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An Electron Microscope Study of Defect-free $YBa_2Cu_3O_{7-x}$ ($x \approx 0{\cdot}15$) with Superconductivity at 93 K

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Abstract

High resolution electron microscopy has been used to characterise sintered preparations of the mixed oxide $YBa_2Cu_3O_{7-x}$ ($x \approx 0{\cdot}15$). By carefully controlled processing techniques a single phase defect-free orthorhombic structure having excellent characteristics for use as a high temperature superconductor was obtained. Surface structures and an image of a dislocation are included in this study.

1. Introduction

It is well known that mixed-phase $YBa_2Cu_3O_{7-x}$ may become superconducting in the temperature range 50–106 K, the precise temperature depending upon the preparation conditions (Wu *et al.* 1987; Syono *et al.* 1987; Strobel *et al.* 1987; David *et al.* 1987; Gopalakrishnan *et al.* 1987). Much interest has centred upon the identification of the phase which has the major contribution to the superconductivity, and to its preparation as a pure phase. This paper reports the results of the analysis of a synthesis of sufficient quality to permit application. Some of the wide field of potential applications have been recently reviewed (Geballe and Hulm 1980; Matisoo 1980; McDonald 1981).

2. Experimental

Several prescriptions for preparation of superconducting $YBa_2Cu_3O_{7-x}$ have been published. We have followed essentially that given by Le Page *et al.* (1987), with slight variation in heating and cooling rates designed to give uniform annealing and oxygen content.

Using a sintered high-density sample ($4{\cdot}8\ g\,cm^{-3}$), samples were made for electron microscope examination by minimal crushing under liquid nitrogen, following a procedure previously found successful for cuprite samples (Moss *et al.* 1987). The crushed powder was suspended in ethanol and evaporated onto holey carbon support films. It was found that, whereas excessive grinding produced a large number of thin electron-transmitting crystallites with a variety of orientations, these crystallites also contained frequent planar defects. Since our aim was to characterise the bulk, a minimal grinding technique was arrived at whereby bulky particles, which could

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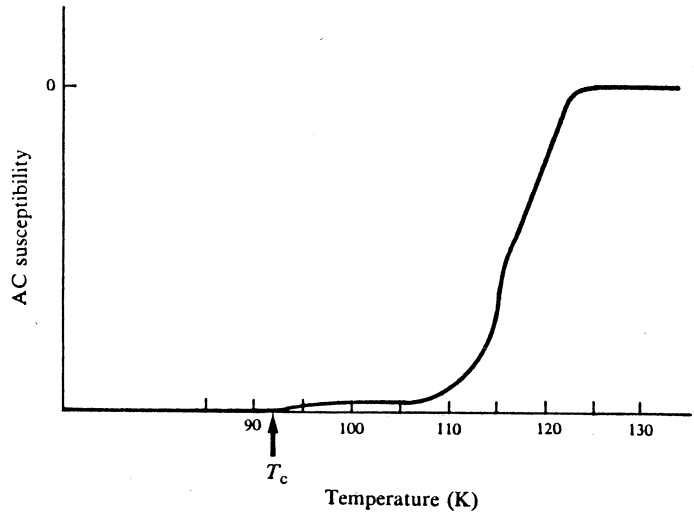

Fig. 1. Experimental AC susceptibility as a function of temperature.

be examined at their thin edge, were mainly produced, with very occasional thin sections.

Fig. 1 shows the AC susceptibility of our sample as a function of temperature. Fig. 2*a* shows the [001] orientation of a bulky particle at high resolution, using the top-entry JEOL 200CX microscope, whose characteristics have been described by Glanvill *et al.* (1986). Simple squares form this lattice image, and three crystal thickness regimes appear. Fig. 2*b* shows an enlarged section from this micrograph. We note that there is no evidence for twin lamellae often reported for this material (Syono *et al.* 1987), nor other extended defects. However, image density variations, seen most readily in Fig. 2*a*, occur in the thin region, often between neighbouring unit cells, which possibly reflect local variations in oxygen content. Such variations should be most evident in the thin crystal regions (Bursill 1985).

