

## Raman scattering from high- $T_c$ superconductors

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Raman scattering experiments from high- $T_c$  superconductors of the  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  type, with  $R = \text{Y, Pr, Nd, Eu, Gd, Dy, and Yb}$ , are reported. Because of the great difficulty in obtaining single-phase samples, spectra from all starting compounds and other known phases of Y-Ba-Cu are presented. This systematic approach has allowed the identification of the lines observed in Raman spectra of the superconducting compounds as well as those of impurity phases. The lines originating from the superconducting yttrium compound were investigated as a function of quench temperature, and oxygen deficiency. Polarization studies on single crystals are also presented.

### I. INTRODUCTION

An important experiment to test the conventional electron-phonon-mediated Bardeen-Cooper-Schrieffer (BCS) mechanism for superconductivity in the recently discovered metallic copper oxides<sup>1,2</sup> is the isotope effect,<sup>3-6</sup> in which  $^{16}\text{O}$  is replaced by  $^{18}\text{O}$ . On substitution no changes were observed in the superconducting properties in Refs. 3 and 4; while in Ref. 5 a small isotope effect is claimed. Nevertheless, a study of the phonon properties is crucial for an understanding of these intriguing materials even if the superconducting mechanism is proven not to be phonon mediated.

During the short time since the discovery of these materials, there have already been numerous reports dealing with phonon properties, including infrared studies,<sup>7-11</sup> Raman studies,<sup>3,9-18</sup> and inelastic neutron scattering studies.<sup>19</sup> Even among the eleven Raman-scattering references substantial discrepancies are present. In agreement with Ref. 15, we find that many of these discrepancies are due to impurity phases, which, because of the usual preparation techniques, are almost always present in these compounds. Many of these phases are not metallic and consequently have much larger cross sections for Raman scattering so, that even though the impurities may be a small volume fraction, they can dominate the Raman spectra.

Here we report the results of a systematic study of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system. We present spectra obtained from the usual starting compounds as well as from the known impurities which are likely to be present in typical samples. A comparison of these spectra with the ones obtained from nominally pure  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has allowed the identification of many impurity lines, and more importantly, those lines belonging to the superconducting compound.

In addition to the identification of the lines originating from the superconducting compound, the behavior of a number of them as a function of quench temperature, oxygen stoichiometry, substitution of Y by a number of rare-earth metals, and polarization studies on single crystals, are presented.

Section II is a detailed factual report of our results. In Sec. III these are discussed and compared with other reports in the literature and our conclusions are given in Sec. IV.

### II. RESULTS

In order to identify the origin of the various Raman lines observed in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system it was neces-

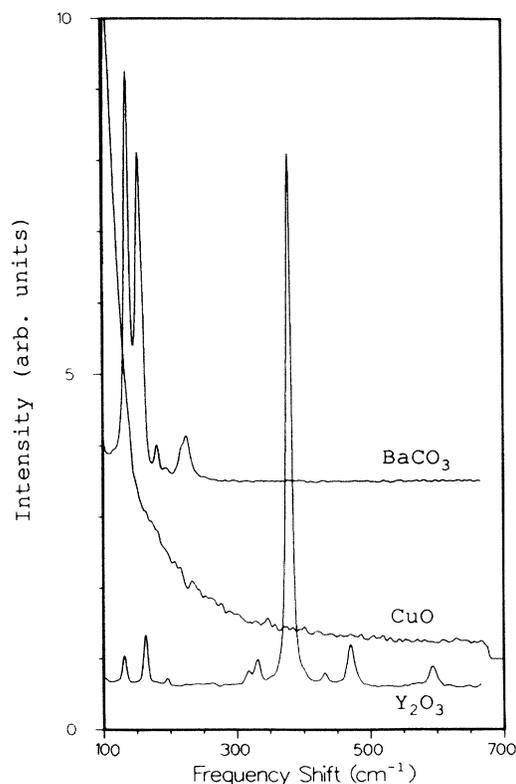


FIG. 1. Raman spectra of the compounds used as starting materials to fabricate  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , viz.,  $\text{BaCO}_3$ ,  $\text{CuO}$ , and  $\text{Y}_2\text{O}_3$ .

