Superstructure along the c axis in $YBa_2Cu_3O_{7-x}$ single crystals having $T_c \approx 92$ K

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We have grown by flux methods $YBa_2Cu_3O_{7-x}$ single crystals, having critical temperature $T_c \approx 92$ K, and orthorhombic distortion not detectable either by x-ray or by electron diffraction (difference between a and b lattice constants smaller than 7×10^{-3} Å). In such crystals, transmission-electron-microscopy investigations have shown the presence of a domain structure, and electron-diffraction measurements have revealed the occurrence of a new superstructure along the c axis. This superstructure consists in a systematic crossing of the Cu-O chains in alternate (001) planes, which causes a doubling of the c lattice parameter and a strong decrease of the orthorhombic distortion. The occurrence of this superstructure is probably induced by tiny dopant impurities, and it can explain the discrepancies existing among the reports by several authors about the amount of orthorhombic distortion of $YBa_2Cu_3O_{7-x}$ single crystals.

In the last year, the properties of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ have been widely investigated in a number of laboratories. The crystal structure of $YBa_2Cu_3O_{7-x}$ was first determined by measurements on polycrystalline samples prepared by solid-state reaction.[1-3] The room-temperature structure of $YBa_2Cu_3O_{7-x}$ samples with critical temperature $T_c = 92$ K was found to be orthorhombic, space group $Pmmm$. The orthorhombic distortion is related to the ordering of the oxygen ions in the basal plane: The oxygen sites at $(0\frac{1}{2}0)$ [hereafter O(1)] are almost completely filled while those at $(\frac{1}{2}00)$ [hereafter O(2)] are mostly empty. Such distribution of oxygen ions gives rise to one-dimensional Cu-O chains in the b direction.

The oxygen stoichiometry plays a central role in determining the structural properties of $YBa_2Cu_3O_{7-x}$.[4] The decrease of the oxygen content per atomic formula unit (a.f.u.) was found to give rise to an increase of the lattice parameter c according to the formula[5]

$$7 - x = 70.512 - 5.454c .\tag{1}$$

Furthermore, the decrease of oxygen content results in a decrease of the orthorhombic distortion and finally (for an oxygen content of about 6.5 per a.f.u.) in a crystallographic phase transition from an orthorhombic to a tetragonal structure (space group $P4/mmm$). By decreasing the oxygen content an increasing number of oxygen vacancies occurs at the O(1) sites while, at the same time, the oxygen occupancy of the O(2) sites slightly increases. Finally, at the structural transition from orthorhombic to tetragonal the O(1) and O(2) sites become equivalent with an occupancy of 0.25. In the tetragonal phase the linear Cu-O chains in the basal plane are completely disrupted and are substituted by highly disordered two-dimensional Cu-O network.

The superconducting properties of the $YBa_2Cu_3O_{7-x}$ compound are strongly related to its structural properties. The transition temperature T_c is 92 K at the highest allowed oxygen contents per a.f.u., and decreases monotonically with the oxygen content. Finally, superconductivity disappears close to the orthorhombic-to-tetragonal phase transition, and the tetragonal phase of $YBa_2Cu_3O_{7-x}$ is no longer superconducting. This striking feature has lead many investigators to infer that the Cu-O one-dimensional chains play a central role in the mechanism of the high-T_c superconductivity.[6,7] However, this point has not been definitely settled: In fact, other authors suggest that the central feature could be the absolute oxygen content per a.f.u. rather then the presence of the linear Cu-O chains.[8]

In this framework, the situation of the $YBa_2Cu_3O_{7-x}$ single crystals is rather confusing. Single crystals of $YBa_2Cu_3O_{7-x}$, about mm^3 sized, were obtained by several research groups, who used conceptually similar procedures, namely flux techniques from strongly non-stoichiometric Y_2O_3, BaO, and CuO mixtures. The data from different authors concerning the crystals are somewhat contradictory, as far as the amount of orthorhombic distortion is concerned. In fact, the reported differences between a and b lattice parameters, even for samples with the same transition temperature of 92 K, range from 0.073 Å,[9] very close to the polycrystalline value, down to about 0.007 Å.[10,11] Other authors do not even mention the orthorhombic distortion of their crystals.[12]

