PHYSICAL REVIEW B VOLUME 39, NUMBER 4 1 FEBRUARY 1989

Raman-active phonons in the high-temperature superconductors and results in $Bi_2Sr_2CuO_6$

Gerald Burns, P. Strobel,* G. V. Chandrashekhar, F. H. Dacol, F. Holtzberg, and M. W. Shafer
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598-0218

(Received 2 September 1988)

We report Raman results from single crystals of the 10-K superconductor $Bi_2Sr_2CuO_6$, which has one Cu-O plane per primitive unit cell. All $4A_{1g}$ phonons are observed, and the spectrum is very similar to that of the two Cu-O plane phase $Bi_2CaSr_2Cu_2O_8$. This similarity is correlated with the structures of these two materials. A general comparison of the Raman-active modes in all the high-T_c cuprate superconductors is given. This comparison highlights the similarities of the phonon spectra.

INTRODUCTION

The rare-earth copper oxide high-T_c superconductors have been intensely studied, but many features in these materials remain unexplained. The discovery[1] of a new family of cuprate superconductors with ideal formula $(Bi/Tl)_2Ca_{n-1}(Sr/Ba)_2Cu_nO_{4+2n}$, with $n=1,2,3$, and perhaps larger values, allows new insights into these materials. This paper deals with the phonon characteristics of these Cu-O plane-containing superconductors. We previously reported[2] single-crystal Raman data on the Bi phase containing two adjacent copper layers, abbreviated Bi($n=2$), as indicated in Table I. We present single-crystal data for the A_{1g} phonons in $Bi_2Sr_2CuO_6$, that is the Bi($n=1$) material. In a separate section, Raman data for all the high-T_c cuprate superconductors are compared, in order to gain further understanding of the general features of these phonons.

All the compounds considered here contain copper layers perpendicular to the c axis in tetragonal or slightly orthorhombically distorted unit cells. They are abbreviated as indicated in Table I. The meaning should be fairly clear. La-Sr-Cu-O has the K_2NiF_4 structure. Where used, n is the number of Cu-O planes in the primitive unit cell. Tl 1:2:3 is a new material,[3] which is structurally very close to Y 1:2:3. La-Sr-Cu-O has one Cu-O plane and both Y 1:2:3 and Tl 1:2:3 have two Cu-O planes. Figure 1 shows many of the structures.

TABLE I. General information for the high-temperature superconductors discussed here.

Symbol	Formula	T_c (K)	n[a]	Raman modes
La-Sr-Cu-O	$La_{2-x}Sr_xCuO_4$	36	1	$2A_{1g}$
Bi($n=1$)	$Bi_2Sr_2CuO_6$	10	1	$4A_{1g}$
Bi($n=2$)	$Bi_2CaSr_2Cu_2O_8$	85	2	$6A_{1g}+B_{1g}$
Tl($n=2$)	$Tl^2CaBa_2Cu_2O_8$	105	2	$6A_{1g}+B_{1g}$
Tl($n=3$)	$Tl_2Ca_2Ba_2Cu_3O_{10}$	125	3	$7A_{1g}+B_{1g}$
Y 1:2:3	$YBa_2Cu_3O_7$	92	2	$4A_{1g}+B_{1g}$
Tl 1:2:3	$TlCaBa_2Cu_2O_7$	60	2	$4A_{1g}+B_{1g}$

[a] Number of Cu-O planes per primitive unit cell.

Throughout this paper we use the tetragonal notation to classify the normal modes; thus, the irreducible representations of the point group $4/mmm$-D_{4h} are used. This has the important advantage that all the high-temperature superconductors can be easily compared. For the materials that are actually orthorhombic, the deviations from tetragonal symmetry are small, and the splitting of the phonon frequencies seems to be small or negligible. If required, the reduction of the irreducible representations from tetragonal to orthorhombic point groups is trivial with the use of correlation tables.

