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Microstructure of High Temperature Superconductors of the Perovskite Type

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Abstract

Combined high resolution electron microscopy and convergent beam electron diffraction (CBED) of the same areas of crystals of $Ba_3La_3Cu_6O_{14}$ reveals defects of various types including ordinary dislocations and polytypic intergrowths. This latter type is considered to be intimately associated with the performance of this material as a high temperature superconductor.

1. Introduction

Mixed valence copper oxides of stoichometry $Ba_3La_3Cu_6O_{14}$, $Ba_2YCu_3O_7$ and $La_{2-x}Ba_{1+x}Cu_2O_y$ are oxygen defect compounds, the former two having oxygen defect perovskite and the latter an oxygen defect intergrowth K_2NiF_4 structure (Michel and Raveau 1984; Er-Rakho *et al.* 1981). Similar compounds have recently been shown to be high temperature superconductors (Bednorz and Muller 1986; Wu *et al.* 1987) and an extensive literature on the subject is now appearing. (At the March 1987 meeting of the American Physical Society over 150 papers were presented in a special panel discussion.)

A common observation by many workers is that complex annealing procedures are necessary to obtain a high proportion of a sample in the superconducting form. Thus, a study of microstructure by high resolution electron microscopy is essential in unravelling the factors determining the macroscopic properties. In this paper we report observations on the microstructure of $Ba_3La_3Cu_6O_{14}$ which is, in a sense, an end member of the series of perovskites as lanthanum is the rare earth cation with the largest radius.

2. Results and Discussion

Fine dried powders of La_2O_3, CuO and $BaCO_3$ in stoichiometric proportions to yield $La_3Ba_3Cu_6O_{14}$ were ground together in a mortar and then reacted in an Al_2O_3 crucible by heating at 560, 720 and 900°C for consecutive 24 hour periods. The dark grey product was lightly crushed and fine crystals were suspended on a holey carbon film and examined in a JEOL 200 CX electron microscope. Both selected

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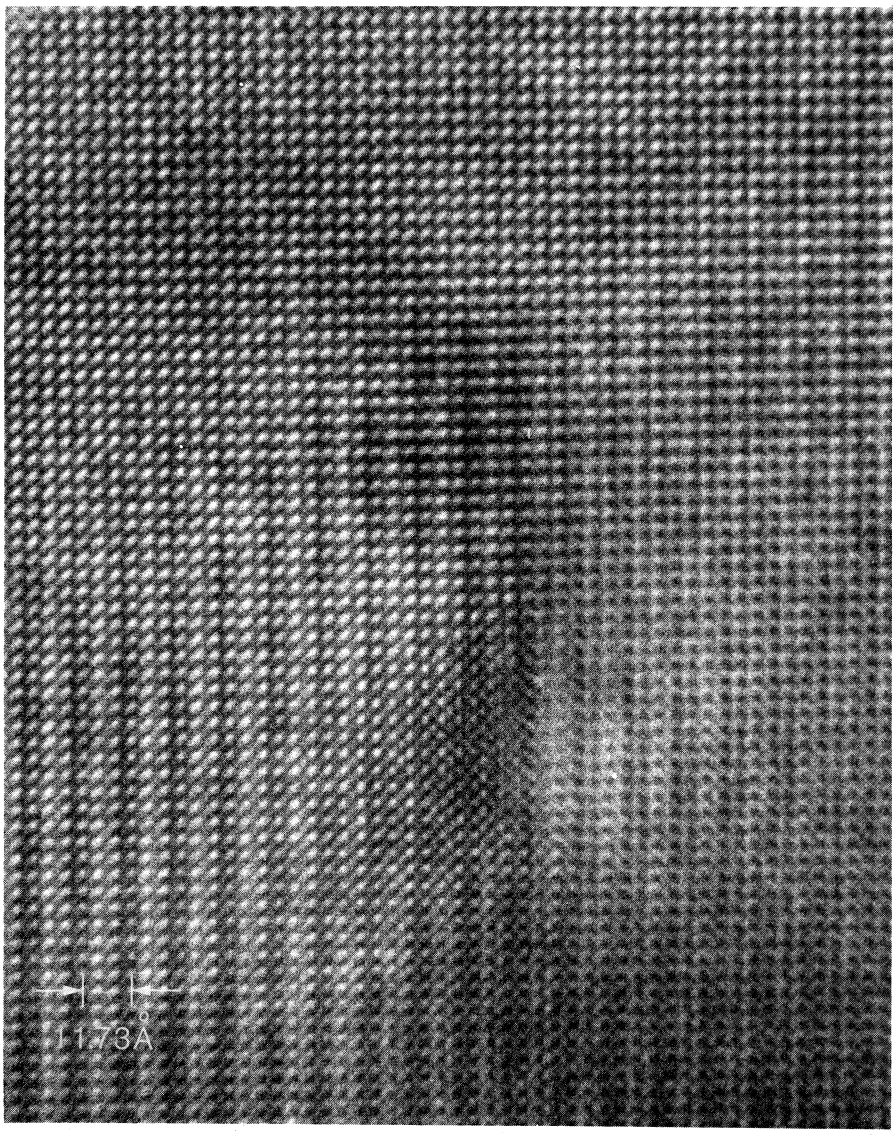


