The effects of Co substitutions for Cu in YBa2Cu3O6+x on the phonon Raman spectrum.

L. Börjesson[a], L. Van Hong[a], M. Käll[a], M. Kakihana[c] and P. Berastegui[b]

[a]Department of Physics, [b]Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

[c] Research Laboratory of Engeneering Materials, Tokyo Institute of Technology, Nagatsua 4259, Midori-ku, Yokohama 227, Japan

Abstract

We have investigated the phonon Raman spectra of $YBa_2Cu_{3-x}Co_xO_{7-\delta}$ ceramic samples prepared by both solid state reaction and a polymerized complex method using Raman microprobe collection optics. With increasing Co content the frequencies of the Ba, Cu(2), O(2)-O(3) and the apical oxygen O(4) c-axis vibrational modes change considerably. The changes are compared with changes of interatomic bond distances as obtained by neutron diffraction and indicate charge transfer effects between the CuO_2 planes and the CuO chains with increasing Co substitution. The CuO_2 plane oxygen mode at 336 cm^{-1} exhibits slightly decreased coupling to the electronic states with increasing Co content.

1. Introduction

High-T_c superconductivity in the cuprate superconductors is highly sensitive to structural and compositional modifications. In particular, in $YBa_2Cu_3O_{6+y}$ it has been found that the oxygen stoichiometry and ordering are of paramount importance for the critical temperature T_c. The role of the the CuO chains (or the BiO and TlO intercalated layers in the Bi and Tl based superconductors) for superconductivity is a much debated issue. It has been suggested that they act as charge reservoirs which provide the CuO_2 planes with holes[1] i.e. as "charge buffer layers". In some reports it is proposed that the oxygen ordering in the CuO chains is essential for the ability of these layers to transfer holes to the CuO_2 conduction plane[1-3].

In this paper we investigate samples of $YBa_2Cu_3O_{6+y}$ in which the ordering of the CuO chains has been distorted by partial substitution of Cu for Co. It is well known that Co predominantly substitutes Cu in the CuO chains and that T_c drops rapidly with increasing Co content[4,5]. Here we report on the phonon properties as studied by Raman scattering. We show that Co substitution results in changes of structure and phonon

frequencies which are indicative of a charge transfer process between the CuO_2 planes and the CuO chains. The transfer of charge has detrimental effects on T_c. The superconducting and the structural properties of the same samples are characterized and compared with Monte Carlo simulations of the CuO chain ordering elswhere in this volume[6].

2. Experimental

Polycrystalline samples of $YBa_2Cu_{3-y}Co_yO_{6+x}$ (y=0, 0.05, 0.1, 0.15, 0.2, 0.3, and 0.5) were prepared either by conventional solid state sintering at 935-965 C for 60 h followed by oxygen annealing at 1 atm pressure and 400 C for 30 h or by a citrate/ethyleneglycol based polymerized complex technique[7]. X-ray powder diffraction showed no impurities within the detection limit which for CuO, $BaCuO_2$ and YBa_2CuO_5 is about 0.5 weight % . The oxygen content, the structural and the superconducting properties of the same samples is reported elsewhere[6].

Room temperature Raman spectra were obtained with a triple spectrometer (SPEX 1877) equipped with microscope (100x) collection optics and a CCD detector (Wright Instruments). The resolution was

about 4 cm^{-1}. The 514.5 nm line of an argon laser was used for excitation. The laser light was focused to a spot of about 2 μm size on individual grains of the polycrystalline pellets. Grains with either the ab plane or the ca(b) plane perpendicular to the incident beam were chosen for the investigations. Spectra of samples prepared by the two different procedures showed almost identical results.

