Effects of oxygen deficiency on the infrared spectra in $YBa_2Cu_3O_{7-\delta}$

S. Sugai
Department of Physics, Faculty of Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka 560, Japan
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The systematic change of lattice vibrations due to oxygen deficiency and the related structural phase transition was observed in $YBa_2Cu_3O_{7-\delta}$ quenched from various temperatures using infrared reflection spectroscopy. Upon decreasing the quenching temperature, the rise and fall of some peaks and a large energy shift in some modes were observed. The decrease of the 356 cm^{-1} mode is attributed to the decrease of bond charge around Cu atoms as a result of increasing attractive force for O atoms, which is related to the insulator-to-metal and superconducting transitions.

The 90-K superconductor $YBa_2Cu_3O_{7-\delta}$ was found in the course of searching for new high-T_c superconductors,[1] which was started by the discovery of the 30-K superconductors $(La_{1-x}M_x)_2CuO_4$ by Bednorz and Müller.[2] It was found that the T_c is almost the same in the compounds in which La or many kinds of lanthanides are substituted for Y, if only the crystal structure is the same. The structure of $YBa_2Cu_3O_{7-\delta}$ includes oxygen deficiency inevitably, and the amount of deficiency is strongly related to the electric properties and the crystal structure.[3-8]

An oxygen deficiency $\delta = 0.70$ at the calcination temperature of 950 °C in air reduces to 0.07 below 400 °C.[8] $\delta = 0.07$ is the lowest oxygen deficiency obtained at an oxygen pressure of less than 1 atm. With decreasing oxygen deficiency the semiconducting material becomes metallic with a superconducting transition. In the compound with large oxygen deficiency O atoms on the Cu-O layer between two Ba atoms are randomly distributed two dimensionally in the tetragonal lattice. The occupation factor is only 15% at 940 °C in air. On increasing the occupation factor the O atoms make one-dimensional chains of Cu-O, and the crystal structure changes into orthorhombic. The occupation factor of O atoms on the chain is 58% near the tetragonal-to-orthorhombic phase-transition temperature and 93% at the samples after sufficient annealing at low temperature.[8]

In order to investigate the effects of oxygen deficiency on the lattice vibrations, far-infrared reflection spectroscopy was executed on the samples obtained by rapid quenching from various temperatures.

The orthorhombic low-temperature phase is classified in the $D_{2h}^1(Pmmm)$ symmetry,[3,9] and the unit cell includes one molecular unit. When we assume the oxygen deficiency δ is zero, that is, the oxygens on the linear chain are fully occupied and the lateral oxygen positions are fully vacant, the normal modes of lattice vibrations are $B_{1u}+B_{2u}+B_{3u}$ from the motion of one Y atom, $A_g+B_{2g}+B_{3g}+B_{1u}+B_{2u}+B_{3u}$ from two Ba atoms, $A_g+B_{2g}+B_{3g}+2B_{1u}+2B_{2u}+2B_{3u}$ from three Cu atoms, $2A_g+2B_{2g}+2B_{3g}+2B_{1u}+2B_{2u}+2B_{3u}$ from four O atoms on the two layers sandwiching the Y atom, $A_g+B_{2g}+B_{3g}+B_{1u}+B_{2u}+B_{3u}$ from two O atoms on the Cu-O line along the z axis, and $B_{1u}+B_{2u}+B_{3u}$ from one O atom on the linear Cu-O chain relating to the oxygen deficiency. The total optical modes are $4A_g+4B_{2g}+4B_{3g}+7B_{1u}+7B_{2u}+7B_{3u}$. The modes from the oxygen-deficient chains are expected to be strongly broadened. All the gerade modes are Raman active. The B_{1u}, B_{2u}, and B_{3u} modes are infrared active for light with polarization along the z, y, and x axes, respectively.

The tetragonal high-temperature phase belongs to the $D_{4h}^1(P4/mmm)$ symmetry.[3] The normal modes are $4A_{1g}+4E_g+7A_{2u}+7E_u$ in the optical branches. The collective modes from the O atoms on the Cu-O plane between two Ba atoms are not expected, because the occupa-

