LBL-31438
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

National Center for Electron Microscopy

Submitted to Physica C

Crystal Structure of Stage-n Iodine-Intercalated Compounds $IBi_{2n}Sr_{2n}Ca_nCu_{2n}O_x$

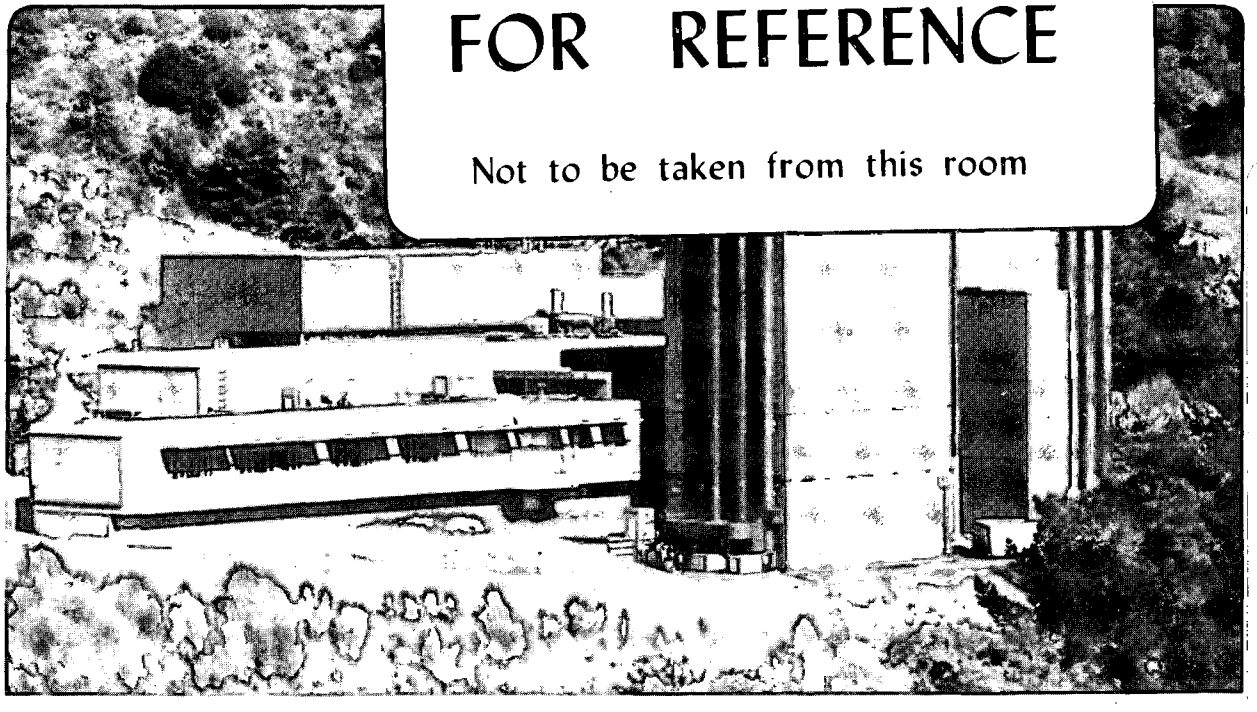
N. Kijima, R. Gronsky, X. Xiang, W. Vareka, A. Zettl,
J. Corkill, and M. Cohen

August 1991

U. C. Lawrence Berkeley Laboratory
Library, Berkeley

FOR REFERENCE

Not to be taken from this room



LBL-31438
Copy 1
Bldg. 50 Library.

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-31438

Crystal Structure of Stage-n Iodine-Intercalated Compounds $IBi_{2n}Sr_{2n}Ca_nCu_{2n}O_x$

N. Kijima*, R. Gronsky, X. Xiang+, W. Vareka+, A. Zettl+, J. Corkill+ & M. Cohen+

Materials Sciences Department
National Center for Electron Microscopy
Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

*Mitsubishi Kasei Corp.
1000, Kamoshida-cho
Midori-ku
Yokohama 227, Japan

+Department of Physics
University of California
and Materials Sciences Dept.
Lawrence Berkeley Laboratory
Berkeley, CA 94720

Submitted to Physica C, 11/1/91

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, National Science Foundation Grant No. DMR88-18404, and support from AT&T Bell Laboratories.

Crystal Structures of Stage-*n* Iodine-Intercalated Compounds $IBi_{2n}Sr_{2n}Ca_nCu_{2n}O_x$

N. Kijima and R. Gronsky

National Center for Electron Microscopy, Materials Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

X.-D. Xiang, W. A. Vareka, A. Zettl, J. L. Corkill, and Marvin L. Cohen

Department of Physics, University of California, and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Abstract

The crystal structure of stage-3 iodine-intercalated superconducting $IBi_6Sr_6Ca_3Cu_6O_x$ has been determined by transmission electron microscopy to belong to the space group *Pma2* with lattice parameters a = 5.4 Å, b = 5.4 Å and c = 49.4 Å. Iodine atoms intercalated between every three Bi-O bilayers expand the distance between the Bi-O layers by 3.6 Å and alter the atomic stacking across Bi-O layers from the staggered configuration characteristic of host superconducting $Bi_2Sr_2CaCu_2O_x$ to an aligned configuration characteristic of stage-1 iodine-intercalated superconducting $IBi_2Sr_2CaCu_2O_x$. Higher-stage intercalation has also been observed as stacking faults which predominantly contain both stage-2 and stage-3 phases. The space groups and c-axis dimensions of the higher-stage phases have been deduced to be *Pma2* with c=3.6+15.3n Å when stage number n is odd, and *Bbmb* with c=2(3.6+15.3n) Å when n is even.

Keywords: superconductor, intercalation, crystal structure, transmission electron microscopy, I-Bi-Sr-Ca-Cu-O system.

