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Raman-active phonons in R_2BaCuO$_5$ (R =La,Nd)

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The polarized Raman spectra of tetragonal La_2BaCuO_5 and Nd_2BaCuO_5 have been measured in various scattering configurations. The Raman lines corresponding to $(3A_{1g}+1B_{1g}+3B_{2g}+3E_g)$ Raman-active modes expected for the $P4/mbm$ structure have been observed. It has been found that the A_{1g} and B_{2g} modes, arising as Davydov's partners from the internal stretching vibrations of oxygen within the CuO_4 structural units, have the same frequencies. This justifies the molecular-site group analysis used parallel to the factor-group analysis to assign the particular phonon lines to definite atomic vibrations.

INTRODUCTION

Most compounds with nominal composition R_2BaCuO_5 (R=rare earth or Y) have an orthorhombic structure described by the space group *Pbnm*.[1] The exceptions are La_2BaCuO_5 (La 2:1:1) and Nd_2BaCuO_5 (Nd 2:1:1) which are tetragonal with space group $P4/mbm$.[2–5] Compounds with a structure of La 2:1:1, namely, the solid solutions $La_{4-2x}Ba_{2+2x}Cu_{2-x}O_{10-2x'}$ have been characterized by Michel, Er-Rakho, and Raveau.[2] These results have recently been supplemented by the results of structural and magnetic studies of Mizuno, Masuda, and Hirabayashi[3] on $La_{4-x}Ba_{2+x}Cu_2O_{10}$. In this Brief Report was found that La 2:1:1 is an insulating ferromagnet at low temperatures. Ba substitution in this compound does not lead to metal-insulator transition but a certain evidence for the hole doping effect as observed. The as established unit cell of La 2:1:1 and Nd 2:1:1 is shown in Fig. 1. The framework is built up from edge- and face-sharing BaO_{10} and $La(Nd)O_8$ polyhedra and isolated CuO_4 planar groups aligned in the $x'z$ planes, where x' is the [110] crystallographic direction.

All R_2BaCuO_5 compounds in comparison with $RBa_2Cu_3O_x$ ones have strong Raman spectra. Therefore presence of small amounts of this phase in $RBa_2Cu_3O_x$ ceramics changes considerably their spectra. The Raman spectra of R_2BaCuO_5 with orthorhombic (*Pbnm*) structure have been reported by Loo, Burns, and Xidis.[6] Abrashev and Ilie[7] assigned all A_g lines to definite atomic vibrations using polarized measurements. The Raman spectrum of Nd_2BaCuO_5 has been reported by Loo, Burns, and Xidis[6] without discussion of the line assignment. Baran *et al.*[8] have measured the nonpolarized Raman and IR spectra of Nd_2BaCuO_5 and discussed the origin of some of the Raman lines within the framework of a molecular model for the single CuO_4 group. As a whole, however, the phonon mode analysis and the line assignment have not been completed.

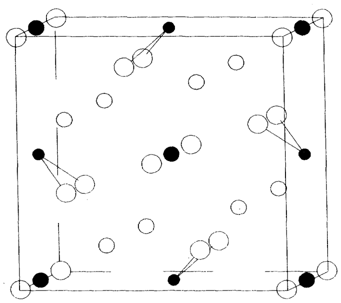


FIG. 1. The unit cell of the La(Nd) 2:1:1 structure. The light hatching circles are the La(Nd) atoms, the black hatching circles are Ba atoms, big empty circles are the O atoms, small black circles are Cu atoms. a-b plane of the structure coincides with the plane of the page.

In this work we present the results of our measurements of polarized Raman spectra of La 2:1:1 and Nd 2:1:1 in some of the most informative scattering configurations. The line assignment is done on the basis of factor-group and molecular-site group analysis for each set of atoms and for CuO_4 groups in the unit cell, respectively, and of the polarization properties of the modes. The additional lines and bands with unclear origin in the spectra of La 2:1:1 and Nd 2:1:1 are observed.

EXPERIMENT

The La_2BaCuO_5 and Nd_2BaCuO_5 samples were prepared following a standard solid state reaction technique.[3–6,8] Appropriate amounts of Nd_2O_3, La_2O_3, $BaCO_3$, and CuO were mixed and calcinated in air at 950° C for 15 h. The as obtained materials were ground and pressed into 1 g pellets. The La pellets were annealed at 960° C for 15 h. As long as the size of microcrystals in the ceramics was small and unsufficient for polarized micro-Raman measurements, the pellets were reannealed at 1050° C for three days. As a result the size of La 2:1:1 microcrystals increased but additional impurity phases $La_{2-x}Ba_xCuO_4$ and BaO appeared. For the Nd 2:1:1 pellet the annealing at 1000° C for three days gave nearly single phase samples.

