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A superstructure in single-crystal $YBa_2Cu_3O_{7-\delta}$

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Abstract. A new form of superstructure with a $\sqrt{2} \times 2\sqrt{2} \times 1$ supercell oriented at 45° to the original unit-cell axes has been found in a $YBa_2Cu_3O_{7-\delta}$ single crystal by means of electron diffraction and electron microscopy. It is suggested that this superstructure results from a substructure modulation.

1. Introduction

To date, some superstructures have been found in $YBa_2Cu_3O_{7-\delta}$ (see, e.g., Van Tendeloo *et al* 1987). Van Tendeloo *et al* found that an $a^*/2$ superstructure reflection appeared in the electron diffraction pattern and that the superstructure was easily destroyed in heating–cooling cycles. In the structure model which they proposed, the oxygen concentration was greater than 7 and the *a* axis was double owing to an alternate arrangement of oxygen atoms in the Cu–O chains along the *a* axis. However, in a later paper (Zanderbergen *et al* 1987), the same researchers concluded that an alternation arrangement with a smaller concentration of oxygen was more likely. A similar superlattice has been found by Cava *et al* (1987). They reported additional electron diffraction features half-way between Bragg reflection along *b* in the form of narrow streaks elongated in the *b* direction. This phenomenon was found in samples with reduced oxygen content and lower T_c. They interpreted the superstructure in terms of the ordering of oxygen vacancies in Cu–O chains and concluded that the spatial arrangement of the oxygen atoms determines the superconducting transition temperature.

These experimental studies demonstrated that, under some specific conditions of prior crystal preparation, oxygen vacancies may form particular arrangements on the oxygen sublattice instead of usual ones in orthorhombic or tetragonal $YBa_2Cu_3O_{7-\delta}$. A positive theoretical treatment has been given by Beal-Monod (1987). The theory concerned a simple mean-field description with two order parameters and interactions between first and second neighbours. According to his results, some superstructures based on oxygen vacancies ordering are possible; in these, modulation may be either along the Cu–O chains or in the diagonal direction of the subcell of the oxygen sublattice between barium layers.

In this paper, we report a new form of superstructure, in which a $\sqrt{2} \times 2\sqrt{2} \times 1$ supercell orients at 45° to the original unit-cell axes. It should be noted that the superstructure, which was localised in some areas in single-crystal $YBa_2Cu_3O_{7-\delta}$, appeared with strong superstructure reflections in the electron diffraction pattern and existed in