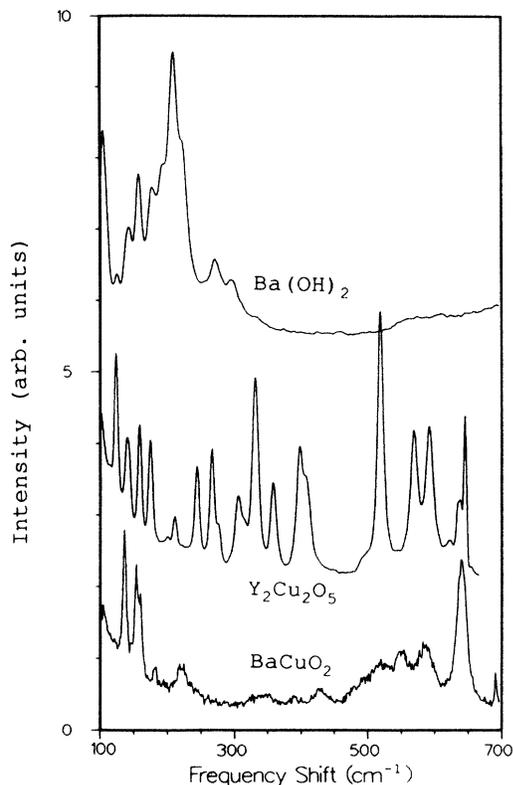


FIG. 2. Raman spectra of possible impurity phases in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-s}$ , viz.,  $\text{BaCuO}_2$ ,  $\text{Y}_2\text{Cu}_2\text{O}_5$ , and  $\text{Ba}(\text{OH})_2$ .

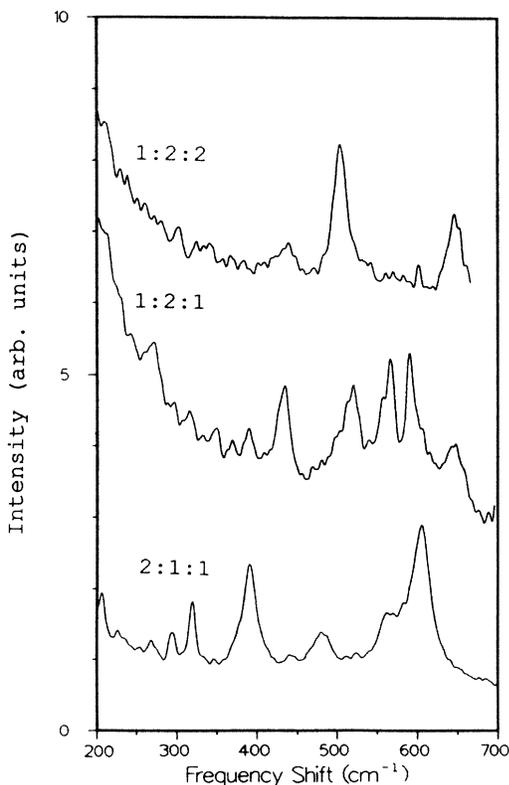


FIG. 3. Raman spectra obtained from pellets fabricated with the atomic ratios of Y to Ba to Cu given by (a) 1:2:2, (b) 1:2:1, and (c) 2:1:1.

sary to perform Raman scattering experiments from (i) the starting materials as well as other possible impurities; (ii) pellets prepared with different Y:Ba:Cu ratios; and (iii) samples prepared by different techniques. Having identified the Raman lines of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-s}$  compound we studied their (iv) polarization characteristics using single crystals, (v) dependence on oxygen stoichiometry, and (vi) dependence on rare-earth substitution of the Y.