Fig. 1. Lattice image of a dislocation including slowly varying contrast due to strain. Contrast reversal in the lattice image due to the tilt induced by the strain field of the dislocation is evident.

area and CBED patterns and X-ray powder patterns are in accord with the unit cell dimensions and intensities reported by Er-Rakho *et al.* (1981). We agree with the refinement of the structure in the space group and unit cell chosen by Er-Rakho *et al.*, but to facilitate comparison of our lattice images and diffraction patterns with the orthorhombic cell of $Ba_2YCu_3O_7$ we have indexed our results in terms of a tetragonal cell of dimensions $a = b = 3{\cdot}91$ Å and $c = 11{\cdot}73$ Å. A number of different types of defects were observed in both the lattice images and CBED of $Ba_3La_3Cu_6O_{14}$.

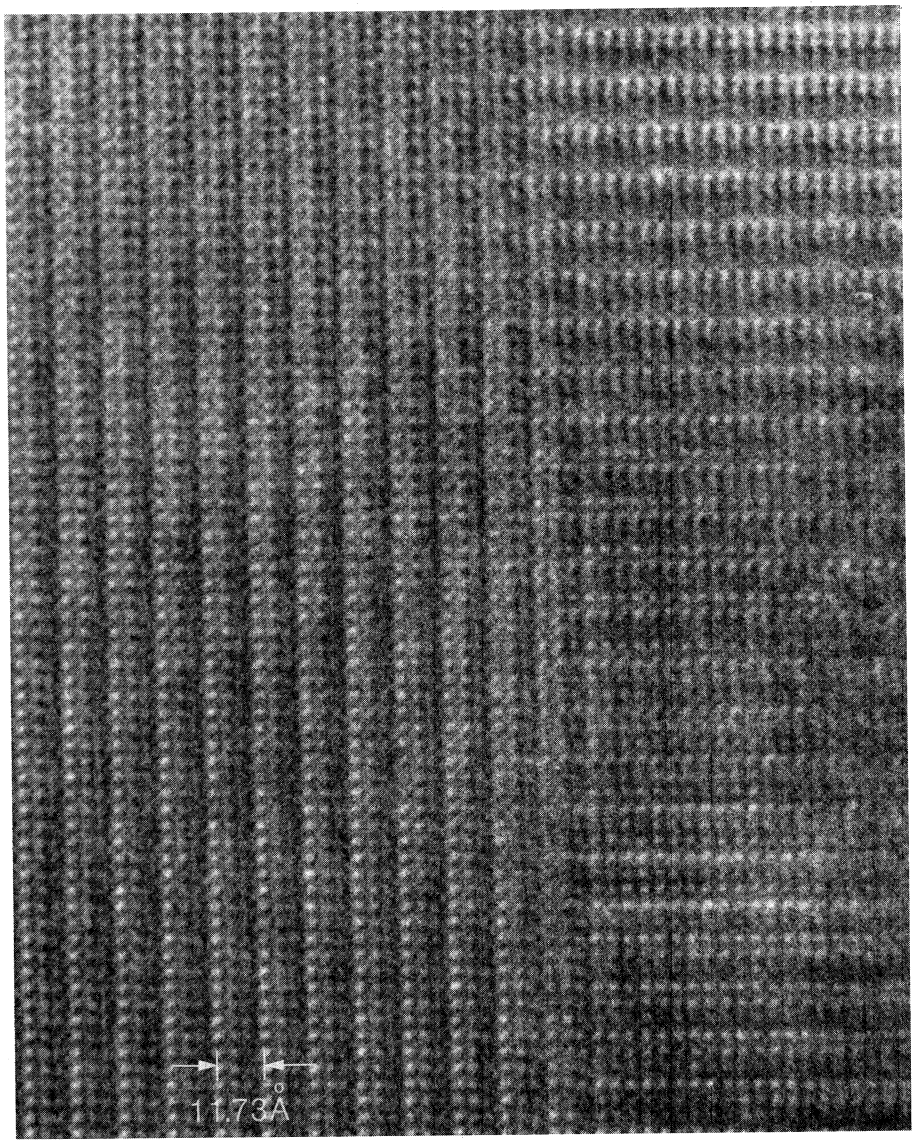


Fig. 2. Lattice image of an interface in $La_3Ba_3Cu_6O_{14}$. The plane of projection is (100) in each crystal and the *c* axes are orthogonal. No strain or tilt can be detected in this one-dimensional intergrowth.

Dislocations

Only a few dislocations have been observed (see Fig. 1). The slowly varying contrast is approximately 'two beam' in character, an observation which can be readily understood by an inspection of the diffraction pattern which is dominated by a sublattice with a spacing of 3.9 Å. Since it is considered that dislocations do not play a central role in determining superconducting properties, no detailed analysis

