

Chain-oxygen vibrations in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$

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The modes of B_{1u} symmetry observed in the infrared spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$ at $\nu \approx 277 \text{ cm}^{-1}$ and 500 cm^{-1} , respectively, are assigned to vibrations of the chain oxygen. This assignment is reached by analysis of the corresponding eigenvectors, influence of Au,Pr,¹⁸O doping on these frequencies, and comparison of the infrared spectra of both materials.

Vibrations of atoms in the CuO_2 planes of oxide superconductors have been at the center of interest because of the natural conjecture that they should couple strongly to the superconducting carriers. It was indeed found in Raman spectroscopy that phonon frequencies, linewidths, and line amplitudes are strongly affected at the transition temperature,¹⁻³ which has led to the determination of a superconducting gap in $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (R = rare earth). Vibrations not involving the CuO_2 planes also couple to the electronic system, but with a smaller coupling constant. For some modes, the coupling is zero to within experimental error. In infrared (ir) spectroscopy, the odd B_{1u} vibrations (z direction) at $\mathbf{k} = 0$ were also found to show anomalies at T_c ,⁴⁻⁸ a detailed interpretation of the results, however, requires an understanding of the vibrational eigenmodes corresponding to each oscillator. While for the case of the even, Raman modes this assignment is well established and generally accepted in the literature,⁹⁻¹¹ we believe that in the case of the odd, ir vibrations the mode at $\sim 277 \text{ cm}^{-1}$ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has been incorrectly assigned; most authors believe it is associated with a plane-oxygen vibration. Instead, we have obtained evidence for it to be a chain-oxygen-related mode. For an interpretation of this mode regarding its behavior in the normal or superconducting state it is rather important to have a reliable eigenmode assignment.

The current understanding is that the vibration at 277 cm^{-1} is related to a vibration in the z direction of the O(2), O(3) oxygen atoms in the CuO_2 planes (see, e.g., (Refs. 4 and 8). Equivalent atoms in neighboring planes are in phase with each other, as is required by symmetry for ir-active (i.e., odd) vibrations. The relative phase of the O(2) and O(3) atoms is, however, not fixed by symmetry, leading to two possible eigenmodes: one in which O(2) and O(3) are in phase and one where they are out of phase. The out-of-phase mode is the one usually assigned to the 277 cm^{-1} peak in the spectra, while the in-phase one is believed to be the higher-frequency mode at 315 cm^{-1} . Corresponding modes exist in the Raman case, except that the two neighboring planes vibrate now out of phase (even parity). The assignment of the two ir modes is supported by frequencies predicted in lattice dynamical calculations,⁹ where the out-of-phase TO mode is found to be at $\sim 200 \text{ cm}^{-1}$ and the in-plane one

at $\sim 320 \text{ cm}^{-1}$. There are, however, a number of serious problems with this assignment.

It is instructive to study the symmetries of these vibrations in the approximate, higher-symmetry tetragonal case (i.e., $\text{YBa}_2\text{Cu}_3\text{O}_6$). There the out-of-phase vibrations of O(2) and O(3) correspond to different representations of the D_{4h} point group, both for the ir and the Raman modes. The odd, out-of-phase mode has B_{2u} (silent), the Raman one B_{1g} symmetry, while the in-phase modes are of A_{2u} (ir) and A_{1g} (Raman) symmetry. The point to make is that the selection rules in the D_{4h} group are different for these representations and, to the extent that the orthorhombic distortion is only small in the superconductor, these modes may be distinguished experimentally. In the Raman case, the B_{1g} selection rule is fulfilled nearly exactly experimentally in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for one of the phonons in question and thus identifies it as the out-of-phase vibration.⁹ Of the tetragonal odd modes the B_{2u} one is silent: because of the symmetry of the displacements, the dipole vector associated with the out-of-phase vibration remains zero. Physically speaking, charge is displaced up by one oxygen [say O(2)] and down by the other [O(3)]. Because of tetragonal symmetry these displacements are exactly equal and the net dipole vector cancels. The mode with out-of-phase displacement in the tetragonal approximation should not be seen at all and it can be expected to remain weak in the orthorhombic material. Experimentally, the 277-cm^{-1} mode is quite strong though, making its assignment to B_{2u} problematic. One may estimate the effect of orthorhombic distortion on phonon strength by consulting lattice dynamical calculations.⁹ They predict in the distorted case an oscillator strength of $S < 0.1$; the experiment finds much larger value for both single crystals¹² and ceramics at room temperature ($S \approx 3$), increasing at lower temperatures to about 8 (Ref. 4) in contradiction with the nearly silent character of this mode. Considering the small predicted strength, we call, for the rest of the paper, the mode of approximate B_{2u} tetragonal symmetry the "silent" mode, knowing that it is not exactly silent in orthorhombic symmetry.

