

## Raman study of the effect of oxygen stoichiometry on the phonon spectrum of the high- $T_c$ superconductor $\text{YBa}_2\text{Cu}_3\text{O}_x$

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We have carried out a study of the effect of oxygen stoichiometry on the  $k=0$  phonon spectrum of the high- $T_c$  superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_x$  using Raman spectroscopy. Polycrystalline samples were prepared with oxygen content  $x$  varying from 7.0, where the material is orthorhombic and superconducting, to 6.0, where it is tetragonal and semiconducting. The frequency and intensity of the  $k=0$  phonon modes of  $A_g$  symmetry at 151, 340, 435, and 502  $\text{cm}^{-1}$  (for  $x=7$ ) were studied as a function of oxygen content.

### I. INTRODUCTION

A striking property of the new family of oxygen-deficient high-temperature superconducting oxides in the Y-Ba-Cu-O system<sup>1-3</sup> having the composition  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (Refs. 4 and 5) is the critical dependence of the superconducting<sup>6-14</sup> and magnetic<sup>15,16</sup> properties on oxygen content. We report here the measurement of first-order Raman scattering to study the effect of this oxygen content on the  $k=0$  phonon modes of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (Y 1:2:3), for  $6 \leq x \leq 7$ .

The superconducting transition temperature of Y 1:2:3 depends strongly on the oxygen stoichiometry, which can be readily and reversibly varied between  $x=6$  and  $x=7$ <sup>6,7,17</sup> by heating in an inert atmosphere. In the fully oxygenated state ( $x=7$ )  $\text{YBa}_2\text{Cu}_3\text{O}_x$  is orthorhombic [see Fig. 1(a)] and superconducting with  $T_c=92$  K and for  $x \lesssim 6.5$  it is tetragonal [Fig. 1(b)] and semiconducting.<sup>1-3,7,8,14,18-20</sup> Two features of the structure<sup>17,21</sup> are the sheets consisting of Cu(2)-O(2),O(3) atoms and the ribbons formed by Cu(1)-O(4),O(1) atoms. For  $x=7$ , the O(1) site at  $(0, \frac{1}{2}, 0)$  is fully occupied and O(5) at  $(\frac{1}{2}, 0, 0)$  is empty. As oxygen is removed, vacancies are formed in the O(1) position, with smaller amounts ( $<10\%$ ) leaving the O(4), O(2), and O(3) positions.<sup>18</sup> These vacancies can be ordered for certain values of  $x$ . For example for  $x=6.8-6.9$  a superlattice with a unit cell of dimensions  $(2\sqrt{2}a, 2\sqrt{2}a, c)$  has been proposed,<sup>22</sup> and for  $x=6.6$  a doubling of the  $a$  axis alone has been observed.<sup>23</sup> Near  $x=6.5$ , there is an orthorhombic-to-tetragonal transition in which oxygen atoms occupy O(1) and O(5) sites equally.<sup>18</sup> The annealing and quenching conditions can apparently affect the value of  $x$  for which the tetragonal structure is formed.<sup>18,24,25</sup> The superconducting transition temperature drops as oxygen is removed and the material is not superconducting in the tetragonal state, whether the oxygens are ordered or not. Continued removal of oxygen to  $x=6$  gives a tetragonal structure in which the O(1) and O(5) sites are both empty. An orthorhombic-to-tetragonal transition also occurs as a function of temperature at 700°C in air.<sup>18</sup>

A number of Raman studies of Y 1:2:3 and related compounds have been carried out.<sup>26-46</sup> The reported

spectra often differ greatly due to the presence of impurity phases or unreacted starting material. Since many of these compounds have higher scattering cross sections than Y 1:2:3, great care is needed to eliminate or carefully identify such impurities.<sup>26,43</sup> We make particular reference here to those Raman studies which have investigated the dependence of the spectrum on oxygen stoichiometry. Stavola *et al.*<sup>28</sup> measured Raman spectra between 400 and 700  $\text{cm}^{-1}$ , for four values of  $x$  and interpreted their results as a superposition of different amounts of tetragonal and orthorhombic phases. In later work, these workers<sup>39</sup> measured the continuous frequency shift of the 502  $\text{cm}^{-1}$  mode between  $x=7$  and  $x=6.3$  and proposed that intensity changes in the vicinity of 600  $\text{cm}^{-1}$  as a function of oxygen content were due to disorder activation of the Cu(1)-O(1) chain mode, forbidden in the ordered  $x=7$  material. Blumenroder *et al.*<sup>38</sup> reported Raman spectra for  $x=6.2$  and  $x=6.8$ . They observed a mode at 644  $\text{cm}^{-1}$  whose intensity depended on oxygen content and they assigned it also to the normally forbidden vibrations

