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Oxygen diffusion and reordering in $RBa_2Cu_3O_{6+x}$

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Abstract

An overview is provided of the thermally activated processes and phase transformations observed in $RBa_2Cu_3O_{6+x}$, in the framework of an interpretation as consistent as possible with them. New measurements are also reported of highly degassed $YBa_2Cu_3O_{6+x}$, where it is shown that the only thermally activated peak left, with an activation energy of 0.11 eV, is reduced in intensity by extreme degassing. This observation supports the hypothesis that such a peak is due to the Snoek-type reorientation of isolated O atoms in the CuO_x plane.

1. Introduction

The dynamics of the O atoms in the CuO_x planes of $RBa_2Cu_3O_{6+x}$ is an intriguing and controversial subject, involving many aspects such as diffusion, ordering and small displacements within the CuO chains in a zig-zag fashion.

All those aspects have been studied by means of anelastic relaxation measurements, and will be briefly summarized in what follows. A more comprehensive overview is made in ref. 1, where an attempt has also been made to provide a consistent picture to explain most of the experimental data. Several points are still controversial, or at least need confirmation. Here we also present some new measurements on highly degassed $YBa_2Cu_3O_{6+x}$, which add new evidence to the hypothesis of an extremely high mobility of the isolated O atoms.

1.1. Possible types of O movements

It seems established that the O(1) positions of the O atoms in the Cu–O chains are in fact split into two off-centre positions, resulting in Cu–O chains which are slightly zig-zagged [2]. As a consequence, the oxygens in the CuO_x planes will undergo two types of jumps and rearrangements: between the O(1) and O(5) positions, and between the much closer off-centre positions. The O(1)–O(5) jumps are most likely responsible for the intense high-temperature dissipation peaks, because they involve a longer distance ($\sqrt{2}\,a$) and a 90° reorientation of the elastic dipole associated with O between the two nearest neighbour Cu(1) atoms. Instead, some of the processes with low intensity and at low temperature could be connected with the off-centre positions.

1.2. High-temperature peaks

The high-temperature processes are characterized by an activation energy of about 1 eV. There are two distinct peaks and their height is a function of the O content, as shown in Fig. 1. The PH2 peak is situated at 700 K (10^3 Hz) in the well oxygenated material. The initial increase of the peak intensity on decreasing the oxygen content induced Xie *et al.* [3] to propose a mechanism based on jumps of O atoms between O(1) and O(5) positions, in the proximity of an O(1) vacancy in the *ortho*-I phase (all Cu–O chains full).

Peak PH1 is observed at around 600 K; it is much broader than a single Debye process and has an activation energy of about 1.2 eV. The fact that it reaches its maximum intensity when the only expected ordered phase is the ortho-II (Cu–O chains alternately filled), strongly suggests that it is associated with O(1)–O(5) jumps within domains of that phase [1, 4]. At low O stoichiometries it is suppressed by quenching from high temperature and develops after ageing above 500 K, so excluding the possibility that it is due to isolated oxygens. No processes are observed above room temperature, which can be ascribed to the Snoek-type relaxation of isolated oxygens.

Elastic anomalies connected with phase transformations are also observed above room temperature: when reducing the O concentration, a frequency-independent dissipation peak and a modulus dip appear around 500 K, which become more intense and structured at the lowest stoichiometries [5].

1.3. Low-temperature peaks

The main effect that is observed in elastic measurements below room temperature is a phase trans-

