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HREM STUDY OF Bi-OXIDE BASED HIGH Tc SUPERCONDUCTORS

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HREM STUDY OF Bi-OXIDE BASED HIGH Tc SUPERCONDUCTORS

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ABSTRACT

A HREM study of the superstructure and structural defects in $Bi_{2-x}Pb_xSr_2CaCu_2O_8$ and $Bi_{2-x}Pb_x(SrCa)_2CuO_6$(for x=0 and x≈0.4) is presented. The superstructures are shown to involve waves of distortion along the b-axis.These waves are locked on to the lattice positions so that they have a local wave length of 4,5,6,7 or 8 times the basic unit cell. The superstructures are composed of roughly periodic combinations of these basic building blocks (waves). The lead doped superconductors show a less pronounced but more complicated superstructure along b where two distinct periodicities close to 4 and 7 times the basic unit cell predominate. In each of the compounds studied the superstructure, in the better ordered crystals, is shown to be commensurate with a unit cell between 5 and 23 times the basic unit cell. The superstructure in $Bi_{2-x}Pb_xSr_2CaCu_2O_8$ is orthorhombic where as the superstructure in $Bi_{2-x}Pb_x(SrCa)_2CuO_6$ is monoclinic. All these superconductors have a low "twin" density (ie density of 90° twist boundaries). They exhibit many dislocations and dislocation arrays associated with the weak bonding between BiO planes. They also form non-stoechiometric stacking faults with local changes in the c-axis spacing between layers.

INTRODUCTION

The recent discovery that certain oxides containing Bi (1,2) or Tl (3,4) are superconducting with a high Tc is important for our understanding of the superconducting phenomenon. A comparative structural study of all the currently known high Tc superconductors will advance our understanding of the structural elements of these oxides and their role in the superconducting phenomenon. As suggested by Michel et al. (5) these superconductors are Aurivillius related phases. The basic structures of $Bi_2Sr_2CaCu_2O_8$ and $Bi_2(Sr,Ca)_2CuO_6$ determined by X-ray and neutron studies (6,7,8,9) are orthorhombic and have approximate unit cell dimensions $a=\sqrt{2}a_p$, $b=\sqrt{2}a_p$ and $c=8a_p$, and $c=6a_p$ respectively. (a_p=3.8Å : the perovskite unit cell.) They consists of layers of perovskite sandwiched between Bi_2O_2 layers. Figure 1 shows the structure of $Bi_2Sr_2CaCu_2O_8$, $Bi_2(Sr,Ca)_2CuO_6$ and $YBa_2Cu_3O_7$ for comparison.The perovskite layer of $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$, are very similar. The Y of $YBa_2Cu_3O_7$ is replaced by Ca in $Bi_2Sr_2CaCu_2O_8$ and the Ba is replaced by Sr while the CuO chains are replaced by Bi_2O_2 layers. The Bi_2O_2 layers have the rock salt configuration which is very different from the Aurivillius type phases which have two Bi planes separated by O planes. Also there is a Cu plane at the centre of the perovskite layers in the Aurivillius phase whereas there is a Ca plane in $Bi_2Sr_2CaCu_2O_8$. $Bi_2Sr_2CaCu_2O_8$, with c=31Å, has two CuO planes between the BiO layers, whereas $Bi_2(SrCa)_2CuO_6$ has only one CuO plane. They are the first two members of a homologous series.

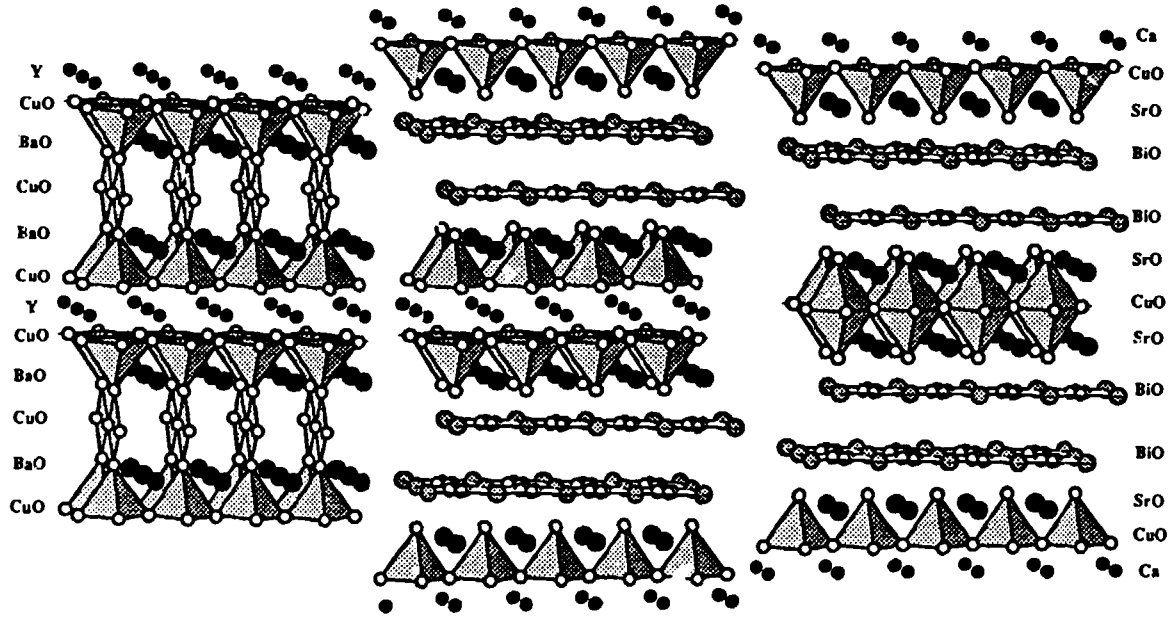

FIG. 1- Structures of $YBa_2Cu_3O_7$, $Bi_2Sr_2CaCu_2O_8$ and $Bi_2(Sr,Ca)_2CuO_6$

Two methods of increasing the Tc of $Bi_2Sr_2CaCu_2O_8$, reported in the literature, are one:- annealing just below the melting point of 885° C for two days (10) and two :- doping with Pb (7).

