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Isotopic and isomorphic substitution of $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$: Far-infrared spectroscopy and assignment of phonons

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We report results of far-infrared spectroscopic measurements on a series of isotopically (^{18}O) exchanged and isomorphically substituted materials in the $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ families. Based upon these measurements, we propose assignments for phonons in both the $YBa_2Cu_3O_6$ semiconducting phase and the $YBa_2Cu_3O_7$ superconducting phase. In $YBa_2Cu_3{}^{18}O_7$, the lowest-frequency phonon at 155 cm^{-1} is seen to shift $\sim 2\%$ to lower frequency when compared to the ^{16}O material, demonstrating the role of oxygen in this vibration (which we have previously assigned as a c-axis-directed Cu-O chain bending mode of B_{1u} symmetry). This transverse-optical branch may be important for phonon-mediated superconductivity in this material, as indicated in a recent theoretical treatment by Weber and Matthiess [Phys. Rev. B **37**, 599 (1988)].

I. INTRODUCTION

There have been many infrared and Raman studies of the recently discovered copper oxide superconductors.[1] These studies have been concerned with establishing the existence and size of the superconducting energy gap, increasing understanding of the electrodynamics and anisotropy in both the normal and superconducting states, and, in general, with the search for clues to the mechanism(s) which underlie the unprecedented high superconducting temperatures. One of the key steps toward the detailed understanding of the infrared spectra of these materials is the assignment of the phonon modes. This problem has received some attention but remains an unsettled issue. We address this question here by examining the far-infrared (FIR) reflectance spectra of an extensive series of isotopically and isomorphically substituted compounds of the general formula $RBa_2Cu_3O_{6+x}$ at temperatures from 10–300 K.

In a previous paper,[2] we described FIR reflectivity measurements on the $RBa_2Cu_3O_x$ system, where $R = Y$, Er, and Nd and x was varied from 6 to 7 for $R = Y$. The FIR reflectivity spectrum of $YBa_2Cu_3O_7$ at 10 K exhibits five phonon features at approximately 155, 194, 276, 312, and 570 cm^{-1}. We suggested the following assignments for those modes. The 155-cm^{-1} phonon has been assigned as a B_{1u} vibration of the linear Cu-O chains. The 194-cm^{-1} mode has been assigned as an Y B_{1u} translational mode. The 276- and 312-cm^{-1} B_{1u} modes originate in the Cu-O planes and the 570-cm^{-1} B_{1u} phonon is a Cu-O stretching vibration along the c axis. In this paper we (1) present additional evidence in support of those assignments, (2) show how our spectroscopic assignments can be logically extended to the semiconducting $RBa_2Cu_3O_6$ stoichiometry, (3) point out some interesting patterns that are beginning to emerge in the relationship between the infrared spectroscopy and the superconducting properties of these materials, and (4) provide phonon frequency data that should be useful for lattice dynamics calculations.

II. EXPERIMENT

Near-normal-incidence reflectance spectra were taken on a Fourier-transform infrared spectrometer over the energy range 30–700 cm^{-1}. Temperatures were varied using a flow-type He cryostat. The spectrometer was equipped with a He-cooled Si composite bolometer. Sample spectra were referenced to an Al mirror and the samples were not polished to avoid surface contamination. Sample surface roughness caused scattering losses, particularly at higher energies, but the phonon frequencies are relatively unaffected by this (see below). This was verified by overcoating some samples with Al and using these coated samples as references. Where appropriate, samples were annealed at low temperature (350 °C) to maximize oxygen content and order while minimizing the crystallite orientation which has been reported to occur during extended high-temperature (> 900 °C) oxygen anneals.[3]

Samples were prepared via standard solid-state techniques using BaO_2, Y_2O_3, and CuO starting materials. Pellets were pressed but not sintered. ^{18}O exchange was accomplished by heating a pellet to 700 °C in vacuum and then admitting 500 Torr of 96% ^{18}O. The progress of the exchange was followed by removing aliqoits from the vapor above the pellet and analyzing the $[^{18}O]/[^{16}O]$ ratio by mass spectroscopy. Equilibrium between oxygen initially in the solid and oxygen initially in the gas phase is reached within 30 min under these conditions. To achieve ^{18}O enrichments in excess of 90%, this procedure was repeated three times. Following the third exchange, the sample was slow cooled in the equilibrated ^{18}O-^{16}O atmosphere and annealed for up to 80 h at 350 °C. ^{18}O content was determined in three ways: (1) by measuring the sample weight gain with a microbalance, (2) from the $[^{18}O]/[^{16}O]$ ratio in the vapor after the final exchange, and (3) by mass spectrometric monitoring of oxygen evolving from the sample during heating to 400° in vacuum after the FIR data had been taken. For samples prepared according to this recipe, [^{18}O]/[^{16}O] ratios in the desorption experiment were in excellent agreement with the [^{18}O]/[^{16}O] ratios from the vapor above the final exchange. In addition, all three measures of the extent of ^{18}O incorporation were consistent with expectations if all sites in the structure reached equilibrium with the exchange gases.

