Title

HIGH RESOLUTION ELECTRON MICROSCOPY OF THE C=30.5A[ANGSTROM] AND C=38.2A[ANGSTROM] POLYTYPOIDS IN THE BI-CA-SR-CU-O SUPERCONDUCTOR

Permalink

https://escholarship.org/uc/item/8d30h83f

Authors

Hetherington, C.J.D
Ramesh, R.
O'Keefe, M.A.

Publication Date

1988-05-01

LBL-25320

Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

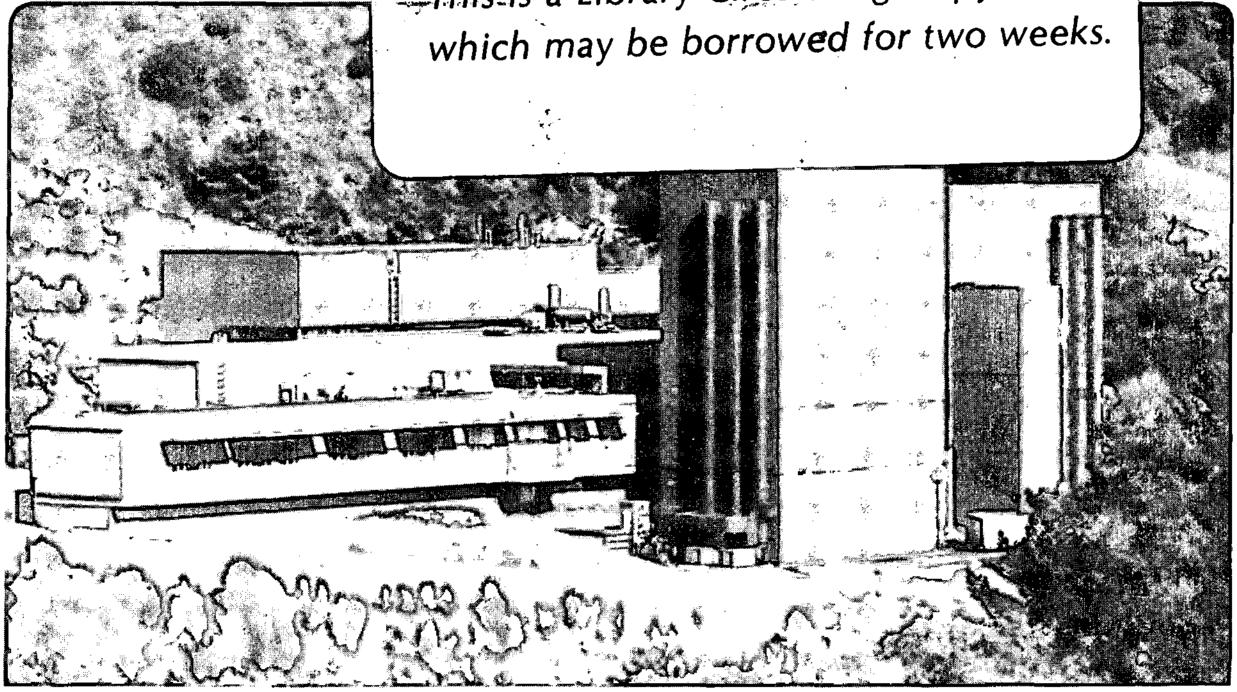
National Center for Electron Microscopy

Submitted to Applied Physics Letters

High Resolution Electron Microscopy of the c=30.5Å and c=38.2Å Polytypoids in the Bi-Ca-Sr-Cu-O Superconductor

C.J.D. Hetherington, R. Ramesh, M.A. O'Keefe, R. Kilaas,
G. Thomas, S.M. Green, and H.L. Luo

May 1988



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

DISCLAIMER

HIGH RESOLUTION ELECTRON MICROSCOPY OF THE c=30.5Å AND c=38.2Å POLYTYPOIDS IN THE Bi-Ca-Sr-Cu-O SUPERCONDUCTOR

C.J.D.Hetherington[1], R.Ramesh[2], M.A.O'Keefe[1], R.Kilaas[1] and G.Thomas[1,2]
[1] National Center for Electron Microscopy, Lawrence Berkeley Laboratory
[2] Department of Materials Science and Mineral Engineering,
University of California, Berkeley, CA 94720.
S.M.Green[3] and H.L.Luo[3]
[3] Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla CA.

We report results of high resolution structure imaging, image processing and simulation of the c=30.5Å (T_C=80K) and c=38.2Å (T_C=115K) superconducting polytypoids in the Bi-Ca-Sr-Cu-O system. The increase in c-parameter is due to the insertion of two layers of Cu-O perovskite + Ca atoms in each unit cell. From the processed image and simulations, it appears that the central Cu layer in the c=38.2Å polytypoid may be oxygen deficient. In addition, the image simulation experiments suggest that the oxygen atoms in the Bi-O layers are located at the face center of the Bi lattice.