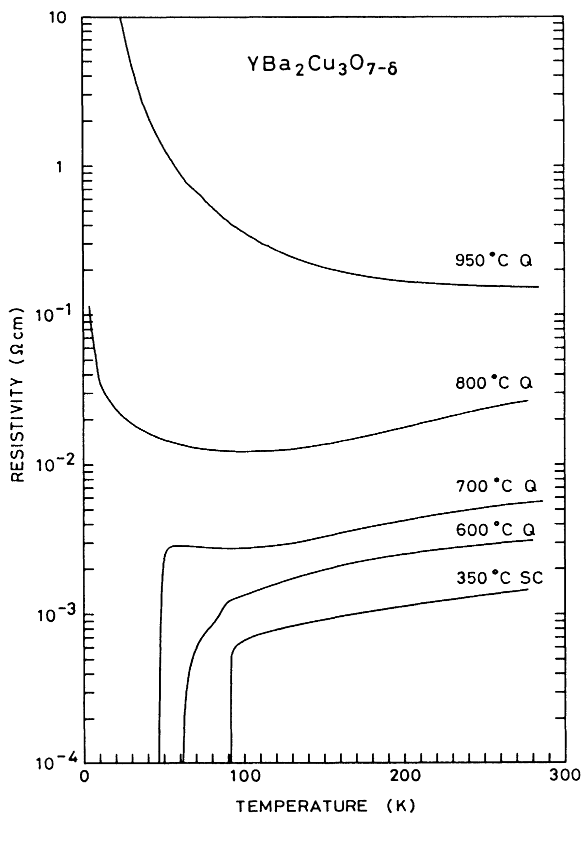

FIG. 1. Electrical resistivity in $YBa_2Cu_3O_{7-\delta}$ samples quenched from 950° ~ 600 °C and cooled slowly after annealing at 350 °C.

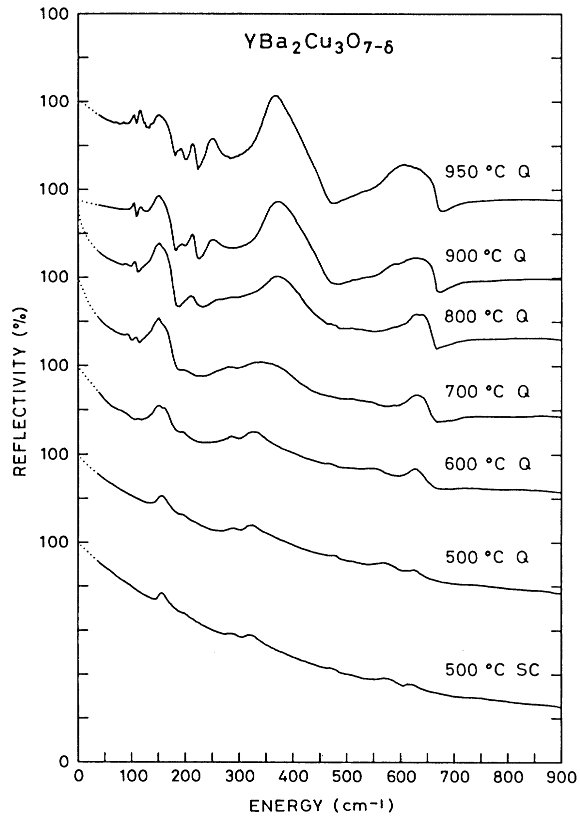

FIG. 2. Reflection spectra in $YBa_2Cu_3O_{7-\delta}$ samples quenched from 950° ~ 500 °C and cooled in a furnace after annealing at 500 °C (the lowest spectra).

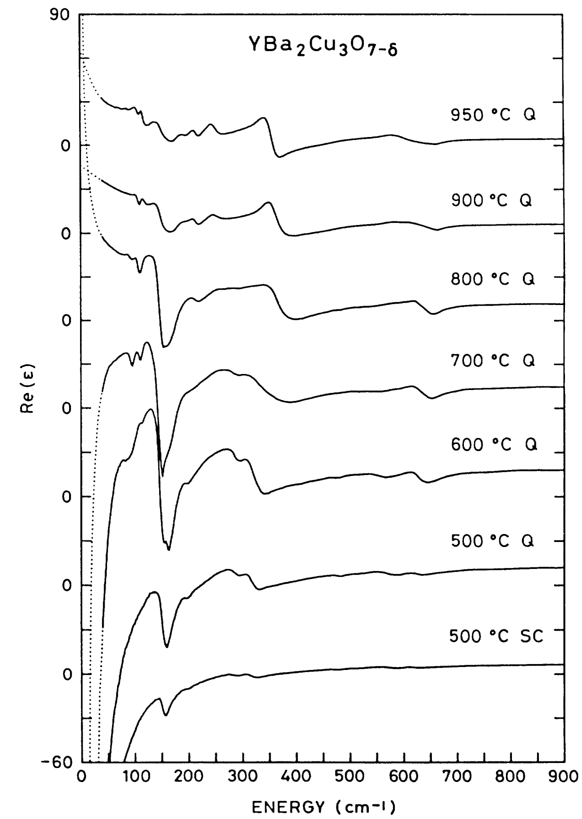

FIG. 3. Re(ϵ) in $YBa_2Cu_3O_{7-\delta}$ obtained by the Kramers-Kronig transformation of reflection spectra in Fig. 2.

tion factor is only 15%–29%. Only localized modes are possible.