1. Introduction

Recently, a number of stage-1 iodine-intercalated $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ (n = 1, 2, 3) superconductors and a stage-2 iodine-intercalated $IBi_4Sr_4Ca_2Cu_4O_x$ 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 [1~5]. Beginning with host superconductors $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ (n=1, 2, 3), iodine was intercalated between every set of Bi-O bilayers at temperatures in the range of 150 to 200°C for times between 10 and 15 days, while iodine was intercalated into every other Bi-O bilayer of a host superconductor $Bi_2Sr_2CaCu_2O_x$ at 300 °C for times between 10 and 15 days. It was found from the temperature dependence of the a.c. and d.c. magnetic susceptibility that the stage-1 iodine-intercalated compounds behave as bulk superconductors with 2 to 10 K lower superconducting transition temperatures than those of the host materials and that the stage-2 iodine-intercalated superconducting $IBi_4Sr_4Ca_2Cu_4O_x$ has 5 K higher T_c than the stage-1 iodine-intercalated superconducting $IBi_2Sr_2CaCu_2O_x$. The crystal structures of the stage-1 iodine-intercalated $IBi_2Sr_2CaCu_2O_x$ and stage-2 iodine-intercalated $IBi_4Sr_4Ca_2Cu_4O_x$ have been determined by x-ray diffraction analysis [2, 3] and transmission electron microscopy [3~5]. These analyses showed that iodine atoms intercalate between the Bi-O bilayers, with a corresponding expansion along the c axis of 3.6 Å for each Bi-O bilayer, and that the intercalated iodine layers occupy epitaxial sites with respect to the adjacent Bi-O layers, but intercalated iodine atoms alter the atomic stacking across Bi-O layers from the staggered configuration characteristic of superconducting $Bi_2Sr_2CaCu_2O_x$ to a registered configuration in $IBi_2Sr_2CaCu_2O_x$ and $IBi_4Sr_4Ca_2Cu_4O_x$. In the crystal structure of the stage-2 iodine intercalated superconductor, however, the c-axis dimension is 7.1 Å shorter than 4 times the c-axis dimension of the stage-1 iodine-intercalated superconductor. It was also found from the atomic spacings apparent in the high-resolution transmission electron microscope images of $IBi_2Sr_2CaCu_2O_x$ and $IBi_4Sr_4Ca_2Cu_4O_x$ that the iodine layers bond to their neighboring Bi-O layers by van der Waals interactions.

Many stacking faults have been observed in those crystals which contain the dominant stage-2 iodine-intercalated compound [5]. In some of these crystals, we observed periodically dispersed stage-3 and other higher-stage phases within the stage-2 compound. In order to determine the crystal structures of these higher-stage iodine-intercalated compounds, this study has been undertaken using high resolution transmission electron microscopy.

2. Experimental

Several plate-like crystals of nominal stage-2 iodine-intercalated superconducting $IBi_4Sr_4Ca_2Cu_4O_x$ were prepared by encapsulating iodine and high-quality single crystals 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.

Transmission Laue patterns of the iodine-intercalated products were used to orient the crystals for precise cutting into thin wafers, which were subsequently sandwiched between silicon wafers, mechanically thinned and dimpled, and then ion-milled to electron transparency. Ion milling was carried out at 77K using argon ions accelerated at 3 kV and 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 [6], and compared with images simulated by the code NCEMSS [7] at the National Center for Electron Microscopy.

3. Results and Discussion

It is commonly observed that stacking faults occur abundantly throughout the stage-2 iodine-intercalated compound. Figure 1 shows a high-resolution transmission electron microscope image of a region wherein stage-3 (S3) stage-4 (S4) and stage-5 (S5) lamellae are dispersed within the stage-2 (S2) matrix. The double arrow identifies a thicker lamella of the stage-3 phase which has the characteristic feature of iodine layers appearing between every third set of Bi-O bilayers. This

amount of long range order (≥ 5 unit cells) was never seen for any of the other higher-stage phases.

Figure 2 shows selected area electron diffraction patterns from the same area of the iodine-intercalated crystal, but in two different zone axes. All primary reflections can be indexed on the assumption that this crystal contains both stage-2 (space group *Bbmb*, lattice parameters a = 5.4 Å, b =5.4 Å and c = 68.5 Å), and stage-3 (space group *Pma2*, lattice parameters a = 5.4 Å, b = 5.4 Å and c = 49.4 Å) phases. Figure 3(a) shows a magnified segment of Fig. 2(a) featuring the 00l reflections, verifying the presence of only these two phases and no higher stage intercalates. Comparison with Fig. 3(b), a Fourier transform of the region of Fig. 1 containing only stage-3 material, and the simulations in Fig. 3(c) of a stage-2 phase diffraction pattern, and Fig. 3(d) of a stage-3 phase diffraction pattern, shows good agreement. X-ray diffraction patterns similarly show no evidence of higher-stage intercalates, indicating that only stage-2 and stage-3 iodine-intercalated crystals are thermodynamically stable in a saturated iodine vapor pressure at 300 °C.

The a and b axial lengths of the pristine host material, which has space group *Bbmb* and lattice parameters a = 5.4 Å, b = 5.4 Å and c = 30.6 Å, are identical to those of all the stage-1, stage-2 and stage-3 iodine-intercalated compounds; however, the c axis dimensions vary from 18.9 Å to 68.5 Å depending upon stage number. The c parameter doesn't linearly increase with stage number, due to the fact that iodine intercalation causes not only the expansion of the distance between the Bi-O layers but also a change in the stacking sequence of the contiguous structure, as revealed in the high resolution images.

Figure 4 shows an original high-resolution transmission electron micrograph (a), corresponding processed image (b) and simulated image (c) of the stage-3 iodine-intercalated compound with a [$\bar{1}$10] incident beam direction along a 6 nm-thick sample. The box in Fig. 4(b) shows a unit cell for comparison, and it is observed with excellent agreement among these figures that iodine atoms marked (I) intercalate between every third set of Bi-O bilayers. Table I

summarizes the atomic positions used during image simulation; the atomic coordinates of the oxygen atoms in the Bi-O layers were fixed at the center of the adjacent four Bi atoms as they were in previous studies of both the stage-1 and stage-2 iodine-intercalated compounds. Figure 5 schematically depicts the crystal structure of the stage-3 iodine-intercalated superconductor $IBi_6Sr_6Ca_3Cu_6O_x$. As in the host material, the basic building blocks of Bi, Sr, Ca, Cu and oxygen in the stage-3 iodine-intercalated compound are staggered by half of the *b* axial length across the Bi-O bilayer in the absence of iodine atoms. With iodine intercalation, the basic building blocks are brought into registration across the Bi-O bilayer. Consequently, only the basic building block in the middle of the unit cell marked "B" in Fig. 5 is displaced relative to the adjacent blocks that border iodine-containing layers. Consequently, the *c* axis parameter of the stage-3 iodine-intercalated compound is longer than those of the host material and the stage-1 iodine-intercalated compound, but shorter than that of the stage-2 iodine-intercalated compound; these differences are summarized schematically in Fig. 6.