(i) *Starting materials and impurities.* Figure 1 shows room-temperature Raman spectra from the materials usually used to fabricate the high- $T_c$  compound, viz.,  $\text{CuO}$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{BaCO}_3$ . Figure 2 contains a spectrum from a pellet fired from a mixture of  $\text{CuO}$  and  $\text{BaCO}_3$  (1:1 atomic ratio of Cu to Ba) which contains mainly  $\text{BaCuO}_2$ , another from a pellet made with  $\text{CuO}$  and  $\text{Y}_2\text{O}_3$  (1:1 atomic ratio of Cu to Y) which is known to yield mainly  $\text{Y}_2\text{Cu}_2\text{O}_5$ , and also a spectrum of the possible impurity  $\text{Ba}(\text{OH})_2$ .

(ii) *Other compounds.* In Fig. 3 we present spectra obtained from pellets which were prepared with various Y:Ba:Cu composition ratios; these ratios are 2:1:1, 1:2:1, and 1:2:2.

(iii) *Sample preparation.* The three curves of Fig. 4 are different samples of nominal 1:2:3 composition. Curves (a) and (b) are spectra obtained from samples

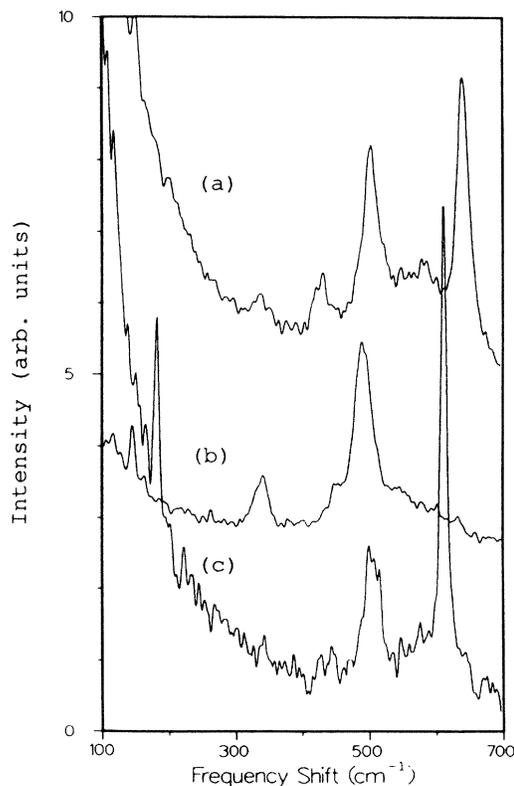


FIG. 4. Raman spectra of three pellets of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-s}$ . The two upper samples are prepared as described in Refs. 20 and 21 (note the line at  $\sim 640 \text{ cm}^{-1}$  indicating the presence of  $\text{BaCuO}_2$  in the upper spectrum). The lower sample was prepared by coprecipitation as described in Ref. 22. (The line at  $\sim 612 \text{ cm}^{-1}$  is due to presence of some of the 2:1:1 compound.)

