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# SUPERSTRUCTURE OF THE SUPERCONDUCTOR $BI_2Sr_2CaCu_2O_8$ BY HIGH RESOLUTION ELECTRON MICROSCOPY

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# SUPERSTRUCTURE OF THE SUPERCONDUCTOR $Bi_2Sr_2CaCu_2O_8$ BY HIGH RESOLUTION ELECTRON MICROSCOPY

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The superstructure of the high Tc superconducting oxide $Bi_2Sr_2CaCu_2O_8$ has been studied by high resolution electron microscopy. Waves of distortion along the b-axis give an incommensurate superlattice slightly larger or smaller than $5\sqrt{2}a_p$ ($a_p$=perovskite unit cell). The building blocks along the b-axis are 4, 5 and 6 times $\sqrt{2}a_p/2$. The incommensurate superlattice is composed of approximately periodic combinations of these building blocks. The symmetry of three major projections are $p_{gm}$ (or possibly $p_{gg}$), $c_{mm}$ and $c_{mm}$ for the ideal superlattice with $b=5\sqrt{2}a_p$. These projections correspond to the space groups Pcnn and Pmnn respectively.

## 1. INTRODUCTION

The basic structure of $Bi_2Sr_2CaCu_2O_8$ as determined by X-ray and neutron studies [1,2,3] is an Aurivillius related phase as suggested by Michel et al. [4], and has approximate unit cell dimensions $a=\sqrt{2}a_p$, $b=5\sqrt{2}a_p$ and $c=8a_p$, where $a_p$=3.8Å. It consists of layers of perovskite sandwiched between $Bi_2O_2$ layers. While electron microscopy does not have sufficient resolution to unambiguously determine the basic structural unit of such a compound, it is an invaluable tool in determining the superstructure.

## 2. METHODS AND MATERIALS

The Bi-Sr-Ca-Cu-oxides were prepared as described in [3] with nominal cation compositions of 2,2,2,4 and 2,2,1,4, with Tc up to 80K. 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 respectively.

## 3. RESULTS

$Bi_2Sr_2CaCu_2O_8$ is seen to be a layered compound which cleaves easily on a preferred plane. The layers slide easily over each other, since Moiré patterns and other contrast phenomenon associated with wrinkling of the layers are seen in practically all crystals. Many of the defects are probably introduced during EM preparation.

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 $\sqrt{2}a_p/2$). In agreement with X-ray and neutron results the unit cell is seen to be $\sqrt{2}a_p$ x $5\sqrt{2}a_p$ and is centered with cmm symmetry. At certain defocus, and especially for slightly tilted crystals, it is evident that there are waves of distortion along the b-axis which give rise to the $5\sqrt{2}a_p$ periodicity. The major component of displacement is perpendicular to the b-axis. This is deduced from the observation that 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 about the b-axis.). See figure 1.

Depending on the preparation, the blocks of x6 or x4 $\sqrt{2}a_p/2$ are inserted along the b-axis to give an average superstructure length slightly greater or less than $5\sqrt{2}a_p$, i.e. an incommensurate superstructure. The insertion of such blocks is not perfectly periodic. This argues in favour of the existence of discrete building blocks, rather than an incommensurate wave of fixed length (fig. 2).

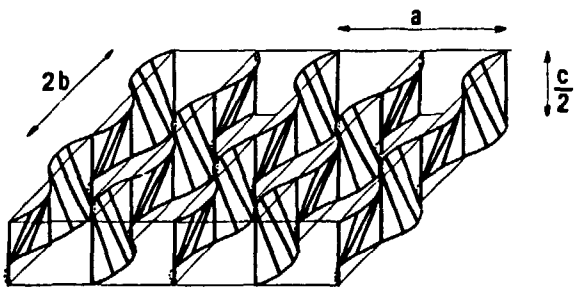


**Figure 1** Schematic representation of displacements of atomic columns.

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 (fig.3). The Bi planes are seen to undulate along the b-axis to give the superlattice. The image down the b-axis has cmm symmetry (fig.3)

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. Depending on the exact orientation, the optical diffraction pattern is consistent with either $p_{gm}$ (c'=c/2) or $p_{gg}$ projection symmetry (fig.4). It is not evident which is correct.

## 4. CONCLUSIONS

The observed projection symmetries are consistent with a space group of either Pcnn or Pmnn for the ideal superlattice with $b=5\sqrt{2}a_p$. With building blocks in this system, it is possible to form many incommensurate phases which destroy the symmetry. Careful control of the preparation conditions will be essential to produce a commensurate phase suitable for the precise determination of the complete superstructure by X-ray and neutron diffraction.

