Vibrational properties of Bi_2CuO_4

Z. V. Popović,* G. Kliche, M. Cardona, and R. Liu

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 80 06 65,
D-7000 Stuttgart 80, Federal Republic of Germany
(Received 18 August 1989)

We report both polarized Raman and unpolarized infrared-reflectivity spectra of Bi_2CuO_4. $5A_{1g}$, $4B_{2g}$, $6E_g$, and 14 ir modes are clearly observed. The assignment of the observed Raman modes is given according to Cartesian symmetry coordinates and preliminary force-constant calculation on the basis of a rigid-ion model and by comparison with the spectra of the isostructural compound Bi_2PdO_4. Similarities between vibrational properties of Bi_2CuO_4 and high-T_c superconducting oxides are discussed.

I. INTRODUCTION

Bi_2CuO_4 is a quasi-one-dimensional oxide system with a linear-chain magnetic behavior.[1] This oxide has a tetragonal[1-4] crystal structure with isolated CuO_4 square-planar units of Cu^{2+} ions which are stacked one on top of another in a staggered manner along the c axis. A schematic representation of the crystal structure of Bi_2CuO_4 projected along [001] and [010] is given in Fig. 1.[2] The arrangement of Bi atoms in (001) plane (at $z = \frac{1}{4}$

(a)

(b)

FIG. 1. Crystal structure of Bi_2CuO_4 in the (a) (001) and (b) (010) plane which is drawn using as unit-cell parameters ($a=8.51$ Å, $c=5.814$ Å, space group $P4/ncc$, $Z=4$) given in Ref. 2. The numbers on these figures are the corresponding distances (in Å) between Bi, Cu, and O atoms. $\bar{1}$ is the center of inversion.

or $\frac{3}{4}$) is rhombic with the nearest-neighbor Bi-atom spacing of 4.05 Å (in plane) and 3.51 Å (between planes). The Cu-O spacing in the CuO_4 squares is about 2 Å and the Cu-Cu spacing between two Cu^{2+} ions along the c axis is 2.9 Å ($=c/2$). Each Bi atom is tetrahedrally surrounded by four oxygen atoms. These deformed tetrahedra are connected via a common edge that forms $(BiO_2)_n$ chains along the c axis. The spacing between Bi and O lies between 2.12 and 2.73 Å [see Fig. 1(a)]. Two different space groups have been reported for the crystal structure of Bi_2CuO_4: $I4$ (C_4^5) (Ref. 3) and $P4/ncc$ (D_{4h}^8).[2,4] It is claimed in Ref. 3 that the Cu^{2+} ions have two distinguishable sites ($I4$ space group) while in Ref. 2 it is shown that there is only one unique Cu site so that the Cu-Cu distances are all uniform ($P4/ncc$ space group). All other crystal structure parameters of Bi_2CuO_4 are practically the same in both works. Recently, an electron diffraction and magnetic susceptibility study of this compound has been performed,[1] but the previously reported[2-4] ambiguity regarding its space group could not be resolved. In this paper we report polarized Raman spectra of Bi_2CuO_4 single crystals and far-infrared spectra of ceramic samples. The factor-group analysis for both space groups is discussed, and normal modes of vibrations are presented. Similarities between vibrational properties of Bi_2CuO_4 and high-T_c superconducting oxides are discussed.
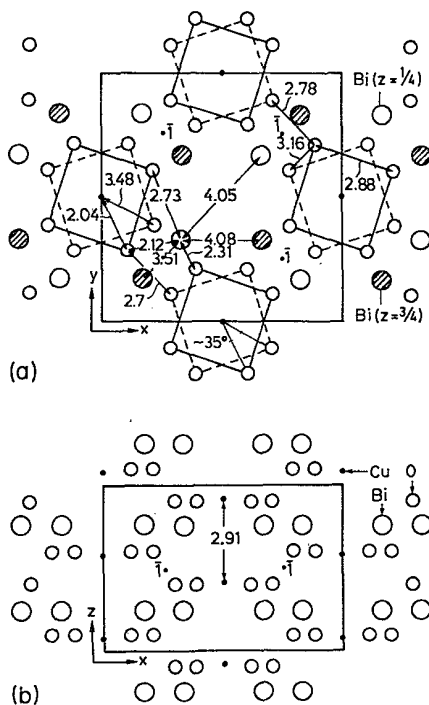
II. EXPERIMENT