PACS No. 74.70b

The recent discovery of superconductivity in alkaline earth based cuprates has stimulated unsurpassed interest in the structure, properties and processing of these ceramics[1-4]. In the case of the Bi-Ca-Sr-Cu-O ceramics one characteristic feature has been the presence of steps in the resistivity plot, suggesting lack of connectivity[5,6]. In addition, two superconducting polytypoids with T_c~75-85K and T_c~110-115K are generally observed[7,8]. It has been suggested that the compound with c=30.5Å corresponds to the lower T_c polytypoid and that with c=38.2Å to the higher T_c polytypoid[7,8]. This is in agreement with the theoretical[9] and experimental observations[10-12] of other researchers. However, the reason for the increase in the c-parameter was not evident. Subsequent to our earlier reports[7,8], we have now carried out atomic resolution imaging of both compounds, the results of which are reported here.

The samples were prepared according to the procedure described in earlier communications[5,6]. It has been found that the addition of a small quantity of Pb to the alloy leads to a dramatic change in the fraction of the higher temperature (T_c~110K) polytypoid, while the sample without Pb addition was made up of predominantly the 75-85K polytypoid[6]. Samples for high resolution imaging were prepared by slicing a piece from the bulk sample, followed by mechanical polishing and finally Argon ion milling at liquid nitrogen temperature to electron transparency. The samples were examined in the Berkeley Atomic Resolution Microscope at 800kV. Images were recorded within a few minutes to avoid excessive specimen damage due to the beam. The [110] zone axis orientation was used for both the samples. Although images in other zone axes were also recorded by tilting the foil, the damage to the region of interest prevented detailed interpretation of the images. Image processing was carried out to filter out the noise in the images using the "SEMPER" program[13] while image simulations were carried out using the "CEMPAS" program[14].

A. Structure of the c=30.56Å polytypoid : Fig.1(a) shows a [110] image of the phase with c=30.5Å, the structure of which was confirmed by convergent beam diffraction. This image was obtained from the edge of the foil, where the sample is most likely to behave as a weak phase object. In this image , the intensity is directly related to the atomic potential upto a certain resolution. Structural information for this phase was obtained from ref.(15) and the [110] projected potential was calculated from this information. This is shown in Fig.1(b). The structure in this orientation consists of the Bi bi-layers, which are shifted with respect to each other by half a Bi-Bi bond distance, due to the presence of the glide plane along the c-direction. This is clearly seen in the image in Fig.1(a). In between these Bi bi-layers, the stacking sequence consists of Sr-Cu-Ca-Cu-Sr, which is repeated in the lower half of the unit cell with a shift of half a unit cell. These atomic positions are also observed in the image in Fig.1. The processed image corresponding to Fig.1(a) is shown in Fig.1(c). The interpretation of the image was confirmed by simulating the [110] image using the "CEMPAS" image simulation program. In Fig.1(d) a calculated image, for a foil thickness of 30Å and objective defocus of +250Å, is presented. The calculated images show a good match with the actual image , except for the Bi bi-layers, which is discussed below. Some additional features in the experimental image in Fig.1(a) are arrowed where the intensity is greater than that expected, indicating heavier atoms compared to the aforementioned structure. This appears to occur predominantly in the Ca atom positions, suggesting that Ca (Z=20) has been replaced by Sr(Z=38) or Bi(Z=83). This is possible since the sizes of these three atoms are quite similar. It is to be noted that the modulation in the b-direction is not observed in this image. However, when viewed at 45° the image shows much waviness due to the non-parallel alignment of the Bi bi-layers and the Sr-Ca-Cu layers along that direction.

B. Structure of the c=38.2Å polytypoid : The addition of Pb to the alloy causes the composition of the superconducting phase to become uniform and also raises its Cu +Ca content. However, it should be noted that the lower T_C polytypoid is also observed through the susceptibility measurements, although as a minor phase. Fig.2(a) is the [110] image of the c=38.2Å polytypoid. Clearly, this image is different from that in Fig.1(a), the difference being in the Sr-Ca-Cu layers, while the Bi bi-layers are still observed. The processed image is shown in Fig.2(b). Xray microanalysis data showed that the increase in c-parameter is concomittant with an increase in Cu+Ca content of the region, while the Sr content remained the same as in the region with c=30.5Å[8]. Hence, the structure of the c=30.5Å polytypoid was modified to accommodate one extra Cu+Ca layer in each half of the unit cell. Fig.3(a) shows the projected potential for the stacking sequence consisting of : Bi-Bi-Sr-Cu-Ca-Cu-Ca-Cu-Sr-Bi-Bi ... and the corresponding calculated images in the under-focussed condition are shown in Fig.3(b). The match between the actual image and the calculated images is quite good, confirming the structural model. The atomic positions corresponding to this phase are given in Table I.