What is the experimental evidence, apart from its strength, that the mode at 277 cm^{-1} is not the silent one, and if it is not, what is its correct assignment? To answer this question, we consider substitutions of metal ions and

of oxygen by an isotope. We also compare the phonons in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (1:2:3) with those in $\text{YBa}_2\text{Cu}_4\text{O}_8$ (1:2:4), the double-chain compound.

In Fig. 1 we show the reflectivity spectra of both the 1:2:3 and 1:2:4 compounds. Apart from the effects of the double chain, the compounds are isostructural and should, hence, possess similar phonon modes and frequencies. The Raman phonons, for instance, are nearly identical in frequency in both compounds, except for additional, chain-related modes in 1:2:4, which are not Raman active in 1:2:3.¹³ The infrared modes not related to chains should thus also be similar in 1:2:3 and 1:2:4 and we found this to be true with one exception.⁵ As may be seen from the figure, the strong mode at 277 cm^{-1} in 1:2:3 is not present in 1:2:4. In view of an assignment of the silent mode to this peak, this is a very surprising result. Why should the silent mode be the only one to disappear from its position in 1:2:3? Furthermore, there is an additional peak in the 1:2:4 spectrum at 500 cm^{-1} . From a group-theoretical point of view, however, the number of ir-active modes is the same in both compounds. No new mode is expected. We may hence conclude that the 277-cm^{-1} (1:2:3) and 500-cm^{-1} (1:2:4) modes are actually the same (as indicated by arrows in Fig. 1), with a significantly different frequency in the two compounds.

Why should the frequency of this mode be so different in the two compounds? If we assume it to be the chain-oxygen vibration along z , the explanation follows naturally from the existence of double chains in 1:2:4. The z vibration of the chain oxygen is a pure bending mode in 1:2:3 and should hence have a characteristically low frequency. In the double-chain compound the unit cell is face centered: there is a shift of $b/2$ in y direction of two primitive cells adjacent in c direction. Consequently the chain oxygen is placed under a copper atom and its z -direction vibration has predominately bond-stretching character. Its frequency should go up significantly as is observed in the spectra. Thus, the comparison of the two spectra in Fig. 1 suggests that the 277-cm^{-1} mode in 1:2:3 is indeed a chain-related mode.

An indication for this assignment may be taken from infrared-reflectivity measurements on the chainless semiconductor $\text{YBa}_2\text{Cu}_3\text{O}_6$ where a chain mode must be absent. Indeed there is no z -polarized phonon in this material in the energy range $220\text{--}440\text{ cm}^{-1}$.¹⁴ However, in view of considerable frequency shifts of other phonons ($\sim 50\text{ cm}^{-1}$), we do not take this point as reliable evidence for our assignment.

Now we present the results of substitution experiments which further support this point. Gold is known to sub-

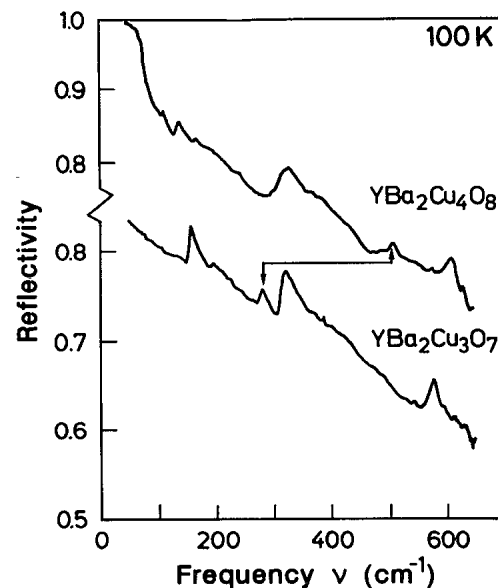


FIG. 1. Reflectivity spectra of $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramics at $T = 100\text{ K}$.

stitute for Cu(1) (the chain copper atom) in the 1:2:3 structure (Ref. 15). Pr, on the other hand, replaces Y in $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. In Table I we list the frequency changes of the five strong ir-active modes in 1:2:3 upon exchange of Cu(1) by Au and Y by Pr. The largest change, $\Delta\nu/\nu = -4.0\%$, for Au substitution occurs for the mode at 277 cm^{-1} , a surprising result if this mode were to be the silent one. As Au substitutes in the chain-copper site such an effect is rather expected for the chain-oxygen mode. For Pr in place of Y, on the other hand, the strongest change ($\Delta\nu/\nu = -1.6\%$) occurs for the 193 cm^{-1} mode, which is known to be a vibration involving mostly the Y atom.¹⁶ The mode at 277 cm^{-1} is barely affected, the in-phase oxygen mode at 315 cm^{-1} considerably more. This gives us further support for the 277-cm^{-1} mode being related to chain-oxygen vibration.

