

Enhancement of Cu-O vibrational modes and superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ studied by x-ray photoelectron spectroscopy and high-resolution electron-energy-loss spectroscopy

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We find peaks around 60 meV ($\sim 484 \text{ cm}^{-1}$) in high-resolution electron-energy-loss spectroscopy spectra for ortho- and tetra- $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. It is found that the peak intensity for superconductors (ortho-Y-Ba-Cu-O) is strongly enhanced as compared with nonsuperconductors (tetra-Y-Ba-Cu-O). From these results, it is suggested that this enhancement is due to the strong coupling of phonons with charge fluctuations.

I. INTRODUCTION

Many studies have been reported on high- T_c oxide superconductors since the La-Ba-Cu-O (Refs. 1 and 2) and Y-Ba-Cu-O (Ref. 3) systems were found. Furthermore, Bi-Sr-Ca-Cu-O (Ref. 4) and Tl-Ba-Ca-Cu-O (Ref. 5) systems with $T_c \sim 100$ – 125 K have been discovered. However, the mechanism of superconductivity for the oxides is unclear even though many have been proposed.

Recently, Tachiki and Takahashi⁶ theoretically investigated the mechanism for high- T_c superconductivity in the oxides. It was reported that the LO phonons strongly interact with the charge fluctuations induced by the interplay of the Cu-O electron transfer and the Coulomb interaction, and they generate the Cu-O charge transfer oscillations. They pointed out that the charge fluctuations enhance the spectral intensity of LO phonons and they could be observed by high-resolution electron-energy-loss spectroscopy (HREELS).

We report the results of measurements of phonons in superconducting and nonsuperconducting oxides using HREELS. It will be shown here that the intensity of vibration related to Cu-O is enhanced in the superconducting oxides.

II. EXPERIMENT

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (abbreviated to Y-Ba-Cu-O below) samples were prepared as follows. The mixtures of barium, yttrium, and copper oxalates were prepared by coprecipitation of corresponding nitrates with NH_4OH and oxalic acid solution at $\text{pH}=4.6$. The powders obtained by the above procedure were heated in an oxygen stream (1 atm) and ground. Ortho-Y-Ba-Cu-O was obtained by repeating these treatments at 900°C for 60 h, and at 930

and 960°C for 10 h. On the other hand, the tetra-Y-Ba-Cu-O was prepared by quenching the above sample from 948 to -196°C . The results of x-ray diffraction measurements confirmed that these samples consist of a single phase. The oxygen content δ was about 0.1 and 0.5 for the former and the latter, respectively.

Characterization of sample surfaces and measurements of phonons were carried out using an ADES-400 (V.G. Scientific) equipped with an x-ray photoelectron spectrometer (XPS) and HREELS. An Al $K\alpha$ source was employed for the XPS measurements and HREELS spectra were measured by an incident electron beam energy of 3.2 eV and an energy resolution of 40 meV. We estimated the electron escape depth in this case to be 50–100 Å.⁷ The surfaces were cleaned by scraping with a grinder *in situ* under UHV condition ($\sim 1 \times 10^{-8}$ Pa).

III. RESULTS AND DISCUSSION

The results of T_c measurements are shown in Figs. 1(a) and 1(b) for the ortho- and the tetra-TBaCuO, respectively. It is found that the zero-resistance temperature is 90 K for the orthorhombic sample. On the other hand, the variation of resistivity as a function of temperature for the tetragonal sample behaves like a semiconductor, which is typically found in tetra-Y-Ba-Cu-O.

Figures 2(a), 2(b), and 2(c) show XPS spectra of C 1s, O 1s, and Cu 2p for the ortho-Y-Ba-Cu-O with (spectrum a) and without (spectrum b) scraping. It is found that a 284.7-eV peak of C 1s has almost vanished after scraping, which implies that typical contaminants such as hydrocarbons are removed. A 531.2-eV peak of O 1s which corresponds to OH group⁸ decreases in intensity. On the other hand, that of a 528.4-eV peak due to the oxide⁸ increases. The intensity of Cu 2p slightly increases by scraping.

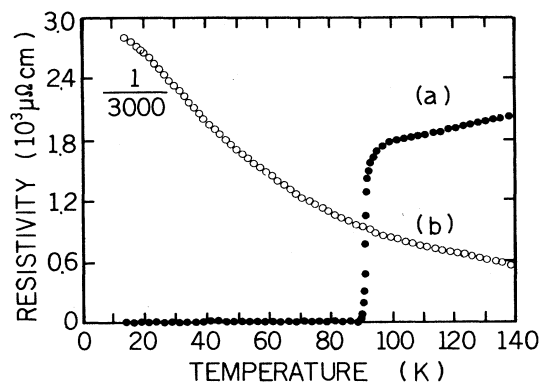


FIG. 1. Changes of resistivity for (a) ortho- and (b) tetra-Y-Ba-Cu-O as a function of temperature.