The samples were obtained by rapid quenching pellets sintered at 950 °C for 24 h into liquid nitrogen from various temperatures after keeping them at those temperatures for 12 h. The quenched pellets were mirror polished without the use of water. The infrared spectra were measured by a Fourier-transform-type spectrometer (Digilab FTS16AS) equipped with a Ge bolometer (Infrared Lab).

Figure 1 shows the resistivity of $YBa_2Cu_3O_{7-\delta}$ samples quenched from 950, 800, 700, and 600 °C, and cooled slowly in a furnace after annealing at 350 °C. The slowly cooled sample shows a superconducting transition at 92 K. The sample quenched from 600 °C shows a resistivity drop by double steps and undergoes a superconducting state at 61 K. This sample is a mixed phase of 92- and 60-K superconductors. The sample quenched from 700 °C shows a resistivity increase below 90 K followed by a superconducting transition at 46 K. The resistivity of the sample quenched from 800 °C decreases at first and then increases below 105 K. The samples quenched from 800° and 950 °C do not show the superconducting transition down to 4.2 K. The oxygen deficiencies estimated from the data by Kishio *et al.*[8] are 0.70, 0.54, 0.40, and 0.21 for the samples quenched from 950°, 800°, 700°, and 600 °C, respectively, and 0.07 for slowly cooled sample.

Figure 2 shows a series of far-infrared reflection spectra in the samples quenches from 950°, 900°, 800°, 700°, 600°, and 500 °C and cooled slowly after annealing at 500 °C in a furnace. The spectra in the sample quenched from 500 °C are in accord with the data by Bonn *et al.*[10] At low temperatures the number of free carriers increases and they screen the electric field accompanying the infrared-active phonons so that the phonon peaks decrease. In the presence of free carriers the reflectivity reaches 100% at energy zero due to the plasma oscillation. The contribution of the plasma term, however, is very small compared with the normal three-dimensional Drude type with the same carrier density. The samples used in this experiment include voids which reduce the reflectivity at small wavelengths less than the radii of the voids. The slow-cooling sample with the smallest number of voids shows a reflectivity of about 60% at 900 cm^{-1}. The reflectivity data were obtained up to 2000 cm^{-1}. No noticeable structure is observed above 900 cm^{-1}.

Figures 3 and 4 show Re(ϵ) and Im(ϵ) obtained by the Kramers-Kronig transformation of the reflection spectra. The peaks of Im(ϵ) correspond to transverse optical (TO) phonons. The Im(ϵ) has rich structure due to phonons at high temperatures. On decreasing temperature the peaks become small in consequence of the screening by free carriers. The peak energies for the sample quenched from 950 °C are 86, 106, 117, 150, 192, 214, 253, 356, 603,

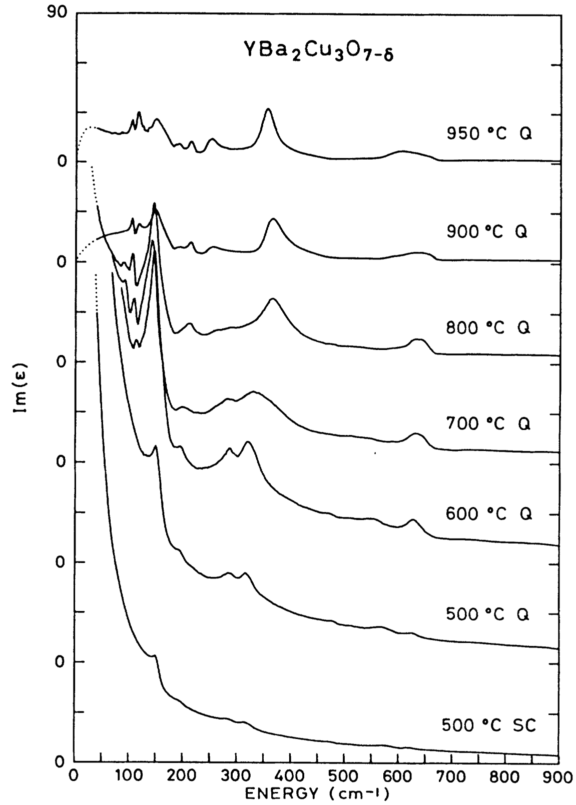

FIG. 4. Im(ϵ) in $YBa_3Cu_3O_{7-\delta}$ obtained by the Kramers-Kronig transformation of reflection spectra in Fig. 2.

