EVIDENCE FOR CHAIN SITE SUBSTITUTION OF NICKEL IN YBa$_2$(Cu$_{1-x}$Ni$_x$)$_4$O$_8$

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We report a Raman scattering study of YBa$_2$(Cu$_{1-x}$M$_x$)$_4$O$_8$ (M=Ni, Zn) ceramic samples in the normal and superconducting phases. The frequency of the Cu(1) chain A$_g$ mode is observed to soften by about 11 cm$^{-1}$ over a Ni doping range of 0-2.5%, while other modes exhibit shifts of 0-4 cm$^{-1}$. The modes show only small shifts in the Zn doped materials. We believe that this large softening indicates that Ni substitutes for Cu in chain sites.

Keywords: A. High T$_c$ superconductors; D. Phonons; E. Inelastic light scattering;

The substitution of Ni and Zn for Cu in YBa$_2$Cu$_3$O$_7$ (Y-123) has been of special interest due to the fact that while Ni and Zn have similar chemical characteristics, the non magnetic Zn suppresses T$_c$ at lower doping than magnetic Ni. Several studies including NMR and NQR studies$^1$ and point contact spectroscopy$^2$ indicate that the filled 3d shell of the Zn$^{2+}$ impurity ion prevents the hopping of holes and therefore causes a carrier localization. The clusters around the Zn ion restore short range antiferromagnetic order$^3$. In contrast, the unfilled d shell of Ni$^{2+}$ is believed not to produce this effect. As such, information regarding whether Ni prefers chain or plane Cu sites is crucial to the understanding of the suppression of superconductivity by Ni as compared with Zn.

Controversial data has been reported for the crystallographic site occupancy of Zn and Ni substituting for Cu. A direct determination of sites and of bond lengths is rendered difficult due to the low contrast between neutron or x-ray scattering factors of Zn and Ni as compared with Cu. Much of the literature appears to favor the view that both Zn and Ni preferentially occupy the Cu(2) sites in the CuO$_2$ layers$^4$-$^6$ in the Y–123 materials, although the possibility of Zn at Cu(1) chain sites has also been discussed$^7$. Information about Ni doped Y–123 comes primarily from bulk ceramic samples$^8$,$^9$. Since the crystal remains orthorhombic up to a solubility limit of 10 at. %, as it does with Zn doping, the implication is that the Cu-O chains remain intact and that a substantial fraction of Ni goes into the CuO$_2$ planes. Dopants with smaller ionic radii$^{10}$ such as Al and Co make the lattice tetragonal above 4 at. %, and are believed to prefer chain sites.

Much of the Raman study of Ni-doped Y–123's has focused on studies of the O(2)-O(3) phonons and associated phonon anomalies$^{11}$,$^{12}$. Previous Raman scattering studies have shown that the anomalies at T$_c$ are substantially suppressed with Zn doping whereas they are not with Ni doping. The calculations of Zeyher and Zwicknagel$^{13}$ using strong electron-phonon coupling predicts changes in linewidth, asymmetry and frequency due to a Fano-type mixing between phonons and the electronic continuum. In addition to phonon anomalies, Raman studies$^{11}$ also showed evidence of weak modes at 590 and 230 cm$^{-1}$, which had sample dependent intensities in some of the films. These group theoretically forbidden chain modes in the 123's were identified as indicative of the presence of some disorder in the chains.

We report a Raman scattering study of the related YBa$_2$(Cu$_{1-x}$M$_x$)$_4$O$_8$ (Y–124) materials doped with M= Zn and Ni. The advantage of studying the 124's is that in addition to the Raman modes seen in the 123's, the 124's exhibit chain modes as well. From our study of these chain modes, we present strong evidence that Ni does substitute for Cu in the chain site.

Experimental Details

Raman spectra are obtained using a Spex Triplemate spectrometer equipped with a liquid nitrogen cooled CCD detector and a holographic supernotch filter. The beam diameter on the sample is between 30 and 80 µm and about 10 to 15mW of laser power is incident on the samples. The ceramic samples, which are about 2 x 2 x 1 mm$^3$ are attached
to the cold finger of a helium refrigerator. Spectra are obtained both in the superconducting phase at 10K and in the normal phase at 100K for the Ni-doped samples and at 10K for the Zn-doped samples. The 5145 and 4880Å lines of the Ar⁺ laser are used to excite the spectra.

