Twins and oriented domains in the orthorhombic superconductor $YBa_2Cu_3O_{7\pm\epsilon}$

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The investigation of the orthorhombic superconductor $YBa_2Cu_3O_{7\pm\epsilon}$ by high-resolution electron microscopy (HREM) shows the existence of two sorts of domains: twinned domains and oriented domains forming slices perpendicular to the *c* axis. The interpretation of these domains and of their boundaries is given, based on the simulated HREM images previously made. It is shown that the orientation of the $(CuO_2)_\infty$ planes formed by the CuO_4 square planar groups plays an important role. A phenomenon of misorientation of those domains is also observed and interpreted.

The high-T_c superconductor of the Y-Ba-Cu-O system[1,2] is an oxygen-deficient perovskite $YBa_2Cu_3O_{7\pm\epsilon}$.[3,4] The structural study by x-ray diffraction on single crystals[5,6] and powder neutron diffraction[7–9] suggests a great tendency of this oxide to twinning. Such properties could affect the superconductivity. The present work is a high-resolution electron microscopy study of the twins and oriented domains in this orthorhombic superconducting oxide ($a=3.821$ Å, $b=3.885$ Å, $c=11.676$ Å, $T_c=92$ K).

The orthorhombic superconductor was prepared as previously described[3] from ultrapure oxides Y_2O_3 and CuO, and barium carbonate. The samples were studied by electron diffraction with a JEM 120 CX electron microscope and with high resolution by a JEM 200 CX electron microscope fitted with a top-entry goniometer providing $\pm$ 10° tilt about two axes. In order to understand the nature of the twins and oriented domains, an accurate study of the structure[10] by high-resolution electron microscopy (HREM) was carried out, using simulation of the images with the program of Sharnulis, Summerville, and Eyring.[11]

The first point that should be noted about this oxide is that most of the crystals exhibit twins, oriented domains, moiré patterns, and strains.

A great number of crystals exhibit an electron diffraction pattern typical of a twin (Fig. 1) in which the

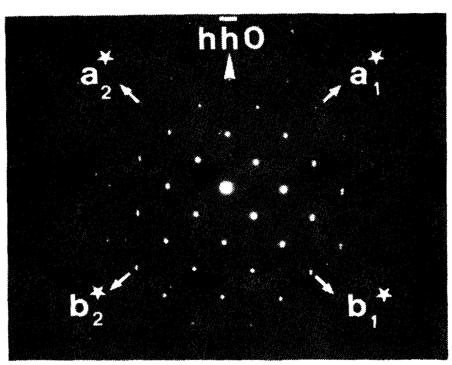


FIG. 1. Typical [001] electron diffraction pattern.

