Strain Relief Twinning Due to Vacancy Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$

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Introduction

The orthorhombic superconducting oxide $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($6.3 < x \leq 7$) [1] is usually heavily twinned. The twin boundaries are likely to influence the intra-grain critical superconducting current density attainable. The twinned microstructure arises from a tetragonal-to-orthorhombic structural symmetry transition due to vacancy ordering. It occurs during cooling and during an increase in oxygen content. In this paper we summarize and analyse the relevant observations and suggest a path of the microstructural transition.

Phase equilibria

The equilibrium oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($6 \leq x \leq 7$) depends on temperature and oxygen partial pressure $p(\text{O}_2)$. By using thermogravimetry, iodometry or reduction combined with weight measurement, [2-5] have measured the oxygen content as a function of temperature for different values of $p(\text{O}_2)$. Fig. 1a shows these results for four levels of $p(\text{O}_2)$. It can be deduced that specimens annealed in pure oxygen at temperatures below about 600 K attain the maximum possible oxygen content O_7 . Equilibration of the oxygen content is determined by $p(\text{O}_2)$ and by the chemical diffusion coefficient $\bar{D}$. Rothman et al. [6] have reviewed literature data of $\bar{D}$. They scatter widely due to differences in specimen quality and to the difficulty to assign correct diffusion lengths in porous samples. However it can be concluded that in dense layers of about 1 mm thickness isothermal equilibration at about 600 K takes months of annealing time. - Using thermal analysis [7,4] the oxidation enthalpy per oxygen atom was reported to be 0.9 or 1.1 eV, respectively. In [8] it was found that the oxidation enthalpy depends on the oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_x$. It ranges from 0.7 eV at lower oxygen contents to 1.0 eV near O_7 .

At high temperatures and/or low oxygen partial pressures $\text{YBa}_2\text{Cu}_3\text{O}_x$ is tetragonal. On cooling in an oxygen atmosphere the oxygen content increases. Concomitantly a phase transition from tetragonal (t) to orthorhombic (o) symmetry occurs at a certain value of x . The t-o-phase transition was shown to be a classical order-disorder transition [9,10]. Its structural features are treated below. The t-o phase boundary $T_o(x)$ has been determined by several authors using x-ray and neutron diffraction [4,11-13], resistivity measurements [4,14] or thermogravimetry [15]. Fig. 1b summarizes the results of these measurements. Disregarding differences in experimental accuracy a least square fit through all data points yields a slope of $1.0 \cdot 10^{-3}/\text{K}$ for $6.3 \leq x \leq 6.7$.

Tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$ is not superconducting. The orthorhombic phase shows a strong dependence of the critical temperature T_c on oxygen content x . The results of [11,16-18] are shown in Fig. 1a. Some authors [11,16,18,19] report a plateau of $T_c \sim 60$ K at $6.6 < x < 6.8$ and claim the occurrence of a second orthorhombic phase in

Fig. 1: (a) Ordering temperature T_0 (see Fig. 1b), Néel-temperature T_N , and critical temperature T_c versus oxygen content x in $\text{YBa}_2\text{Cu}_3\text{O}_x$. Equilibrium oxygen content as function of temperature and oxygen partial pressure as reported by different authors. (b) Ordering temperature T_0 as a function of the oxygen content x in $\text{YBa}_2\text{Cu}_3\text{O}_x$ as derived by different authors.

this range. However, the evidence is not conclusive when taking the scatter of the data into account. - Tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$ orders antiferromagnetically at low temperatures. The Néel temperature T_N according to [20] is included in Fig. 1a.

With all the above mentioned data the tentative pseudo-binary phase diagram for $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($6 \leq x \leq 7$) in Fig. 1a contains the most likely phase relations and critical temperatures to our knowledge. Below $x = 6$ and above $x = 7$ $\text{YBa}_2\text{Cu}_3\text{O}_x$ tends to decompose or form precipitates [21,22]. The quasi-ternary $\text{BaO}-\text{Y}_2\text{O}_3-\text{CuO}$ phase diagram has been studied by [23]. At high temperatures the "green" phase Y_2BaCuO_5 , BaCuO_2 , CuO and the melt occur in equilibrium with $\text{YBa}_2\text{Cu}_3\text{O}_x$.

Structures and Microstructures.