The samples of Bi_2CuO_4 were obtained by solid-phase reaction of CuO and Bi_2O_3 (in a molar ratio of 1:1). The initial oxides (99.95% purity, Ventron, G.m.b.H., Karlsruhe, FRG) were well mixed and annealed in air at 800 °C for 4 days. The powder obtained, with polycrystalline grains, was first checked by x-ray diffraction and then reground and reheated (in an alumina crucible) to 860 °C. The melt was held at this temperature for several hours, and then cooled to 600 °C at about 5 °C/h. The single crystals so obtained were platelike in habit, with the c axis normal to the major surface. Crystal dimensions were typically 1.5 mm on edge and 300 μm thick.

The infrared-reflection measurements were performed, both at room and liquid-helium temperature, using a Bruker (Karlsruhe, FRG) IFS-113-V spectrometer in the spectral range from 30 to 650 cm^{-1}. Raman spectra were obtained in backscattering geometry at 300 K. The excitation source was the 5145-Å line of an Ar^+-ion laser. The monochromator was a SPEX Industries, Inc. (Metuchen, NY, USA) model 1403 with a Mepsicron (Surface Science, Mountain View, CA, USA) detection system. For the spectral range below 70 cm^{-1} the same monochromator, with a standard photon-counting system, was used.

III. FACTOR-GROUP ANALYSIS (FGA)

As mentioned earlier, Bi_2CuO_4 crystallizes in a tetragonal space group with four formula units comprising 28 atoms in all. In the $I4$ space group the Cu_I and Cu_{II} atoms have C_4 (2a) site symmetry while Bi, O_I, and O_{II} have C_1 (8c) site symmetries. Since the number of formula units per primitive cell[5] is two, the total number of vibrational modes at $k=0$ is 42 (including the acoustic ones). Using the tables given by Rousseau $et\ al.$[6] and subtracting the acoustic modes $(1A+1E)$ we obtain the following irreducible representations of $k=0$ modes of Bi_2CuO_4 (for the $I4$ space group):

$$\Gamma_{opt}=10A+9B+10E . \tag{1}$$

The $9B$ modes are only Raman active $(\alpha_{xx}-\alpha_{yy},\alpha_{xy})$ while the $10A$ $(\alpha_{xx}+\alpha_{yy},\alpha_{zz};E\|\hat{z})$ and $10E$ $(\alpha_{xz},\alpha_{yz};E\|\hat{x},E\|\hat{y})$ modes are both Raman and infrared active.

The $P4/ncc$ space group is centrosymmetric, hence the modes should be odd (u) or even (g), with mutually exclusive Raman and ir activities. The Cu, Bi, and O atoms have C_4 (4c), C_2 (8f), and C_1 (16g) site symmetries, respectively. The irreducible representations of the corresponding phonons are

$$\Gamma^{Cu}=A_{1g}+A_{1u}+A_{2g}+A_{2u}+2E_g+2E_u , \tag{2a}$$

$$\Gamma^{Bi}=A_{1g}+A_{1u}+2A_{2g}+2A_{2u}+2B_{1g}+2B_{1u}+B_{2g}$$
$$+B_{2u}+3E_g+3E_u , \tag{2b}$$

$$\Gamma^O=3A_{1g}+3A_{1u}+3A_{2g}+3A_{2u}+3B_{1g}+3B_{1u}+3B_{2g}$$
$$+3B_{2u}+6E_g+6E_u . \tag{2c}$$

Summarizing the representations which are given in Eqs. (2a)–(2c) and deleting acoustic $(A_{2u}+E_u)$ and silent $(A_{2g},A_{1u},B_{1u},B_{2u})$ modes, we obtain the irreducible representation of the Raman- and ir-active modes of Bi_2CuO_4 with the space group $P4/ncc$:

$$\Gamma_{opt}=5A_{1g}+5B_{1g}+4B_{2g}+11E_g+5A_{2u}+10E_{2u} . \tag{3}$$

Table I lists these phonons, their symmetries, the atoms involved, and the polarizations necessary for their observation.

