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Polarized Raman spectra of Y_2BaCuO_5: Normal-mode assignment from substitutions for Y and Ba

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Using the micro-Raman-spectroscopy technique, three types of phonon Raman spectra of R_2BaCuO_5 ($R = Y$, Ho, Gd) and $Y_2Ba_{0.5}Sr_{0.5}CuO_5$ corresponding to the main crystallographic directions were obtained in the range 100–700 cm^{-1} in both parallel and crossed polarizations. Comparing the line shifts upon cation substitution, the polarization properties of the three types of spectra, and taking into account the particular site environments, all A_g lines were assigned to definite atomic vibrations.

INTRODUCTION

The Y_2BaCuO_5 (green) phase often occurs in the Y-Ba-Cu-O superconducting ceramics. Its crystal structure has been determined as an orthorhombic one (space group *Pbnm*) with lattice parameters $a = 7.1$ Å, $b = 12.2$ Å, and $c = 5.6$ Å.[1,2] The unit cell contains four formula units, the atom sites and interatomic distances being well established.[2–4] The Cu atoms are surrounded by five oxygen atoms forming twisted quadratic pyramids, the Y atoms occupy two different [Y(1) and Y(2)] sites in an environment of seven oxygen atoms, the Ba atoms sit in a complex eleven-oxygen-atom environment. The oxygen atoms occupy three different sites [O(1), O(2), and O(3)], and two thirds of them form two types of chains extended along the **c** axis. The YO_7 trigonal prisms form distorted chains parallel to the **b** axis.

The strong ir and nonpolarized Raman spectra of Y_2BaCuO_5, with large number of lines have been reported by several groups.[5–8] Using a molecular-unit structural model and comparing the CuO_5 pyramids in Y_2BaCuO_5 and $YBa_2Cu_3O_{7-x}$, Popovic *et al.*[8] made an attempt to assign some of the phonon modes of Y_2BaCuO_5. Raman spectra of substituted R_2BaCuO_5 ($R =$ Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, and Lu) have been reported by Loo, Burns, and Xidis.[9] A more precise assignment of the Raman lines to definite atomic vibrations, however, was not done in that study.

In this work we present the polarized Raman spectra of R_2BaCuO_5 ($R =$ Y,Ho,Gd) and $Y_2Ba_{0.5}Sr_{0.5}CuO_5$ for incident polarization along definite crystallographic directions. The substitutions of Ho and Gd for Y and Sr for Ba allowed us to analyze the modes related to heavier cations (Y,Ba,Cu) and to the oxygen modes. In the latter case the different environments of the O(1), O(2), and O(3) sites were taken into account.

EXPERIMENT

The samples were prepared by a standard solid-state reaction technique. The starting powders (Y_2O_3, Ho_2O_3, Gd_2O_3, $BaCO_3$, $SrCO_3$, and CuO) were mixed in appropriate ratios and calcinated in air at 950 °C for 20 h. The material thus obtained was finely ground and pressed into 1-g pellets under 100-atm pressure. The sintering procedures were made in air at different temperatures between 850 and 1050 °C for 20 h, and then the samples were quenched to room temperature. The purity and stoichiometry of the samples were tested by x-ray diffraction and scanning electron microscopy. Similar to some earlier reports,[10,11] our attempts to obtain Y_2SrCuO_5 were unsuccessful. In the samples with the nominal composition [Y]:[Sr]:[Cu] = 2:1:1 only the distinct phases Y_2O_3, Y_2SrO_4, and $(Sr_{1-x}Y_x)_{14}Cu_{24}O_{41}$ were found. The samples with $Y_2Ba_{0.5}Sr_{0.5}CuO_5$ stoichiometry, however, were practically free of impurity phases. Depending on the sintering temperature the average size of the microcrystals on the polished surface varied between 3 and 30 μm. Most of the grains were of irregular shape.

The Raman spectra were collected at room temperature using a triple-multichannel spectrometer (Microdil 28) in conjunction with an optical microscope. An objective of 100× magnification ensured a 1–2-μm laser spot. The 488-nm Ar^+ laser line was used for excitation in the backscattering geometry.