Basically $\text{YBa}_2\text{Cu}_3\text{O}_x$ has a crystal structure derived from three cubic unit cells of perovskite (ABO_3) stacked along the c -axis, Fig. 2. The cube corners are occupied by Cu, the centres of the edges by O and the body centres by Y and Ba in the succession Ba-Y-Ba along the c direction [24-27]. Stable oxygen vacancies in the Y layer are lowering the oxygen stoichiometry from 9 for the perfect perovskite structure to 7. Further structural vacancies of

Fig. 2: Unit cell of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Fig. 3: The lattice parameters a and b of $\text{YBa}_2\text{Cu}_3\text{O}_x$ plotted against the temperature of quenching after heating in different atmospheres [5].

variable concentration occur in the basal plane, i.e. $\text{Cu}(1)(\text{CuO})$ layers between the Ba layers, such that $6 \leq x \leq 7$. The $\text{Cu}(2)(\text{CuO}_2)$ layers adjacent to the Y atoms show a "dimpled" form. By neutron powder diffraction experiments [9,10] it was shown that in the low temperature phase the oxygen vacancies in the $\text{Cu}(1)$ layers are ordered and located in $\frac{1}{2}00$ sites. Thus, Cu-O chains are remaining along the b axis. This leads to an orthorhombic structure of Pmm space group with parameters $a_0=0.3823$ nm, $b_0=0.3886$ nm, $c_0=1.1681$ nm [27], actually shown in Fig. 2. At high temperatures, i.e. at $T > T_0$, the structural vacancies are disordered and distributed randomly on the $\frac{1}{2}00$ and $0\frac{1}{2}0$ sites. This leads to a tetragonal symmetry of space group $\text{P4}/\text{mmm}$. Fig. 3 gives the results of neutron diffraction work showing the variation of the lattice parameters a_0 , b_0 and a_1 with temperature and oxygen partial pressure. It should be noted that x is determined by T and $P(\text{O}_2)$ such that the oxygen concentration in the basal plane x_b may vary in the range $0 \leq x_b \leq 1$.

TEM investigations are showing streaks and $\frac{1}{2}00$ superlattice reflections in the diffraction patterns. They indicate further variants of vacancy ordering in the $\text{Cu}(1)$ layers of oxygen deficient material [28,29]. The observed doubling of the a_0 axis was interpreted as being due to the formation of Cu-O chains on every other (100) plane only. This structure was proposed to occur as a phase near $x = 6.5$ called O-II [30,31]. It may account for the plateau in $T_c(x)$ near 60 K mentioned above. Still further structural variants due to oxygen ordering have been invoked from the observation of superlattice reflections and theoretical considerations [32]. But they are not immediately relevant to this paper because the present state of investigation does not permit to take these refinements into account.

Fig. 4: Micrographs of twinned orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$. (a) Optical micrograph in reflected polarized light, (b) TEM-micrograph showing two perpendicular sets of twins observed along $[001]$.

The twins observed in light and electron micrographs of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$, Figs. 4a and b, are down to 100 nm (occasionally even less) wide. Most crystals show two sets of twin orientations (never more) intersecting at 90° or at oblique angles. Some grains appear to be twinned in only one direction. They may be twinned solely on one twinning system or may be oriented such that their c-axis lies in the plane of the section; in this case only one trace of the $hk0$ type twin planes can occur even if two twin systems are present. Analysis of electron diffraction patterns of twinned regions yields that twinning occurs on (110) and $(\bar{1}\bar{1}0)$ planes. Fig. 5a shows a $[001]$ diffraction pattern of a twinned

Fig. 5: Electron diffraction pattern of a twinned area of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$ along $[001]$ (a), and (b) schematic key diagram to Fig. 5a, showing the splitting of spots due to (110) twinning (for the sake of clarity the orthorhombicity has been greatly exaggerated).

region with splitting of (110) reflections. The angular deviation of the (110) planes in the two twin orientations is $\varphi \approx 1.6^\circ$, in accordance with other studies yielding $1.6 < \varphi < 1.8^\circ$ [33].

If grains are containing two sets of twin orientations the twins of one set are tapered either at or near the perpendicular twin boundary, Fig. 4b. In TEM investigations interactions of the electron beam may affect the twin configuration. Beam heating or radiation damage by direct displacement of oxygen may lead to disordering and thus to a transformation from the orthorhombic into the tetragonal structure. If oxygen loss to the vacuum inside the microscope is not extensive twins will reappear after some minutes. This re-transformation produces a similar but not identical twin configuration [34].

Across a (110) type twin boundary the a_c and b_c axes are interchanged so that the direction of the Cu-O chains changes by about 90° . Several models of the 110 twin boundary structure have been discussed [35]. Most lattice images of twin boundaries show a width of only one or two cell units [35]. However, at bent or irregular twin boundaries or after beam heating experiments greater widths of up to 5 nm have been observed [36]. To our knowledge no conclusive correlation has been established between twin spacing and superconducting properties such as T_c and J_c as yet.