IV. RESULTS AND DISCUSSION

Figure 2 shows the polarized Raman spectra of Bi_2CuO_4 at 300 K. $5A_{1g}$, $4B_{2g}$, and $6E_g$ modes are clearly observed. Far-infrared-reflection spectra of Bi_2CuO_4 at 300 and 10 K are shown in Fig. 3. These spectra are measured from ceramic samples because the dimensions of our single crystals were not large enough for far-infrared-reflection measurements. We observed 14 oscillators in all, with E_u or A_{2u} symmetry. The numbers in Fig. 3 are the TO (LO) frequencies of corresponding oscillators which are obtained using Kramers-Kronig analysis performed on the reflection spectrum of Bi_2CuO_4 measured at 10 K.

Comparing the number of experimentally observed Raman-active modes with FGA predictions [Eqs. (1) and (3)] we conclude that the space group of Bi_2CuO_4 is $P4/ncc$. Namely, according to the FGA of the $I4$ space group [Eq. (1)] for $(xx+yy$ or $zz)$ polarization we expect to see 10 A modes. Actually, only five modes are observed for this polarization, in agreement with FGA results for the $P4/ncc$ space group [see Table I, or Eq. (3)]. The same is also valid for (xy) polarization. In the case of $I4$ space group, nine B modes exist. We observed only 4 modes for this polarization according to the prediction of FGA for the $P4/ncc$ space group. Further, Eq. (1) predicts 10 A and 10 E infrared and Raman doublets.

TABLE I. Zone-center modes of Bi_2CuO_4 $[P4/ncc\ (D_{4h}^8),\ Z=4]$.

		Number of modes			Activity	
	Total	Acoustic	Optic	Atoms involved	Raman	ir
A_{1g}	5		5	all	$xx+yy,zz$	
A_{1u}	5			all		
A_{2g}	6			all		
A_{2u}	6	1	5	all		$E\|z$
B_{1g}	5		5	Bi,O	$xx-yy$	
B_{1u}	5			Bi,O		
B_{2g}	4		4	Bi,O	xy	
B_{2u}	4			Bi,O		
E_g	11		11	all	xz,yz	
E_u	11	1	10	all		$E\|x,E\|y$

Unfortunately, we have no polarized infrared spectra and direct symmetry correspondence between observed infrared (Fig. 3) and Raman (Fig. 2) spectra is not possible. Nevertheless, the number of experimentally observed infrared modes (14) is closer to the prediction of 15 [Eq. (3)] than that of 20 [Eq. (1)]. Although a number of the observed LO and TO frequencies can be construed to be nearly degenerate with A- and E-like Raman modes (a fact which would speak for the lack of inversion symmetry, i.e., $I4$ space group) several Raman peaks of A and E character, in particular those at 50, 190, and 260 cm^{-1}, have no counterpart in the ir spectra. Moreover, no Raman peaks of A and E character (i.e., which should be ir active in $I4$ group) show any signs of an LO-TO splitting. Thus, we conclude that the observed spectra of Bi_2CuO_4 are to be interpreted within the $P4/ncc$ space group.

Figure 2(a) shows Raman spectra of Bi_2CuO_4 for $z(xx)\bar{z}$ and $y(zz)\bar{y}$ polarization together with the normal modes of the A_{1g} vibrations of Bi_2CuO_4. These normal modes as well as the mode assignment were obtained using preliminary lattice-dynamical calculations for Bi_2CuO_4 performed on the basis of a rigid-ion model.[7]

