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Charge redistribution in $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ probed by Raman spectroscopy: CuO_2 -plane phonon as a probe of carrier dynamics in the CuO_2 plane

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Raman-scattering spectra were investigated for the $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$ system which undergoes a metal-to-insulator transition under variation of carrier concentration. As the system approaches the metal-to-insulator phase boundary, the intensity of CuO_2 -plane phonon modes decreases. We found that the intensity of the CuO_2 -plane mode scales with the inverse of the hole concentration within the CuO_2 conducting planes. A remarkable correlation is found between the CuO_2 -plane mode intensity and T_c for $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$. We suggest that this correlation as well as the CuO_2 -plane mode intensity offer a simple and useful probe for metal-to-insulator transition and carrier dynamics in the CuO_2 plane for substituted materials. © 2002 American Institute of Physics. [DOI: 10.1063/1.1529082]

Change of carrier concentration on the conducting CuO_2 plane, which determines T_c of the system, is the most important parameter in the high- T_c cuprates.^{1,2} The approach to study superconductivity and superconducting materials through chemical modification of the structure has been used extensively, as it provides not only means for the design of new materials but also a way to adjust the physical properties of the material in a controlled manner.^{2,3} It is, however, almost always very difficult to monitor *how* the carrier concentration will change in the conducting CuO_2 plane with substitution. Such a problem is especially exposed in the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ (Y123), where equally with the conducting CuO_2 planes CuO chains are present as well. In the interpretation of much experimental data, it is not obvious how the features of the superconducting CuO_2 planes can be distinguished from those of the CuO chains.

Here, we show that CuO_2 -plane phonons, particularly those accessible by Raman spectroscopy, provide a very simple probe of a metal-to-insulator transition and carrier dynamics in the CuO_2 plane. As a result of our study of $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$ with various carrier concentrations, we find that the intensity of the CuO_2 -plane mode scales with the inverse of the hole concentration within the CuO_2 planes. Furthermore, a remarkable correlation is found between the CuO_2 -plane mode intensity and T_c for $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$.

Ceramic samples with compositions of

$$\text{YBa}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d} \quad (0 \leq y \leq 0.5)$$

and

$$\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d} [0 \leq (x, y) \leq 0.3]$$

were prepared by the polymerized complex method,⁴ a technique which is known to give very pure and homogeneous cuprate superconductors that are crucial for the present study with doping. Oxygen contents were determined either by the standard iodometric titration technique or from Rietveld refinement of neutron diffraction data.⁵ The agreement in the determinations between the two methods was excellent. T_c 's were determined by complex magnetic susceptibility measurements as reported previously.⁶ Room temperature Raman spectra were excited using 514.5 nm line of an Ar laser, the laser beam was focused to a spot of about 2 μm size with microscope (90 \times) collection optics on individual grains of the polycrystalline pellets, the scattered light was analyzed with a triple spectrometer (Jobin-Yvon/Atago Bussan T64000) with the first two stages connected in a subtraction dispersion, and collected with a liquid-nitrogen-cooled CCD detector. The resolution was about 2 cm^{-1} .

Figure 1 shows typical Raman spectra of $\text{YBa}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$ with $0 \leq y \leq 0.5$. Grains with the a - b plane perpendicular to the incident beam were chosen for the investigations. The modes at about 110, 150, 340, 440, and 500 cm^{-1} have previously been assigned to the Ba, Cu(2), O_{Cu} out-of-phase, O_{Cu} in-phase and O_{ap} vibrational modes, respectively,⁷ where Cu(2) and O_{Cu} denote the atoms in the conducting CuO_2 planes, while O_{ap} denotes the apical oxygen connecting the CuO_2 plane and the CuO chain. The increase of Co content from $y=0$ to $y=0.5$ has induced lots of changes in the Raman spectrum of Y123, and the full interpretation of the Raman spectra of Co-doped Y123 can be found elsewhere.^{8,9}

The application of Raman spectroscopy for study of a

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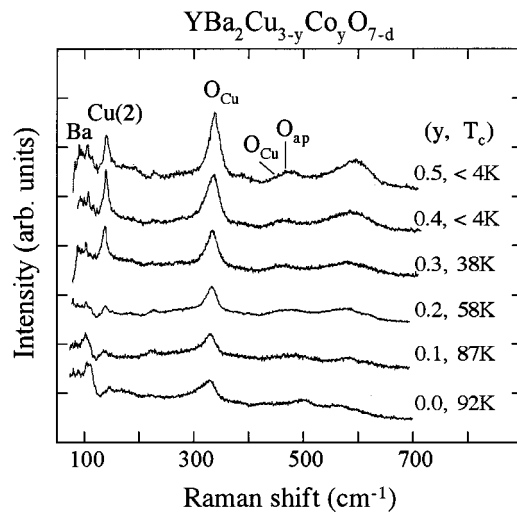
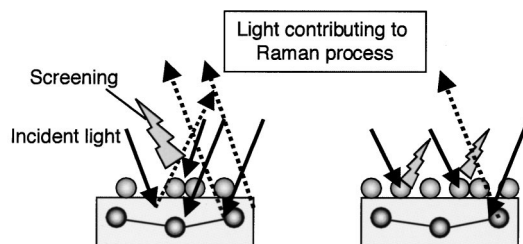