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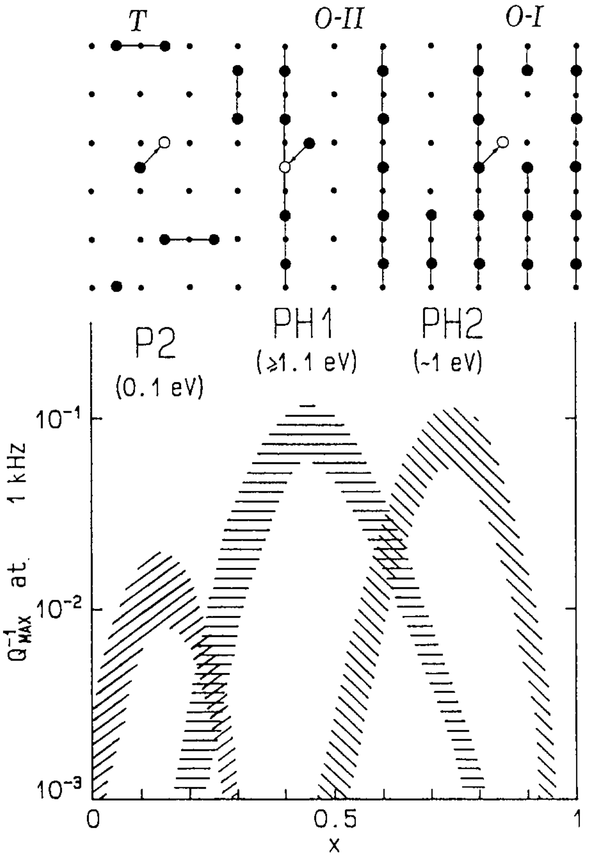

Fig. 1. Intensities of the thermally activated peaks which are attributed to different types of O(1)–O(5) jumps, as a function of the O stoichiometry x. The upper part represents the CuO_x planes with the various jumps (adapted from Ref. [1]).

formation starting below 220 K. It generally appears as a dissipation peak accompanied by a hysteresis of the modulus below 220 K, whose amplitude and extension can vary strongly from sample to sample, and is reduced at low O contents. It seems related to the formation of new twins [6], and attempts have been made to associate such a transformation with the x, T phase diagram [1, 7].

In the fully oxygenated material three thermally activated processes are observed. According to the labelling adopted in ref. 1, they are P1 (≈ 35 K at ≈ 1 kHz), P3 (85 K) and P4 (110 K), and have relatively small intensities (less than 10^{-3}). For none of them has a definitive interpretation been provided. Peak P4, which disappears with O degassing, is the best candidate for the anelastic relaxation of the O atoms within the off-centre positions in the Cu–O chains [8]. Other interpretations for these peaks are based on relaxations of an electronic nature [9] or spin excitations [10].

The observation of a phase transformation around 120 K is not straightforward; it is measured only after ageing below about 80 K, and manifests itself in Q^{-1} and modulus anomalies which quickly disappear upon heating, suggesting the dissolution of a new phase nucleated below about 80 K. The phase transition at 120 K was systematically observed by us, also when substituting Y with Pr, and its existence was recently confirmed by another laboratory [11]. In the same temperature range, anomalies of the dielectric constant have also been observed [12]. Such anomalies could be associated with (anti)ferroelastic and (anti)ferroelectric ordering of the oxygens within the off-centre positions [13]. In fact, a slight displacement of an O(1) ion from the axis of the Cu–O chain also gives rise to an electric dipole.

When the O stoichiometry x is lowered below 0.2, all the above processes disappear and an intense (up to 10^{-2}) nearly single-time relaxation peak develops, labelled as P2. In spite of its low activation energy of 0.11 eV, it has been attributed to the Snoek type hopping of isolated O atoms between the O(1) and O(5) sites [14].

2. Experimental details and results

The sample was a 44×4×0.4 mm^3 bar of ceramic $YBa_2Cu_3O_{6.35}$ prepared as described in ref. 15. It was electrostatically excited on its first and fifth flexural modes (0.6 and 8 kHz). The O content was reduced by heating in vacuum (better than 10^{-5} mbar) for about 2 h at progressively higher temperatures (from 840 to 1000 K) and rapidly cooling to room temperature. After

