

Oxygen-isotope effect on the high-frequency Raman phonons in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

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Raman spectra have been obtained from single-crystal samples of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ with varying degrees of oxygen-isotope exchange. A comparison of the high-energy ($\geq 400 \text{ cm}^{-1}$) vibrational spectra obtained from an unexchanged sample, a partially exchanged sample and a fully exchanged crystal has been carried out to obtain an unambiguous assignment of the A_{1g} modes at 465 and 630 cm^{-1} . The 465 mode is assigned to c -axis vibrations of O(3) atoms in the Bi-O layers and the 630 mode to the O(2) apical oxygen atoms in the Sr-O layers. [S0163-1829(98)03334-7]

I. INTRODUCTION

A detailed knowledge of the symmetry and atomic eigenvectors associated with each vibrational mode provides important information concerning the structure and mechanical properties of a material. Given such information one can learn about other excitations in the system from a study of their interactions with the phonons. In high-temperature superconductors, for example, one can use phonon measurements to obtain valuable information on the nature of the electronic excitations and the transition to the superconducting state.^{1,2} As a result a great deal of effort^{3,4} has been expended in obtaining and interpreting the vibrational spectra of many of the high-temperature superconductors (HTS's). These compounds have complex structures, however, and as a result the vibrational spectra are often complicated and difficult to interpret. This is particularly true in the case of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212) where the structure is further complicated by the presence of an incommensurate structural modulation which can lead⁵ to the presence of additional modes in the spectra. For these reasons the origin of the high-frequency oxygen vibrations in the Raman spectrum of Bi2212 remains controversial despite many investigations⁶⁻¹³ by different groups.

The unit cell of Bi2212 has orthorhombic symmetry with the orthorhombic x and y axes in the CuO_2 planes and directed at an angle of 45° with respect to the direction of the planar Cu-O bonds. As is the case in other HTS cuprates, however, the orthorhombic distortions are small and it is appropriate¹⁴ to use the symmetry operations of the tetragonal group (D_{4h}) to describe the mode symmetries. At the center (Γ) of the Brillouin zone Bi2212 one should then have 45 modes of vibration:

$$\Gamma \equiv 6A_{1g} + B_{1g} + 7E_g + 7A_{2u} + 8E_u + B_{2u}, \quad (1)$$

where the even modes are Raman active. Although additional modes appear in the Bi2212 spectra because of the incommensurate modulation and orthorhombic distortion, the strongest modes should transform as the even representations in Eq. (1) as has been demonstrated¹⁰ for the B_{1g} mode. Different polarizations of the incident and scattered light can then be used to probe the symmetries of the different vibrations. We use a backscattering configuration with the incident light directed parallel to the z axis of the crystal. Then if (\hat{e}_s, \hat{e}_i) designates the unit polarization vectors of the scattered and incident light, respectively, the $(\hat{x}\hat{y})$ geometry allows¹⁴ coupling to the B_{1g} phonons and the $(\hat{x}\hat{x})$ spectra arise from $(A_{1g} + B_{2g})$ vibrations. There appears to be a consensus on the origin of the strong B_{1g} phonons and the relatively intense low frequency A_{1g} vibrations. This is not the case, however, for two of the strongest features in the Raman spectrum of Bi2212 that appear at higher frequencies. These are the A_{1g} modes that appear with nominal frequencies of 465 and 630 cm^{-1} in spectra obtained from optimally doped compounds. Most authors (Table I) have assigned the 465 cm^{-1} mode to vibrations of the apical oxygen atoms located on the Sr planes and the 630 cm^{-1} phonon to vibrations of oxygen atoms located in the Bi-O planes. Recently however, after reviewing the situation in other cuprates, Kakihana *et al.*¹¹ suggested that the assignments should be reversed on the basis that the mode appeared strongly in $(\hat{z}\hat{z})$ geometry and because the higher-frequency mode usually involves the apical oxygen atoms.

II. EXPERIMENT AND DISCUSSION

Direct information on the vibrational origin of a phonon can be obtained from the study of atomically substituted

TABLE I. Measured frequencies and assignments of the high-frequency Raman active phonons in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$.

Authors	465 cm^{-1} mode		630 cm^{-1} mode	
	Frequency	Assign.	Frequency	Assign.
Present work	467	O(3)	629	O(2)
Liu <i>et al.</i> (Ref. 5)	465	O(2)	630	O(3)
Martin and Lee (Ref. 6)	458	O(2)	627	O(3)
Denisov <i>et al.</i> (Ref. 7)	460	O(3)	634	O(2)
Boekholt <i>et al.</i> (Ref. 8)	463	O(2)	625	O(3)
Sugai and Sato (Ref. 9)	469	O(2)	632	O(3)
Cardona <i>et al.</i> (Ref. 10)	469	O(2)	631	O(3)
Kakihana <i>et al.</i> (Ref. 11)	463	O(3)	627	O(2)
Kim <i>et al.</i> (Ref. 12)	464	O(2)	623	O(3)

samples. Previous Raman work on Bi2212 has involved studies of crystals doped with Y,¹¹ Pb,¹⁵ and oxygen-isotope exchanged samples in the form of single crystals⁶ and polycrystalline samples.¹² To gain information on the vibrational spectra the use of isotopic substitution is probably preferable in that it should not lead to any significant chemical or structural changes. For example, the study of isotopically exchanged [$^{18}\text{O} \rightarrow ^{16}\text{O}$ and $^{65}\text{Cu} \rightarrow ^{63}\text{Cu}$] samples has been used^{16,17} to determine the eigenvectors and degree of hybridization of several phonons in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y123). In the case of Bi2212 Martin and Lee⁶ have carried out Raman experiments on $^{18}\text{O} \leftrightarrow ^{16}\text{O}$ exchanged single crystals and Kim *et al.*¹² on $^{18}\text{O} \leftrightarrow ^{16}\text{O}$ exchanged polycrystalline samples. In contrast to the assignments of Kakihana *et al.*¹¹ both of these groups (Table I) assigned the 465 mode to the vibrations of the O(2) atoms on the Sr-O layers and the 630 mode to vibrations of the O(3) atoms in the Bi layer.