Higher stage phases such as those appearing as stacking faults in Fig. 1 seem to bear similar structural characteristics to the lower stage intercalates. For example, the stage-4 iodine-intercalated phase has 4 basic building blocks with a staggered stacking sequence between 2 iodine layers across which the building blocks are in registry, to form the stacking sequence: A-I-A-B-A-B-I-B-A-B-A-I-A. The stage-5 iodine-intercalated phase would therefore be expected to have 5 basic building blocks with the staggered stacking sequence between 2 iodine layers across which the building blocks are in registry, to form the stacking sequence: A-I-A-B-A-B-A-I-A. Consequently, the stage-5 phase has a shorter *c*-axis dimension than the stage-4 phase since the registration of building blocks in the stage-5 phase does not require a doubling of the *c* axis parameter to complete a unit cell. Since any single intercalated iodine layer expands the distance between Bi-O layers by 3.6 Å and since the length of a basic building block along the *c* axis is 15.3 Å, it follows that the *c* parameter of the stage-4 phase should be 129.6 Å and that of the stage-5 phase should be 80.1 Å. These values correspond to the actual dimensions measurable in Fig. 1.

It is concluded from these results that the c-axis dimension of a general stage-n iodine-intercalated phase is $m(3.6+15.3n)$ Å where m=1 when n is odd and m=2 when n is even (c.f. Fig. 6). Considering the stacking sequence of iodine layers and basic building blocks in the stage-1, stage-2 and stage-3 iodine-intercalated compounds, it is also possible to surmise the space group of a stage-n compound to be *Pma2* when n is odd or *Bbmb* when n is even.

Figure 7 is another high-resolution transmission electron microscope image revealing even higher-stage iodine-intercalated phases than those discussed so far, i.e., stage numbers 4, 5, 6,7,10,11, and 20 appear in the same field of view (see labels in Fig. 7). The incident direction of the electron beam in this image is $[\bar{1}10]$. For each intercalate, the measured c-axis dimension agrees well with the above formula. Note also that the image also captures a two phase interface at the position marked "D" where a single intercalated iodine layer is responsible for the transformation of the stage-20 phase into two unit cells of stage-10 phase. There is considerable lattice distortion accompanying the 3.6Å expansion of the crystal due to the localized intercalation of iodine, which induces both a compressive stress along the c axis and a pure shear in the a-b plane, as seen in the image.

Table II summarizes the lattice parameters, space groups and the distances between adjacent cation layers in the pristine crystal and iodine-intercalated compounds. It is seen that although the presence of iodine expands the distance between the Bi-O layers between which it intercalates and causes a shift of the basic building blocks along the a or b axes by half of their lattice parameters, it causes no fundamental structural changes within the building blocks themselves. This behavior of the iodine is associated with its formation of weak van der Waals bonds to adjacent atomic layers..

Acknowledgement

The Atomic Resolution Microscope, image analysis facilities, and technical support at the National Center for Electron Microscopy are gratefully acknowledged. This research is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences

Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098, National Science Foundation Grant No. DMR88-18404 and support from Bell Laboratories.

References

[1] X.-D. Xiang, S. McKernan, W.A. Vareka, A. Zettl, J. L. Corkill, T. W. Barbee III, and Marvin L. Cohen, *Nature* **348** (1990) 145.

[2] X.-D. Xiang, A. Zettl, W. A. Vareka, J. L. Corkill, T. W. Barbee III, and Marvin L. Cohen, *Phys. Rev. B* **43** (1991) 11496.

[3] X.-D. Xiang, W. A. Vareka, A. Zettl, J. L. Corkill, T. W. Barbee III, Marvin. L. Cohen, N. Kijima, and R. Gronsky, submitted to *Science.*

[4] N. Kijima, R. Gronsky, X.-D. Xiang, W. A. Vareka, A. Zettl, J. L. Corkill, and Marvin. L. Cohen, *Physica C.*(accepted for publication).

[5] N. Kijima, R. Gronsky, X.-D. Xiang, W. A. Vareka, A. Zettl, J. L. Corkill, and Marvin. L. Cohen, submitted to *Physica C.*

[6] W. O. Saxton, T. J. Pitt, and M. Horner, *Ultramicroscopy* **4** (1979) 343.

[7] R. Kilaas, *in proceedings of the 45th Annual Meeting of the Electron Microscopy Society of America*, G. W. Bailey (ed.), Baltimore, Md. (1987) 66.

Table I. Atomic positions for the stage-3 iodine-intercalated superconductor $IBi_6Sr_6Ca_3Cu_6O_x$ used in image simulations.

Atom	Site	x	y	z
I	2c	0.25	0.75	0.0
Bi1	2c	0.25	0.28	0.069
Bi2	2c	0.25	0.22	0.313
Bi3	2c	0.25	0.78	0.378
Bi4	2c	0.25	0.72	0.622
Bi5	2c	0.25	0.28	0.687
Bi6	2c	0.25	0.22	0.931
Sr1	2c	0.25	0.75	0.123
Sr2	2c	0.25	0.75	0.258
Sr3	2c	0.25	0.25	0.432
Sr4	2c	0.25	0.25	0.568
Sr5	2c	0.25	0.75	0.742
Sr6	2c	0.25	0.75	0.877
Cu1	2c	0.25	0.25	0.157
Cu2	2c	0.25	0.25	0.224
Cu3	2c	0.25	0.75	0.467
Cu4	2c	0.25	0.75	0.533
Cu5	2c	0.25	0.25	0.776
Cu6	2c	0.25	0.25	0.843
Ca1	2c	0.25	0.75	0.191
Ca2	2c	0.25	0.25	0.500