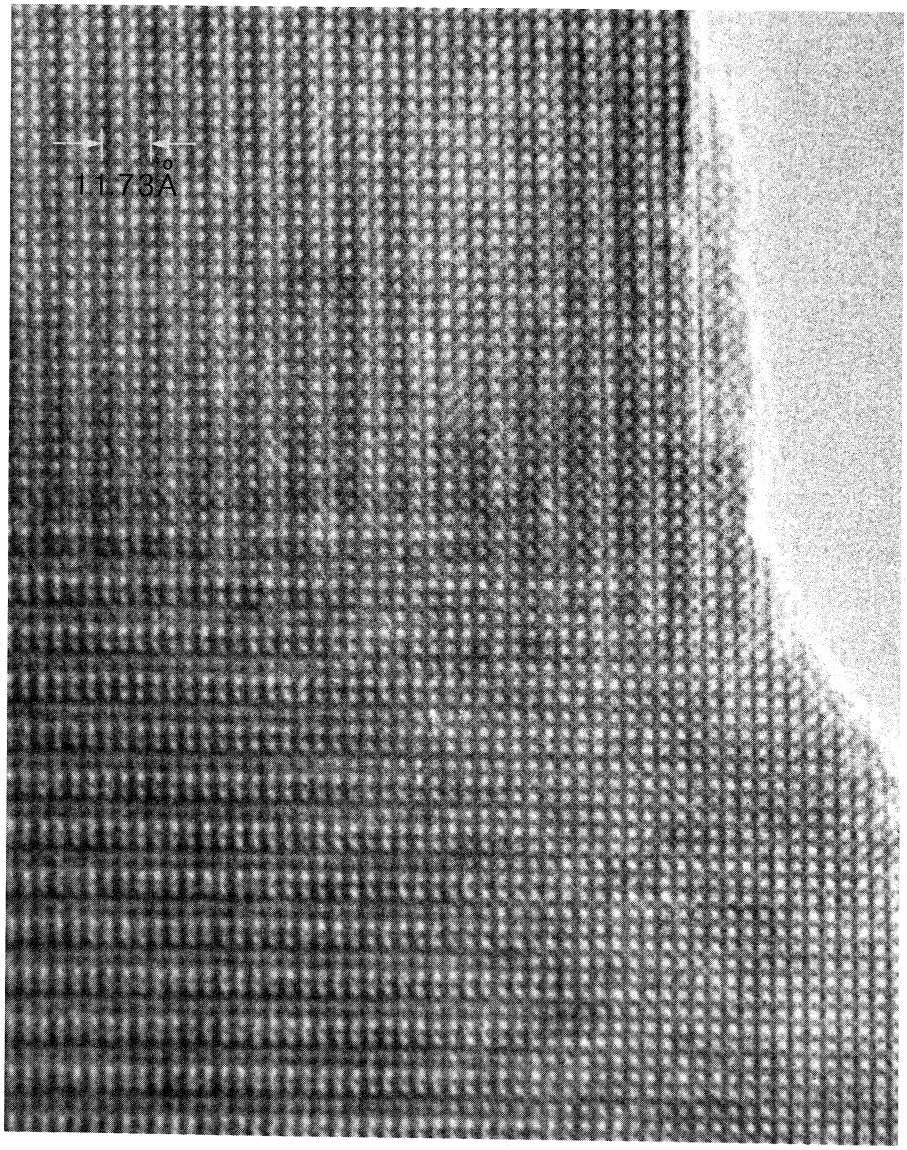
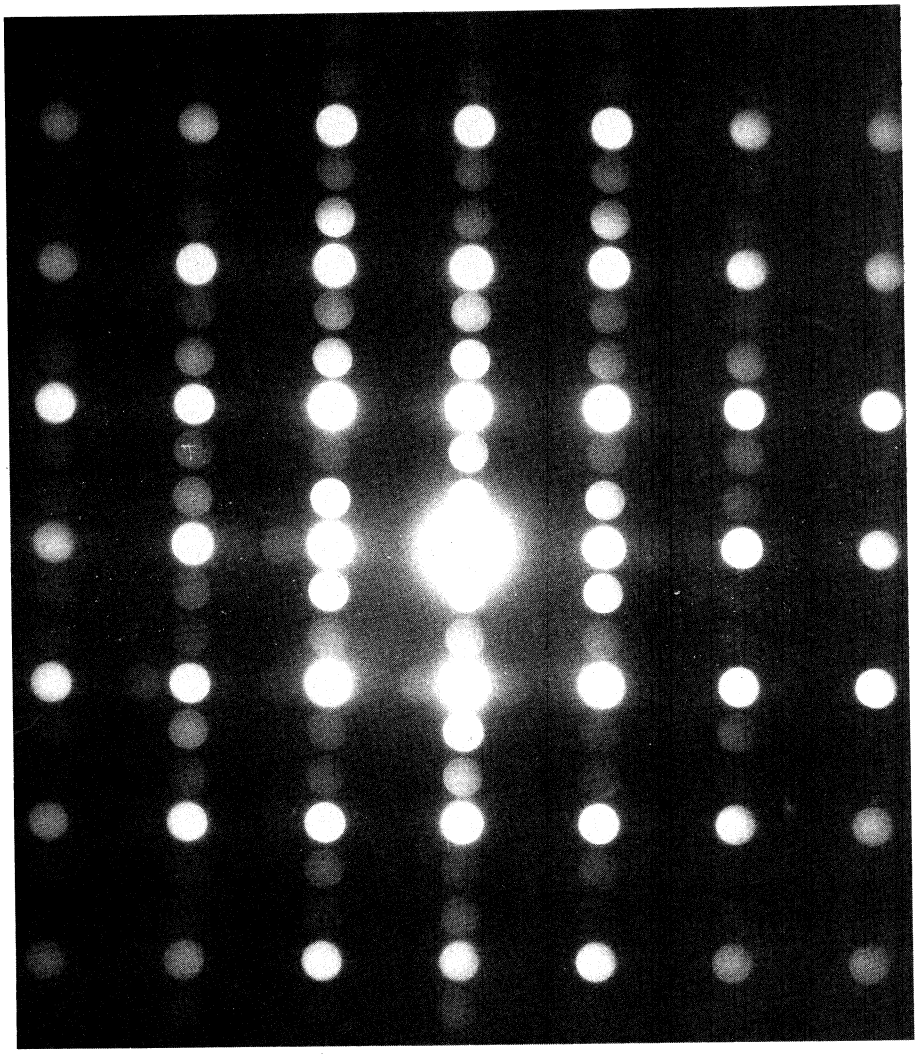


Fig. 3. Lattice image of two-dimensional overgrowth in $La_3Ba_3Cu_6O_{14}$.

has been attempted, but direct counting on a circuit gave a value of $\frac{1}{3}c$ for the value of the Burgers vector in one instance; that is, an additional 'cubic unit' was involved. The change in contrast in the lattice images due to tilt induced by the strain field is often striking. In Fig. 1 the contrast is in fact reversed.