RAMAN SPECTRA ANALYSIS

Because of the orthorhombic structure of Y_2BaCuO_5, different Raman spectra are expected for the parallel incident and the scattered polarizations that vary with respect to the crystallographic axes. To determine the crystallographic orientation, numerous spectra in the parallel-scattering configuration were collected for a polarization along or perpendicular to the apparent straight edges of the microcrystals. In most cases one of the three types of spectra assigned as type I (Fig. 1), type II (Fig. 2), and type III (Fig. 3) were obtained. In the type-I spectra the 604-cm^{-1} line (all frequencies are for Y_2BaCuO_5) is the strongest one, whereas the line at 318 cm^{-1} is weak. In the spectra of type II both the 604- and the 318-cm^{-1} lines are strong. In the spectra of type III the 604-cm^{-1} line is relatively weak, but the one at 318 cm^{-1} is strong. There are lines that are observed only in some types of spectra, e.g., the 560-cm^{-1} line (in types II and III) and the 375-cm^{-1} line (in type III). The suggestion

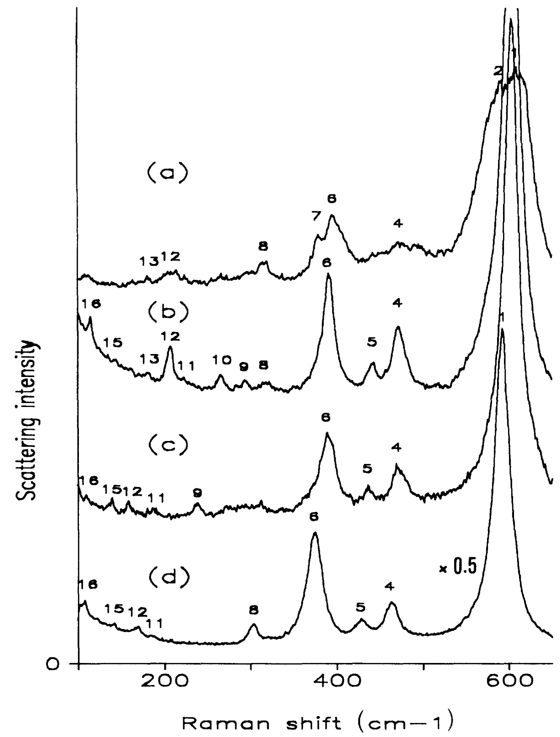

FIG. 1. Type-I spectra in parallel polarization: (a) $Y_2Ba_{0.5}Sr_{0.5}CuO_5$, (b) Y_2BaCuO_5, (c) Ho_2BaCuO_5, and (d) Gd_2BaCuO_5. The line numbers correspond to those in Table II.

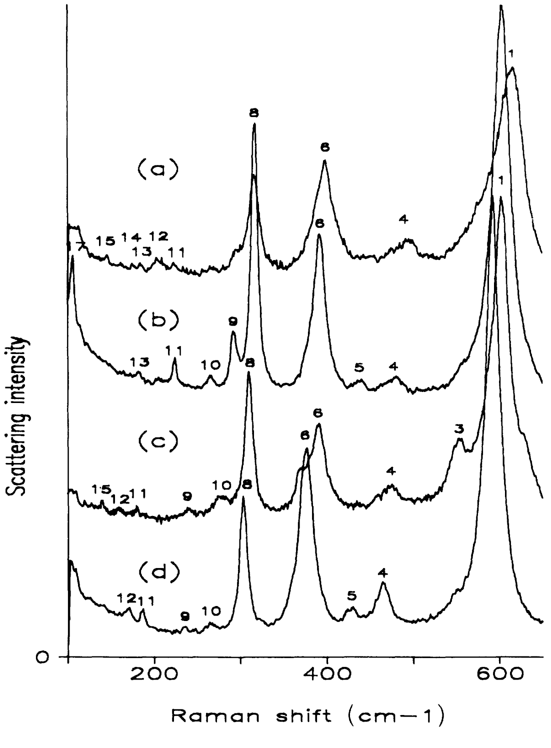

FIG. 2. Type-II spectra in parallel polarization: (a) $Y_2Ba_{0.5}Sr_{0.5}CuO_5$, (b) Y_2BaCuO_5, (c) Ho_2BaCuO_5, and (d) Gd_2BaCuO_5. The line numbers correspond to those in Table II.