Ca3	2*c*	0.25	0.75	0.809
O1	2*c*	0.25	0.78	0.069
O2	2*c*	0.25	0.72	0.313
O3	2*c*	0.25	0.28	0.378
O4	2*c*	0.25	0.22	0.622
O5	2*c*	0.25	0.78	0.687
O6	2*c*	0.25	0.72	0.931
O7	2*c*	0.25	0.25	0.110
O8	2*c*	0.25	0.25	0.271
O9	2*c*	0.25	0.75	0.420
O10	2*c*	0.25	0.75	0.581
O11	2*c*	0.25	0.25	0.729
O12	2*c*	0.25	0.25	0.890
O13	2*a*	0.0	0.0	0.157
O14	2*a*	0.0	0.0	0.224
O15	2*a*	0.0	0.0	0.467
O16	2*a*	0.0	0.0	0.533
O17	2*a*	0.0	0.0	0.776
O18	2*a*	0.0	0.0	0.843
O19	2*b*	0.0	0.5	0.157
O20	2*b*	0.0	0.5	0.224
O21	2*b*	0.0	0.5	0.467
O22	2*b*	0.0	0.5	0.533
O23	2*b*	0.0	0.5	0.776
O24	2*b*	0.0	0.5	0.843

Table II. Comparison of the lattice parameters (Å), space groups and distances (Å) between adjacent cation layers in the host superconducting $Bi_2Sr_2CaCu_2O_x$ and the iodine-intercalated superconductors. The distances between the layers are defined using the *z* coordinates of the cations.

	Pristine	Stage-1	Stage-2	Stage-3	Stage-*n*
	$Bi_2Sr_2CaCu_2O_x$	$IBi_2Sr_2CaCu_2O_x$	$IBi_4Sr_4Ca_2Cu_4O_x$	$IBi_6Sr_6Ca_3Cu_6O_x$	$IBi_{2n}Sr_{2n}Ca_nCu_{2n}O_x$
a	5.4	5.4	5.4	5.4	5.4
b	5.4	5.4	5.4	5.4	5.4
c	30.6	18.9	68.5	49.4	$m(3.6+15.3n)$ m=1 when n is odd m=2 when n is even
Space Group	*Bbmb*	*Pma2*	*Bbmb*	*Pma2*	*Pma2* when n is odd *Bbmb* when n is even
I-Bi	---	3.31	3.40	3.40	3.40
Bi-(I)-Bi	3.24	6.62	6.80	6.80	6.80
Bi-Sr	2.70	2.80	2.70	2.70	2.70
Sr-Cu	1.70	1.70	1.70	1.70	1.70
Cu-Ca	1.65	1.65	1.65	1.65	1.65

Figure Captions

Fig. 1 Phase contrast high-resolution transmission electron microscope image of an area where the stage-3 iodine-intercalated compound is precipitated among the other stage phases. The incident electron beam of the image is along the [$\bar{1}$10] direction. "S2", "S3", "S4" and "S5" represent the iodine-intercalated phases with four different stage numbers which indicate the number of the basic building blocks sandwiched by two iodine layers.

Fig. 2. Selected area electron diffraction patterns of the iodine-intercalated superconductor. (a) [110]-c^* plane, (b) a^*-c^* and b^*-c^* planes.

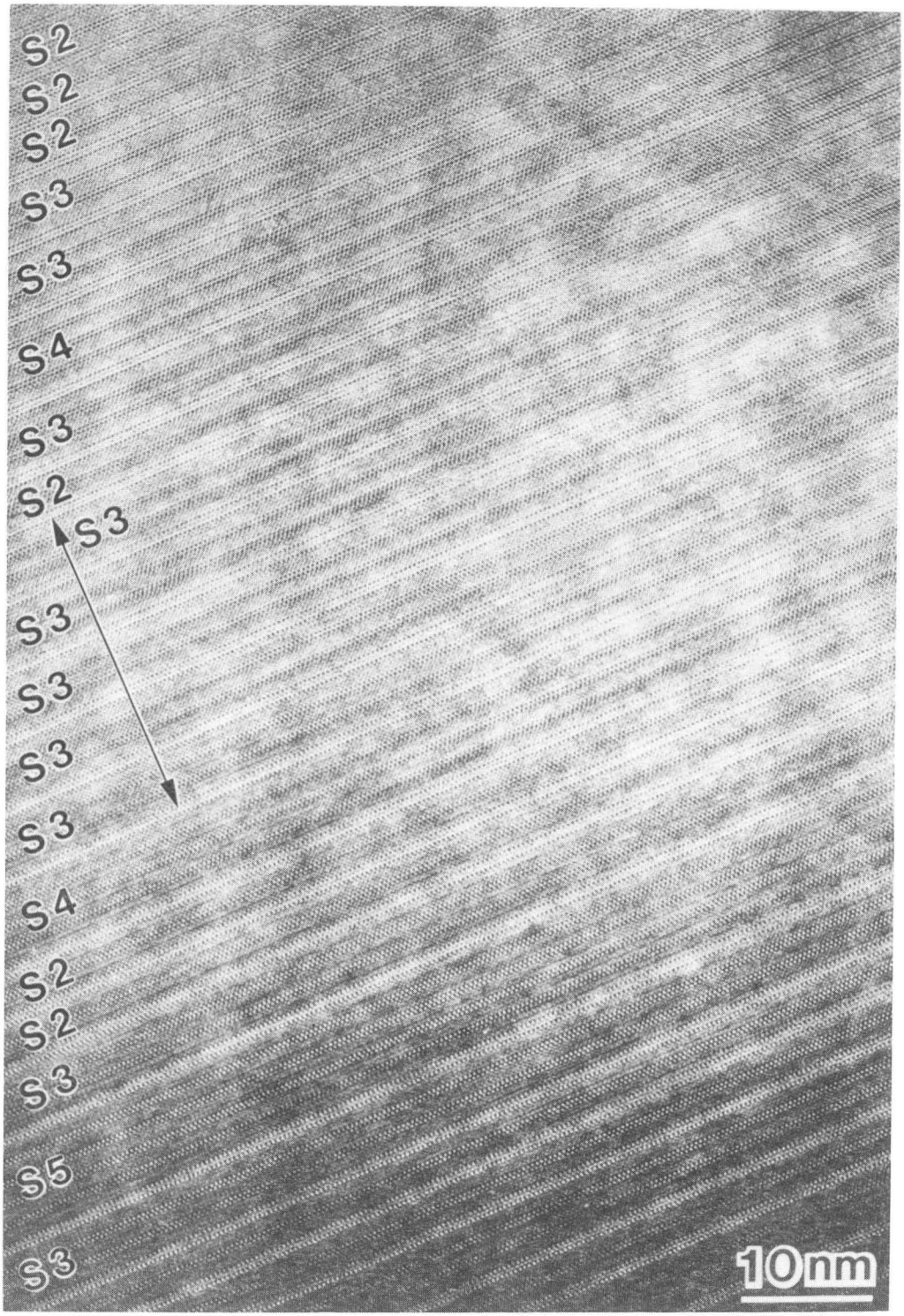
Fig. 3. (a) Magnified version of the selected area electron diffraction pattern shown in Fig. 1(a). The l indices of 00l reflections of the stage-2 iodine-intercalated compound are shown on the left of the reflections, while those of the stage-3 iodine-intercalated compound are shown on their right. (b) Electron diffraction pattern Fourier-transformed from the area which includes only the stage-3 iodine-intercalated compound, (c) simulated electron diffraction pattern for the stage-2 iodine-intercalated compound [5], (d) electron diffraction pattern for the stage-3 iodine-intercalated compound simulated with the atomic positions listed in Table I assuming lattice parameters a =5.4 Å, b =5.4 Å, c = 49.4 Å and space group *Pma2*. Zone axis of all the electron diffraction patterns is [$\bar{1}$10].