We have grown single-crystal platelets of $YBa_2Cu_3O_{7-x}$ sized up to about $4 \times 2.5 \times 0.1$ mm^3 by the flux method, using as a solvent the eutectic mixture of two of the constituent oxides, namely CuO(72%) and BaO(28%). Alumina crucibles were used for the growth. Details on the growth procedure are given in Ref. 13. The

structural properties of these crystals were investigated by x-ray diffraction, while the chemical composition and homogeneity were measured by electron microprobe analysis. T_c was determined from dc and ac susceptibility and from dc resistivity measurements. The transition temperatures for the as-grown crystals range between 50 and 70 K. Very sharp resistive transitions at 92 K (transition width less than 1 K) were obtained after a one-day annealing treatment at 600 °C in flowing O_2 followed by a slow cooling to room temperature.[14] Susceptibility measurements also showed sharp transitions, indicative of a homogeneous composition.

In this paper we report on a structural investigation on such single crystals of $YBa_2Cu_3O_{7-x}$ having T_c =92 K. The crystals have first been investigated by electron microprobe analysis, and no spurious elements were found in a detectable concentration. Laue photographs showed the platelet-shaped crystals to be normal to the c crystallographic direction. The lattice parameters were measured with a Bragg-Brentano single-axis diffractometer using Co $K\alpha$ radiation. The c lattice parameter was obtained from the symmetrical reflection (0011) $(2\theta_B = 115°)$. The diffraction peaks of the annealed crystals were pretty sharp indicating a well-defined value of c and therefore an homogeneous oxygen distribution throughout the sample. A typical value of c for the annealed samples was $11.678 \pm 3 \times 10^{-3}$ Å. Such a value, according to Eq. (1), corresponds to the high oxygen content of 6.82 per a.f.u., close the the maximum value allowed for polycrystalline $YBa_2Cu_3O_{7-x}$ samples. This result is in agreement with the very sharp superconducting transition at 92 K detected by dc resistivity measurements.

For such high oxygen contents a strong orthorhombic distortion is expected. The a and b values were investigated using the (0 2 11),(2 0 11) $(2\theta_B = 148°)$ and (039),(309) $(2\theta_B = 156°)$ asymmetrical reflections. In the case of a twinned orthorhombic structure a splitting of both the (0 2 11) and (039) peaks is expected. The diffraction spectrum of the (039) reflection is shown in Fig. 1 (no other peaks were observed over an angular range of 10° around the peak shown). No splitting was observed either for the (0 2 11) or the (039) peaks even though such high-angle reflections are very sensitive to the
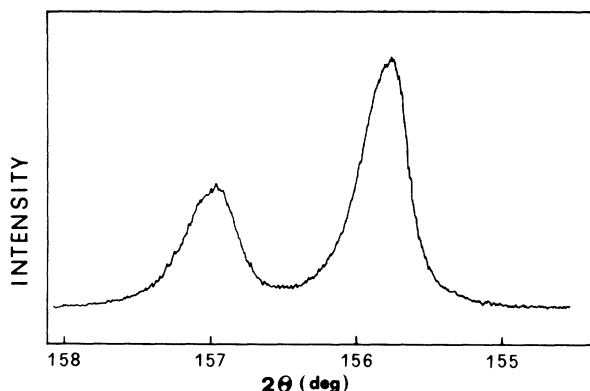
value of the lattice parameter. The lattice parameters deduced from these reflections were $a = b = 3.867 \pm 3 \times 10^{-3}$ Å. The possible existence of an orthorhombic twinned structure was also investigated by the Buerger's precession camera: No evidence for an orthorhombic twinned structure was found in any case from x-ray diffraction experiments.

All these data lead us to conclude that for our single crystals with T_c =92 K the difference between a and b, if any, is less than 6×10^{-3} Å.