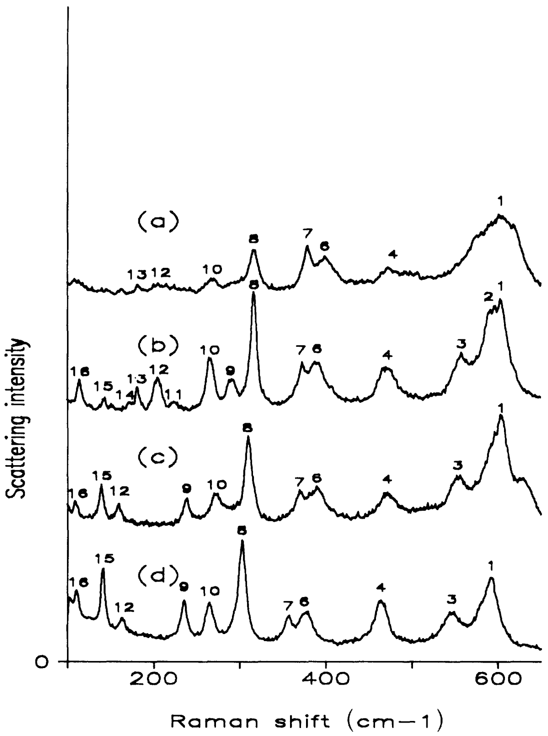

FIG. 3. Type-III spectra in parallel polarization: (a) $Y_2Ba_{0.5}Sr_{0.5}CuO_5$, (b) Y_2BaCuO_5, (c) Ho_2BaCuO_5, and (d) Gd_2BaCuO_5. The line numbers correspond to those in Table II.

that each of these three types of spectrum corresponds to a polarization along a definite crystallographic axis (x, y, or z along the **a**, **b**, and **c** vectors, respectively) is supported by the fact that a number of Raman lines have exact polarizations: i.e., they are of zero or of negligible intensity in some types of spectra.

Further analysis is based on the following assumptions.

(i) Each normal mode is dominated by vibrations of mainly one type of atom. [This is presumed by analogy with some high-temperature superconductivity (HTS) compounds. Checking its validity would require isotope studies and/or actual lattice-dynamics calculations.]

(ii) The lines corresponding to the same atoms in different materials are of nearly the same intensity and exhibit the same polarization properties.

(iii) The lines of equal or very close frequencies in parallel and crossed polarizations are due to vibrations of the same atom.

(iv) As a rule, a Raman line has its strongest intensity for incident polarization along the direction of atomic vibrations.

The factor-group analysis of the Y_2BaCuO_5 structure (see Table I) predicts in total 54 $(16A_g+16B_{1g}+11B_{2g}+11B_{3g})$ Raman-active phonons.[8] Eight of the A_g modes are related to the oxygen and the rest of the A_g modes to heavier Y, Ba, and Cu. It is logical to assume that the eight high-frequency phonons, namely, those above 300 cm^{-1} (No. 1 to No. 8) correspond to oxygen vibrations, whereas the other lines ($\omega_{ph}<300$ cm^{-1}) are related to Cu, Ba, and Y(Ho, Gd). Table II summarizes the frequencies of all observed phonon lines and their polarization properties.