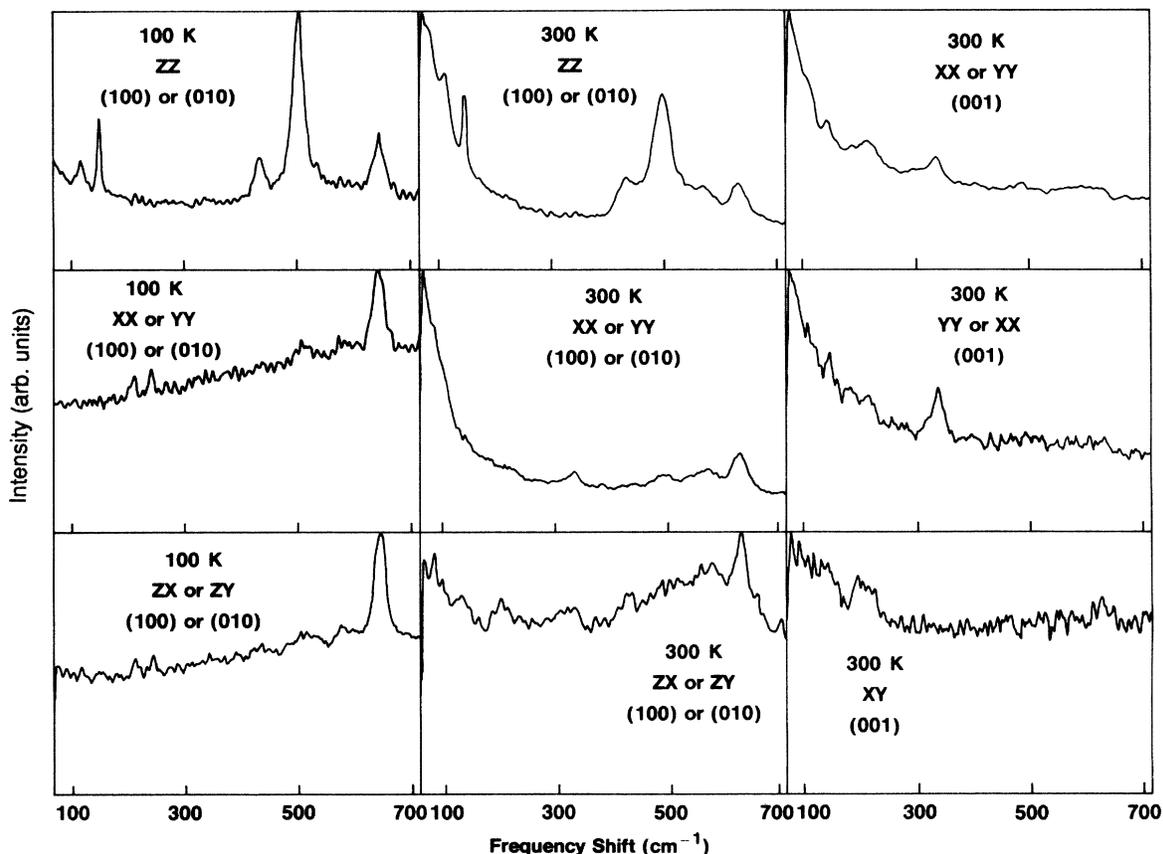


FIG. 5. Raman spectra obtained from a "single crystal" of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at  $\sim 100$  K and room temperature. (Uncertainties in the polarization and scattering faces are due to the fact that the  $a$  and  $b$  axes are not identifiable.) Scattering from the  $a$  or  $b$  faces (which are not as well formed as the  $c$  face) shows evidence for some  $\text{BaCuO}_2$ . Note that all the lines which we assign to the 1:2:3 compound, viz.  $\sim 116$ ,  $\sim 149$ ,  $\sim 336$ ,  $\sim 434$ , and  $\sim 504$   $\text{cm}^{-1}$ , appear in polarizations labeling them as Ag symmetry.

prepared by sintering the oxides  $\text{CuO}$ ,  $\text{BaCO}_3$ , and  $\text{Y}_2\text{O}_3$  (Refs. 20 and 21) by two independent groups in our laboratory. Curve (c) is from a sample prepared by coprecipitation before firing.<sup>22</sup>

(iv) *Single crystals.* Figure 5 contains spectra obtained from "single crystals" of the 1:2:3 compound,<sup>23</sup> typically  $\sim 200$   $\mu\text{m}$  on a side, with well-defined (001) faces and rough (100) and (010) surfaces. In the present experiments we did not distinguish between the [100] and [010] directions because of microtwinning. This leads to the ambiguities in the polarizations given in Fig. 5. In the low-temperature experiments the temperature was estimated to be  $\sim 100$  K; however, since typically a  $\sim 100$  mW beam was focused on a  $\sim 100$   $\mu\text{m}$  diameter spot and the crystallites were bonded with grease, the quoted temperature should be treated with caution.