While electron microscopy does not have sufficient resolution to unambiguously determine the basic structural units of such compounds, it is an invaluable tool in determining the superstructures and defects. We present here a high resolution electron microscope study of the superstructures and defects in $Bi_{2-x}Pb_xSr_2CaCu_2O_8$ and $Bi_{2-x}Pb_x(SrCa)_2CuO_6$ (for x=0 and x≈0.4). A brief account of our results on $Bi_2Sr_2CaCu_2O_8$ have been presented in references (11 and 12). Some HREM results on the Bi-oxide based superconductors will be found in references (13,14,15,16,17,18) among others.

MATERIALS AND METHODS

2.1 Sample preparation.

The Bi-Sr-Ca-Cu-oxides were prepared as described in Bordet et al. (8) with nominal cation compositions of 2224, 2214, 2212 and 2.4 1.65 0.7 2. The Pb doped compounds were prepared in a similar manner with a cation ratio Bi-Pb-Sr-Ca-Cu of 1.8 0.4 2 1 2. A second annealing to induce crystallization was carried out at 970 C° for 20 hours followed by cooling at a rate of 20° C/hour. The undoped Bi-oxides all had a majority phase with c=31 Å as shown by X-ray powder scans, and Tc onset up to 84°K, except the 2.4 1.65 0.7 2 compound which had a majority of the c=24Å phase (reported Tc≈6° to 20°K) and about 20% of the 31Å phase. The Pb doped material (c=31 Å majority phase) had a Tc of 79°K (majority phase) and 100°K (minority phase) before recrystallization. After recrystallization individual crystals were extracted from the pellet and shown to be either the 24 Å or 31Å (Tc=92 K) phase by X-ray diffraction. For the 24 Å Pb doped phase a Tc=87°K measured in several crystals has not been confirmed in others. The Tc given are mid-point values of the ac susceptibility curves.

2.2 Electron Microscopy.

Specimens were prepared for electron microscopy as described in reference (19). The individual crystals were crushed and prepared separately. Electron microscope observations were performed on a JEOL 200CX at 200kV and a JEOL 4000EX at 400kV. These microscopes have a point resolution of 2.3Å and 1.7Å , and tilting stages of $\pm 7^{\circ}$ and $\pm 15^{\circ}$ respectively.

RESULTS

All the compounds studied are lustrous black layered compounds which cleave easily on a preferred plane to give very thin flakes. They have the slippery feel of graphite since the layers slide easily over each other. Moiré patterns and other contrast phenomenon associated with wrinkling of the layers are seen in most crystals. The specimen preparation technique of grinding in a pestle and mortar must introduce many of the defects.

3.1 $Bi_2Sr_2CaCu_2O_8$

Viewed down the c-axis, the preferred orientation of the sheets, the image is dominated by a square net of 2.7Å x 2.7Å ($\sqrt{2}a_p/2$ x $\sqrt{2}a_p/2$). (plate Ia). In agreement with X-ray and neutron results the unit cell is seen to be $\sqrt{2}a_p$ x (approx)$5\sqrt{2}a_p$ (plate Ib), and is centred with cmm symmetry. It is evident that there are waves of distortion along the b-axis which give rise to the approximate $5\sqrt{2}a_p$ periodicity. See also plate IIf. There is a major component of displacement perpendicular to the b-axis. This is deduced from the observation that in certain images there is a repetition of two rows where the atomic columns are imaged as spots then three rows which become continuous lines (the c-axis atomic columns are tilted locally about the b-axis.). See plate Ic. This is in agreement with X-ray and neutron results which indicate that the Bi atoms are displaced along the x-axis (8).

Tilting about the b-axis by 10° gives the [101] projection. In this orientation the 111 reflection appears indicating that the structure is not body centred. The 101 reflection also appears indicating that it is not centred on all faces.The [101] image has pmm symmetry. See plate Id. The indices are given with respect to the basic unit cell . $a \approx \sqrt{2}a_p$, $b \approx \sqrt{2}a_p$ and $c \approx 8a_p$. $a \neq b$.

Tilting away from the [001] zone axis about the a-axis by only a few degrees (not an exact projection) gives some useful information about the superstructure. The repeat periodicity is then clearly $\approx 5x\sqrt{2}a_p$ as is expected for a thin crystal. As usual the atomic columns become blurred in the direction of tilt , except that at regular intervals ie $\approx 5x\sqrt{2}a_p$ along the b-axis distinct spots are visible. See plate Ij. This is the case irrespective of the number of layers, including regions one layer thick. ie. 1/2 c as seen on the right of plate Ij. Hence the contrast in these images must be determined largely by atomic displacements from the ideal lattice positions. The displacements of the Bi atoms along z, as seen in plate IIf and shown schematically in figure 2, can explain qualitatively the contrast in these images . However other displacement models for the superstructure can explain this contrast.

