

Analysis of the oxygen relaxation spectrum in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ at high temperature

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Abstract

In the present work, a systematic study of the mechanical loss peak due to the diffusion of oxygen atoms within the Cu–O planes is presented. It is observed that the height of the peak varies dramatically as the oxygen concentration is changed. The variation of the peak height can be explained by a two-dimensional model. Moreover, the shape of the peak is asymmetrical and therefore cannot be interpreted by a single relaxation mechanism. Instead, the peak can be dissociated into two broadened Debye peaks which are controlled by an energy distribution. This method of decomposition of the observed peak is more meaningful when taking into account the structural transformation which is related to the variation of the oxygen content in the specimen.

1. Introduction

An energy dissipation peak was reported by a number of research groups in YBaCuO (YBCO) at temperatures higher than room temperature (depending on the frequency) [1–10]. This is a relaxation peak which has an activation energy of approximately 1.1 eV and a pre-exponential factor of an order of 10^{-13} s. The obvious dependence of the relaxation parameters on the oxygen concentration confirms that the peak is due to the oxygen relaxation mechanism. Furthermore, the activation energy of the peak presents a value quite similar to the migration energy of the oxygen atom within the Cu–O basal planes studied by other techniques [11, 12].

However, the peak differs from a classical point defect relaxation peak in two features. First, the oxygen concentration dependence of the peak height is not classical. Different research groups obtained different results. Xie *et al.* [1] reported a sharp increase in the peak height for a decreasing concentration of oxygen. On the contrary, Cost and Stanley [4] and Mi *et al.* [5] observed a continuous decrease of the peak height as they annealed their samples in vacuum. Nevertheless, the reported data show that they did work on the same peak. Second, the shape of the peak is obviously asymmetric. Some authors even saw two separate peaks [7–10]. Bonetti *et al.* [7] and Cannelli *et al.* [8] attributed the two peaks to oxygen jumps in two different orthorhombic phases (Orth. I and Orth. II). While Xie and Chen [9] believed that two peaks could be connected

with the oxygen jumping in the orthorhombic and tetragonal phases respectively.

In order to have a better understanding of the mechanism which is responsible for this energy dissipation peak, a systematic study of the evolution of the peak as a function of oxygen content (x) has been performed. The results have been analyzed by continuous relaxation spectra, by taking into account the structural features of this material.

2. Experiments

$\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ samples were prepared from commercial YBCO (Strem Chemicals, Inc. Newburyport, MA, USA) powder. Before compacting the powder into samples of individual dimensions, 20wt.% silver oxide powder had been mixed with YBCO in order to improve the mechanical strength of the specimen. Compressed bulk samples were sintered at 1203 K in oxygen for 40 h and slowly cooled down to room temperature. Subsequently, the received samples were re-annealed in air at different temperatures, in order to obtain homogeneous specimens with different oxygen content x . The previous experiments [13] have shown that addition of silver does not influence the electrical properties and crystal structures of YBCO. X-Ray diffraction data indicate that the silver exists as a separate phase. Oxygen content x was determined by iodometric titration [14].

Mechanical loss (Q^{-1}) measurements were carried out in a forced torsional pendulum. The apparatus

permits one to measure Q^{-1} as a function of either frequency, temperature, applied stress or time. The technique of measurements and the anelastic formalism has been described elsewhere [15, 16].

3. Results

Measurements of the mechanical loss spectrum (Q^{-1}) have been carried out for different oxygen content samples during thermal cycling from 300 K to 640 K. A stationary spectrum can be observed starting from the first cooling curve. This spectrum is always reproducible in further thermal cycling. The results are shown in Fig. 1, where the mechanical loss spectrum Q^{-1} is plotted as a function of the inverse temperature $1/T$. From Fig. 1, we see that the evolution of the damping peak as a function of the oxygen content can be roughly separated into three stages. Starting from high oxygen content samples, a relatively small peak can be observed in three samples which have oxygen content x as 0.89, 0.79 and 0.66 respectively. The height of the peak increases slightly as the oxygen content decreases. There is no obvious shift in the peak temperature, as the oxygen content is changed. The X-ray diffraction measurements reveal that these three samples are in the orthorhombic state.