The lattice parameters of the La 2:1:1 phase, as calculated from the x-ray powder diffractometry (Cu $K\alpha$ radiation, URD-6 powder diffractometer), are $a=6.849$ Å,

$c = 5.871$ Å, which corresponds to $La_{3.9}Ba_{2.1}Cu_2O_{10}$ stoichiometry.[3] For the "impurity" $La_{2-x}Ba_xCuO_4$ phase, they are, respectively, $a = 3.784$ Å, $c = 13.368$ Å, which corresponds to $x = 0.15$,[9] i.e., to the "Bednorz and Müller" phase.

The SEM microprobe analysis (Philips 515, EDAX 9100) confirmed that the ratio R:Ba:Cu (R=La,Nd) is close to the nominal 2:1:1. It is worth noting that for a pellet of a nominal composition $La_{1.5}Ba_{1.5}CuO_5$, the microcrystals of the main phase were of the same $La_{3.9}Ba_{2.1}Cu_2O_{10}$. For the latter ceramics, however, an increase of BaO in favor of $La_{2-x}Ba_xCuO_4$ was observed.

The Raman spectra were measured at room temperature using a micro-Raman setup containing a triple multichannel spectrometer Microdil 28 equipped with an optical microscope. A 100× objective was used to focus the incident beam in a spot of about 1 μm diameter on the polished surface of the pellet and to collect the backward scattered light. Both 488.0 and 514.5 nm Ar^+ laser lines were used for the excitation. As the microcrystals are of a needlelike shape with c axis along the long edge,[3] it was easy to identify the [001] direction on the crystal surface. The microcrystals exhibiting ab plane on the polished surface of the pellet were seen as squares with edges supposed to be along the [110] and [$\bar{1}$10] directions [it is natural that the (110) plane is a plane of easy cleavage as the tightly bound CuO_4 squares lie in this plane]. The polarized Raman spectra confirmed such a supposition.

FACTOR-GROUP AND MOLECULAR-SITE ANALYSIS

The unit cell of La_2BaCuO_5 and Nd_2BaCuO_5 (space group $P4/mbm$) contains two formula units. There are five sets of equivalent atoms; namely, four La(Nd) atoms occupying sites of C'_{2v} symmetry, two Ba atoms (C_{4h}), two Cu atoms (D'_{2h}), two O1 atoms (C_{4h}), and eight O2 atoms (C_s^d). Only motions of La(Nd) and O2 atoms participate to the in total 12 ($3A_{1g}+2B_{1g}+3B_{2g}+4E_g$) Raman-active modes. Of the rest Γ-point phonon modes 15 ($5A_{2u}+10E_u$) are IR active, 10 ($2A_{2g}+3A_{1u}+4B_{1u}+B_{2u}$) are silent, and 2 ($A_{2u}+E_u$) are acoustical modes. The Raman-active A_{1g} modes have to be observed in parallel xx, yy, and zz; the B_{1g}, in parallel xx and yy; B_{2g}, in crossed xy and yx, and E_g, in crossed xz, yz, zx, and zy polarizations of the exciting and scattered light, respectively.

