

Raman scattering from $\text{Ba}_2\text{YCu}_3\text{O}_7$ above and below the 90-K superconducting transition: Evidence for oxygen vacancies in the Cu-O chains

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Raman scattering data from different types of samples of the normal and superconducting phases of $\text{Ba}_2\text{YCu}_3\text{O}_7$ ($T_c \approx 90$ K) and $\text{Ba}_2\text{Y}_{0.75}\text{Sc}_{0.25}\text{Cu}_{2.4}\text{Ni}_{0.6}^{2+}\text{O}_7$ ($T_c \approx 65$ K) are reported and assigned. A Raman line observed at 632 cm^{-1} is assigned to the stretching mode of the Cu-O chains. This mode is Raman inactive in the ordered O-deficient lattice but appears to be activated by oxygen vacancies along the chains. Another sample-dependent line is observed at 365 cm^{-1} which gains intensity below 150 K but disappears in the superconducting phase. In the Ni-alloyed material the Raman results suggest that the Ni^{2+} ions primarily occupy Cu sites in the Cu-O chains.

Materials such as $\text{La}_2\text{CuO}_{4-\delta}$ and its solid solutions $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_{4-\delta}$ have been known for a number of years.^{1,2} However, it is only recently that their high- T_c superconducting properties have been identified.³⁻⁵ Subsequent pressure-dependent measurements by Chu *et al.*⁶ led to possible superconducting-phase onsets that were as high as 52 K in these materials. Since even higher pressure did not raise T_c any further it was realized that T_c could only be raised by compositional variations that could lead to new phases. One choice was to replace La by the lighter elements Y and Sc in the same column of the periodic table, since apart from the intrinsic pressure effect of the smaller ions the critical phonon frequency would be raised if there is some coupling of the Cu-O modes with the modes of the counter-ion sublattice. This process led Wu *et al.*⁷ and many others independently⁸ to report on a new Y-Ba-Cu oxide phase with a transition temperature approaching 90 K. The Y-Ba-Cu oxide phase was identified as $\text{Ba}_2\text{YCu}_3\text{O}_7$ by single-crystal x-ray diffraction by Rietman *et al.*⁹ and independently by many others.¹⁰ The correct positions of the O atoms in the structure were worked out by powder neutron diffraction by Beech, Miraglia, Santoro, and Roth¹¹ and Jorgensen.¹² In this communication we will report on a detailed, temperature-dependent Raman scattering study of samples of $\text{Ba}_2\text{YCu}_3\text{O}_7$ prepared by different methods. In addition results on the Raman spectrum of a modified composition with the $\text{Ba}_2\text{YCu}_3\text{O}_7$ structure involving the partial replacement of Y^{3+} by Sc^{3+} and Cu^{2+} by Ni^{2+} will also be discussed.

The $\text{Ba}_2\text{YCu}_3\text{O}_7$ samples used in this work were obtained by three different routes. Sample A was synthesized by heat treatment in air of high-grade Y_2O_3 , BaCO_3 , and CuO , which were thoroughly ground in a dry box and placed in a SiO_2 boat in a tube furnace coupled to a temperature controller. The heat treatment in air was for ≈ 24 h at $T = 935 \pm 2^\circ\text{C}$, with two intermediate grindings. The material was finally ground, sieved (100 mesh) and pelletized at a pressure of 10^4 psi. The pellets were placed in the furnace under flowing O_2 and annealed at $910 \pm 1^\circ\text{C}$ for 12 h followed by slow furnace cooling. Sample B was synthesized via the heat treatment of the ci-

