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Charge-transfer and compression effects of isomorphous substitutions in $YBa_2Cu_3O_7$

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The influence of partial isomorphous substitutions at the Cu and Ba sites of $YBa_2Cu_3O_{7-\delta}$ on the phonon spectrum and the structure has been investigated systematically by Raman scattering and neutron diffraction. For partial substitution of Sr for Ba the vibrational frequency of the apex oxygen, O(4), increases as expected from the observed compression of the structure in the region between the CuO_2 planes and the CuO chains. Substitutions of trivalent ions such as Co, Fe, and Al for Cu change the coordination of the apex oxygen in a way consistent with an elimination of holes in the CuO_2 planes. The O(4) vibrational frequency decreases rapidly with increasing trivalent substitution. The changes cannot be explained in a simple way by the bond-length changes observed in the neutron-diffraction experiments. A remarkable correlation is found between T_c and the O(4) Raman mode for trivalent substitutions on the Cu(1) site and for oxygen deficiency. We suggest that this correlation as well as the rapid decrease of T_c and the structural changes we observe are caused by a hole charge transfer from the CuO_2 planes to the CuO chains.

I. INTRODUCTION

High-T_c superconductivity in the cuprate superconductors is very sensitive to structural and compositional modification.[1] In particular, in $YBa_2Cu_3O_{7-\delta}$ (Y 1:2:3), it has been found that the stoichiometry and oxygen ordering are of paramount importance for the critical temperature T_c.[2] Furthermore, T_c has been shown to decrease rapidly with various magnetic and nonmagnetic partial substitutions for Cu both in the CuO chains and in the CuO_2 planes.[1,2] In contrast, replacement of Y by various rare-earth metals (except Pr) has only minor effects on T_c (it may even increase) regardless of whether the substituting ion carries a magnetic moment or not.[2] These observations lead to the conclusion that both the CuO_2 planes and the CuO chains are of crucial importance for the superconductivity in Y 1:2:3. As superconductivity and metallic conductivity are generally thought to occur in the CuO_2 planes through hole charge carriers, the question on the nature of the possible coupling between chains and planes in Y 1:2:3 presents itself. The role of the CuO chains (or the BiO and TLO intercalated layers in the Bi and TL based superconductors) for superconductivity is a much debated issue. In some reports it is maintained that they act as charge reservoirs, which provide the CuO_2 planes with holes,[3,4] i.e., acting as a "charge buffer layer." More active roles have also been proposed for the CuO chains in which they take a direct part in superconductivity through, e.g., proximity effects[5] or through an excitonic mechanism.[6]

It has been 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 planes.[4,7,8] Quenching of Y 1:2:3 causes the chain oxygen to be randomly distributed on the O(1) and O(5) sites and leads to a destruction of superconductivity[9] (the atomic notation of Jorgensen *et al.*[3] is used). Recovery of superconductivity and progressive ordering of the chains occur on annealing at room temperature.[9,10] In a recent model by Poulsen *et al.*[4] these effects could be accounted for by assuming that a minimal cluster size of undistorted chains is necessary for the transfer of a hole to the CuO_2 planes. Thus the experiments and the model both emphasize the importance of local orthorhombic distortions for superconductivity in Y 1:2:3. Moreover, a recent band-structure calculation[8] shows that nondistorted chains are needed for charge transfer to occur, while broken chains lead to localization of holes in the chains. On the other hand, powder neutron and x-ray-diffraction experiments on Y 1:2:3 samples subjected to trivalent substitutions (Co, Al, Fe) for Cu show that their average structures become tetragonal for 3–4 % substitutional ions, while the samples remain superconducting with T_c as high as 80 K.[11,12] This has been taken as evidence that orthorhombic distortion and oxygen ordering in the CuO chain layers are not required to obtain high-T_c superconductivity in Y 1:2:3.[13] However, recently it was shown that a superconducting $YBa_2Cu_{2.85}Al_{0.15}O_7$ single crystal with tetragonal average symmetry exhibited local orthorhombic distortions with a correlation length of about 40 Å,[14] i.e., larger than the superconducting coherence length and the minimal size cluster for the charge transfer proposed by Poulsen *et al.*[4] In a recent Monte Carlo simulation of CuO chain layers with partial Co substitution for Cu, Andersen *et al.*[15] showed that the oxygen atoms tend to order locally in CuO chains even in the "average" tetragonal phase and that the minimal cluster model is able to explain the dependence of T_c on Co concentration.