Unlike infrared-active modes, only certain atoms participate (vibrate) in the Raman-active modes, with only two kinds of motion. For Raman-active modes that have A_{1g} and B_{1g} symmetry, the vibrating atoms can only move along the c axis. For modes that have E_g symmetry, the atoms only move in the ab plane (perpendicular to the c axis). These latter modes seem to be very weak, and very few have been reported in these materials. Thus, *throughout the paper, only modes with A_{1g} and B_{1g} symmetry will be mentioned and discussed.*

EXPERIMENT

The Bi($n=1$) superconductor first reported by Michel *et al.*,[4] was largely neglected in recent physico-chemical studies of cuprate superconductors. The reasons for this are, (i) its low T_c, (ii) difficulties in the synthesis of the superconducting phase in the Bi-Sr-Cu-O system. Superconductivity in the Bi($n=1$) occurs only in a narrow range of compositions.[5] Single crystals of both superconducting and nonsuperconducting Bi($n=1$), with a similar structure, were grown by slow cooling from CuO-rich melts[5,6] at 900–1200 °C. Crystals were characterized by x-ray diffraction (precession camera) and analyzed by electron microprobe.[5]

The Raman measurements of Bi($n=1$) were carried out in backscattering from large ab-face crystals. Then, the four A_{1g} ($4A_{1g}$) allowed phonons should be observable. In terms of polarizations and directions, this can be written as $z(xx)\bar{z}$ to denote z as the direction of the laser and signal, and x as the direction of polarization of the light in both cases, which yields modes that have A_{1g} and