The next stage concerns two samples whose oxygen content x are reduced to 0.55 and 0.46 respectively. A

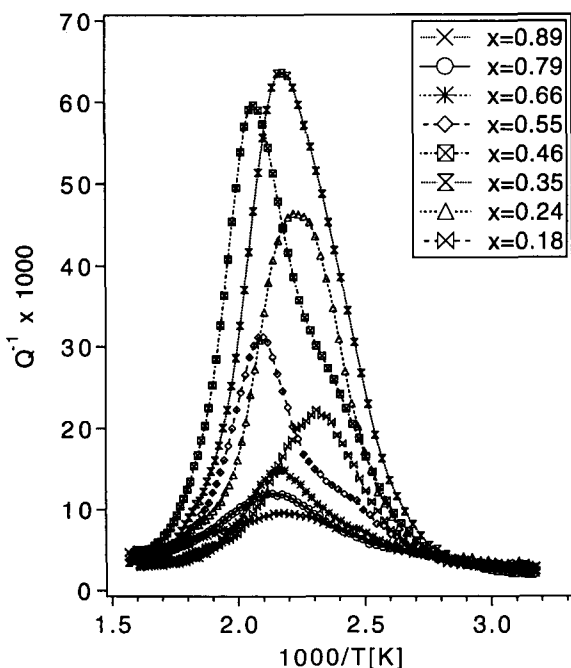


Fig. 1. Oxygen relaxation spectra plotted vs. inverse temperature for samples containing different oxygen content (x). All curves were measured during the first cooling at a cooling speed 2 K min^{-1} , and frequency 1.0 Hz.

sharp increase of the peak height can be observed in this stage. Meanwhile, the peak shifts towards higher temperature. X-Ray diffraction shows that the specimen with $x=0.55$ is still in the orthorhombic phase, while the sample with $x=0.46$ is dominated by a tetragonal symmetry. In fact, the second stage should be a case of co-existence of orthorhombic and tetragonal phases. We can see that a small shoulder appears in the low temperature side of the peak and makes the shape of the peak asymmetric.

The third stage is represented by three samples which have an oxygen content of $x=0.35$, 0.24 and 0.18. They are all in the tetragonal phase. The height of the peak drops proportionally to the oxygen decrease. In the meantime, the position of the peak shifts towards the lower temperature.

4. Analysis and discussions

The variation of the peak height as a function of the oxygen content can be explained by a two-dimensional bi-energy level model proposed earlier [17]. In that paper, we assumed that there exists a potential difference (defined as $2\Delta E$) between the two crystallographic oxygen sites in the basal plane. A fit of the experimental results by the bi-energy level model, and detailed discussion of the physical meaning of the existence of ΔE will be published elsewhere [18]. Here, only the analysis of the asymmetric features of the energy dissipation peak is developed.

From the theory of anelasticity, an asymmetric or enlarged peak is explained by either a “discrete relaxation spectrum” or a “continuous relaxation spectrum” [19]. The former expresses the energy dissipation Q^{-1} as:

$$Q^{-1} = \sum_{i=1}^n \Delta^{(i)} \frac{\omega\tau^{(i)}}{1 + [\omega\tau^{(i)}]^2} \quad (1)$$

The latter describes the anelastic behavior in terms of a *dynamic response function* $J_2(\omega)$. A normalized relaxation peak is expressed as:

$$Q_{\text{nor}}^{-1} = \frac{J_2(\omega)}{\delta J} = \int_{-\infty}^{\infty} \Psi(\ln \tau) \frac{\omega\tau}{1 + \omega^2\tau^2} d(\ln \tau) \quad (2)$$

with a normalized distribution function $\int_{-\infty}^{\infty} \Psi(\ln \tau) d(\ln \tau) = 1$

Equation (1) implies that the total energy dissipation value is a sum of n independent mechanisms. Each of n mechanisms is characterized by a different relaxation strength $\Delta^{(i)}$ and relaxation time $\tau^{(i)}$. On the other hand, eqn. (2) considers the relaxation time τ as a distribution function, instead of a few separated “lines”. Here, in the YBaCuO case, both “discrete” and “continuous” relaxation spectra actually have their own physical meanings.