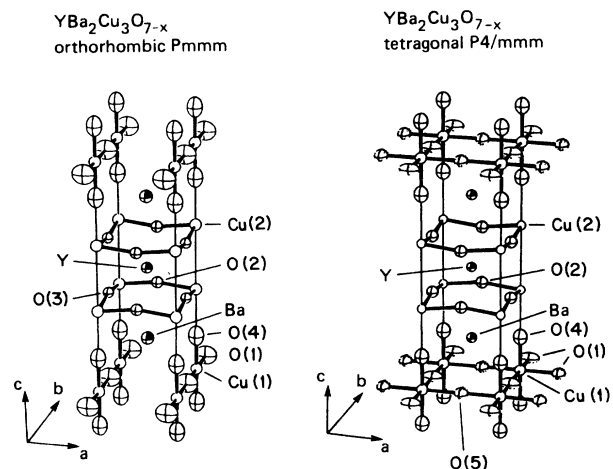


FIG. 1. (a) Crystal structure of the orthorhombic phase of  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , (b) the tetragonal structure of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  (from Ref. 20).

of the Cu(1)-O(1) chains. On the other hand, we assign this, and the mode at  $585\text{ cm}^{-1}$ , to BaCuO<sub>2</sub> impurities and discuss them further below. Bhadra *et al.*<sup>43</sup> measured the Raman spectra of three samples of Y 1:2:3 of different but unknown oxygen content. They observed a qualitative shift to low frequency of the  $502\text{ cm}^{-1}$  mode, as oxygen is removed and proposed that the  $340\text{ cm}^{-1}$  mode, which they only observed at low oxygen content, is normally forbidden for  $x=7$  but is rendered Raman active by oxygen vacancies. They further proposed that its observation in nominally  $x=7$  samples is due to inhomogeneity of the stoichiometry. However, we observe the mode in all samples, and at all oxygen contents, and find a substantial increase in intensity as oxygen is removed. Thomsen *et al.*<sup>42</sup> studied the Raman shift of the four strongest modes as a function of oxygen content. Our results agree with the overall behavior observed there but the dependence on oxygen content is different. Recent work by Kirillov *et al.*<sup>45</sup> proposes that the  $585$  and  $640\text{ cm}^{-1}$  modes are intrinsic to the Y 1:2:3 structure, in disagreement with our assignment. In addition they find a dependence of several modes on oxygen content which differs from those reported here.

In our study we have made measurements of the frequency and intensity of four Raman modes at  $151$ ,  $340$ ,  $435$ , and  $502\text{ cm}^{-1}$  for more than 10 different oxygen stoichiometries using material that was characterized by chemical, x-ray, and magnetic measurements.

## II. EXPERIMENT

The preparation of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> from Y<sub>2</sub>O<sub>3</sub>, BaCO<sub>3</sub>, and CuO followed the procedure described recently.<sup>47</sup> Finely ground starting materials were reacted in flowing oxygen for 12 h, pressed into pellets, and sintered for a further 12 h in oxygen at  $950^\circ\text{C}$ . Variation in the oxygen content was effected by equilibrating a pellet of material of the  $x=7$  compound, in a high-purity argon atmosphere at various temperatures. Oxygen content was determined by a gravimetric method in which batches of 10 g of Y 1:2:3 were heated in argon at a given temperature until the resulting weight due to oxygen loss remained constant.<sup>25</sup> This required at least 24 h, and the standard processing time was chosen to be 36 h. Following this anneal, samples were cooled in argon to room temperature in 8 h. The weight loss provided a gravimetric determination of oxygen content (see Fig. 2). Each run was checked by reheating in oxygen at  $500^\circ\text{C}$  to produce the weight gain appropriate to the  $x=7$  compound. Two other methods of oxygen determination were used, and calibrated against the gravimetric results: thermogravimetric analysis and iodometric titration (Fig. 2). Agreement between the different techniques of  $\leq 0.05$  oxygen equivalents could be obtained.

Raman scattering measurements were made on pressed pellets of finely ground ( $\sim 10\ \mu$ ) material that had been annealed in argon, as described above, to produce material with different oxygen content. The pellets were stored in dry N<sub>2</sub> or air. Raman measurements were made at room temperature with samples in a helium atmosphere to eliminate the rotational Raman spectrum of air. Approx-

mately 100 mW of  $514.5\text{ nm}$  Ar<sup>+</sup> laser light was focused with a cylindrical lens to a line ca.  $6\times 0.1\text{ mm}^2$  on the sample surface producing a power density of  $\sim 15\text{ W/cm}^2$ . Scattered light was collected at  $90^\circ$  and spectrally analyzed with a 1-m J-Y double monochromator using a spectral resolution of  $4\text{ cm}^{-1}$ , and single-channel detection. Data acquisition time per run was approximately 16 h. Spectra measured on samples after three months of storage showed no significant changes due, for example, to decomposition, chemical reaction with atmospheric moisture or loss of oxygen by out diffusion.