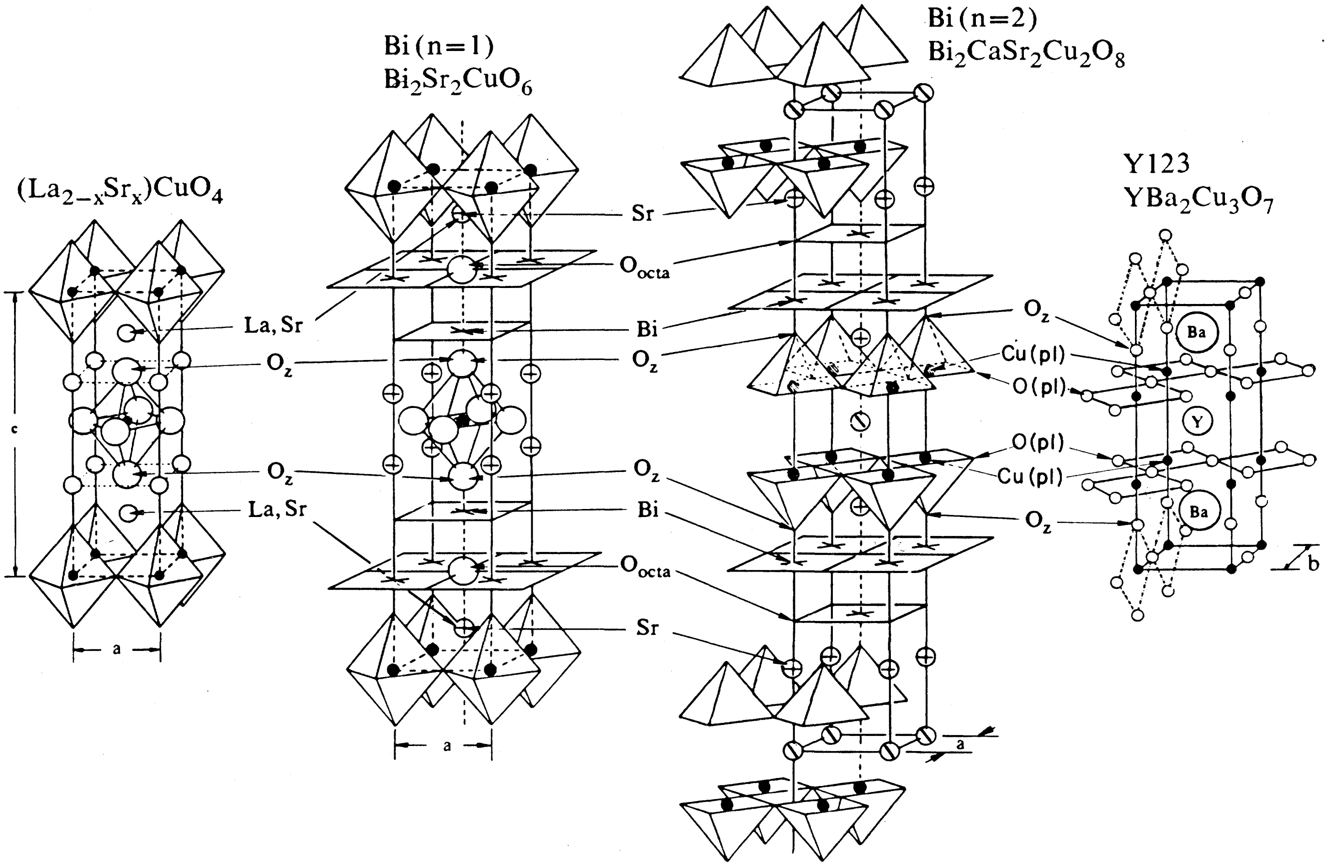

FIG. 1. The structures of some of the high-temperature superconductors, with the conventional crystallographic unit-cell outlined. Labeled atoms are those that can vibrate in phonon modes transforming as the A_{1g} and B_{1g} irreducible representations of the $4/mmm$-D_{4h} point group. (See the text.)

B_{1g} symmetries. [However, remember that for Bi($n=1$), only A_{1g} modes are allowed.]

RESULTS FOR Bi($n=1$)

The upper part of Fig. 2 shows the experimental Raman data from superconducting single crystals of Bi($n=1$). Four lines are observed, in agreement with the number expected from group theory[2] (Table I), and the frequencies are given in the figure. The feature labeled *P* is a plasma line.

These spectra can be compared to two published results on ceramics[7] and "highly oriented polycrystals."[8] The ceramic data show some intense sharp lines[7] but are in poor agreement with the results shown here and in Ref. 8. The highly oriented polycrystals[8] show broad, weak, and unlabeled features. However, some of these features are in reasonable agreement with the lines reported here.

We have measured Bi($n=1$) samples that are not superconducting as well as those that have $T_c \approx 10$ K, and find essentially the same Raman results so that the frequencies in the figure seem appropriate to the Bi($n=1$) phase in general and are listed in Table II.

In the lower part of Fig. 2, our Raman results for Bi($n=2$) single crystals ($T_c \approx 85$ K) are shown.[2] The similarity to the Bi($n=1$) spectrum is striking, in spite of the structural difference established by single-crystal x-ray diffraction. The reason for the similarity will be discussed in the next section.

RESULTS FOR OTHER HIGH HIGH-T_c SUPERCONDUCTORS

Many Raman measurements have been reported for Y 1:2:3, but for other cuprate superconductors less data are available. For each of the high-temperature superconducting materials listed in Tables I and II, the data that we use are briefly discussed, and the quoted papers should be consulted for complete references. *Only results from single crystals* will be considered, because some impurity modes have been found in ceramic samples. Also, only A_{1g} and B_{1g} phonons are discussed. We follow the order of Table II (from left to right).

La-Sr-Cu-O. The results from single crystals seem fairly conclusive.[9] The frequencies at 226 and 430 cm^{-1} (Table II) are reasonably independent of the amount of substituted Sr, and of the orthorhombic distortion.