Fig. 3*a* shows the [010] orientation at intermediate enlargement, to display a large image field. Again, no extended defects are evident, unlike those frequently found in alternative preparations and thought to arise from ex-solution of $Ba(OH)_2$, from inadequate annealing, or from sample grinding (cf. Ourmazd *et al.* 1987; Hyde *et al.* 1987).

Fig. 3*b* shows an enlargement of part of Fig. 3*a*, together with a representation of the crystal structure for the [010] projection. Note the one-to-one correspondence of light and dark spot contrast with the positions of Y, Ba and Cu atoms of the structure, demonstrating that the atomic columns have been resolved. Computer simulations we have made (cf. Hewat *et al.* 1987) confirm this assignment of atomic sites.

It is remarkable for such a structure that the only notable departure from crystal perfection is an extremely low density of dislocations, one of which is shown in Fig. 4. These were found in only one fragment observed at this [010] orientation. The dislocations have edge character with one additional (100) plane of atoms occurring in the top part of the crystal compared with the lower part. The Burger's vector thus has a component [100] indicating a degree of plastic deformation which is attributed to damage introduced during specimen preparation. Of further interest is the observation

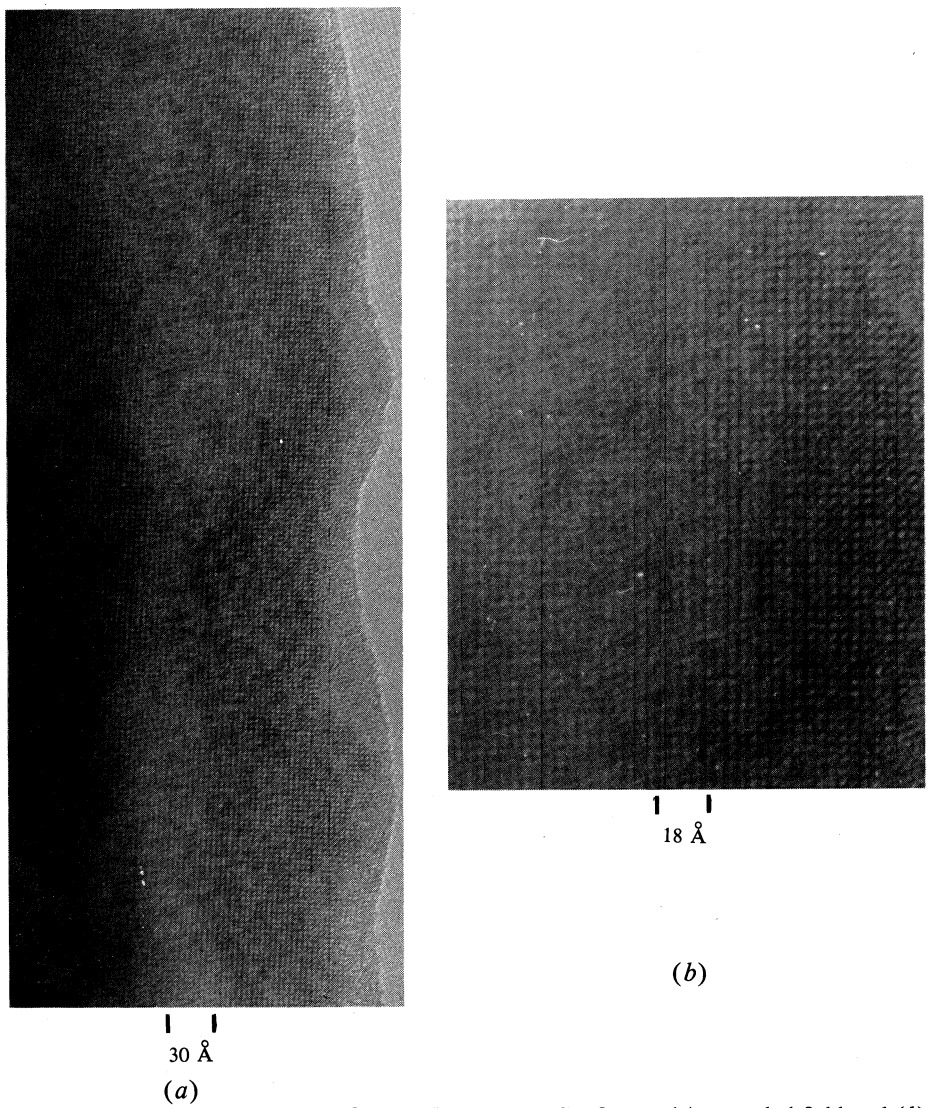

Fig. 2. High resolution image of [001] projection of $YBa_2Cu_3O_{7-x}$: (*a*) extended field and (*b*) enlarged section.

