

## Phase transformations in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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(Received 24 October 1988)

Isothermal annealing experiments have been carried out over a wide temperature range (200–700°C) to study the mechanisms of the tetragonal-to-orthorhombic phase transformation. The annealed samples were analyzed by means of x-ray diffraction, electrical resistivity and magnetization measurements, and polarized light microscopy. The x-ray diffraction and magnetization results show that the tetragonal-to-orthorhombic phase transformation proceeds isothermally, indicating an oxygen diffusion-controlled process. Data from the polarized light microscopy show that a phase boundary exists between the tetragonal-to-orthorhombic phases, which moves gradually as a result of oxygen diffusion, from the sample surface towards the center, as annealing time is extended. Twinning occurs as oxygen is increased to just above 6.5, and twin boundaries are found to extend through all the grains even near the moving phase boundary. This twinning clearly indicates a martensite-related shear transformation. Transport properties, diffusion mechanisms, and the tetragonal-to-orthorhombic phase transformation process are discussed.

### I. INTRODUCTION

Since the discovery of 90-K superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,<sup>1,2</sup> research has been carried out to understand the superconducting and structural properties of the compound. The structural behavior and the phase transition have been extensively studied by neutron-,<sup>2-4</sup> electron-,<sup>5-8</sup> and x-ray-diffraction<sup>9,10</sup> methods. The results have shown that the compound has an orthorhombic crystal structure with space group *Pmmm*. The unit cell consists of  $\text{CuO}_2$  sheets in the *a-b* planes and  $\text{CuO}_3$  linear chains along the *b* axis, which are associated with the 90-K superconductivity. The orthorhombic structure has been found to undergo an order-disorder transition at near 700°C. The phase above 700°C has been identified to have a closely related tetragonal structure which exhibits semiconducting behavior.

Using neutron diffraction,<sup>11-12</sup> researchers have determined that the orthorhombic-to-tetragonal phase transition is accompanied by a decrease in oxygen occupancy along the *b* axis between the Cu(1) atoms. As the total oxygen content of the sample is decreased to near 6.5, the occupancies along both the *a* and *b* directions between Cu(1) atoms become equal, and the orthorhombic-to-tetragonal phase transition occurs. This observation suggests that high- $T_c$  superconductivity is related to the one-dimensional chains in the unit cell.

Previous studies on crystal structure and phase transitions have concentrated mainly on the structural properties in the thermodynamic equilibrium of the system. Very few data have been reported on the kinetics of the phase transformations, which is in an important area enabling an understanding of the mechanism of phase transformation.

Based on the temperature and time dependence of the transformed phase, two groups of transformation have been established: "nucleation and growth" and "martensite" reactions. In the first group, the new phase nucleates heterogeneously in certain regions of the sample matrix

and then grows into the old one through an interphase boundary movement at relatively slow speed. Diffusion is usually involved, since the atoms need to go across the interphase boundaries during the transformation to achieve the concentration equilibrium. As the transformation proceeds isothermally at a given temperature, the fraction of the new phase increases with time. In the second group, large amounts of atoms are moved in a shear fashion. The transformation is very rapid (virtually independent of time) and usually diffusionless. The amount of transformation is dependent on temperature (instead of on time as in the case of nucleation and growth reactions) below a temperature threshold ( $M_s$ ). High reversibility of the transformation is also a common feature of martensitic reactions.

In this paper, we discuss the mechanisms of phase transformation in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and associated electronic behavior. Some previous studies of phase transformations are summarized.

### II. TETRAGONAL-TO-ORTHORHOMBIC PHASE TRANSITION

Previous results<sup>13,14</sup> have indicated that tetragonal (*T*) to orthorhombic (*O*) phase transition is accomplished through the nucleation and growth process governed by oxygen diffusion. Some typical x-ray diffraction plots are shown in Fig. 1 for samples annealed at 400°C for different times. These 1-g sample pellets with approximately 11-mm diam. and 1.7 mm thick were sintered in air at 950°C for 4 h. After sintering, the samples were quenched to 400°C and held isothermally. After annealing at 400°C for different times, the samples were quenched in air to room temperature on an Al plate. The detailed preparation procedures can be found elsewhere.<sup>13</sup> As shown in Fig. 1, the diffraction peaks for the *T* phase disappear as the annealing time is extended. Simultaneously, the *O* phase peaks intensify indicating that the