The A_{1g} mode at 50 cm^{-1} originates from in-plane Bi-

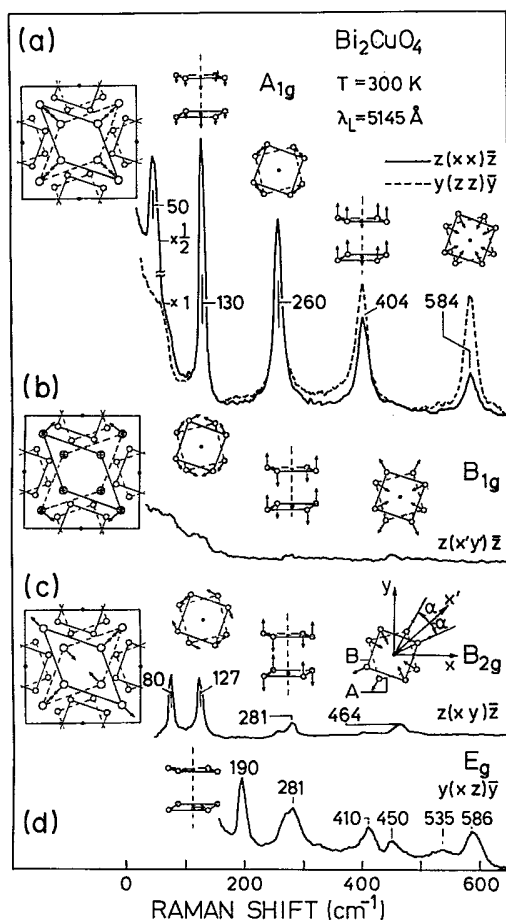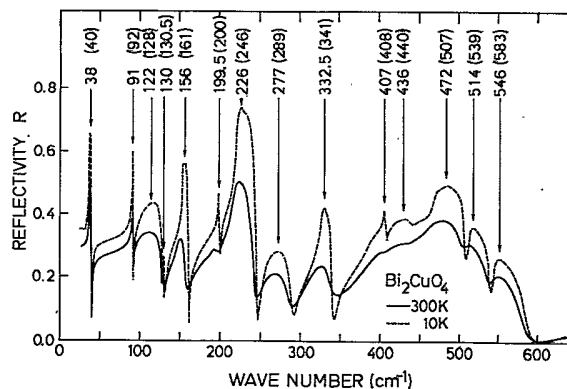FIG. 3. Far-infrared nonpolarized-reflectivity spectra of Bi_2CuO_4 polycrystalline sample at 300 K (solid line) and 10 K (dashed line). Numbers on the arrows pointing peaks are the values of the TO (LO) frequencies of corresponding oscillators obtained by Kramers-Kronig analysis of reflectivity spectra measured at 10 K.

Bi motion. The polarization of this mode, if assumed to be of the Bi—Bi bond-stretching type, should lie mainly in the $\langle 110 \rangle$ directions. This explains the strong intensity of this mode for the (xx) configuration as compared with the (zz) configuration. The next A_{1g} mode, at 130 cm^{-1}, originates from translational vibrations of the CuO_4 planes along z as shown in Fig. 2(a).

The A_{1g} mode at 260 cm^{-1} corresponds to the rotation of two stacked $[CuO_4]$ squares in opposite directions. If one considers the Bi environment, this mode can be described as a O—Bi—O bending, whereas the 404 cm^{-1} mode has Bi—O stretching character, mixed with an out-of-plane bending vibration of the $[CuO_4]$ squares. The 584-cm^{-1} A_{1g} mode is mainly an in-plane breathing of the $[CuO_4]$'s. The assignment of the highest-frequency A_{1g} mode of Bi_2CuO_4 as a breathing mode of the isolated $[CuO_4]$ squares is in good agreement with previously published data for this mode of $[CuO_4]$ planar squares which, as similar units, are found in copper-oxalato and -acetylacetonato complexes.[8] The enhancement of intensity of this mode for (zz) polarizations leads to the conclusion that the normal mode of this vibration has components of oxygen motion in z direction also (like the A_{1g} vibration at 404 cm^{-1}), which may come from coupling of oxygen vibrations of two $[CuO_4]$ squares along the z axis (via O—Bi—O bridges). Normal coordinate calculations[7] show indeed some contributions in the z direction. But because of the lack of accurate Cu-O and Bi-O potentials (there are large differences in the literature[9-11]), and because of the unknown A_{2u} and E_u TO- and LO-phonon modes, a refinement of the calculations is necessary and in progress (a large range of Cu-O and Bi-O force constants was studied with the result that the breathing-mode character dominates for this highest-frequency A_{1g} Raman mode). Although the shortest Bi-O distance in Bi_2CuO_4 is 2.12 Å [see Fig. 1(a)] we conclude that the highest A_{1g} mode of Bi_2CuO_4 at 584 cm^{-1} is mainly the breathing vibration of the isolated $[CuO_4]$ square, because the Bi-O spacing is the same as in Bi_2O_3

FIG. 2. Polarized Raman spectra of Bi_2CuO_4 at 300 K together with normal modes of some of the observed vibrations.

(Ref. 12) which has the highest-frequency Raman mode at 513 cm^{-1}.[13]

Our assignments of the A_{1g} Raman-active modes of Bi$_2$CuO$_4$ were checked also by comparing with Raman spectra of a ceramic sample of the isostructural Bi$_2$PdO$_4$.[7] The exchange of the Cu atom by the heavier palladium causes a shift of the 130- and 404-cm^{-1} modes towards smaller wave numbers. The other A_{1g} modes appear at the same frequencies in both compounds, in support of our conclusions.

