Polydomain structure of $YBa_2Cu_3O_7$ single crystals

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An x-ray diffraction analysis has revealed a system of oriented structural domains in yttrium-barium cuprate crystals. The appearance of a regular substructure is linked with a high-temperature martensitic transition from a tetragonal phase to an orthorhombic phase ($P4/mmm \rightarrow Pmmm$).

A diffraction study of $YBa_2Cu_3O_7$ was undertaken in order to find features of the actual structure which are related to the possible occurrence of a phase transition[1] in the high-temperature interval. $YBa_2Cu_3O_7$ single crystals were grown by slowly cooling a molten mixture of the oxides Y_2O_3, BaO, and CuO. The crystals were rectangular wafers, black with mirror-finish faces, with a diameter up to 1.5 mm and a thickness of 30–50 μm.

The x-ray studies were carried out by recording Laue patterns, rocking and fixed-crystal x-ray diffraction patterns, and angular-scanning topograms at room temperature with URS-60, DRON-3, and URS-0.02 instruments and an RKV-86 camera. The symmetry of the arrangement of the spots on the Laue patterns corresponds to the diffraction class *mmm*. From the x-ray rocking diffraction patterns of an oriented crystal we determined the constants of the orthorhombic lattice: $a = 3.86$ Å, $b = 3.92$ Å, $c = 11.59$ Å. We observed no systematic extinction of the reflections, so that, according to the data in the literature,[2] we can classify this crystal as being of space group *Pmmm*.

A characteristic feature of all the samples is a blurring or splitting of the diffraction spots, which indicates a developed substructure. An important point is that the reflections of the substructure are not distributed in a disordered way; they instead form oriented combinations which are strictly determined by the crystallographic indices of the reflections. Figure 1a illustrates the situation with schematic Laue patterns. From these patterns we see that planes running parallel to [001] cause a splitting of the reflections along the perimeter of the zonal ellipse. In contrast, the reflections belonging to a [100] zone (Fig. 1b) are split across the perimeter of the zonal ellipse. It can be seen quite well that the (00*l*) reflections remain unsplit focused points in all reflection orders. All of these structural features of the diffraction pattern can be explained in a consistent way through a detailed crystallographic analysis of a suggested conversion of the lattices through a uniform displacement. The primary assertion is that this structure is formed through the twinning of a prototypical (initial) tetragonal lattice along a {110}/{110}.

The diagram in Fig. 2a shows how the original lattice can change into a rectangular lattice with unit cell OABC through a tilting of the sides of the square OEDB through an arbitrary angle ϕ. In this version of the twinning displacement, the new

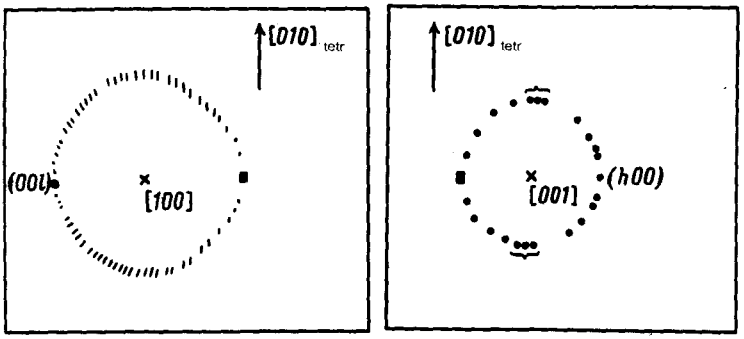


FIG. 1. Schematic diagrams of Laue patterns of the $YBa_2Cu_3O_7$ single crystal. a—The axis of the zone of reflections runs parallel to $[100]_{tetr}$ of the tetragonal phase; b—the axis of the reflection zone is parallel to $[001]_{tetr}$.

phase forms in orientation state I; II is the mirror-symmetry domain. In an alternative twinning system, domains III and IV appear (Fig. 2b). The diffraction pattern undergoes corresponding changes. Figure 2d is a superposition of the reciprocal lattices of all four orientation states. We wish to call attention to the point that in this scheme with uniform deformations a transition occurs from the $4/mmm$ group to its mmm subgroup, and the symmetry of the original tetragonal phase is preserved in the combined reciprocal lattice. This crystal-geometry model corresponds completely to the observed diffraction patterns. In this scheme, only the $(00l)$ sites of the reciprocal lattice remain unchanged during the transition, and the component of the splittting of the other sites lie in planes parallel to x^*y^*0. The particular features of the splitting of the reflections along the zonal ellipse in Fig. 1b then also become obvious.