To obtain additional insight into the origin of these two modes we have carried out experiments on ^{18}O exchanged Bi2212 single crystals. The coupling between adjacent Bi-O layers in Bi2212 is very weak and as a result crystals cleave rather easily on planes situated between the Bi-O layers. In addition foreign species can be intercalated¹⁸ into the spaces between the Bi-O layers. Thus it is perhaps not too surprising that when the oxygen concentration δ is increased or decreased the oxygen atoms are either added or lost from the Bi-O planes. Oxygen intercalation on the Bi-O planes was suggested by electron microscopy¹⁹ and neutron scattering experiments²⁰ but the most direct evidence was provided by scanning tunneling microscopy investigations.²¹ It is thus reasonable to expect that the O(3) sites in the Bi-O planes would be the easiest to exchange when one attempts to replace ^{16}O with the heavier ^{18}O isotope in Bi2212, and that the O(2) sites in the Sr-O planes would be relatively more difficult to exchange, as is suggested by the results of Kim *et al.*¹² Thus one should be able to identify the relevant sites associated with each mode by carrying out experiments on partially exchanged samples of Bi2212.

To prepare partially exchanged samples the quartz ampoule containing the single crystals was evacuated and then backfilled with either high purity ^{16}O or ^{18}O to a pressure of 1 atmosphere. The ampoule was then annealed at 750°C for 4 h. Spectra obtained from the two different samples prepared in this way are shown in Fig. 1. From this figure it can be seen that the 465 mode appears at 467 cm^{-1} in the spectrum obtained from the unexchanged ^{16}O crystal but at

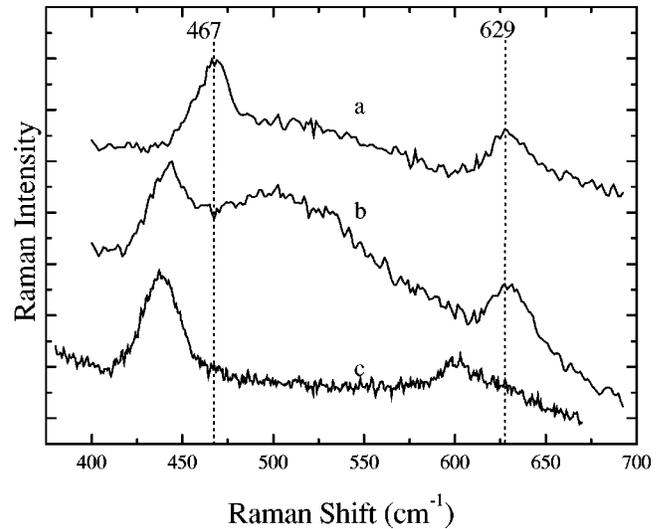


FIG. 1. Room-temperature Raman spectra obtained from (a) an optimally doped Bi2212 single crystal containing the ^{16}O isotope (top curve), (b) a crystal in which the oxygen isotope is partially exchanged with ^{18}O (middle curve), and (c) a more completely exchanged crystal (bottom curve).

441 cm^{-1} in the spectrum from the sample annealed in ^{18}O . The 630 cm^{-1} mode on the other hand appears at 629 cm^{-1} in both spectra, that is, its frequency is unaffected by the partial exchange of oxygen isotopes. It is clear from these results that the 465 cm^{-1} mode is associated with vibrations of oxygen atoms. The normalized frequency shift $[\omega(16) - \omega(18)]/\omega(16)$ is about 5.6%, which is close to the maximum value obtainable and thus further suggests that the site involved in this vibration is completely exchanged. Given the above discussion one must conclude that the 465 cm^{-1} mode involves vibrations of oxygen atoms only and that these atoms are located in the Bi-O planes. This means that the 630 cm^{-1} mode, which previous workers^{6,12} have shown to be associated with oxygen vibrations, must involve the O(2) apical sites which are more difficult to exchange. These results thus provide direct support for the assignments of Kakihana *et al.*¹¹

To further corroborate these results we have also tried to prepare a fully exchanged sample. In this case the sample was first annealed in vacuum at 500°C for four hours. The ampoule containing the sample was then evacuated again and backfilled with ^{18}O to a pressure of one atmosphere. The sample was then annealed in the ^{18}O atmosphere for 24 h at 850°C after which it was gradually cooled over a period of 15 h to a temperature of 300°C .

A spectrum obtained from this sample is shown in Fig. 1(c). In this spectrum the 465 cm^{-1} mode again appears at 441 cm^{-1} (fully shifted) but now the 630 cm^{-1} mode is also shifted by approximately 5% and appears at 598 cm^{-1} . This result is consistent with previous measurements⁶ of this phonon in fully exchanged crystals. Finally, on comparing the results from the unexchanged, partially exchanged, and fully exchanged samples (Fig. 1), and given that exchange takes place in the Bi-O planes, we must assign the 630 cm^{-1} mode to *c*-axis vibrations of the apical O(2) oxygen atoms.

In summary we have demonstrated that the 465 cm^{-1} phonon of Bi2212 arises from vibrations of the O(3) atoms

in the Bi-O planes and the 630 cm^{-1} mode from vibrations of the O(2) apical oxygen atoms in the Sr-O planes.

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