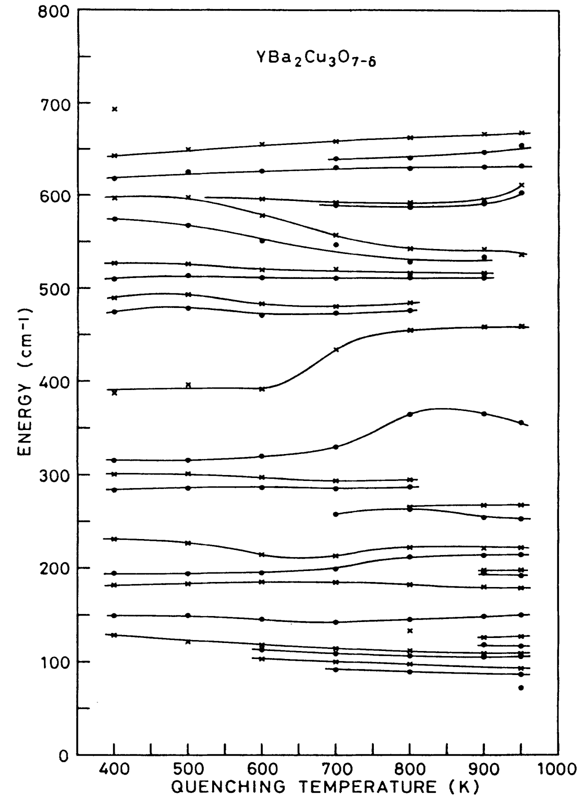

FIG. 5. TO (circles) and LO (crosses) phonon energies as a function of quenching temperature. The energies for the sample cooled in a furnace are shown at the position of 400 °C.

632, and 655 cm^{-1}. Those for the sample cooled in the furnace are 149, 195, 284, 316, 474, 510, 574, and 618 cm^{-1}. The characteristic features of the quenching temperature dependence are the following. (1) The peaks at 86, 106, 117, 192, 253, 603, and 655 cm^{-1} at 950 °C disappear in the orthorhombic phase and new peaks appear at 284, 474, 510, and 574 cm^{-1} instead. The 574-cm^{-1} peak has large temperature dependence in energy. (2) The energies of the 214- and 356-cm^{-1} peaks at 950 °C decrease at the phase-transition temperature. (3) The 150-cm^{-1} peak increases near the phase-transition temperature at 600°–800 °C. The peak energies of the TO and LO modes are plotted in Fig. 5. The LO mode energies were obtained from the peaks of $-\mathrm{Im}(1/\epsilon)$.

In the perfect two-dimensional metal the electric field accompanying the phonons with the polarization in the xy plane is completely screened, but the field parallel to the z axis is not affected. Therefore only the modes polarized parallel to the z axis are infrared active. The two dimensionality of $YBa_2Cu_3O_{7-\delta}$ is good enough to satisfy this condition. The observed modes in the metallic samples obtained from low temperatures are B_{1u} modes with the polarization along the z axis. Generally the number of infrared-active modes in the high-symmetric phases at high temperatures are smaller than those in the low-symmetric phase at low temperatures. Many modes which appear only in the high-temperature tetragonal phase nevertheless are the E_g modes with the polarization in the xy plane. These modes are activated by the decrease of free carriers. The peaks which appear only in the orthorhombic phase are those which come in sight as a result of narrowing due to the decrease of randomness caused by oxygen deficiency.

It is very difficult to assign the modes even in the metallic region, because $7B_{1u}$ modes are mixed together. Tentative assignment is done as follows. The 149-, 195-, 284-, and 316-cm^{-1} modes are related to the motion of Cu, Ba, and Y atoms, the 474- and 574-cm^{-1} modes are from O atoms in the Cu-O plane sandwiching Y atoms, and the 618-cm^{-1} mode is from O atoms on the Cu-O line along the z axis.

Generally, lattice constants decrease on cooling, which increases phonon energies. The behavior of the 316-cm^{-1} mode is contrary. The decrease in energy reflects the decrease of the bond charge around the Cu atoms. With decreasing temperature the formation of the linear Cu-O chains with increasing oxygen occupation factor increases the attractive force for electrons from Cu atoms on the Cu-O planes sandwiching Y atoms, which increases the electric conductivity and causes superconductivity.

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