The lattice dynamics of materials with the K_2NiF_4 structure have been studied extensively by Geick and co-workers,[10] and extended to La-Sr-Cu-O by Prade *et al.*[11]

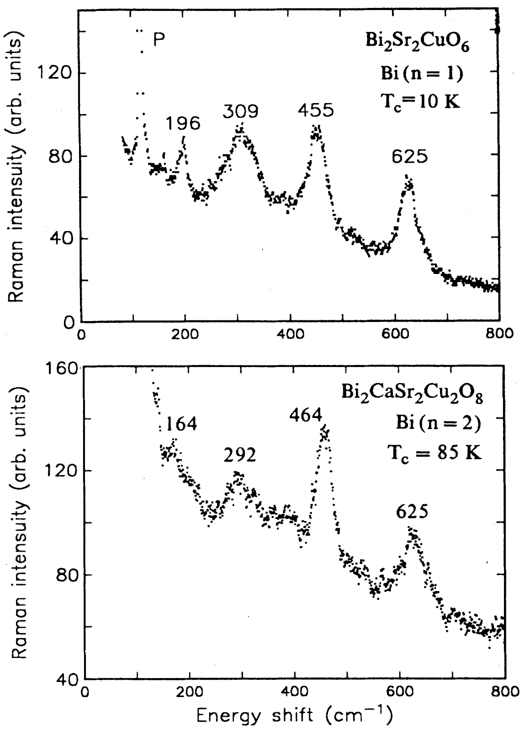

FIG. 2. The room-temperature polarized Raman data from single-crystal $Bi_2Sr_2CuO_6$, Bi($n=1$) (top), and $Bi_2CaSr_2Cu_2O_8$, Bi($n=2$) (bottom).

The high-frequency A_{1g} Raman-active mode involves the motion of mostly the light O_z atoms moving against each other along the c axis. The lower-frequency A_{1g} mode involves the same sort of motion, but mostly of the heavy La atoms.

Bi(n=1). The Raman spectrum is described above (Fig. 2). The frequencies measured in single crystals are listed in Table II.

Bi(n=2). Frequencies from single crystals[2] (Fig. 2) are listed in Table II.

This material has two Cu-O planes per primitive unit cell, so Raman vibrations due to motion of the atoms in these planes become allowed.[2] With 45° crossed polarization Raman measurements, Cardona *et al.*[8] have detected the B_{1g} plane mode at 282 cm^{-1} which is also listed in Table II. Two A_{1g} modes have not as yet been detected.

Tl(n=2). McCarty *et al.*[12] have obtained Raman spectra from this material and the frequencies are listed in Table II. Using the micro-Raman technique, they were able to separate domains with different n values in the same "single" crystal.

The group theory for Tl($n=2$) and Bi($n=2$) is the same if we assume tetragonal symmetry. If sharper Raman or infrared lines can be observed in Tl and Bi compounds, it will be interesting to look for indications of the lowering of the symmetry, but for now we neglect this effect.

Tl(n=3). McCarty *et al.*[12] have reported Raman spectra for this material and the frequencies are listed in Table II.

By use of the group-theoretical results already obtained[2] for Bi($n=2$), it is straightforward to determine under which irreducible representations the phonons in this material transform.[13] The Raman modes of interest are listed in Table I.

Y 1:2:3. The frequencies listed in Table II are from previous single-crystal studies,[14-16] and these papers should be consulted for further references. Also available are several lattice-dynamic calculations[17,18] on Y 1:2:3, which are helpful for the analysis.

Tl 1:2:3. McCarty *et al.*[19] have reported Raman data in this material, and the frequencies are listed in Table II. This material is essentially isotstructural with Y 1:2:3, with Tl replacing the chain Cu atoms, Ca replacing the Y atoms, and a rearrangement of the chain O atoms which causes the Tl atoms to become octahedrally coordinated.

DISCUSSION OF THE RAMAN-ACTIVE MODES

Fortunately, the frequencies of all the allowed modes for the relatively simple La-Sr-Cu-O and Bi($n=1$) structures are known. This allows us to progress from the simplest to the more complex materials, discussing the Raman-active modes and their frequencies (from left to right in Fig. 1 and Table II). Assignments for some of the modes that are discussed here have already been suggested by many workers,[7-19] and we do not claim extensive originality. Our aim here is to present a rather complete and unified picture of these phonons in all the cuprate superconductors.