trates of Y, Ba, and Cu. The citrates were formed by the addition of citric acid to an aqueous solution of water-soluble nitrates and acetates of Y, Ba, and Cu. The water was evaporated off to give a residue composed of an x-ray amorphous mixture of the citrates, which was heat treated in air at 700°C for 1 h to give the oxides and then at 900°C for 1 h to give $\text{Ba}_2\text{YCu}_3\text{O}_7$. The material was then pelletized and O_2 annealed as described for sample A. Sample C was prepared by a method similar to sample A except that barium peroxide, BaO_2 , was used instead of BaCO_3 . This allowed for an excess of O_2 to be present in the first stages of formation of the $\text{Ba}_2\text{YCu}_3\text{O}_7$ phase. The samples of composition $\text{Ba}_2\text{Y}_{0.75}\text{Sc}_{0.25}\text{Cu}_{2.4}\text{Ni}_{0.6}^{2+}\text{O}_7$ were prepared via the BaCO_3 route using high-grade NiO and Sc_2O_3 . The samples studied were carefully checked by power x-ray diffraction and found to contain $> 95\%$ of the orthorhombic $\text{Ba}_2\text{YCu}_3\text{O}_7$ phase. Samples B and C were nearly 100% single phase while sample A and the Sc, Ni-alloyed composition contained $\approx 1\%$ - 2% of the semiconducting Y_2BaCuO_5 and BaCuO_2 phases. Sample B, however, was found to contain smaller-size microcrystals. A four-probe ac lock-in resistivity measuring setup coupled to a computer-driven variable-temperature system was used to check the superconducting transitions in the samples. Transitions down to the noise level of our system were observed for all samples. The transitions were ≈ 1 to 3 K wide for samples A and C and about 5-K wide for sample B. T_c corresponding to zero resistance and taken as the average between a cooling and warming scan was 90 K for sample A, 87 K for samples B and C, and 65 K for the sample containing Sc^{3+} and Ni^{2+} . Magnetometry data on these samples indicated bulk superconductivity¹³ with T_c consistent with the conductivity measurements. Electron microprobe analyses showed that the compositions of all the samples were close to $\text{Ba}_2\text{YCu}_3\text{O}_7$. However, Auger depth profiles and x-ray photoemission measurements¹⁴ indicated that the O content of sample B was 5% higher on a relative scale compared with sample A.

The Raman data were obtained in the backscattering geometry with pelletized samples mounted on the cold finger of a closed-cycle He-Displex[®] attached to a temperature regulator and a controller. The temperature stabi-

ty during a run was $\pm 0.5^\circ\text{C}$. The temperature was monitored by a GaAs diode sensor placed near the bottom of the pellet. Excitation was provided by one of the lines of a Kr-Ar laser. Typically, laser power at the sample ranging from 30 to 100 mW was focused into a line $\approx 2\text{-mm}$ long and $\approx 0.5\text{-mm}$ wide using a cylindrical lens. The scattered beam was analyzed by a conventional double monochromator with holographic gratings, an S-20 response phototube, and photon counting detection. The dark count in this system was maintained at ≈ 1 count/sec. Spectra were recorded typically with slits set at a resolution of 10 cm^{-1} . Most of the spectra were reproduced at least by two excitation wavelengths—typically at 4880 and 5145 Å. Poorer-quality spectra could be obtained with excitation at 4579 and 6471 Å. This is in agreement with the observation that the plasma-edge antiresonance in $\text{Ba}_2\text{YCu}_3\text{O}_7$ is near 5000 Å,¹⁵ which allows for a somewhat greater penetration depth of the incident beam in the spectral range around 5000 Å.

The Raman spectra observed can be interpreted in terms of the layered, O-deficient structure of $\text{Ba}_2\text{YCu}_3\text{O}_7$,¹¹ shown in Fig. 1. The local environments at the Cu(1) and Cu(2) sites are indicated by the dotted lines. The structure has space-group symmetry $Pnmm$ (D_{2h}^{14}) with Cu(1)-O(4) chains along the b axis and puckered planes involving Cu(2)-O(2)-Cu(2)-O(3) atoms parallel to the a - b plane. The Cu-O distances at the Cu(1) site are Cu(1)-O(1)=1.846 Å and Cu(1)-O(4)=1.9429 Å. The corresponding distances at the Cu(2) site are Cu(2)-O(2)=1.9299 Å and Cu(2)-O(3)=1.9607 Å.¹¹ The short Cu-O distance orthogonal to the chain direction is notable. In addition, the neutron scattering results of Beech *et al.* indicate that the O(4) positions are fully occupied ($\text{O}=7.0$ per formula unit) in their O_2 -annealed samples but their unannealed samples have $\text{O}=6.8$. However, our O_2 -annealed sample B examined at the National Bureau of Standards (NBS)¹⁶ and a number of O_2 -annealed samples examined by Jorgensen show an oxygen content corresponding to around 6.8 per formula unit.