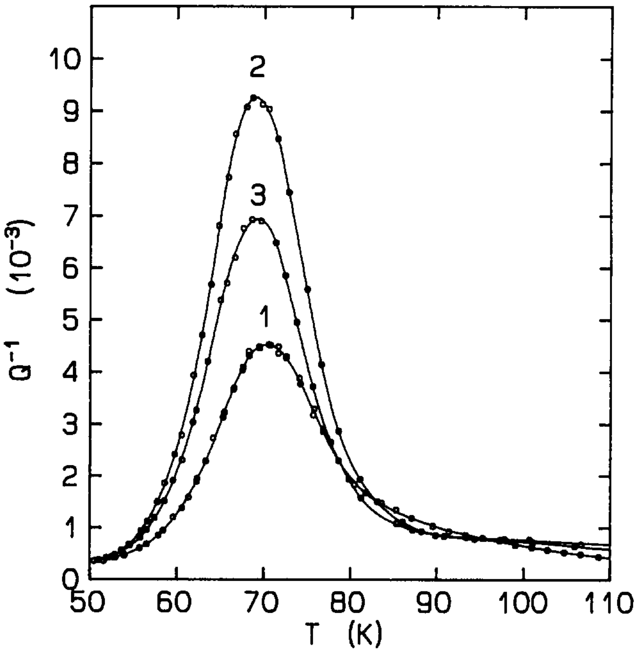

Fig. 2. Elastic energy dissipation of $YBa_2Cu_3O_{6+x}$, starting from $x \approx 0.3$ (1), after 2 h in vacuum at 980 K (2) and after an additional 2 h in vacuum at 1000 K (3). The initial vibration frequency was 8.3 kHz.

degassing at the highest temperatures, traces of decomposed green phase appeared on the sample surface. From X-ray analysis the fraction of spurious phases was estimated to be in the order of a few per cent, and therefore they could contribute to no more than a few per cent of the reduction of the intensity of P2.

Figure 2 represents the evolution of peak P2 during the outgassing treatments, starting from a stoichiometry lower than 0.3, obtained after heating in vacuum up to 840 K. Curves 2 and 3 were obtained after two subsequent vacuum treatments of 2 h at 980 and 1000 K, respectively; the final stoichiometry (curve 3) was $x = 0.05 \pm 0.05$, as estimated from the X-ray analysis. Curve 3 shows for the first time that the intensity of P2 decreases after severe degassing.

3. Discussion

The mechanism proposed for peak P2 [14] encountered several objections. It was noted [16] that only the rise of P2 was reported, but not the expected decrease on approaching $x = 0$. The present results show that indeed P2 starts decreasing after annealing in vacuum at 1000 K.

A second objection was raised by de Brion *et al.* [17], who observed a lowering of P2 after a few months of annealing at room temperature, implying a time constant of a few months for reaching thermal equilibrium at room temperature. They considered the reordering of initially isolated oxygens, taking into account only O pairing, assuming a mean hopping time of about 10^{-11} s for free O at room temperature (extrapolated from the relaxation time of P2), and a characteristic time for reaching equilibrium of 1 month. They found that the molar concentration x of initially free oxygens should be lower than 10^{-7}, a value which is clearly in conflict with the high intensity of P2.

The above reasoning is an oversimplification, since it identifies the time for reaching equilibrium at room temperature with that required for most of the free oxygens to aggregate, starting from a configuration in which they are all free. However, thermodynamic equilibrium will be reached after several steps of aggregation and dissociation, and the limiting step in this process is the jump of an O atom out of a chain fragment. Such a jump should require an activation energy close to that of processes PH1 and PH2, *i.e.* 1–1.2 eV, which means one dissociation every few hours or months at room temperature. As a consequence, a slow time constant for reaching thermal equilibrium does not necessarily imply a negligible concentration of mobile free oxygen.

In conclusion, the following arguments support a Snoek-type mechanism of isolated O atoms for peak P2: Snoek-type relaxation is expected to exist for symmetry reasons and is a nearly single Debye process; peak P2 is the only stable thermally activated peak in the tetragonal material from 50 to 750 K and has a relaxation strength compatible with a significant reorientation of the elastic dipole; none of the other peaks present in the Q^{-1} curves vs T can be associated with the above mechanism; finally, the peak height decreases when the O stoichiometry is reduced to very low values.

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