One interesting feature of the image in Fig.2(a), and more obviously in the processed image in Fig.2(b), is that the image of the central layer of Cu atoms is quite different from that of the other two layers, as indicated in Figs.2(a&b) by arrows. The black and white spots are darker and brighter than the corresponding spots for the other two Cu atoms. In the case of Y-Ba-Cu-O superconductors, it is known that the ordering of oxygen atoms is responsible for the presence of the Cu-O chains in the orthorhombic structure. Thus, in order to check the possible origin of this difference in contrast, image simulations were carried out with a unit cell from which certain of the oxygen atoms (four in each unit cell) were removed, forming Cu-O chains along the 110 direction. Fig.4(a) shows the projected potential in the [110] orientation for the perfect structure corresponding to which Fig.4(b) shows the calculated image. Fig.4(c) is the projected potential for the "defect" structure showing the missing oxygen atoms along the Cu-O chain. The corresponding calculated image is shown in Fig.4(d). It can be seen that the image corresponding to the central layer of Cu + oxygen atoms bears a close resemblance to the actual image and the processed image in Figs.2(a&b) respectively. It is hence suggested that the central Cu layer, which has an environment quite different from that of the other two Cu layers, may, in addition, be oxygen deficient.

C. Bi-O bonding in the unit cell : One aspect of speculation has been the Bi-O bonding in the double Bi layers. Figs.5(a&b) schematically show the two possible positions of the oxygen atom with respect to the Bi atoms. In (a) the oxygen atom is located in between two Bi atoms, while in (b) the oxygen is located in the face centered position. When examined in the [110] zone axis orientation, either the oxygen atoms fall in between the Bi atoms, (a), or they fall on top of the Bi atoms, (b). Consequently, the images might show a difference between the two cases. The simulated images for (a) and (b) in the under-focussed condition are shown in (c) and (d) respectively. The difference between these two images is that in (c) the intensity at the Bi sites are "smeared" out while in (d) the intensity at the Bi positions are not "smeared". Referring to the actual images in Fig.2(a) and in Fig.1(a), no "smearing" of the intensity of the Bi atomic positions can be observed. This suggests that the oxygen atoms lie at the face centred position and not along the edges.

Discussion : In this paper, three important aspects of the structure of the superconducting phase have been examined. The first is that the change in c-parameter from 30.5Å to 38.2Å is due to the insertion of two Cu-O + two Ca layers. This is consistent with the earlier findings of a higher Cu+Ca content in the c=38.2Å phase[8]. This is thought to be directly responsible for the increase in the T_c from 80K to 110K, as predicted by Grant[9]. The second is the Bi-O bonding. It has been shown through a combination of high resolution imaging and image simulation, that the oxygen atoms should lie at the face centred positions. Thirdly, in the case of the c=38.2Å polytypoid, image simulation experiments suggest that the central Cu layer may be oxygen deficient. It has also been observed that in the un-doped sample, there is a likelyhood for the replacement of Ca atoms by either Bi or Sr. The capability of high resolution imaging to distinguish between two atoms of different atomic numbers occupying the same site, even when the two atoms are of the same size, is suggested. In this case the substitution of Ca (Z=20) by Bi (Z=83) alters the relative intensity at that site. Since Bi can take different oxidation states while Ca and Sr generally are in the +2 oxidation state, the implications of the presence of Bi in between the Cu-O layers may be quite significant. Further atomic resolution experiments to study the nature of such replacements are in progress.

ACKNOWLEDGEMENTS: We gratefully acknowledge the technical assistance of Mr. J.Turner. This work was supported by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract No. DE-Ac03-76SF00098. The work at UC, San Diego was supported by the California MICRO program and the Hughes Aircraft Co.

REFERENCES

(1) C.Michel, et. al., Z.Phys., B-Condensed Matter, 68, 412(1987).

(2) H.Maeda, et. al., Jap. Jl. of Appl. Phys. Lett. 27(in press).

(3) R.M.Hazen, et. al., Phys. Rev. Lett. 60, 1174(1988).

(4) C.W.Chu, et. al., Phys. Rev. Lett., 60, 941 (1988).

(5) S.M.Green, C.Jiang, Yu Mei, H.L.Luo and C.Politis, submitted to Phys. Rev. Lett., April 19, 1988.

