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Raman spectra of bismuth cuprate high-T_c superconductors and 3d-metal-substituted phases

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Raman spectra are presented for $Bi_2Sr_2CuO_{6+y}$, $Bi_2Sr_2CaCu_2O_{8+y}$, and compounds formed by cationic substitution of Cu by Fe, Mn, and Co. For $n=1$ materials, the spectra show a greater number of modes than those predicted by group theory using the undistorted pseudotetragonal unit cell. These extra modes, however, are consistent with group-theory predictions based on the space group of the supercell of $Bi_2Sr_2CoO_{6+y}$, which is caused by commensurate modulation over several periods of the smaller unit cell. Similar analysis is made of the supercell of $Bi_2Sr_2SrFe_2O_{8+y}$; predictions are consistent with the rearrangement of low-frequency modes as compared with $Bi_2Sr_2CaCu_2O_{8+y}$. Accompanying changes in oxygen stoichiometry cause strong shifts in the corresponding high-frequency oxygen stretch modes in both $n=1$ and 2 materials. Additional substitution of strontium by calcium in $n=2$ compounds leads to a more disordered structure, with consequent broadening of all modes in the spectrum. Overall, consideration of the supercell structure where it exists is essential in interpreting Raman spectra from the superconducting cupric oxides and their substituted compounds.

INTRODUCTION

Recently Tarascon and co-workers[1-4] have made cationic substitutions for Cu in the $n=1$ and 2 bismuth oxide superconductors and have studied the effect of these substitutions on superstructure modulation,[1-4] valence,[1,3,4] and magnetic properties.[1,4] The details of the superstructure in these compounds, which are isostructural to $Bi_2Sr_2CuO_{6+y}$ (Refs. 1 and 2) and $Bi_2Sr_2CaCu_2O_{8+y}$,[2-4] have been obtained from single crystal x-ray-diffraction and transmission-electron-microscopy (TEM) studies; the effect of the superstructure on oxygen stoichiometry has also been investigated.[1-4] The undoped bismuth compounds have been extensively studied by Raman spectroscopy,[5-14] and the spectra have been interpreted both experimentally[5-14] and theoretically[5-15] in terms of the basic unit cell without taking the superstructure into account. We present here Raman spectra of some of the 3d-metal-substituted compounds and interpret the mode patterns as a function of the newly determined supercell structure. In two cases, where the space group and atom positions of this supercell have been determined, the group theoretical analysis of the number and type of possible modes has been performed and related to the corresponding spectra.

EXPERIMENT

Raman data were obtained with a microprobe system that has been described in detail elsewhere,[16] but with the added capability of a television camera for improved viewing of the sample and placement of the focused beam. The measured spot size used here was 1 μm, the diffraction limit.[16] Exciting radiation was provided by an Ar^+ laser operated at 5145 Å for all samples except $Bi_2Sr_2CaCu_2O_{8+y}$, whose spectrum was taken with 4880-Å excitation.

Sample preparation has been described in detail elsewhere.[1,2,17] All samples were in the form of pellets containing crystallites in various orientations. Under the microscope, it was possible to find crystallites which appeared to have the c axis perpendicular to the surface, as well as regions where the c axis was roughly parallel to the surface. The former were uniformly bright regions a few micrometers in size; the latter appeared as regions characterized by a random array of very small spots, giving an overall mottled appearance. It was relatively simple to focus on the uniformly bright regions of the perpendicular c axis, but no spectra were obtained; it may be that such crystallites were too thin along the c axis. Therefore all of the spectra shown in this paper were obtained from regions where the c axis was parallel to the surface, although finding a suitable spot was difficult, again because of possible lack of sufficient density into the surface. Indeed, the greater success with this orientation may only be due to its greater availability, since it is estimated that the surface area containing the platelets with perpendicular c-axis orientation made up less than 10% of the total area. Backscattering geometry was used, so that the **k** vector of the beam was nominally perpendicular to the c axis, but it was not possible to determine the direction of the **E** vector with respect to the c axis. The scattered radiation was not analyzed for polarization. Each spectrum shown was taken with refocusing on at least two different spots to assure reproducibility.

