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Low-Activation Energy Relaxations in Oxide Superconductors

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Abstract. A brief survey is made of the numerous anelastic relaxation processes with activation energies below 0.2 eV, which are found in the oxide superconductors with the 123 and 214 structure. Up to now there is no general agreement on their mechanisms, although some kind of electronic relaxation is often invoked. New measurements are presented of the process with the lowest activation energy, ~80 meV, in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. It is shown that the intensity of this peak is maximum at the maximum oxygen stoichiometry, $x = 1$, and steeply decreases in the restricted range $0.9 < x < 1$, disappearing below it. It is proposed that the anelastic relaxation is caused by the reorientation of pairs of the p_z holes, which are observed at $x > 0.8$ by X-ray absorption spectroscopy.

1. INTRODUCTION

The oxide superconductors, especially those with 123 and 214 structure, present several anelastic relaxation processes with activation energies unusually low for the oxides, but at the moment there is no general agreement on their mechanisms. For all of these processes some kind of electronic relaxation has been proposed; this seems an attractive possibility, in view of the uncommon electric properties of these oxides, but up to now no detailed mechanism or conclusive evidence has been found. In some cases it is not even ascertained whether these peaks are due to some intrinsic property of the material, or to impurities or imperfections not yet determined.

2. LOW ACTIVATION ENERGY PEAKS AND POSSIBLE MECHANISMS

In conducting and superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ three peaks are found with activation energies of 0.08, 0.15 and 0.2 eV [1-5], which we label P1, P3 and P4, respectively. When the O stoichiometry is lowered below $x \sim 0.3$, the material becomes superconducting, the above peaks disappear and a new one, P2, develops [6]. All the peaks in the conducting material have been shown to be affected by some cation substitution, which is regarded as a sign of the involvement electronic effects. For example, P3 and P4 seem to be affected by the partial substitution of Y^{3+} with Ca^{2+} [4], but also by the atmosphere in which the sample is sintered [5]. Peak P2 in the semiconducting material is the only one which approximates well a single Debye relaxation, and has also been detected with a completely different technique, as a peak of the NQR rate as function of temperature [7].

In $\text{La}_{2-x}(\text{Sr/Ba})_x\text{CuO}_{4+y}$ a dissipation peak with an activation energy of 40-80 meV has been found [8], whose intensity depends on x . The fact that the peak intensity is maximum when the superconducting critical temperature is maximum, suggests some connection between the peak and the holes [8].

The mechanisms which have been proposed to explain some of these processes include hopping of interstitial or off-centre atoms and the movement of dislocations or domain boundaries, besides electronic effects. The hopping of isolated O atoms in the nearly empty CuO_x planes of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ can quantitatively explain peak P2 both in the acoustic [6] and NQR [7] experiments, but this is the only case in which a Snoek-like effect of a heavy atom can possibly require such a low activation energy. Indeed, it is also proposed that P2 is due to polaron hopping [7].

Regarding the hopping of off-centre atoms, the only case known in these oxides is that of the O atoms in the Cu-O chains in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [9,10], which could be responsible for P4 [1]. Other off-centre configurations can be supposed to occur in correspondence with some impurity or imperfection, which has not yet been detected by diffraction methods.

Finally, dislocations can hardly be considered, since they are far less abundant and mobile than in metals [11,12].

3. EXPERIMENTAL AND RESULTS

The sample was a bar ($43 \times 4.3 \times 0.9 \text{ mm}^3$) of polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, which was electrostatically excited on its 1st and 5th flexural modes (1.7 and 22 kHz). The starting material was oxygenated at 500 °C for few hours in flowing O_2 , and the oxygen content was estimated from the lattice parameters as $x = 6.93 \pm 0.03$. The superconducting transition had the midpoint at 90.3 K with a width of 1.3 K and zero resistance at 88 K. We will refer to this state of the sample as to the $x = 0.93$ state. The accurate determination of the O stoichiometry requires the destruction of the sample, and therefore the values of x during the subsequent treatments are not known with high accuracy, but are deduced from the resistance curves and the p_xT diagram of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$.

Figure 1: Elastic energy loss of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ at three different stoichiometries $x \geq 0.9$. As prepared, $x \sim 0.93$ (1); after a vacuum anneal at 200 °C, $x \sim 0.9$ (2); after a full oxygenation, $x \sim 1$ (3).

Figure 2: Normalized experimental data of peak P1 at 1.7 and 22 kHz in the $x=0.93$ and $x=1$ states (same symbols as in Fig. 1), after subtraction of the background. The closed triangles are the difference between the experimental curves 2 and 1. For the dashed and continuous lines, see the text.