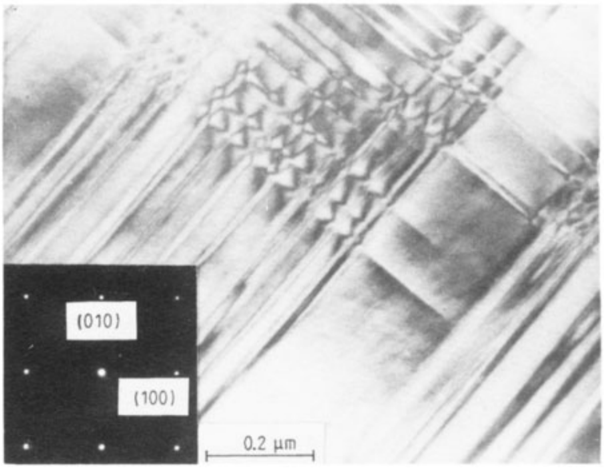
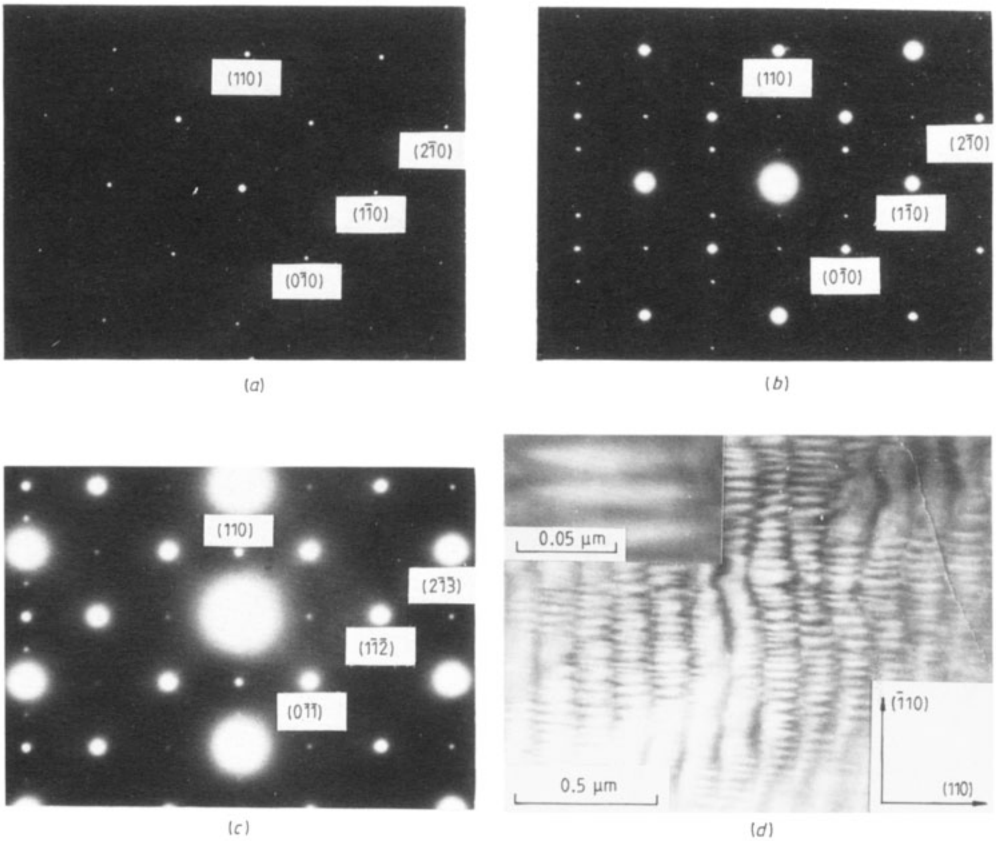


Figure 1. (110) and (1$\bar{1}$0) twins in orthorhombic $YBa_2Cu_3O_{7-\delta}$.



(a) (b)

(c) (d)

Figure 2. (*a*) Diffraction pattern along the [001] zone in orthorhombic $YBa_2Cu_3O_{7-\delta}$; (*b*) diffraction pattern along the [001] zone in the superstructure; (*c*) tilted 23° about the [110] zone; (*d*) bright-field image of dense microtwins.

both the orthorhombic and the tetragonal phase. This superstructure probably results from a substructure modulation and not simply from an oxygen ordering on the oxygen sublattice between barium layers.

2. Experiments and discussion

The preparation of single-crystal $YBa_2Cu_3O_{7-\delta}$ was carried out as described in an earlier paper (Lu *et al* 1987). The single-crystal specimen for transmission electron microscopy (TEM) observation was prepared by ion milling in an argon ion beam at 4 kV for about 5 h. A JEOL-200CX electron microscope, equipped with a double-tilting stage, a heating stage and quantitative Link System energy-dispersive x-ray spectrometer, was used at 200 kV.

From electron diffraction, it was determined that the specimen was aligned along the [001] zone. The bright-field image shows that (110) or $(1\bar{1}0)$ twins, characteristic of orthorhombic $YBa_2Cu_3O_{7-\delta}$, dominate large areas (figure 1). However, when electron diffraction was selected from some dense microtwin areas, as shown in figure 1 or figure 2(*d*), $(\frac{1}{2}\,\overline{\frac{1}{2}}\,0)$ and $(\frac{1}{4}\,\frac{1}{4}\,0)$ superstructure reflections appeared, as shown in figures 2(*b*) and 2(*c*).