(v) *Oxygen stoichiometry.* It is known that for  $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $T_c$  depends substantially on the oxygen stoichiometry.<sup>21,24-26</sup> The stoichiometry may be controlled by rapid cooling of the sample to low temperature from an appropriate high temperature and/or by oxygen pressure. Raman scattering from the 1:2:3 compound, quenched in one atmosphere  $\text{O}_2$  from different temperatures between 500 and 900  $^\circ\text{C}$  by dropping it into liquid

nitrogen, exhibits shifts in at least the Raman line at 500  $\text{cm}^{-1}$ . However, since quenching from different temperatures is a rather difficult process to perform reproducibly, the results showed substantial scatter. Rather than present these results we show Raman spectra of samples that were quenched from 500  $^\circ\text{C}$  (where kinetics are relatively slow and constant from sample to sample) into liquid nitrogen. Oxygen pressures were varied to control the stoichiometry. Figure 6 shows the spectra from samples in which the oxygen content ( $\text{O}_{7-\delta}$ ) is (a)  $\delta=0.16$ ,  $T_c=90$  K, (b)  $\delta=0.44$ ,  $T_c=57$  K; and (c)  $\delta=0.72$ ,  $T_c < 4$  K.

(vi) *Substitution.* In Fig. 7 we present data on compounds where the Y has been replaced by varying amounts of Pr and in Fig. 8 from samples with half the Y replaced by Pr, Nd, Eu, Gd, Dy, or Yb.

### III. DISCUSSION

(i) *Impurities.* The spectra for  $\text{CuO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Y}_2\text{Cu}_2\text{O}_5$ ,  $\text{BaCuO}_2$  (Figs. 1 and 2) are in good agreement with those of Ref. 15, and the spectrum for the 2:1:1 compound (Fig. 3) agrees with the spectra shown in Refs. 12 and 15. De-

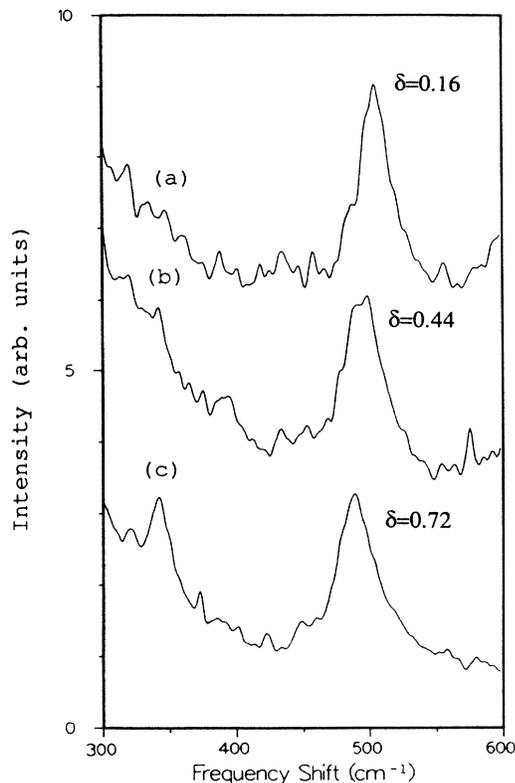


FIG. 6. Raman spectra of  $\text{YBa}_2\text{CuO}_{7-\delta}$  cooled under various oxygen pressures. The upper sample has a  $T_c$  of 90 K, the middle one 57 K, and the lowest was not superconducting. The  $\sim 336 \text{ cm}^{-1}$  peak is only intense in samples which have a large oxygen deficiency.

pending on the exact location in the Y:Ba:Cu phase diagram, the Raman spectra (Figs. 3 and 4) show, as expected, various fractions of the superconducting 1:2:3 compound,  $\text{BaCuO}_2$ ,  $\text{Y}_2\text{Cu}_2\text{O}_5$ , and the 2:1:1 compound. However, samples prepared in the nominal 1:2:3 ratio show mostly additional lines from  $\text{BaCuO}_2$  (characterized by its strong peak at  $\sim 640 \text{ cm}^{-1}$ ) and the 2:1:1 compound (characterized by a strong peak at  $\sim 612 \text{ cm}^{-1}$ ). The spectra in Figs. 1–3 should be helpful to those involved in sample preparation in order to identify possible impurities.