According to Table I, we expect to see the B_{1g} modes for $z(x'y')\bar{z}$ polarization. However, no modes were clearly identified for this polarization [Fig. 2(b)] for the reasons discussed below.

The B_{2g} symmetry modes of Bi$_2$CuO$_4$ are shown in Fig. 2(c). According to Eq. (2) there are one Bi and three oxygen modes of B_{2g} symmetry. The mode at 80 cm^{-1} is an in-plane bond-bending vibration of the Bi rhombohedra, as indicated in Fig. 2(c). The next three B_{2g} modes originate mainly from oxygen motion. The mode at 127 cm^{-1} is a bond-bending oxygen mode (deformation of the CuO$_4$ squares), the mode at 281 cm^{-1} also corresponds to CuO$_4$ deformation with oxygen motion in the z direction while the peak at 464 cm^{-1} is an in-plane bond-stretching deformation of the [CuO$_4$] squares, as indicated in Fig. 2(c).

By analyzing the normal modes of these vibration, we obtain that for $\alpha=0$ [Fig. 2(c), right] the Raman tensor of the motion of the square labeled B is (with respect to x,y axes)

$$\underline{R}_B = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

for $\alpha \neq 0$, but small (as is the case here). We expand this tensor to first order in α and obtain

$$\underline{R}_B = \begin{bmatrix} -\alpha & 1 & 0 \\ 1 & \alpha & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \underline{R}_A = \begin{bmatrix} \alpha & 1 & 0 \\ 1 & -\alpha & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

where $\underline{R}_A$ corresponds to the square labeled A in Fig. 2(c).

Thus, the total Raman tensor for B_{2g} mode is

$$\underline{R}(B_{2g}) = \underline{R}_B + \underline{R}_A = \begin{bmatrix} 0 & 2 & 0 \\ 2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

For the B_{1g} modes we have to subtract the two Raman tensors given above ($\underline{R}_A - \underline{R}_B$) and obtain

$$\underline{R}(B_{1g}) = \begin{bmatrix} 2\alpha & 0 & 0 \\ 0 & -2\alpha & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

Note that $\alpha \simeq 15°$ ($\simeq 0.26$ rad); hence, $2\alpha = 0.5$. So the signals for these B_{1g} modes should be $(0.5/2)^2 = 0.06$ times smaller than for the B_{2g} configuration. Similar arguments hold for the other B_{1g} modes, which explain their small intensity in the Raman spectrum [Fig. 2(b)].

The lowest spectrum in Fig. 2 contains the E_g modes. This spectrum [for $y(xz)\bar{y}$ geometry] was obtained from a surface normal to the layers, whose quality is bad when compared to the layer surface. Because of this, low-frequency modes are masked by elastically scattered light and only six E_g modes are clearly seen. The mode at 190 cm^{-1} originates from Cu-Cu motion as indicated in Fig. 2(d). This assignment was made on the basis of the strong frequency shift obtained by replacing Cu with Pd in Bi$_2$PdO$_4$.[7] The next mode in (xz) polarization appears at the same frequency as the out-of-plane B_{2g} mode [Fig. 2(c)] and thus, its assignment to an E_g mode is not reliable. The next four E_g modes at 410, 450, 535, and 586 cm^{-1} originate from bond-stretching oxygen vibrations of the [CuO$_4$] squares.

From the unpolarized infrared spectra of ceramic samples shown in Fig. 3 it is not possible to resolve the A_{2u} or E_u symmetry of the 14 observed modes, and therefore, we are not able to assign the observed peaks to normal modes as was done in the case of polarized Raman spectra. Hence, the assignment of ir modes of Bi$_2$CuO$_4$ is given by comparison with analogous spectra of isostructural Bi$_2$PdO$_4$ (Fig. 4). At first glance these spectra can be divided into three regions. One of them is above 400 cm^{-1}, where the substitution of Cu by the approximately two times heavier Pd does not cause any frequency change. All of these modes are bond-stretching modes of the [CuO$_4$] squares with motion mainly of oxygen atoms. No frequency shift is observed also in the spectral range below 130 cm^{-1}. Thus we assign these modes to vibrations of the bismuth atoms. In the spectral range from 150 to 400 cm^{-1} all modes (except that at 277 cm^{-1}) shift by 10–20 cm^{-1} upon replacing Cu by Pd. These modes thus originate from bond-bending vibrations of [CuO$_4$] squares, which may be coupled with Bi—O stretching and O—Bi—O bending modes.