3. Results

In Fig. 1 we show the obtained Raman spectra of YBa$_2$Cu$_{3-y}$Co$_y$O$_{6+x}$ with Co contents in the range 0≤y≤0.5. The incident and the scattered light was polarized along the c-axis of the grains. In this configuration we observe all the four A$_{1g}$ (tetragonal notation) modes with displacements along the c-axis. The modes at about 115, 155, 440, and 500 cm^{-1} have previosly been assigned to the Ba, Cu(2), O(2)-O(3) in phase, and apical O(4) vibrational modes, respectively[8]. In some of the spectra some leakage of the O(2)-O(3) out-of-phase mode (B$_{1g}$symmetry) at 340 cm^{-1} is observed. The most prominent changes of the phonon frequencies with increasing Co content are observed for the Ba and the O(4) modes (see Fig.2). The frequency of the Ba mode shifts by ~13 cm^{-1} to higher frequencies and the O(4) mode shifts by ~21 cm^{-1} to lower frequencies over the investigated range of Co concentrations. Smaller frequency shifts are observed for the other A$_{1g}$ modes; the Cu(2) mode shifts downwards by ~6 cm^{-1} and the O(2)-O(3) mode shifts upwards by ~7 cm^{-1}.
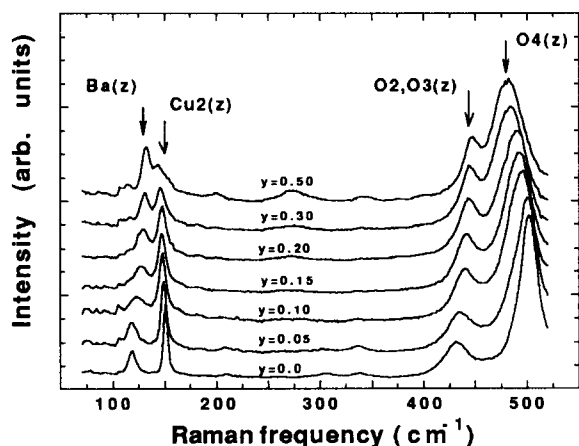

Figure 1. Raman spectra of YBa$_2$Cu$_{3-y}$Co$_y$O$_{6+x}$ taken with microscope optics from microcrystals within polycrystalline pellets. The polarization of the incident and scattered light is along the c-axis. The assignment of the various c-axis vibrational modes are depicted.
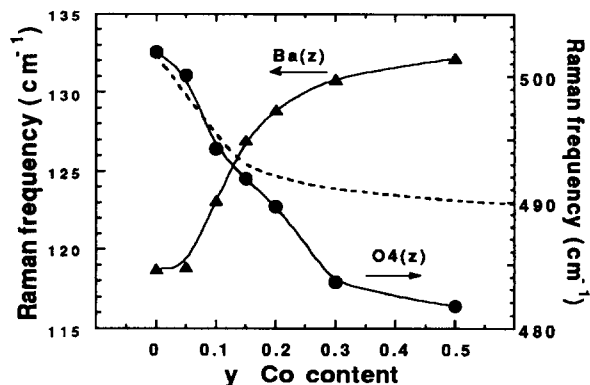

Figure 2. Frequencies of the Ba and the apex oxygen (O(4)) Raman modes as a function of Co content in YBa$_2$Cu$_{3-y}$Co$_y$O$_{6+x}$. Dashed line represents calculated frequencies of the O(4) mode based on the Cu(1) - O(4) and Cu(2)-O(4) distances using (Eq. 2).

Raman spectra of the O(2),O(3) B$_{1g}$ mode are shown in Fig. 3 for 0≤y≤0.5. The line shape of the mode is assymetric for all investigated Co concentrations.This asymmetry has been analysed in detail for pure YBa$_2$Cu$_3$O$_{6+x}$ and has been attributed to Fano interference effects between the phonon and a strong electronic continuum[8] typical of the cuprate superconductors.
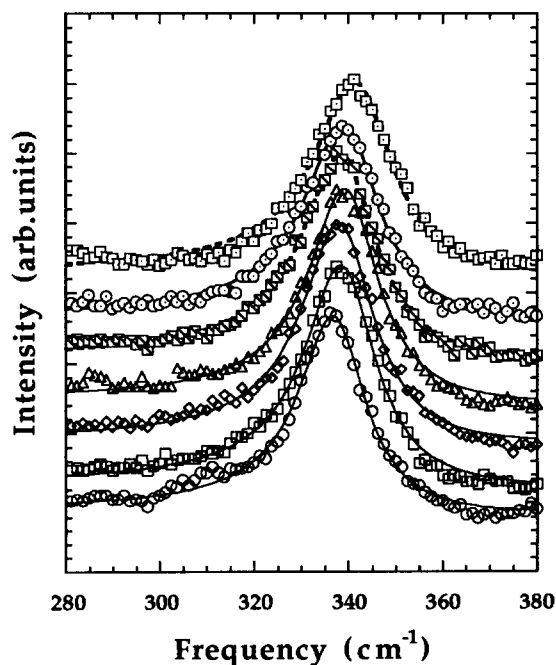