(ii) *Identification of 1:2:3 Raman lines.* From a detailed comparison of all the spectra it is possible to conclude that the Raman lines associated with the 1:2:3 compound are located around 116, 149, 336, 434, and  $504 \text{ cm}^{-1}$ . Care must be taken however because  $\text{BaCuO}_2$  also has features at  $\sim 435$  and  $\sim 500 \text{ cm}^{-1}$  which can be mistakenly assigned to the 1:2:3 compound. Only if the relative intensities compared to that at  $640 \text{ cm}^{-1}$  are clearly different from that expected for  $\text{BaCuO}_2$  (Fig. 2), can these peaks be assigned to the 1:2:3 compound. The low-lying lines at 116 and  $149 \text{ cm}^{-1}$  can also be ruled out as being due to impurities by a similar process based on relative intensities or absence of other peaks. The intense line close to  $500 \text{ cm}^{-1}$  is reported in all references.<sup>3,9–18</sup> The other features, however, are often either too low in frequency, or are masked by strong  $\text{BaCuO}_2$  lines. Below,

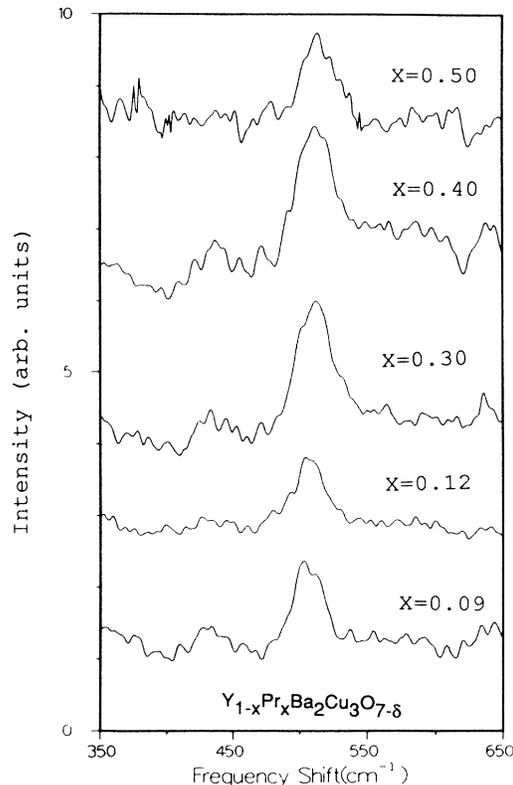


FIG. 7. Raman spectra of  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  obtained for  $x = 0.09, 0.12, 0.30, 0.40,$  and  $0.50$ . The peak at  $\sim 504 \text{ cm}^{-1}$  increases in frequency as Pr is added.

we compare our assignment only with those references in which the impurity lines are readily identifiable: Reference 12 reports lines at 142, 338, and  $483 \text{ cm}^{-1}$  (the difference between 483 and  $504$  will be discussed below); Ref. 9 reports a line at  $495 \text{ cm}^{-1}$ ; Ref. 10 has prominent lines at 155, 335, 440, and  $509 \text{ cm}^{-1}$  and others at 175, 295, 581, and  $638 \text{ cm}^{-1}$ ; Ref. 15 identifies lines at 337 and  $502$  and weak structures at 187 and  $563 \text{ cm}^{-1}$ . Thus, of the five Raman lines we have identified here, four have also been assigned independently to the 1:2:3 compound. The remaining line at  $116 \text{ cm}^{-1}$  was checked as a Raman line using 5825- and  $4767\text{-\AA}$  radiation and agrees with a line assigned to a plasma line in Ref. 12 where  $5145\text{-\AA}$  radiation was used.