It will be noted that in the thin region of plate Ij the positions of Bi atoms can be seen on the $a_p x a_p$ lattice as expected for a sheet one (or 2n+1) layer(s) thick ie.for a thickness of c/2 with one Bi plane on either surface. See figure 3. The inset in plate Ij shows an edge on view of of a neighbouring region of this same crystal which has curled up to reveal that it is in fact just one layer thick. The diffraction pattern of this region also shows the 110 reflections expected from a crystal (n+1/2)c thick. Layers (n+1/2)c and 2nc thick may be distinguished by the presence or absence of the 110 reflections respectively. (Plate Ig,h)

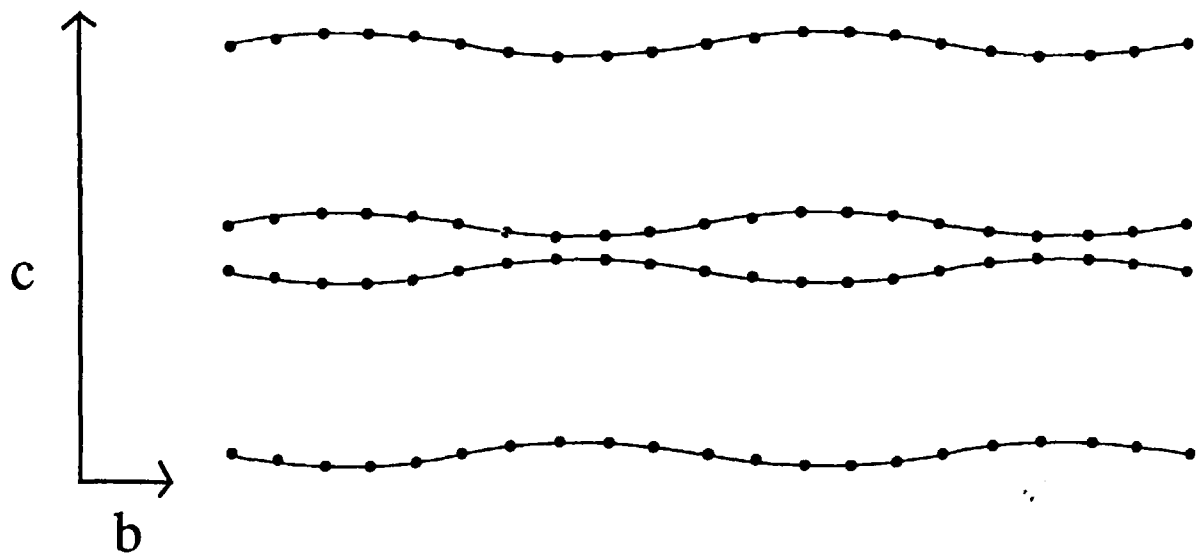

FIG. 2-Schematic representation of the displacements of the Bi atoms along z for $Bi_2Sr_2CaCu_2O_8$.

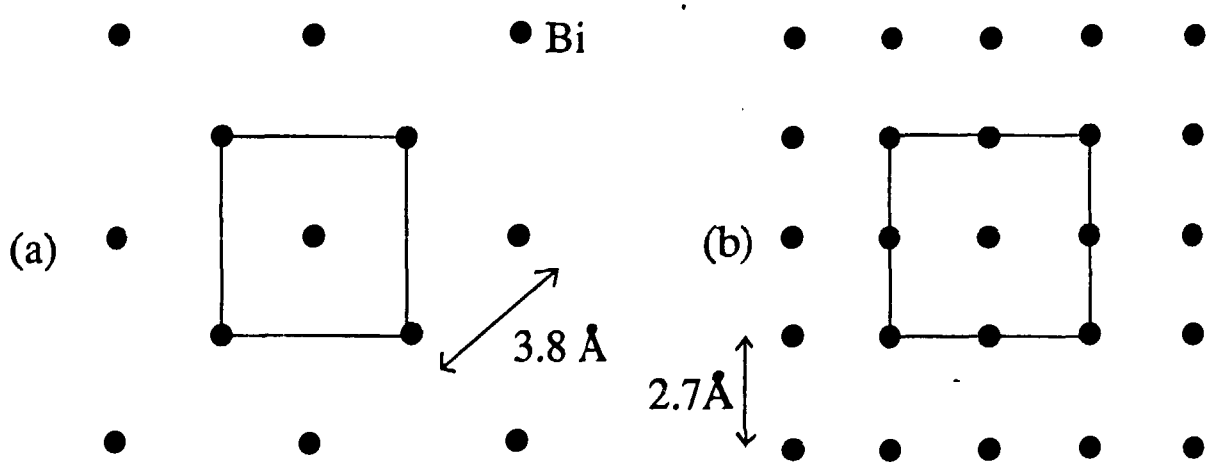

FIG. 3- [001] projection of $Bi_2Sr_2CaCu_2O_8$ sheets (a) one and (b) two layers thick . Only the Bi atoms are shown for simplicity. The unit cell is indicated.

The existence of the superstructure modulations even in sheets one layer thick must be taken into account when considering the possible causes of this modulation.

Viewed parallel to the layers, the pairs of very dark lines must correspond to layers of Bi_2O_2. Bi (atomic number 83) is a very strong scatterer. It is clear that the layers cleave between the Bi bilayer, leaving a monolayer of Bi; plate IIf . The crystals seen in this orientation are usually too small to be oriented by electron diffraction. They are very often the curled up edges of large sheets. The Bi planes are seen to undulate along the b-axis to give the superlattice. The image down the b-axis has cmm symmetry and has no superstructure. Images slightly off the short a-axis reveal fascinating moiré patterns, due to the variation of inclination of atomic columns approximately parallel to the c-axis. The [001] projection symmetry is difficult to determine from our images but X-ray patterns give cmm symmetry .

It is clear from the [001] images and diffraction patterns that the superstructure modulation along the b-axis is not usually an integral multiple of the basic unit cell, $b=\sqrt{2}a_p$ ie. 5.4 Å. The average period as measured from the diffraction pattern ranges between 4.6 and 5.2 times b and peaks at 4.67 and 4.75 x b. These diffraction patterns can often be indexed on a 14 ie.(5+5+4) or 19 ie (5+5+5+4) times bunit cell and so are commensurate with a large unit cell. The average repeat periods are 14/3=4.67 and 19/4=4.75 times brespectively for these superstructures. See plate IIc,d. This is in agreement with the images where blocks of x6 or x4 b/2 are inserted along the b-axis to give an average superstructure length slightly greater or less than 5b.(Plate IIa,b). The insertion of such blocks is not perfectly periodic. This also argues in favour of the existence of discrete building blocks, rather than an incommensurate wave of fixed length. If the superstructure were perfectly periodic it would be practically impossible to distinguish , from the image, between an ordered superstructure of the type proposed and an incommensurate wave of fixed length.