Figure 3. Raman spectra of the O(2)-O(3) mode in YBa$_2$Cu$_{3-y}$Co$_y$O$_{6+x}$, for y=0 (bottom) to y=0.5 (top), taken with polarization vectors in the ab plane.
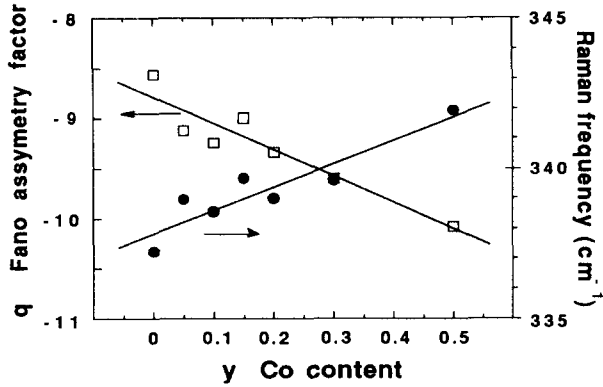
Figure 4. Fano asymmetry parameter and peak frequency of the O(2),O(3) B_{1g} phonon as a function of Co content in $YBa_2Cu_{3-y}Co_yO_{6+x}$.

The lineshape has been analysed using the Breit-Wigner-Fano response function

$$I(\varepsilon) \propto (q+\varepsilon)^2 / (1+\varepsilon^2) \qquad (1)$$

where $\varepsilon = (\omega-\omega_0)/\gamma$ is the reduced energy and q is an asymmetry parameter describing the interaction betweenthe phonon and the electronic continuum. Here ω_0 is the frequency of the "naked" phonon and γ is the half width. Equation 1 was fitted to the 340 cm⁻¹ mode (see curves in figure 3) and results for q and ω_0 are presented in figure 4 as a function of the Co content. Note that large q ($\sim\pm\infty$) describes symmetric (non-interacting) phonons. Fig. 4 shows that the phonon frequency increases and the Fano parameter change slightly towards increasingly negative numbers (the interaction decreases) with increasing Co content. It should be noted that the asymmetry is appreciable for the y=0.4 and 0.5 samples which are not superconducting. Thus, the electron-phonon interaction is significant even for these non-superconducting samples[6].

4. Discussion

In order to compare the observed frequency changes of the O(4) mode with those expected from the changes of the interatomic bond lengths we assume that the force constants follow a simple $1/r_{ij}^3$ relation of a harmonic ionic crystal. In the case of the O(4) vibration there are two relevant r_{ij}, i.e. the Cu(1)-O(4) and the Cu(2)-O(4) distances. The corresponding frequency can then be approximated by

$$\omega^2_{O(4)} = \frac{A}{r^3_{Cu(1)-O(4)}} + \frac{B}{r^3_{Cu(2)-O(4)}} \qquad (2)$$

The constants A and B have been determined from reported changes of the interatomic distances and the O(4) vibrational frequency induced by pressure, rare-earth substitution for Y, and Sr substitution for Ba[5]. These alterations represent only compressional distortions of the structure and should therefore give reasonable estimates of A and B. In neither of these cases it is thought that any significant charge redistribution takes place between the chains and the planes for fully oxygenated samples. We obtain A= 5.27 ·10⁵ cm⁻² Å³ and B=2.04 ·10⁶ cm⁻² Å³ .