Morphological and structural investigations were also carried out by transmission electron microscopy (TEM) with a Jeol 200 B instrument operating at 200 kV on thin specimens prepared by crushing the brittle single crystals. Preferential cleavage of the samples along the c planes gave rise mainly to platelets thin enough for TEM observation, having the c axis perpendicular to the surface. An electron diffraction pattern recorded with the electron beam parallel to the c axis is reported in Fig. 2. The typical feature of the orthorhombic twinned structure, namely the spot splitting parallel to a $(110)^*$ crystallographic direction, was not observed. Moreover, streaking of the diffraction spots in both the $(110)^*$ directions as well as the presence of some diffuse scattering along the $(100)^*$ directions can be noticed. Micrographs were then taken with the method of the diffraction contrast in two beam conditions exciting a (100) reflection. Two sets of overlapping domains whose boundaries lay normal to each other could be observed as shown in Fig. 3. Both kinds of boundaries occur perpendicular to a $(110)^*$-type direction. Extinction of contrast for one of the two sets is obtained when a two beam image is recorded with a (110)-type reflection exactly satisfying the diffraction conditions (see Fig. 4). Alternatively, the second set disappears if the (110) reflection perpendicular to the previous one is excited. From analysis of the diffraction spot size it is possible to estimate an upper limit for the orthorhombic distortion in our samples. $(a-b)/a$ results to be less than about 2×10^{-3}, in agreement with the x-ray diffraction measurements. However, the presence of domain contrast in the electron micrographs supports the hypothesis that some orthorhombic distortion should be present. In fact, the contrast in the domain structure arises from a difference in the excitation error of the operating

FIG. 1. The (039) x-ray diffraction peak of our $YBa_2Cu_3O_{7-x}$ crystals (Co $K\alpha_1$ and $K\alpha_2$ radiation). It is seen that neither peak is split.
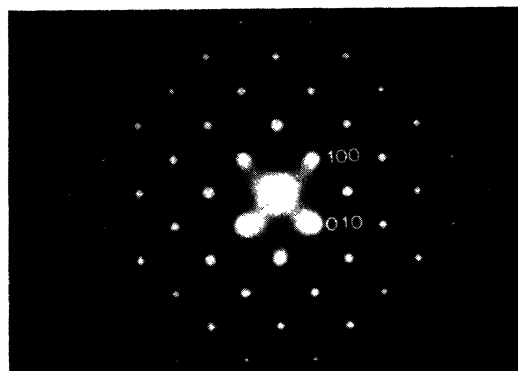

FIG. 2. Electron diffraction pattern along the [0,0,1] zone axis.
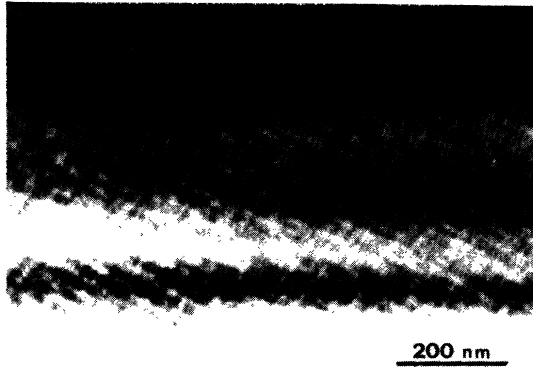
FIG. 3. Diffraction contrast image, taken in two beam condition with a (200) reflection exactly excited, showing two sets of domains with boundaries both normal to a (110)* direction.