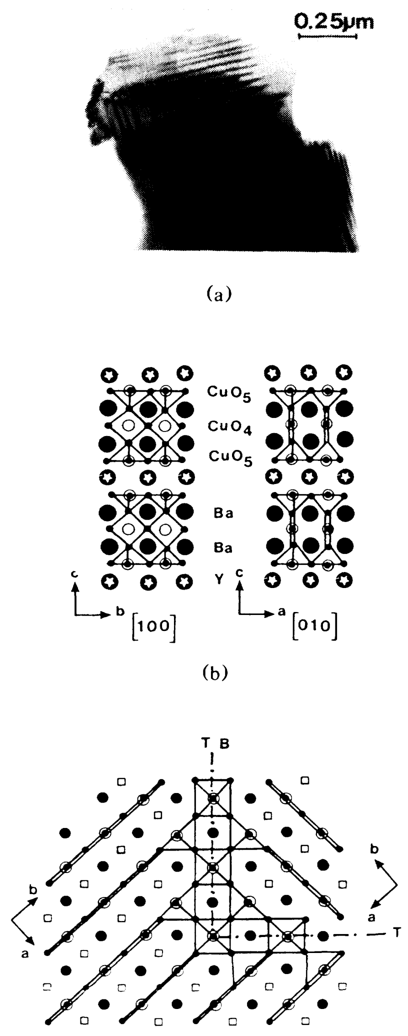
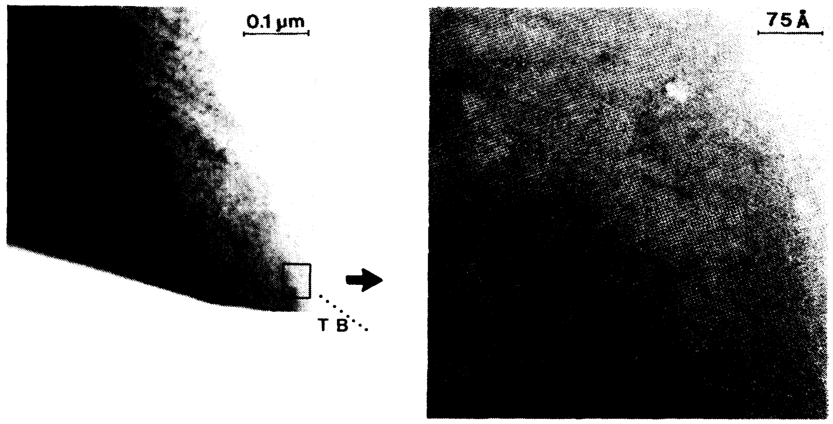


FIG. 2. (a) Low-resolution image of quasiperpendicular twinned domains. (b) $YBa_2Cu_3O_7$: idealized model of the triple layers of polyhedra along [100] and [010]. (c) Orientation of the CuO_4 groups through the quasiperpendicular twin boundaries (TB).



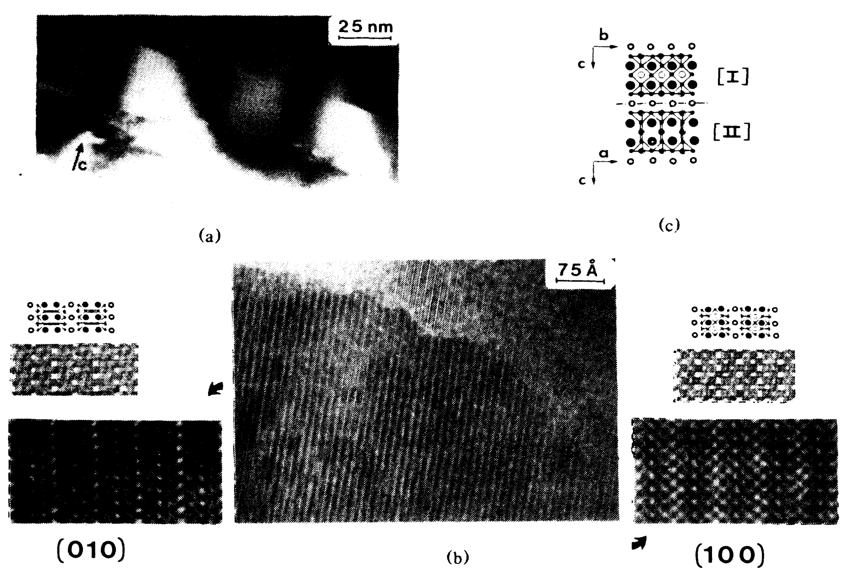
(a) (b)

FIG. 3. (a) Twin boundaries appear along [001] as black lines. (b) Enlargement of the boundary area.

$h\bar{h}0$ reflections which are not split belong to both components; the observed value of the angle between the two reciprocal directions [110]* of each domain is in agreement with the calculated one from the directions $[110]_1$ and $[110]_2$. Different models based on the consideration of the change of orientation of the rows of oxygen vacancies along the [010] direction can explain the formation of such twinned domains. One of these models, developed elsewhere,[10] involves the presence of additional CuO_6 octahedra and CuO_5 pyramids at the twin boundary. A phenomenon which is often observed in the low-resolution images of thick crystals deals with the simultaneous existence of perpendicular twinned domains [Fig. 2(a)] due to the equivalence of the $[110]_1$ and $[110]_2$ directions. This is explained by the fact that the $(CuO_2)_\infty$ planes of CuO_4 square planar groups belonging to the triple layers of polyhedra [Fig. 2(b)] can take two perpendicular orientations involving quasiperpendicular twin boundaries [Fig. 2(c)].