It will be noted that in the case of an incommensurate wave of length pb, where p is an irrational number, the major spots in the diffraction pattern will exhibit satellites which can be indexed as nb*/p where n is an integer. However, the satellites from neighbouring lattice reflections cannot be indexed on the same superlattice grid, since n/p is not an integer. They can only be indexed with respect to their own lattice reflection.

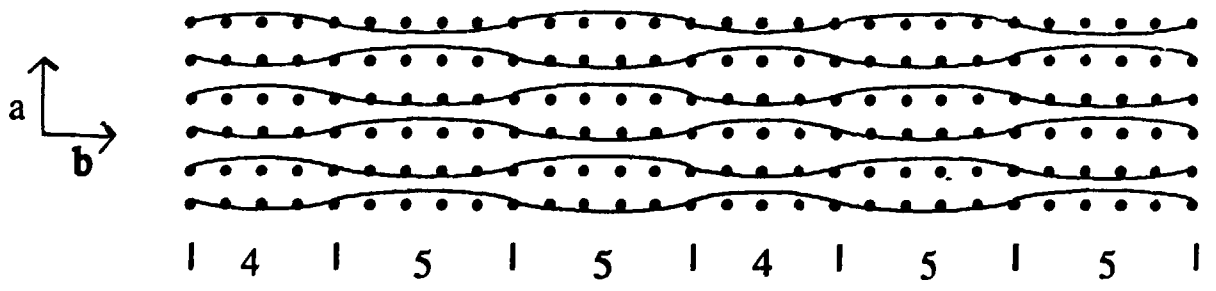

FIG. 4- Schematic representation of the superstructure corresponding to plate IIc, the [001] projection.

3.2 $Bi_2(SrCa)_2CuO_6$

The phase $Bi_2(SrCa)_2CuO_6$ with c=24 Å is also modulated along the b-axis with a periodicity close to 5xb, but it differs from $Bi_2Sr_2CaCu_2O_8$ in that its superstructure is described on a monoclinic lattice where as $Bi_2Sr_2CaCu_2O_8$ has an orthorhombic lattice.While our electron micrographs along the a-axis are not good enough to establish this point, X-ray diffraction patterns (20) show this quite clearly.

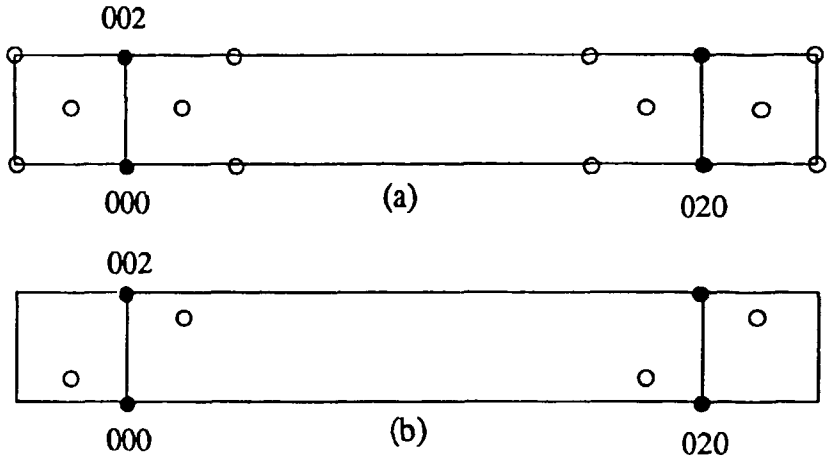

FIG. 5- Reflections seen in [100] X-ray diffraction patterns for (a) $Bi_2Sr_2CaCu_2O_8$ and (b) $Bi_2(SrCa)_2CuO_6$. The superstructure is orthorhombic in (a) and monoclinic in (b). ● - lattice reflection. o - superlattice reflection.

The [001] images are consistent with this evidence. See plate IVa. In this image there is a superstructure of exactly 5xb, as confirmed in the diffraction pattern, plate IIIa. (The superstructure is not always exactly 5xb.) This image resembles a superposition of three images of the $Bi_2Sr_2CaCu_2O_8$ type but displaced by 5b/3 along b. The X-ray diffraction patterns obtained so far correspond to a superposition of only two such images. An explanation for this is that the superlattice periodicity along c is variable but commensurate. It will be noted that the [010] direction of the lattice is not a principal direction for the superlattice in this phase.

The c-axis can be verified by observing the order at which the Ewald sphere cuts the second Laue zone. This provides a means of checking whether the crystal observed is of the c=24 Å or c= 31 Å phase.

3.3 $Bi_{2-x}Pb_xSr_2CaCu_2O_8$ and $Bi_{2-x}Pb_x(SrCa)_2CuO_6$ (x≈0.4)