(6) R.Ramesh, G.Thomas, S.M.Green, C.Jiang, Yu Mei, H.L.Luo, submitted to Appl. Phys. Lett., 9 May 1988.

(7) R.Ramesh, et. al., Appl. Phys. Lett. (in press).

(8) H.W.Zandbergen, et. al., Nature, 332, 620(1988).

(9) P.M.Grant, unpublished.

(10) C.C.Torardi, et. al., Science , (in press).

(11) J.M.Tarascon, et. al., Phys. Rev. (communicated).

(12) T.M.Shaw et. al, Phys. Rev. (in press).

(13) W.O.Saxton, T.J.Pitt and M.Horner, Ultramicroscopy 4, 343(1979).

(14) R.Kilaas, in Proc. of the 45th Annual Meeting of the Electron Microscopy Society of America, Published by San Fransisco Press, San Fransisco, CA 94101-6800, (1987).

(15) P. Bordet, et. al., Proc. Int. Conf. on High Temp. Superconductor Materials and Mechanisms of Superconductivity, (in press).

FIGURE CAPTIONS

Figure 1: (a) High resolution structure image of the c=30.5Å polytypoid in the [110] zone axis ; (b) calculated projected potential for the c=30.5Å polytypoid in the [110] orientation ; (c) processed image corresponding to (a) ; (d) [110] calculated image obtained using the structure in ref.(15) for a foil thickness of 30Å and an objective defocus of +250Å.

Figure 2: (a) High resolution structure image of the c=38.2 polytypoid in the [110] zone axis. Note the extra layer of Cu and Ca inserted ; (b) processed image corresponding to (a). Note the difference in contrast between the central Cu layer and the other two Cu layers.

Figure 3: (a) [110] projected potential for the c=38.2 polytypoid obtained using the atomic basis given in Table I and the space group No.69. The "a" and "b" parameters are the same as for the c=30.5Å phase, i.e., a=5.41Å and b=5.39Å ; (b) a series of calculated images in the [110] zone axis in the under-focussed condition.

Figure 4: (a) [110] projected potential for the "perfect" structure of the c=38.2 compound ; (b) calculated image corresponding to (a) ; (c) [110] projected potential of a "defect" structure in which the oxygen atoms along the central Cu-O chain have been removed ; (d) image calculated using (c). Note the difference in intensity for the central Cu layer in (d), while it is uniform in (b).

Figure 5: (a) Schematic representation of the Bi-O positions when the oxygen atoms have the atomic positions of (0,0.5, z) ; (b) same as in (a) but for oxygen atomic position of (0.5, 0.5, z) ; (c) calculated [110] image for the c=38.2Å polytypoid corresponding to the Bi-O coordination in (a) ; (d) same as in (c), but corresponding to the Bi-O coordination in (b). Note the "smearing" of the calculated image in the Bi- bi-layers, which is absent in the actual images in Figs.1(a) and 2(a).

TABLE I

a=5.41Å ; b=5.39Å ; c=38.2Å.

ORTHORHOMBIC STRUCTURE ; SPACE GROUP : Fmmm1 (No. 69)

ATOM	x	y	z
Bi	0.2112	0.0	0.0
Sr	0.0	0.5	0.1354
Ca(1)	0.0	0.5	0.0456
Ca(2)	0.0	0.5	0.9544
Cu(1)	0.0	0.0	0.0
Cu(2)	0.0	0.0	0.0908
O(1)	0.25	0.25	0.0
O(2)	0.25	0.25	0.0908
O(3)	0.0	0.0	0.1612
O(4)	0.5	0.5	0.2134