Fig. 4 Phase contrast high-resolution transmission electron microscope image (a), corresponding processed image (b) by means of Fourier filtering, and simulated image (c) using the atomic parameters in Table I. The incident electron beam is along the [$\bar{1}$10] direction. The specimen thickness is 6 nm. The box shows the unit cell, which includes an iodine layer and three basic building blocks of Bi, Sr, Cu, Ca and oxygen atoms. Compare with Fig. 6(d).

Fig. 5 Crystal structure of the stage-3 iodine-intercalated compound $IBi_6Sr_6Ca_3Cu_6O_x$.

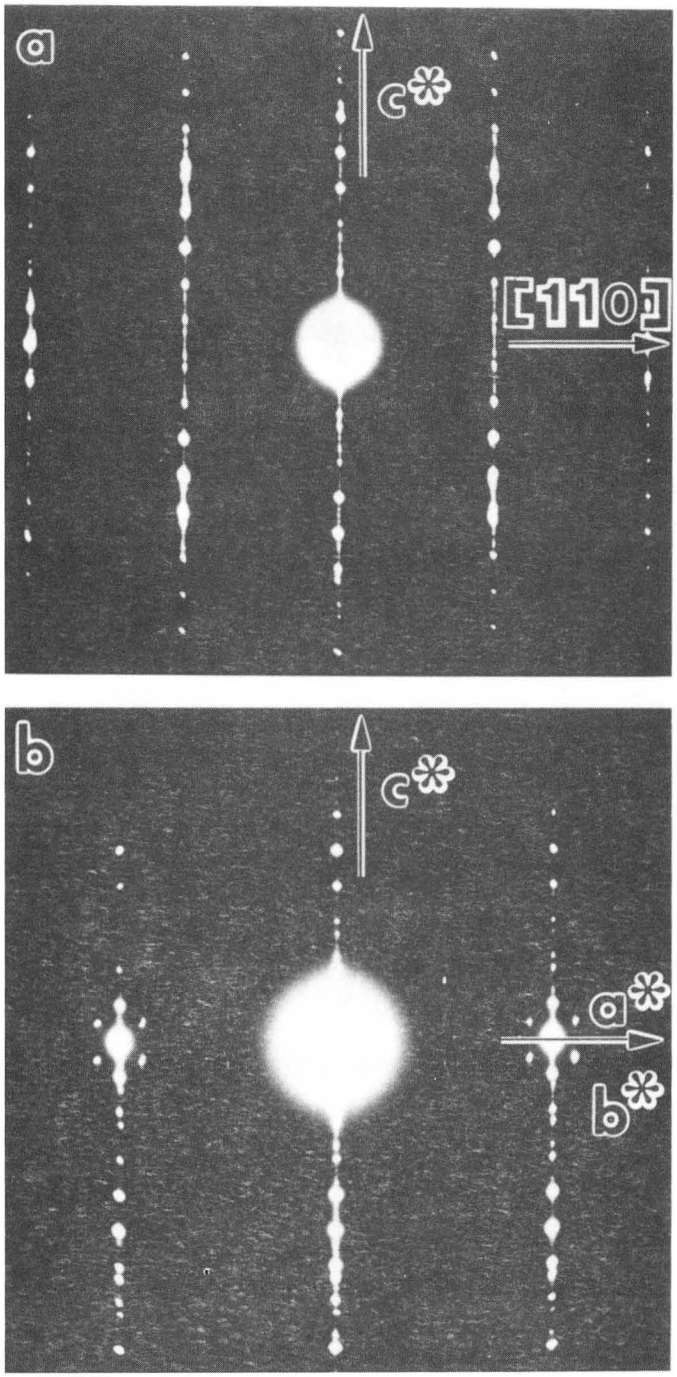
Fig. 6 Comparison of the crystal structures of the host material $Bi_2Sr_2CaCu_2O_x$ (a), stage-1 iodine-intercalated compound $IBi_2Sr_2CaCu_2O_x$ (b), stage-2 iodine-intercalated compound $IBi_4Sr_4Ca_2Cu_4O_x$ (c), stage-3 iodine-intercalated compound $IBi_6Sr_6Ca_3Cu_6O_x$ (d), stage-n iodine-intercalated compound $IBi_{2n}Sr_{2n}Ca_nCu_{2n}O_x$ when its stage number is odd (e) and even (f). The c lattice parameters C(odd) and C(even) are $m(3.6+15.3n)$ Å, where $m = 1$ when n is odd and $m = 2$ when n is even.

Fig. 7 Phase contrast high-resolution transmission electron microscope image of the area where the higher-stage (>stage-3) iodine-intercalated phases are precipitated in the same crystal that the stage-2 and stage-3 compounds are dominantly precipitated in. The incident electron beam of the image is along the $[\bar{1}10]$ direction. "S4", "S5", "S6", "S7", "S10", "S11" and "S20" represent the iodine-intercalated phases with different stage numbers which indicate the number of the basic building blocks sandwiched by two iodine layers.