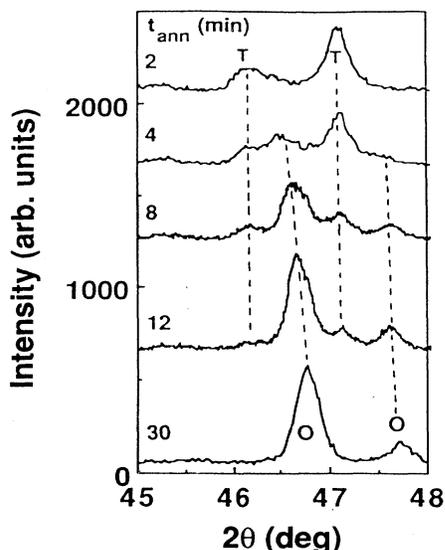


FIG. 1. X-ray diffraction intensity vs  $2\theta$  in the region around  $2\theta=46^\circ$  showing the growth of orthorhombic phase in the tetragonal matrix with increasing annealing time.

amount of transformed *O* phase increases with time.

Electrical resistivity data are consistent with the x-ray diffraction results. As can be seen in Fig. 2, a resistive drop is observed for the sample annealed for 4 min at 400°C, indicating that a small amount of *O* phase has

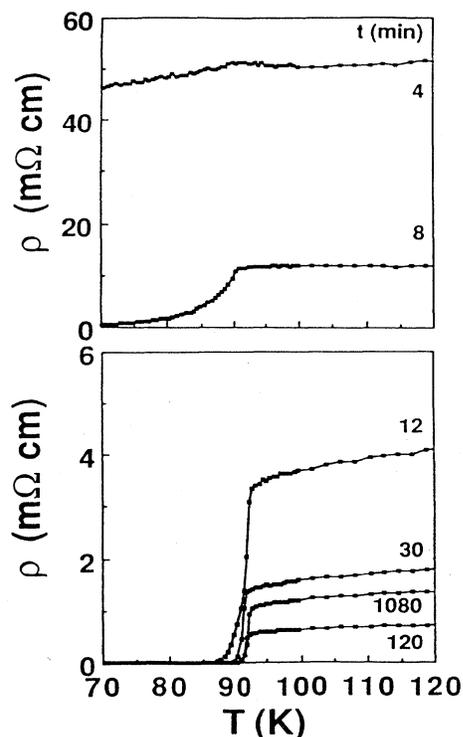


FIG. 2. Resistivity vs temperature near 90 K for the samples annealed at 400°C for the times indicated. The onset temperature is the same for all the samples examined.

formed. However, the entire sample is not yet superconducting. Percolative superconductivity is established as the annealing time is extended to 8 min. However, the transition is rather broad, indicating a great inhomogeneity of oxygen content in the sample. As expected, the transition sharpens with the increasing annealing time. Using an iodine titration technique, we have measured the oxygen content of these samples. The oxygen concentration is plotted against annealing time shown in Fig. 3. As can be seen from this figure, the total oxygen content of the sample increases gradually from  $x=6.28$  to 6.92 as annealing time extends from 2 min to 18 h. Previous studies<sup>15</sup> have shown that  $T_c$  values are near 60 K for  $6.5 \leq x \leq 6.75$  and 90 K for  $6.75 \leq x \leq 7$  in the well-equilibrated states. However, as shown in Fig. 2, all the samples have a single resistive drop at 90 K, although their oxygen content is ranging from  $x=6.28$  to 6.92. This means that the sample consists of a mixture of *T* phase and 90-K *O* phase. The increase in total oxygen content is caused by the increasing amount of the 90-K *O*-phase in the sample.

In order to study the mechanism of the *T*-*O* transformation, a magnetization experiment was carried out to determine the volume fraction of 90-K *O* phase  $\xi$  transformed at time  $t$  at 400°C. The experimental details can be found in Ref. 14. The relation between the volume fraction of transformed *O* phase  $\xi$  and annealing time  $t$  obtained from the magnetization experiment is shown in Fig. 4. The isothermal transformations can generally be expressed by

$$\xi = 1 - \exp(-Kt^n),$$

where  $K$  is associated with the nucleation and growth rate and  $n$  depends, over a wide temperature range, only on the growth geometry.<sup>16</sup>  $K$  and  $n$  are determined by plotting  $\ln\{1 - (1 - \xi)\}$  vs  $\ln t$  [Fig. 5(a)]. The slope and intercept of the line obtained give the values of  $n$  and  $K$ , respectively. The Avrami relation obtained is