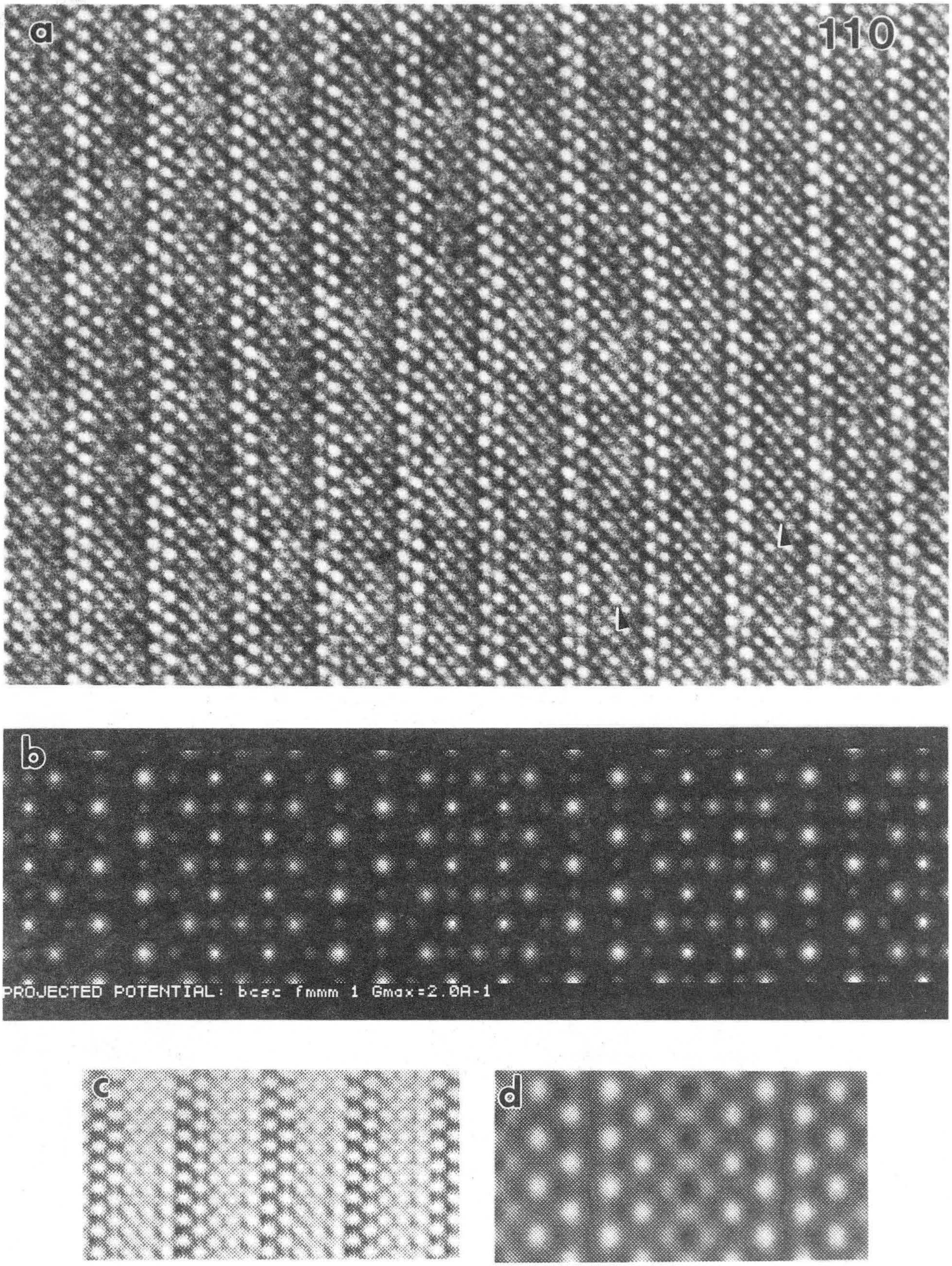


Fig.1

XBB 885 4985

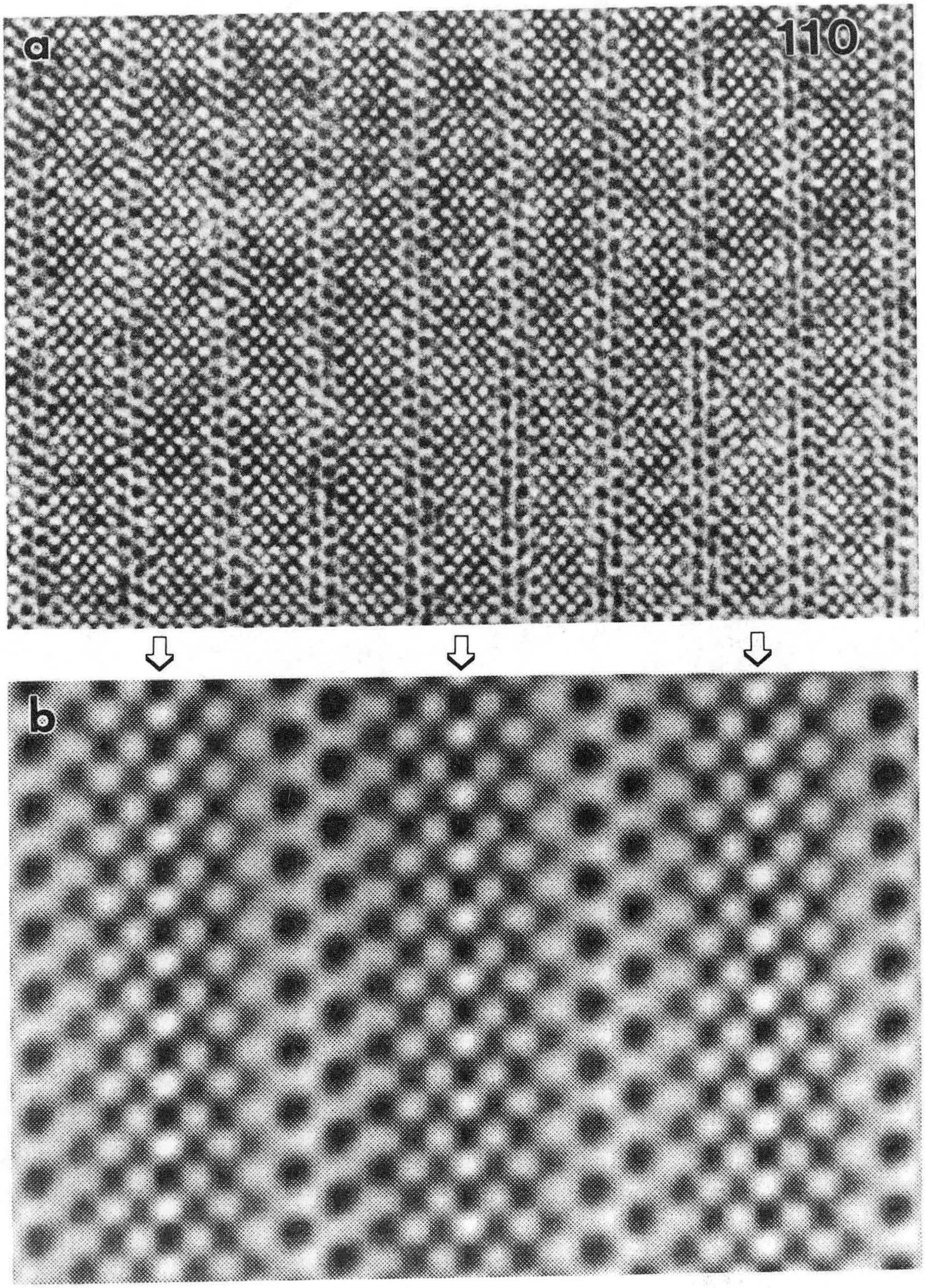