The lead doped Bi-oxides display a much weaker but even more complicated superstructure with two distinct periodicities of close to 4 and 7xb which are present simultaneously. The [001] diffraction patterns of both compounds display diffuse lines along <110> directions passing through 2n,2n,0 reflections and also in the [100] direction passing through 2n+1,2n+1,0 reflections. This may be associated with short range order of the Pb. In $Bi_{2-x}Pb_xSr_2CaCu_2O_8$ the superlattice reflections are extremely variable in intensity but remain essentially in the same position. Thus the superstructure apparently remains constant but the degree of order varies. The crystals of $Bi_{2-x}Pb_x(SrCa)_2CuO_6$ observed were particularly well ordered; plate IIIb and IVc.The diffraction pattern can be indexed on

a 21xb unit cell; the very weak diffraction spots define this lattice. The brighter reflections occur at 6, 10 and 18xb*/21. These correspond to a periodicity of 7/2, 4.2/2 and 7/3 times b. The periodicity of 4.2b is equal to an average periodicity of (5+4+4+4+4)/5. Interpretation of the [001] image is not simple because the superstructure is monoclinic as for the un-doped phase. However the optical diffraction pattern of this image plate IIIe shows all the major electron diffraction spots. The 4.2 and 7xb periodicities can be seen more easily in slightly tilted images as in plate IVc. Similarly the $Bi_{(2-x)}Pb_xSr_2CaCu_2O_8$ diffraction pattern can be indexed on a 23b unit cell with bright reflections at 6,10 and 20b*/23. These correspond to periodicities of 4.6/2 and (7.67/2)xb , ie. (5+5+5+4+4)/5 and (8+8+7)/3. The 4.6 periodicity is seen to be centred (plate IVb) as for $Bi_2Sr_2CaCu_2O_8$ (plate Ia). The 7.67 periodicity is only seen very faintly in some images.

Thus it appears that the shorter periodicity (≈4b) is a wave of distortion very similar to that occurring in the undoped materials, but modified in frequency by the presence of Pb. The longer periodicity only occurs in the Pb doped oxides and so may be associated with ordering of the Pb.

DEFECTS

The oxides studied can form non-stoechiometric stacking faults with different numbers of perovskite blocks between the Bi_2O_2 layers. The specimen in which we saw intergrowths of the 24 Å and 31 Å phase had a nominal composition 2.5 1.65 0.7 2. (Plate IVd). One of the specimens contained a few intergrowths of a 16 Å phase which is not one of the homologous series. These Bi-oxides also form twist boundaries (or "twins") where successive layers have the a- and b-axes interchanged. (See plate IVe) . This is possible because b is approximately equal to a for the basic unit cell. The twist boundary plane is on (001). This type of defect is often associated with over-lapping crystals. They do not form twins on (101) planes as seen in $YBa_2Cu_3O_7$. Moiré patterns and dislocation arrays in the basal plane are very common. The dislocation arrays in the Pb doped oxides show a greater tendency to dissociate to form extended nodes than is the case for the undoped oxides. See plate IV e.f.

DISCUSSION

The origin of the superstructure in the Bi-oxide based superconductors which involves waves of distortion of the BiO layers is not well understood. It could be induced by a difference in lattice parameter between the Bi_2O_2 layer and the perovskite layer, or by an ordering of Ca^{++} and Sr^{++} cations which have atomic radii 0.94Å and 1.10Å respectively, or by an ordering of Sr^{++} vacancies (21),or by a displacement of Bi cations associated with a small number of additional oxygen atoms in the Bi_2O_2 layer, or by a combination of these and other factors. The existence of single layer thick $Bi_2Sr_2CaCu_2O_8$ sheets which retain the superstructure modulation probably argues against the insertion of oxygen between the BiO planes. The observation that the superstructures are composed of combinations of waves of distortion which are each an integral number times the basic unit cell is consistent with the existence of an ordering of atomic species or vacancies at specific lattice positions.

Does the superstructure play any direct role in the superconducting phenomenon? It seems unlikely that it is involved in any type of resonance phenomenon because the Tc of $Bi_2Sr_2CaCu_2O_8$ and $YBa_2Cu_3O_7$ are very similar and $YBa_2Cu_3O_7$ has no superstructure. However it may well be involved in the mechanism which controls the valence on the Cu atoms. It is well establishes that a requirement for a high Tc in this type of cuprate is the presence of an average Cu valence of about 2.3. The formal valence of all the Bi-oxides studied is 2, hence one must suppose that some additional oxygen or cation vacancies produce the required valence. The correlation between the crystal order and stoechiometry, and the Tc are very difficult to establish in these oxides with 4 or 5 cations. Even in some of the best samples, which appeared to be nearly single phase specimens of $Bi_2Sr_2CaCu_2O_8$ as judged by diffraction experiments, appeared to be multi-phased as regards their Tc.The preparation of pure single phase materials is one of the major hurdles in the characterization of these materials.

The difference of twining behaviour in the Bi-oxides and $YBa_2Cu_3O_7$ implies that twining does not play an essential role in high Tc superconductivity.

The determination of the structure of $Bi_2Sr_2CaCu_2O_8$ is a good example of the complementary roles played by X-ray, neutron and electron diffraction/microscopy. X-rays can determine the position of the cations, neutrons the position of the oxygen in the basic structure and electron microscopy the nature of the superstructure.

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Plate I

All scale bars represent 10 Å.

(a)[001] projection of a $Bi_2Sr_2CaCu_2O_8$ crystal .400 kV.

(b)[001] projection of a thicker $Bi_2Sr_2CaCu_2O_8$ crystal highly defocused. 200 kV. Note the cmm symmetry.

(c)[001] projection of $Bi_2Sr_2CaCu_2O_8$ crystal at a defocus which shows the sequence of dotted and continuous lines corresponding to atomic columns aligned and tilted with respect to the incident beam.

(d)[101] projection of a $Bi_2Sr_2CaCu_2O_8$ crystal showing pmm symmetry.

(e)Optical diffraction pattern (ODP) of(b)

(f) ODP of (d). Note the presence of the 111 and 101 reflections (arrowed).

(g)ODP of (j) :- 2n+1 layers thick. Note the presence of the <110> reflections (arrowed).

(h) ODP of (j) :- 2n layers thick.

(j) Projection of a $Bi_2Sr_2CaCu_2O_8$ crystal tilted by a few degrees about the a-axis away from [001]. Note the periodicity of close to 5xb along b even in the layer just one layer (c/2) thick. Inset :- Edge of a neighbouring region of the same crystal curled up showing that it is in fact one layer thick.