$$\xi = 1 - [\exp(-0.001t)].$$

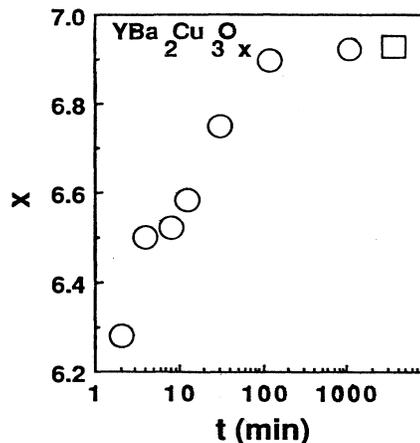


FIG. 3. The oxygen content  $x$  in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  as a function of annealing time for samples annealed at 400°C. The sample annealed in flowing  $\text{O}_2$  is indicated by the square. These data are obtained from an iodine titration technique. The size of the symbol approximates the error in the value of  $x$ .

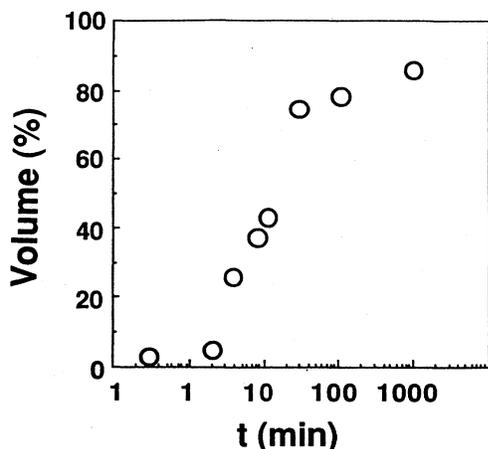


FIG. 4. The volume fraction of a superconductor as a function of annealing time at 400 °C.

The actual Avrami fitting of the experimental data is shown in Fig. 5(b). Possible interpretations of the fitting result are as follows. For interface-controlled growth such as polymorphic changes and order-disorder transitions, the exponent  $n=1$  corresponds to the growth condition of

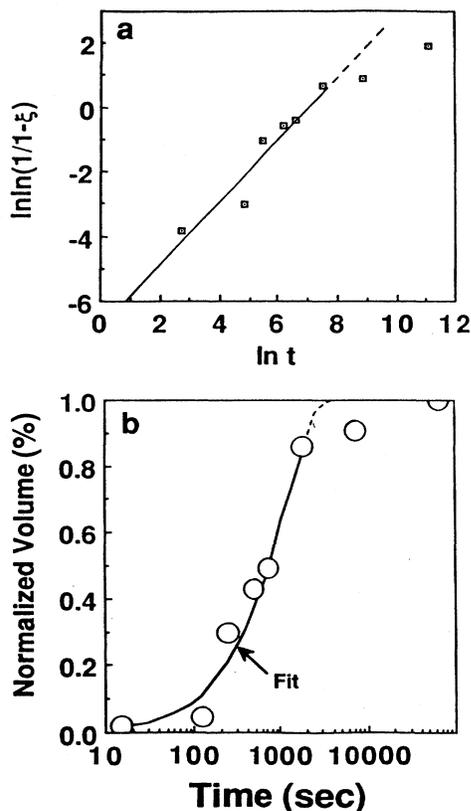


FIG. 5. (a)  $\ln[\ln(1/(1-\xi))]$  vs  $\ln t$  from which the exponent  $n$  is obtained. The line shown has a slope corresponding to  $n=1$ . (b) The volume obtained using the parameters from (a). The volume of the transformed 90-K orthorhombic phase has been normalized to the value obtained after 18 h of annealing at 400 °C.

grain boundary nucleation after saturation. This means that the nucleation occurs at grain boundaries where oxygen diffusion may be more rapid relative to the bulk. After the nucleation has saturated, the  $O$  phase grows into the grains as planar growth fronts. It is possible that the  $T$ - $O$  phase transition is interface controlled, since the oxygen composition difference is small [oxygen content  $x=6.5$  has been found to be a rather sharp boundary between the parent ( $T$ ) and product ( $O$ ) phases]. On the other hand, in principle, the growth of order-disorder transitions is generally interface controlled.<sup>17</sup>

For diffusion-controlled growth, as pointed out by Ham<sup>18,19</sup> and Wert and Zener,<sup>20</sup>  $n=1$  represents a growth condition of rods with long dimensions compared with the grain separation. A scanning electron microscopy photograph reveals the elongated rodlike grains in the sample (Fig. 6). This suggests that the growth fronts are directed to the longer axes ( $a$  or  $b$ ) of the grains along which oxygen diffusion is likely more rapid compared with diffusion along  $c$  axis.