reflection for crystals lying on the two sides of the boundary.[15] Moreover, the disappearance of one set of domains when imaged with a (110)-type reflection supports the hypothesis. In fact, this reflection is common to the crystal on both sides of the twin boundary in the generally accepted twin structure observed in polycrystalline $YBa_2Cu_3O_{7-x}$. The overlapping domains with boundaries perpendicular to each other should be separated by planar defects in the (001) planes. Such planar defects probably consist in permutation twins where the a and b directions are interchanged. The same defects have been already observed and characterized by both x-ray diffraction by You et al.[16] and by high-resolution microscopy by Van Tendeloo and co-workers.[17,18] In fact such permutation twins can explain the presence of overlapping domains whose boundaries are both normal to a (110)*-type direction. On the basis of the above considerations, the morphology of our single crystals does not appear to be basically different from that generally observed on polycrystalline $YBa_2Cu_3O_{7-x}$, since the same crystal defects are found, exception made for the domain size. The average domain size, as derived from Figs. 3 and 4, is of the order of 100 Å, roughly one order of magnitude smaller than usually observed in $YBa_2Cu_3O_{7-x}$ polycrystals. Such narrow domains can well account for the observed

streaking of the diffraction spots (see Fig. 2) along crystallographic directions perpendicular to the domain boundaries. Moreover, the presence of two orthogonal sets of domains is observed even in the thinnest areas of the specimen, so that a rather short domain size along the c axis and a high density of the (001) twins can be deduced. This fact, as we will see, can account for the experimentally observed small values of the orthorhombic distortion that appears anomalous in $YBa_2Cu_3O_{7-x}$ crystals with high oxygen content and good superconducting properties.

Indeed, the presence of a growing density of (001) permutation twins gives rise to an increasing fraction of crystal where the Cu-O linear chains are oriented orthogonally to each other in two successive (001) crystallographic planes. An extreme situation can be modeled with the presence of a permutation twin for each (001) plane. Since the origin of the orthorhombic distortion is the presence of linear Cu-O chains exclusively along the a crystallographic direction, no orthorhombic distortion is expected for such spatially alternate ordering of the oxygen ions. A regular superstructure results, consisting of linear Cu-O chains perpendicular to each other in alternate (001) planes: Diffraction spots from the superstructure should then become observable. On the basis of the model reported in Fig. 5 the geometric structure factor can be computed for the sublattice of the relevant oxygen ions. Hereafter, we will indicate with the expression "original lattice" the usual orthorhombic structure with the oxygen vacancies ordered exclusively along the b axis. A new unit cell is obtained by doubling only the c lattice parameter, which yields new Miller's indices h,k,l related to the old indices h',k',l' by the obvious relations: $h=h'$, $k=k'$

FIG. 4. The same area of Fig. 3 imaged with a (110) reflection exactly excited, showing extinction of contrast for one set of domains. Diffraction conditions are reported in the inset.

(a)   (b)
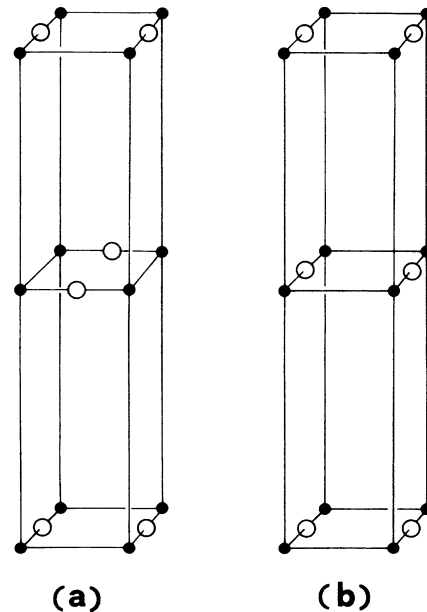
FIG. 5. (a) Sketch of the unit cell of the $YBa_2Cu_3O_{7-x}$ superstructure described in the text; (b) sketch of two unit cells of "normal" $YBa_2Cu_3O_{7-x}$ stacked along the c axis. Only the elements making (a) different from (b) are shown, namely the linear chains of Cu ions (filled circles) and of O ions (open circles).

$2l = l'$. Reflections are allowed when the following conditions for the Miller's indices of the superstructure cell are satisfied:

h odd, then $(k+l) = 2n$,

h even, then $(k+l) = 2n + 1$.