The $Q^{-1}(T)$ curve in the initial state is labelled as 1 in Fig. 1, and it was stable over 6 years. The sample was then aged for 20 hours in a vacuum better than 10^{-5} mbar at 200 °C and cooled to room temperature at 0.85 K/min. After this treatment, we estimate the O contents as $x = 0.90$ or higher. In fact, according to Ref. [13] a longer vacuum anneal at 320 °C changes the O stoichiometry of ceramic samples from 0.94 to 0.90. We measured again the electrical resistance, which showed $T_C = 92.0$ K and zero resistance at 89.6 K. A slight increase and sharpening of the superconducting transition after a mild vacuum anneal was found also in [13] and may indicate that the sample was initially in the overdoped state. According to [14], the optimal doping is at $x = 0.94$, which would imply that our sample passed from $x > 0.94$ to $x \sim 0.94$; we will label this state as " $x = 0.9$ ". After this slight reduction of x , the $Q^{-1}(T)$ curve remained unaffected, except for peak P1 which was reduced by more than 3 times (curve 2).

The sample was again oxygenated in order to achieve a stoichiometry as close as possible to 1 (" $x = 1$ " state): it was heated up to 600 °C in a UHV system with a quartz tube; then a static atmosphere of 1250 mbar O_2 was admitted and the furnace was slowly cooled to room temperature at a rate of -0.2 K/min. The cooling rate was reduced to -0.1 K/min between 490 °C and 300 °C, in order to maximize the O uptake. The oxygenation raised the whole $Q^{-1}(T)$ (curve 3), but while P3 and P4 remained nearly unaffected, P1 became more than twice higher than in the as prepared state ($x = 0.93$).

The reproducibility of the phenomenology was checked by observing the disappearance of P1 after partially outgassing to $x \sim 0.87$, and by observing the recovery of P1 to the maximum height after a full oxygenation.

Figure 2 shows the experimental data after subtraction of the background and of the contribution of the other two peaks, and after normalization of the intensities. The peak is much broader than a single Debye relaxation (shown as a dashed line), but its shape and temperature do not change with the intensity. This fact is unusual, since normally the shapes and temperatures of very broad peaks are scarcely reproducible. We also made a check of the consistency of the background subtraction, using as a background the experimental curve 1, where P1 is small. These are the closed triangles, and fall exactly on the same curves as the others. It is possible to fit P1 with the expression first proposed by Jonscher for the dielectric relaxation of complex and correlated systems [15]:

$$Q^{-1} = \Delta \frac{1}{(\omega\tau)^{-m} + (\omega\tau)^{1-n}}$$

where $\tau(T) = (1.5 \times 10^{-13} \text{ s}) \exp[(945 \text{ K})/T]$. The Debye relaxation (dashed line) is obtained for $m = 1 - n = 1$, while the solid lines are obtained with $m = 0.41$ and $n = 0.67$.

4. DISCUSSION

The main characteristic of P1 is its strong dependence on x in an interval where most of the physical properties are nearly constant, and its disappearance below $x \sim 0.9$. This fact excludes any relaxation of domain boundaries or geometrical defects, which certainly do not disappear below that stoichiometry; it is also difficult to imagine an off-centre occupation which is so sensitive to x . We remain with the possibility of polaron relaxation.

A model for the distribution of the holes in $YBa_2Cu_3O_{6+x}$ as a function of x has been proposed by Tolentino *et al.* [16], based on spectroscopic observations of the characters of the holes. According to [16], the holes doped by the O atoms in the CuO_x planes are distributed among the $2p_x$ and $2p_y$ orbitals of the O atoms in the Cu-O chains and CuO_2 planes. Increasing x above 0.8, they observed that some holes start occupying also the $2p_z$ orbitals of the apical oxygens. These p_z holes seem the natural candidates for explaining P1, even though we do not know whether their mobility is compatible with an Arrhenius law with the activation energy of P1. The only problem is with their z symmetry, which is the same as that of the lattice and therefore cannot cause anelastic relaxation. Such a problem can be solved by assuming that these holes may form pairs (bipolarons), whose reorientation requires an activation energy of ~ 80 meV and causes peak P1. This would also explain the very steep dependence of the intensity of P1 on x , because the number of bipolarons would be roughly proportional to the square of the concentration of the p_z holes.

It has been observed that the partial substitution of Cu with Fe suppresses P1 [2], while the partial substitution of Y with Pr progressively transforms P1 into another peak [3]. We do not know whether

these observations are in contrast or confirm our model, since we are not aware of any study of the effects of the above substitutions on the p_z holes. We note, however, that great care must be taken that the substitutions do not affect also the O content, since P1 is extremely sensitive to it.

5. CONCLUSION

In the oxide superconductors several relaxation processes have been found with unusually low activation energies. An attractive and plausible explanation for many of them would be the hopping of polarons, but it has not yet been possible to find precise mechanisms or conclusive evidences of the involvement of polarons.

New measurements are presented of the peak with the lowest activation energy in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, and it is shown that it can be interpreted in terms of holes which have been observed by X-ray spectroscopies. The peak develops itself only for $x > 0.9$, becoming maximum at $x=1$. In this restricted range most of the physical properties are nearly constant, but XAS experiments revealed that the p_z orbitals of the apical oxygens start being occupied by holes. It is proposed that the dissipation peak is due to the reorientation of pairs of such holes.

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