The microtwins suggest that the symmetry of unit cell is orthorhombic, although the difference between a and b is too small to be determined by means of electron diffraction ($a \simeq b = 3.88$ Å, $c = 11.24$ Å). It is easy to deduce that the supercell oriented at 45° to the original unit-cell axes with a size of $a' = |\boldsymbol{a} - \boldsymbol{b}| = \sqrt{2}a = 5.49$ Å, $b' = 2|\boldsymbol{a} + \boldsymbol{b}| = 2\sqrt{2}a = 10.97$ Å and $c' = c = 11.24$ Å, as illustrated in figure 3. It is worth noting that the structural modulation in the superstructure occurred along $[1\bar{1}0]$ and [110] directions, which is quite different from previously reported superstructures. Additionally, the superstructure reflections were so strong that they cannot be simply attributed to oxygen modulation, as for previously reported superstructures.

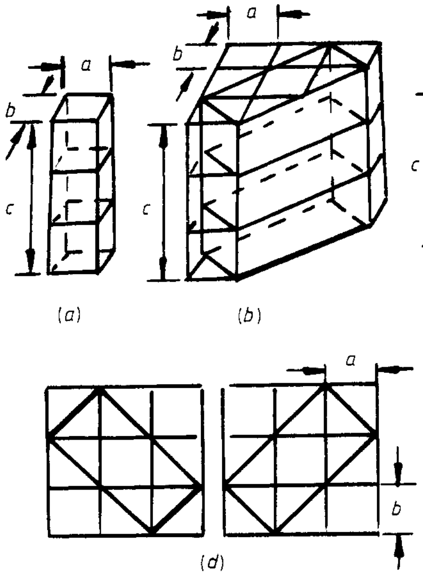
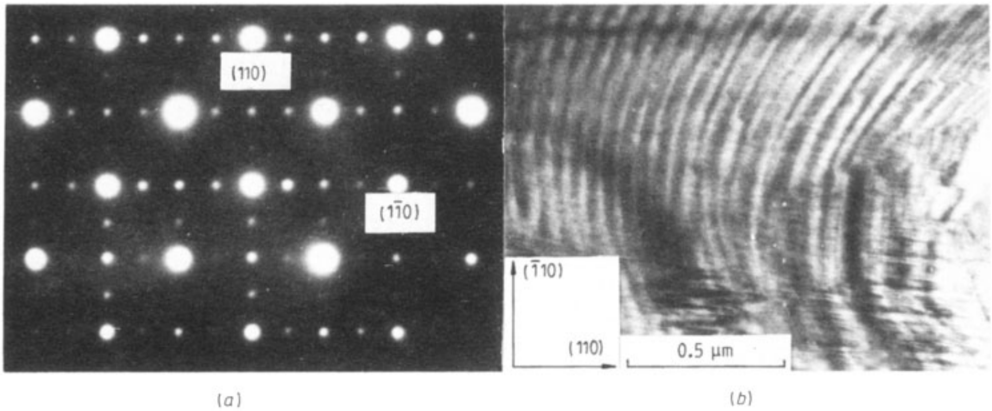


Figure 3. (*a*) Original unit cell; (*b*) substructural modulation on the unit cell; (*c*) supercell; (*d*) models for two variants of the superstructure.



(*a*) (*b*)

Figure 4. (*a*) Diffraction pattern showing two variants of the superstructure; (*b*) bright-field image showing bent boundaries.

Our results revealed that this superstructure has two variants, as shown in figure 4(*a*). The bright-field image (figure 4(*b*)) shows bent boundaries. The models for two variants of the superstructure are given in figure 3(*d*).

Quantitative energy-dispersive x-ray spectrometer analyses (figure 5) show the same Y : Ba : Cu stoichiometry for both orthorhombic $YBa_2Cu_3O_{7-\delta}$ and the superstructure. Thus the possibility that other Y : Ba : Cu stoichiometry phases, such as yttrium-rich or barium-rich phases, exist (Eaglesham *et al* 1987, Nakada *et al* 1987) was excluded. The origin of the superstructure is then narrowed down to a substructure modulation in $YBa_2Cu_3O_{7-\delta}$.