The method of isomorphous substitution has been applied extensively to Y 1:2:3 in order to investigate the importance of various structural units for the superconducting properties. In particular, the structural changes that occur on the substitution of trivalent metals for Cu and their relation to superconductivity have been the subject of several reports.[2,16–18] Thus, Miceli and coworkers[17,18] studied the effects of Co and Al substitutions in Y 1:2:3 by neutron diffraction. Their results, which are confirmed by the present study, were explained in terms of a redistribution of charge between the CuO chains and the CuO_2 planes. In this paper the effects of trivalent metal substitutions (Co, Al, and Fe) at the Cu(1) chain site on the lattice dynamics, the crystal structure, and T_c are investigated systematically by a combination of Raman spectroscopy and neutron diffraction in order to reveal the role of the CuO chains. A comparison is made with the effect of chemical internal pressure induced by Sr substitutions on the Ba site. The same samples have been used throughout the various experiments to ensure that the results can be interrelated. This care has been taken, since it is well known that results from samples of the same composition prepared under similar, but not identical, conditions may deviate considerably. We show that the changes in phonon dynamics and structure for substitution of Sr for Ba are fully consistent with a pure compression effect. On the other hand, the trivalent substitutions for Cu(1) result in changes of structure and phonon frequencies that are indicative of a charge-transfer process.

II. EXPERIMENTAL

Samples of formula $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ and $YBa_2Cu_{3-x}M_xO_{7-\delta}$ (M = Co, Al, and Fe) 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. The latter technique has been shown to be capable of producing extremely pure and homogeneous superconducting materials.[19] X-ray powder diffraction showed no impurities, the detection limit being about 0.5% by weight for CuO, $BaCuO_2$, and YBa_2CuO_5 in Y 1:2:3. The oxygen content of the samples was determined by iodometric titration (for experimental details see Eriksson and coworkers).[20,21]

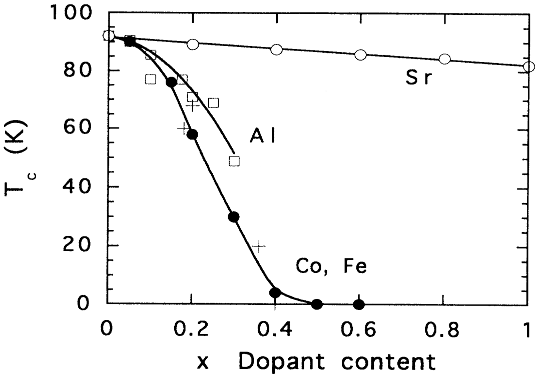

FIG. 1. T_c as a function of dopant concentration (x) in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ (open circles) and $YBa_2Cu_{3-x}M_xO_{7-\delta}$, M=Co (filled circles), Al (open squares), and Fe (crosses). T_c values signify the midpoint of the resistive transition. Full lines are guides for the eye.

The neutron-diffraction experiments were performed at the pulsed neutron source ISIS, Rutherford-Appleton Laboratory, United Kingdom using the POLARIS high-flux, medium-resolution powder diffractometer. The atomic coordinates were determined by Rietveld refinements of the neutron data using standard procedures. A more complete presentation of the results from the Rietveld refinement of the neutron-diffraction data will be given elsewhere.[21] Room-temperature Raman spectra were obtained with a double monochromator (SPEX 1403) with a resolution of 8 cm^{-1} using the 514.5-nm line of an argon laser for excitation in a backscattering geometry. The superconducting properties of the samples were characterized by resistivity measurements using a standard four-probe technique. In Fig. 1 the dependence of the T_c (midpoint of the transition) of the dopant concentration of Sr (for Ba) and Co, Al, and Fe (for Cu) for Y 1:2:3 is presented. Sr substitution has only minor effects on T_c, while the substitutions for Cu show large effects on T_c.