First, it is well known that YBaCuO has different crystal structures (orthorhombic and tetragonal phases) as the oxygen content x is changed. Oxygen relaxation diffusion, in each phase, may have different relaxation parameters. If the sample is not purely in one single phase, diffusion of oxygen in both phases could have contributions to the measured energy dissipation Q^{-1} values. Hence, i in eqn. (1) can be set as two, which correspond to the contribution of orthorhombic and tetragonal phases respectively. Moreover, the physical environment may not be exactly the same around each oxygen atoms jumping. So, conditions for oxygen jumping may not be the same in each grain of the polycrystalline specimen. Therefore, the relaxation time τ is not an individual value but a distribution function. So, the experimental value of Q^{-1} in YBaCuO should obey the following mathematical expression:

$$Q^{-1} = \int_{-\infty}^{\infty} \delta J^{(o)} \Psi^{(o)}(\ln \tau^{(o)}) \frac{\omega \tau^{(o)}}{1 + [\omega \tau^{(o)}]^2} d(\ln \tau^{(o)}) + \int_{-\infty}^{\infty} \delta J^{(T)} \Phi^{(T)}(\ln \tau^{(T)}) \frac{\omega \tau^{(T)}}{1 + [\omega \tau^{(T)}]^2} d(\ln \tau^{(T)}) \quad (3)$$

Here, the superscripts ‘‘o’’ and ‘‘T’’ are used to indicate orthorhombic and tetragonal cases.

We can now fit our experimental data by eqn. (3). The distribution function Ψ is chosen as a gaussian distribution form. From the Arrhenius equation, $\tau = \tau_0 e^{(E/kT)}$, the distribution of relaxation time τ may come either from τ_0 , E or both. Here, to simplify calculation, τ_0 is set as a constant of 10^{-13} s. So, $\int d(\ln \tau)$ in eqn. (3) becomes $\int dE$. As an example, two fitted results are plotted in Fig. 2. The graphics of (a) and (b) of Fig. 2 represent different oxygen content cases. It is seen clearly, from Fig. 2, that the measured mechanical loss spectrum is composed of two enlarged Debye peaks in this temperature range. Referring to the X-ray diffraction data, the analyzed results in Fig. 2 can be explained as follows.

The peak, which is located at higher temperature, originates from oxygen relaxation in the orthorhombic phase. Another peak is due to oxygen relaxation in the tetragonal state. As the oxygen content is reduced, the ratio of the orthorhombic phase in the specimen decreases. Therefore, the contribution to the total energy dissipation due to oxygen diffusion in the orthorhombic phase, is reduced. On the other hand, the peak associated with the tetragonal phase is gradually increased. Meanwhile, the positions of two peaks move more closely together as the oxygen content decreases. This reflects the fact that the activation energy values in the two phases are close to each other, because, in the low oxygen content case, the occupation of oxygen