In order to study the thermodynamic behaviour of the superstructure, the micrographs shown in figure 6 were taken during a heating experiment. In the experiment, the heating rate was controlled to about 2.5 °C min^{-1}. As the temperature was raised, the intensity of the superstructure reflections decreased gradually with their location remaining unchanged. The contrast of the microtwins also weakened gradually and

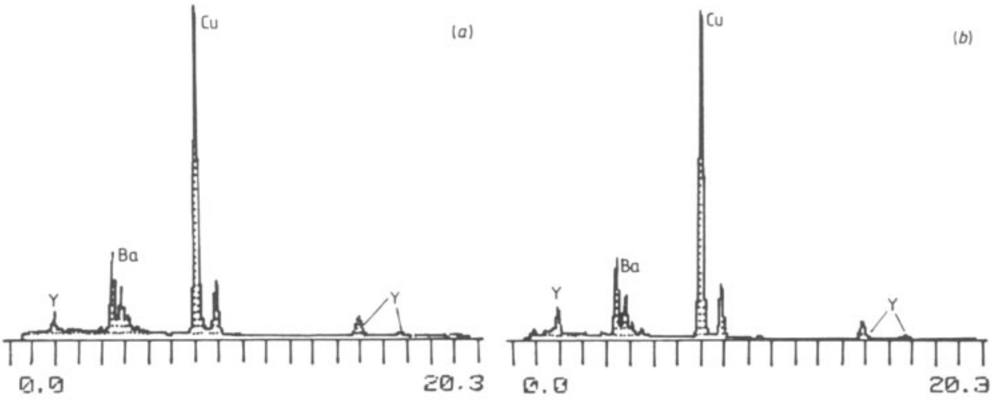


Figure 5. Quantitative energy-dispersive x-ray spectrometry analysis for (*a*) orthorhombic $YBa_2Cu_3O_{7-\delta}$ and (*b*) the superstructure.