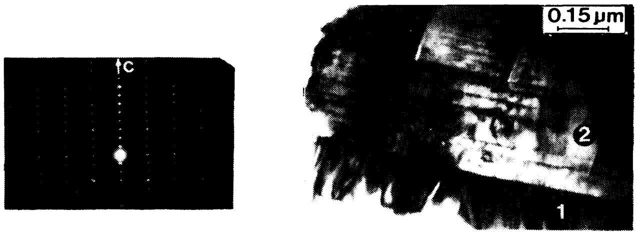
From the observation of those twinned crystals along [110] and [001] it appears that no particular defect seems to be coupled with the domain boundaries. Similar contrasts are indeed observed from one domain to the other, as shown for a well-oriented crystal along [001] [Fig. 3(a)]; in this case, domain boundaries appear as black lines in the thick part of the crystal, and the defects are not particularly localized in the boundary area but over all the matrix, as shown from the enlargement corresponding to the thin part of the crystal [Fig. 3(b)].

A second family of domains is often observed, which



(a) (c) (b)

FIG. 4. (a) Oriented slices perpendicular to the c axis. (b) High-resolution image of the boundary; enlargement of regular zone on each side of the boundary area and corresponding calculated images (for -430 Å defocus and 30 Å thickness). (c) Idealized drawing of two oriented domains (labeled I and II).



(a) (b)

FIG. 5. (a) Electron diffraction pattern of a crystal exhibiting misoriented domains. (b) Low-resolution image of such domains.

corresponds to the formation of oriented slices perpendicular to the *c* axis [Fig. 4(a)]. Such domains are shown on the HREM image of Fig. 4b; in this case the "ideal" crystal has its *c* axis parallel to the edge of the thin crystal. In Fig. 4(c), the area labeled [I] exhibits a contrast characteristic of a [100] image (see simulation, Ref. 10), whereas the area labeled [II] is characteristic of a [010] image.[10] Thus an idealized model of the oriented domains can be proposed [Fig. 4(c)] which corresponds to different orientation of the CuO_4 groups belonging to the $(CuO_2)_\infty$ layers. It is worth pointing out that, contrary to the twinned domains, those domains are characterized by a junction involving a juxtaposition of two different parameters *a* and *b*, respectively, at the boundary. Consequently the domain interfaces are particularly disturbed as observed in the thickest part of the bulk.

Another type of phenomenon appears rather frequently that will be called misorientation of crystals, as shown from the electron-diffraction patterns [Fig. 5(a)] of such crystals, where we can clearly see the contribution of every component. However, in that case the angle between the domains varies from one crystal to the other. The low-resolution image of those crystals [Fig. 5(b)] shows that both types of domains are observed perpendicular to *c*: twinned domains (area labeled 1) and oriented domains (area labeled 2). One also observes significant strains and bending of the crystals. Such a phenomenon may result from the formation of microfractures which just started on the edge of the crystal but did not develop.

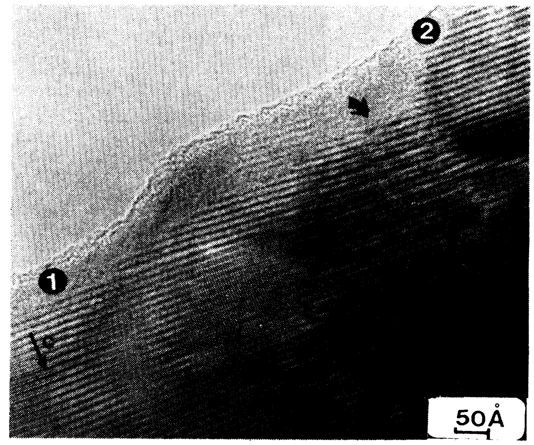


FIG. 6. High-resolution image of a boundary between the oriented domains.

