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Properties of Y-Ba-Cu-O thin films with ordered defect structure: $Y_2Ba_4Cu_8O_{20-x}$

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Properties of both unfaulted and faulted *c*-axis-oriented $Y_2Ba_4Cu_8O_{20-x}$ thin films are reported. Their superconducting transition temperatures are 81 and 93 K, respectively. This implies that the precise ordering of copper-oxygen layers in $YBa_2Cu_3O_{7-x}$ is not crucial for the high T_c. $Y_2Ba_4Cu_8O_{20-x}$ exhibits lower resistivity and lower Hall coefficient than $YBa_2Cu_3O_{7-x}$. The extra copper-oxygen layers seem to play an important role in the normal state.

Recently, we presented an analysis, using both x-ray and electron diffraction, of an ordered defect structure in epitaxial films of Y-Ba-Cu-O.[1] We determined that significant volume fractions of a film could be characterized by a *c*-axis parameter which is expanded by the width of one atomic layer from the normal $YBa_2Cu_3O_{7-x}$ (1:2:3) structure.[2] Using a model originally proposed by Zandbergen *et al.*[3] for isolated defects in bulk materials, we proposed the existence of an ordered defect structure in which an extra copper-oxygen layer appears in every unit cell of the parent 1:2:3 material (see the inset in Fig. 1). The composition of this structure would be $Y_2Ba_4Cu_8O_{20-x}$ (2:4:8). In this paper, we report additional evidence for the 2:4:8 model as well as the synthesis of films in which the new material appears as nearly a single phase with a high degree of ordering perfection. Upon changes in growth and postannealing conditions, samples could be made either as 1:2:3, or 2:4:8, or more commonly, as faulted structures that mix the two. We report normal-state and superconducting properties for the new phase as well as its structurally faulted variations. We find that the new phase is characterized by significant changes in the normal-state transport properties when compared to the 1:2:3 compound, while its critical temperature is decreased by only 10 K. Our interpretations of the observed properties are discussed in terms of the proposed 2:4:8 structure.

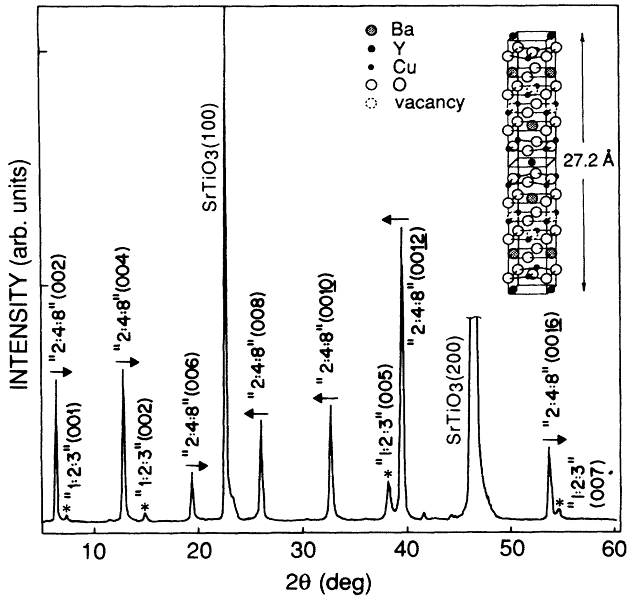

FIG. 1. X-ray diffraction data of a *c*-axis-oriented 2:4:8 sample. Peaks marked with an asterisk belong to the 1:2:3 phase of the sample. Each arrow on the 2:4:8 peaks denotes the direction it moves when the stacking faults appear. Inset shows a unit cell of 2:4:8 structure.

Samples were prepared by both electron-beam evaporation and reactive magnetron sputtering. Detailed descriptions of the deposition techniques were published elsewhere.[4,5] BaF_2 was used as the Ba source in the evaporation,[6] and a Ba metal target was used in the sputtering. Microprobe analysis showed no fluorine in the samples made with BaF_2 after a wet O_2 anneal. In order to achieve the well-ordered new phase, the films had to be rich in Cu with slightly Y-rich composition ($Y_{15}Ba_{28}Cu_{57}$) according to the microprobe. Films made with Ba metal have properties consistent with those of films made with BaF_2. For transport measurements, samples were patterned into 0.4-mm-wide and 2-mm-long strips by regular photolithographic techniques. Low-resistance contacts were made using silver evaporated on the pads. The x-ray diffraction data in this paper were obtained using a four-circle x-ray diffractometer in a symmetrical scattering geometry (diffraction vectors normal to the film).[1] Despite a clear interest in determining oxygen concentrations in the new structure, we have not yet found a reliable analytical method which is applicable to thin films.