It may be of interest to look for similarities between the spectra of Bi$_2$CuO$_4$ and Bi- or Y-based high-T_c superconductors.[14] Even though the structures are different [the CuO$_4$ squares in Bi$_2$CuO$_4$ are isolated and in Y-Ba-Cu-O or Bi-Ca-Sr-Cu-O mutually connected] it is possible to find some similarities in their vibrational properties. For example, two ir-active modes at 277 and 332 cm^{-1} of Bi$_2$CuO$_4$ are close in frequencies to the ir modes of

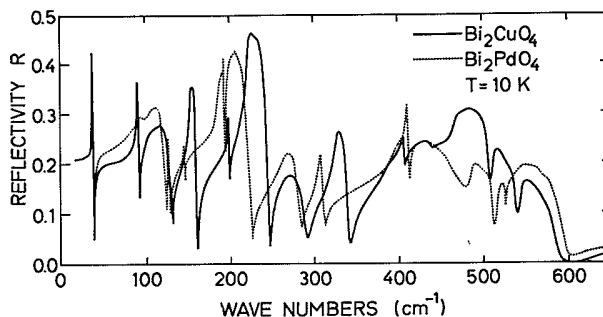FIG. 4. Far-infrared nonpolarized-reflectivity spectra of Bi$_2$CuO$_4$ (solid line) and Bi$_2$PdO$_4$ (dashed line) measured at 10 K.

YBa$_2$Cu$_3$O$_7$ at 270 and 310 cm^{-1}. In YBa$_2$Cu$_3$O$_7$ these modes probably are out-of-plane oxygen motions [(CuO$_2$) plane] (Ref. 15) and may correspond to the same oxygen motion of CuO$_4$ squares in Bi$_2$CuO$_4$. Furthermore, an analog of the low-frequency Raman mode of Bi in Bi$_2$CuO$_4$ at 50 cm^{-1} is also found in Bi$_2$CaSrCu$_2$O$_8$.[16] Finally, the B_{1g} mode of Bi$_2$CaSrCu$_2$O$_8$ has an eigenvector[14] similar to the B_{2g} of Bi$_2$CuO$_4$ and both appear at the same frequency [282 cm^{-1} in Bi$_2$CaSrCu$_2$O$_8$, and 281 cm^{-1} in Bi$_2$CuO$_4$, in Fig. 2(c)].

ACKNOWLEDGMENTS

*Permanent address: Institute of Physics, P.O. Box 57, YU-11000 Belgrade, Yugoslavia.

[1]K. Sreedhar, P. Ganguly, and S. Ramasesha, J. Phys. C **21**, 1129 (1988).

[2]J. C. Boivin, J. Tréhoux, and D. Thomas, Bull. Soc. Fr. Mineral. Crystallogr. **99**, 193 (1976).

[3]R. Arpe and Hk. Müller-Buschbaum, Z. Anorg. Allg. Chem. **426**, 1 (1976).

[4]B. G. Kakhan, V. B. Lazarev, and I. S. Shaplygin, Russ. J. Inorg. Chem. **24**, 922 (1979).

[5]W. G. Fateley, F. R. Dollish, N. T. McDevitt, and F. F. Bentley, *Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: The Correlation Method* (Wiley, New York, 1972), p. 2.

[6]D. L. Rousseau, R. P. Bauman, and S. P. S. Porto, J. Raman Spectrosc. **10**, 253 (1981).

[7]G. Kliche (unpublished).

[8]K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1978), pp. 234 and 251.

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

[10]H. C. Gupta, Physica (Amsterdam) C **157**, 257 (1981).

[11]S. Mase and T. Yasuda, J. Phys. Soc. Jpn. **58**, 658 (1989).

[12]H. A. Harwig, Z. Anorg. Allg. Chem. **444**, 151 (1978).

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

[14]C. Thomsen and M. Cardona, in *Physical Properties of High Temperature Superconductors I*, edited by D. M. Ginsberg (World Scientific, Singapore, 1989), p. 409.

[15]M. Bauer, L. Genzel, and Th. Wolf, Solid State Commun. (to be published).

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