A recent study<sup>21</sup> using polarized light microscopy on some isothermally annealed samples at 400 °C showed some interesting features of the  $T$ - to- $O$  phase transformation. As shown in Fig. 7(a), the sample annealed at 400 °C for 4 min has a layer of transformed  $O$  phase on the surface. A clear phase boundary separating both  $T$  and  $O$  phases can be seen in the figure. In the transformed  $O$ -phase region, each grain is twinned, whereas the tetragonal-phase region possesses rather uniform and untwinned microstructure. The phase boundary moves towards the center of the sample gradually as the result of oxygen diffusion. This movement is depicted in Fig. 7(b), which shows that the layer of transformed region has thickened as the annealing time has increased to 8 min. A magnified phase boundary of this sample is shown in Fig.

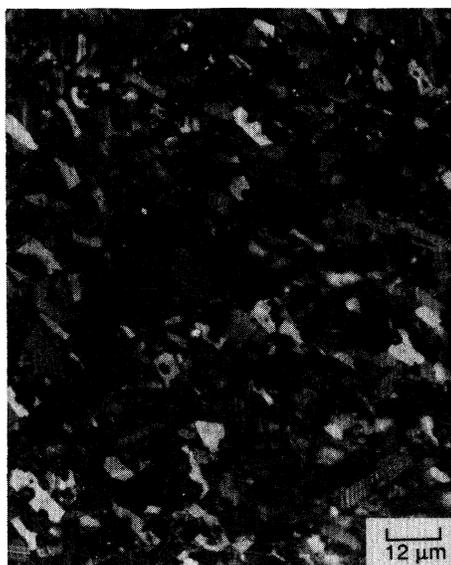


FIG. 6. A polarized light photo showing the elongated rodlike grains in a sample that was slowly cooled from sintering temperature 950 °C to room temperature in air.

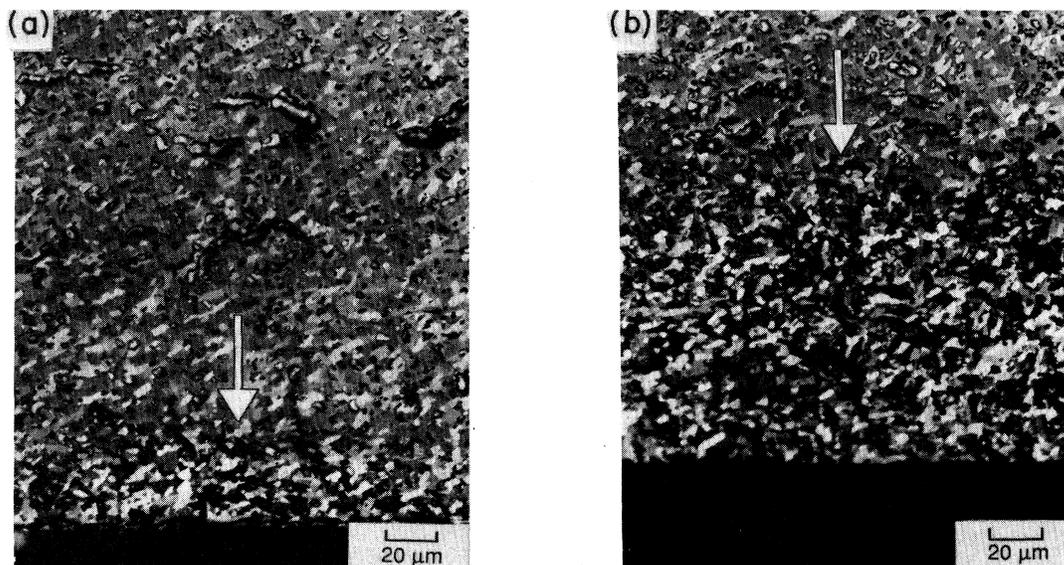


FIG. 7. Polarized light photographs showing the oxygenated layer in the samples that are annealed at 400°C for (a) 4 min and (b) 8 min.

8. At 30 min, the entire sample has transformed into the orthorhombic phase after the two phase boundaries have met at the center of the sample.

It appears that the  $T$ - $O$  phase transition occurs through homogeneous shear, which is related to the martensitic reaction. Only very small amounts of oxygen diffusion may be involved for such shear transformation since the  $T$  and  $O$  phases have virtually the same composition at the beginning of the phase transition. After the shear process, oxygen gradually increases from 6.5 to near 7.0 as anneal-

ing proceeds. Clearly, a critical oxygen concentration value of 6.5 is required for nucleation to occur and to continue. As oxygen diffuses into the sample matrix from the surface, nucleation takes place in the regions where the oxygen content has just exceeded 6.5. The nuclei then grows rapidly to the maximum size (the grain size) through mechanical twinning. A coherent interface may be considered between the  $T$  and  $O$  phases during the transformation. This interface could be the (110) plane as the twin boundary observed by transmission electron microscopy.<sup>22,23</sup> The motion of the phase boundary is obviously controlled by the oxygen diffusion. If assuming the boundary the "interphase boundary" between the two phases, the  $T$ - $O$  transition may be considered a nucleation and growth reaction instead of a martensitic reaction.