Polytypic Intergrowths

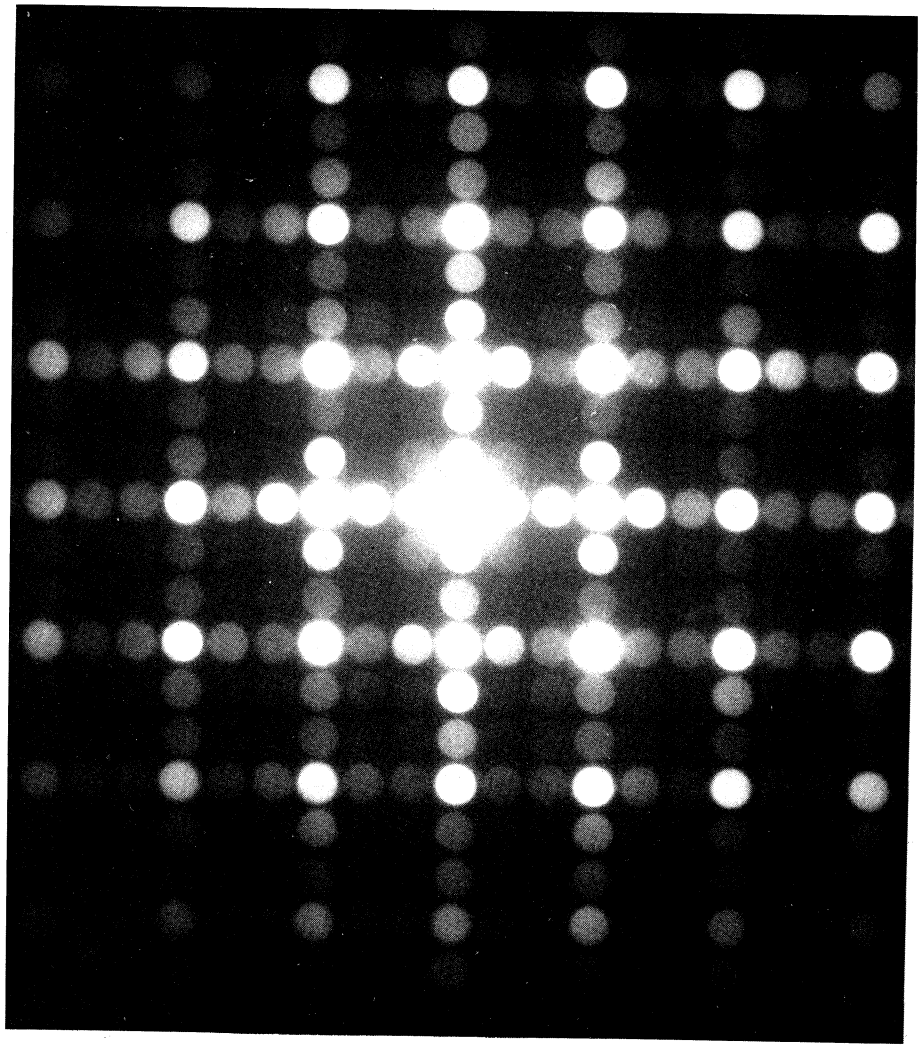
These intergrowths are the most prominent and also the most numerous of the features in the microstructure; we believe them to be also the most significant from the point of view of the superconducting properties.



(*a*)

Fig. 4. (*a*) CBED pattern of predominantly single crystal region of $La_3Ba_3Cu_6O_{14}$ viewed down [100] with $a = b = 3{\cdot}91$ Å and $c = 11{\cdot}73$ Å. Patterns of this type permit the assignment of space group. (*b*) CBED pattern from two-dimensional polytype overgrowth of $La_3Ba_3Cu_6O_{14}$. (*c*) Selected area diffraction pattern from two-dimensional overgrowth in $La_3Ba_3Cu_6O_{14}$ emphasising long range registry.