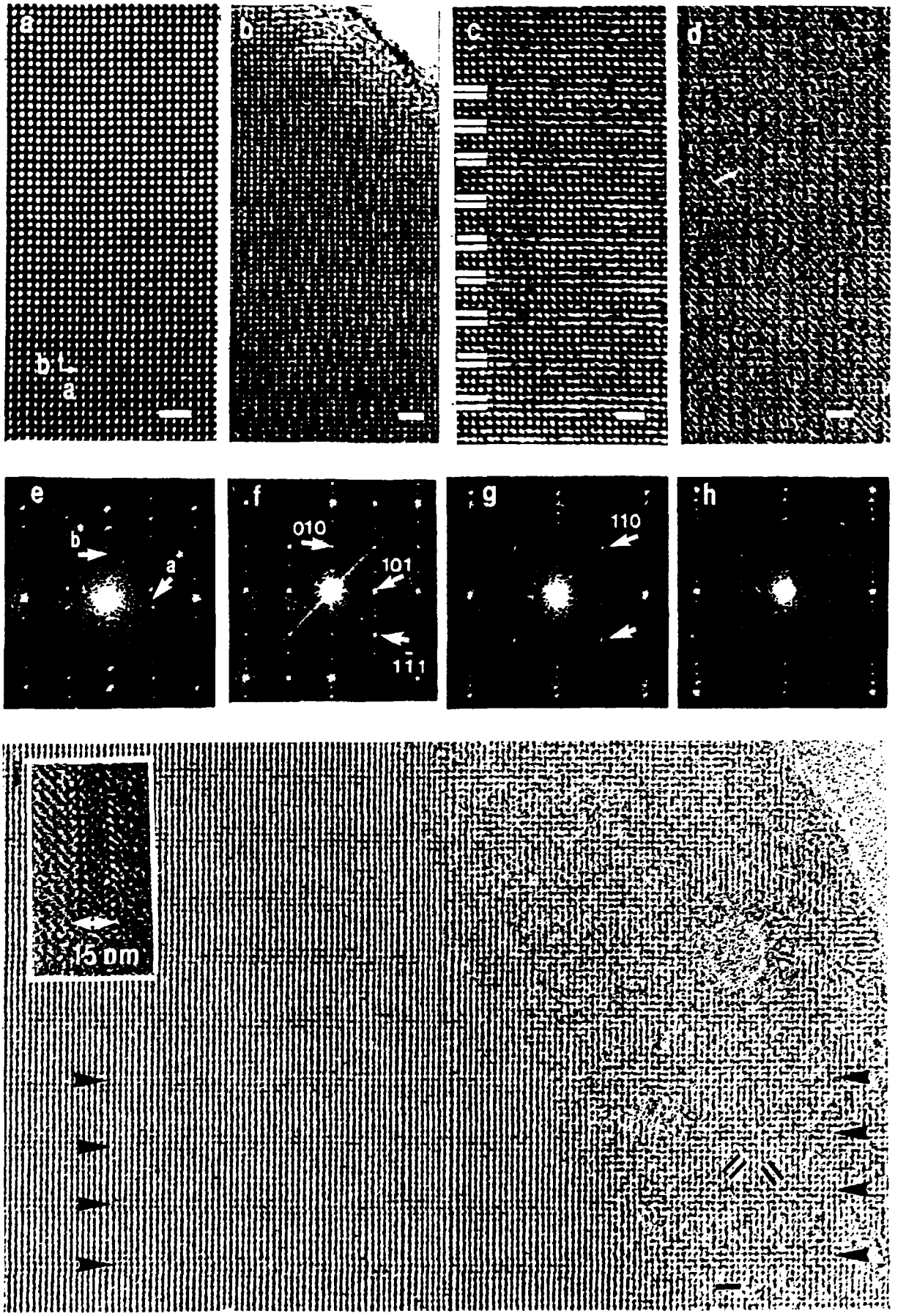

a
b
c
d
b
a
e
f
g
h
b
a
010
101
111
110
1.5 nm

Plate II

All scale bars represent 10 Å.

(a),(b) [001] projection of $Bi_2Sr_2CaCu_2O_8$ crystals. The insertion of blocks of x4 and x6 b/2 is not perfectly periodic.

(c) Electron diffraction pattern corresponding to (a). It can be indexed on aunit cell along b of 14b. The 3b*/14 spot comes from the first Laue zone. See IIe. The bright spot at 6b*/14 corresponds to 2.33b, so the true periodicity is 4.67b.

(d) Electron diffraction pattern of the other most commonly seen $Bi_2Sr_2CaCu_2O_8$ superstructure. It can be indexed on a unit cell of 19b.The 4b*/14 spot comes from the first Laue zone. See IIe. The bright spot at 8b*/19 corresponds to 2.375b, so the true periodicity is 4.75b.

(e) Optical diffraction pattern corresponding to f.

(f) Image of $Bi_2Sr_2CaCu_2O_8$ close to [100]. Note the undulations in the Bi layer and the single Bi plane at the surface.