RESULTS AND DISCUSSION

$n=1$

Figure 1 shows the Raman spectrum of $Bi_2Sr_2CuO_{6+y}$ together with the spectra for the materials resulting from

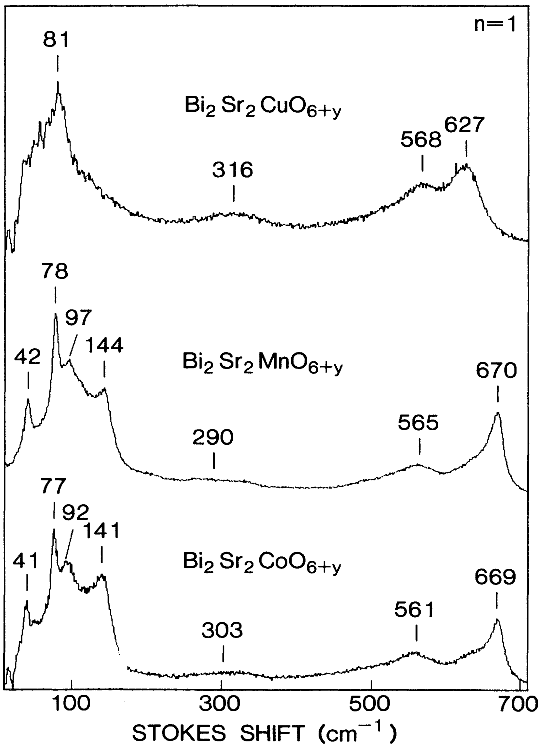

FIG. 1. Raman spectra of the $n=1$ bismuth oxide superconductor and its resultant substituted compounds. The scale for each spectrum and its offset have been adjusted for convenient display.

cation substitution of Mn and Co for Cu. Sample preparation is described in detail elsewhere.[1,2,17] $Bi_2Sr_2MnO_{6+y}$ and $Bi_2Sr_2CoO_{6+y}$ are both insulators,[1,2] whereas $Bi_2Sr_2CuO_{6+y}$ is a superconductor with $T_c = 10$ K.[17] The undistorted unit cell of $Bi_2Sr_2CuO_{6+y}$ is body-centered tetragonal with space group $I4/mmm$;[11,12] standard group-theoretical analysis predicts four modes with symmetry A_{1g}.[11] The number of modes seen in the $Bi_2Sr_2CuO_{6+y}$ spectrum is in agreement with the predicted number. The modes at 627 cm^{-1} (vibration along the c axis of the oxygen in the bismuth plane[12]) and at 316 cm^{-1} (similar motion of Sr[12]) found for $Bi_2Sr_2CuO_{6+y}$ are in good agreement with data also obtained from single-crystal samples.[8,12] However, these data[8,12] show the oxygen stretch in the Sr plane[12] at 455 cm^{-1}, whereas the mode here is shifted up to 568 cm^{-1}. Such discrepancies may be due to differences in processing conditions and composition, giving rise to stacking irregularities[18] and other defects.[19] The lowest frequency mode is at 81 cm^{-1}, which appears in previous work at 196 cm^{-1}.[8,12] (No data below 100 cm^{-1} were shown by other workers for $Bi_2Sr_2CuO_{6+y}$.[8,12]) Although it is reasonable to ascribe the lowest-frequency mode to the Bi stretch,[11] the mode shown is anomalously strong and broad.

Since the undistorted unit cell of each of the doped compounds $Bi_2Sr_2MnO_{6+y}$ and $Bi_2Sr_2CoO_{6+y}$ is isostructural with that of $Bi_2Sr_2CuO_{6+y}$,[1] once again only four bands are expected for analysis based on tetragonal symmetry ($I4/mmm$).[11,12] However, the two lower spectra of Fig. 1 show that the broad mode at 81 cm^{-1} for $Bi_2Sr_2CuO_{6+y}$ is "resolved" into four sharp bands, giving a total of seven bands, four of which are spaced closely together at the low end of the spectrum.