## III. RESULTS

Before discussing the detailed dependence of the Raman spectrum on oxygen content, we will examine the two limiting cases corresponding to the structures shown in Fig. 1, i.e., orthorhombic *Pmmm* for  $x=7.0$ , and tetragonal *P4/mmm* for  $x=6.0$ . Figure 3 shows the Raman spectra for these between  $25$  and  $800\text{ cm}^{-1}$  at room temperature. We believe that these spectra are essentially free of contributions from impurity phases. In particular, the BaCuO<sub>2</sub> peaks at  $585$  and  $640\text{ cm}^{-1}$  and the strongest Y<sub>2</sub>BaCuO<sub>5</sub> peaks at  $318$ ,  $390$ , and  $605\text{ cm}^{-1}$  are absent. There is considerable confusion in the literature caused by the occurrence of impurity modes, particularly those at  $585$  and  $640\text{ cm}^{-1}$ . These have been assigned to various intrinsic Cu-O stretching modes<sup>19,45</sup> or to disorder induced Cu(1)-O(1),<sup>30,38</sup> or Cu(2)-O(2),O(3) vibrations.<sup>31</sup> This situation arises, in part, from the variation in the amount of BaCuO<sub>2</sub> present under different oxygenation conditions. When BaCuO<sub>2</sub> is mixed with Y 1:2:3, it is transformed by heating in Ar to give different compounds, as yet unidentified, but probably including nonstoichiometric BaCuO<sub>x</sub>. The result, as shown in Fig. 4, is that under the argon annealing treatment that changes the oxygen content of Y 1:2:3, the absolute intensity of the  $640\text{-cm}^{-1}$  mode and its intensity relative to the  $585\text{-cm}^{-1}$  mode of BaCuO<sub>2</sub> change markedly. In addition small shifts in the frequency of the  $640\text{-cm}^{-1}$  mode are ob-

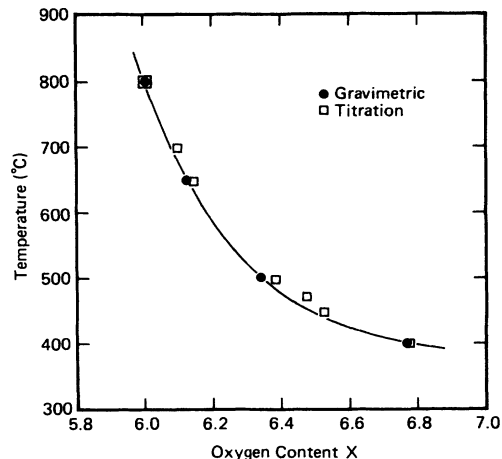


FIG. 2. Dependence of the oxygen content of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> on argon annealing temperature.

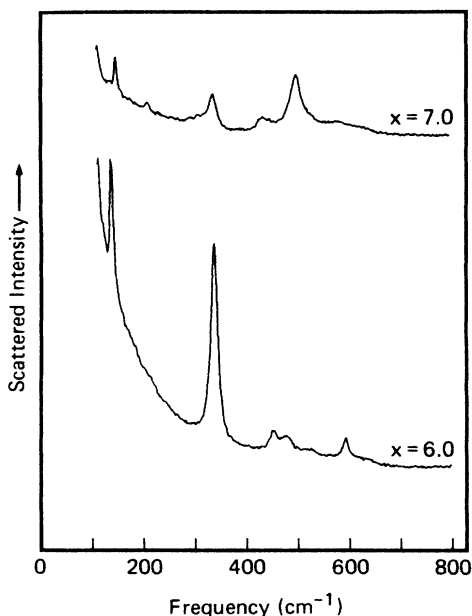


FIG. 3. (a) Raman spectrum of a polycrystalline pellet of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at room temperature, (b) the same for tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$ .

served. Thus, the reduction in intensity or disappearance of the  $640\text{-cm}^{-1}$  mode with sample reduction should *not* be interpreted as evidence for this mode being intrinsic to Y 1:2:3.

The main features of the  $x=7$  spectrum are four lines at 151, 340, 435, and  $502\text{ cm}^{-1}$ . In addition, there are weaker lines at 115,<sup>34</sup> 233, and  $325\text{ cm}^{-1}$ , and broad weak structure between 550 and  $650\text{ cm}^{-1}$ . This is distinct from the  $\text{BaCuO}_2$  peaks noted above. In the tetragonal  $x=6$  compound, an additional mode appears at  $596\text{ cm}^{-1}$  and substantial changes in the frequency of other modes can be seen. In addition large intensity changes occur which are particularly striking for the 340- and  $500\text{-cm}^{-1}$  modes.