These "undeveloped microfractures" would allow the strain to be reduced and prevent the splitting of the crystals. This hypothesis is in agreement with the fact that the angle between the domains varies from one crystal to the other. The HREM image of such a misorientation (Fig. 6) shows the angle between these domains and their overlapping. Moreover, it appears from the observation of the contrast on the edge of the crystal that the microfracture has occurred close to the twin boundary.

This study shows that the existence of domains appears to be the rule in the orthorhombic superconductor $YBa_2Cu_3O_{7\pm\epsilon}$. It also shows that the stoichiometry and especially the copper coordination may be changed at the domain boundaries, so that the electron-transport properties of the crystals could be dramatically influenced. Moreover, many defects have been observed during this investigation, which are promising subjects for future work.

Note added. After having written this manuscript we received a copy of unpublished work by Van Tendeloo, Zandbergen, and Amelinckx,[12] showing the existence of twinned domains, in agreement with our results.

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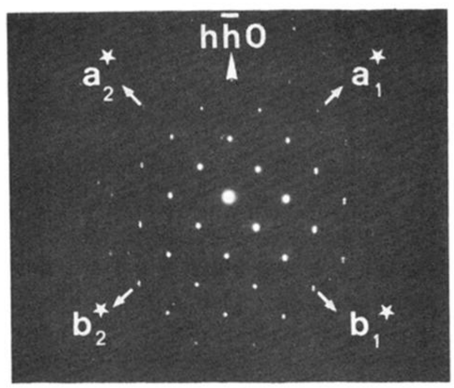
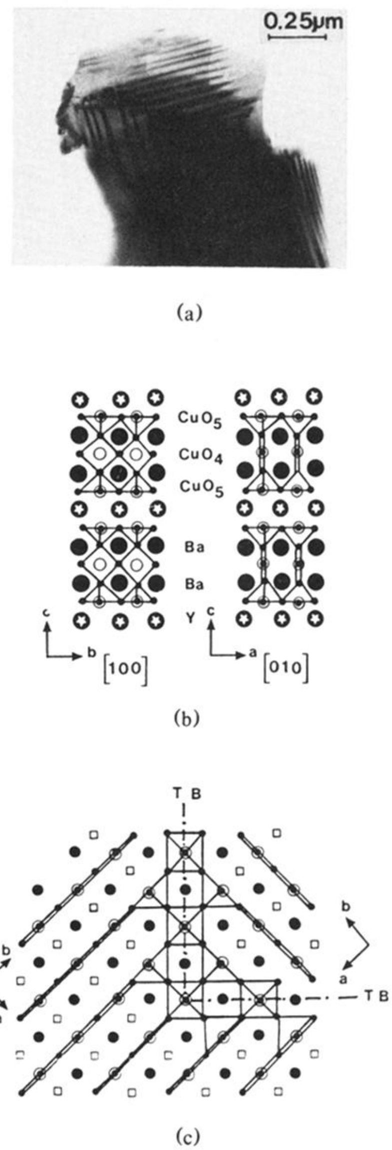


FIG. 1. Typical [001] electron diffraction pattern.