Figure 9 is an isothermal transformation diagram

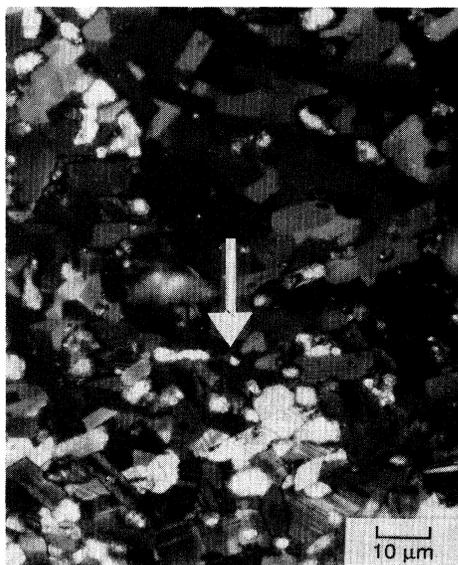


FIG. 8. The magnified phase boundary shown in Fig. 7(b) separating the orthorhombic (twinned) and tetragonal (untwinned) phase regions.

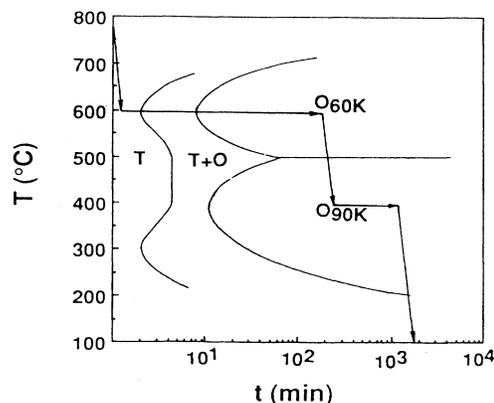


FIG. 9. The time-temperature-transformation diagram established based on the electrical behavior and x-ray-diffraction results of the samples. The actual cooling path for studying 60- to 90-K phase transition is drawn in the diagram.

[time-temperature transformation (TTT) diagram] based on the kinetics of the transformation over a wide temperature range (200–700 °C) in air.<sup>13</sup> As can be seen in this figure, two distinct superconducting phase regions occur within which the samples have sharp  $T_c$  values of 60 and 90 K, respectively. The two-phase regions are separated by a sharp boundary at 500 °C. This is consistent with the previously observed plateau in the  $T_c$  versus oxygen content diagram<sup>15</sup> and with results from quenching experiments.<sup>24</sup> As can also be seen in Fig. 7 that there are two “noses” being the starting and finishing lines of the transformation indicating two different kinetics of the transformation.

The TTT diagram established for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is useful for understanding kinetics of phase transformation during different heat treatments. For instance, if a sample is rapidly quenched from above 700 °C to room temperature through the single tetragonal phase region, the resulting structure is a single tetragonal phase. A single 90-K orthorhombic phase can be obtained by slowly cooling through the 90-K phase region. Obviously, quenching a sample from the 60-K phase region to room temperature can produce a 60-K orthorhombic structure. It has often been observed that insufficient quenching rates result in resistive drops at different temperatures, indicating that the samples have simply gone through the  $T$  and  $O$  phase region.

It should be noted that the shape and the location of the isothermal curve may be affected by any change of oxygen diffusion rates in the material since the phase transformation is sensitively diffusion controlled. At a given temperature, the time required for the phase transformation to complete is prolonged if diffusion is slowed down by increasing the relative density of the sample. The TTT diagram established in this research is for the samples with relative density of 85%. Other factors such as sample and grain size and stoichiometry can also affect oxygen diffusion, in turn affecting the shape and location of the isothermal curve.

### III. 60- TO 90-K PHASE TRANSITION

Many previous studies have shown that two phases exist in the material with 60- and 90-K superconductivity.<sup>15</sup> Transmission electron microscopy work has indicated that there are structural differences between these two phases. A model proposed by Alario-Franco *et al.*,<sup>5</sup> for example, shows that every other Cu(1)-O(1) chain along the  $b$  axis is removed for oxygen near  $x=6.6$ .<sup>5</sup> The result is a doubling of the unit cell having a stoichiometry of  $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$ . The corresponding  $T_c$  value is near 60 K.