The substitutions of Gd and Ho for Y and of Sr for Ba would not affect the Cu vibrations. One finds that the position of the 144 cm^{-1} (No. 15) line, which is strongest in the type III spectra, remains unchanged for all samples. Comparing the CuO_5 pyramid with the one in 1:2:3 HTS compounds, we assign this mode to Cu-O(3) stretching vibration. Following this analogy, the other A_g mode of Cu [vibrations within the O(1)-O(2) plane] must be over 200 cm^{-1}. The presence of four lines (No. 9 to No. 12) of $\mathrm{Y_2BaCuO_5}$ in this region complicates the assignment. Analyzing the 294- (No. 9) and 268-cm^{-1} (No. 10) lines of $\mathrm{Y_2BaCuO_5}$ and the 239- (No. 9) and 273-cm^{-1} (No. 10) ones of $\mathrm{Ho_2BaCuO_5}$, we note that the No. 9 lines have stronger partners in cross polarization than the No. 10 lines (see Fig. 4). The ratio of frequencies of the No. 9 lines $\omega_{\mathrm{Y}}/\omega_{\mathrm{Ho}}=1.23$ is close to $(m_{\mathrm{Ho}}/m_{\mathrm{Y}})^{1/2}=1.36$, whereas the frequency of the No. 10 line remains nearly unchanged. This argues that the 268-cm^{-1} line (No. 10) in $\mathrm{Y_2BaCuO_5}$ has to be assigned to Cu and the 294-cm^{-1} (No. 9) line to Y. We assume further that two of the remaining three A_g Y vibrations are those at 225 (No. 11) and 209 cm^{-1} (No. 12); as in the Ho (Gd) samples, they soften to 189 (185) cm^{-1} and 159 (169) cm^{-1}, the corresponding $\omega_{\mathrm{Y}}/\omega_{\mathrm{Ho}}$ being 1.19 and 1.31, respectively. For all samples the No. 11 line is strongest in the type-II spectra, whereas the No. 12 line is characterized by a strong partner in crossed polarization. From arguments that follow, the last of the four A_g modes related to Y has to be either the line at 116 (No. 16) or at 106 cm^{-1} (No. 17). In $\mathrm{Y_2BaCuO_5}$ the No. 16 line is stronger in type-III spectra and has strong crossed polarization partner. The No. 17 line is stronger in the type-II spectra. In the Ho (Gd) substituted samples one finds in this area only one phonon at 110 (109) cm^{-1} (No. 16), which is stronger in type-III polarization. Only the Ba line could remain in the same frequency range for the Ho (Gd) substituted samples, whereas the A_g line of Ho (Gd) would shift to lower wave numbers. Hence, we could assign the 116- (No. 16) and 106-cm^{-1} (No. 17) lines in $\mathrm{Y_2BaCuO_5}$ to Ba and Y, respectively. The other line of Ba is most likely below 100 cm^{-1} and coincides with the one at 72 cm^{-1} reported by Udagawa *et al.*[6] and Loo, Burns, and Xidis.[9]

Although all phonon lines corresponding to A_g modes are already assigned, the two weak lines at 182 (No. 13) and 173 cm^{-1} (No. 14) still remain unidentified. The comparison with the ir spectra of $\mathrm{Y_2BaCuO_5}$ (Refs. 8 and 12) shows that these two lines correspond to ir-active phonons and thus they are not proper A_g phonons.

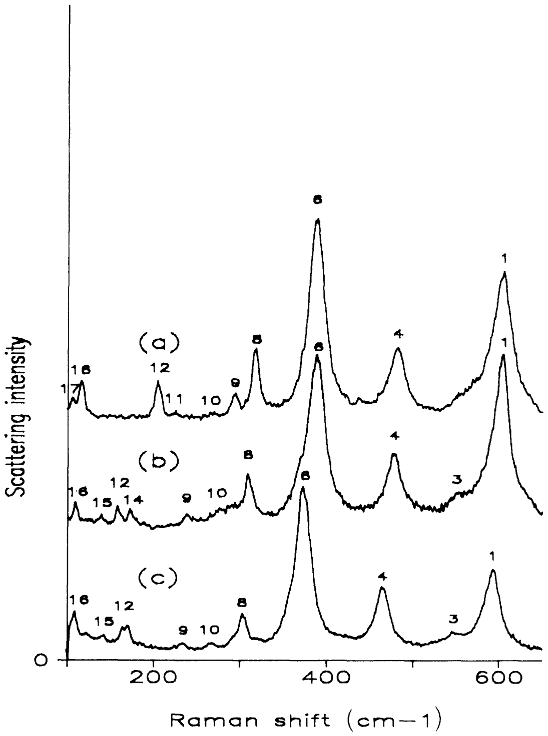

FIG. 4. Type-I spectra in crossed polarization. The scattering configuration corresponds to $z(xy)\bar{z}$ in Portó notations: (a) $\mathrm{Y_2BaCuO_5}$, (b) $\mathrm{Ho_2BaCuO_5}$, and (c) $\mathrm{Gd_2BaCuO_5}$.

