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Stoichiometry dependence of oxygen anelastic relaxation in $YBa_2Cu_3O_{7-x}$ and the orthorhombic-to-tetragonal phase transition

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Abstract

Measurements of the elastic energy dissipation coefficient and of the dynamic Young modulus were performed on polycrystalline YBCO samples by the vibrating-reed technique and torsional pendulum, in the frequency range 5–5000 Hz. Two relaxational damping peaks with activation energy $H_{o1}=(1.5\pm0.1)$ eV and $H_{o2}=(1.3\pm0.1)$ eV have been observed above room temperature and their origin is discussed in terms of the short-range oxygen dynamics. The dynamic modulus shows a relaxation in correspondence to the two peaks and a softening attributed to the orthorhombic-to-tetragonal phase transition.

1. Introduction

It is now well established that oxygen plays a key role in high-T_c superconductivity. The structural stability of the well-oxygenated superconducting phase in $YBa_2Cu_3O_{7-x}$ (YBCO) is limited by the oxygen out-diffusion that occurs predominantly in the CuO basal plane (O(4) chain sites) [1, 2]. Several sub-stoichiometric phases can be obtained, characterized by different order degrees of the oxygen sublattice [3]. Observations by electron microscopy have indicated that the so-called ortho-II phase is the most stable among the sub-stoichiometric ones [4]. Corresponding to different degrees of oxygen ordering, differences have been observed in the elementary cell lattice parameters, indicating a strain associated with the fraction of oxygen occupancy in either the ($\frac{1}{2}$ 0 0) or (0 $\frac{1}{2}$ 0) sites. In these conditions anelastic relaxation effects can be observed. Experimental results obtained by different research groups have indeed confirmed that in the temperature range where appreciable oxygen mobility is expected, strong relaxational damping maxima can be detected [5–9]. The results obtained by the different authors show both similarity and differences. Amongst the differences is the number of observed anelastic relaxation peaks.

In this research we have extended our previous measurements to gain further insight into the microstructural features of the orthorhombic-to-tetragonal transformation. Measurements of the elastic energy dissipation coefficient have been performed in controlled stoichiometric conditions to monitor how the oxygen deficiency affects the damping spectra. Finally we try to compare the results with those obtained by other research groups.

2. Experimental

The measurements were made on polycrystalline YBCO specimens prepared by solid-state reaction procedure [10]. Thin bar-shaped specimens obtained by successive consolidation and sintering stages were employed for the anelasticity measurements. A vibrating-reed technique with electrostatic drive and frequency modulation detection of flexural vibrations (10^2–10^4 Hz) and a torsional pendulum (1–10 Hz) were employed. All measurements were performed in an oxygen partial pressure of about 0.5 Pa and at a maximum strain amplitude below 10^{-5}. The oxygen content after specimen preparation and following thermal treatment was determined by iodometric titration. Some thermogravimetric (TG) and derivative thermogravimetric (DTG) measurements were also performed in the same conditions as used for the anelastic measurements.

3. Results

Shown in Figs. 1 and 2 are the energy dissipation coefficients Q^{-1} and modulus M of a YBCO sample brought from room temperature up to about 850 K under diffusion pump vacuum at 3 K min^{-1}. All these measurements, except for the one on the 6.97 oxygen stoichiometry specimen, refer to the same sample. The

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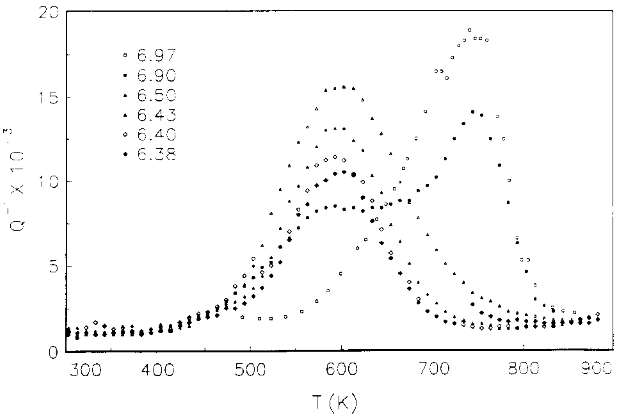

Fig. 1. Elastic energy dissipation in YBCO. All the measurements, except the one on the 6.97 oxygen stoichiometry sample, are successive runs on the same specimen. Room temperature frequency at the beginning of first run: 1.5 kHz.

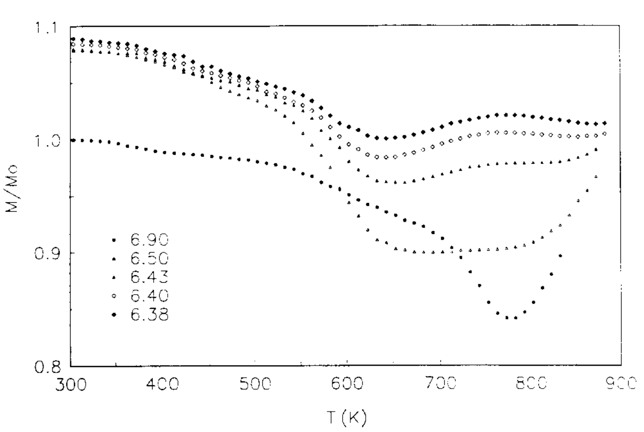

Fig. 2. Normalized dynamic modulus in YBCO. The values listed in the figure are the oxygen stoichiometry of the sample, measured at the beginning of each run. All the measures are successive runs on the same sample; the data are normalized at the first run room temperature value.

same kinds of result were achieved on other YBCO polycrystals (apart from minor differences). In successive runs on the same specimen, the oxygen content (measured at the beginning of each run) is always decreasing: 6.90 on the first run, 6.50 on the second run and so on.