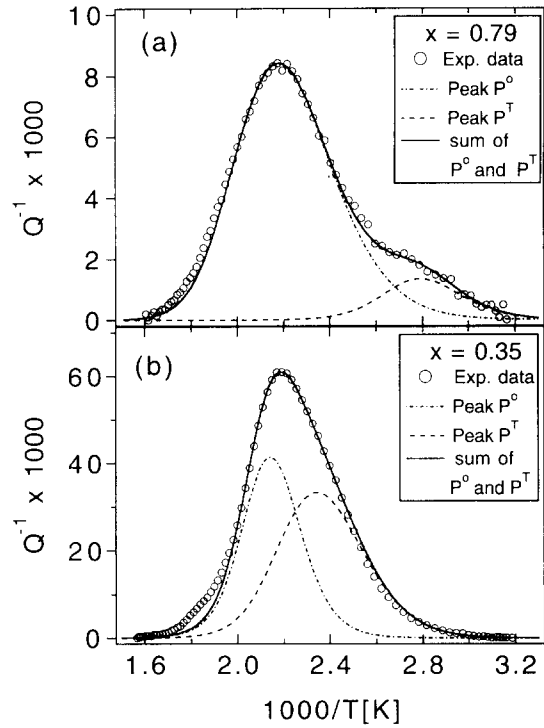


Fig. 2. A few examples of simulating experimental data by two enlarged Debye peaks which are controlled by an energy distribution in gaussian type. The pre-exponential factor τ_0 was chosen as 10^{-13} s. Two Debye peaks signify an oxygen relaxation in two different phases: (O) experimental data; (—) simulated results; (---) peak is assumed to be due to oxygen relaxation in the orthorhombic phase; (-.-) peak is assumed to be due to oxygen relaxation in the tetragonal phase.

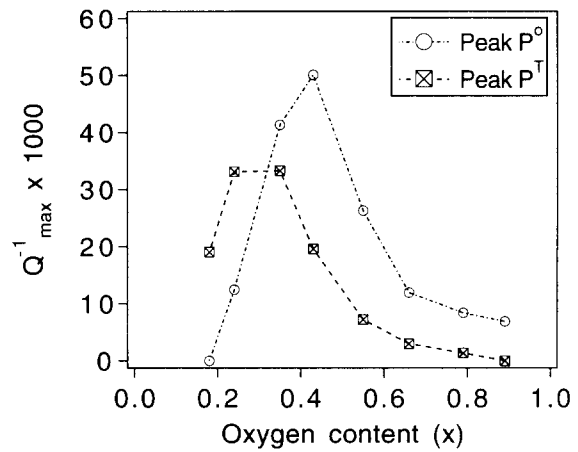


Fig. 3. The variations in peaks’ heights as a function of oxygen content x . (O) and (X) represent two peaks which are believed to be due to the oxygen relaxation in the orthorhombic phase (jumping of oxygen between CuO chain and vacancy) and tetragonal phase (jumping of oxygen between two vacancy sites) respectively.

sites in the basal plane becomes random. The two phases become less distinguishable in this case. The above simulation has been applied to other samples. The results are presented in Fig. 3, where the heights

of two peaks, which may reflect the contribution to the energy dissipation from different phases, are plotted as a function of the oxygen content x . One can see that the variation of the peaks' heights have general agreement with the X-ray diffraction results. An "Orth peak" is dominating when the orthorhombic phase is observed by X-ray diffraction. Otherwise, a "Tetra peak" dominates the mechanical loss spectrum. A detailed analysis of crystal structure [10] shows that the Orth. II phase can be separated into Orth. I and Tetra. phases. So, jumping of oxygen in Orth. II phase may not give rise to a new internal friction (IF) peak. Hence, two energy dissipation peaks observed in YBCO at high temperature could be explained by oxygen diffusional jumping in the orthorhombic phase (jumping takes place between the Cu-O chain and vacancy) and tetragonal phase (jumping takes place between two vacancy sites) respectively. This analyzed result supports more or less Xie's explanation [9].

5. Conclusions

A study of oxygen relaxation in YBaCuO has been performed by mechanical spectroscopy. The experimental results have been analyzed by a distribution spectrum controlled by an energy distribution. The results show that the experimental curves can be fitted by two enlarged Debye peaks which represent the contributions of oxygen relaxation in the orthorhombic and tetragonal phases respectively. This analysis makes the picture of oxygen relaxation in YBaCuO clearer.

Acknowledgment

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