#### A. Mode assignments

In the orthorhombic  $Pmmm$  structure, there are 15 Raman active modes, five each of  $A_g$ ,  $B_{2g}$ , and  $B_{3g}$  symmetry. The five lines at 115, 151, 340, 435, and  $502\text{ cm}^{-1}$  have been assigned to  $A_g$  modes from polarized single-crystal data.<sup>33,40,44</sup> These involve atomic displacements along the  $c$  axis. The normal mode atomic displacements corresponding to the Raman and ir active modes have been given by Bates and Eldridge.<sup>48</sup> They also carried out a normal coordinate calculation of the mode frequencies using a modified Wilson GF matrix method with empirical force constants obtained from other related materials. A lattice dynamical calculation with potentials adjusted from related compounds has also been carried out.<sup>44</sup> An assignment which combines these results with those of the single-crystal Raman scattering<sup>33,40,44</sup> is as follows:  $115\text{ cm}^{-1}$  (Ba  $c$ -axis motion);  $151\text{ cm}^{-1}$  [Cu(2)  $c$ -axis motion];  $340\text{ cm}^{-1}$  [Cu(2)-O(2,3)] bend with O(2), O(3)

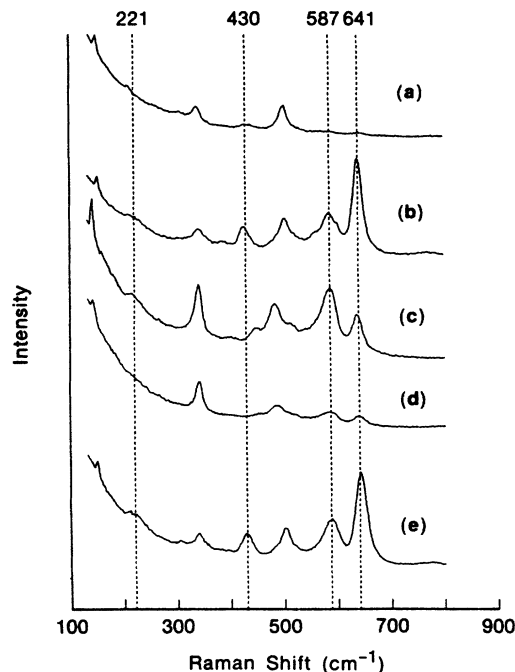


FIG. 4. Raman spectra showing the role of  $\text{BaCuO}_2$  impurities in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (Y 1:2:3) and the effect of Ar annealing. (a) Y 1:2:3; (b) Y 1:2:3 + 10%  $\text{BaCuO}_2$ ; (c) sample *b* annealed in argon for 24 h at  $500^\circ\text{C}$ ; (d) sample *b* annealed in argon for 24 h at  $800^\circ\text{C}$ ; (e) sample *d* reoxygenated by heating for 24 h in an oxygen atmosphere. The spectrum of *b* is restored.

out of phase;  $437\text{ cm}^{-1}$  [Cu(2)-O(2,3)] bend with O(2) and O(3) in phase, and  $502\text{ cm}^{-1}$  [Cu(1)-O(4) stretch]. Alternative assignments have been given.<sup>30,31,37,38</sup> The  $233\text{ cm}^{-1}$  mode may be defect induced.<sup>44</sup>

The assignment of the  $B_{2g}$  and  $B_{3g}$  modes is more difficult because they are weaker and very few are identified. The  $B_{2g}$  and  $B_{3g}$  modes become degenerate  $E_g$  modes in the tetragonal phase. Since  $a \approx b$ , the separation of these pairs of  $B_{2g}$  and  $B_{3g}$  modes in the orthorhombic phase is not expected to be large. The largest difference will be in the  $B_{2g}$  and  $B_{3g}$  modes involving O(4) motion along  $a$  and  $b$  since this corresponds to motion in and perpendicular to the plane of the Cu(1)-O(4) ribbons. We might, therefore, expect to see four nearly degenerate pairs and one more widely separated doublet for these nontotally symmetric modes. Assignments based on the calculated frequencies of Bates and Eldridge,<sup>48</sup> and Liu *et al.*<sup>44</sup> and the observations of Kourouklis *et al.*<sup>39</sup> are  $325\text{ cm}^{-1}$  [ $B_{2g}$  Cu(1)-O(4)] bend along  $a$  axis],  $550\text{-}650\text{ cm}^{-1}$  region [2 pairs of  $B_{2g}$ ,  $B_{3g}$  Cu(2)-O(2), O(3) in plane bend]. The  $B_{3g}$  Cu(1)-O(4) bend along the  $b$  axis is probably in the vicinity of the  $440\text{-cm}^{-1}$  and  $503\text{-cm}^{-1}$   $A_g$  modes, which mask it. The two  $B_{2g}$ ,  $B_{3g}$  pairs of lower frequency modes involving Ba and O(2), O(3) motion are not expected to be below  $160\text{ cm}^{-1}$  (Ref. 44).

#### B. Dependence on oxygen content

Raman spectra taken on a number of samples with different oxygen stoichiometry between  $x=7$  and  $x=6$

are shown in Fig. 5. We concentrate attention on the four strongest modes with frequencies of 151, 340, 435, and  $502\text{ cm}^{-1}$  at  $x=7$ . These have  $A_g$  symmetry in the orthorhombic phase and since  $A_g$  modes do not arise from the doubly degenerate  $E_g$  modes of the tetragonal phase, none of the frequency shifts can be attributed to splitting arising from the reduction in symmetry which occurs for  $x$  less than 6.5.