These anomalies are difficult to explain based solely on the unit-cell structure. Even if the symmetry is somewhat lowered from tetragonal to orthorhombic by considering a slight difference in the lengths of the a and b axes,[20] the effects on the mode structure should be negligible.[12] Even if one considers the cell to be doubled,[20] the additional modes should be practically degenerate with those of the unit cell.[15] If any extra modes were visible from these causes, they would therefore be expected to be distributed among the four tetragonal modes, rather than appearing only at low frequencies. The explanation must lie in consideration not just of the unit cell, whether tetragonal, orthorhombic, or doubled, but also of the superstructure modulation and the resulting[1–4] "supercell."

The superstructure modulation is incommensurate[1,2] for $Bi_2Sr_2CuO_{6+y}$ and commensurate[1,2] for $Bi_2Sr_2CoO_{6+y}$ and $Bi_2Sr_2MnO_{6+y}$. The space group for the latter two compounds is *Imma* No. 74 (D_{2h}^{28}) with axes relabeled ($Z=4$).[2] The upper part of Table I gives the positions of each of the equivalent atoms in the $Bi_2Sr_2CoO_{6+y}$ supercell, which are well illustrated in Figs. 2 and 3 of Ref. 1 and Fig. 2b and Fig. 3b of Ref. 2. The bottom part of Table I gives the number of Raman active modes at each position, so that more than 30 A_g modes alone would be expected without a reasonable con-

TABLE I. $Bi_8Sr_8Co_4O_{25}$ ($n=1$) with space group *Imma* (D_{2h}^{28}) No. 74 with axes relabeled ($Z=4$). O-Bi refers to the oxygen atoms within the Bi-O layer, O-Sr to the oxygen atoms within the Sr-O layer, and O-Co to the oxygen atoms within the Co-O layer.

	Atomic positions
Atom	Wyckoff notation
Bi(1,5)	4e
Bi(2–4)	8i
Sr(1,5)	4e
Sr(2–4)	8i
Co(1)	4e
Co(2)	8i
Co(3)	4c
O-Bi(1)	8h
O-Bi(2–5)	16j
O-Sr(1)	4e
O-Sr(2–5)	8i
O-Co(1,2)	16j

	Raman active modes at each position
Position	Modes
4c	None
4e	$A_g+B_{2g}+B_{3g}$
8h	$2A_g+B_{1g}+B_{2g}+2B_{3g}$
8i	$2A_g+B_{1g}+2B_{2g}+B_{3g}$
16j	$3A_g+3B_{1g}+3B_{2g}+3B_{3g}$

sideration of mode energy overlap. For example, a total of eight A_g modes are predicted for the five different Sr atom positions; yet just one broad mode at 316 cm^{-1} is seen. As pointed out by Prade *et al.*,[15] we can expect modes from each half of the cell above and below the Bi-Bi cleavage plane to be very nearly degenerate, since the subunits involved in the vibrations are well separated. If the remaining four modes are each vibrational stretches along the *c* axis, the distance between Sr atoms along *c* changes very little for the different Sr atoms considered in Table I (see Fig. 3 of Ref. 1 or Fig. 3b of Ref. 2). Hence it is reasonable to expect all modes for Sr to be sufficiently alike in energy to result in one broadened mode. Similar arguments can be made for closely spaced energies in the modes for the Bi atoms shown in Table I, as well as the oxygen atoms in the Bi-O and Sr-O planes, so that the spectrum would still appear to have four modes from the atoms just discussed.