TABLE II. The frequencies (in cm^{-1}) of the measured A_{1g} and B_{1g} Raman modes active in the various materials. See text for the labeling of these modes.

La-Sr-Cu-O	Bi($n=1$)	Bi($n=2$)	Tl($n=2$)	Tl($n=3$)	Y 1:2:3	Tl 1:2:3
				92		
	196 Bi	164 Bi	134 Tl	129 Tl	108 Ba	120 Ba
			[157 Cu(pl)]		152 Cu(pl)	148 Cu(pl)
226 La						
(284 Sr)	309 Sr	292 Sr				
		282 B_{1g}			340 B_{1g}	278 B_{1g}
			409 O(pl)		440 O(pl)	
430 O_z	455 O_z	464 O_z	493 O_z	498 O_z	504 O_z	525 O_z
	625 O_{octa}	625 O_{octa}	599 O_{octa}	599 O_{octa}		

La-Sr-Cu-O. This material has only $2A_{1g}$ allowed modes and they only involve motion of La and O_z atoms, as has been discussed. From the mass ratios and lattice-dynamic calculations, it is clear that the lower-frequency mode involves mostly the heavy La atoms, and is listed as 226 La in Table II. Similarly, the higher-frequency mode is listed as 430 O_z in Table II. The assignment in this material is particularly simple because there are only two atoms involved in two modes.

Note the positions of the La and O_z atoms. For the A_{1g} motion, O_z vibrates along the c axis with a heavy metal atom above it and a Cu-O plane below it; the bonding of O_z to the Cu-O plane atoms is probably weak, as indicated by the large distance to the Cu-O plane. The La atom vibrates with an O_z atom below it and a "vacancy" in the Cu-O plane above it.

The other materials considered here contain Sr atoms in a similar environment as the La atoms in La-Sr-Cu-O. The corresponding frequency is 226 cm^{-1} multiplied by the square root of the La/Sr atom mass ratio, which yields 284 cm^{-1} (listed in Table II as 284 Sr). This is approximately the expected frequency of this mode in La-Sr-Cu-O if Sr atoms replace the La atoms without significantly changing the force constants.

Bi(n=1). The structure of this material is shown in Fig. 1. Like La-Sr-Cu-O, it has only one Cu-O plane per primitive unit cell, but it contains more atoms, and this leads to $4A_{1g}$ Raman-allowed modes.

There are two important structural units in this material, from a Raman vibration point of view: (i) the Cu-O plane, (ii) the ordered sequence of atoms along the c axis O_z-Bi-O_{octa}-Sr (see Fig. 1). In fact, with only small modifications, this ordered sequence is common to all cuprate superconductors that have a body-centered structure.

As in La-Sr-Cu-O, only atomic motion along the c axis (perpendicular to the Cu-O plane) gives rise to the $4A_{1g}$ Raman-active modes. The four atoms involved in the Raman-active modes are precisely the atoms in the ordered sequence O_z-Bi-O_{octa}-Sr. However, the local environment of two of these atoms is the same as in La-Sr-Cu-O (Fig. 1). For this reason, and because of the proximity of the frequency to the 430 O_z mode in La-Sr-Cu-O, the 455-cm^{-1} mode in Bi($n=1$) can be assigned to vibrations involving mostly O_z atoms (455 O_z in Table II).

The same reasoning allows us to assign the 309-cm^{-1} mode in Bi($n=1$) to a phonon involving mostly Sr atom vibration, and this is listed as 309 Sr in Table II. For Bi($n=1$) this leaves the 193- and 625-cm^{-1} phonons to be assigned. The light O_{octa} atom, which has six metal atom neighbors (5Bi+Sr), should be more strongly bonded than O_z, and thus vibrate at a higher frequency. So the 625-cm^{-1} vibration is assigned to this oxygen atom (625 O_{octa} in Table II). The lowest-frequency mode at 196 cm^{-1} should be assigned to atomic motion of the heavy atoms, namely Bi, and is listed accordingly in Table II. The validity of these assignments can be tested by comparison to the other superconductors.