^{18}O-exchanged samples of $YBa_2Cu_3O_6$, the semiconducting phase, were prepared similarly to the -O_7 material, but the final cooling cycle was done in vacuum. All ^{18}O samples were compared with ^{16}O control samples prepared in an identical manner except for the use of ^{16}O rather than ^{18}O. Superconducting (-O_7) samples were also examined by SQUID magnetometry to ascertain the existence of an isotope effect upon T_c. That work is described elsewhere.[4]

$RBa_2Cu_3O_6$ and $YBa_{2-x}Sr_xCu_3O_6$ samples were first prepared as -O_7 materials. These compounds were then reduced at 750 °C for 12 h under a flowing argon atmosphere or by vacuum annealing at 700 °C overnight. Oxygen contents were measured by vacuum thermogravimetric analysis (TGA) as reported previously.[5]

Transverse-optical phonon frequencies reported in this paper have been determined from the maxima in the imaginary part of $\epsilon(\omega)$, derived from the reflectance spectra by Kramers-Kronig analysis. This procedure will yield reasonably accurate frequencies for phonon modes which are not heavily damped. Phonon frequencies determined from our data in this way are in good agreement with other published results in which the frequencies were estimated from the reflectance spectra directly,[1,2] extracted by oscillator fits to the reflectivity,[6] or derived from a Kramers-Kronig analysis of reflectivity data taken over a wide energy range and corrected for geometric sample scattering.[3] It should be noted that the oxygen content will affect the phonon frequencies and, therefore, all matched samples in this study were prepared identically in order to assure the same oxygen content and thus allow accurate frequency shifts for isotopically substituted samples to be determined.

III. RESULTS AND DISCUSSION

A. $YBa_2Cu_3O_7$

In Fig. 1 we show the far-infrared reflectance of a 91% ^{18}O-exchanged sample of $YBa_2Cu_3O_7$ and its ^{16}O control sample. Frequency shifts for each of the five phonon modes are given in Table I. (For clarity, the structure and atom numbering scheme used for $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ appear in Fig. 2.)

Group theory predicts 21 infrared-active modes at $k = 0$ for $YBa_2Cu_3O_7$, yet only five appear in the far-infrared spectrum. We believe that this is a result of the highly anisotropic conductivity in this material. Of the 21 modes ($7B_{1u}+7B_{2u}+7B_{3u}$), only seven ($7B_{1u}$) are polarized along the low-conductivity c direction. These modes are less effectively screened than are those polarized in the high conductivity a-b plane ($7B_{2u}+7B_{3u}$). (The fact that only five modes appear, while seven are predicted, may be due to small oscillator strengths for the other two modes. It should also be noted that it is an approximation to attribute a given phonon feature to a particular structural element since, by symmetry, all the ions in the $YBa_2Cu_3O_7$ structure can participate in the B_{1u} modes.)

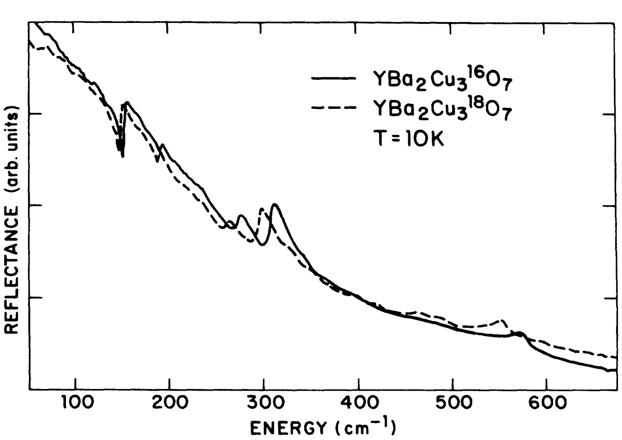

FIG. 1. Far-infrared reflectance spectra from 30–700 cm^{-1} of $YBa_2Cu_3{}^{16}O_7$ and $YBa_2Cu_3{}^{18}O_7$ at 10 K. Frequency information is given in Table I.

There are several observations which can be made to support the importance of anisotropic screening in $YBa_2Cu_3O_7$. First, single-crystal data in which the electric field of the incident infrared radiation is perpendicular to the c axis show little, if any, evidence of the phonons which appear quite strongly in powdered material.[7] Since single crystals having appreciable length *along* the c axis have not yet been grown, it has not been possible to take an infrared spectrum where E is parallel to c. The study of c-axis phonons has, therefore, been restricted to powders and thin films for $YBa_2Cu_3O_7$. Oriented thin films, where the c axis is parallel to the film surface, would be interesting in this regard, particularly if epitaxial growth maintained a particular c-axis direction in the film plane so that a "pure" c-axis spectrum could be obtained. In the other oxide superconductors $Ba(Pb,Bi)O_3$ and $La_{1.85}Sr_{0.15}CuO_4$ the effects of screening are also seen. The $Ba(Pb,Bi)O_3$ structure yields more isotropic (three-dimensional) screening and therefore phonons do not appear in the far-infrared reflectance spectra.[8] In $La_{1.85}$-$Sr_{0.15}CuO_{14}$ the dominant phonons are c-axis directed, including the very strong mode at 240 cm^{-1}, consistent with the two-dimensional nature of this material.[9] In the related structure La_2NiO_4 both c-axis and a-b plane phonons appear in the infrared reflectivity, but the c-axis phonons

TABLE I. Phonon energies for $YBa_2Cu_2{}^{16}O_7$ and $YBa_2Cu_3{}^{18}O_7$ (91% ^{18}O) at 10 K.

Energy (cm^{-1})		
$YBa_2Cu_3{}^{16}O_7$	$YBa_2Cu_3{}^{18}O_7$	$\nu(^{16}O)/\nu(^{18}O)$
155.5	152.6	1.019
193.2	192.2	1.005
276.2	262.7	1.051
312.0	299.4	1.042
569.9	549.5	1.037