If space group *I4/mmm* is used, no Raman active modes are predicted from any of the atoms in the Cu-O plane. However, Table I shows that, for the supercell (space group *Imma*), one A_g mode can be expected from Co1, two from Co2, and none from Co3. Further, each of the two oxygens in the Co-O plane has three A_g modes. These modes arise because the supercell contains two Co-O planes, analogous to the activity of the two Cu-O planes of the $Bi_2Sr_2CaCu_2O_{8+y}$ cell considered without any supercell modulations (space group *I4/mmm*). These modes for $Bi_2Sr_2CaCu_2O_{8+y}$ consist of various symmetric and antisymmetric stretches along the *c* axis, and it is not unreasonable to consider analogous motions for the Co-O plane atoms for the supercell. Since the bond lengths would have to extend across the Bi-Bi cleavage plane, they are considerably greater than those corresponding to the axial stretches of the atoms of the Bi-O and Sr-O planes. This longer bond length would tend to lower frequencies, as observed. Detailed calculations of these modes and their corresponding frequencies are beyond the scope of this paper.

As shown in Ref. 2, $Bi_2Sr_2CoO_{6+y}$ and $Bi_2Sr_2MnO_{6+y}$ have the same space group. Their spectra in Fig. 1 are nearly identical. Since the atomic weights of Co and Mn are 59 and 55, respectively, the expected shift in frequency from this mass difference is within the error due to the linewidth of the modes. The space group for the $Bi_2Sr_2CuO_{6+y}$ supercell is indeterminate, since the modulation is incommensurate. It is not surprising that this more amorphous structure should cause a broadening of the low-frequency modes so that they appear to coalesce.

The commensurate modulation of $Bi_2Sr_2CoO_{6+y}$ and $Bi_2Sr_2MnO_{6+y}$ is accompanied by the insertion of an extra oxygen row every eight Bi rows;[1,2] for $Bi_2Sr_2CuO_{6+y}$ the extra row occurs approximately every ten rows. These extra oxygens in $Bi_2Sr_2CoO_{6+y}$ and $Bi_2Sr_2MnO_{6+y}$ (as compared to $Bi_2Sr_2CuO_{6+y}$) apparently have a "stiffening" effect on the highest-frequency mode, which is ascribed to the stretch vibration along the *c* axis of the oxygen in the bismuth planes of the unit cell. Thus we see for this mode in $Bi_2Sr_2CoO_{6+y}$ and $Bi_2Sr_2MnO_{6+y}$ an upward shift of more than 40 cm^{-1} to 670 cm^{-1}. Another structural difference that may contribute to the large shift is the fact that the Bi atoms form "ribbons" in the Bi-O plane in $Bi_2Sr_2CuO_{6+y}$,[1,2] whereas the ribbons are converted to equal spacing[1,2] in $Bi_2Sr_2CoO_{6+y}$ and $Bi_2Sr_2MnO_{6+y}$. The oxygen atoms are correspondingly rearranged and in this way may affect the stretching mode along the *c* axis. The modes from vibrations in the Sr plane (316 and 568 cm^{-1}) do not change with the substitution within the uncertainty due to the mode widths.

$n=2$

Figure 2 shows the Raman spectra for the $n=2$ bismuth compounds with and without substitution. The discussion of the appearance of the samples for $n=1$ also holds for all of the $n=2$ compounds. A spectrum of $Bi_2Sr_2CaCu_2O_{8+y}$ on the same material as used here has been published previously[5] from 10 to 550 cm^{-1}; the top spectrum of Fig. 2 was taken from 10 to 710 cm^{-1}. The mode positions of both spectra are in agreement, but the relative intensities are different, possibly because of different orientations among the spots used. The modes shown in the top spectrum of Fig. 2 at 60, 128, 225, and 458 cm^{-1} are in approximate agreement with those found in single crystals[6,8-14] of $Bi_2Sr_2CaCu_2O_{8+y}$. The high-frequency mode in these data[6,8-14] range from 625 to 635 cm^{-1}. However, it is found to be 649 cm^{-1} in a material determined to be[7] $Bi_2(Sr_{1-x}Ca_x)_2CuO_{6+\delta}$ with