of surface steps, shown in Fig. 5. Clearly, such steps must appear in images of clean specimens having atomic resolution [see Smith *et al.* (1987) for a review of surface profile imaging at atomic resolution]. Of particular interest here is the predominant occurrence of steps having a height of 1/3 on (001), i.e. 3·86 Å or only one-third of the complete unit cell. Furthermore, images exhibiting different contrasts occur for terminations at different planes within the unit cell. Further image simulations are proceeding in order to identify precisely the nature of the surface layers; i.e. whether surface terminations are predominantly O, Cu, Y or Ba. This will be informative concerning the surface polarity of the superconductor. Techniques for identification of surface polarity have been developed only recently, and applied successfully to ruby

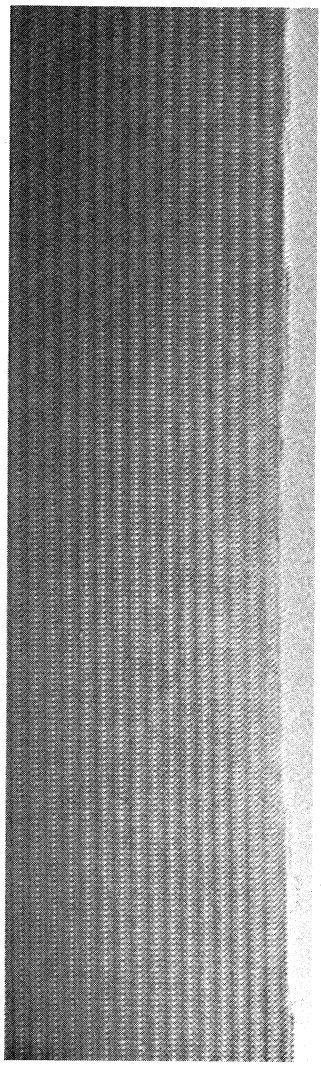

Fig. 3*a*. [010] image of $YBa_2Cu_3O_{7-x}$ showing an extended area free of defects.

and sapphire (Bursill *et al.* 1987). A number of distinct types of surface terminations are included in Fig. 5.

3. Discussion

The present study has shown clearly that homogeneous $YBa_2Cu_3O_{7-x}$ may be achieved in bulk quantities. Furthermore it is clear that defect-free material leads to an optimisation of superconducting properties; i.e. single-phase orthorhombic crystals achieve $T_c \geqslant 93$ K. Material prepared with inadequate annealing or with insufficient oxygen, increasingly contain tetragonal or multi-phase admixtures, thereby reducing T_c below 90 K.