Note in Fig. 1 the presence of two peaks: one at about 600 K and the other at about 750 K, whose strength depends on the oxygen stoichiometry. The lower temperature peak, P_{o2}, increases in intensity as x increases (oxygen outflows the specimen), with a maximum around $x = 0.5$, and decreases afterwards. The other peak, P_{o1}, is generally decreasing as x increases and is completely lost in the background when $x > 0.3$.

The corresponding modulus behaviour is relatively more complicated, although the relaxation (M/M_o decrease) corresponding to the peaks P_{o1} and P_{o2}, the rising trend at higher temperatures, and the room-temperature modulus upward shift with oxygen deficiency are reasonably clear.

4. Discussion

Measurements of the elastic energy dissipation have recently been applied extensively to study oxygen mobility and diffusion in YBCO [6–9,11]. One of the main points to be addressed, and up to now not completely clarified, is the number and nature of thermally activated relaxation processes, observed in the temperature range where appreciable oxygen mobility sets up. Measurements performed by different experimental groups have shown that strong anelastic relaxation effects, dependent on oxygen, may be detected above room temperature at acoustic frequencies. These measurements have also indicated that there is a measurable stoichiometry effect upon the relaxation time τ of the processes: *i.e.* a peak temperature shift by varying the oxygen content in the superconducting orthorhombic phase. This militates against an accurate determination of the anelastic relaxation parameters because measurements in carefully controlled conditions are needed. Another problem concerns the number of relaxation peaks: many authors have reported at first the presence of one peak only [6,8,9,12], but nowadays our observation of two peaks has been largely confirmed. In these measurements we also report the contemporary presence of the two peaks, first seen in $EuBa_2Cu_3O_{7-x}$ [13].

In our measurements, in nearly stoichiometric conditions ($x < 0.1$) an anelastic relaxation peak, previously labelled P_{o1}, is observed [7,13]. At kHz frequency the peak temperature just precedes the modulus instability, clearly seen in Fig. 2, which is the sign of a phase transition between the orthorhombic I and tetragonal phases. Only with measurements performed at lower frequency (reported in Fig. 3), to shift the peak at lower temperature, can the intrinsic anelastic nature of this peak be clearly evinced. The measured activation energy is $H_{o1} = (1.5 \pm 0.1)$ eV [14]. A second peak, previously labelled P_{o2}, was observed at significantly lower temperatures in sub-stoichiometric samples ($x > 0.1$). The corresponding activation energy is $H_{o2} = (1.3 \pm 0.1)$ eV. This value is close to the one recently deduced by Woirgard *et al.* [12] for a peak observed by isothermal measurements. Both peaks can be observed in the internal friction spectrum for intermediate oxygen deficiency values, $0.1 < x < 0.3$ (Fig. 1). The experimental data regarding the relaxation time taken from the measurements of Fig. 1 and from similar measurements not shown here are reported in Fig. 3, together with those obtained from different experimental groups and recently reviewed by Cost and Stanley

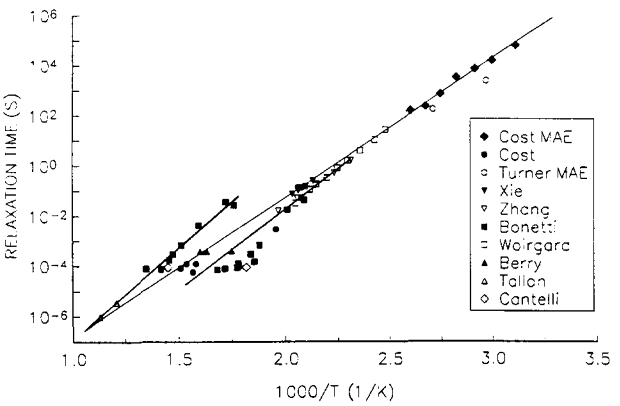

Fig. 3. Arrhenius plot of the relaxation time in YBCO measured by internal friction and in two cases by mechanical after effect (MAE) by different authors. The longer line refers to a fit of all the data with a single peak; the two short lines represent a fit of the internal friction data with two peaks of different activation energy.