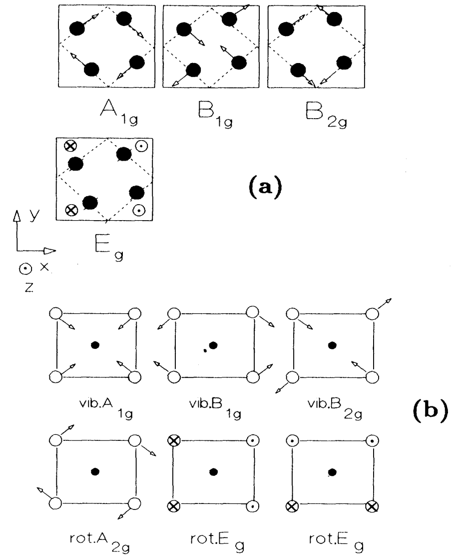
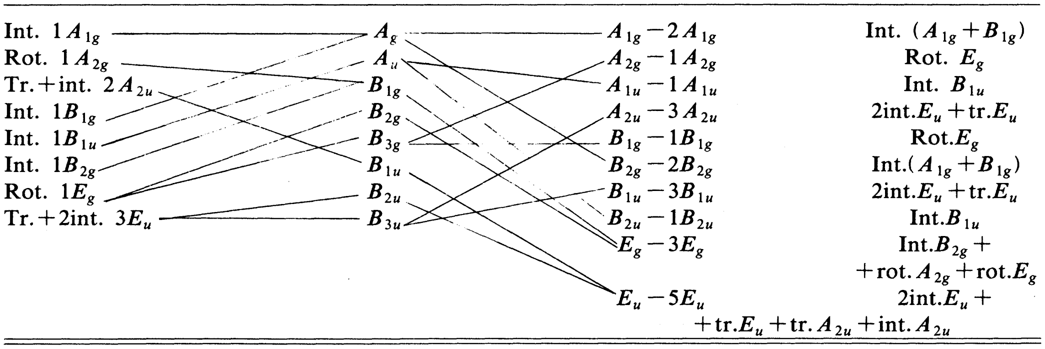


FIG. 2. The shapes of the Raman allowed normal modes for La(Nd) atoms in the unit cell (a) and the shapes of these modes in CuO_4 molecule give rise to Raman modes of O2 in the 2:1:1 crystal (b).

The atomic displacements for the four ($A_{1g}+B_{1g}+B_{2g}+E_g$) Raman-active modes related to La(Nd), as obtained from the symmetry coordinates,[11] are shown in Fig. 2(a). In order to analyze the normal vibrational modes related to displacements of O2, we will further treat the CuO_4 groups as isolated ones and will use the molecular-site group analysis.[10,11]

Table I shows the correlation between the symmetries of the vibrational modes of a free CuO_4 molecule (D_{4h} symmetry) and of the CuO_4 group (D_{2h}), Cu(D'_{2h}), and O2 (C_s^d) in the crystal lattice of R_2BaCuO_5 (R=La,Nd).

TABLE I. Correlation table connecting the modes of free CuO_4 molecule and modes of CuO_4 cluster in R_2BaCuO_5 (R=La,Nd) crystal $z_{\mathrm{molec}} \equiv x_{\mathrm{cryst}} + y_{\mathrm{cryst}}; x_{\mathrm{molec}} \equiv z_{\mathrm{cryst}}$.



Modes of CuO_4 free molecule D_{4h} symmetry	Site sym. of molec. in crystal D_{2h}	Sym. of crystal D_{4h}	Vibrational modes in crystal and their mol. origin
Int. $1A_{1g}$	A_g	$A_{1g}-2A_{1g}$	Int. $(A_{1g}+B_{1g})$
Rot. $1A_{2g}$	A_u	$A_{2g}-1A_{2g}$	Rot. E_g
Tr.+int. $2A_{2u}$	B_{1g}	$A_{1u}-1A_{1u}$	Int. B_{1u}
Int. $1B_{1g}$	B_{2g}	$A_{2u}-3A_{2u}$	2int.E_u+tr.E_u
Int. $1B_{1u}$	B_{3g}	$B_{1g}-1B_{1g}$	Rot.E_g
Int. $1B_{2g}$	B_{1u}	$B_{2g}-2B_{2g}$	Int.$(A_{1g}+B_{1g})$
Rot. $1E_g$	B_{2u}	$B_{1u}-3B_{1u}$	2int.E_u+tr.E_u
Tr.+2int. $3E_u$	B_{3u}	$B_{2u}-1B_{2u}$	Int.B_{1u}
		E_g-3E_g	Int.B_{2g}+ +rot.A_{2g}+rot.E_g
		E_u-5E_u	2int.E_u+ +tr.E_u+tr.A_{2u}+int.A_{2u}