Fig.2

xbb 885-4984

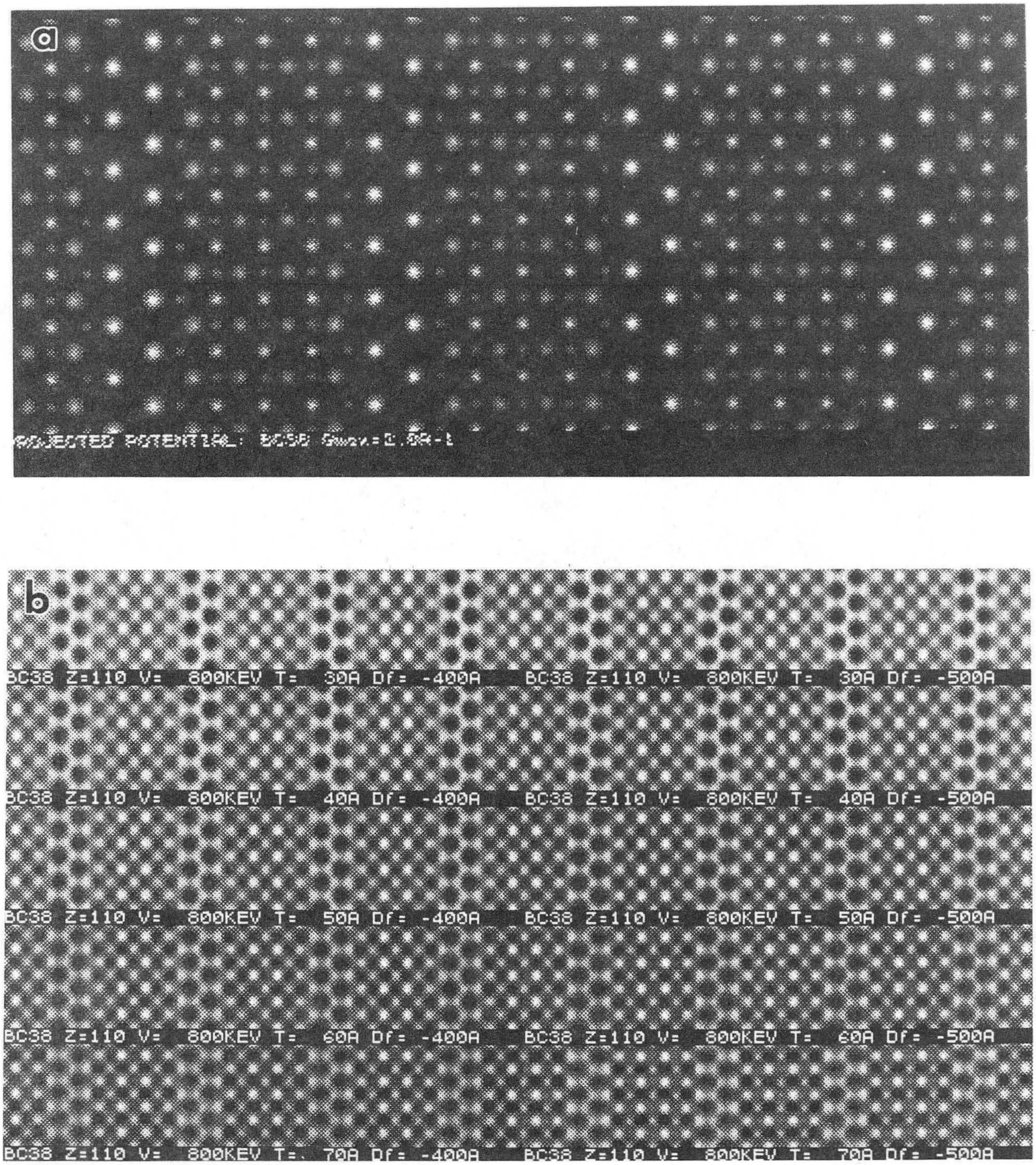


Fig.3

XBB 885-4981