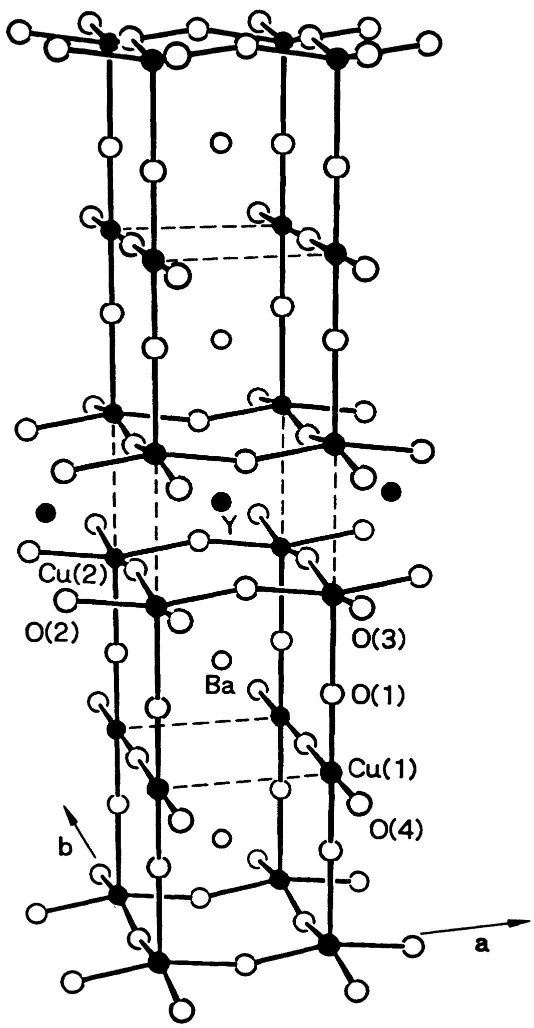

FIG. 2. Crystal structure and atom numbering scheme for $YBa_2Cu_3O_7$. In $YBa_2Cu_3O_6$, atom O(4) is missing and atoms O(2) and O(3) are equivalent and are therefore referred to as O(2).

again dominate the spectrum.[10] Apparently screening in the *a*-*b* plane is not as effective in $LaNiO_4$ as in the copper oxide superconductors.

Upon isotopic substitution, all five modes in $YBa_2Cu_3O_7$ shift to lower energy, with the highest-energy modes shifting by the largest fractional amount. For a pure oxygen vibration, 91% ^{18}O exchange would be expected to shift the frequency by 5.5%. If instead one assumes that it is the Cu-O reduced mass which is the relevant quantity then a shift of 4.3% would be expected. Without knowing the exact form of the normal vibrations for each mode one cannot predict the precise dependence on oxygen mass. However, the higher frequency modes exhibit ^{18}O isotope shifts of 4%–5% and thus must involve large contributions due to oxygen motion.

The 194-cm^{-1} mode, which we have previously assigned[2] as a fairly isolated Y vibration of B_{1u} symmetry, exhibits the smallest ^{18}O isotope shift (< 1%), consistent with that assignment. Most likely the Y ion is weakly coupled vibrationally to the eight oxygen ions which surround it (the Cu-O planes). The fact that the 276 and 313 cm^{-1} modes in $YBa_2Cu_3O_7$, which we have assigned as Cu-O plane vibrations, appear slightly shifted in $RBa_2Cu_3O_7$ (Fig. 3 and Table II) also suggests weak coupling between oxygen in the Cu-O planes and the *R* layer.

The 155 cm^{-1} mode shifts by 2% when ^{18}O is substituted for ^{16}O. This indicates that oxygen has an appreciable vibrational amplitude in this mode, although the fractional shift is smaller than that of the high-frequency modes. There are several possible causes for this smaller isotope shift. For example, other ions in the $YBa_3Cu_3O_7$ structure may participate in this vibration. Ba^{2+} is a likely candidate since modes of the same symmetry which are close in frequency can interact, and Ba^{2+} should have a mode of B_{1u} symmetry at low frequency. In fact, in $YBa_3Cu_3O_6$ there are two modes near 110 cm^{-1} which most likely are the A_{2u} (*c* axis) and E_u (*a*-*b* plane) Ba vibrations.[6] However, a mode in the 100–120-cm^{-1} region that could be assigned primarily to Ba^{2+} does not appear in the $YBa_2Cu_3O_7$ spectrum. We shall return to this point in subsequent discussion.

A different explanation for the small isotope shift in the 155 cm^{-1} phonon mode is anharmonicity in the vibration-

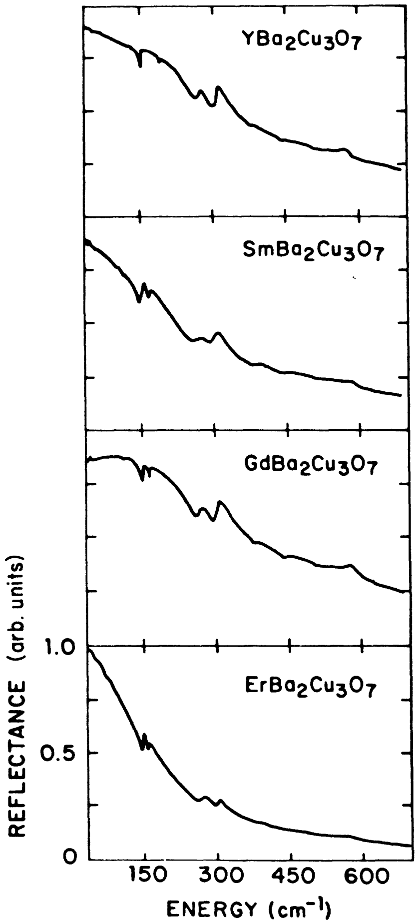

FIG. 3. Far-infrared reflectance spectra from 30–700 cm^{-1} of $RBa_2Cu_3O_7$, where $R = Y$, Sm, Gd, and Er at 10 K. The phonon at 194 cm^{-1} in $YBa_2Cu_3O_7$ shifts to between 160 and 170 cm^{-1} when rare-earth metals substitute for Y.

TABLE II. Phonon energies for $R\mathrm{Ba_2Cu_3O_7}$ ($\mathrm{cm^{-1}}$) at 10 K.