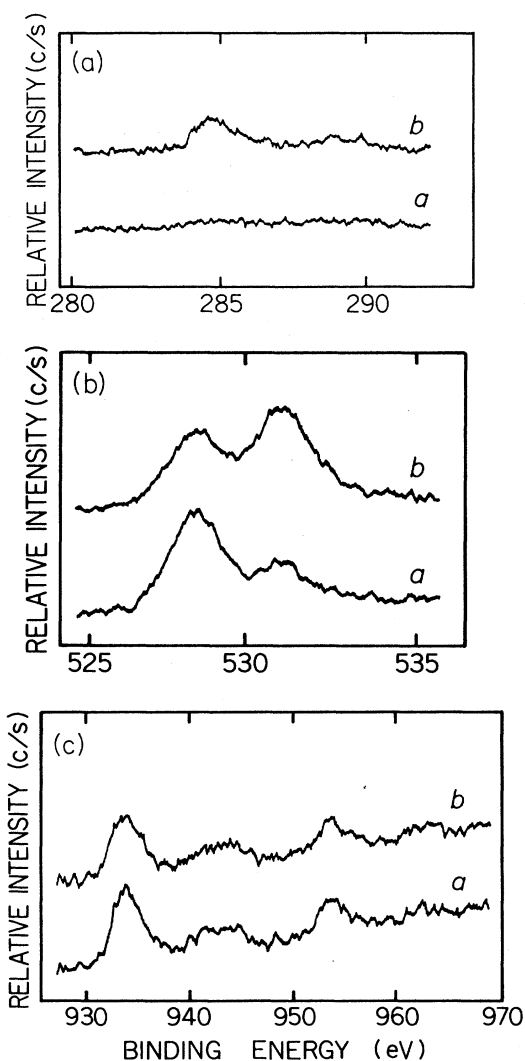


FIG. 2. (a) XPS spectra of $C 1s$ for ortho-Y-Ba-Cu-O with (spectrum *a*) and without (spectrum *b*) scraping. (b) XPS spectra of $O 1s$ for ortho-Y-Ba-Cu-O with (spectrum *a*) and without (spectrum *b*) scraping. (c) XPS spectra of $Cu 2p$ for ortho-Y-Ba-Cu-O with (spectrum *a*) and without (spectrum *b*) scraping.

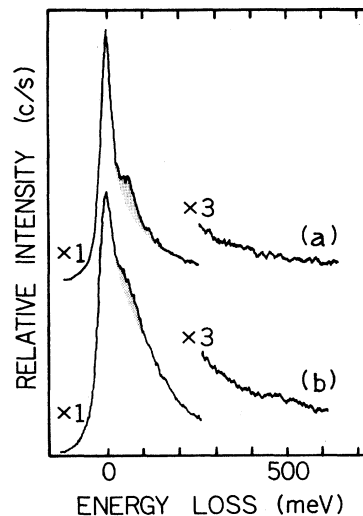


FIG. 3. Typical HREELS spectra for (a) ortho- and (b) tetra-Y-Ba-Cu-O.

Similar results are obtained for tetra-Y-Ba-Cu-O. These results reveal that the surfaces are almost cleaned by scraping.

Typical HREELS spectra for ortho- and tetra-Y-Ba-Cu-O are displayed in Fig. 3. Broad peaks are found around 60 meV ($\sim 484 \text{ cm}^{-1}$) for ortho- and tetra-Y-Ba-Cu-O. In order to obtain the intensity of both peaks, smooth backgrounds were subtracted between 30 and 110 meV and the obtained peak areas (shaded in Fig. 3) were measured electronically. The relative peak intensity (normalized to the elastic peak intensity) is obtained on three ortho- and tetra-Y-Ba-Cu-O: the averaged values are 0.54 ± 0.10 and 0.25 ± 0.12 for the former and the latter, respectively. From these results, we emphasize that the peak intensity for ortho-Y-Ba-Cu-O is strongly enhanced as compared with tetra-Y-Ba-Cu-O.

The peak around 60 meV ($\sim 484 \text{ cm}^{-1}$) would consist of some peaks which are unresolved due to poor spectrometer resolution ($40 \text{ meV} = 322 \text{ cm}^{-1}$). Since the peak ranges from $\sim 30 \text{ meV}$ (242 cm^{-1}) to $\sim 110 \text{ meV}$ (888 cm^{-1}), it would be convoluted by the following peaks: 340 cm^{-1} [$Cu(2)-O(2,3)$] bend with $O(2)$, $O(3)$ out of phase; 437 cm^{-1} [$Cu(2)-O(2,3)$] bend with $O(2)$ and $O(3)$ in phase, and 502 cm^{-1} [$Cu(1)-O(4)$] stretch which were assigned by single-crystal Raman scattering.⁹⁻¹² However, it is hard to determine which vibrational modes contribute mainly to the 60-meV peaks because of polycrystalline samples.

The enhancement in the 60-meV peak for ortho-Y-Ba-Cu-O was not observed using Raman spectroscopy.¹² However, we do find it in this study using HREELS. It was predicted theoretically⁶ that the enhancement of the spectral intensity due to the coupling Cu-O vibration with charge fluctuations occurs for excitations with finite wave numbers q , but not for the $q=0$ excitation observed in Raman spectroscopy. Our finding agrees completely with the above prediction. Therefore, we suggest that the enhancement observed here is due to the above mecha-

nism, and that the interaction mediated by the coupled vibration of Cu-O and charge fluctuations may yield a strong attractive force accountable for the high- T_c superconductivity in the oxides.⁶

In summary, we find a strong enhancement of the spectral intensity of the 60-meV peak in ortho-YBaCuO using HREELS. From this result, it is suggested that this

enhancement is due to the coupling of Cu-O vibrations with charge fluctuations, which was previously predicted theoretically.⁶

It must be made clear which vibrational modes are enhanced in order to elucidate the mechanism of superconductivity in the oxides. For this purpose, we are planning a HREELS study using single crystals.

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