Other studies suggest that the two phases also have different electronic and magnetic characteristics. One recent experiment, for example, indicates that 60-K phase has very low upper critical field ( $B_{c2}=15$  T) compared with the 90-K phase ( $B_{c2}=98$  T).<sup>25</sup> The derived superconducting and normal-state parameters based on these data reveal electronic and magnetic differences for the 60 and 90-K phases.

The phase transition between these two thermodynamic equilibrium states is of great interest. An experiment to

study the 60- to 90-K phase transition was carried out.<sup>26</sup> The samples were equilibrated at 600 °C in air for 2 h to obtain a 60-K superconducting phase. These well-equilibrated samples were then quenched from 600 to 400 °C in air for the phase transition to occur. Each sample was quenched to room temperature in air after different annealing times at 400 °C. The cooling path is indicated in Fig. 9. The  $T_c$  values and oxygen content of the samples were subsequently measured (see Fig. 10). As can be seen in Fig. 10, the 60-K phase transformed into the 90-K phase very abruptly (< 20 sec). No intermediate  $T_c$  values are observed in both resistivity and Meissner effect experiments. As can also be seen from Fig. 10, the 60- to 90-K phase transition takes place over a very narrow oxygen content range. This means that the transition does not require significant diffusion as in the case of the  $T$ - $O$  transformation. These experimental observations suggest that the 60- to 90-K phase transition may also be related to the martensitic reaction.

In the sample being equilibrated at 600 °C, shear occurred and resulted in twins with rather fine twin boundary separations. The corresponding equilibrium oxygen content ( $x=6.62$ ) is associated with 60-K superconductivity. When the sample's temperature was rapidly lowered to 400 °C, the twin boundary separations tended to widen to around 1200 Å, which may involve a further mechanical shear process driven by higher external stress in the lower temperature range. It is consistent with rapid shear process that the  $T_c$  value of the system abruptly in-

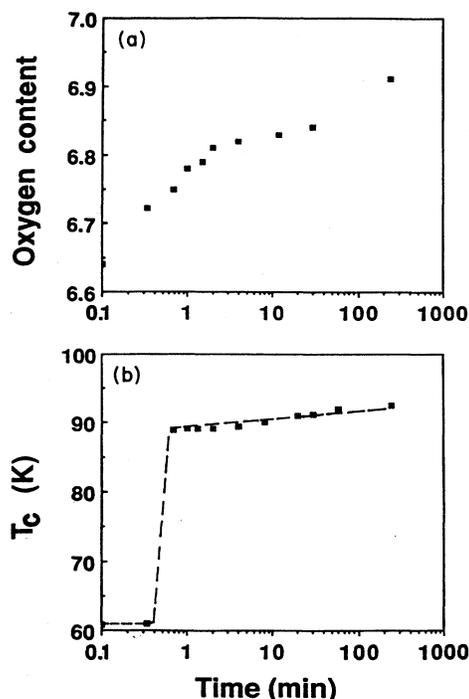


FIG. 10. (a) Oxygen content  $x$  in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  as a function of annealing time for samples annealed at 400 °C. The oxygen content data are obtained from an iodine titration technique. (b) Superconducting transition temperature  $T_c$  (on set) vs annealing time for the samples annealed at 400 °C.

creased from 60–90 K as the sample was quenched from 600 to 400 °C annealed at 400 °C for only 40 sec. Such fast change in  $T_c$  values is not possible if the transition involves a diffusion-controlled nucleation and growth process.

#### IV. DISCUSSION

$T$ - $O$  phase transformation has been found to proceed isothermally, and experimental results suggest that it is an oxygen diffusion-controlled isothermal shear transformation. However, this observation does not preclude the possibility of isothermal martensitic transformation which is completely diffusionless. Some indications of martensitic transition are summarized as follows.<sup>27–30</sup>

(1) The martensitic transformation is accomplished by a cooperative movement of large amounts of atoms in a shear fashion. The parent-product interface (habit plane) can move at a high velocity over a wide temperature range. Thus, at a constant temperature, the parent phase transforms into the product phase very rapidly. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , mechanical shear occurs simultaneously as the local oxygen concentration is increased to above 6.5.