Bi (n=2). The Bi superconductor with two Cu-O planes has mode frequencies very similar to those found for Bi($n=1$). This may seem surprising since there are three more Raman-active modes expected in Bi($n=2$) than in Bi($n=1$), as noted in Table I. By polarization measurements, one of these modes, the B_{1g} mode, is found at 282 cm^{-1} and listed in Table II. However, there are still $2A_{1g}$ modes to be accounted for.

These new $2A_{1g}$ modes in Bi($n=2$) are due to the motion of the Cu and O atoms in the Cu-O planes. Their symmetry-adapted vectors are shown in Fig. 3, along with the normal mode of the other (B_{1g}) Raman-active mode from the Cu-O plane. These $2A_{1g}$ modes have been observed in other materials (see below), but are often weak. This may explain why they have not been observed as yet in Bi($n=2$).

The four observed modes in Bi($n=2$) can be understood by our taking into account the ordered sequence O_z-Bi-O_{octa}-Sr, which occurs with the same surroundings in the Bi($n=2$) as in Bi($n=1$) (Fig. 1). Thus, similar frequencies and eigenvectors can be expected for phonons involving the motion of these atoms. This is indeed observed and the modes for Bi($n=2$) are labeled accordingly in Table II. The correspondence of the frequencies between Bi($n=1$) and Bi($n=2$) for this ordered sequence of atoms is remarkable.

Tl(n=2). The lowest-frequency mode and the two highest-frequency modes in the spectrum are intense. Since the structure is essentially the same as that of Bi($n=2$), similar frequency modes should be expected. The two highest-frequency modes are very close to those observed in Bi($n=2$) and are thus assigned similarly. The 134-cm^{-1} mode undoubtedly involves mostly the heavy Tl-atom motion, and is so labeled. It appears that the mode that primarily involves the motion of the heavy alkaline-earth atoms is not observed. This compound includes two particular modes at 157 and 409 cm^{-1}, which have no obvious correspondence in the compounds previously discussed.

Structures with two or more Cu-O planes have

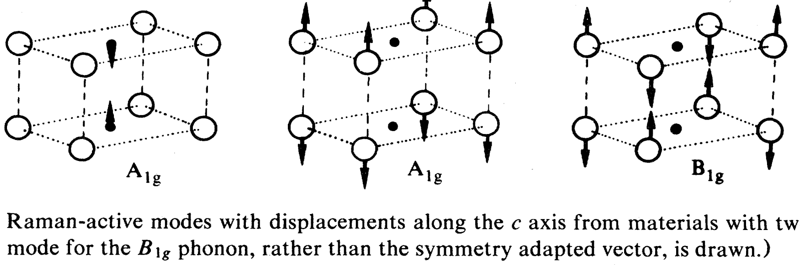

FIG. 3. The $2A_{1g}+B_{1g}$ Raman-active modes with displacements along the c axis from materials with two Cu-O planes per primitive unit cell. (The normal mode for the B_{1g} phonon, rather than the symmetry adapted vector, is drawn.)

$2A_{1g}+B_{1g}$ modes due to atoms in these planes, as shown in Fig. 3. This is also the case in Y 1:2:3 where these modes were identified (see below). Considering the similarity of the frequencies between Tl($n=2$) and Y 1:2:3, and the lack of correspondence to any other modes observed in Bi($n=1$) and Bi($n=2$), we assign the weak 409-cm^{-1} mode in Tl($n=2$) to the high-frequency Cu-O plane mode (Fig. 3), and it is labeled 409 O(pl) to note that it involves mostly motion of oxygen atoms in the Cu-O plane. The other Cu-O plane A_{1g} mode, which involves mostly motion of the heavier Cu atoms (Fig. 3), must be at a lower frequency, and is assigned, and labeled as 157 Cu(pl) in Table II. It is shown in parentheses because it is a weak shoulder in the measured spectrum[12] and not noted as a mode by the authors of Ref. 12.

