bi atoms in the Bi–O bilayer of the stage-2 iodine-intercalated crystal is the same as that in the stage-1 iodine-intercalated crystal, that is, the positional relationship between iodine atoms and adjacent Bi atoms in the stage-2 iodine-intercalated superconductor is the same as that between Bi atoms in the upper basic building block and Bi atoms in the lower basic building block of the host pristine crystal. As
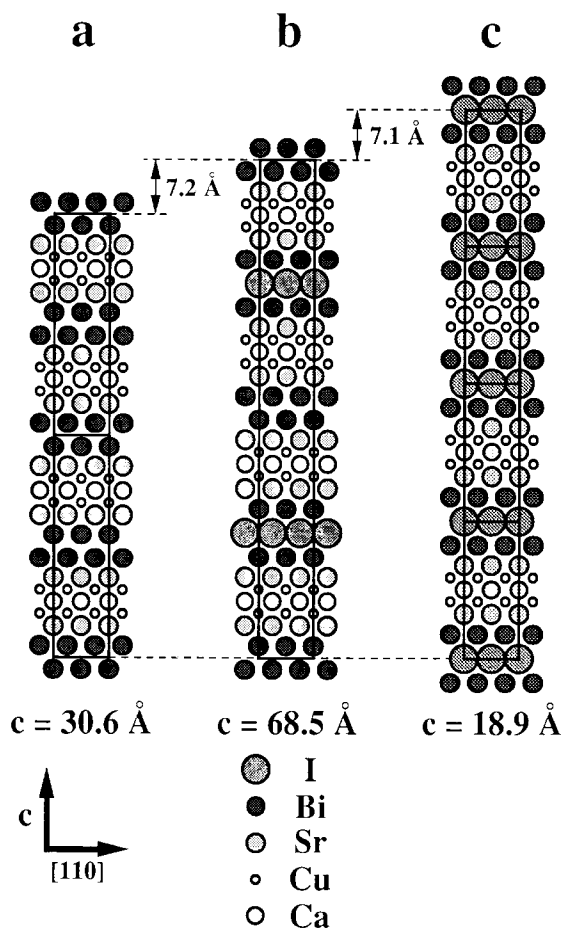
in the stage-1 iodine-intercalated crystal, therefore, it is possible to model iodine intercalation between every other Bi–O bilayer as the simple substitution of I for Bi atoms in one of the Bi–O layers, resulting in the shift of the outwardly displaced Bi atoms by half of the a axial length, so that the Bi atoms in the upper (displaced) Bi–O layer occupy lattice sites equivalent to Bi atoms in the lower basic building block. In the stage-2 iodine-intercalated crystal, however, there are no iodine atoms between every other Bi–O bilayer, and the two basic building blocks in the unit cell retain their staggered configuration at those sites. The structural rearrangement in the stage-

1 iodine-intercalated crystal, where the basic building blocks are brought into registry throughout the crystal, results in a halving of the c axial length of $IBi_2Sr_2CaCu_2O_x$ relative to $Bi_2Sr_2CaCu_2O_x$. On the other hand, the structural rearrangement in the stage-2 iodine-intercalated crystal, where the basic building blocks are in registry across every other Bi–O bilayer (those containing intercalated iodine atoms), and staggered across alternate Bi–O bilayers (those without intercalated iodine atoms), results in a doubling of the c axial length of $IBi_4Sr_4Ca_2Cu_4O_x$ relative to $Bi_2Sr_2CaCu_2O_x$.

Table 2 is a comparison of the distances between adjacent cation layers in the host superconductor and the stage-1 and stage-2 iodine-intercalated superconductors, showing that the amount of expansion of the crystal along the c-axis is simply the distance between the two Bi–O layers, to an accuracy of 5% on lattice parameters. That is, as shown in fig. 7, the c parameter (68.5 Å) in the stage-2 iodine-intercalated crystal is 7.2 Å longer than double the c parameter (30.65 Å) of the host material, corresponding to twice the distance (3.6 Å) between Bi–O bilayers bearing iodine atoms. Furthermore, since there are two Bi–O bilayers without iodine atoms in every unit cell of the stage-2 iodine-intercalated crystal, its c lattice parameter (68.5 Å) is 7.1 Å shorter than 4 times the c parameter (18.9 Å) of the stage-1 iodine-intercalated compound. This amount also corresponds to the summation of the shrinkage distance between two Bi–O bilayers without iodine atoms to an accuracy of 1% on lattice parameters.

Table 2
Comparison of the distances (Å) between adjacent cation layers in the host superconducting $Bi_2Sr_2CaCu_2O_x$, the stage-2 iodine-intercalated superconducting $IBi_4Sr_4Ca_2Cu_4O_x$ and the stage-1 iodine-intercalated superconducting $IBi_2Sr_2CaCu_2O_x$. The distances between the layers are defined using the z coordinates of the cations

Layers	$Bi_2Sr_2CaCu_2O_x$[a]	$IBi_4Sr_4Ca_2Cu_4O_x$	$IBi_2Sr_2CaCu_2O_x$
I–Bi	–	3.40	3.31
Bi–(I)–Bi	3.24	6.80	6.62
Bi–Sr	2.70	2.70	2.80
Sr–Cu	1.70	1.70	1.70
Cu–Ca	1.65	1.65	1.65

[a] Ref. [8].

From the distance between Bi–O layers and intercalated iodine layers in the stage-2 iodine-intercalated crystal, it is probable that the iodine layers bond to their neighboring Bi–O layers by van der Waals interactions, as in the stage-1 iodine-intercalated crystal. According to the prevailing models of the Cu-based oxide superconductors [9], only the Cu–O planes are critical structural components in superconductivity; the other structural components appear to act as charge reservoirs which control the local charge concentration within the Cu–O planes, and the superconducting transition temperature is closely related to the effective valence of the Cu atoms in the plane. Nevertheless, in the stage-2 iodine-intercalated superconducting $IBi_4Sr_4Ca_2Cu_4O_x$, as well as in the stage-1 iodine-intercalated superconducting $IBi_2Sr_2CaCu_2O_x$, the intercalated iodine atoms have no such effect on the transition temperature. If the intercalated iodine could have extracted electrons from the Bi–O layer, the resulting increase in holes within the Cu–O bands might have increased the carrier concentration, and consequently, T_c. In practice, however, the van der Waals interaction between iodine layers and adjacent Bi–O layers cannot bring about the necessary change in valence to increase T_c. The iodine layers in the iodine-intercalated superconductors, on the contrary, have a negative effect on the transition temperature since iodine layers bonded to Bi–O layers by the van der Waals interaction block the interaction between superconducting electrons across the Bi–O bilayer along the c-axis. The reason why the stage-2 iodine-intercalated superconductor has a 5 K higher T_c than the stage-1 iodine-intercalated superconductor is thought to be that only half of the Bi–O bilayers contain iodine layers that block the interaction between the superconducting electrons along the c-axis.

Acknowledgements

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