$\mathrm{YBa_2Cu_3O_7}$	$\mathrm{SmBa_2Cu_3O_7}$	$\mathrm{GdBa_2Cu_3O_7}$	$\mathrm{ErBa_2Cu_3O_7}$
155.3	156.0	154.5	151.4
193.8	171.4	170.0	162.0
275.8	274.4	272.4	271.0
312.5	312.0	309.1	304.7
571.9	580.6	580.0	569.0

al potential for this mode. Anharmonicity is known to reduce the isotope effect in molecular vibrations.[11] The oxygens in the Cu-O chains are weakly bound and oxygen loss from these sites proceeds readily at relatively low temperatures. The binding energy for this oxygen can be no more than ΔH for oxygen loss, ~20 kcal/mol (0.9 eV), and may be substantially less.[5] If the 155 $\mathrm{cm^{-1}}$ mode is a c-axis Cu-O bending mode, as we have suggested, it may well represent the reaction coordinate for mobilizing the oxygen atoms. In that case, anharmonic behavior for this mode seems reasonable. Furthermore, the large thermal parameters in the a and c directions determined by neutron diffraction[12] also are consistent with an anharmonic potential and may be related to tunneling phenomena.

The Cu-O chain mode may be better represented as a translational mode of the chain [$\mathrm{CuO_4}$] groups along the c axis rather than as a pure Cu-O bend. In that case, 91% ^{18}O exchange would cause a shift in frequency, assuming harmonic motion, of 2.8%. Such a mode has been predicted (at 254 $\mathrm{cm^{-1}}$) by lattice dynamics calculations.[13] (Several other low-frequency modes of B_{1u} symmetry involving the Cu-O chains are indicated in Ref. 13. At this stage a precise determination of the form of the vibration we observe at 155 $\mathrm{cm^{-1}}$ is not possible. The isotope shifts we measure should aid in such a determination.) Physically, one can understand this mode as arising from a difference in bond strengths between the strong Cu(1)—O(1) bonds and the weaker Cu(2)—O(1) bonds, allowing the [$\mathrm{CuO_4}$] group to vibrate as a whole. The $\mathrm{CuO_4}$ group will, of course, have internal modes in addition to this external translational mode. It should also be noted that this mode, at the Brillouin-zone center where the infrared absorption occurs, does not involve any Cu—O bond bending, but gains more bond bending character as one moves toward the zone boundary.

A recent theoretical calculation predicted a maximum for the Eliashberg function, $\alpha^2F(\omega)$, at frequencies between 15-20 meV (120-160 $\mathrm{cm^{-1}}$). The phonon responsible for this strong enhancement of electron-phonon coupling is a Brillouin-zone boundary c-axis Cu-O chain-bending mode.[14] Although the maximum T_c derived from this theoretical treatment is 30 K, it is interesting that the calculation singles out a phonon frequency and assignment that agree with our observations of the Cu-O chain mode at 155 $\mathrm{cm^{-1}}$. Perhaps the small oxygen isotope effect on T_c that has been reported for $\mathrm{YBa_2Cu_3O_7}$ (Refs. 4 and 15) originates from an electron/phonon contribution to the superconductivity (even if an additional mechanism is necessary to attain the >90 K transition temperatures), and the 155 $\mathrm{cm^{-1}}$ optical-phonon branch is responsible for this coupling. In the same context we point out that the 240 $\mathrm{cm^{-1}}$ mode in $\mathrm{La_{2-x}Sr_xCuO_4}$, which is reported to scale in strength with T_c,[16] has been assigned as an A_{2u} symmetry mode.[9] Far-infrared measurements in our laboratory on ^{18}O exchanged samples indicate that this mode is a Cu-O plane bending vibration in which the Cu and O atoms move parallel to the c axis. These observations highlight the possibly important role played by Cu—O bond-bending vibrations in the Cu-O superconductors.

As stated above, the higher energy phonons in $\mathrm{YBa_2Cu_3O_7}$ (279, 312, and 570 $\mathrm{cm^{-1}}$) exhibit frequency shifts upon substitution of ^{18}O for ^{16}O which are indicative of the large vibrational amplitude of oxygen in these modes. This is consistent with our previous assignments for the phonons.[2] The 279 and 314 $\mathrm{cm^{-1}}$ features are Cu-O plane vibrations of B_{1u} symmetry, split by the orthorhombic distortion in this material. Further support for this assignment is seen in Fig. 4, where we display reflectance spectra of $\mathrm{YBa_{2-x}Sr_xCu_3O_7}$. In these materials the unit-cell parameters a, b, and c are all decreasing functions of x, with b and c decreasing most rapidly.[17] There may be a decrease in oxygen content for higher x values

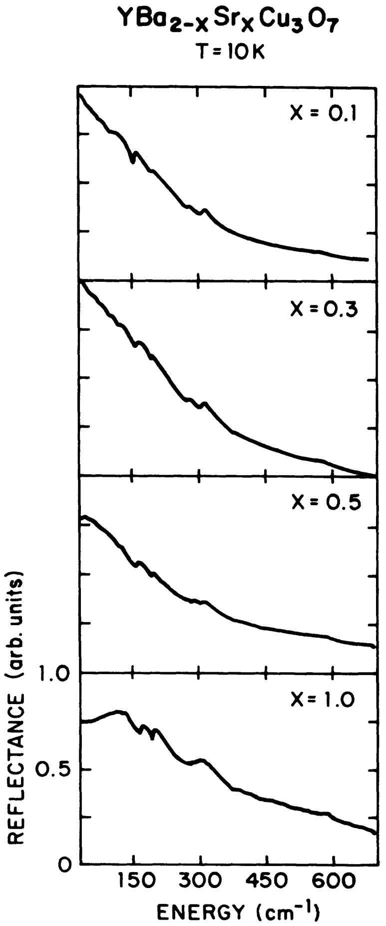

FIG. 4. Far-infrared reflectance spectra from 30-700 $\mathrm{cm^{-1}}$ of $\mathrm{YBa_{2-x}Sr_xCu_3O_7}$, where $x=0.1$, 0.3, 0.5, and 1.0, at 10 K. The two phonons near 300 $\mathrm{cm^{-1}}$ at $x=0.1$ have nearly collapsed into one reflectance peak for $x=1.0$ (see text).