Figure 1 shows x-ray diffraction data of an oriented 2:4:8 sample (curve A in Fig. 3) with *c* axis perpendicular to the $SrTiO_3$ (100) substrate. As indicated in the figure, each major peak can be assigned to either the substrate, *c*-axis-oriented 1:2:3, or *c*-axis-oriented phase having a lattice parameter of 27.19 Å with odd-order reflections missing. We note that, relative to a film made up almost entirely of 1:2:3, the intensity of the 1:2:3 is about 8%. Furthermore, each peak of the 27.19 Å phase is sharp and falls at a scattering vector whose magnitude is an integer multiple of $2\pi/27.19$ Å^{-1} within our experimental precision of ± 0.003 Å^{-1}. For the remainder of this paper, we refer to samples which satisfy this criterion as "well ordered" or "unfaulted," in contrast to the "faulted" structure described next.

As reported earlier,[1] we also observed diffraction patterns having broad peaks close to, but not precisely aligned with, the well-ordered positions. Figure 2 shows diffraction and resistivity data for (a) a well-ordered sample and (b) the same sample after further annealing. After a further anneal the peaks shifted. We interpret these results to imply that the well-ordered structure is not stable at higher temperatures. This may be a reason why our films made with BaF_2 have a more well-ordered material since they were annealed at lower temperatures and for less time. We believe that the peak shifts are due to layering disorder in the structure. Support for this interpretation is found by considering the diffraction patterns expected for layered structures with random faults.[7] As random faults are introduced, diffraction peaks broaden and shift. The magnitude and direction of the shift depend on the details of the model. A simple relevant model is the case of stacking monoatomic layers with two possible interlayer distances: 11.7 and 13.6 Å. These spacings reproduce the observed sets of well-ordered peak positions. Taking the 13.6 Å spacing as the norm and introducing 11.7 Å spacings as faults, the peak shifts are found to oscillate with scattering angle with the same direction as our observations. The amplitude of the shifts increase with an increasing density of faults. These considerations lead us to refer to material showing such oscillatory peak shifts as "faulted." More complete calculations taking into account the multicomponent nature of our films are underway. We have also found that upon further anneal, a Bragg peak at $2\theta = 35.5$ appears, which we attribute to CuO. Note that there is a clear change in its superconducting transition temperature, associated with the structural change (see the insets in Fig. 2).

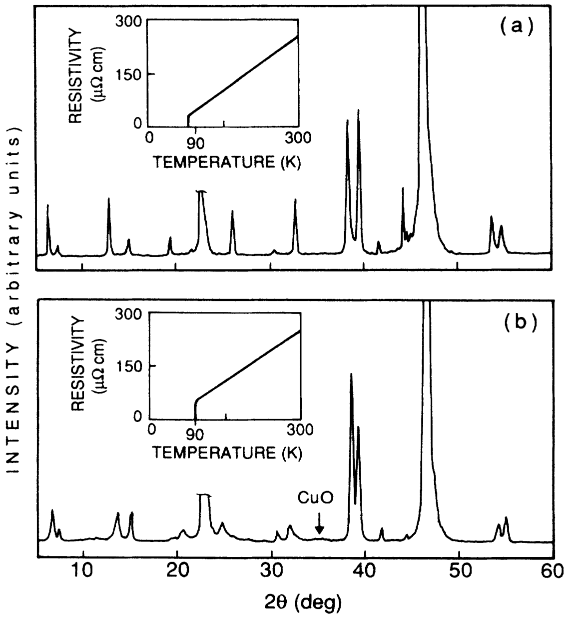

FIG. 2. X-ray diffraction data of a c-axis-oriented 2:4:8/1:2:3 mixed but unfaulted sample (a), and the same sample after high-temperature annealing (b). The shifts of the peaks are consistent with random 2:4:8 stacking faults. Inset shows the resistivity vs temperature data.

Resistivity versus temperature data for the unfaulted 2:4:8 sample (curve A) are shown in Fig. 3 along with a 1:2:3 phase (curve B),[8] a faulted 2:4:8 phase (curve C) and a 1:2:3/2:4:8 mixed but unfaulted phase sample (curve D). There are three points to note. (1) The transition temperature of the unfaulted 2:4:8 phase is about 10 K lower than the 91 K normally seen in the 1:2:3 structure. (2) The 2:4:8 phase has a lower resistivity: 150 μΩ cm at 300 K and 30 μΩ cm at 100 K compared with 300 μΩ cm at 300 K and 100 μΩ cm at 100 K for the 1:2:3 phase. (3) The resistivity of the 2:4:8 sample extrapolates to zero around 55 K while the resistivity of the 1:2:3 extrapolates to zero at (or slightly above) 0 K. This intriguing point is discussed below. Some samples with faulted 2:4:8 structure have been observed with onset temperatures as high as 96 K and zero-resistance temperatures as high as 93 K. These values are repeatedly about 3–4 K higher than those of our well-ordered 1:2:3 samples made under the same conditions. Whether this higher T_c is just a sample to sample variation or a special property of this faulted 2:4:8 structure (e.g., due to strain or doping of the 1:2:3 structure produced by the stacking faults or some kind of superstacking) is yet to be clarified. The sample with unfaulted 2:4:8 and 1:2:3 phases (curve D) that are presumably mixed on a macroscopic scale clearly has one transition at 90 K and another transition at 81 K