As far as suggestions that defects may contribute positively towards raising T_c (Ourmazd *et al.* 1987), we conclude that, to the contrary, defect-free material is to be preferred. With the extensive investigations now undertaken in many parts of the world it becomes apparent that, apart from phase purity, the most important

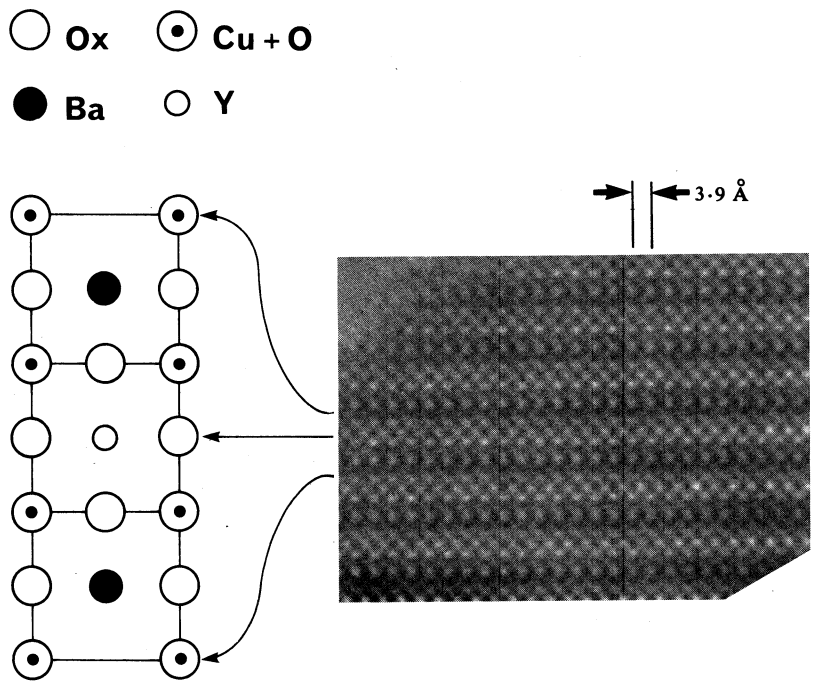

Fig. 3*b*. Enlargement of a section of Fig. 3*a* showing the interrelation of the image with Y, Ba and Cu atom columns.

parameter is the Cu_3^+/Cu_2^+ ratio. This is revealed directly in the value of x achieved in the preparation (see Gopalakrishnan *et al.* 1987). Recent studies at Japanese (see Syono *et al.* 1987) and French (see Bordet *et al.* 1987) laboratories suggest that the occurrence of chains of four coordinated Cu ions, as well as of square-pyramidally coordinated layers, are important in the superconducting mechanism.

Site substitution. Attention is now being given to replacing the oxygen by fluorine or sulfur, with favourable results (see Ovshinsky *et al.* 1987; Taylor *et al.* 1987). Given the relatively narrow superconducting energy gap, and the key role played by the $[CuO_4]$ and $[CuO_5]$ polyhedra, it is very likely that initial Cu purity may be of great significance in achieving good material. Substitution of alternative ions at Cu sites is likely to introduce additional states overlapping with the energy gap. Thus, semiconductor grade copper oxides appear to be essential for the production of high quality device material. It is already clear that substitution of yttrium by other rare earths does not significantly affect T_c (Ohshima and Wakiyama 1987), whereas replacement of barium by strontium does not have a positive effect.