If the modes involving primarily Ba motion (expected in the 240-cm^{-1} range) and the B_{1g} mode are observed, it will be interesting to compare their frequencies to the other modes listed in Table II.

Tl($n=3$). The insertion of an extra Cu-O plane and an extra Ca atom in Tl($n=2$) to form Tl($n=3$) adds only one extra Raman mode (Table I and Ref. 13). The reason for this is that the central plane is at a mirror plane, and thus yields no Raman-active modes. The new mode comes from mostly Ca-Ca vibration. Thus, Raman modes in Tl($n=3$) and Tl($n=2$) should be very similar, except for this additional Ca-Ca mode.

As yet, only a few modes have been reported in Tl($n=3$) as indicated in Table II. Note that the two highest modes have very similar frequencies to those found in Bi($n=1$), Bi($n=2$), and Tl($n=2$). This is consistent with the presence of the similar ordered sequence of atoms O_z-Bi/Tl-O_{octa}-Sr/Ba in all these compounds, and these frequencies can be assigned accordingly. The assignment of the 92-cm^{-1} mode is not made and more experimental results should lead to a better understanding.

Y 1:2:3. The structure of Y 1:2:3 is fundamentally different from that of the materials discussed above. It contains Cu-O planes, but no O_z-heavy-atom-O_{octa}-alkaline-earth ordered sequence. The Cu-O planes lead to three phonons, $2A_{1g}+B_{1g}$ (Fig. 3), which we expect to occur at similar frequencies as in the Bi and Tl cuprates. These are the 152- and 440-cm^{-1} modes, which are the $2A_{1g}$ phonons, and the 340-cm^{-1} B_{1g} mode.

Of the two other A_{1g} modes in Y 1:2:3, the highest-frequency one of 504 cm^{-1} is clearly associated with the light O_z atoms. Note that in Y 1:2:3, the O_z atom is bonded on one side to a Cu-O plane, and on the other side to a Cu atom that is part of a Cu-O chain, instead of a heavy Bi or Tl atom in the previously discussed materials. Yet this results in a fairly close frequency correspondence.

The 108-cm^{-1} mode found in Y 1:2:3 must be associated with the heavy Ba atoms which can vibrate in an A_{1g} mode (labeled 108 Ba in Table II). The atomic environment of Ba in Y 1:2:3 is different from that found in the materials discussed previously, and in that sense it should not be directly compared to the previously discussed heavy atom vibrations.

Tl 1:2:3. This material has a structure very similar to that of Y 1:2:3. Four of the five allowed phonon frequencies have been reported (Table II). Since the structures are so similar, the labeling of the various phonons by analogy with Y 1:2:3 is straightforward.

It is interesting to note that the largest phonon frequency differences between this material and Y 1:2:3 should come about when the chain Cu atom is replaced by a heavy Tl atom, and the Y atom is replaced by a lighter Ca atom. However, at these sites, Tl or Ca atom motion is not allowed in any Raman-active mode. Nevertheless, some large frequency changes should be expected in, for example, infrared-active modes.

In summary, we have shown the similarities and differences in the Raman spectra of the Cu-O plane containing superconductors. All of the phonon modes can be assigned, in a consistent manner, on the basis of a comparison of the structures and group theory, with the exception of the 92-cm^{-1} mode in Tl($n=3$). The similarity of the Raman spectra of superconducting and nonsuperconducting Bi($n=1$) shows that the occurrence or absence of superconductivity in this compound is probably not due to structural changes.