Inspection of the outline of this type of material reveals the possibility of substantially strain free growth parallel to any of three mutually perpendicular axes. From an initially disordered cubic material, ordering of the La and Ba atoms along the *c* axis of the tetragonal ordered phase and concomitant ordering of oxygen vacancies is equally probable in any of three orthogonal directions. That this is in fact realised

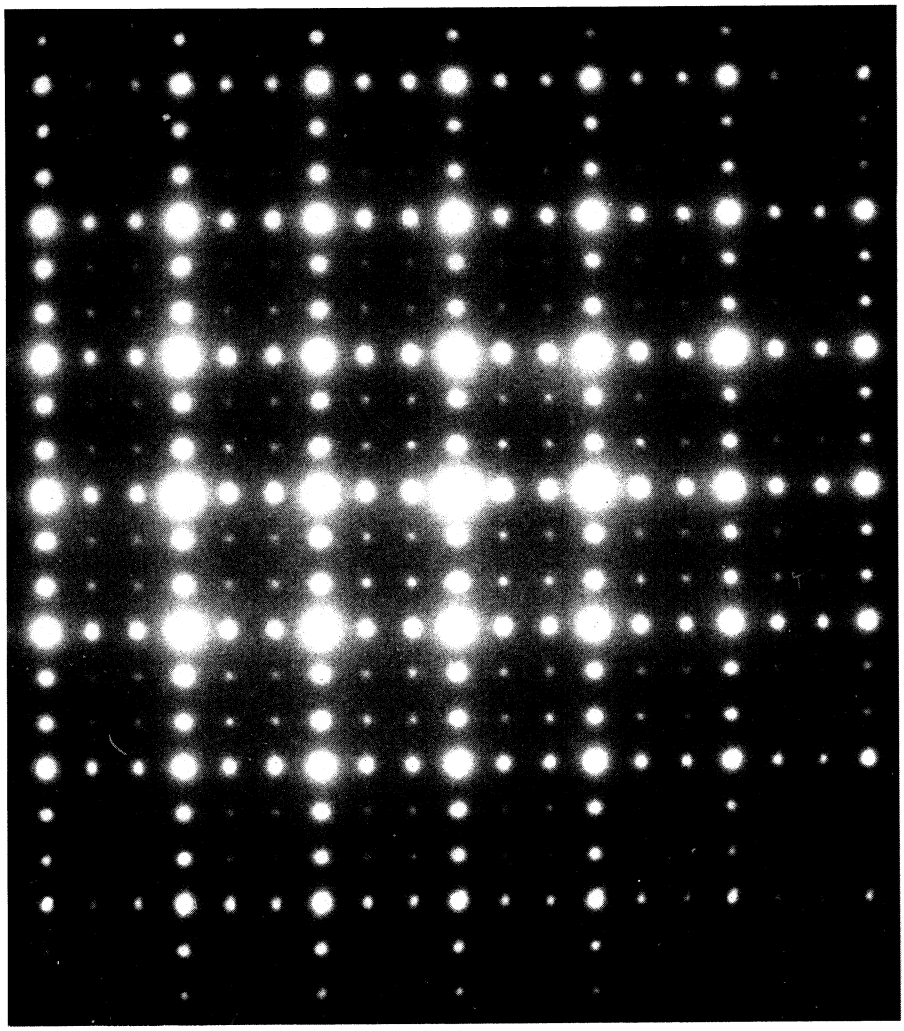


(*b*)

Fig. 4. (*Continued*)

can be seen from micrographs and diffraction patterns. Fig. 2 shows a boundary sufficiently long and straight to illustrate with some clarity the freedom from strain at the interface. This may be described as one-dimensional intergrowth.

Two-dimensional overgrowth can be seen in Fig. 3, while the analogous three-dimensional microdomain texture can be deduced to occur in the thicker part of the specimen. The diffraction evidence which supports this conclusion is shown in Fig. 4. Here the importance of obtaining CBED patterns and high resolution lattice images from the same portion of crystal (Moodie and Whitfield 1984) is particularly evident, since volumes of single crystal can only be identified with confidence at high resolution.