(2) Many martensitic transformations are associated with mechanical twinning. The martensitic transformation is a shear process transforming the initial crystal to a different structure by producing the twinning shear. A martensite plate usually has an internal twinned structure. The coherent twin boundaries as the mirror symmetric planes are often observed in the martensite structure. For  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound, the orthorhombic phase has been found to be severely twinned. As the  $T$ - $O$  phase transformation proceeds, a volume change in unit cell takes place due to the oxygen ordering along the  $b$  axis. A shear stress is created when the  $a$ - $b$  plane changes from a square to a rectangle. To accommodate the volume stress, the lattice structure must deform plastically so that the energy of the system is lowered. Twinning is one way of deforming the material plastically in systems that are lacking slip planes. Therefore, when the shear stress reaches a critical value (probably corresponding to  $x=6.5$ ) resulting from the oxygen ordering, twinning occurs very rapidly.

(3) The martensite transformation does not require thermally activated diffusion as does a nucleation and growth reaction. The parent and product phases usually have the same composition. Since shear process occurs at low-oxygen content level (just above 6.5) in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , the oxygen contents of both the  $T$  and  $O$  phases should be very close at the beginning of the transformation. Therefore, the shear process may not require any oxygen diffusion. The oxygen content of the sample gradually increases from 6.5 to 7.0 after the completion of the mechanical shear process. However, the nucleation of the  $O$  phase is induced by oxygen diffusion, which can be seen from the movement of the phase boundary shown in Fig. 8.

(4) The amount of transformation is temperature dependent, rather than time dependent as are nucleation and growth reactions. Spontaneous transformation occurs at a fixed temperature ( $M_s$ ). The fraction of transformed

martensite increases with the decreasing temperature until the temperature ( $M_f$ ) is reached. At a given temperature below  $M_s$ , transformation does not proceed isothermally. It has been observed in this research that the  $T$ - $O$  phase transformation is a diffusion-controlled isothermal process, which may appear to be a typical nucleation and growth reaction. However, if we imagine the case that the tetragonal phase had an oxygen content of 7.0, the  $T$ - $O$  transformation would be completely athermal since diffusion were no longer required. Previous analysis<sup>23</sup> of 60- to 90-K phase transition has shown that after 40 sec of annealing at 400 °C, the entire sample is already a single 90-K phase, with the Meissner effect measurements indicating a typical martensite-related athermal transformation.

(5) The relative movement of the atoms is very small during the transition (usually less than the nearest-neighbor separation). It has been observed by transmission electron microscopy (TEM)<sup>31</sup> that in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , there is only one-degree splitting of the spots in the selected area diffraction across the twin boundary (110). This indicates extremely small movement of the atoms associated with the phase transformation.

(6) During the martensitic transformation below  $M_s$ , transformation does not continue immediately if the sample is held at a given temperature for a period of time and cooled again (a process called stabilization). The martensitic transformation is often incomplete as a result of stabilization of the parent phase; that is a certain percent of the parent phase remains untransformed. A recent study<sup>22</sup> has shown that the orthorhombic phase formed at different temperatures during slow cool may have different structural properties which could, in turn, affect the superconducting properties. In particular, the  $T$ - $O$  phase transition process generates shear bands on the surface of the grains against the same type of bands formed from adjacent grains. This may create high stress fields at grain boundaries which could decrease superconducting properties such as  $T_c$  and  $H_{c2}$  in these regions. The weak links may, therefore, be associated with the nature of the shear transformation.

(7) High reversibility of the transformation is another characteristic of martensitic transformation. Some *in situ* TEM experiments<sup>22,23</sup> have shown that twinning occurs very rapidly as the temperature is lowered below 400 °C. Twin boundaries become sharper and disappear quickly as temperature is raised above 400 °C. This process is highly reversible during thermal cycling.

#### V. CONCLUSION

$T$ - $O$  phase transformation in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is an oxygen diffusion-controlled isothermal shear transformation. However, the mechanical shear process may not involve diffusion, so the transformation may also be martensitic. The 60- to 90-K phase transition is accomplished through further shear driven by higher external stress in the lower temperature ranges. Shear transformation usually forms shear bands on sample surfaces. These bands are located at grain boundaries in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and cause highly stressed regions. The stressed regions are sensitive to

externally applied magnetic field because of their low  $T_c$  and  $H_{c2}$  values and thus are responsible for weak links.

#### ACKNOWLEDGMENTS

The author would like to thank P. C. Clapp for valuable discussions on martensitic transformation mechanisms.

The author would also like to thank D. W. Capone II, K. C. Goretta, K. Zhang, G. T. Gourdey, W. L. Kwok, and A. Umezawa for stimulating discussions and experimental assistance. The author acknowledges A. Essling and D. Graczyk for their oxygen content measurements. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences—Materials Sciences, under Contract No. W-31-109-ENG-38.