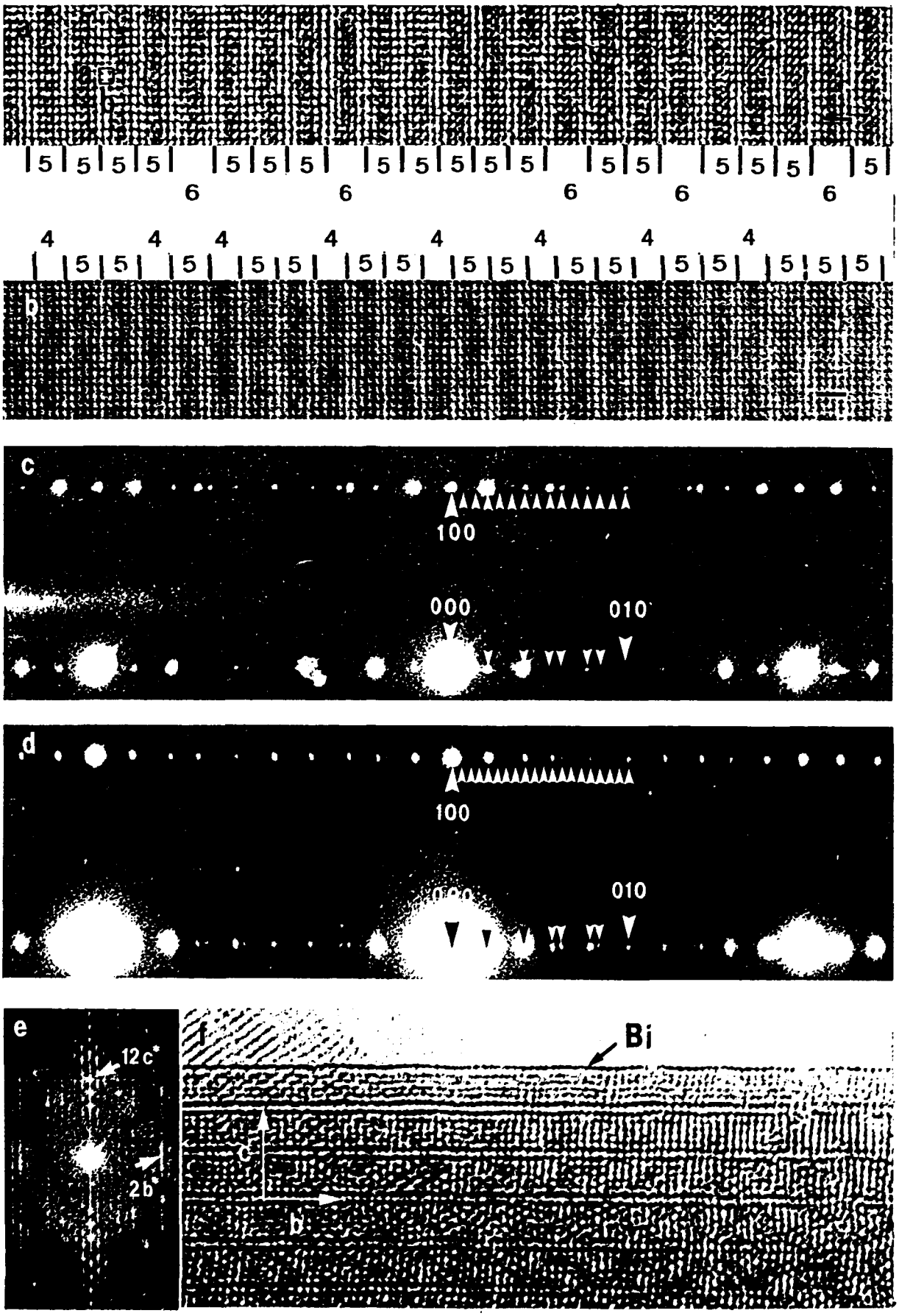

5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
6 6 6 6 6
4 4 4 4 4 4 4 4
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
b
c
100
000
010
d
100
010
e
12c*
2b*
Bi
c
b

Plate III

(a)[001] Electron diffraction pattern of $Bi_2(SrCa)_2CuO_6$. The superlattice reflections can be indexed as nb*/5.

(b)[001] Electron diffraction pattern of $Bi_{2-x}Pb_x(SrCa)_2CuO_6$. The superlattice reflections can be indexed as nb*/21. The superlattice is defined by the very small spots.

(c)[001] Electron diffraction pattern of $Bi_{2-x}Pb_xSr_2CaCu_2O_8$. The superlattice reflections can be indexed as nb*/23

(d)ODP of $Bi_2(SrCa)_2CuO_6$ image corresponding to (a).

(e)ODP of $Bi_{2-x}Pb_x(SrCa)_2CuO_6$ image corresponding to (b).

(f) ODP of $Bi_{2-x}Pb_xSr_2CaCu_2O_8$ image corresponding to (c).