The analysis of oxygen-atom vibrations is favored by the fact that the different oxygen sites have different environments. Comparing the $\mathrm{Y_2BaCuO_5}$ and $\mathrm{Y_2Ba_{0.5}Sr_{0.5}CuO_5}$ spectra, one finds that only three (No. 1, No. 4, and No. 6) out of the eight oxygen A_g phonon lines (No. 1 to No. 8) change significantly their frequencies. The lines at 604 (No. 1) and 393 cm^{-1} (No. 6) harden by nearly 10 cm^{-1}, whereas the one at 472 cm^{-1} (No. 4) transforms in an unresolved triple band shifted towards higher wave numbers. It is reasonable to assume that the oxygen modes that are most sensitive to substitution of Ba by Sr are related to the shortest Ba-O bonds.

TABLE I. Atomic positions (Ref. 3) and Raman active modes in $\mathrm{Y_2BaCuO_5}$.

Atom	x	y	z	Multiplicity	Site symmetry	Raman active modes	Directions of vibrations	
							A_g,B_{1g}	B_{2g},B_{3g}
Y(1)	0.115	0.288	0.250	4	C_s^{xy}	$2A_g+2B_{1g}+B_{2g}+B_{3g}$	x,y	z
Y(2)	0.396	0.073	0.250	4	C_s^{xy}	$2A_g+2B_{1g}+B_{2g}+B_{3g}$	x,y	z
Ba	0.931	0.904	0.250	4	C_s^{xy}	$2A_g+2B_{1g}+B_{2g}+B_{3g}$	x,y	z
Cu	0.713	0.659	0.250	4	C_s^{xy}	$2A_g+2B_{1g}+B_{2g}+B_{3g}$	x,y	z
O(3)	0.081	0.100	0.250	4	C_x^{xy}	$2A_g+2B_{1g}+B_{2g}+B_{3g}$	x,y	z
O(1)	0.166	0.432	0.000	8	C_1	$3A_g+3B_{1g}+3B_{2g}+3B_{3g}$	x,y,z	x,y,z
O(2)	0.356	0.228	0.508	8	C_1	$3A_g+3B_{1g}+3B_{2g}+3B_{3g}$	x,y,z	x,y,z

TABLE II. Raman frequencies (in cm^{-1}) of Gd_2BaCuO_5, Ho_2BaCuO_5, Y_2BaCuO_5, and $Y_2Ba_{0.5}Sr_{0.5}CuO_5$ for parallel (||) and crossed (⊥) scattering configurations. For each line the type of the spectrum corresponding to highest intensity ($I_{\parallel}$) and the proposed assignment to definite atomic vibrations are also given.

	Gd_2BaCuO_5		Ho_2BaCuO_5		Y_2BaCuO_5		$Y_2Ba_{0.5}Sr_{0.5}CuO_5$		Spectrum of		Direction of
Line	∥	⊥	∥	⊥	∥	⊥	∥	⊥	highest $I_{\parallel}$	Atom	vibration
No. 1	592	592	604	604	604	604	614	605	I	O(3)	*x*
No. 2					591		591		III	O(1)	*y*
No. 3	547	547	554	554	560	558			III	O(1)	*z*
No. 4	465	464	470	478	472	482			I	O(2)	*x*
No. 5	429		438		441		441		I	O(1)	*x*
No. 6	375	375	391	388	393	388	398	398	II	O(3)	*y*
No. 7	356		371		375		377		III	O(2)	*z*
No. 8	303	303	310	310	318	318	317	317	II	O(2)	*y*
No. 9	234	233	239	239	294	294	295		II	Y(2)	*y*
No. 10	266	266	273	273	268	267	270	269	III	Cu	*y*
No. 11	185		189		225	225	225		II	Y(1)	*y*
No. 12	169	163	159	159	209	206	210	203	I	Y(1)	*x*
No. 13					182		183		III ir		
No. 14					173		174		II ir		
No. 15	141	141	140	140	144		145		III	Cu	*x*
No. 16	109	109	110	110	116	116			III	Ba	*y*
No. 17					106	106			II	Y(2)	*x*