which would account for the more rapid decrease of b vs a (as well as the increased width of the chain bending mode in the 150–160 cm^{-1} region due to oxygen vacancies in the Cu-O chains.) However, the most important observation is that the 276 and 312 cm^{-1} modes increase unequally in frequency, to 308 and 322 cm^{-1}, respectively. This difference in magnitude of the shift allows us to assign the 276 cm^{-1} mode as a b-axis B_{1u} mode and the 312 cm^{-1} phonon as an a-axis B_{1u} mode, since b decreases more drastically than a as the Sr content increases. The larger frequency shift for the 276 cm^{-1} bending mode would then be a result of the larger lattice contraction along the b direction.

The 570 cm^{-1} mode, which we have previously assigned as the Cu(1)-O(1) B_{1u} stretch, will be discussed further below in relation to the spectroscopy of $YBa_2Cu_3O_6$. Its shift due to ^{18}O substitution is consistent with that assignment.

In a complex vibrational system such as $YBa_2Cu_3O_7$ the frequency shift of a given mode due to isotopic substitution is hard to predict. It will differ depending upon the vibrational amplitude of the substituted atom in that particular mode. Nevertheless, the product of the isotopic frequencies for all modes of a given symmetry must follow the Teller-Redlich product rule[11]

$$\frac{\nu_1' \nu_2' \cdots \nu_m'}{\nu_1 \nu_2 \cdots \nu_m} = \left[\left(\frac{m_1}{m_1'}\right)^{\alpha} \left(\frac{m_2}{m_2'}\right)^{\beta} \cdots \left(\frac{m_m}{m_m'}\right)^{\gamma} \left(\frac{M'}{M}\right)^{t} \right]^{1/2}, \tag{1}$$

where $\nu_1', \nu_2', \ldots, \nu_m'$ are the phonon frequencies in the isotopically (^{18}O) substituted material, $\nu_1, \nu_2, \ldots, \nu_m$ are the frequencies in the unsubstituted (^{16}O) material, $m_1, m_2, \ldots, m_m$ are the unsubstituted ion masses, $m_1', m_2', \ldots, m_m'$ are the isotopic masses, $\alpha, \beta, \ldots, \gamma$ are the number of modes of the given symmetry species contributed by each set of equivalent ions, M' and M are the unit-cell masses for ^{18}O-exchanged and unexchanged samples, and t is the number of translations (acoustic modes) which belong to the species considered. $YBa_2Cu_3O_7$ has four distinct oxygen sites. Assuming each site is 91% ^{18}O substituted (to yield an average oxygen mass of 17.8 amu), the right-hand side of (1) is equal to 1.23. From the far-infrared data the left-hand side of (1) is equal to 1.17 and therefore the product rule is not saturated. Since we only observe five of the predicted $7B_{1u}$ modes it may be that some of the isotope shift resides in the remaining two modes. The Ba A_{2u} mode, visible in $YBa_2Cu_3O_6$ (see below), can be used to estimate the expected isotope shift for the Ba B_{1u} mode in $YBa_2Cu_3O_7$, bringing the observed ratio of frequencies to 1.18. Since the remaining unobserved B_{1u} mode may contribute to the ratio somewhat, we can only conclude that the Teller-Redlich product rule does not contradict our assignment of the observed far-infrared phonons in YBa_2- Cu_3O_7 as all being of B_{1u} symmetry. Furthermore, the Teller-Redlich product rule assumes harmonic vibrations and this assumption, particularly for the 155 cm^{-1} Cu-O chain bending mode, is probably incorrect. To the extent that the modes are anharmonic, the total isotope shift is reduced; therefore the lack of saturation for the product rule seems reasonable.

B. $YBa_2Cu_3O_6$

$YBa_2Cu_3O_6$ is expected to have eleven infrared active vibrations, $5A_{2u}+6E_u$, in which the $6E_u$ modes are doubly degenerate. Some mode assignments have previously been made in $RBa_2Cu_3O_6$ based upon frequency shifts obtained when Sm replaces Y.[6] Using these results, combined with our assignments for the $YBa_2Cu_3O_7$ material described above, our previous results,[2] and the isotopic substitution data displayed in Fig. 5, we can obtain a more complete understanding of the vibrations in $RBa_2Cu_3O_6$. In general, more structure appears in the spectra of the $RBa_2Cu_3O_6$ materials at 5 K than at room temperature, giving at least nine strong modes and possibly several weaker ones. All the modes predicted by group theory appear and some additional structure, due possibly to residual oxygen in the chain sites, also appears. Due to the additional structure at low temperature we will discuss only the strongest reflectivity features, which can be assigned with more certainty. Transverse-optical phonon frequencies are listed in Table III. (Our suggested mode assignments are given in Table V.)