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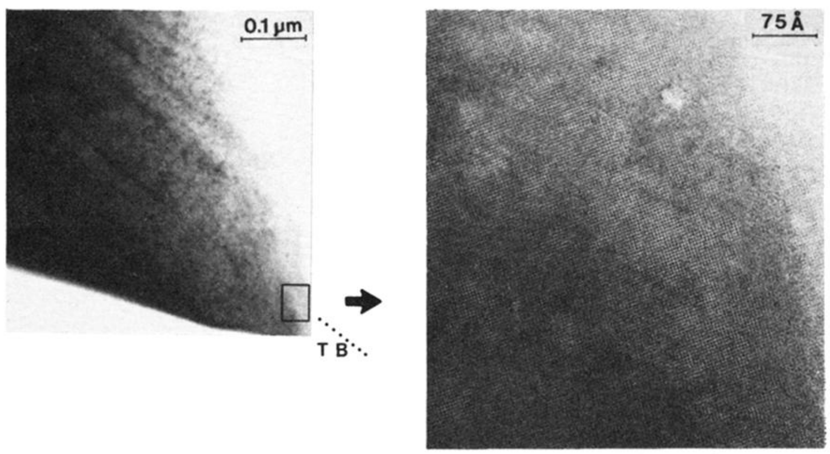

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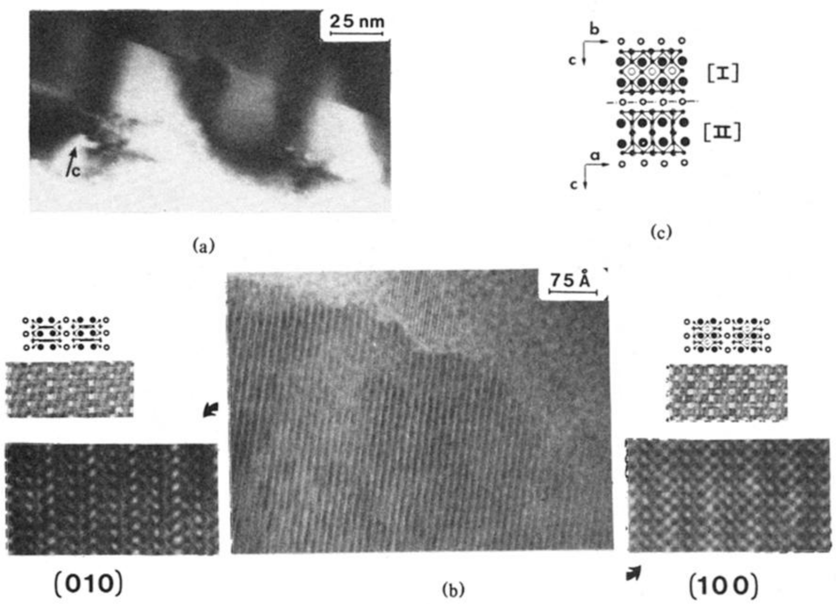

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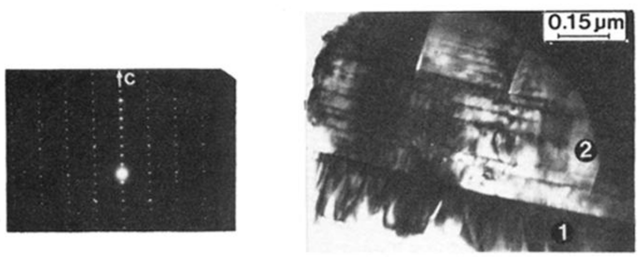

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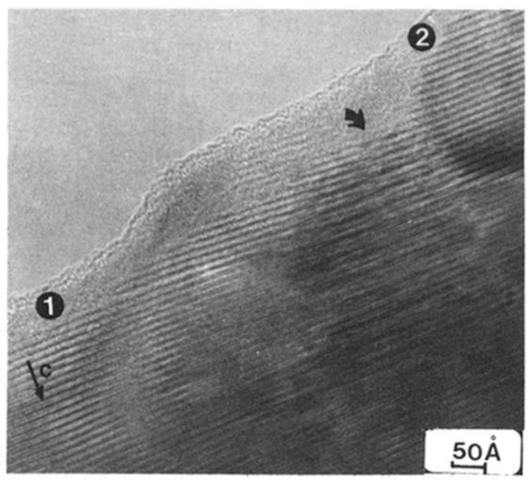

FIG. 6. High-resolution image of a boundary between the oriented domains.