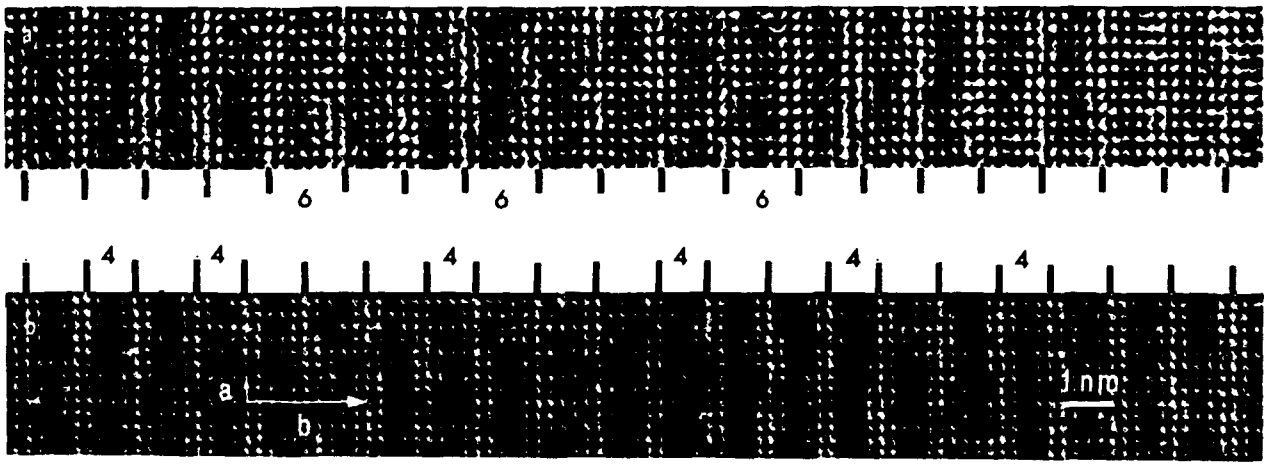


**Figure 2a,b)** [001] projections of $Bi_2Sr_2CaCu_2O_8$ crystals. The insertion of blocks of x4 and x6 $(\sqrt{2}a_p)/2$ is not perfectly periodic.

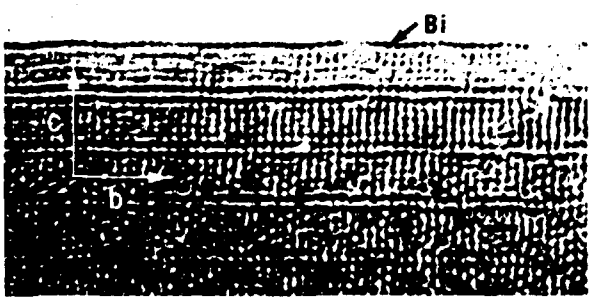


**Figure 3a.** Image of $Bi_2Sr_2CaCu_2O_8$ close to [100]. Note the undulations in the Bi layer and the single Bi plane at the surface.

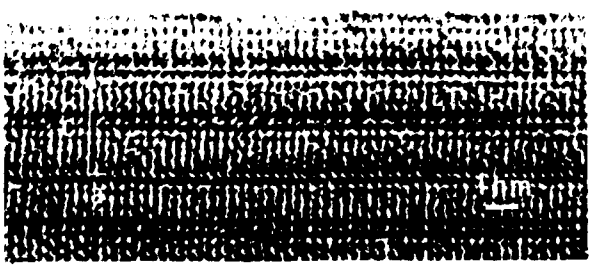


**Figure 3b.** Image of $Bi_2Sr_2CaCu_2O_8$ close to [010].

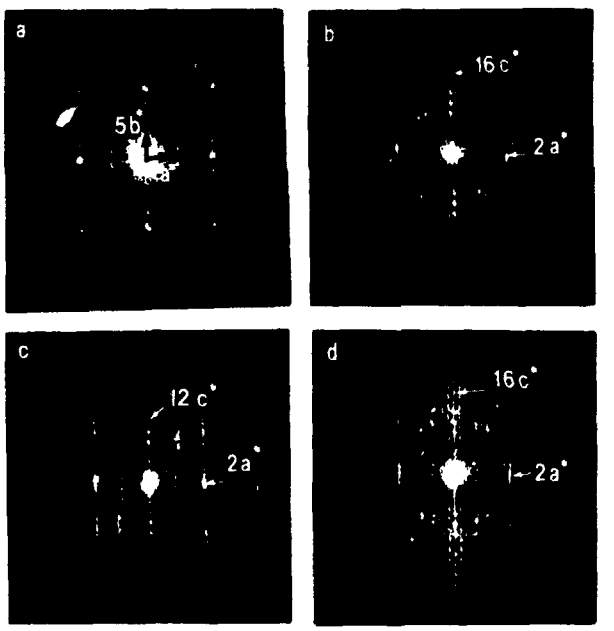


**Figure 4a)** Optical diffraction pattern (ODP) of figure 2a has cmm symmetry. **b)** ODP of figure 3a **c)** ODP of figure 3b has cmm symmetry **d)** ODP of crystal shown in figure 3a at a slightly different orientation, close to [100].

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REFERENCES

1 J.M. Tarascon, Y. Le Page, P. Barboux, B.G. Bagley, L.H. Greene, W.R. McKinnon, G.W. Hull, M. Giroud, & D.M. Hwang **Phys.Rev.** (1988) submitted.
2 S.A. Sunshine, T. Siegrist, L.F. Schneemeyer, D.W. Murphy, R.J. Cava, B. Batlogg, R.B. van Dover, R.M. Fleming, S.H. Glarum, S. Nakahara, R. Farrow, J.J. Krajewski, S.M. Zahurak, J.V. Waszczak, J.H. Marshall, P. Marsh, L.W. Rupp Jr. & W.F. Peck (1988) preprint.
3 P. Bordet, J.J. Capponi, C. Chaillout, A.W. Hewat, J.-L.Hodeau & M. Marezio (these proceedings)
4 C. Michel, M. Hervieu, M.M. Borel, A. Grandin, F. Deslandes, J. Provost & B. Raveau **Z.Phys.B68**,421.