III. RESULTS AND DISCUSSION

A. Sr substitution for Ba

Substituting Sr for Ba results in a linear decrease of T_c with a slope of about 10 K/atom (cf. Fig. 1). Rietveld refinements of the neutron-diffraction data for Sr-substituted $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ show that Sr exclusively enters the Ba site. Neutron diffraction as well as chemical analysis indicate that the oxygen content does not change significantly.[21] Sr doping results in an average compression of the orthorhombic unit cell; *a*, *b*, and *c* decrease linearly with increasing Sr concentration without any tendency towards tetragonalization. The compression in the c direction takes place in the region between the planes and the chains as shown in Fig. 2, where some relevant interatomic distances are presented as a function of Sr content. The Cu(2)-O(4) bond length decreases rapidly with the amount of Sr doping, while the Cu(1)-O(4) distance is only slightly shortened, i.e., O(4) is displaced towards the CuO_2 plane. Ba(Sr) moves in the same direction as O(4) so that the relative position of O(4) and Ba(Sr) in the z direction does not change.

Veal *et al.*[22] reported results on solid solubility and T_c depression of Sr-substituted Y 1:2:3 that are similar to ours. However, their finding that Sr substitution results in a tetragonalization of the unit cell was not substantiated by us. In a more recent study by Karen *et al.*[23] a refinement of the structure of differently substituted $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ was attempted. Their results are in qualitative agreement with this work; however their neutron data are characterized by rather poor statistics. The atomic displacements we observe are consistent with the local structure obtained from extended x-ray-absorption fine structure (EXAFS) experiments, which exhibits a distortion around Sr; O(4) shifts towards Sr, and Sr moves closer to the CuO_2 plane.[24]

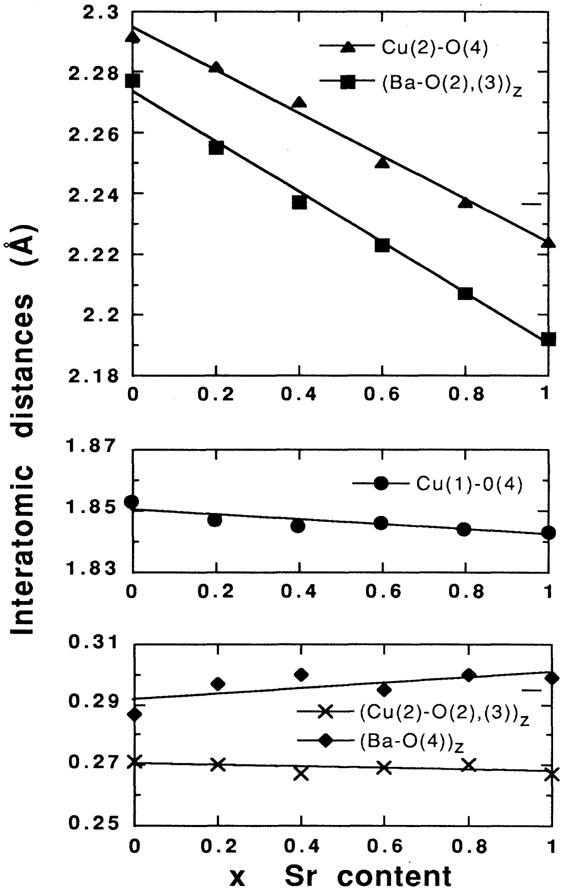

FIG. 2. Some representative interatomic distances in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$. Standard deviation error bars are smaller than the symbols. Lines are guides to the eye.

It may be noted that the disorder on the Ba site introduced by the Sr substitution does not tend to create an average tetragonal symmetry. This indicates that the order in the CuO chains is not strongly affected by Sr doping. The joint movement of Ba(Sr) and O(4) towards the CuO_2 layer with Sr doping indicates that no redistribution of charge between planes and chains occurs. Such a redistribution is expected to change the relative position of O(4) and Ba(Sr) along the c axis because of coloumbic forces. The fact that the corrugation of the CuO_2 planes, i.e., the displacement of Cu(2) and O(2), O(3) along the c axis, is left unchanged by Sr substitution (see Fig. 2) is a further indication that the electronic environment of Cu(2) does not change.