In summary, this analysis shows that the actual structure of the $YBa_2Cu_3O_7$ crystals may contain subgrains of four orientation states of an orthorhombic phase.

A direct experiment confirms that conclusion. The photographs in Fig. 3a, recorded by angular-scanning topography,[3] reveal four groups of contrast diffraction images of the crystal [(200) CuK_α reflection]. Measurements of the vertical component of the splitting on the basis of these topograms put the twinning angle at $\phi = 0.9°$. The angle ϕ can be determined independently from Fig. 2a if the parameters a and b of the orthorhombic cell are known [if the parameter values are approximately the same, the relation $\phi \approx 1 - (a/b)$ can be used]. The value $\phi = 0.86°$ calculated in this manner agrees with the data obtained from measurements on the topogram.

These results can be used to construct a preliminary model of the substructure of the low-temperature phase of $YBa_2Cu_3O_7$ (Fig. 3b). We wish to call attention to the characteristic partitioning of the crystal of the orthorhombic phase parallel to $\{110\}$ of the original tetragonal phase, by plane boundaries of two types: coherent boundaries, which are invariant twinning planes, and incoherent boundaries, which separate domain complexes. Correspondingly, there are two length scales for the observed elements of the substructure. For the structural domain of one orientation state, the thickness estimated from our data ranges downward from 10 μm. For a domain com-

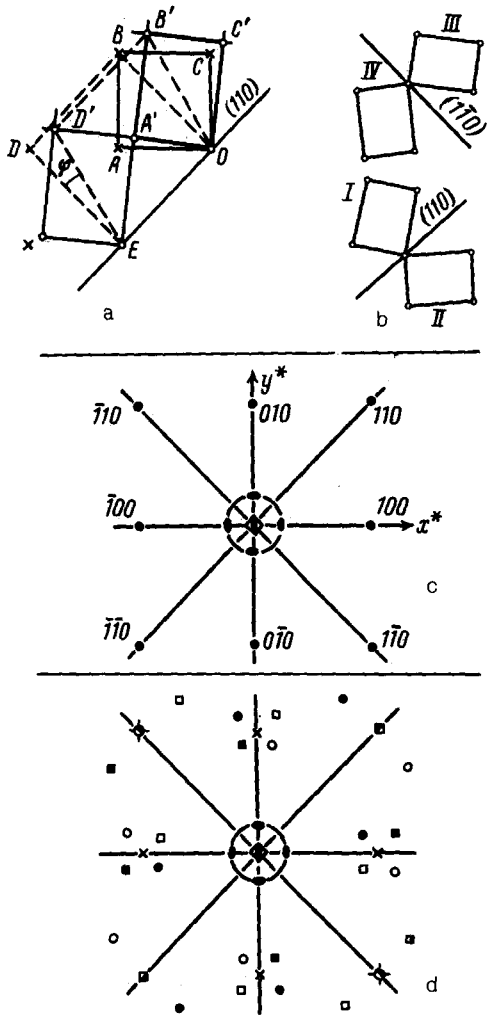
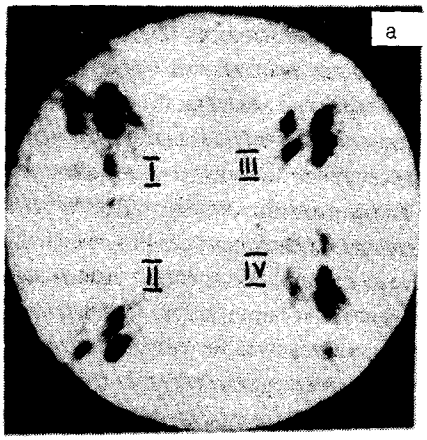