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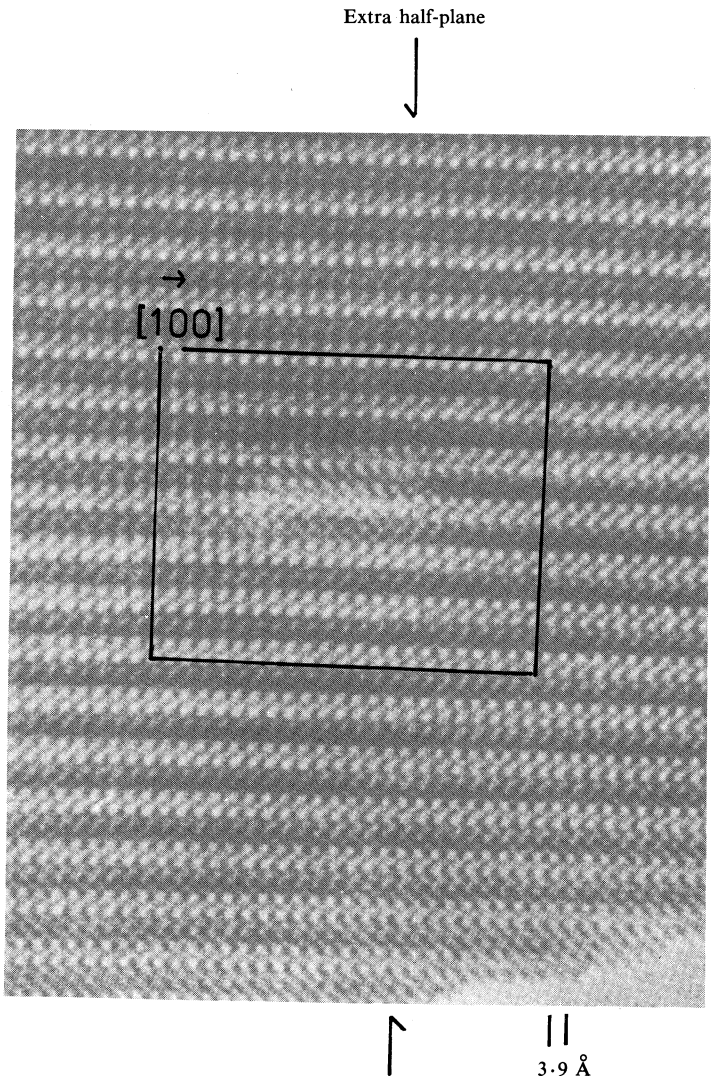

Fig. 4. Enlargement of an area from the [010] oriented image showing a solitary edge dislocation with Burger's vector [100].

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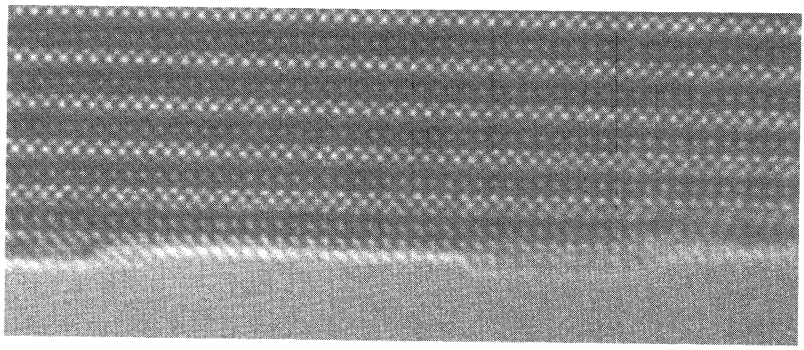
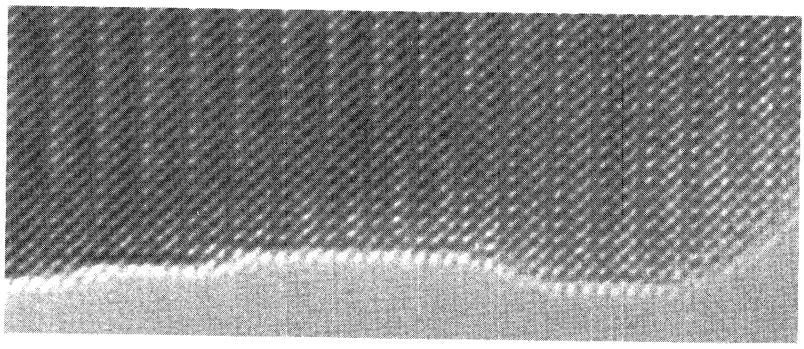


Steps on (001)



Steps on (100)

Fig. 5. Selection of surface step images showing atomic steps of height 1/3 on (001) and of unit height on (100).

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