Obviously for l odd the superlattice reflections overlap with the reflections from the original lattice. Therefore the search for superlattice reflections should be subject to the following conditions:

l even, $h = 2n$, $k = 2n+1$ or $h = 2n+1$, $k = 2n$.

Accordingly, (011)-, (013)-, etc. type reflections are allowed, so that the oxygen ordering described above should result in superlattice reflections with indices $(01\frac{1}{2})$, $(01\frac{3}{2})$, etc. when referred to the Miller's indices of the original lattice. The superlattice reflections predicted by the present model have been observed systematically for different specimens and for different zone axis orientations. Two examples are reported in Fig. 6 where the $(01\frac{1}{2})$ and $(01\frac{3}{2})$ reflections can be observed. Summarizing, the structure of our single crystals can be described on the basis of a high density of (001) permutation twins. This also agrees with the absence of sharp and well-defined twin boundaries normal to the (110)* directions (see Figs. 3 and 4), owing to the lack of stacking order along the c axis. The presence of sharp superstructure spots in the electron diffraction patterns clearly indicates that at least a sizable fraction of the crystal can be described on the basis of the above outlined supercell. Obviously no orthorhombic distortion is expected at all for such superstructure of tetragonal symmetry, with periodically crossed Cu-O chains. The residual small orthorhombic distortion originating the domain contrast in the two beam electron images can be due to residual regions of orthorhombic $YBa_2Cu_3O_{7-x}$ lattice.

The microstructure of our crystals can be described either as a large amount of (001) twins in the original lattice, or equivalently as a complementary number of antiphase boundaries in the ordered superlattice. In any case, a high density of these planar defects is required to account for the small domain size along the c direction. In this frame, the average as well as the local orthorhombic distortion will depend on the amount and spatial distribution of these defects, which in turn define the relative amounts and domain size of new and original phases. In fact, the elastic strain of both structures caused by the coherent interfaces will play a role in the description of the detailed atomic arrangement.

It is important to note that by varying the amount and spatial distribution of the (001) planar defects it is probably possible to change in a continuous way the average orthorhombic distortion, from the upper limit of the origi-
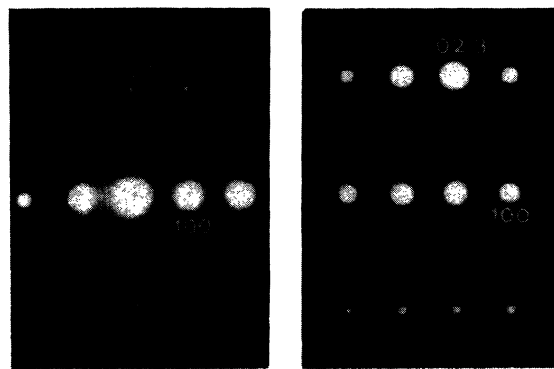

FIG. 6. Electron diffraction patterns in two different orientations showing superlattice spots. On the left side the specimen is oriented along the $[0,\bar{1},2]$ zone axis and $(11\frac{1}{2})$ reflections are present, while on the right side the orientation is along $[0,\bar{3},2]$ and the $(0\,2\,\frac{1}{2})$ superlattice spot can be observed.

nal structure to the negligible value expected for the tetragonal supercell. This can possibly account for the large spread of results obtained for this parameter by different authors[9-11] in single crystals having essentially the same superconducting properties. The different crystallographic behavior between crystals and polycrystalline samples can possibly be ascribed to slight contamination of the former by impurities from either the melt or the crucible. In fact it has been shown that the inclusion of a large number of elements, even in small amounts, can lead to a strong decrease of the orthorhombic distortion in $YBa_2Cu_3O_{7-x}$.[19-21]

In conclusion, we have found and determined, for the first time, a superstructure along the c axis, in $YBa_2Cu_3O_{7-x}$ single crystals with $T_c = 92$ K. The occurrence of such a superstructure is sufficient to explain the discrepancies about the amount of orthorhombic distortion of $YBa_2Cu_3O_{7-x}$ crystals reported in previous papers by several authors, and demonstrates the possibility of having (presumably, as a consequence of small dopant impurities) $YBa_2Cu_3O_{7-x}$ samples with high T_c, and yet a *tetragonal* structure, down to a microscopic scale.