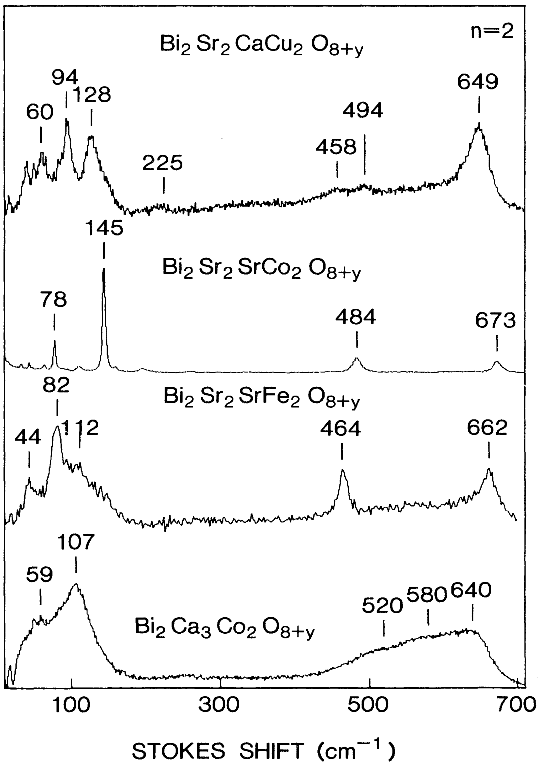

FIG. 2. Raman spectra of the $n=2$ bismuth oxide superconductor and its resultant substituted compounds. The scale for each spectrum and its offset have been adjusted for convenient display.

$(0 \leq x \leq 0.3)$ and $T_c \leq 80$ K, in good agreement with the value reported here. This material[7] also shows the 494-cm^{-1} mode shown here in the top spectrum of Fig. 2 and in earlier work.[5] It can only be concluded that the mode structure is strongly dependent on the stoichiometry of a given sample. Table II summarizes the mode positions in different samples.

The undistorted unit cell of $Bi_2Sr_2CaCu_2O_{8+y}$ has the same space group as the undistorted unit cell of $Bi_2Sr_2CuO_{6+y}$ $(I4/mmm)$.[11] Group theory predicts six A_{1g} modes and one B_{1g} mode for this symmetry.[11] X-ray,[3,21] electron-microscope,[22] and scanning-tunneling-microscope[23] data show an incommensurate superstructure modulation of period 4.7 for $Bi_2Sr_2CaCu_2O_{8+y}$, so that the space group is indeterminate. However, if Fe is substituted for Cu and Sr for Ca to give $Bi_2Sr_2SrFe_2O_{8+y}$, the modulation becomes commensurate.[2] Its space group has been found to be $B222$ No. 21 (D_2^6) with axes relabeled $(Z=4)$.[2] The upper part of Table III gives the position of each of the equivalent atoms in $Bi_2Sr_2SrFe_2O_{8+y}$, which are well illustrated in Figs. 1 and 2 of Ref. 3 and Fig. 2a and Fig. 3a of Ref. 2. The bottom part of Table III shows that every atom can have every symmetry, so that once again mode frequency overlaps must be considered.

The high-frequency mode at 662 cm^{-1} is ascribed to the motion of oxygen in the bismuth planes along the c axis as in the $n=1$ material of Fig. 1. From Table III, a total of 16 A modes are predicted for the six different O-Bi positions, where O-Bi indicates oxygen atoms within the Bi-O layer. It is reasonable to use the arguments presented previously for the $Bi_2Sr_2CoO_{6+y}$ and conclude that all of these modes are sufficiently degenerate that no splitting is seen. This mode is shifted up by 13 cm^{-1} from that of $Bi_2Sr_2CaCu_2O_{8+y}$, smaller than that seen in Fig. 1 for $Bi_2Sr_2CoO_{6+y}$ as compared with $Bi_2Sr_2CuO_{6+y}$. Here the shift cannot be explained by the addition of extra oxygen in the Bi-O plane since $Bi_2Sr_2CaCu_2O_{8+y}$ has an incommensurate period of 4.7 (indeterminate space group) compared to the commensurate periodicity of 5 for $Bi_2Sr_2SrFe_2O_{8+y}$; this difference implies a negligible change in oxygen content between the