At  $x=7$ , the oxygen atoms are ordered, with O(1) sites full and O(5) sites empty. As oxygen is removed, the dominant process is vacancy formation on O(1).<sup>18,20</sup> These vacancies, or the chains of Cu(1)-O(1) might be expected to show ordering in the orthorhombic phase<sup>22,23</sup> particularly at "simple" values of  $x$  such as 6.5, where every second oxygen is missing, 6.66 (one in three missing) or 6.33 (one in three present) and so on. For other values of  $x$ , and especially when the system becomes tetragonal for  $x < 6.5$ , disorder in the O(1) and O(5) position is most likely.

As oxygen is removed, the overall dimensions of the unit cell change, reflecting the changes in bond lengths and packing.<sup>49</sup> At  $x=7$ ,  $a=3.824(2)\text{ \AA}$ ,  $b=3.888(2)\text{ \AA}$ , and  $c=11.678(7)\text{ \AA}$ .<sup>21</sup> On going to  $x=6$ , the  $c$  axis lengthens by  $0.18\text{ \AA}$  and  $(b-a)$  changes from  $0.064\text{ \AA}$  to zero. The dependence of the individual bond lengths on oxygen content has been determined by Johnston *et al.*<sup>14</sup> Other structural features to note are the short O(4)-O(1) distance of  $2.68\text{ \AA}$  and the large "thermal" amplitude of the O(4) atom.

Figures 6 and 7 show the frequency shifts of the 151-, 340-, 435-, and  $502\text{-cm}^{-1}$  modes as a function of oxygen content  $x$ . The 340 and  $435\text{ cm}^{-1}$  modes which are assigned to Cu(2)-O(2,3) out of plane bending, move to higher frequencies as oxygen is removed (the former by a very small amount), while the Cu(1)-O(4) oxygen stretch

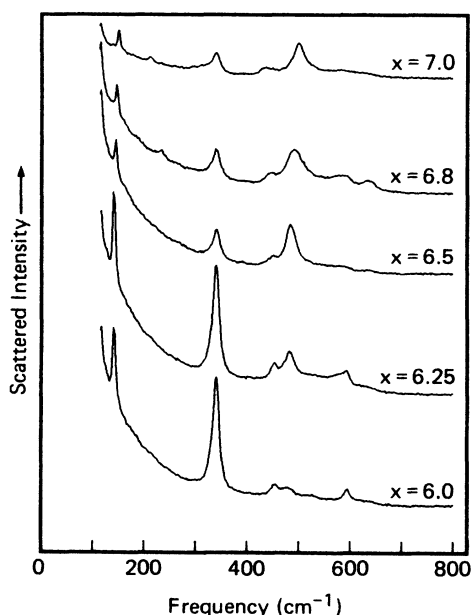


FIG. 5. Raman spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  for several values of  $x$ , measured at room temperature.

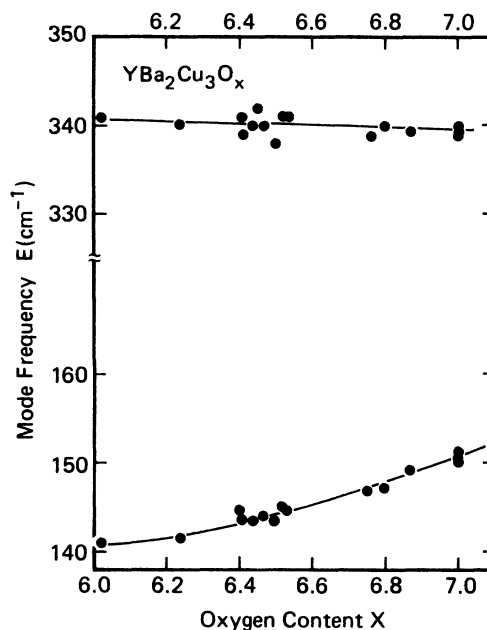


FIG. 6. Dependence of the  $k=0$  mode frequency of oxygen content  $x$  in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  for the  $151\text{-}$  and  $340\text{-cm}^{-1}$  modes.

at  $502\text{ cm}^{-1}$  and the Cu(2) mode at  $151\text{ cm}^{-1}$  decrease in frequency upon oxygen removal. These data are similar to those reported by Thomsen *et al.*,<sup>42</sup> but the functional dependence on oxygen content clearly differs. This is particularly true for the  $435\text{-cm}^{-1}$  mode which they find to

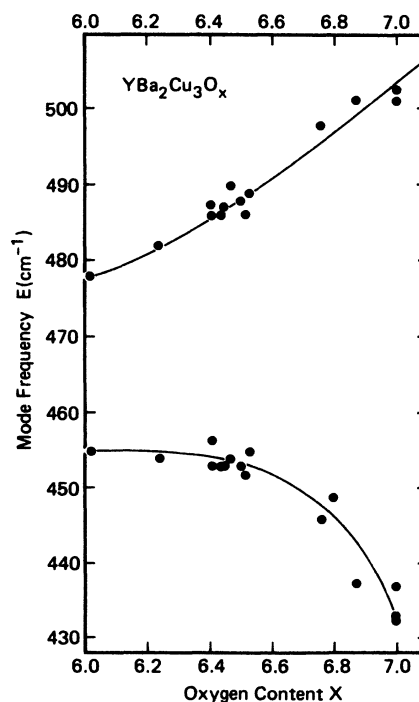


FIG. 7. Dependence of the  $k=0$  mode frequency as a function of oxygen content  $x$  in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  for the  $435\text{-}$  and  $502\text{-cm}^{-1}$  modes.