The lowest frequency modes (106 and 116 cm^{-1}) can be attributed to vibrations of Ba parallel and perpendicular to the c axis, of A_{2u} and E_u symmetry.[6] As the heaviest atom in the structure, Ba vibrations are expected to have the lowest frequencies. These modes are nearly unaffected by exchange of ^{18}O for ^{16}O, shifting by an amount which is roughly consistent with the Ba ions vibrating against remaining ions in the unit cell (center-of-mass conservation). This suggests that there is only weak coupling of Ba to oxygen motion, at least in $YBa_2Cu_3O_6$. (In $YBa_2Cu_3O_7$, it has been suggested that the 155 cm^{-1} mode is predominantly a Ba vibration.[18] It is possible that Ba motion is more strongly coupled to Cu-O motions in the $-O_7$ material through the O(4) oxygen which is absent in $YBa_2Cu_3O_6$. It seems more probable, however, that the

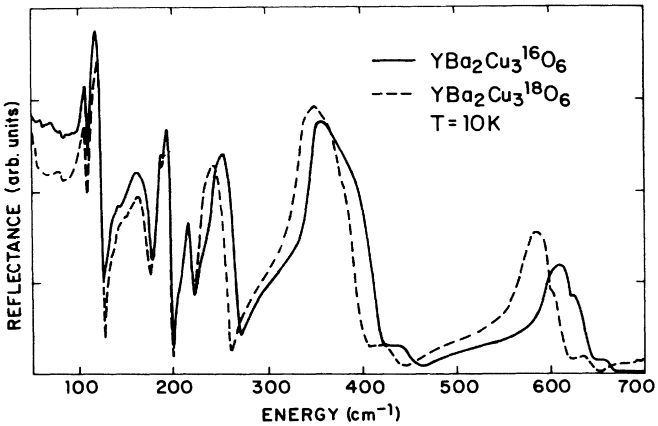

FIG. 5. Far-infrared reflectance spectra from 30–700 cm^{-1} of $YBa_2Cu_3{}^{16}O_6$ and $YBa_2Cu_3{}^{18}O_6$ at 10 K. The shift in the higher frequency modes is evident.

TABLE III. Phonon energies for $YBa_2Cu_3{}^{16}O_6$ and $YBa_2Cu_3{}^{18}O_6$ (87% ^{18}O) at 10 K. (sh) stands for shoulder.

ν (cm^{-1}) $YBa_2Cu_3{}^{16}O_6$	$YBa_2Cu_3{}^{18}O_6$	$\nu(^{16}O)/\nu(^{18}O)$
106	105	1.01
116	115	1.01
144 (sh)	142 (sh)	1.01
166	163	1.02
192	191	1.01
218	217	1.00
253	240	1.05
361	344	1.05
432	416	1.04
610	588	1.04
625 (sh)	603 (sh)	1.04
657	636	1.03

155 cm^{-1} mode is predominantly a Cu-O chain vibration, as discussed earlier.)

The far-infrared reflectance of $YBa_{2-x}Sr_xCu_3O_6$ for various values of x appears in Fig. 6. As expected, substitution of Sr for Ba affects the lowest frequency modes most strongly, whereas the higher frequency phonons change slightly, probably due to the overall lattice contraction. In $YBaSrCu_3O_6$ the modes near 110 cm^{-1} are broadened, possibly due to disorder in the Ba sublattice. More work remains to be done on this system, but the substitution-induced changes strongly imply involvement of Ba vibration in the 110 cm^{-1} modes. Changes also occur in the mode at 253 cm^{-1} when Sr is substituted for Ba, possibly as a result of the near proximity of the Sr and Cu-O planes. Since this mode shifts to lower energy when Sr is substituted for Ba it is likely that the Sr-O force constants are smaller than those of Ba-O, lowering the frequency of the Cu-O plane A_{2u} bending mode at 253 cm^{-1} (this mode is discussed below).

If these assignments for the modes near 110 cm^{-1} in the tetragonal materials are correct, then why is a c-axis-directed Ba mode at similar frequency not observed in $YBa_2Cu_3O_7$? In the O_7 material the E_u mode splits into a B_{2u} and a B_{3u} mode, both of which would be screened by the conduction electrons. The A_{2u} mode should become a B_{1u} mode. This is presumably one of the two "missing" symmetry-allowed modes in $YBa_2Cu_3O_7$. It is possible that a c-axis electron plasma may screen this low-frequency mode in $YBa_2Cu_3O_7$. A low-frequency plasma response has been reported previously both in $YBa_2Cu_3O_7$ (Ref. 19) and $La_{1-x}Sr_xCuO_4$.[20] In this regard it is interesting that the structure in the 100–120 cm^{-1} region is lost at oxygen contents near $O_{6.6}$ as the oxygen content is increased from O_6 to O_7.[2] This may signal the oxygen content at which a c-axis plasma response at this frequency develops.

The mode near 160 cm^{-1} in $YBa_2Cu_3O_6$ we assign as a c-axis translational mode of the CuO_2 groups which remain when the chain oxygens are removed. The O(1) atoms are tightly bound to the two-coordinated Cu(1) and quite far removed from the four-coordinated Cu-O plane Cu(2) atoms [Cu(1)-O(1) distance 1.792 Å, Cu(2)-O(1) distance 2.463 Å].[21] Thus one might expect the CuO_2 moiety to vibrate as a whole along the c axis (A_{2u} mode symmetry). The isotope shift for such a vibration should depend upon the *total* CuO_2 mass, so for 87% ^{18}O exchange one would expect the mode frequency to decrease by ~1.8%. We observe a 2% shift, which is close to this value. This mode would obviously be closely related to the [CuO_4] c-axis translational mode which we previously discussed as a possible candidate for the 155 cm^{-1} mode in $YBa_2Cu_3O_7$.