Raman activity at the Γ point of the Brillouin zone is indicated for the modes of Γ_g , B_{2g} , and B_{3g} symmetry by factor group analysis, at the O(1), O(2), and O(3) sites. However, no Raman activity is predicted by group theory at the O(4) site associated with the copper-oxygen chains. The A_g symmetry phonons involve stretching vibrations within the Cu-O planes, whereas the phonons of B_{2g} and B_{3g} symmetry are associated with deformations out of the Cu-O planes at the two Cu sites. Raman activity is also predicted for vibrational modes involving the Ba and Cu(2) atoms.

The Raman spectrum of sample A of $\text{Ba}_2\text{YCu}_3\text{O}_7$ is shown in Fig. 2. Four lines at 430, 497, 583, and 632 cm^{-1} (values at 300 K) are observed. These lines can be detected at different excitation frequencies, at power levels down to 30 mW, and in samples that had been cooled down to ≈ 30 K before exposure to the laser beam. Data collected between 50 and 300 cm^{-1} and from 700 to 1000 cm^{-1} showed no scattering above the background level. The Raman spectrum of sample B displayed in Fig. 3 shows that in the normal metallic phase the lines near

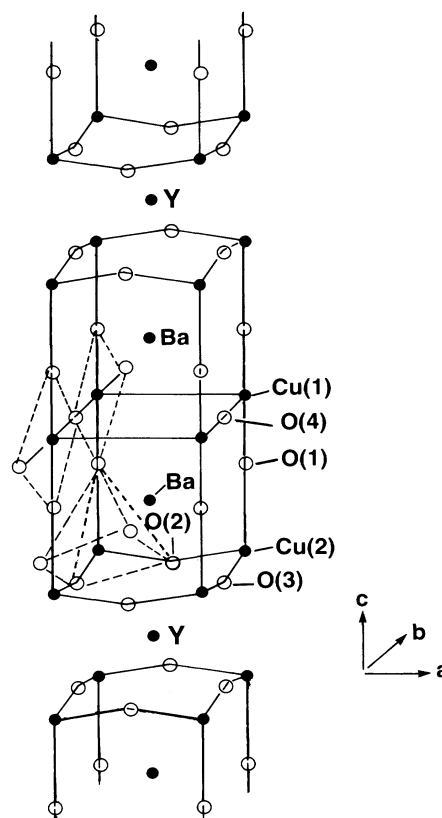


FIG. 1. The structure of the $\text{Ba}_2\text{YCu}_3\text{O}_7$ phase. The sites are labeled in accordance with Refs. 9 and 11.

430, 497, and 583 cm^{-1} can be detected in the same intensity ratio as in sample A, but the strongest line: that at 632 cm^{-1} , is absent. In the spectrum of sample C (not shown here) all four lines are observed but the intensity of the 632 cm^{-1} line is sizably depressed relative to that of the 497 cm^{-1} line. The observed Raman lines with increasing frequencies at 430, 497, 583, and 632 cm^{-1} correlate with decreasing Cu—O bond lengths at the O(3), O(4), O(2), and O(1) sites, respectively, and are assignable to the Cu-O stretching modes of A_g symmetry at these sites. However, the A_g mode at the O(4) chain site is forbidden by group theory but Raman activity may be induced as a result of disorder due to oxygen vacancies along the chains. Since the line at 632 cm^{-1} is extremely sensitive to sample preparation, it is suggested that due to the expected strong electron-phonon interaction along the chains, this line rather than the one at 497 cm^{-1} is associated with the Cu(1)-O(4) stretching mode. This interpretation is consistent with the neutron scattering results but not with the observation that O_2 -annealed samples prepared at NBS do not show vacancies in the chain direction. Moreover, our O_2 -annealed sample B which shows an O content corresponding to 6.8, displays no Raman activity at 632 cm^{-1} . Surface-sensitive techniques, however, show that the O content in samples B and C is higher than in sample A. Since Raman scattering is sampling the surface regions of these materials, it is likely that the surface rather than the bulk oxygen vacancy determines