have a linear shift with  $x$ . On the other hand, Kirillov *et al.*<sup>45</sup> finds discontinuities in the shifts of the 502- and 435-cm<sup>-1</sup> modes at  $x=6.4$ . The source of these discrepancies is not immediately clear, but may be related to the homogeneity of the oxygen content and to the accuracy of its determination.

A detailed understanding of the frequency shifts with  $x$  involves a knowledge of electron-phonon interactions and ion-ion potentials, which are not yet available. However, some insights can be obtained by considering bond-length changes associated with oxygen removal. One of the most interesting modes is that at 502 cm<sup>-1</sup> assigned to Cu(1)-O(4) stretch; [recall that Cu(1)-O(1) is not Raman active]. When oxygen is removed, the  $c$  axis lengthens as the structure becomes more open. Because of the short O(1) to O(4) distance, it might be expected that the 502-cm<sup>-1</sup> mode would be very sensitive to the removal of O(1) and, indeed, it does show a rather strong dependence on  $x$  (Fig. 6). As noted by Kourouklis *et al.*,<sup>39</sup> the Cu(1)-O(4) bond *decreases* in length as oxygen is removed yet the mode frequency *drops*. In the rare-earth analogs  $R\text{Ba}_2\text{Cu}_3\text{O}_7$ , increasing the radius of the rare earth, also increases the  $c$  axis and results in shorter Cu(1)-O(4) bonds. In that case, however, the 502-cm<sup>-1</sup> mode *increases* in frequency as the Cu(1)-O(4) bond decreases<sup>50</sup>—a more intuitive result. The anomalous shift of the 502-cm<sup>-1</sup> mode has been ascribed<sup>39</sup> to changes in the force constant associated with changes in the Cu valence as oxygen is added to, or removed from, the system. More generally, it has been proposed by Shafer, Penney, and Olson<sup>51</sup> that in the metallic and superconducting phases of these oxide materials, the covalent nature of the copper-oxygen bonding makes it more correct to think of  $(\text{Cu-O})^+$  complexes sharing the electron deficiency. These holes are believed to be the major charge carriers, since there is a good correlation between  $T_c$  and the hole concentration.<sup>51,52</sup>

As oxygen is removed from  $x=7$  to  $x=6.5$ , we find that there is a rapid increase in the Cu(2)-O(2), O(3) bend at 435 cm<sup>-1</sup> (and a smaller but noticeable increase in the frequency of the 340-cm<sup>-1</sup> mode). Below  $x=6.5$  on the other hand, where the material is semiconducting, the mode frequency is relative constant. This suggests that electronic screening of the force constants for these modes is important in the highly conducting regime.<sup>42</sup> There is evidence that the conductivity occurs mainly in the Cu(2) planes,<sup>52</sup> and the behavior of the 435-cm<sup>-1</sup> mode provides support for this. It is not clear, however, why the related 340-cm<sup>-1</sup> mode in which the O(2) and O(3) atoms vibrate out of phase, shows such a small frequency shift. Electronic screening also appears to be involved in the anomalous temperature dependence of the 340-cm<sup>-1</sup> mode which softens below the superconducting transition temperature.<sup>29,35,46</sup>

#### IV. CONCLUSION

We have used Raman spectroscopy to study the effect of oxygen stoichiometry on the phonon spectrum of  $\text{YBa}_2\text{Cu}_3\text{O}_x$ . The dependence of the frequency of the four strongest  $A_g$  modes on  $x$  was measured for  $6 \leq x \leq 7$ . We find that the Raman spectrum can provide a sensitive non-destructive method of determining oxygen stoichiometry, once it has been calibrated by chemical assays. Mode frequency shifts provide evidence for changes in the nature of the Cu(1)-O(4) bond as oxygen is removed and for screening by conduction electrons in the Cu(2)-O(2), O(3) planes. In many cases the results are significantly different from those of other workers. In part this may arise from procedures for oxygen determination. It is pointed out that care must be taken to identify purity modes due to other oxide phases.

<sup>1</sup>M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.* **58**, 908 (1987).

<sup>2</sup>J. M. Tarascon, L. H. Greene, W. R. McKinnon, and G. W. Hull, *Phys. Rev. B* **35**, 7115 (1987).

<sup>3</sup>H. Takagi, S. Uchida, K. Kishio, K. Kitazawa, K. Fueki, and S. Tanaka, *Jpn. J. Appl. Phys.* **26**, L320 (1987).