TABLE III. $Bi_{10}Sr_{15}Fe_{10}O_{46}$ $(n=2)$ with space group $B222$ (D_2^6) No. 21 with axes relabeled $(Z=4)$. Sr* refers to Sr between Fe-O layers, O-Bi to the oxygen atoms within the Bi-O layer, O-Sr to the oxygen atoms within the Sr-O layer, O-Fe to the oxygen atoms within the Fe-O layer, and O-Sr* to oxygen atoms within the Sr*-O layer.

Atomic positions

Atom	Wyckoff notation
Bi(1–5)	$8l$
Sr(1–5)	$8l$
Fe(1–5)	$8l$
Sr*(1,2)	$8l$
Sr*(3)	$4k$
O-Bi(0)	$4g$
O-Bi(1–5)	$8l$
O-Sr(1–5)	$8l$
O-Fe(1,12)	$4g$
O-Fe(2–5,8–11)	$8l$
O-Fe(6,7)	$4h$
O-Sr*(1,2)	$8l$
O-Sr*(3)	$4k$

Raman active modes at each position

Position	Modes
$4g$	$A+2B_1+B_2+2B_3$
$4h$	$A+2B_1+B_2+2B_3$
$4k$	$A+B_1+2B_2+2B_3$
$8l$	$3A+3B_1+3B_2+3B_3$

TABLE II. Mode positions of samples which approximate $Bi_2Sr_2CaCu_2O_{8+y}$. Weak modes are enclosed in parentheses.

Mode positions (cm^{-1})						
Ref. 6	Ref. 7	Ref. 8	Ref. 9	Ref. 10	Ref. 12	Ref. 5 and this work
				27.5		
			56	51.5		
				61		60
						94
120		122	115	118		128
	130	(133)				(148)
		(156)			164	
195		184	190			
		(219)			(282)	(225)
295		296	290	300	292	
		313				
		(391)		385		(347)
462	462	469	463	463	464	458
	492					494
	587					
625		631	620	620	625	
	650	659				649

Bi planes as a result of the Fe substitution. In addition, both $Bi_2Sr_2CaCu_2O_{8+y}$ and $Bi_2Sr_2SrFe_2O_{8+y}$ have the "ribbon" structure.[1-3] However, in $Bi_2Sr_2SrFeO_{8+y}$, extra oxygens are found not only between the Bi planes but are also inserted into the Sr* plane,[2,3] where Sr* indicates the Sr between Fe-O planes. The presence of these extra oxygens apparently has the effect of "stiffening" the bond to cause a net upward shift of 13 cm^{-1}.

The mode at ≈ 460 cm^{-1} corresponds to stretching motion of oxygen in the Raman active Sr-O planes, and is not shifted appreciably. Lattice-dynamic calculations[15] for the undistorted unit cell of $Bi_2Sr_2CaCu_2O_{8+y}$ indicate that the Raman modes coming from the Cu-O planes are at the lowest frequencies of the spectrum; all of these modes can be expected to shift because of the substitution of Fe for Cu and the change in modulation periodicity. It is also necessary to consider the modes from the Sr*-O plane, which do not arise in the simpler unit cell,[11] and can be expected in the lower-frequency part of the spectrum for reasons given for the extra modes with $n = 1$. An overall rearrangement of modes below 200 cm^{-1} is clear, but no detailed conclusions can be drawn.