Finally, a recent lattice-dynamics calculation[21] for Bi($n=2$) presents the $k=0$ results (including the Raman- and infrared-active modes). The ordering of the calculated A_{1g} mode frequencies is in good agreement with our results. The two highest-frequency modes (calculated values 493 and 517 cm^{-1}) involve primarily oxygen atom motion, as discussed in this paper. The two midfrequency modes (calculated values 182 and 387 cm^{-1}) arise from the Cu-O plane and are mostly due to Cu(pl) and O(pl) motion, respectively. The lowest-frequency modes (calculated values 87 and 167 cm^{-1}) are basically similar to those discussed here, but have slightly more complicated eigenvectors. This type of lattice-dynamic calculation is helpful in the understanding of these complicated materials, and hopefully will be extended to other materials with a different number of Cu-O planes.

---

[*] Permanent address: Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Grenoble, France.

[1] For a short review, see A. Khurana, Phys. Today **41** (No. 4), 21 (1988).

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

[3] B. Morosin, D. C. Ginley, P. F. Hlava, M. J. Carr, R. J. Baughman, J. E. Schirber, E. L. Venturini, and J. F. Kwak, Physica C **152**, 413 (1988); S. S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, R. Beyers, and S. La Placa, Phys. Rev. Lett. **61**, 750 (1988).

[4] C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

[5] P. Strobel, K. Kelleher, F. Holtzberg, and T. Worthington, Physica C **156**, 434 (1988).

[6] G. V. Chandrashekhar and M. W. Shafer (unpublished).

[7] Z. V. Popovic, C. Thomsen, M. Cardona, R. Liu, G. Stanisic, R. Kremer, and W. Konig, 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] G. Burns, G. V. Chandrashekhar, F. H. Dacol, and M. W. Shafer, Solid State Commun. **68**, 67 (1988); W. H. Weber, C. R. Peters, B. M. Wanklyn, C. Chen, and B. E. Watts, *ibid.* **68**, 61 (1988).

[10] H. Rauh and R. Geich, Phys. Status Solidi (b) **127**, 55 (1985); H. Bürger, K. Strobel, R. Geick, and W. Mülle-Lierheim, J. Phys. C **9**, 4213 (1976); K. Strobel and R. Geick, *ibid.* **15**, 2105 (1982); H. Rauh, R. Geick, N. Lehner, J. Bouillot, and G. Eckold, Phys. Status Solidi (b) **115**, 463 (1983).

[11] J. Prade, A. D. Kulkarni, F. W. de Wett, W. Kress, M. Cardona, R. Reiger, and U. Schroder, Solid State Commun. **64**, 1267 (1987).

[12] K. F. McCarty, D. S. Ginley, D. R. Boehme, R. J. Baughman, and B. Morosin, Solid State Commun. **68**, 77 (1988).

[13] The complete of $k=0$ phonon modes for Tl($n=3$) is $7A_{1g}+B_{1g}+8E_g+9A_{2u}+2B_{2u}+11E_u$.

[14] G. Burns, F. H. Dacol, F. Holtzberg, and D. Kaiser, Solid State Commun. **66**, 217 (1988).

[15] S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Price, and D. M. Ginsberg, Phys. Rev. B **37**, 5920 (1988).

[16] C. Thomsen, M. Cardona, B. Gegenheimer, R. Liu, and A. Simon, Phys. Rev. B **37**, 9860 (1988).

[17] F. E. Bates and J. E. Eldridge, Solid State Commun. **64**, 1435 (1987).

[18] W. Kress, U. Schroder, J. Prade, A. D. Kulkarni, and F. W. de Wett, Phys. Rev. B **38**, 2906 (1988); R. Liu, C. Thomsen, W. Kress, M. Cardona, B. Gegenheimer, F. W. de Wette, J. Prade, A. D. Kulkarni, and U. Schroder, *ibid.* **37**, 7971 (1988).

[19] K. F. McCarty, D. S. Ginley, D. R. Boehma, R. J. Baughman, E. L. Venturini, and B. Morosin, Physica C **156**, 119 (1988).

[20] G. Burns, G. V. Chandrashekhar, F. H. Dacol, and P. Strobel, Phys. Rev. B **39**, 775 (1989).

[21] J. Prade, A. D. Kulkarni, F. W. de Wette, U. Schröder, and W. Kress, Phys. Rev. B (to be published).