Looking at the environments of O(1), O(2) (Fig. 5), and O(3) (Fig. 6), one finds that the Ba-O bonds are shortest for O(3), where the nearest three Ba and one Y(1) atoms form a square oriented approximately in the *yz* plane. Of the O(2)-Ba and O(1)-Ba bonds the former is shorter. The two A_g modes corresponding to O(3) are the Y(1)-O(3)-Ba (out of the *xz* plane) and the Cu-O(3)-Y(2) (out of the *yz* plane) stretching vibrations, respectively. Among the three A_g modes related to O(2) the one corresponding to out-of-*yz*-plane vibrations (close to the *x* direction) would be more sensitive to Ba substitution.

Taking into account that the O(3)-Cu bond (2.22 Å) is much shorter than the O(3)-Ba bond (2.62 Å). Further, we assign the 604-cm^{-1} (No. 1) line to O(3) vibrations along the *x* axis. Note that there is a close correspondence between the environments and bond lengths of the O(3) atom in Y_2BaCuO_5 and the apex oxygen in $YBa_2Cu_3O_{7-\delta}$ [the latter environment is obtained by the former one if Y(2) is replaced by Cu(1) and Y(1) by Ba]. Hence, the Y(2)-O(3)-Cu stretching vibrations in Y_2BaCuO_5 correspond to the Cu(1)-O(1)-Cu(2) vibrations in $YBa_2Cu_3O_{7-\delta}$ ($\approx 500\ cm^{-1}$).

Of the two remaining Ba-sensitive lines, the one assigned to the Y(1)-O(3)-Ba stretching should be strong for incident polarization along *y*, whereas the line related to the out-of-*yz*-plane O(2) vibrations is expected to be most intensive for incident polarization close to *x* and weak for polarization along *y*.

The lines at 604 (No. 1) and 472 cm^{-1} (No. 4) are strong in the type-I spectra, whereas the one at 393 cm^{-1} (No. 6) is stronger in the type-II spectra. On the basis of above considerations one concludes that the type-I and -II spectra correspond to polarizations along *x* and *y*, respectively. Obviously the type-III spectra correspond to *z* polarization. Only two oxygen lines, namely, at 560 (No. 3) and 375 cm^{-1} (No. 7) are stronger in the type-III

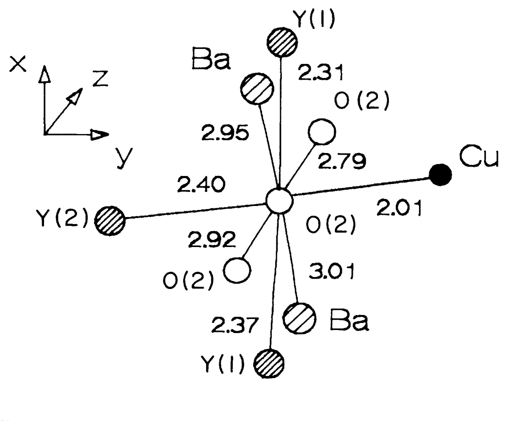

FIG. 5. Environment of the O(2) atom in Y_2BaCuO_5 (Ref. 3). The interatomic distances are in units of Å.

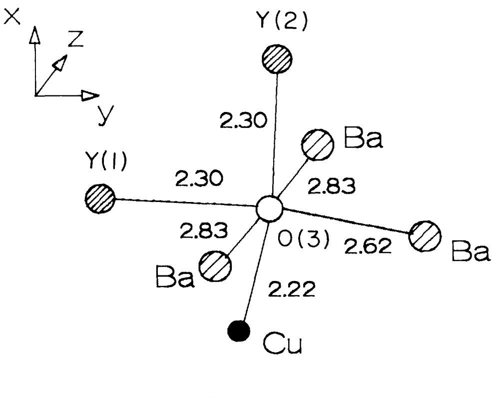

FIG. 6. Environment of the O(3) atom in Y_2BaCuO_5 (Ref. 3). The interatomic distances are in units of Å.