The bottom spectrum of $Bi_2Ca_3Co_2O_{8+y}$ in Fig. 2, which contains Ca instead of Sr and Co instead of Cu, is characterized chiefly by a broadening of all mode widths. In this compound, which is an insulator, Bi and Ca have nearly equal ionic radii (0.98 and 0.96 Å, respectively) so that Bi replaces Ca at random;[4] however, Ca does not occupy Bi sites.[4] The observed broadening is consistent with the introduction of this type of disorder. The ≈ 460 cm^{-1} mode appears to be shifted upward into a broad continuum. Thus the oxygen stretch appears to be affected by the substitution of Ca or Bi for Sr. X-ray data indicate an incommensurate modulation of periodicity 28.4 Å along the a axis.[4] Since there is no indication of inclusion of extra oxygen in the Bi-O layers,[4] the highest-frequency mode does not appear to be shifted up.

The remaining spectrum of Fig. 2 for $Bi_2Sr_2SrCo_2O_{8+y}$, which is an insulator like all the substituted compounds, is markedly different from the others in Fig. 2 in that there are only four sharp strong modes. This compound forms a complicated structure which is not entirely understood.[4] Two modulations have been found,[4] one commensurate with reciprocal period $(3a^*+b^*)/18$, the other incommensurate with period $\sim a^*/11.3$. X-ray data indicate the presence of long-range order.[4] There are some small features seen in the Raman spectrum which may be additional modes. Whereas the general features of the other spectra shown are consistent with the structural determination, results from this compound are at present anomalous.

CONCLUSION

Cation substitution of $Bi_2Sr_2CuO_{6+y}$ $(n = 1)$ and $Bi_2Sr_2CaCu_2O_{8+y}$ $(n = 2)$ causes the superstructure modulation to change from incommensurate to commensurate as determined by x-ray and TEM studies. Raman spectra of the $n = 1$ materials display more modes than predicted by group theory analysis based on the space group of the undistorted unit cell. Analysis based on the space group of the commensurate supercell of $Bi_2Sr_2CoO_{6+y}$ along with considerations of frequency overlap among some of the predicted modes explain many features of the observed spectra, including the appearance of additional modes at low frequencies. A similar analysis of $Bi_2Sr_2SrFe_2O_{8+y}$, which also shows commensurate modulation and therefore has a determinate space group, is consistent with an overall rearrangement of the low-frequency modes (below 200 cm^{-1}) as compared with $Bi_2Sr_2CaCu_2O_{8+y}$. Relative shifts of the higher-frequency oxygen stretch modes among the various doped compounds can be explained in terms of structural details and mode frequency overlaps to form single broad modes. As shown most clearly for the $n = 1$ superconductors, interpretation of the Raman spectra of these materials must consider the presence of the larger cell consisting of modulations over a number of periods of the unit cell considered in earlier work.

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[1] J.-M. Tarascon, P. F. Miceli, P. Barboux, D. M. Hwang, G. W. Hull, M. Giroud, L. H. Greene, Y. LePage, W. R. McKinnon, E. Tselepis, G. Pleizier, M. Eibschutz, D. A. Neumann, and J. J. Rhyne, Phys. Rev. B **39**, 11 587 (1989).

[2] J.-M. Tarascon, Y. LePage, W. R. McKinnon, E. Tselepis, P. Barboux, B. G. Bagley, and R. Ramesh, in *Proceedings of the Symposium on High Temperature Superconductors: Relationships Between Properties, Structure, and Solid-State Chemistry, San Diego, 1989,* edited by J. D. Jorgensen, K. Kitazawa, J.-M. Tarascon, M. S. Thompson, and J. B. Torrance (MRS, Pittsburgh, PA, 1990), p. 317.

[3] Y. LePage, W. R. McKinnon, J.-M. Tarascon, and P. Barboux, Phys. Rev. B **40**, 6810 (1989).

[4] J.-M. Tarascon, R. Ramesh, P. Barboux, M. S. Hegde, G. W. Hull, L. H. Greene, M. Giroud, Y. LePage, W. R. McKinnon, J. V. Waszczak, and L. F. Schneemeyer, Solid State Commun. **71**, 663 (1989).