Having established the structural changes induced by Sr in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$, we now turn to the Raman results. The main change of the Raman spectrum induced by Sr doping is a rapid increase of the c-axis vibrational frequency of O(4) at about 500 cm^{-1} (cf. Fig. 3). An increase of the frequency is expected, since the Cu(1)-O(4) and the Cu(2)-O(4) atomic distances decrease considerably (see Fig. 2). In order to compare the observed frequency changes of the O(4) mode with those expected from the bond-length changes we assume that the force constant follows a simple $1/r_{ij}^3$ relation (i.e., $\omega \sim r_{ij}^{-3/2}$) valid for a harmonic ionic crystal and shown to apply to various materials of zinc-blende structure for different de-

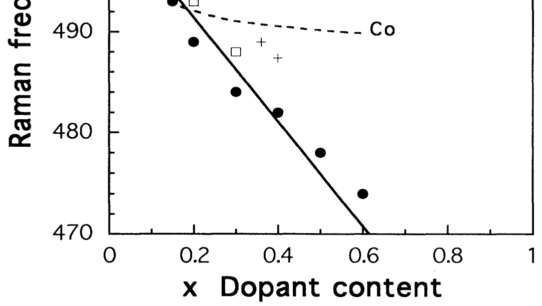

FIG. 3. Frequency of the apex oxygen [O(4)] Raman mode as a function of dopant concentration in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ and $YBa_2Cu_{3-x}M_xO_{7-\delta}$, M=Co, Al, and Fe. The symbols have the same meaning as in Fig. 1. Dashed lines designate calculated frequencies of the O(4) mode in Co-, Al-, Fe-, and Sr-doped samples. The calculations are based on the coordination distances $r_{Cu(1)-O(4)}$ and $r_{Cu(2)-O(4)}$ using a $r^{-3/2}$ frequency dependence [see Eq. (1)].

grees of covalency.[25] In the case of the O(4) vibration of $YBa_2Cu_3O_{7-\delta}$ (YBCO) there are two relevant r_{ij}'s, i.e., the Cu(1)-O(4) and the Cu(2)-O(4) distances. The corresponding frequency is then given by

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

As shown above, the changes of the interatomic distances may be explained as a compression of the unit cell around Sr. Thus, we would expect Eq. (1) to hold for the case of partial Sr substitution for Ba in YBCO. In fact, a rough estimation of the concentration dependence of $\omega_{O(4)}$, based on the assumption $A \approx B$ and using $r_{Cu(1)\text{-}O(4)}$ and $r_{Cu(2)\text{-}O(4)}$ as determined by the neutron-diffraction experiments, results in a trend similar to that given by the experimental frequencies. This encourages us to determine A and B in Eq. (1) from the results for the $x=0$ and 1 samples. We then obtain $A = 5.27\times10^5$ cm^{-2} Å^3 and $B = 2.04\times10^6$ cm^{-2} Å^3, and the dashed line in Fig. 3 indicates the resulting concentration dependence using the experimentally determined r_{ij} of the same samples. It is reassuring for the validity of the simple relationship of Eq. (1) and the calculated A and B that they reproduce (within the experimental accuracy) the pressure dependence of $\omega_{O(4)}$,[26,27] as well as the frequency changes induced by replacing Y for other lanthanides[28] using the neutron-diffraction-determined $r_{Cu(1)\text{-}O(4)}$ and $r_{Cu(2)\text{-}O(4)}$.[29–31] In neither of these cases is it thought that any significant charge redistribution takes place between the chains and the planes for fully oxygenated samples.

The fact that the O(4) vibrational frequency changes may be explained on the basis of bond-length considerations is a further indication that Sr substitution does not significantly change the distribution of charge around O(4), i.e., between layers and chains in the structure. Thus, both the structural and dynamical results are consistent with the conclusion that the hole carrier concentration in the CuO_2 planes does not change significantly as Ba is partly replaced by Sr. These findings are in accordance with the reported Hall effect[32] measurements and with the weak influence Sr doping has on T_c.