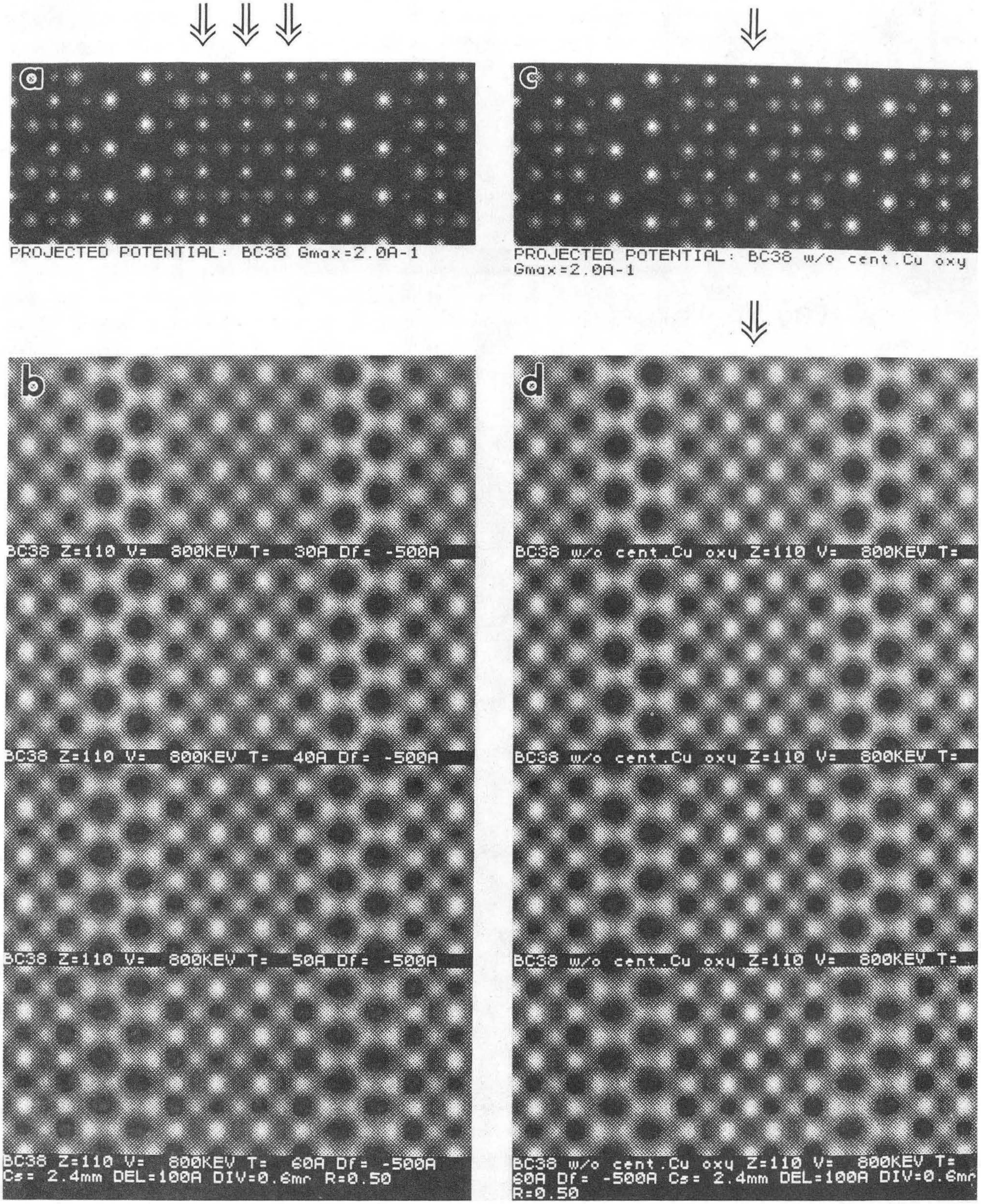


Fig.4

XBB 885-4983

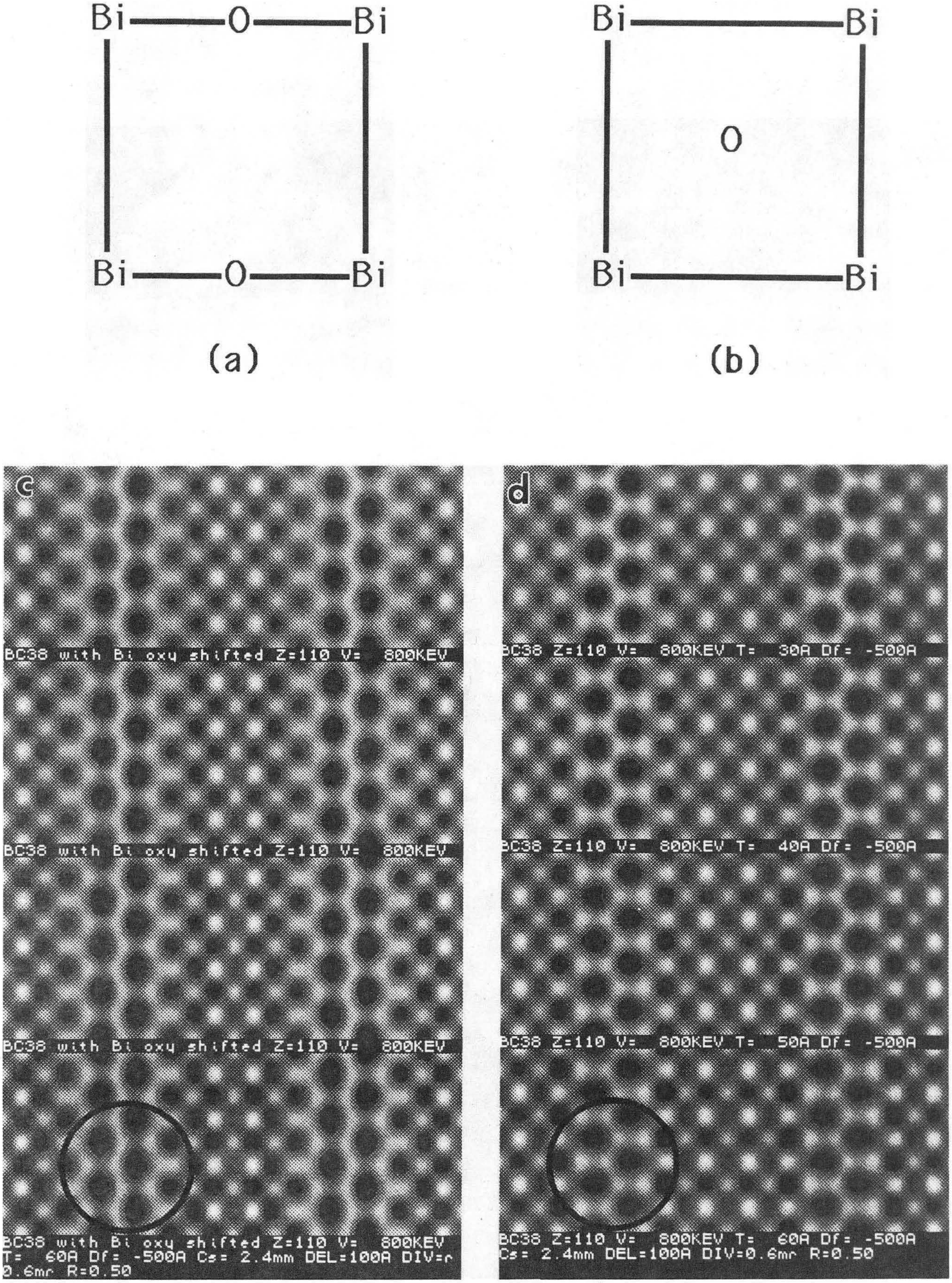


Fig.5

XBB 885-4982

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