Discussion

The evidence shows that vacancy ordering of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ compound associated with the t-o structural transition proceeds by increasing the oxygen partial pressure and/or by lowering the temperature through the $x(p(\text{O}_2), T)$ phase boundary shown in Fig. 1a. With decreasing oxygen content and increasing cooling rate the ordering process may remain incomplete or can be suppressed completely. The case of slow cooling under high oxygen partial pressure is most suitable to analyse the path and the structural features of the transformation. According to [9,10] the ordering transition occurs essentially in the temperature range $1 > T/T_o > 0.8$. The rate of vacancy diffusion in this temperature range is sufficient [6] such that with technical cooling rates on the order of deg/min the fractional site occupancy on the $\frac{1}{2}00$ and $0\frac{1}{2}0$ sites can essentially follow thermodynamic equilibrium. For example the average displacement time for the site exchange at 800 K is of the order of 10^{-5} s.

The t-o structural and the accompanying microstructural transitions are most likely to proceed in two stages. Immediately below T_o local fluctuations will lead to the formation of domains with two different orientation variants of the a_c and b_c axes evolving from the two equivalent a_c axes, Fig. 6a. In well fired specimens where each grain consists of a single crystallite of the tetragonal high temperature phase only two orientation variants are possible and they will form elastically strained domain boundaries. On further cooling b_c/a_c increases causing an increase in strain energy density. The continuing enhancement of the internal strains associated with the rapid increase of the axial ratio towards the

Fig. 6: Schematic representation of the structural and microstructural transitions, (a) initial state of ordering with roughly collinear unit cell axes and a diffuse, strained domain boundary, (b) after stress relaxation twinning, strain free (110) twin boundary, (c) illustration of the maximum shear displacement of a twin lamella (all length changes and angles are exaggerated for clarity).

final value of $b_o/a_o \sim 1.018$ may be relieved by twinning. This is a common secondary microstructural change when ordering transformations involve a change in crystal symmetry [37,38]. To this end fluctuations in domain size and configuration will lead to regions of maximum local stress concentration which act as nucleation sites for stress relaxation twins. These may form from two adjacent domains which undergo a rotation such that their common (110) composition plane becomes a (110) (or a $(\bar{1}\bar{1}0)$) twin plane as shown schematically in Fig. 1b. The twinning shear $\bar{S}$ is derived experimentally from the observed orientation difference as $\bar{S} = \tan(\phi/2) = 0.014$. Based on an average twin thickness of $D = 100$ nm the macroscopic shear is $S = 1.4$ nm accordingly which corresponds to $2.5|\langle 110 \rangle|$. This means that reversal of the twinning shear direction is caused by displacements equivalent to about 2.5 basal plane diagonals only. Such a small displacement indicates a small nucleation energy for reversal of the a_o and b_o axes by vacancy re-ordering i.e. an extreme sensitivity of directional diffusion to local stress.

An indirect but very conclusive proof of the two-stage microstructural transition has been found by thermal analysis: on cooling $\text{YBa}_2\text{Cu}_3\text{O}_x$ powders a small exothermic peak is occurring reproducibly at temperatures slightly below T_o . Two examples are shown in Fig. 7. This peak can be attributed to recalescence due to the release of the stored strain energy of the coherency strains associated with the domain structure formed initially. This heat

Fig. 7: Thermal analysis on cooling at 10K/min from above 800°C of $\text{YBa}_2\text{Cu}_3\text{O}_x$ powder samples, particle size $17\mu\text{m}$ FSSS.

release occurs when nucleation and rapid growth of the strain relief twins leads to an almost strain-free microstructure. On heating, thermal analysis shows no such effect, in keeping with the second order characteristics of the transition. Differences in the rate of change of electrical resistivity during cooling and heating [39] may be interpreted correspondingly.

Analogous two-stage ordering processes as suggested in the present case are a common feature of substitutional and interstitial structural order-disorder transitions which are associated with a lowering of crystal symmetry [38]. Antiferromagnetic ordering associated with magnetostrictive symmetry changes such as in Mn-(Cu,Ni) alloys is a further example [40].

Due to the short jump distance for vacancies between the $\frac{1}{2}00$ and $0\frac{1}{2}0$ sites and the correspondingly low nucleation energy of reverse twin formation two conclusions may be drawn: (i) minimal internal shear stresses suffice to induce directional vacancy ordering in orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$ such that strain relief twins occur and are re-arranged to minimize the strain; therefore, (ii) it is practically impossible to obtain twin-free states in samples which extend in size substantially beyond the twin thickness observed in bulk samples, i.e. 100 nm. Moreover, from the assessment of all evidences which were compiled above it is concluded, that a two-step microstructural transition is associated with the t-o phase transformation.

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