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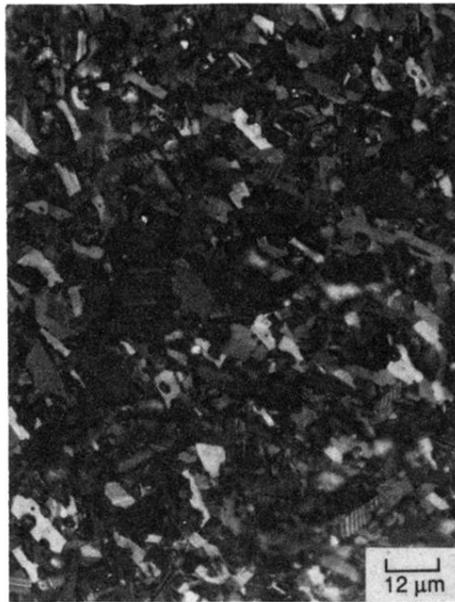


FIG. 6. A polarized light photo showing the elongated rodlike grains in a sample that was slowly cooled from sintering temperature 950°C to room temperature in air.

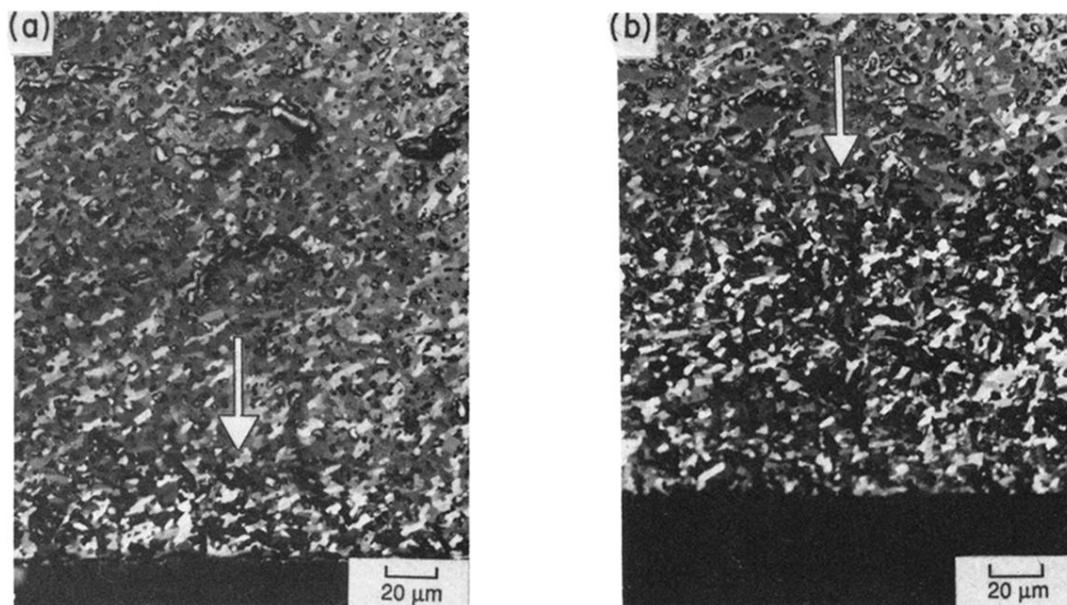


FIG. 7. Polarized light photographs showing the oxygenated layer in the samples that are annealed at 400°C for (a) 4 min and (b) 8 min.

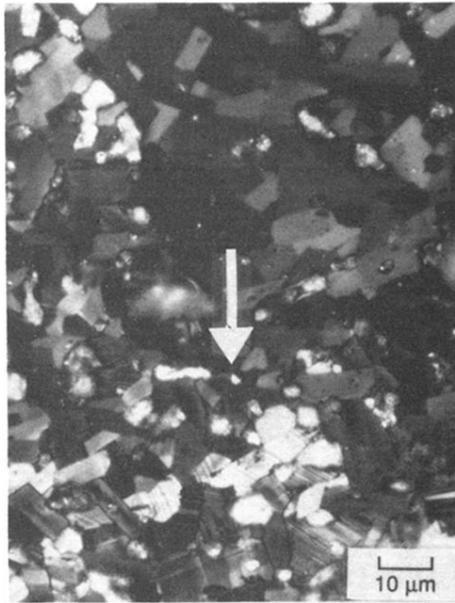


FIG. 8. The magnified phase boundary shown in Fig. 7(b) separating the orthorhombic (twinned) and tetragonal (untwinned) phase regions.