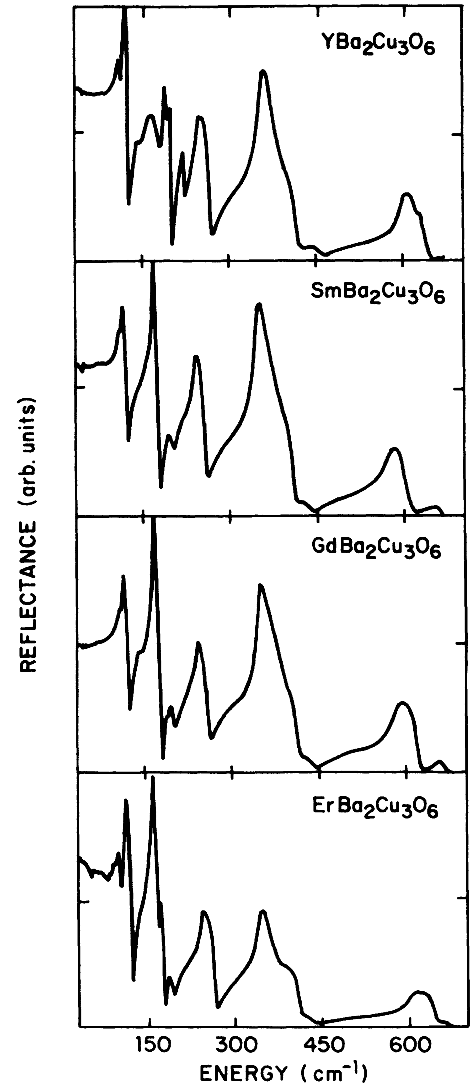

FIG. 6. Far-infrared reflectance spectra from 30–700 cm^{-1} of $RBa_2Cu_3O_6$, where R = Y, Sm, Gd, Er, at 10 K. The modes at 218 and 192 cm^{-1} shift 20–30 cm^{-1} to lower energy when rare-earth metals substitute for Y.

We assign the feature at 193 cm^{-1} to the A_{2u} Y mode due to its close similarity in energy to the 195 cm^{-1} B_{1u} Y vibration in $YBa_2Cu_3O_7$. The mode at 218 cm^{-1} would then be the doubly degenerate Y E_u vibration. These modes both undergo large shifts in energy when rare earths are substituted for Y (Fig. 7 and Ref. 6). As can be seen in Table IV, the modes at 192 and 218 cm^{-1} in $YBa_2Cu_3O_6$ shift by ~25 cm^{-1} to lower energy when rare earths occupy the Y site. Since the masses of the rare

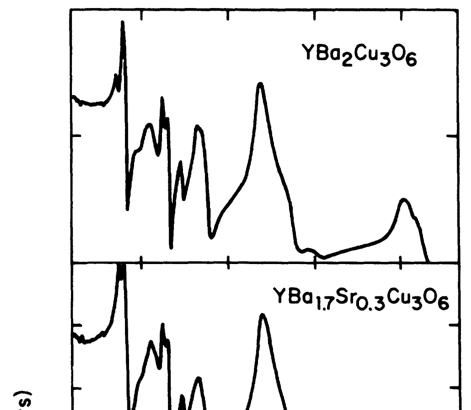

FIG. 7. Far-infrared reflectance spectra from 30–700 cm^{-1} of $YBa_{2-x}Sr_xCu_3O_6$ at 10 K. Strong changes in the modes near 110 cm^{-1} in $YBa_2Cu_3O_6$ demonstrate that these are the Ba A_{2u} and E_u modes.

earths are all rather similar, the variation in phonon frequencies for different rare earths probably results from changes in force constants and unit-cell dimensions. Comparable changes in frequency are observed for the 195 cm^{-1} Y B_{1u} vibration in $YBa_2Cu_3O_7$ when rare earths are substituted for Y (Table II).

The phonon modes at 253 and 361 cm^{-1} in $YBa_2Cu_3O_6$ also shift toward lower energy when rare earths occupy the Y site (Table IV). These modes exhibit a 5% decrease in energy when ^{18}O is substituted for ^{16}O (Table III). It therefore seems reasonable to assign these modes to bending vibrations of the Cu-O planes. Based upon our previous study of the effect of oxygen stoichiometry on the far-infrared spectra of $YBa_2Cu_3O_x$,[2] the 254 cm^{-1} mode correlates with the 276 cm^{-1} B_{1u} mode in $YBa_2Cu_3O_7$, which identifies it as an A_{2u} Cu-O plane vibration. The infrared-inactive B_{2u} mode in $YBa_2Cu_3O_6$ would then correlate with the 312 cm^{-1} $YBa_2Cu_3O_7$ B_{1u} vibration.

TABLE IV. Phonon energies for $RBa_2Cu_3O_6$ (cm^{-1}) at 10 K.

$YBa_2Cu_3O_6$	$SmBa_2Cu_3O_6$	$GdBa_2Cu_3O_6$	$ErBa_2Cu_3O_6$
106	109	109	102
116	115	117	115
144	143	143	144
166	160	159	157
192	166	165	160
218	198	196	189
253	245	250	247
361	349	354	350
432	423	428	421
610	575	591	626
657	650	657	660

From our oxygen stoichiometry study[2] this mode appears near an oxygen content of $O_{6.5-6.6}$, which is consistent with it being symmetry allowed only in the orthorhombic structure.

We also assign the 435 cm^{-1} mode in $YBa_2Cu_3O_6$ as a O(1)-Cu(1)-O(1) bending mode. This is the E_u binding mode of the CuO_2 chain group. It would be expected to have the highest bending frequency in $YBa_2Cu_3O_6$ due to the short (1.792 Å) Cu(1)–O(1) bond. This mode shifts by about 4% upon ^{18}O substitution, implying a fairly large amplitude oxygen vibration. Assuming this vibration to be similar to that of a linear triatomic molecule (CuO_2) one expects a 4% shift in frequency, as observed.