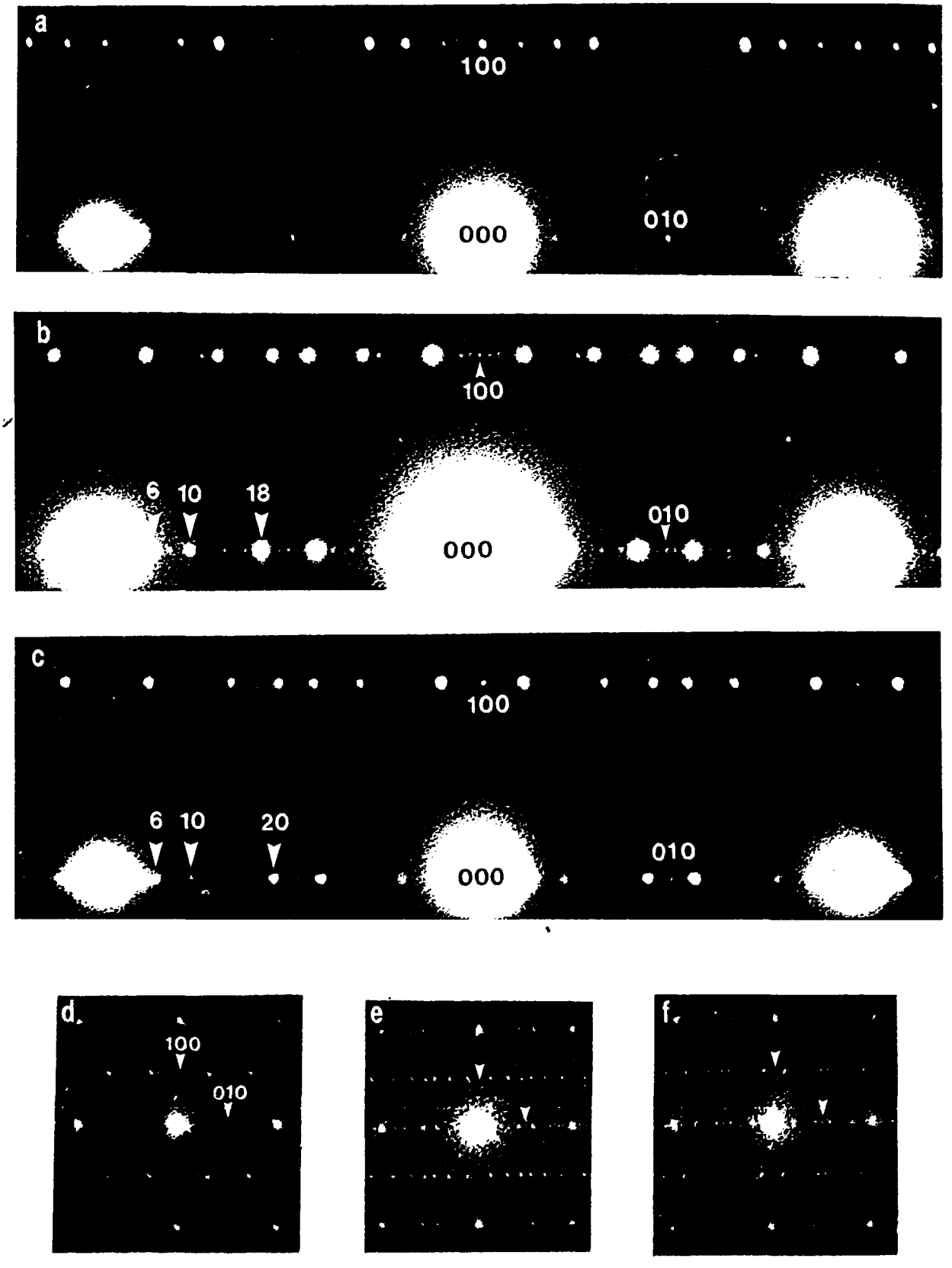

a
100
000
010
b
100
6
10
18
000
010
c
100
6
10
20
000
010
d
100
010
e
f

Plate IV

The scale bars represent 10 Å except in e and f where they represent 100 Å.

(a) [001] image of $Bi_2(SrCa)_2CuO_6$. This image resembles a superposition of three images of the $Bi_2Sr_2CaCu_2O_8$ type displaced by 5b/3 along b.

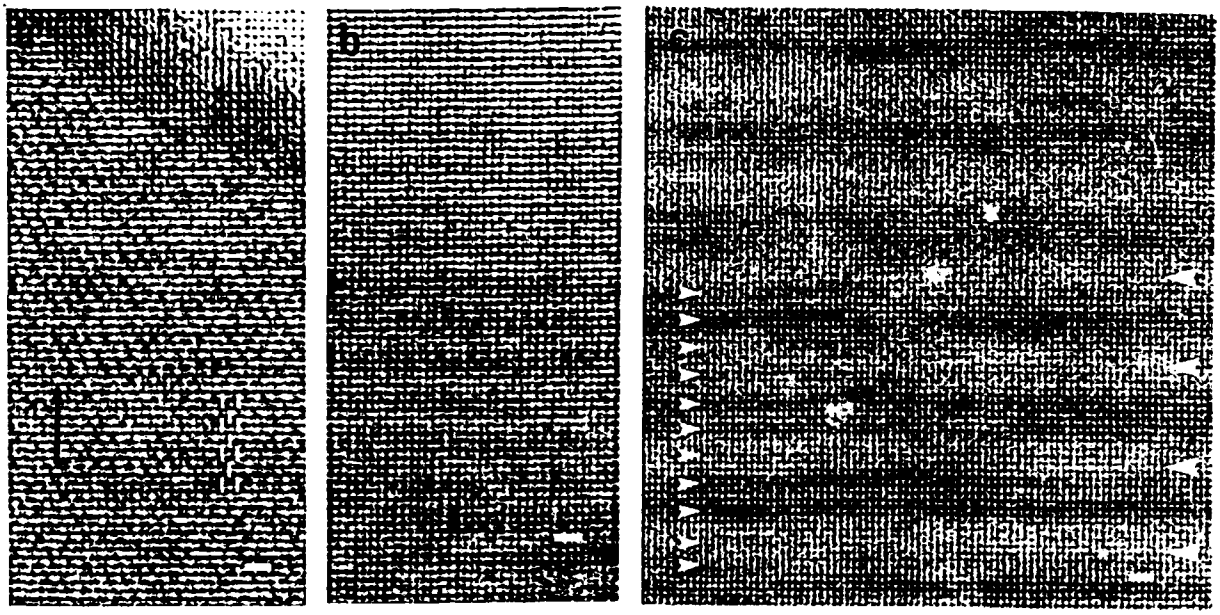
(b) [001] image of $Bi_{2-x}Pb_xSr_2CaCu_2O_8$. The 4.7 period with cmm symmetry is evident.

(c) Image of $Bi_{2-x}Pb_x(SrCa)_2CuO_6$ tilted away from [001] about [100]. Note the two periodicities ≈4.2b and ≈7b.

(d) [110] image of undoped oxide showing intergrowths of the 24 A and 31 A phases.

(e) 'Twin" or 90° twist boundary in $Bi_2Sr_2CaCu_2O_8$. Note the superstructure in two perpendicular directions. There is also an array of screw dislocations — The boundary is not exactly at 90°. Inset :- ODP of a 90° twist boundary.

(f) Dislocation array in $Bi_{2-x}Pb_xSr_2CaCu_2O_8$ with extended nodes.



d