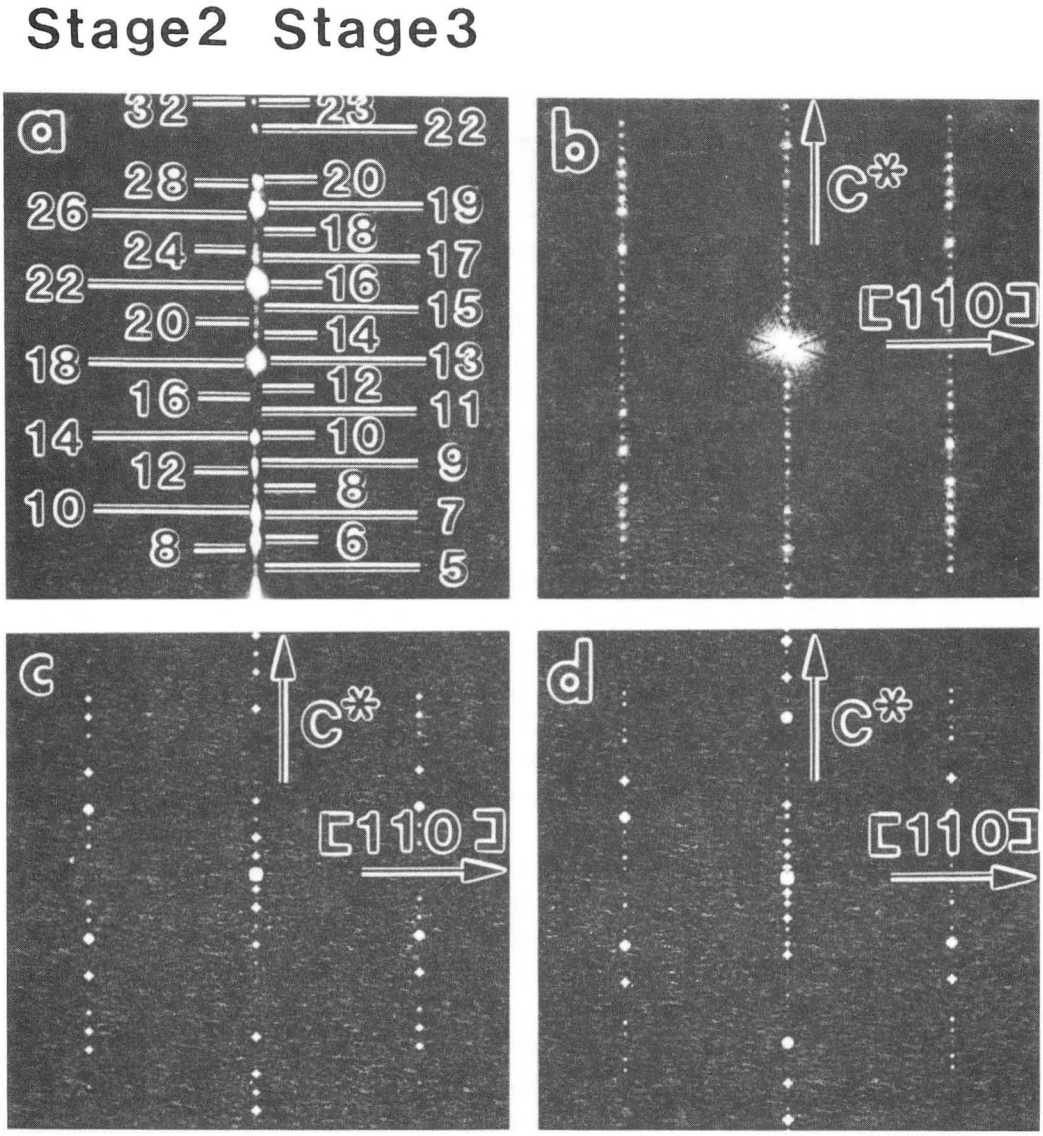
XBB 910-9125

Figure 1



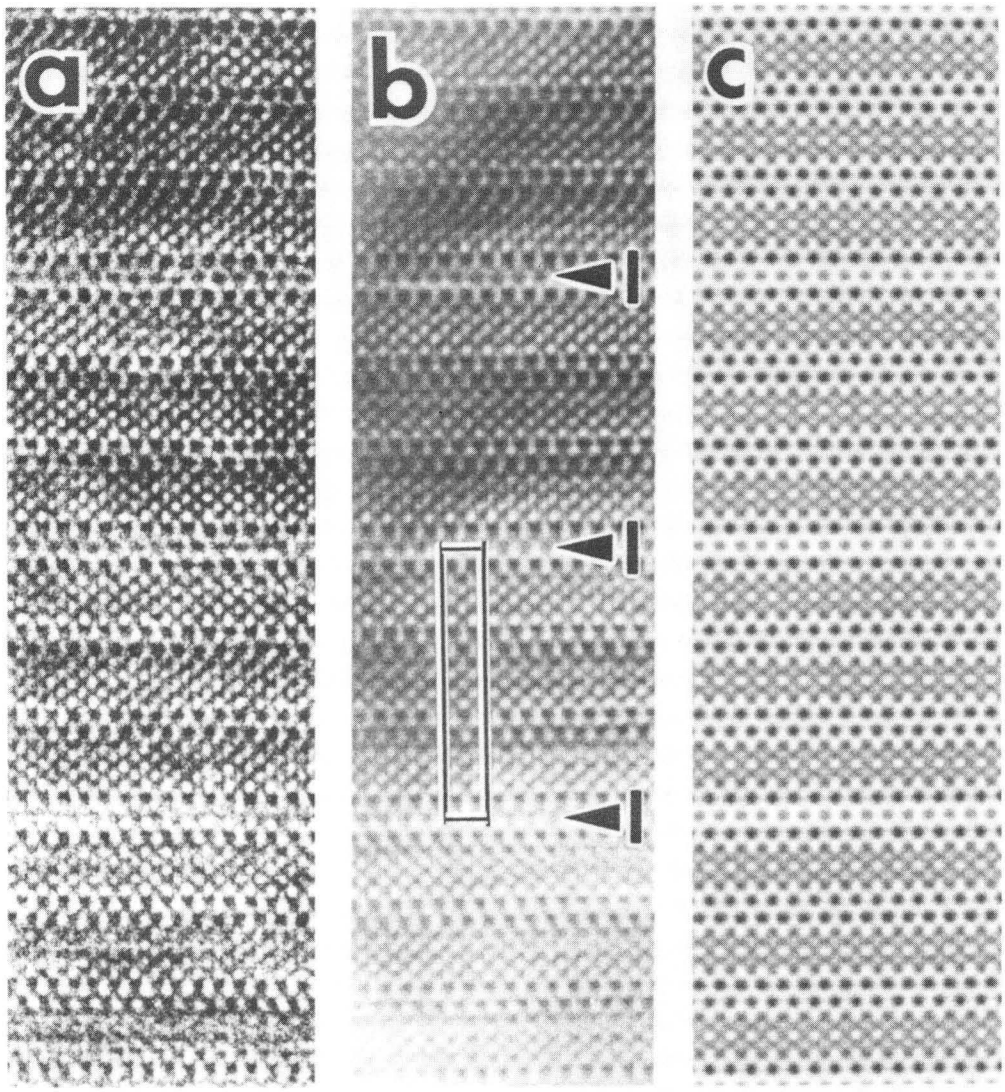
XBB 910-9126

Figure 2