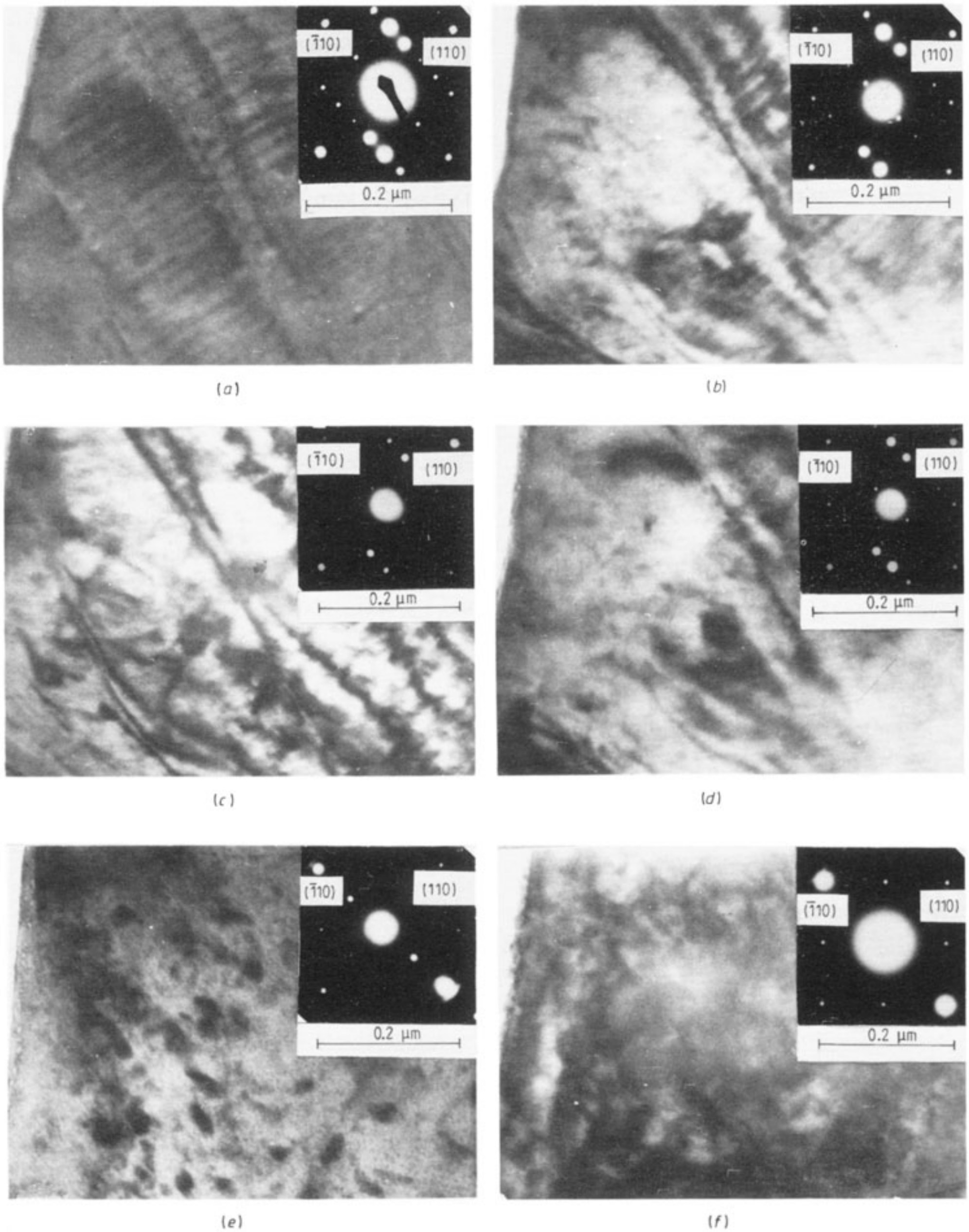


Figure 6. Micrographs demonstrating the effects of the heating and cooling processes: (*a*) room temperature; (*b*) after heating to 80 °C; (*c*) after heating to 130 °C; (*d*) after heating to 160 °C; (*e*) after heating to 310 °C; (*f*) after cooling to 100 °C.

became undetectable at about 160 °C. At this point, $YBa_2Cu_3O_{7-\delta}$ was transformed into the tetragonal phase. However, the superstructure reflections persisted after the phase transformation. This behaviour is like that of the incommensurate phase in barium sodium niobate (BSN), in which incommensurate modulation extends far into the tetragonal phase after BSN has been transformed from the orthorhombic to the tetragonal phase (Pan *et al* 1985). The structure modulation in this superstructure is commensurate.

At higher temperatures (up to about 310 °C) the superstructure reflections intensity decreased markedly. In the subsequent cooling process, they continued to decrease and disappeared eventually at about 150 °C. By then, the heating had lasted for about 3 h. This suggests that the superstructure is related to the oxygen content. The successive reduction in superstructure reflection intensity on heating is regarded as being caused by the irreversible loss of oxygen atoms within the high-vacuum chamber of the electron microscope. When a certain amount of oxygen atoms was lost, the superstructure was destroyed.

3. Conclusions

A new form of superstructure with a $\sqrt{2} \times 2\sqrt{2} \times 1$ supercell oriented at 45° to the original unit-cell axes was found in single-crystal $YBa_2Cu_3O_{7-\delta}$ by means of electron diffraction and electron microscopy. The superstructure was suggested to result from a substructure modulation and not from oxygen ordering on the oxygen sublattice between barium layers. This suggestion was supported by energy-dispersive x-ray spectrometry examination and a thermodynamic behaviour study. However, further investigation is needed to understand the formation and the detailed structure of this superstructure and its effect on superconducting behaviour.

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