FIG. 1. Raman spectra of $\text{YBa}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$ taken with microscope optics from microcrystals within polycrystalline pellets with different Co contents ranging from $y=0$ to $y=0.5$. T_c determined by complex magnetic susceptibility measurements is depicted for each sample.

metal-to-insulator transition is based on the observation of the CuO_2 -plane mode. In the Raman spectra of Co-substituted $\text{YBa}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$, we find that the vibrational modes involving atoms in the CuO_2 planes, i.e., A_{1g} Cu(2) at 150 cm^{-1} and B_{1g} -like O_{Cu} at 340 cm^{-1} , increase in intensity relative to the non- CuO_2 -related phonons with increasing Co content. These CuO_2 plane phonons are weak in superconducting metallic samples ($y < 0.4$), while their intensities increase as the system approaches the metal-insulator phase boundary. This effect is most probably a direct manifestation of the charge-transfer across the metal-to-insulator transition. The larger number of holes in the superconducting samples leads to an increased metallic screening within CuO_2 planes, leading to smaller CuO_2 bond polarizabilities and thereby phonon intensities. A schematic illustration of charge redistribution and Raman-scattering process on CuO_2 plane is depicted in Fig. 2.

This effect is not unique for Y123 case. Similar intensity changes have been observed for the corresponding CuO_2 -plane modes in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+d}$ and $(\text{Pb}_2,\text{Cu})\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+d}$ with increasing Y con-



Hole concentration, T_c	low	→	high
Screening effect	small	→	large
Light contributing to Raman process	large	→	small

FIG. 2. Schematic picture of how the contributing light to phonon Raman scattering reduces with increasing the number of mobile carriers in the CuO_2 plane induced by doping (screening effect).

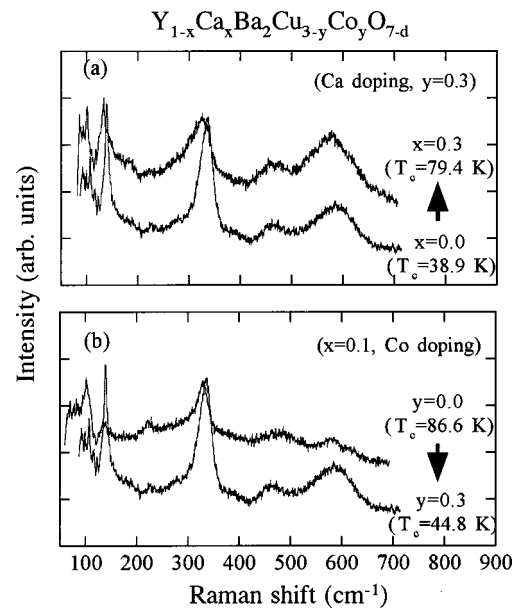


FIG. 3. Raman spectra of (a) $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$ with different Ca contents at $y=0.3$ and (b) $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$ with different Ca contents at $y=0.1$. T_c determined by complex magnetic susceptibility measurements is depicted for each sample.

tent.^{10,11} The fact that the effect is qualitatively similar for modes of different symmetry and for different high- T_c cuprates indicates that the origin is not simply a shift in some specific electronic resonance or a result of a difference in bond polarizabilities. One may also note that a variation in the macroscopic optical properties (i.e., optical penetration depth and refractive index) with carrier concentration changes the overall Raman scattering intensity, whereas Fig. 1 shows a change in relative phonon intensities.

More quantitative interpretation of “charge-redistribution” processes on the conducting CuO_2 plane is made using the case of $\text{YBa}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7-d}$ for different degree of Ca doping. A (Ca/Co)-coupled substitution in Y123 can introduce additional holes on the CuO_2 planes when compared with the corresponding single Co-doping system, from which we can expect a decrease in the Raman intensity for CuO_2 -plane mode as a result of the increased metallic screening in the hole-reintroduced Ca doped samples. Figure 3(a) shows such an example, wherein a series of Raman spectra is displayed as a function of Ca content (x) while keeping Co content constant at $y=0.3$. When comparing the spectrum of $x=0$ with that of $x=0.3$, a significant reduction of the CuO_2 -plane mode intensity becomes obvious, which is consistent with the observed rise in T_c on going from $\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{6.91}$ ($T_c=38.9\text{ K}$) to $(\text{Y}_{0.7}\text{Ca}_{0.3})\text{Ba}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{6.90}$ ($T_c=79.4\text{ K}$). The driving force of the reintroduction of holes on the CuO_2 planes from the CuO chains would come from a reduced positive charge in the $\text{CuO}_2-(\text{Y}^{3+}/\text{Ca}^{2+})-\text{CuO}_2$ layer upon Ca^{2+} doping for Y^{3+} , which tends to transfer the holes localized once in the CuO chains to the CuO_2 conduction planes to re-establish the charge balance of the whole system. On the contrary, when the Co content is increased, while keeping Ca at a given concentration, the CuO_2 -plane mode progressively gains intensity as shown for the case of $x=0.1$ in Fig. 3(b). This clearly indicates a decreased number of holes within the