B. Trivalent substitutions for Cu

When Al, Co, and Fe are substituted for Cu, the superconducting properties rapidly deteriorate (see Fig. 1). The Co- and Fe-substituted materials become nonsuperconducting close to $x=0.4$. T_c decreases somewhat more slowly for the Al-doped samples up to $x=0.3$, which is the highest dopant level studied in this work. The iodometric titrations and the Rietveld refinements both show that the oxygen content increases as the trivalent dopant ions enter the structure.[20,21] Hence, the formal average valence of Cu decreases only slightly with increasing Co content (assuming Co^{3+}) from 2.23 for $x=0$ to about 2.21 at the end of the superconducting composition range ($x=0.4$). For Al doping the formal valence of Cu stays approximately constant, while in the case of Fe doping the possibility of fourvalent Fe (Ref. 33) makes such a calculation less meaningful.

The Rietveld refinements show that Al, Co, and Fe occupy the Cu(1) position.[21] At high levels of substitution Fe also occupies the Cu(2) position. The three dopants cause a transition to tetragonal symmetry for $x \approx 0.1$. Substitutions of Co, Al, and Fe for Cu(1) cause perturbations of the average structure, especially in the region between the CuO chains and the CuO_2 planes. In Fig. 4 some relevant interatomic distances obtained from the Rietveld refinements are shown as a function of dopant concentration. The structural changes caused by Al and Co substitution are almost identical. The effects of Fe substitution are similar but smaller. The somewhat less pronounced effects of Fe may be connected to the tendency of Fe to also occupy the Cu(2) site in the CuO_2 plane. The most significant change for Al, Co, and Fe substitution is the displacement of the apex oxygen relative to the CuO_2 plane and the CuO chain. The Cu(2)-O(4) bond length increases by ~0.3 Å/atom at low Co concentrations (up to $x=0.15$), while the Cu(1)-O(4) bond length decreases by ~0.1 Å/atom in the same range. The Ba site is displaced towards the oxygens of the CuO_2 plane [O(2),O(3)] with increasing x. Thus, the Ba and O(4) sites move in opposite directions along z. This is in contrast to the case of Sr doping for which the O(4) and Ba move jointly towards the CuO_2 plane with increasing substitu-

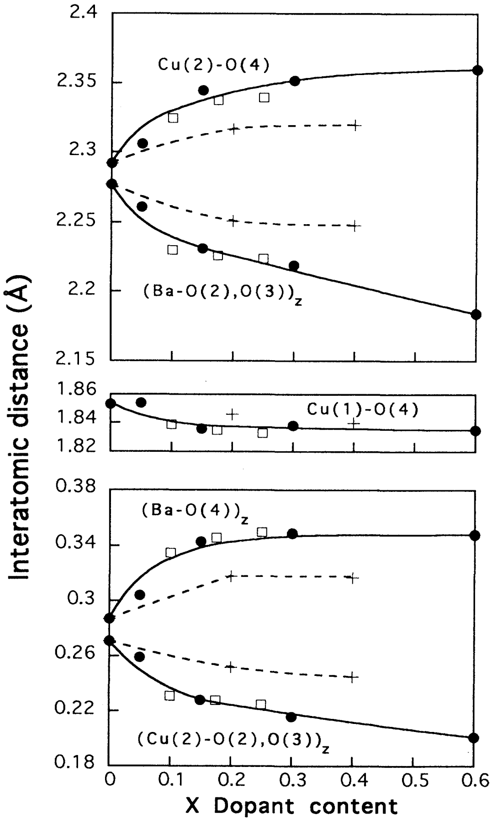

FIG. 4. Some representative atomic distances in $YBa_2Cu_{3-x}M_xO_{7-\delta}$, M=Co, Al, and Fe. Standard deviation error bars are smaller than the symbols. The symbols have the same meaning as in Fig. 1.

tion (cf. Fig. 2). Moreover, the trivalent substitutions for Cu tend to decrease the degree of puckering of the CuO_2 plane, which is also in contrast to the case of Sr doping. In the orthorhombic region ($x < 0.10$) the atomic displacements are most marked, whereas the atomic displacements tend to saturate in the tetragonal region (cf. Fig. 4). Interestingly, the influence on T_c is different; the decrease of T_c is less pronounced in the orthorhombic region ($\sim$40 K/atom) than in the tetragonal region ($\sim$140 K/atom); see Fig. 1. Our results on the site preferences, the transition to tetragonal average symmetry, and the overall trends of the coordination distances with increasing substitutions are in general agreement with several other studies, e.g., EXAFS (Ref. 34) and neutron-diffraction investigations.[17,18,35–37]