In order to further verify this new assignment we have also performed a partial oxygen-substitution experiment. By treating a sample of $\text{ErBa}_2\text{Cu}_3(^{16}\text{O}_{6.84-x}\text{^{18}O}_x)$ with $x = 0$ in ^{18}O atmosphere at high annealing temperatures ($T = 600^\circ\text{C}$) in a thermogravimetric environment we could substitute small concentrations of oxygen ($0 \leq x \leq 1.2$). High-temperature annealing means that ^{18}O and ^{16}O will be roughly equally distributed over all oxygen sites, provided sufficient time to equilibrate is

TABLE I. Relative change of TO frequency for five infrared-active modes of $\text{YBa}_2(\text{Cu}_{2.9}\text{Au}_{0.1})\text{O}_7$ and $(\text{Y}_{0.9}\text{Pr}_{0.1})\text{Ba}_2\text{Cu}_3\text{O}_7$ with respect to the $\text{YBa}_2\text{Cu}_3\text{O}_7$ at $T = 100\text{ K}$. Frequencies in the upper row are given in cm^{-1} .

Assignment	Ba	Y	O1	O2/O3	O4
ν_{TO} ($\text{YBa}_2\text{Cu}_3\text{O}_7$)	155.1	193.3	276.8	314.5	564.8
$\Delta\nu_{\text{TO}}/\nu_{\text{TO}}$ (Cu/Au)	-2.6%	-0.3%	-4.0%	-2.0%	0
$\Delta\nu_{\text{TO}}/\nu_{\text{TO}}$ (Y/Pr)	-0.3%	-1.6%	-0.3%	-0.8%	-0.4%

given. In a low-temperature annealing experiment ($T = 300^\circ\text{C}$) we achieved also an exchange of $x = 1.03$; under this condition, however, the exchange with oxygen in the CuO_2 planes is suppressed and, to first approximation, we may say that the O(1) oxygen position is substituted by ^{18}O while the other oxygen sites consist mostly of ^{16}O .^{17,18} In Fig. 2 we plot the frequencies of the ir-active modes at 274 and 306 cm^{-1} (shifted from the Y values due to the replacement with Er) for small values of x . The vibrational frequencies for small concentrations of a heavier atomic mass are expected to shift approximately linearly with x to lower frequencies. This is indicated in the figure by the dashed lines through the open points, which came from the spectra of well-annealed, homogeneous samples. The black points correspond to the low-temperature annealed sample. While for the 306- cm^{-1} mode the $x = 1.03$ point lies approximately on the curve, the mode at 274 cm^{-1} has shifted much more to lower frequencies. This may only be understood if it is assumed that the lower-frequency mode is a chain vibration which, due to an ^{18}O concentration in the chains higher than average, shifts more than in the high-temperature annealed samples. The facts that the higher mode softens at all and the frequency of the lower mode is higher than that of fully ^{18}O substituted material ($x = 6.84$, $\nu = 261 \text{ cm}^{-1}$) results from a mixing of ir modes of equal symmetry.

Having presented what we believe is convincing evidence to assign the 277- cm^{-1} mode to a chain-oxygen dominated eigenmode, we discuss briefly its unusual temperature dependence in the normal state. Between room temperature and $\sim 100 \text{ K}$ this mode has been reported to soften significantly in undoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, contrary to the other modes in the ir spectra.^{4,7,16,20} In doped samples, this tendency appears to be enhanced: For Au- and Pr-doped samples the mode softens by about 8 cm^{-1} ,¹⁹ for Zn-doped samples a shift of $\sim 12 \text{ cm}^{-1}$ has been reported.⁸ We do not believe that the soften-

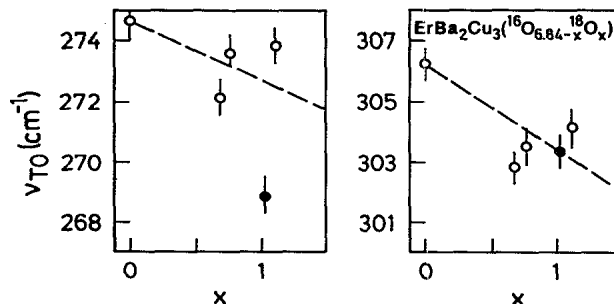


FIG. 2. Frequencies of ir-active vibrations in $\text{ErBa}_2\text{Cu}_3(^{16}\text{O}_{6.84-x}^{18}\text{O}_x)$ as a function of x at $T = 100 \text{ K}$. The open points represent data for the high-temperature-annealed samples with random distribution of ^{18}O ions over the possible sites, the closed points correspond to a low-temperature-annealed sample with site-selective O(1) substitution. The dashed lines are the linear interpolations of the phonon frequencies obtained for samples with $x = 0$ and $x = 6.84$.

ing in the normal state has anything to do with superconductivity, since it occurs even in nonsuperconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$.²⁰ Rather, we propose that it comes from a suitably placed singularity in the density of two-phonon states available for the virtual decay of the phonon being considered.

In conclusion, we have presented evidence that the 277- cm^{-1} mode in the ir spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is related to chain-oxygen vibrations and not to the CuO_2 planes as previously assumed.

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