(*c*)

Fig. 4. (*Continued*)

CBED of small areas can show predominantly single crystal character (see Fig. 4*a*) corresponding to the field shown in Fig. 5. CBED patterns from two-dimensional intergrowths (Fig. 4*b*) again illustrate the perfect matching of the lattices. Selected area diffraction patterns which average over comparatively large volumes emphasise the long range registry between the lattices (Fig. 4*c*).

Thicker crystals give rise to upper layer lines at a repeat distance corresponding to three-dimensional microdomain texture.

Another type of polytypism derives from variation in the basic unit cell of the structure so that, for instance, the *c*/*a* ratio can be four, rather than three. An example of this can be seen in Fig. 5.

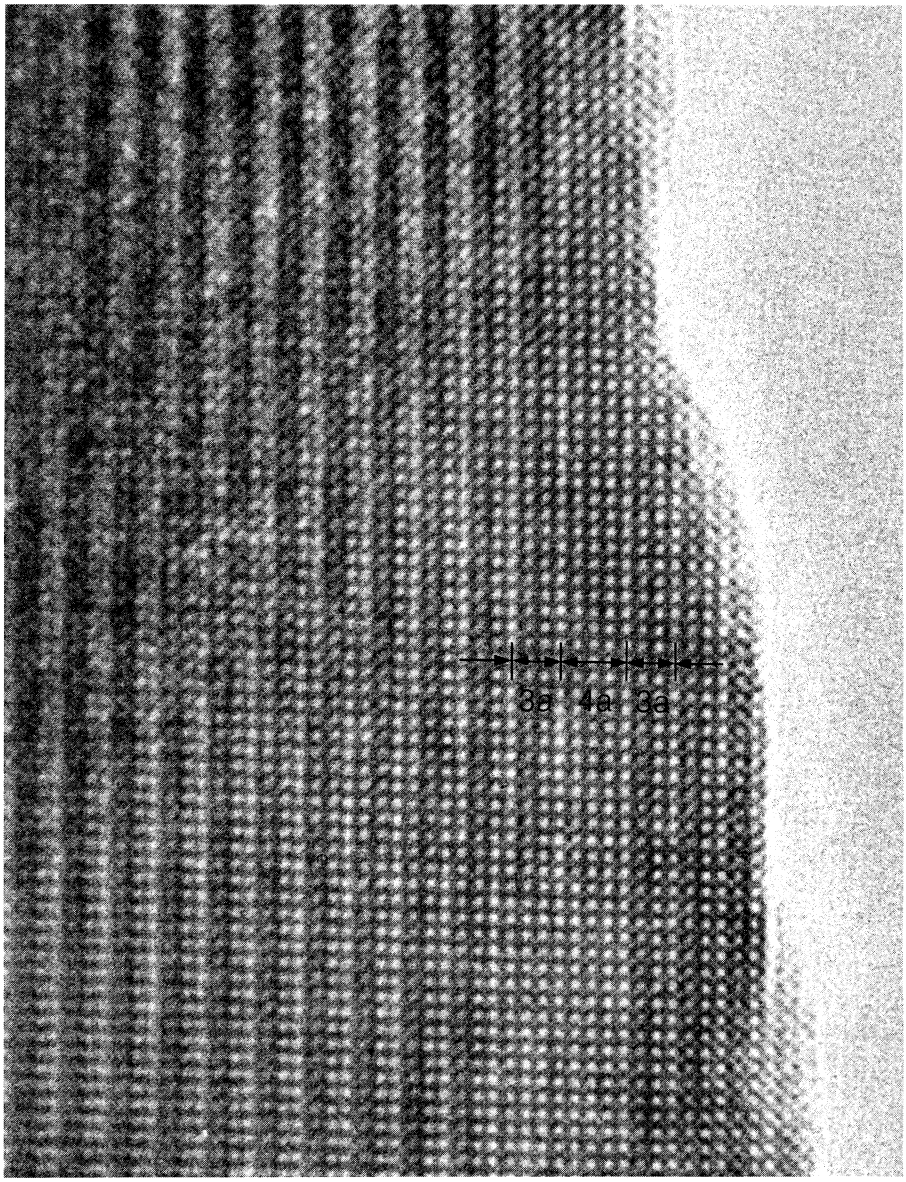


Fig. 5. Lattice image of $La_3Ba_3Cu_6O_{14}$ showing intergrowth of a plate of crystal with $c/a = 4$.