Samples of YBa₂(Cu₁₋ₓMₓ)₄O₈ doped with M = Zn or Ni with 0 < x < 0.1 are prepared by conventional solid state reaction followed by high pressure oxygen annealing. Appropriate quantities of Y₂O₃, BaO, CuO, and NiO or ZnO are thoroughly mixed and reacted in air for 24 h at 650˚C, 750˚C, and 880˚C respectively. The reacted powders are well mixed and cold pressed into pellets. These pellets are sintered at 950˚C and annealed at 500˚C in oxygen for 16 h. The sintered ceramic samples are finally annealed in Morris Research, Model HPD-5010P, high pressure furnace at 990˚C for 48 h under an oxygen pressure of 100 bar.

A Rigaku X-ray diffractometer with Cu-Kα radiation is used to record powder diffraction patterns at room temperature. Silicon is used as an internal standard to follow the shifts in peak positions due to substitution at the Cu site. Lattice parameters are determined from least-square fits to the diffraction lines indexed with the space group Ammm. DC magnetic susceptibility measurements are made using Quantum Design SQUID magnetometer in the "field cooled" mode in an external field of 10 G. The superconducting transition temperature (Tc) denotes the temperature where the onset of diamagnetic signal is observed.

**Results and Discussion.**

Fig. 1 shows the transition temperatures of both Ni- and Zn-doped samples. As is the case for Y–123's and previous works in the doped Y–124's, doping with Zn suppresses Tc at lower concentrations than does doping with Ni. X-ray data, analyzed using about 25 lines, show no significant change in the lattice parameter within an error bar of 0.1% (Fig. 2). This is consistent with x-ray studies of doped 123's, where the lattice parameter changes stayed within 0.3% up to x = 0.2.

The Raman spectra of Ni-doped Y–124 is shown for a few representative values of Ni doping in Fig. 3. Raman spectra are taken using an exciting wavelength of 4880 Å. The primary modes observed in undoped Y–124 at 10K are the A_g mode corresponding to the Cu(2) in-plane mode at 150 cm⁻¹, the A_g Cu(1) chain mode at 254 cm⁻¹, the B₃g Cu(1) chain mode at 312 cm⁻¹, the O(2)-O(3) in-plane modes at 337 cm⁻¹ (B₁g, out of phase) and 434 cm⁻¹ (in phase), the O(4) bridging oxygen mode at 499 cm⁻¹, and the O(1) chain mode at 603 cm⁻¹. The O(1) B₂g mode near 210 cm⁻¹ and the Ba A_g mode at 101 cm⁻¹ are barely observable, making their frequencies difficult to track.

Figs. 4 and 5 show the frequencies of the observed modes as a function of Ni doping. The filled squares denote the frequencies at 10K while the open triangles denote frequencies at 100K. The lines are least squares fits to the data, with linear or quadratic functions as appropriate, and are meant primarily as a guide to the eye. Since most of the data was obtained in the 0-2.5% range with only one other sample at 5%, we will discuss primarily the data in the 0-2.5% range. Fig. 4 shows the oxygen associated modes. The two in-plane O(2)-O(3) modes experience softening of two to four cm⁻¹.

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**Fig. 1.** Superconducting transition temperatures in Ni- and Zn-doped YBa₂(Cu₁₋ₓMₓ)₄O₈.

**Fig. 2.** Room temperature lattice parameters of Ni- and Zn-doped YBa₂(Cu₁₋ₓMₓ)₄O₈.
while the O(4) bridging oxygen mode and the O(1) chain mode show a negligible shift in frequency. The small shifts in the in-plane modes are consistent with previous studies in the doped Y-123 materials

Fig. 5 shows the frequencies of the Cu associated modes in Ni-doped Y–124 as a function of Ni doping. The Raman frequency of the $A_{g}$ $254 \text{ cm}^{-1}$ Cu(1) chain mode softens by almost 11 cm$^{-1}$ in the range 0 – 2.5%, both in the normal and superconducting phases. This softening is also seen using an exciting laser wavelength of 5145Å. In contrast, the $B_{3g}$ mode of the same Cu(1) atom experiences virtually no shift in frequency, while the in-plane Cu(2) mode softens by about 3 cm$^{-1}$.