(iii) *Mode symmetries.* A group-theoretical analysis based on the orthorhombic structure of the crystal<sup>27</sup> predicts 15 Raman active phonons: 5  $A_g$  modes which appear in  $xx$ ,  $yy$ , and/or  $zz$  polarization, 5  $B_{2g}$  modes in the  $xz$  polarization, and 5  $B_{3g}$  modes in  $yz$  polarization. Group theory also determines that the only atoms involved in these vibrations are (following the nomenclature of Ref. 27) the Ba, Cu(2), O(2), O(3), and O(4). A simple analysis indicates that for each vibrational symmetry we expect two low-lying modes associated with motion of the Ba and Cu atoms and three high-frequency modes associated mainly with oxygen atom motion. The single-crystal results shown in Fig. 5 imply that the observed modes are all of  $A_g$  symmetry and hence (also based on group theoretical considerations) that the atomic motion in all

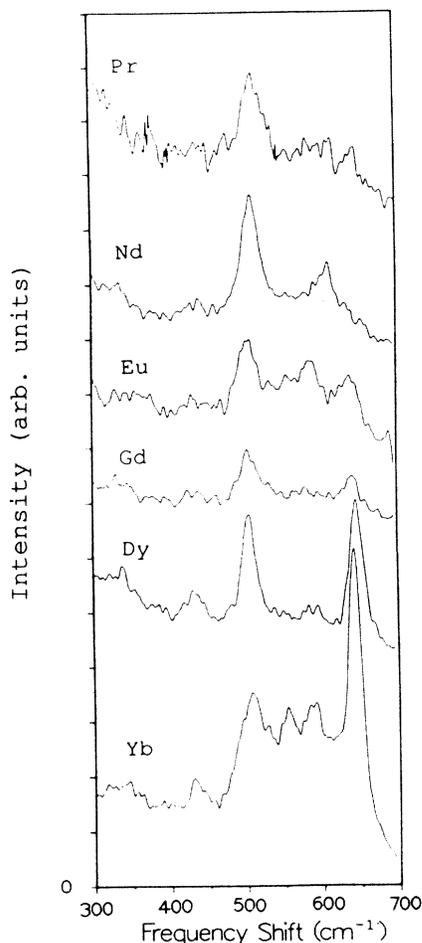


FIG. 8. Raman spectra of  $Y_{0.5}R_{0.5}Ba_2Cu_3O_{7-\delta}$  with  $R = Pr, Nd, Eu, Gd, Dy,$  and  $Yb$ . As the radius of the substituted rare earth increases ( $Yb \rightarrow Pr$ ) the  $504\text{ cm}^{-1}$  line increases in frequency.

cases is along the  $z$  direction. Given the almost tetragonal symmetry<sup>27</sup> of the plane containing the O(2) and O(3) atoms, the modes involving these atoms are expected to have very similar frequencies, and therefore only four  $A_g$  modes would be present. The presence of an additional line is discussed in the next paragraph.

(iv) *Oxygen stoichiometry.* The behavior of the  $336$  and  $504\text{ cm}^{-1}$  lines as a function of oxygen content (Fig. 6) shows two interesting features: The intensity of the  $336\text{ cm}^{-1}$  line increases as the oxygen content is reduced (this fact is statistically confirmed by measurements on many samples—it is always present in oxygen-deficient samples, it is sometimes observed in *nominally* high oxygen-content samples also). Second, the  $504\text{ cm}^{-1}$  line decreases in frequency as oxygen is removed. In Ref. 9 the  $495\text{ cm}^{-1}$  line is also reported to decrease in frequency as oxygen is removed but additional structure is reported at  $590$  and  $625\text{ cm}^{-1}$ . In Refs. 10 and 17 Raman spectra from  $YBa_2Cu_3O_6$  (i.e.,  $\delta = 1$ ) also show that the  $334\text{ cm}^{-1}$  line is very intense. A comparison with the results of Ref. 12 in which the  $336\text{ cm}^{-1}$  line was observed to be very intense and the other line was at  $483\text{ cm}^{-1}$ , indicates