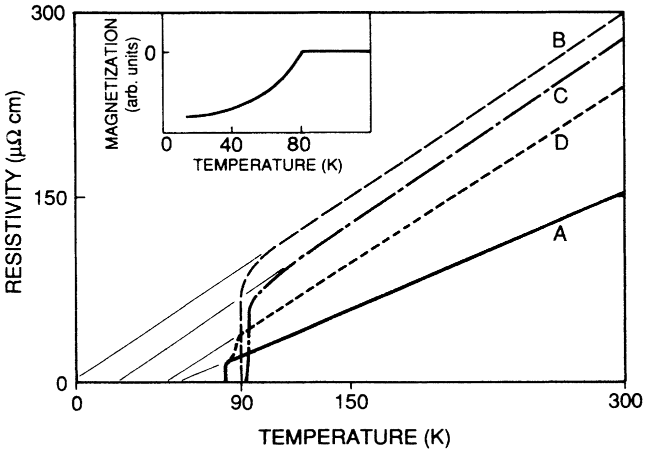

FIG. 3. Resistivity vs temperature data of a c-axis-oriented unfaulted 2:4:8 sample (curve A), a typical c-axis-oriented 1:2:3 sample (curve B), a c-axis-oriented faulted 2:4:8 sample (curve C), and a 1:2:3/2:4:8 mixed but unfaulted sample (curve D). Inset shows magnetization vs temperature data of a c-axis-oriented unfaulted 2:4:8 sample.

corresponding to the 1:2:3 transition and the 2:4:8 transition, respectively.

In order to establish further that the change in T_c is due to the 2:4:8 phase, magnetization versus temperature data taken while heating an unfaulted 2:4:8 sample in a perpendicular field of 100 G are shown in the inset in Fig. 3. The sharp transition temperature at 81 K is in excellent agreement with the resistivity measurement. The critical current density J_c determined from the magnetic hysteresis loop is about 4×10^6 A/cm^2 in 3 kG at 4.2 K and 1×10^6 A/cm^2 in 3 kG at 60 K. These values are comparable to those of good c-axis-oriented epitaxial 1:2:3 films.[5,9]

In Fig. 4, we show that the Hall coefficient data R_H for this unfaulted 2:4:8 sample (curve A) are smaller than those of the 1:2:3 material (curve B),[10] implying higher carrier density, at least within the framework of a simple single-band theory. The 1:2:3/2:4:8 mixed sample (curve C) with stacking faults has the Hall coefficient value in between those of the 1:2:3 sample and the unfaulted 2:4:8 sample. The linear temperature dependence of $1/R_H$ of the unfaulted 1:2:3 phase takes on more curvature as the new stacking sequence appears as seen in Fig. 2. The unfaulted 2:4:8 case displays more complex behavior in this temperature range. It is interesting to note that the temperature at which the inverse Hall coefficient for the unfaulted 2:4:8 phase extrapolates to zero coincides with the temperature at which the resistivity extrapolates to zero. All the samples showed hole-type Hall effects. Finally, we have made preliminary ir reflectance measurements on the unfaulted 2:4:8 material. The results show behavior similar to the 1:2:3 material but with a generally higher reflectance, consistent with the higher carrier density.

We will now interpret these data in terms of the proposed 2:4:8 structure. The fact that the T_c of the unfaulted 2:4:8 sample is only slightly lower than that of a good 1:2:3 sample indicates that high-T_c superconductivity does not depend on the precise ordering of the copper-oxygen layers in the 1:2:3 structure. Furthermore, if 2:4:8 has a different Cu—O chain configuration from 1:2:3, this would imply that the Cu—O chains are not crucial for high T_c, in contrast to models[11] which assign the Cu—O chains a crucial role in the superconducting mechanism of the high T_c. A possible role of these layers is to couple together the two adjacent Cu—O_2 planes; thus, by adding another copper-oxygen layer between the Cu—O_2 planes, the coupling between the Cu—O_2 planes becomes weaker, resulting in a slightly lower T_c. Another possible role of the copper-oxygen layers between the Ba—O layers is to dope the system with carriers.