The large shift in the $A_{g}$ Cu(1) mode is compared with the frequency of the same mode in Zn-doped Y$\text{Ba}_2\text{Cu}_3\text{O}_7$ (Fig. 6), where it is found to increase in frequency by about 4 cm$^{-1}$ up to a Zn doping of 1%, after which it stays a constant. The other modes of Zn-doped Y124 (not shown) exhibit a similar trend.

The large shift of the $A_{g}$ Cu(1) chain mode over a rather small range of Ni concentration leads us to conclude that Ni substitutes for Cu in the chain sites. This argument is fortified by the rather small shift in the Cu(2) in-plane mode. Note that a different vibrational mode of the same Cu(1) atom, the $B_{3g}$ mode, barely shifts over the same range of concentrations.
concentration (Fig. 5). Fig. 7 is a schematic sketch of the three Cu-associated modes. The A\_g Cu(1) chain mode, corresponding to a vibration perpendicular to the chain along the c direction, causes the two chains to vibrate against each other. In contrast, the B\_3g mode corresponds to a vibration along the chain and hence along the O(1)-Ni-O(1) bond, shearing the chains against each other. Since the short range potentials between Ni-O and Cu-O are expected to be about the same, it is not surprising that substitution of Ni for Cu does not change the frequency of a vibration along the Ni-O(1) bond. However, the A\_g vibration pushes the Cu(1) atom against the O(1) in the neighboring chain on one side and against the bridging O(4) on the other side. The calculated Born Mayer potentials for the same chain O(1) and bridging O(4) are the same, but they are different for the neighboring chain O(1). These values could be affected by the substitution of Ni for Cu, and cause a change in the frequency. We note that the differences in Cu and Ni mass can account (in a simplistic harmonic model) for only about a 0.1% decrease in the frequency of the mode, as contrasted to the 4% change seen.

The small change in the Cu(2) in plane mode frequency as compared to the large change in the Cu(1) chain mode does not rule out the substitution of Ni in the planes. It is possible that Ni substitutes in both sites. The chain and plane Cu atoms are in different crystalline environments, which results in different hybridization of their electronic states. The asymmetric bonds in the Cu(1) A\_g vibration as compared with the symmetric bonds in the CuO\_2 planes could preferentially change force constants and frequencies of the chain mode.

Factors that influence frequency shifts include changes in the compressibility with Ni doping. A change in the c-axis compressibility, however, would affect both the Cu(1) and the O(1) chain mode at 603 cm\(^{-1}\). The negligible frequency shift of the O(1) as contrasted to the Cu(1) mode rules out this possibility. Changes due to lattice constant changes are ruled out by the data in Fig. 2.

Softening caused by T\_c associated phonon anomalies is, of course, well known in these materials. In pure Y–124, the Cu(1) A\_g mode is observed to have a dip of about 2 cm\(^{-1}\) at T\_c, while the O(2)-O(3) modes have more pronounced anomalies, with shifts of 2 to 4 cm\(^{-1}\), with similar numbers for the Y–123's. It is possible that some of these shifts have been folded into our data for the same modes, shown in Fig. 4, but due to the small magnitude of these shifts we believe this to be an unlikely source of the softening we observe for the Cu chain mode. As a rough measure we show in Figs. 4 and 5 data from both the normal and superconducting phases, taken at constant temperatures of 10 and 100K. The data for all peaks overlap for both temperatures.

The presence of Ni in the chain sites, which are considered the charge reservoirs, could affect the charge transfer mechanism differently from its presence in a plane site. The O-Cu-O network in the charge reservoir may not function as effectively with Ni in random positions. Indeed the destruction of superconductivity may occur less effectively due to Ni in chain sites than in plane sites, and thus provide an additional mechanism for the lack of suppression of T\_c with Ni doping.

In conclusion, we have presented Raman scattering data where A\_g Cu chain modes exhibit a large softening in Ni-doped Y–124 as compared to B\_3g Cu chain mode, Cu in-plane modes, or the oxygen associated modes. In contrast Zn-doped modes show only small changes in mode frequencies. We suggest that this implies that Ni substitutes in the chain sites.

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References