The superstructure found preserves the existence of linear Cu-O chains, whose directions in alternate (001) planes are perpendicular (see Fig. 5). The possible occurrence of this type of superstructure must, therefore, be considered when studying the correlation between the vanishing of orthorhombic distortion and the disruption of linear Cu-O chains in $YBa_2Cu_3O_{7-x}$.

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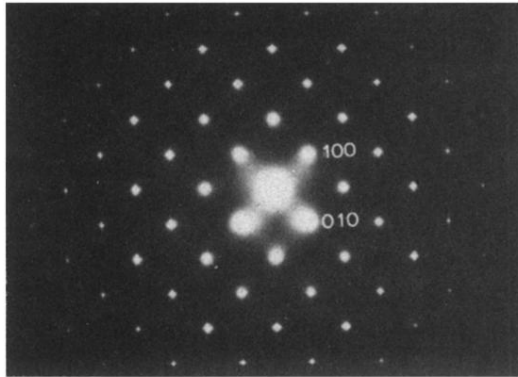
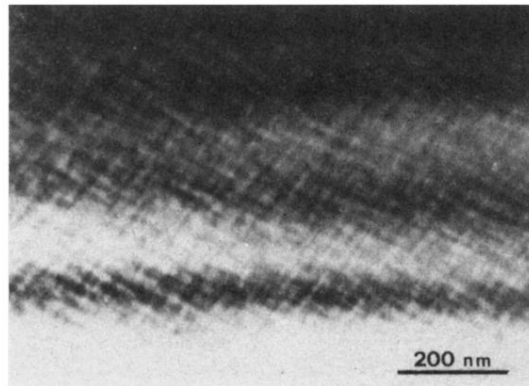FIG. 2. Electron diffraction pattern along the [0,0,1] zone axis.

FIG. 3. Diffraction contrast image, taken in two beam condition with a (200) reflection exactly excited, showing two sets of domains with boundaries both normal to a (110)* direction.
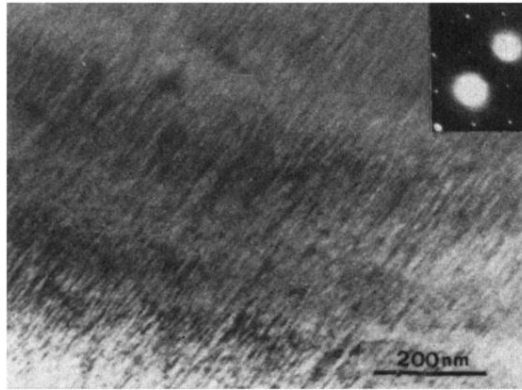
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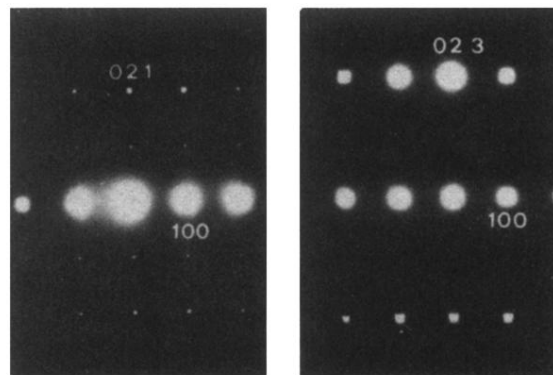
FIG. 6. Electron diffraction patterns in two different orientations showing superlattice spots. On the left side the specimen is oriented along the $[0,\bar{1},2]$ zone axis and $(11\frac{1}{2})$ reflections are present, while on the right side the orientation is along $[0,\bar{3},2]$ and the $(0\,2\,\frac{3}{2})$ superlattice spot can be observed.