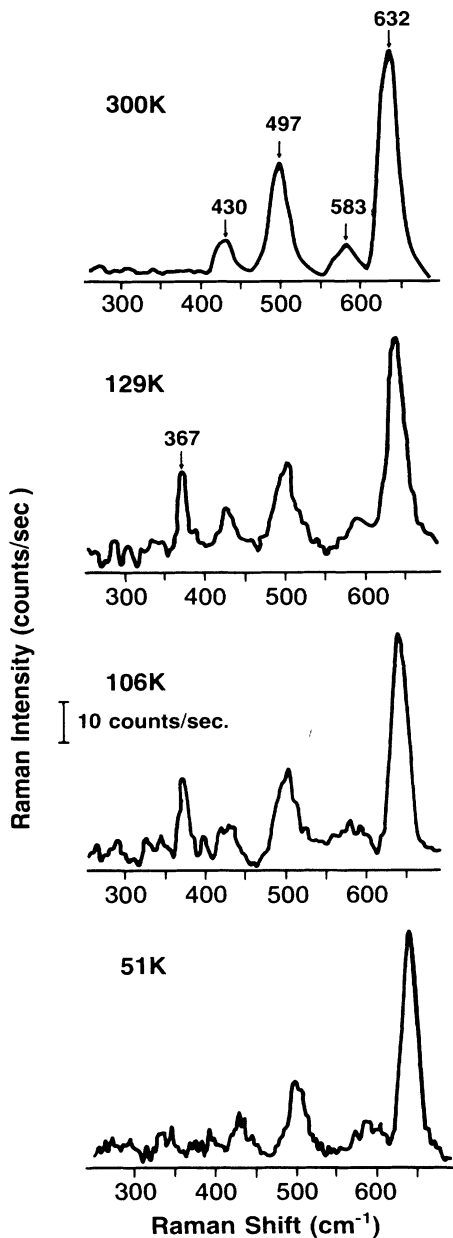


FIG. 2. The Raman spectra of $\text{Ba}_2\text{YCu}_3\text{O}_7$: Sample A as a function of temperature. See text for details regarding the sample. Excitation: 4880 \AA , $\approx 100 \text{ mW}$; the background has been subtracted.

the Raman activity of the 632 cm^{-1} line. The oxygen-deformation and heavy atom modes predicted by group theory are expected to lie at relatively lower frequencies, and hence their absence in the observed spectra indicates that only the O-stretching modes are resonance enhanced, probably via an electron-phonon coupling mechanism involving a Cu $3d$ hole creation and annihilation process. Note the much greater Raman intensity of the lines assigned to modes at the Cu(1) site, indicating that the electron-phonon interaction is greater along the Cu-O chains.

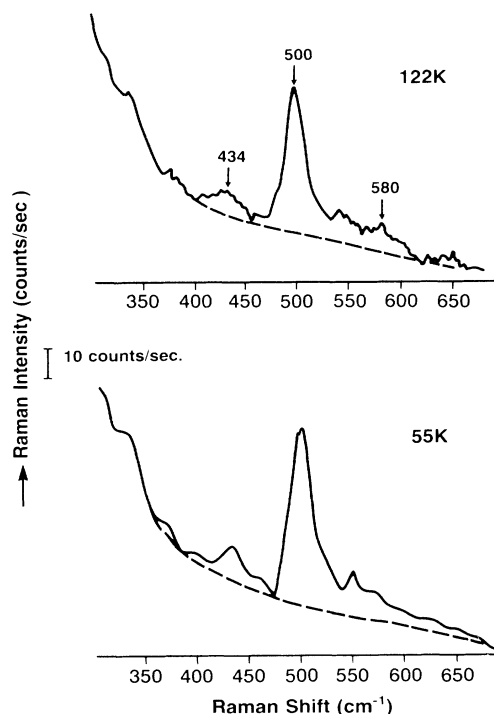


FIG. 3. The Raman spectra of $\text{Ba}_2\text{YCu}_3\text{O}_7$: Sample B, at two representative temperatures. See text for details regarding the sample. Excitation: 4880 \AA , $\approx 100 \text{ mW}$. The spectra are shown without background subtraction.