The Rietveld refinements show that the introduction of Co, Al, or Fe on the Cu(1) site causes disorder among the oxygens in the Cu(1) plane, O(1) being statistically distributed on a less symmetric site $(x,\frac{1}{2},0)$. Similar oxygen disorder phenomena were reported by Zolliker *et al.*[36] from a neutron-diffraction study of Co-doped Y 1:2:3. In an EXAFS study by Bridges *et al.*[34] it was reported that the Co atoms in doped Y 1:2:3 reside in a distorted oxygen environment. The authors propose a model that includes the displacement of Co from the lattice position of Cu(1) creating a zigzag chain. The present results do not support their interpretation, since the Debye-Waller factors of the dopant ions obtained in the Rietveld refinements are reasonably small and comparable to that of Cu(1).[21]

The displacements of average atomic positions that we register are consistent with the view that the hole carriers in the plane are eliminated as Co, Al, and Fe enter the structure. The filling of holes in the CuO_2 plane is expected to change the balance of coulombic forces in the region between the planes and the chains in such a way as to result in the observed effects, i.e., a displacement of Ba towards the oxygens in the plane, a movement of the apex oxygen away from Cu(2) in the plane, and a depuckering of the plane itself. It should be noted that the changes in the coordination around O(4) caused by the substitution of Co, Al, and Fe for copper in Y 1:2:3 are similar to the changes induced by decreasing the oxygen content.[3,17,18,38] These coordination changes have been explained largely in terms of an elimination of holes in the superconducting CuO_2 plane.[3,17,18,38]

Having seen that the structural data indicate a redistribution of charge between the CuO_2 planes and CuO chains when the chain Cu is replaced by trivalent metal ions, we now discuss our Raman results. The most prominent changes of the oxygen vibrational Raman frequencies with increasing Co concentration are the shifts of the O(4) vibration at 500 cm^{-1} to lower frequencies and the shift of the 440 cm^{-1} mode to higher frequencies.[39] The effects on the oxygen-phonon frequencies of the substitution of Cu are similar for the different trivalent ions. The change of frequency of the 500-cm^{-1} mode with increasing M^{3+} dopant concentration is shown in Fig. 3. Note that the change of the frequency is in the opposite direction to that observed for Sr doping. The half width of the O(4) mode as a function of Co concentration is shown in Fig. 5. The width increases rapidly for small Co concentrations and tends to saturate at higher dopant levels. Another important change of the Raman spectrum on trivalent doping is a rapid increase of the intensity in the 530–600-cm^{-1} range. These modes are attributed to infrared chain modes[40] becoming Raman active because of disorder-induced symmetry breaking.[41,42] This indicates a rapidly increasing disorder in the CuO chains and that the different trivalent ions predominantly enter the Cu(1) position, in agreement with our neutron-diffraction results. The increasing width of the O(4) mode is further indication of increasing disorder as Co is introduced on the Cu(1) site. It should be noted that the intensity and frequency changes of the oxygen vibration modes observed for samples of increasing dopant concentration are strikingly similar to those observed for pure Y 1:2:3 as a function of oxygen deficiency.[39,43]

Next we compare the frequency changes of the O(4) mode induced by trivalent substitutions Cu with those expected from the bond-length changes. The calculated frequencies obtained from Eq. (1), using the bond-length changes obtained from the neutron experiments on the same samples and with the constants A and B determined from the results of Sr substitution as described above (see Sec. III A) are shown in Fig. 3 (dashed lines) for Al, Co, and Fe substitutions, respectively. Although the Raman frequencies so obtained decrease slightly and follow the experimental data for low dopant contents, they start to deviate significantly for $x \approx 0.15$. At higher dopant concentrations the observed frequencies decrease much faster than the calculated ones. Thus, for the M^{3+} substitutions the frequency shifts of the O(4) c-axis vibration cannot be described solely by a change of the coordination distances to Cu(1) and Cu(2) as was the case for the Sr substitution. This provides further evidence that the trivalent substitutions substantially alter the bond potentials of O(4). This in turn indicates a redistribution of charge between the CuO_2 planes and the CuO chains. This conclusion is supported by reported Hall experi-