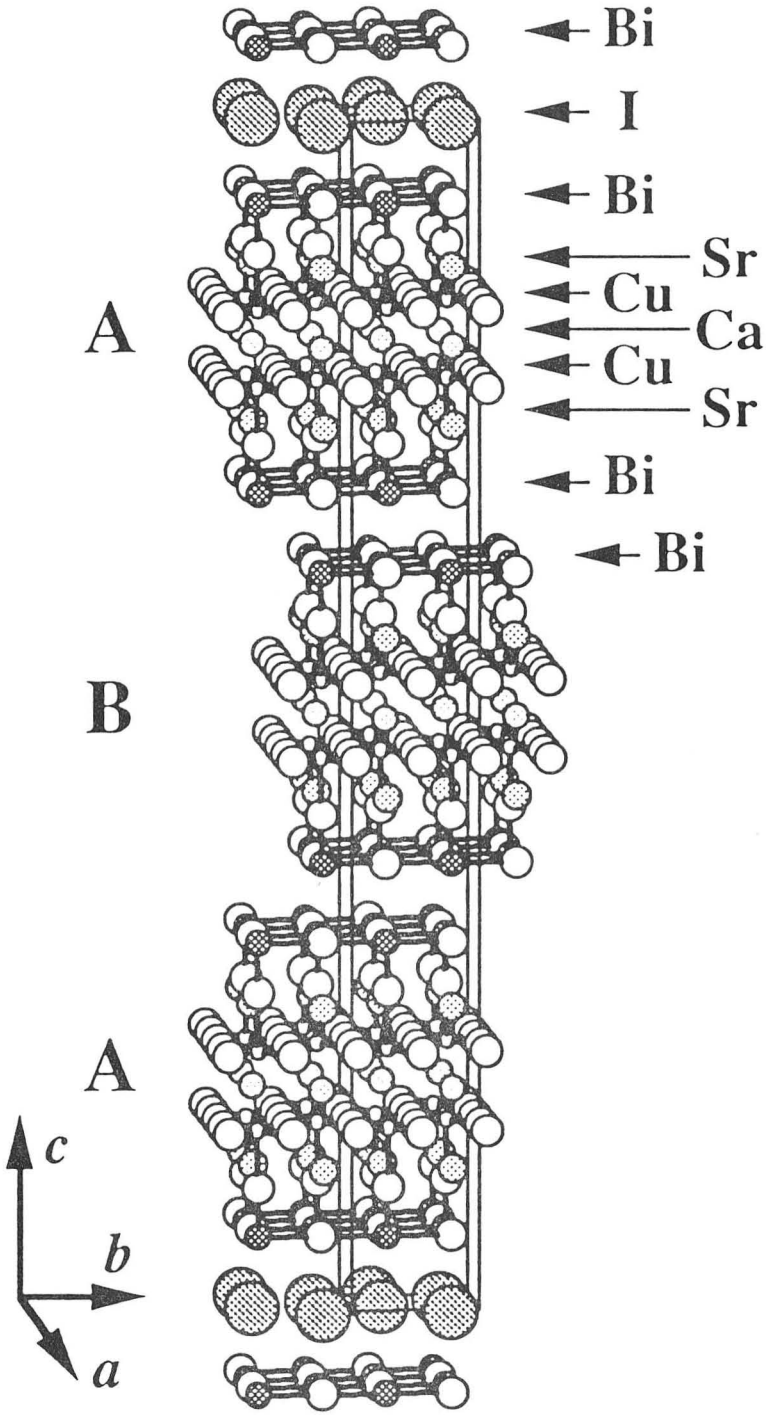
XBB 910-9127

Figure 3



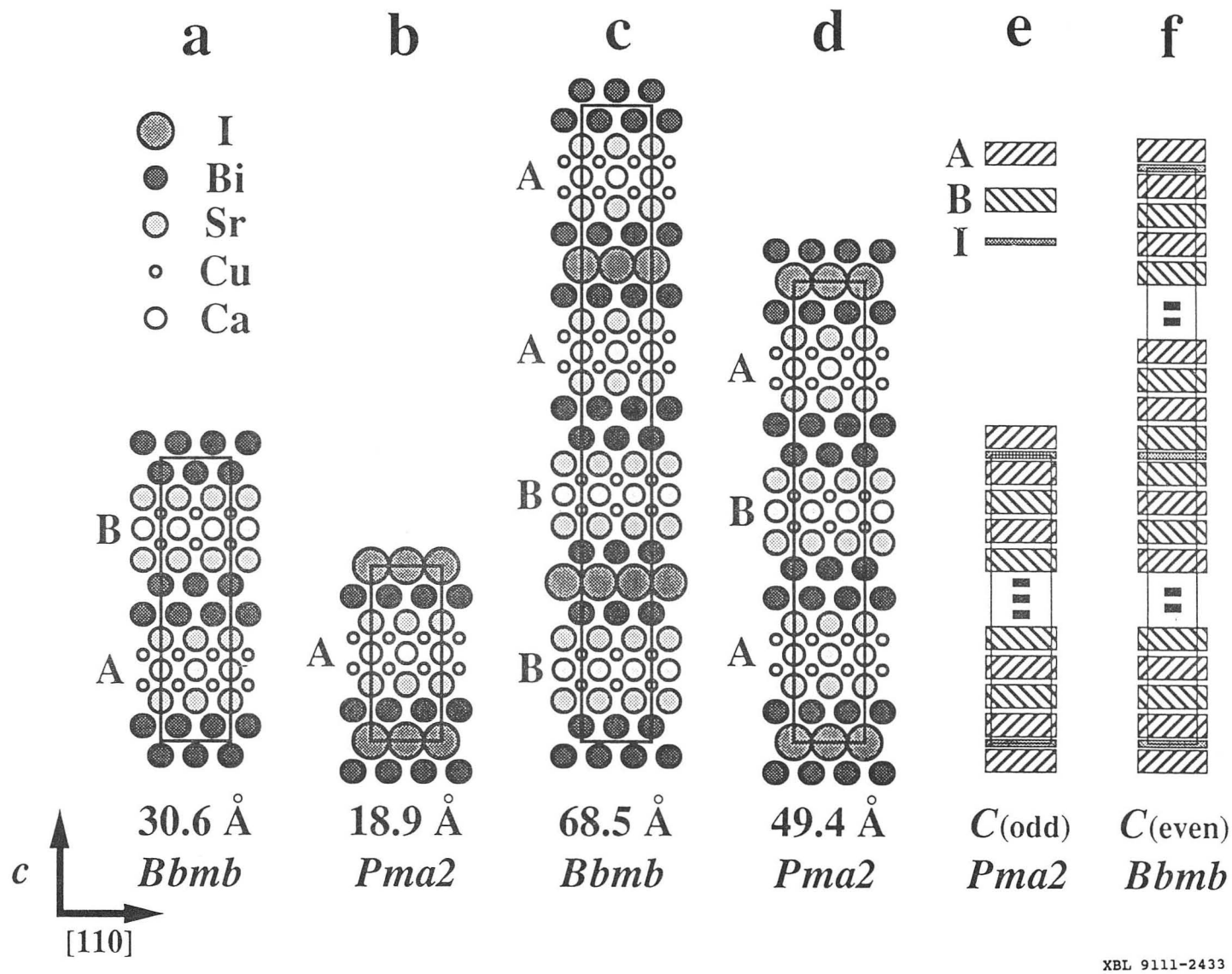
XBB 910-9128

Figure 4



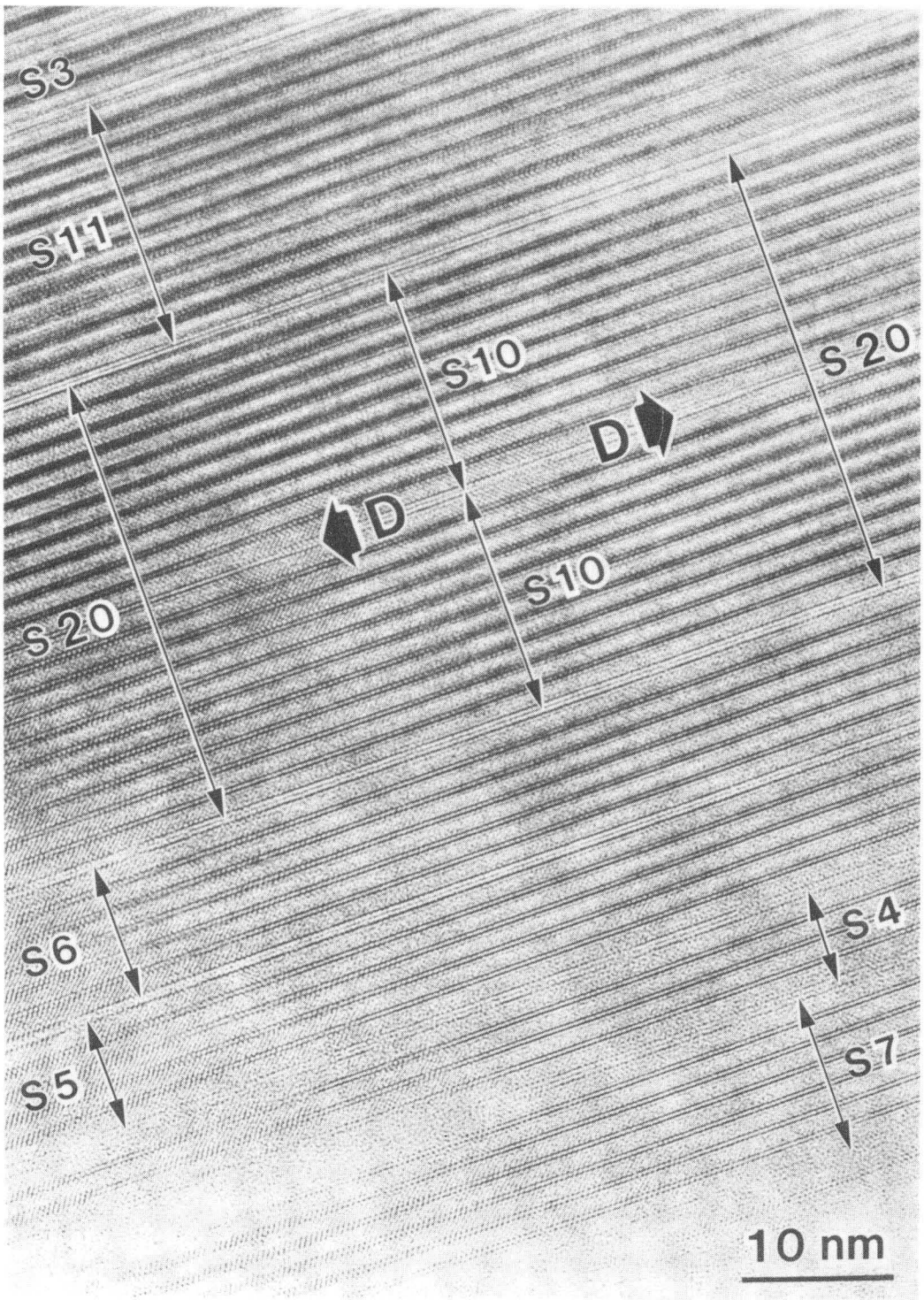
XBL 9111-2432

Figure 5



XBL 9111-2433

Figure 6



XBB 910-9129

Figure 7

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720