<sup>4</sup>R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remicka, E. A. Rietman, S. Zahurak, and G. P. Espinosa, *Phys. Rev. Lett.* **58**, 1676 (1987).

<sup>5</sup>P. M. Grant, R. B. Beyers, E. M. Engler, G. Lim, S. S. P. Parkin, M. L. Ramirez, V. Y. Lee, A. Nazzari, J. E. Vazquez, and R. J. Savoy, *Phys. Rev. B* **35**, 7242 (1987).

<sup>6</sup>J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, *Phys. Rev. B* **36**, 226 (1987).

<sup>7</sup>P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, and D. W. Murphy, *Mater. Res. Bull.* **22**, 995 (1987).

<sup>8</sup>H. Nozaki, Y. Ishizawa, O. Fukunaga, and H. Wada, *Jpn. J. Appl. Phys.* **26**, L1180 (1987).

<sup>9</sup>P. Monod, M. Ribault, F. D'Yvoire, J. Jegoudez, G. Collin, and A. Revcolevschi, *J. Phys. (Paris)* **48**, 1369 (1987).

<sup>10</sup>K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, and K. Fueki, *Jpn. J. Appl. Phys.* **26**, L1228 (1987).

<sup>11</sup>E. Takayama-Muromachi, Y. Uchida, M. Ishii, T. Tanaka, and K. Kato, *Jpn. J. Appl. Phys.* **26**, L1156 (1987).

<sup>12</sup>D. E. Morris, U. M. Scheven, L. C. Bourne, M. L. Cohen, M. F. Crommie, and A. Zettl, in *Novel Superconductivity*, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987).

<sup>13</sup>R. J. Cava, B. L. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, *Nature* **329**, 423 (1987).

<sup>14</sup>D. C. Johnston, A. J. Jacobsen, J. M. Newsam, J. T. Lewandowski, D. P. Goshorn, D. Xie, and W. B. Yelon, in *Chemistry of High Temperature Superconductors*, ACS Symposium Series, No. 351, edited by D. L. Nelson, M. S. Whittingham, and T. F. George (American Chemical Society, Washington, DC, 1987).

<sup>15</sup>N. Nishida, H. Miyatake, D. Shimada, S. Okuma, M. Ishikawa, T. Takabatake, Y. Nakazawa, Y. Kuno, R. Keitel,