On lowering the temperature towards the superconducting state, sample A shows the appearance of a relatively sharp line at 365 cm^{-1} . This line appears at temperatures below $\approx 150 \text{ K}$ and disappears as the sample goes into the superconducting state. It is not recovered on cooling but is observed again in a freshly annealed sample. This line is not observed in sample B. We tentatively assign this feature to a Raman-active Ba-O mode (since its frequency is near the Raman frequency of the BaF_2 crystal¹⁷) whose Raman cross section is possibly enhanced by some fluctuation mechanism. Further work would be needed in order to identify the origin of this feature.

In the superconducting phase there is no indication of any new features down to temperatures of 25 K , except for some sharpening of the 632 cm^{-1} line in sample A. This is in agreement with the neutron-diffraction data which show no phase transitions down to 10 K . There is no evidence of Raman transitions in the region around $2\Delta \approx 3.5k_B T_c \sim 200 \text{ cm}^{-1}$, where 2Δ is the expected BCS gap, if BCS theory indeed applies to this material. Note that Raman activity at the BCS gap has been observed in one previous case: that in the layered compound 2H-NbSe_2 by Sooryakumar and Klein.¹⁸ In 2H-NbSe_2 the Raman activity at the BCS gap is provided by strong coupling of the superconducting gap excitation with a charge-density wave oscillation.

The spectra of $\text{Ba}_2\text{Y}_{0.75}\text{Sc}_{0.25}\text{Cu}_{2.4}\text{Ni}_{0.6}\text{O}_7$ in the normal and the superconducting states are shown in Fig. 4. Here two lines corresponding to the Cu(1)-O(1) stretching mode as assigned above are observed. The other lines

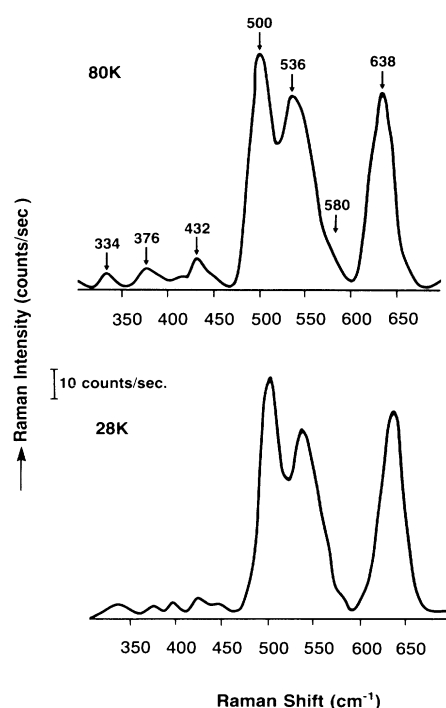


FIG. 4. The Raman spectra of $\text{Ba}_2\text{Y}_{0.75}\text{Sc}_{0.25}\text{Cu}_{2.4}\text{Ni}_{0.67}\text{O}_7$ at two representative temperatures. Excitation: 4880 \AA , $\approx 100 \text{ mW}$; the background has been subtracted.

at 638 , 580 , and 432 cm^{-1} are located at about the same position as in sample A. In addition weaker lines assignable to deformation modes are detectable in this sample. We identify the splitting of the $\text{Cu}(1)\text{-O}(1)$ stretching mode as due to two $\text{Cu}(1)\text{-O}(1)$ distances resulting from the insertion of Ni^{2+} ions into some of the $\text{Cu}(1)$ sites in the lattice. This partial insertion of Ni^{2+} ions into the copper-oxygen chains probably leads to the observed substantial reduction of T_c to 65 K , although the structural integrity and the O deficiency of the $\text{Ba}_2\text{YCu}_3\text{O}_7$ structure remain largely unchanged.

In conclusion, we have presented and assigned the Raman spectra of a number of superconducting samples in the $\text{Ba}_2\text{YCu}_3\text{O}_7$ phase. The intensity of the highest-frequency Raman-active mode was found to be extremely sensitive to the preparation conditions. It is suggested that this is due to oxygen vacancies present along the Cu-O chains in the surface regions of the samples. The effect of inserting Ni^{2+} ions in the $\text{Ba}_2\text{YCu}_3\text{O}_7$ lattice has been shown to result in a strong depression of T_c . Raman spectroscopy emerges as an important tool for probing the oxygen vacancies and local structure of the Cu-O chains.

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