Finally, the structure of the facets on a naturally grown crystal (Fig. 6) indicate that the preferred crystal growth pattern is in integral units of the unit cell, a somewhat unusual behaviour pattern for oxides which normally grow in units of single atomic layers.

Further work is in progress on the superconducting properties of $Ba_3La_3Cu_6O_{14}$ and related compounds in an attempt to correlate the extent of polytype intergrowth

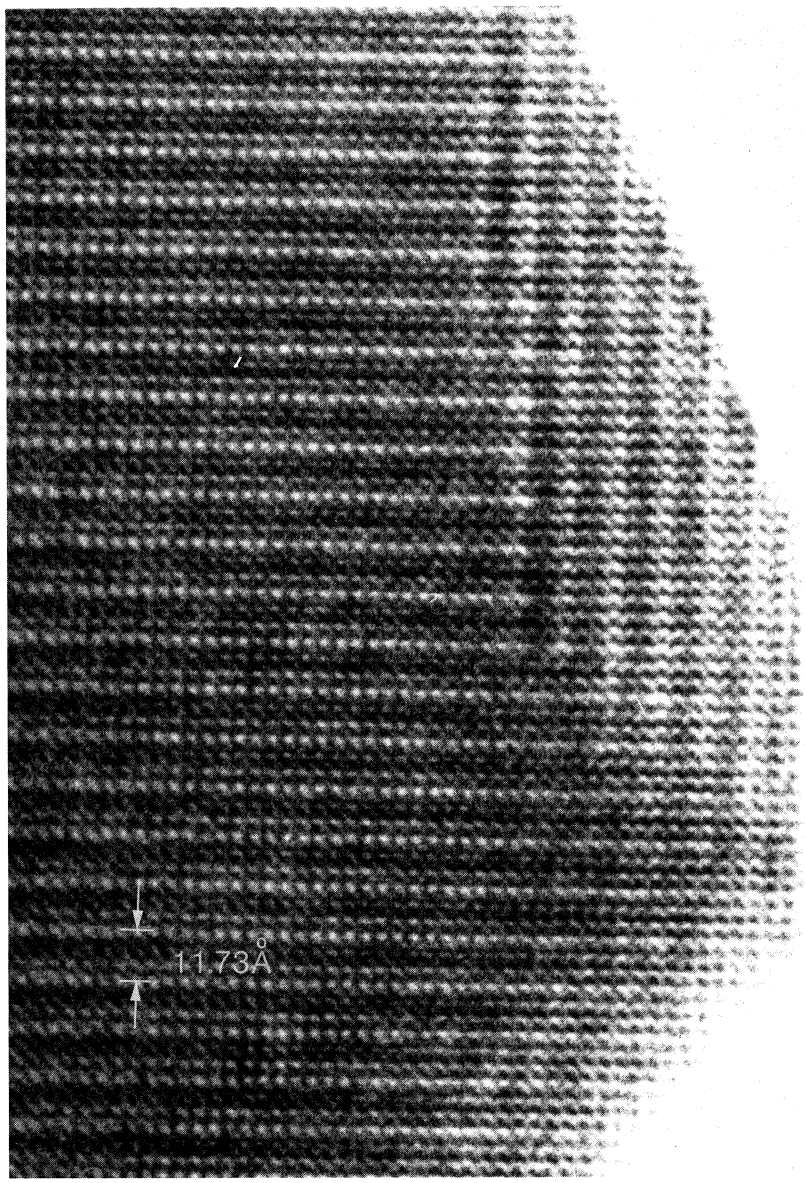


Fig. 6. Lattice image of naturally grown facets in $La_3Ba_3Cu_6O_{14}$. Contrast due to surface steps is superimposed on the lattice images. Steps can also be seen in profile.

with sample history and superconducting properties, and in particular the Meissner rejection ratio. The microstructure reported here represents a particularly simple intergrowth. Our observations on the related compound $Ba_2YCu_3O_7$ indicate a much more complex intergrowth on the (110) plane. These results will be the subject of a later communication.

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