Finally, we discuss the high-frequency modes in $YBa_2Cu_3O_6$. Modes in the frequency range 500–700 cm^{-1} must be Cu-O stretching vibrations, of which there are only two expected in $YBa_2Cu_3O_6$, the Cu(2)-O(2) in plane stretch of E_u symmetry and the Cu(1)-O(1) bridge stretch of A_{2u} symmetry. All the high frequency reflectivity peaks in $YBa_2Cu_3{}^{16}O_6$ shift to lower energy by 3%–4% in $YBa_2Cu_3{}^{18}O_6$. For a vibration in which the reduced mass is that of Cu and oxygen one would expect a 4.3% frequency shift, which is consistent with the observed vibrations being predominantly Cu-O vibrations. The large 610 cm^{-1} phonon peak is seen to shift dramatically to lower energy when rare earths replace Y, implying that this mode is the doubly degenerate Cu(2)-O(2) stretch in the planes[6] adjacent to the rare-earth layer (Table V). The 657 cm^{-1} mode can then be assigned as the Cu(1)-O(1) A_{2u} bridge stretch. It is interesting that this mode, which is correlated to the 570 cm^{-1} Cu(1)-O(1) bridge stretch of B_{1u} symmetry in $YBa_2Cu_3O_7$, shifts to higher energy when oxygen is removed from the Cu-O chains. Removal of oxygen from the square-planar coordinated Cu in the chains causes the O(1) oxygens to move *toward* the chain Cu atom. This bond tightening increases the Cu(1)-O(1) vibrational frequency rather than decreasing it as suggested previously.[3,22] Thus it is not the increase in *c* axis length in $YBa_2Cu_3O_6$ (11.8037 Å) compared to $YBa_2Cu_3O_7$ (11.6655 Å), but rather the decrease in Cu (1)–O(1) bond length in $YBa_2Cu_3O_6$ (1.792 Å) compared to $YBa_2Cu_3O_7$ (1.850 Å), which is important for the variation in frequency of this mode (see Ref. 21 for structural information).

TABLE V. Summary of phonon assignments in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$.

Energy (cm^{-1})	$YBa_2Cu_3O_7$ ($7B_{1u}+7B_{2u}+7B_{3u}$) Assignment	Symmetry	Symmetry	$YBa_2Cu_3O_6$ ($5A_{2u}+6E_u$) Assignment	Energy (cm^{-1})
			A_{2u}	Ba translations	106
			E_u		116
155	O(4)-Cu(1)-O(4) bend or {O(4)-Cu(1)-$[O(1)]_2$-O(4)} *c*-axis translation	B_{1u}			
			A_{2u}	O(1)-Cu(1)-O(1) translation	166
194	Y translation	B_{1u}	A_{2u}	Y translation along *c*	192
			E_u[a]	Y translation in *a*-*b* plane	218
276	Cu(2)-O(3) out-of-plane bend	B_{1u}	A_{2u}	Cu(2)-O(2) out-of-plane bend	253
312	Cu(2)-O(2) out-of-plane bend	B_{1u}	B_{2u}[b]	Infrared inactive	. . .
			E_u	Cu(2)-O(2) in-plane bend	361
			E_u	Cu(1)-O(1) in-plane bend	432
			E_u	Cu(2)-O(2) in-plane stretch	610
572	Cu(1)-O(1) *c*-axis stretch	B_{1u}	A_{2u}	Cu(1)-O(1) *c*-axis stretch	657

[a] Modes which are E_u in tetragonal symmetry are doubly degenerate and are split into $B_{2u}+B_{3u}$ modes in orthorhombic symmetry. The *a*-*b* plane oriented B_{2u} and B_{3u} modes are screened by conduction electrons in $YBa_2Cu_3O_7$.

[b] The infrared inactive B_{2u} mode in tetragonal symmetry becomes an infrared active B_{1u} mode in orthorhombic symmetry.

As described above, the results of the ^{18}O isotope exchange spectroscopic measurement should be considered in light of the Teller-Redlich product rule. In $YBa_2Cu_3O_6$ there are two inequivalent oxygen sites. The plane site contributes one A_{2u} mode and two E_u modes, while the bridging oxygen site contributes one A_{2u} and one E_u mode. Thus, for 87% ^{18}O exchange, the right-hand side of Eq. (1) for the A_{2u} modes is equal to 1.10, while for the E_u modes it is equal to 1.16. The experimentally measured values determined from Table III are

$$A_{2u}=1.12\,,$$

$$E_u=1.15\,.$$

Since we have only identified with reasonable certainty five of the $6E_u$ modes we cannot be certain how closely the product rule would be satisfied for that case. The agreement of the measured and calculated values is reasonable and consistent with our vibrational assignments.

The results of the far-infrared vibrational mode assignments discussed in this paper are summarized in Table V. The discussion has been limited to $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$, where the predictions of group theory at the Brillouin zone centers are most nearly correct. For the intermediate oxygen contents, oxygen disorder, and other types of inhomogeneity may complicate spectra interpretation and one may expect to see such effects as infrared transitions which violate conservation of wave vector due to loss of lattice translational symmetry. If oxygen superordering occurs at particular oxygen stoichiometries between six and seven[23] the situation may again simplify although the increase in unit-cell size will increase the number of infrared transitions expected. For $YBa_2Cu_3O_6$, single-crystal measurements will be very useful since the platelike *a*-*b* plane oriented morphology of $YBa_2Cu_3O_6$ will allow preferential observation of the E_u modes. Furthermore, single crystal studies will allow the effect of photon propagation direction to be properly addressed.[9,24]

IV. CONCLUSION

In conclusion, we have proposed assignment of far-infrared optical phonons in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ based upon the results of isotopic and isomorphic substitution. In particular, the phonon at 155 cm^{-1}, which we have previously assigned as a Cu-O chain bending mode in which the oxygen and Cu ions move parallel to the *c* axis, is observed to shift to lower frequencies upon ^{18}O substitution, confirming the role of oxygen in this vibration. The fact that this mode is similar in form and energy to a vibration which calculations indicate is strongly coupled to the electrons in $YBa_2Cu_3O_7$ may imply that any phonon-mediated superconductivity in $YBa_2Cu_3O_7$ is largely due to this particular optical-phonon branch.

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