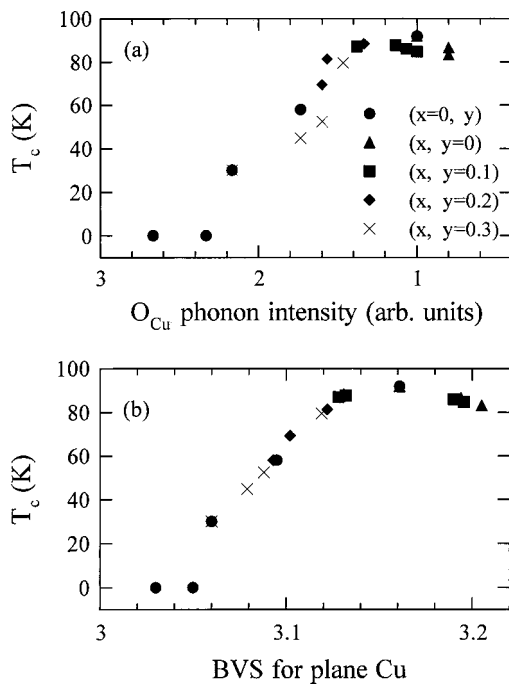


FIG. 4. (a) T_c vs Raman intensity of the O_{Cu} mode [$I(O_{Cu})$] for $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{7-d}$: (●) ($x=0, y=0-0.5$), (▲) ($x=0-0.2, y=0$), (■) ($x=0-0.3, y=0.1$), (◆) ($x=0-0.3, y=0.2$), and (×) ($x=0-0.3, y=0.3$). Data are normalized by the intensity of pure Y123 ($x=y=0$); (b) T_c vs hole concentration estimated by bond-valence-sums for CuO_2 plane in $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{7-d}$.

CuO_2 planes upon Co doping, which is consistent with the observed decrease in T_c on going, for instance from $(Y_{0.9}Ca_{0.1})Ba_2Cu_3O_{6.76}$ ($T_c=86.6$ K) to $(Y_{0.9}Ca_{0.1})Ba_2Cu_{2.7}Co_{0.3}O_{6.90}$ ($T_c=44.8$ K).

Figure 4(a) shows T_c plotted against the O_{Cu} mode intensity [$I(O_{Cu})$] for all the (Ca/Co)-doubly substituted Y123 including singly doped samples. Here we plotted the variation of the B_{1g} -like O_{Cu} phonon, since the depolarized character of this phonon allows one to monitor selectively the changes in the CuO_2 phonon. It is obvious that there is a correlation between T_c and $I(O_{Cu})$. T_c emerges below $I(O_{Cu})=2.2$, and it increases dramatically as $I(O_{Cu})$ decreases from 2.5 to 2.2 displaying insulator-to-metal transitions. However, between $1.0 < I(O_{Cu}) < 1.4$ T_c levels off to an approximately constant value of 90 K. For heavily overdoped samples with $I(O_{Cu}) < 1.0$, T_c would be expected to fall again. We also note that the hole concentration estimated by bond-valence-sums (BVS)^{12,13} for CuO_2 plane in $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{7-d}$ also shows a similar abrupt jump across the insulator-to-metal transition [Fig. 4(b)]. As it is evident from Fig. 5, the intensity of this mode is proportional to the inverse of the hole concentration estimated as bond-valence sums for CuO_2 plane. Thus the sharp drop of the O_{Cu} intensity is due to an abrupt increase in positive

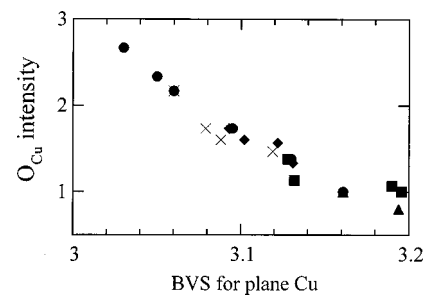


FIG. 5. Raman intensity of the O_{Cu} mode [$I(O_{Cu})$] vs hole concentration estimated by bond-valence-sums for CuO_2 plane in $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{7-d}$. The symbols are the same as in Fig. 4.

charge in the CuO_2 plane, i.e., an onset of the effective charge transfer to the CuO_2 plane inducing the superconductivity. We therefore suggest that the relation between T_c and $I(O_{Cu})$ and the observation of the CuO_2 plane phonon can be used as a convenient means to detect a relative change in the charge carriers within the CuO_2 plane and to study charge transfer or charge redistribution effects in Y123-based oxides.

We should now remind the characteristics and sensitivity of Raman spectroscopy. Compared to other techniques, Raman spectroscopy offers a nondestructive and convenient means for *in situ* observation with high spatial resolution as a function of polarization and temperature. Together with these features, our results clearly indicate the feasibility of Raman scattering technique in addressing some fundamental issues of the insulator-to-metal transition and charge dynamics in the high- T_c superconductors, as well as constitute a quick, nondestructive method for material characterization in practical devices. We want to stress that the method may also be applied for characterization of different high- T_c cuprates and other conducting compounds.

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