[11]. The peak temperature shift observed by Berry *et al.* [8] of the order of 20 K, by varying the oxygen content with prolonged vacuum annealing, suggests a stoichiometry effect on the relaxation time τ. A similar stoichiometric effect was previously observed, by measurements at lower frequency by Xie *et al.* [10], who determined a 20 K [6] peak temperature shift by increasing x from 0.12 to 0.46. This is perhaps why the plot in Fig. 3 shows a wide scatter of the experimental data, particularly evident for the measurements at temperatures higher than about 480 K. At these temperatures, in the usual experimental set up, *i.e.* under vacuum, some oxygen outflow may occur during the measurements. However, the points referring to our P_{o1}, P_{o2} peaks and to the P_{H1}, P_{H2} peaks from Cannelli *et al.* [13], apparently belong to two well separated groups (more than 100 K apart at kHz frequency). So it seems realistic to assume that the internal friction data correspond to two distinct relaxation mechanisms involving oxygen in different environmental habits, *e.g.* those corresponding to the ortho-I and ortho-II phases. The lines shown in Fig. 3 refer to a fit of all the data with one peak only, as suggested by Cost and Stanley [11], and to a fit of the internal friction data with two peaks (P_{o1} and P_{o2}) [14]. It is possible that the calculated values of their activation energy, reported above, are affected by the stoichiometry differences between samples.

The higher activation energy for peak P_{o1} may result from the higher number of nearest O(4) oxygen atoms around the O(5) sites in the ortho-I phase that, on account of the positive interaction energy between O(4) and O(5) [16], should lead to a higher barrier for the oxygen jumps between the (0 ½ 0) and (½ 0 0) sites. Up to now the alternative hypothesis already proposed [7], that P_{o1} is due to an anelastic relaxation process involving the twinned interfaces, cannot be excluded.

We believe the uncertainty between models could be eliminated with the following experiments. A compound very close to YBCO exists, which is claimed to be produced without twins: $YBa_2Cu_4O_8$ [17]. The presence (or lack) of peak P_{o1} in this compound will indicate whether it is due to twins. Peak P_{o1} disappears when the sample undergoes the orthorhombic-to-tetragonal phase transition, with a simple exponential decrease [15]. It is possible to measure, for example with neutron scattering, the kinetics of the phase transformation, in particular during an isothermal annealing in vacuum at a temperature around 690–710 K. From the comparison of the kinetics with which the ortho-I phase turns into the tetragonal phase it should be possible to check if P_{o1} is only present in the ortho-I phase, as it is supposed. This experiment has already been scheduled on a powder neutron diffractometer. The alternative approach, which is to check if P_{o2} is only present in the ortho-II phase, is more difficult to measure, as an oxygen-deficient sample is usually made of very small microdomains with all possible orientations. So the macroscopic symmetry is tetragonal even if the microscopic symmetry is not [18].

To explain the modulus behaviour as a function of temperature as observed in Fig. 2, it is useful to refer to a phase diagram of this compound (Fig. 4). Line 1 in Fig. 4 gives an idea of what happens to a specimen with oxygen content above 6.9 when it is heated up to 850 K and then cooled down to room temperature under vacuum. The orthorhombic–tetragonal phase boundary is crossed at a point whose exact position depends on the details of the oxygen outflow as function of temperature. The point corresponds to the deep minimum seen in Fig. 2 for the curve with oxygen content 6.90. The second line represents the typical

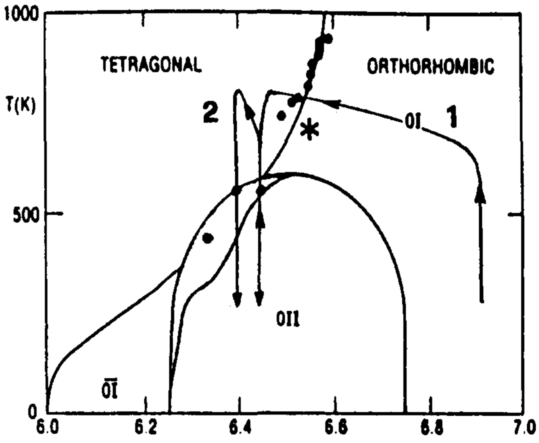

Fig. 4. Computed phase diagram of the YBCO system [19]. The lines numbered 1 and 2 sketch the path followed in such a phase diagram during the first and second run of YBCO samples in measurements like the one shown in Fig. 1.

path of a following run. The orthorhombic II–tetragonal phase boundary is crossed and a little more oxygen is lost.

We have a signature of all this in the modulus behaviour. Up to 500 K at kHz frequency there is a monotonic decrease due to anharmonic effects. Then the relaxation accompanying the P_{o2} peak (feeble in the 6.90 specimen, more intense for all the others) sets in. For all runs except for the first, where a relaxation is in correspondence of P_{o1}, a successive slow decrease, again due to anharmonicity, would then be expected. But a minimum around 650 K is present, instead. This should be due to the orthorhombic II–tetragonal transformation. The minimum is not so deep as in the first run because the transformation is broad, the oxygen content is constant and we are probably in a mixture of the two phases. Finally, at the higher temperatures, the modulus grows, and this is reasonably an effect of the small oxygen outflow. The effect is weaker as the oxygen lost in successive runs is reduced. It is evident from the phase diagram that as some oxygen is lost in each run, the minimum corresponding to the ortho II–tetragonal transition should move to lower temperatures: as it does, in fact, in spite of the uncertainty in its position due to the broadness of the minimum.

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