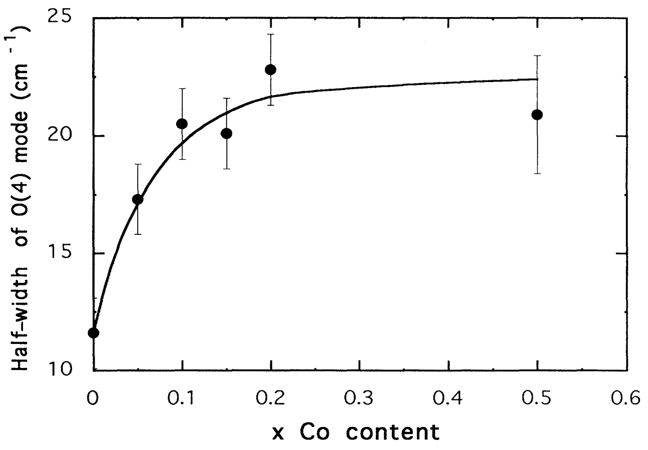

FIG. 5. Half width at half maximum of the O(4) Raman mode at $\sim$500 cm^{-1}. Error bars are indicated by vertical lines. The line is a guide to the eye.

ments, which show that the charge carrier density decreases rapidly with Co doping.[44] The fact that the formal Cu valence does not change significantly with increasing doping therefore implies that holes become localized in the chains, not because Co, Al, and Fe act as hole sinks, but rather because the CuO chain ordering is disturbed by the partial substitution of trivalent ions for Cu. Similar conclusions on the effects of chain ordering on the charge balance were drawn by Jorgensen *et al.*,[10] who studied the effect of aging of quenched oxygen-deficient Y 1:2:3 with respect to changes in crystal structure and T_c. Thus, the idea that the chain ordering is important for superconductivity is not new. However, recently Poulsen *et al.*[4] have shown 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 present results on the O(4) vibrational frequency and the atomic displacements [O(4), Ba, CuO_2 puckering, etc.] seem to be in accordance with such a picture, i.e., the disordering of the chains caused by trivalent substitutions leads to a reduced ability for the transfer of holes from the chains to the planes, despite the nearly constant average oxidation state of copper. Recent Raman experiments on Y 1:2:3 quenched from high temperatures and with oxygen contents in the range 6.25–6.52 show that the O(4) frequency increases with an almost identical rate as T_c with increasing annealing time.[45] This shows that 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.

An interesting empirical correlation is found between T_c and the frequency shift of the O(4) *c*-axis vibrational frequency for samples of Y 1:2:3 subjected to trivalent substitutions (Co, Al, and Fe) and various amounts of oxygen deficiency. In Fig. 6 it is shown that T_c scales almost identically with the O(4) frequency. This 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, i.e., it is directly related to the hole charge carrier density in the CuO_2 planes. The Fe-doped samples deviate somewhat from this correlation and exhibit a more rapid decrease of T_c with decreasing frequency of O(4). This is probably due to the tendency of the Fe ion to also occupy the Cu(2) site. T_c will then be affected either by a magnetic pair-breaking mechanism or by the disorder brought into the planes, while the change in the O(4) vibrational frequency will be smaller, since the amount of Fe in the chains is less. The correlation between T_c and the vibrational frequency found in oxygen-depleted and Co-, Al-, and Fe-doped Y 1:2:3 implies that O(4) is delicately involved in a charge transfer mechanism between the chains and the planes and that the bonding of the O(4) atom is connected to the systematic variations of T_c. This is in agreement with the Raman data on quenched oxygen-deficient Y 1:2:3 (Ref. 45) and with the universal curve for T_c vs bond length for trivalent substituted and oxygen-deficient samples reported by Miceli and co-workers.[17,18] Note that substitutions for the Cu(2) position (Ni,Zn) do not lead to any frequency shift of the 500 cm^{-1} mode.[12] On the other hand, the increasing O(4) vibrational frequency and the slowly decreasing T_c for the Sr-doped samples underline the different nature of the Sr/Ba substitution (compression effect) as compared to the (Co, Al, Fe)/Cu substitutions (charge-transfer effect).