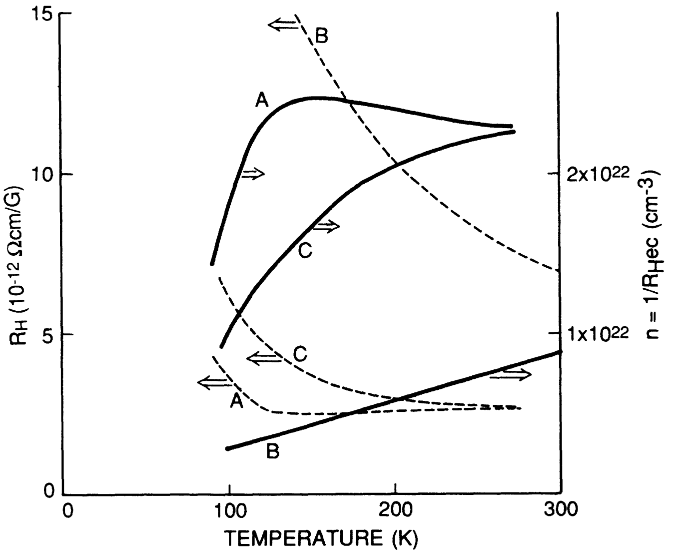

FIG. 4. Hall coefficients R_H and $n=1/R_Hec$ of a c-axis-oriented unfaulted 2:4:8 sample (curve A), a typical c-axis-oriented 1:2:3 sample (curve B), and a c-axis-oriented faulted 2:4:8 sample (curve C).

While the effect of the extra copper-oxygen layer on T_c is relatively small, the effect on the normal-state properties is significant. For example, even though both the 1:2:3 and the 2:4:8 materials show a linear temperature dependence of the resistivity, the absolute value of the resistivity of 2:4:8 is lower than 1:2:3 and its extrapolates to zero at 55 K whereas the 1:2:3 material extrapolates to zero near 0 K. The lower resistivity might originate from the higher carrier density in 2:4:8 material. However, the extrapolation to zero resistivity at 55 K, which we have not seen in any of our other materials, presents a more difficult problem. One possible explanation is that there exists a scattering mechanism in these materials with a characteristic temperature higher than room temperature such that, in the temperature range over which we have been measuring, the temperature dependence of the resistivity is actually a linear approximation to an underlying nonlinear dependence. If this is true, it follows that the apparent linear temperature dependence in these materials is an artifact (similar to the Gruneisen-Bloch formula[12] for pure metals). However, this interpretation requires that the residual resistivity of the 1:2:3 material be much greater than that of the 2:4:8. Finally, the temperature dependence of $1/R_H$ for the 2:4:8 phase is different from that of 1:2:3. The former is not monotonically decreasing and the latter is. Metals that can be described by single-band theory have temperature-independent Hall coefficient. Evidently, a single-band theory is inadequate and two or more bands would be necessary to adequately account for both the anomalous Hall coefficient and resistivity in a single-electron picture.

In summary, we have found additional evidence that stacking faults in the form of extra copper-oxygen layers can be ordered to form a new phase, the 2:4:8 phase. While the unfaulted 2:4:8 phase has T_c of 81 K, faulted 2:4:8 phase can have T_c as high as 96 K, higher than normally seen in good 1:2:3 films. The small change in T_c implies that the precise ordering of copper-oxygen layers in 1:2:3 is not crucial for the high T_c. The normal-state properties of 2:4:8 phase differ significantly from those of the 1:2:3 phase: the 2:4:8 phase has lower resistivity, which extrapolates to zero at temperature of 55 K; its Hall coefficient is smaller and it has a different temperature dependence from that of 1:2:3 phase. The extra copper-oxygen layers seem to play an important role in the normal state.

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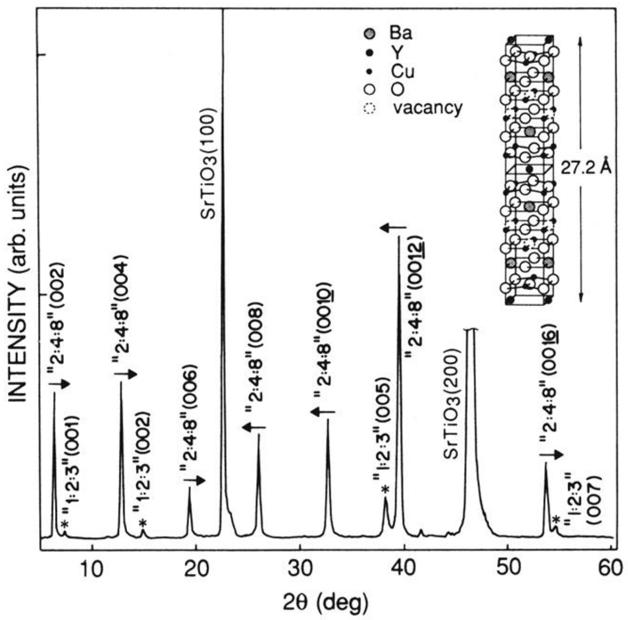

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