FIG. 2. Twinning of a tetragonal lattice along the {110}/{110} system. a—Twinning diagram; b—set of four orientation states that have formed; c—fragment of the reciprocal lattice of the original phase; d—superposition of the reciprocal lattices of four orientation states of the orthorhombic phase. ×—Position of a site of the tetragonal phase.

plex consisting of orientation states I + II or III + IV, the transverse dimension estimated from the topogram ranges upward from 50 μm. Fitting in a natural way into this model is the plane antiphase boundary with the (001) orientation, which has already been mentioned in the literature, and which corresponds to a "relinking" of a chain along the z axis:

$$\mathrm{Y-Ba-Y-Ba-Y-Ba=\!=\!\Vert=\!=Ba-Y-Ba-Y-Ba}\ -\text{etc.}$$

This picture is similar to the domain structure of the uniaxial ferroelectric KH_2PO_4 (KDP), which has been studied in detail elsewhere.[4,5] For KDP, experimental data are already available on the configuration of the incoherent boundary. Diffraction effects have been detected from a transition layer $\sim$1000 Å thick in which ortho-



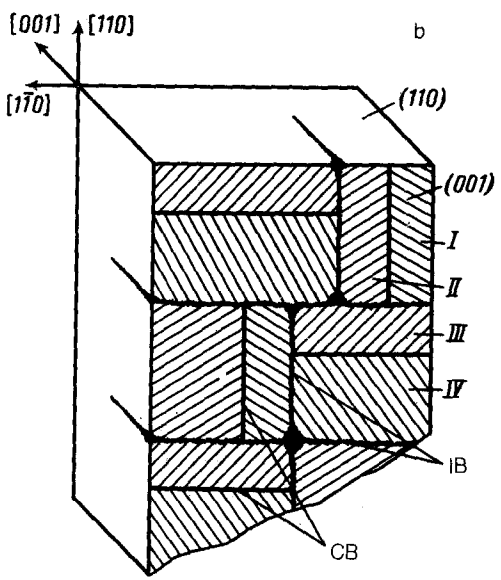


FIG. 3. a: Angular-scanning topogram [(200) CuK_α reflection]. I, II, III, IV—Reflections from four orientation states. b: Diagram of a polydomain crystal of the orthorhombic phase. CB—Coherent boundary; IB—incoherent boundary.

rhombic cells with orientations I-II gradually convert into a tetragonal lattice ($\phi \to 0$), which then also undergoes a gradual "flipping" into orientation states III-IV.

We note in conclusion that the fact that a developed domain structure appears in $YBa_2Cu_3O_7$ requires further study in order to identify the roles played by these plane boundaries in the formation of the superconductivity critical parameters. No less interesting is the problem of the mechanism for the phase transition.

In the literature we find, for example, many pieces of evidence that changes in the oxygen concentration occur during various types of heat treatment at temperatures of

400 °C and above in various atmospheres (O_2, vacuum, etc.), and in addition both oxygen and oxygen vacancies may undergo an ordering. Evidence for this possibility comes from the dependence of T_c on T_{quench} over the range 400–800 °C in which the orthorhombic phase exists. If this were the extent of the matter, then we could use the representation of the ordering of the oxygen as a second-order phase transition for an explanation. However, the fact that there exists a spontaneous plastic deformation of the single crystal, which builds up and which is realized through a twinning, is evidence for a parallel process involving a structural change in the lattice through a uniform deformation, as occurs in the case of first-order phase transitions.

It is thus possible that the entire process can be described as a two-step process: 1) a redistribution of the oxygen (e.g., involving the formation of chains along edge *b* of the unit cell); 2) a regular cooperative change in the lattice structure. In this case, the process has features reminiscent of the bainite transition in steels, where the first step is a redistribution of carbon, and the second is a spontaneous deformation of the ion lattice.

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