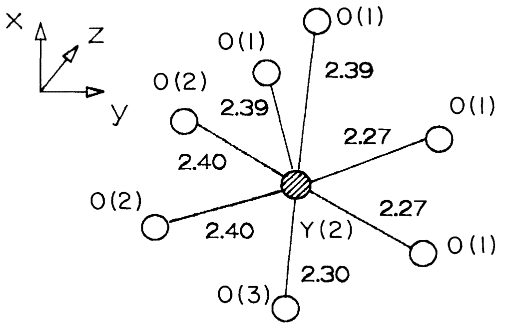

FIG. 7. Environment of the Y(2) atom in Y_2BaCuO_5 (Ref. 3). The interatomic distances are in units of Å.

spectra. Therefore, they represent the O(1)-O(1) and O(2)-O(2) vibrations along z, respectively [the O(1)-O(1) distances are shorter]. On the basis of the same polarization and bond-length arguments, the remaining three oxygen lines at 591 cm^{-1} (No. 2), 441 cm^{-1} (No. 5), and 318 cm^{-1} (No. 8) are assigned, respectively, to O(1)-O(1) (along y), O(1)-O(1) (along x), and O(2)-O(2) (along y) vibrations. Within the above accepted relation between the type of the Raman spectrum and the incident polarization, and if we take into account that the mode frequency is governed by the number and length of the interatomic bonds, we could make some speculations on the assignment of the low-frequency lines to definite atomic vibrations too. It follows from Figs. 7 and 8 that highest frequency of the Y modes is expected for the Y(2) vibrations along y [four Y(2)-O(2) bonds: nearest distance of 2.27 Å] We accept that this mode is represented by the Y line at 294 cm^{-1} (No. 9),which is more intensive in the type-II spectra. The next Y line is the one at 225 cm^{-1} (No. 11). It is also more pronounced in the type-II spectra, and we tentatively assign it to Y(1) vibrations along y (three bonds: average distance 2.29 Å). The Y line at 209 cm^{-1} (No. 12), which is stronger in the type-I spectra, is assigned to Y(1) vibrations along x (four bonds: 2.31 Å). The last Y line, at 106 cm^{-1} (No. 17), is then assigned to Y(2) vibrating along x (three bonds: average length 2.36 Å).

Analyzing the Ba environment from the bond-length arguments one comes to the conclusion that Ba 116 cm^{-1} (No. 16) is due to vibration along y, whereas the second A_g phonon of Ba would correspond to vibrations along x. We note here that the No. 16 line is better seen in types III and I rather than in the type-II spectra. Similarly, one finds that the polarization of strongest intensity of the Cu lines does not correspond to the direction of vibrations. The same situation takes place in some other cases, e.g., in the tetragonal $YBa_2Cu_3O_{7-\delta}$ the intensity of the A_g phonon of Cu(2) (≈ 140 cm^{-1}) for incident polarization within the xy plane, while the vibration itself is along the z axis.

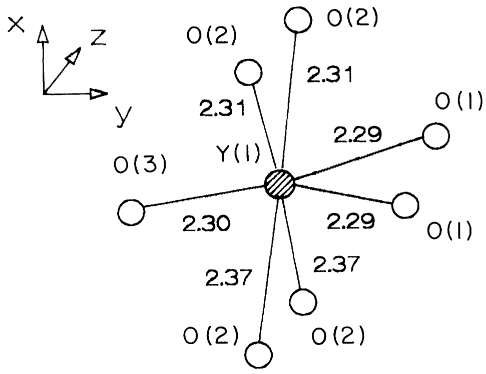

FIG. 8. Environment of the Y(1) atom in Y_2BaCuO_5 (Ref. 3). The interatomic distances are in units of Å.

Among the numerous spectra collected from as grown or cleaved samples of Y_2BaCuO_5 the dominating number could be considered as type I, type II, or their superposition, all corresponding to scattering from the xy plane. This indicates that the xy plane containing tightly bound YO_7 chains could be the plane of easy cleavage of Y_2BaCuO_5 crystals.

CONCLUSIONS

Three types of Raman spectra corresponding to incident polarizations along the main crystallographic directions in Y_2BaCuO_5 were distinguished. Using isomorphic substitutions for Y and Ba and taking into account some general considerations concerning the variations of the A_g frequencies on the atomic masses and interatomic distances, we were able to assign all 16 A_g modes to definite atomic vibrations.

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