The O(4) vibrational frequencies calculated from eq. (2) and using the bond length changes obtained from neutron experiments[5] are shown in fig. 3 (dashed line) for variations of the Co content. Although the Raman frequencies so obtained decrease slightly and follow the experimental data for low dopant contents, they start to deviate significantly for x≈0.15. At higher dopant concentrations the observed frequencies decrease much faster than the calculated ones. Thus, the changes of the O(4) vibration frequency cannot be described solely by changes of the coordination distances to Cu(1) and Cu(2). This indicates that the Co substitutions for Cu(1) substantially alter the bond potentials of O(4) and that a redistribution of charge occurs between the CuO_2 planes and the CuO chains. The changes of the other phonon modes reported here seem to qualitatively support such a picture. The reduction of holes in the CuO_2 plane would increase the coulombic interaction between Ba and O(2), O(3) and lead to increased frequencies of the corresponding vibrational modes as observed. Similarly the downshifts of the Cu(2) and O(4) modes may be explained by a decreased coulombic interaction between Cu(2) and O(4). Recent Raman experiments on oxygen deficient $YBa_2Cu_3O_{6+x}$ quenched from high temperatures show that the O(4) frequency increases with an almost identical rate as T_c with increasing annealing time[9]. Thus, the O(4) frequency is indeed sensitive to the oxygen ordering in the CuO chains and to the charge balance between the CuO_2 planes and the CuO chains.

Similar conclusions on the effects of chain ordering on the charge balance were drawn by Jorgensen et al[10], who studied changes in crystal structure and T_c induced by ageing of quenched, oxygen deficient $YBa_2Cu_3O_{6+x}$ samples. Recently,

Poulsen et.al[4] have shown, using Monte Carlo simulations of the 2-D ASYNNI model, that the transfer of holes from the CuO chains to the CuO_2 planes requires a certain minimum size of well ordered chain regions. The model has recently been applied also to Co substituted $YBa_2Cu_3O_{6+x}$ and the requirement of minimal size regions of CuO chain ordering for superconductivity can well explain the decrease of T_c with increasing Co concentration[6,11]. The present results seem to be in accordance with such a picture, i.e. the disordering of the chains caused by Co substitution leads to a depletion of holes in the CuO_2 planes and to supression of T_c.

An interesting empirical correlation is found between T_c and the frequency shift of the O(4) c-axis vibrational frequency for samples of Y123 subject to Co substitution for Cu and various amounts of oxygen deficiency. In fig. 5 it is shown that T_c scales almost identical with the O(4) frequency. This shows that the bonding of the O(4) atom is systematically connected to variations of T_c. The remarkable correlation is attributed to the sensitivity of the O(4) vibration to changes in the distribution of charge between the chains and the planes.
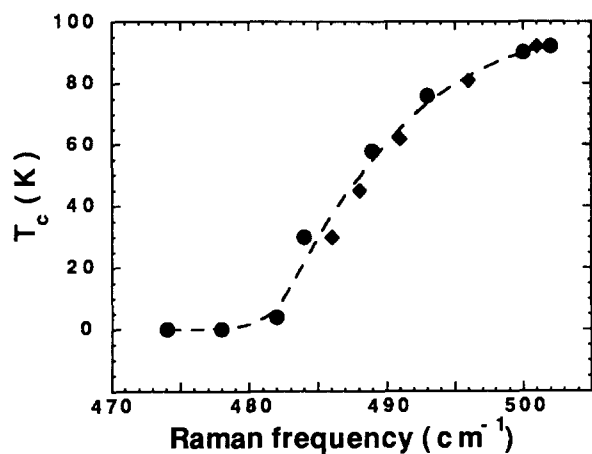

Figure 5. T_c versus Raman frequency of the O(4) mode for $YBa_2Cu_{3-y}Co_yO_{6+x}$ ($0 \leq y \leq 0.5$) (●), and for oxygen deficient $YBa_2Cu_3O_{6+x}$ ($0.3 \leq x \leq 0.9$) (◆). Dashed curve is a guide to the eye.

5. Conclusion

Substituting the chain copper site in $YBa_2Cu_3O_{6+x}$ with Co produces changes of Raman phonon frequencies indicative of a reduction of holes in the CuO_2 plane. The effects are strikingly similar to those reported for oxygen deficient samples. The depletion of hole carriers in the plane

and the drop of T_c is suggested to be caused by chain oxygen disordering. A remarkable common correlation between the apical oxygen Raman frequency and T_c is found for the Co substituted and oxygen-deficient samples. The results indicate that the bonding of the apex oxygen is closely connected to the charge balance between the CuO chains and the CuO_2 planes and that it may play a role for the superconducting properties.

Assymetric lineshapes were observed for the O(2),O(3) out-of-phase mode, typical of Fano interference with electronic states, for all the investigated Co concentrations. This indicates appreciable electron-phonon coupling for this mode even for samples which are non-superconducting.

Acknowledgement

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