- J. H. Brewer, T. M. Riseman, D. L. Williams, Y. Watanabe, T. Yamazaki, K. Nishiyama, K. Nagamine, E. J. Ansaldo, and E. Torikai, *Jpn. J. Appl. Phys.* **26**, L1856 (1987).
- <sup>16</sup>J. M. Tranquada, D. E. Cox, W. Kunmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S. K. Sinha, M. S. Alvarez, A. J. Jacobsen, and D. C. Johnston, *Phys. Rev. Lett.* **60**, 156 (1987).
- <sup>17</sup>Z. Gabelica, E. C. Derouane, J. P. Vigneron, Ph. Lambin, M. Renier, A. A. Lucas, G. Deconninck, F. Bodart, and G. Demortier, *Solid State Commun.* **64**, 1221 (1987).
- <sup>18</sup>J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, *Phys. Rev. B* **36**, 3608 (1987).
- <sup>19</sup>D. W. Murphy, S. A. Sunshine, P. K. Gallagher, H. M. O'Bryan, R. J. Cava, B. Batlogg, R. B. van Dover, L. F. Schneemeyer, and S. M. Zahurak, in Ref. 14, Chap. 18, p. 181.
- <sup>20</sup>J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas, *Phys. Rev. B* **36**, 5731 (1987).
- <sup>21</sup>M. Francois, E. Walker, J.-L. Jorda, K. Yvon, and P. Fischer, *Solid State Commun.* **63**, 1149 (1987).
- <sup>22</sup>M. A. Alario-Franco, C. Chailout, J. J. Capponi, and J. Chenavas, *Mater. Res. Bull.* (to be published).
- <sup>23</sup>C. Chailout, M. A. Alario-Franco, J. J. Capponi, J. Chenavas, J. L. Hodeau, and M. Marezio, *Phys. Rev. B* **36**, 7118 (1987).
- <sup>24</sup>R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, *Phys. Rev. B* **36**, 5719 (1987).
- <sup>25</sup>E. M. Engler, V. Y. Lee, S. S. P. Parkin, R. Jacowitz, G. Lim, A. I. Nazzal, K. Roche, M. Ramirez, J. Vazquez, E. Hadziioannou, and P. Grant (unpublished).
- <sup>26</sup>R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.* **58**, 2340 (1987).
- <sup>27</sup>H. J. Rosen, E. M. Engler, T. C. Strand, V. Y. Lee, and D. Bethune, *Phys. Rev. B* **36**, 726 (1987).
- <sup>28</sup>M. Stavola, D. M. Krol, W. Weber, S. A. Sunshine, A. Jayaraman, G. A. Kourouklis, R. J. Cava, and E. A. Rietman, *Phys. Rev. B* **36**, 850 (1987).
- <sup>29</sup>R. M. Macfarlane, H. J. Rosen, and H. Seki, *Solid State Commun.* **63**, 831 (1987).
- <sup>30</sup>Z. Iqbal, S. W. Steinhauser, A. Bose, N. Cipollini, and H. Eckhardt, *Phys. Rev. B* **36**, 2283 (1987).
- <sup>31</sup>R. Liu, R. Merlin, M. Cardona, Hj. Mattausch, W. Bauhofer, and A. Simon, *Solid State Commun.* **63**, 839 (1987).
- <sup>32</sup>G. Burns, F. H. Dacol, P. Freitas, T. S. Plaskett, and W. Konig, *Solid State Commun.* **64**, 471 (1987).
- <sup>33</sup>A. Yamanaka, F. Minami, K. Watanabe, K. Inoue, S. Takekawa, and N. Iyi, *Jpn. J. Appl. Phys.* **26**, L1404 (1987).
- <sup>34</sup>Y. Morioka, M. Kikuchi, and Y. Syono, *Jpn. J. Appl. Phys.* **26**, L1499 (1987).
- <sup>35</sup>A. Wittlin, R. Liu, M. Cardona, L. Genzel, W. Konig, W. Bauhofer, Hj. Mattausch, and A. Simon, *Solid State Commun.* **64**, 477 (1987).
- <sup>36</sup>J. Chrzanoski, S. Gygax, J. C. Irwin, and W. N. Hardy, *Solid State Commun.* **65**, 139 (1987).
- <sup>37</sup>M. Cardona, L. Genzel, R. Liu, A. Wittlin, Hj. Mattausch, F. Garcia-Alvarado, and E. Garcia-Gonzalez, *Solid State Commun.* **64**, 727 (1987).
- <sup>38</sup>S. Blumenroder, E. Zirngiebl, H. Schmidt, G. Guntherodt, and H. Brenten, *Solid State Commun.* **64**, 1229 (1987).
- <sup>39</sup>G. A. Kourouklis, A. Jayaraman, B. Batlogg, R. J. Cava, M. Stavola, D. M. Krol, E. A. Rietman, and L. F. Schneemeyer, *Phys. Rev. B* **36**, 8320 (1987).
- <sup>40</sup>D. M. Krol, M. Stavola, W. Weber, L. F. Schneemeyer, J. V. Waszczak, S. M. Zahurak, and S. G. Kosinski, *Phys. Rev. B* **36**, 8325 (1987).
- <sup>41</sup>P. B. Kirby, M. R. Harrison, W. G. Freeman, I. Samuel, and M. J. Haines, *Phys. Rev. B* **36**, 8315 (1987).
- <sup>42</sup>C. Thomsen, R. Liu, M. Bauer, A. Wittlin, L. Genzel, M. Cardona, E. Schonherr, W. Bauhofer, and W. Konig, *Solid State Commun.* **65**, 55 (1988).
- <sup>43</sup>R. Bhadra, T. O. Brun, M. A. Beno, B. Dabrowski, D. G. Hinks, J. Z. Liu, J. O. Jorgensen, L. J. Nowicki, A. P. Paulikas, I. K. Schuller, C. U. Segre, L. Soderholm, B. Veal, H. H. Wang, J. M. Williams, K. Zhang, and M. Grimsditch, *Phys. Rev. B* **37**, 5142 (1988).
- <sup>44</sup>R. Liu, C. Thomsen, W. Kress, M. Cardona, B. Gegenheimer, F. W. de Wette, J. Prade, A. Kulkarni, and U. Schröder (unpublished).
- <sup>45</sup>D. Kirillov, J. P. Collman, J. T. McDevitt, G. T. Yee, M. J. Holcomb, and I. Bozovic (unpublished).
- <sup>46</sup>R. Feile, U. Schmitt, P. Leiderer, J. Schubert, and U. Poppe (unpublished).
- <sup>47</sup>E. M. Engler, V. Y. Lee, A. I. Nazzal, R. B. Beyers, G. Lim, P. M. Grant, S. S. P. Parkin, M. L. Ramirez, J. E. Vazquez, and R. J. Savoy, *J. Am. Chem. Soc.* **109**, 2848 (1987).
- <sup>48</sup>F. E. Bates and J. E. Eldgridge, *Solid State Commun.* **64**, 1435 (1987).
- <sup>49</sup>A. Ono, *Jpn. J. Appl. Phys.* **26**, L1223 (1987).
- <sup>50</sup>H. J. Rosen, R. M. Macfarlane, E. Engler, R. D. Jacowitz, and V. Y. Lee, *Phys. Rev. B* (to be published).
- <sup>51</sup>M. W. Shafer, T. Penney, and B. L. Olson, *Phys. Rev. B* **36**, 4047 (1987).
- <sup>52</sup>Z. Z. Wang, J. Clayhold, N. P. Ong, J. M. Tarascon, L. H. Greene, W. R. McKinnon, and G. W. Hull, *Phys. Rev. B* **36**, 7222 (1987).