[5] L. A. Farrow, L. H. Greene, J. M. Tarascon, P. A. Morris, W. A. Bonner, and G. W. Hull, Phys. Rev. B **38**, 752 (1988).

[6] M. Stavola, D. M. Krol, L. F. Schneemeyer, S. A. Sunshine, R. M. Fleming, J. V. Waszczak, and S. G. Kosinski, Phys. Rev. B **38**, 5110 (1988).

[7] Z. V. Popovic, C. Thomsen, M. Cardona, R. Liu, G. Stanisic, R. Kremer, and W. König, Solid State Commun. **66**, 965 (1988).

[8] M. Cardona, C. Thomsen, R. Liu, H. G. von Schnering, M. Hartweg, Y. F. Yan, and Z. X. Zhao, Solid State Commun. **66**, 1225 (1988).

[9] D. Kirillov, I. Bozovic, T. H. Geballe, A. Kapitulnik, and D. B. Mitzi, Phys. Rev. B **38**, 11 955 (1988).

[10] J. Sapriel, L. Pierre, D. Morin, J. C. Toledano, J. Schneck, H. Savary, J. Chavignon, J. Primot, C. Daguet, J. Etrillard, and H. Boyer, Phys. Rev. B **39**, 339 (1989).

[11] G. Burns, G. V. Chandrashekhar, F. H. Dacol, M. W. Shafer, and P. Strobel, Solid State Commun. **67**, 603 (1988).

[12] G. Burns, P. Strobel, G. V. Chandrashekhar, F. H. Dacol, F. Holtzberg, and M. W. Shafer, Phys. Rev. B **39**, 2245 (1989).

[13] V. G. Hadjiev and M. N. Iliev, in *Proceedings of the Eleventh*

International Conference on Raman Spectroscopy, edited by R. J. H. Clark and D. A. Long (Wiley, New York, 1988), p. 1009.

[14] M. N. Iliev and V. G. Hadjiev, Physica C **157**, 495 (1989).

[15] J. Prade, A. D. Kulkarni, F. W. de Wette, U. Schröder, and W. Kress, Phys. Rev. B **39**, 2771 (1989).

[16] J. B. Hopkins and L. A. Farrow, J. Appl. Phys. **59**, 1103 (1986).

[17] J. M. Tarascon, W. R. McKinnon, P. Barboux, D. M. Hwang, B. G. Bagley, L. H. Greene, G. W. Hull, Y. LePage, N. Stoffel, and M. Giroud, Phys. Rev. B **38**, 8885 (1988).

[18] C. C. Chang, T. Venkatesan, M. S. Hegde, D. M. Hwang, R. Ramesh, C. T. Rogers, A. Frenkel, E. W. Chase, L. Nazar, X. D. Wu, and A. Inam, in *Proceedings of the SPIE, Processing of Films for High T_c Superconducting Electronics, Santa Clara, CA, 1989,* edited by T. Venkatesan (SPIE, Bellingham, WA, 1989), Vol. 1187, p. 216.

[19] R. Ramesh, B. G. Bagley, J. M. Tarascon, S. M. Green, M. L. Rudee, and H. L. Luo, J. Appl. Phys. **67**, 379 (1990).

[20] C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, E. M. McCarron, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, Phys. Rev. B **38**, 225 (1988).

[21] Y. Gao, P. Lee, P. Coppens, M. A. Subramanian, and A. W. Sleight, Science **241**, 954 (1988).

[22] C. J. D. Hetherington, R. Ramesh, M. A. O'Keefe, R. Kilaas, G. Thomas, S. M. Green, and H. L. Luo, Appl. Phys. Lett. **53**, 1016 (1988).

[23] M. D. Kirk, J. Nogami, A. A. Baski, D. B. Mitzi, A. Kapitulnik, T. H. Geballe, and C. F. Quate, Science **242**, 1673 (1988).