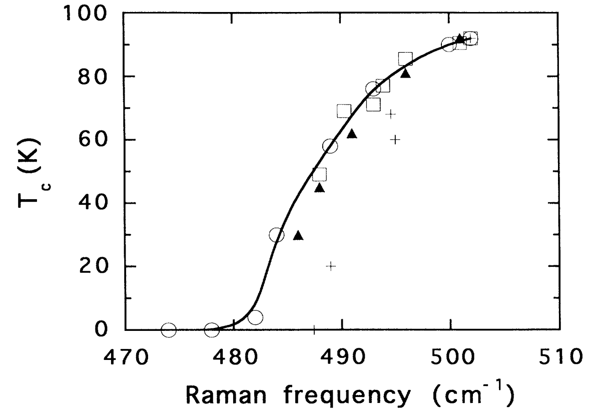

FIG. 6. T_c vs Raman frequency of the apex oxygen [O(4)] mode for $YBa_{2-x}Sr_xCu_3O_{7-\delta}$, $YBa_2Cu_{3-x}M_xO_{7-\delta}$ (M=Co, Al, and Fe), and for oxygen-deficient Y 1:2:3 (Ref. 37). The symbols have the same meaning as in Fig. 1. The line is a guide to the eye.

It is generally believed that insulating, oxygen-deficient Y 1:2:3 contains Cu d^9 ions in the CuO_2 planes, the hole occupying the Cu $d_{x^2-y^2}$ orbital. As the planes become oxidized as a consequence of, e.g., increasing oxygen content in the chains, the extra holes will mostly occupy O p_σ orbitals in the plane. However, experiments show that the positive holes in superconducting Y 1:2:3 (Ref. 46) and in $La_{1-x}Sr_xCuO_4$ (Ref. 47) also have significant Cu d_{z^2} character.

Di Castro, Feiner, and Grilli[48] have proposed that the apex oxygen p_z orbital is important for superconductivity in the planes because of its ability to influence the relative stability of a_1 symmetry holes (e.g., in Cu d_{z^2}) as opposed to b_1 symmetry holes (e.g., in Cu $d_{x^2-y^2}$). In this context the curvature of the T_c vs doping and atomic displacements vs doping graphs noted above may be considered. We suggest that the positive holes in the planes eliminated by small additions of dopants in the chains (in the orthorhombic region) have strong d_{z^2} character. This is in accordance with the experimental results of Bianconi *et al.*[46] and the calculations by di Castro *et al.*[48] showing that the d_{z^2} character of the holes in the planes increases with hole concentration. The filling of d_{z^2} holes would result in a weakening of the bond between Cu(2) and the apex oxygen, in accordance with the decreasing frequency of the O(4) mode, the elongation of the Cu(2)-O(4) bond, and the depuckering of the planes that we observe as a result of small additions of trivalent ions in the chain. The slight influence on T_c in this doping range may be connected with the plateau in the T_c vs carrier concentration–effective mass curve at 92 K reported by Uemura *et al.*[49]

IV. CONCLUSION

Substituting the chain copper site in Y 1:2:3 with Co, Al, and Fe produces changes in coordination distances and apex oxygen Raman frequency 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 is suggested to be the main cause for the rapid decrease in T_c. Since the formal valency of copper is only slightly affected by trivalent substitutions for Cu, a transfer of charge must occur between the copper atoms in the chains and in the planes. This charge transfer may be connected to the observed increasing disorder in the CuO chain. A remarkable common correlation between the apical oxygen Raman frequency and T_c is found for the trivalent substituted and oxygen-deficient samples. The results indicate that the bonding of the apex oxygen is closely connected to the charge transfer between chains and planes and that it may play a role for the superconducting properties.

In contrast, the changes in Raman frequencies and interatomic distances that we observe for Sr substitution at the Ba site are fully consistent with a compression of the region between the chains and the planes and do not indicate any redistribution of charge within the structure.

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