that the sample was probably very oxygen deficient. Furthermore, it was also reported<sup>12</sup> that the  $336\text{ cm}^{-1}$  line appears in the  $xy$  polarization, a polarization in which no mode is predicted by group theory for  $YBa_2Cu_3O_7$ . All these facts imply that the  $336\text{ cm}^{-1}$  line, although originating from the 1:2:3 compound, is probably a forbidden Raman mode which is rendered Raman active by oxygen vacancies. The above conclusion is confirmed by very recent results by Timofeev<sup>28</sup> who from single-crystal measurements identifies the symmetry of this line as  $B_{1g}$  in a crystal of  $D_{4h}$  symmetry; consequently it cannot be from  $YBa_2Cu_3O_7$ . It also explains why in Ref. 12 it appeared in  $xy$  polarization since a reassignment of the  $x$  and  $y$  axes by a rotation of  $45^\circ$  in the plane produces exactly this effect. (In such a coordinate system  $B_{1g}$  modes appear in  $x'y'$  but not in  $x'x'$  or  $y'y'$  while  $A_g$  modes still appear in  $x'x'$  and  $y'y'$ .) The fact that the  $336\text{ cm}^{-1}$  line is sometimes observed in nominally fully oxygenated samples must be ascribed to the unproven possibility of changes in sample stoichiometry close to the surface or to other sample inhomogeneities. The fact that the  $336\text{ cm}^{-1}$  line is observed to have an anomalous temperature dependence<sup>16,29</sup> around  $100\text{ K}$  and which is assumed to be related to superconductivity is probably also only an unfortunate coincidence.

(v) *Substitution.* The increase in frequency of the  $504\text{ cm}^{-1}$  line as  $Y$  is replaced by  $Pr$ , shown in Fig. 7, can be used to identify the atoms involved in this vibration. The structure<sup>27</sup> implies that the O(2) and O(3) atomic motions along the  $z$  direction will be determined mainly by their interactions with the Ba and  $Y(Pr)$  atoms while that of the O(4) is possibly dominated by its interaction with Cu(1) atoms. Hence, the observed increase in frequency as  $Y$  is replaced by the larger  $Pr$  atom indicates that the  $504\text{ cm}^{-1}$  line corresponds to vibrations of O(2) and O(3) atoms. The substitution of  $Y$  by other rare earths that are smaller than  $Pr$  produce smaller changes as can be seen in Fig. 8. The shifts we observe in the  $504\text{ cm}^{-1}$  line for various rare earths is consistent with similar data ( $Sm, Eu, Gd,$  and  $Ho$ ) presented in Ref. 10.

#### IV. CONCLUSIONS

We have identified Raman lines from  $YBa_2Cu_3O_{7-\delta}$  at  $116, 149, 336, 434,$  and  $504\text{ cm}^{-1}$ . From the dependence on oxygen stoichiometry, the  $336\text{ cm}^{-1}$  line is assigned to a defect-induced Raman mode and is consistent with its  $B_{1g}$  symmetry<sup>28</sup> which precludes it as arising from  $YBa_2Cu_3O_7$ . From polarization studies on single crystals, the remaining four modes are found to have  $A_g$  symmetry. Since only Cu(2), Ba, O(2), O(3), and O(4) contribute to first-order Raman spectra, mass considerations suggest that the  $116$  and  $149\text{ cm}^{-1}$  lines arise from vibrations of Cu(2) and Ba. Based on structural considerations, a degeneracy is expected for the O(2) and O(3) vibrations; therefore, one of the  $434$  and  $504\text{ cm}^{-1}$  lines is assigned to O(4) and the other to O(2)+O(3). The frequency change in the  $504\text{ cm}^{-1}$  line as a function of  $Y$  substitution suggests that this line might be due to O(2)+O(3) but this assignment should be taken with caution.

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