Note, that when considering the CuO_4 group as a free molecule, the x and y directions are assumed perpendicular to the O2-O2 distances and the z direction is perpendicular to the plane of molecule. The symmetries of the vibrational modes for the free CuO_4 group are as follows: internal vibrations, $A_{1g}+A_{2u}+B_{1g}+B_{1u}+B_{2g}+2E_u$; rotations, $A_{2g}+E_g$, and translations, $A_{2u}+E_u$. Figure 2(b) shows the vibrational modes related to displacements of O2 atoms within the CuO_4 group which give rise to Raman-active phonons. The fully symmetric A_{1g} stretching vibration of an isolated molecule gives rise to a A_{1g},B_{2g} pair of Davydov's partners in the crystal (Davydov's partners appear because the elementary cell contain two CuO_4 groups on equivalent sites). The A_{1g} and B_{2g} counterparts correspond, respectively, to in-phase motion and out-of-phase motion (along the Cu-O bonds) of the equivalent O2 atoms of neighboring CuO_4 groups. As the Cu-O2 bond is the shortest one in R_2BaCuO_5 (R=La,Nd), one expects these A_{1g} and B_{2g} modes to be of highest frequency. Next in the order of decreasing frequency should be the E_g mode, originating from the internal B_{2g} vibrations, whereas the rest Raman-active modes, related to the rotational A_{2g} and E_g motions of the CuO_4 molecule should be of lower frequency. The internal antisymmetric B_{1g} bending vibration of the molecule gives rise to another A_{1g},B_{2g} Davydov's pair.

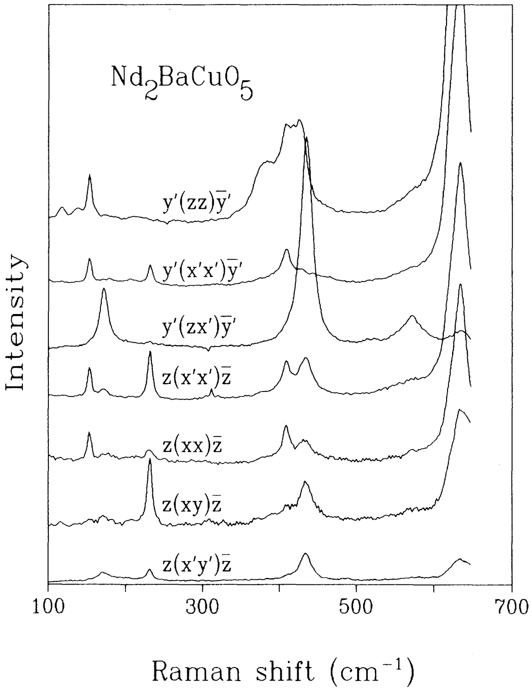


FIG. 3. Polarized Raman spectra obtained from $x'z$ surface of the Nd 2:1:1 crystal (the top three spectra) and from xy surface (the bottom four spectra).

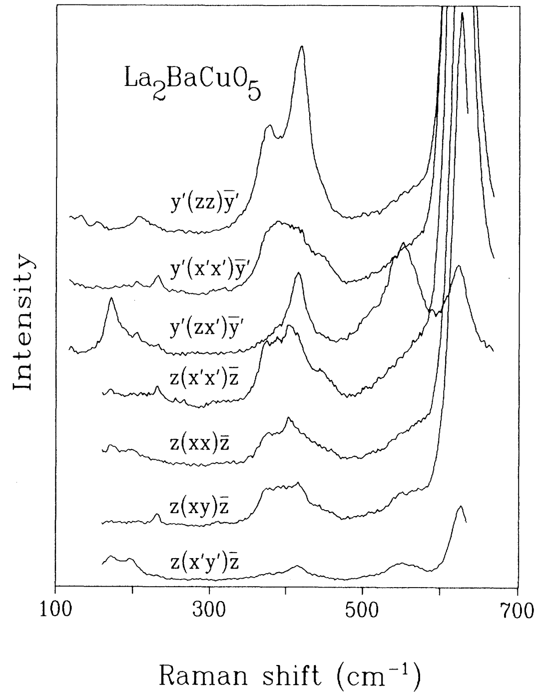


FIG. 4. Polarized Raman spectra obtained from $x'z$ surface of the La 2:1:1 crystal (the top three spectra) and from xy surface (the bottom four spectra).

RESULTS AND DISCUSSION

Figures 3 and 4 show the Raman spectra of Nd_2BaCuO_5 and La_2BaCuO_5 in various backward scattering configurations. We remind that x' and y' denote the [110] and [$\bar{1}$10] directions, whereas x,y, and z are [100], [010], and [001], respectively.

Table II summarizes the Raman line frequencies and their assignment to definite atomic vibrations. The assignment is made on the basis of polarization properties of the modes of different symmetry and taking into account that the modes involving vibrations of heavier Nd(La) atoms should be of lower frequency.

We assign the weak line at 154 cm^{-1} for La 2:1:1 (pro-

TABLE II. Observed peaks in Raman spectra of R_2BaCuO_5 (R=La,Nd).

Line	Nd 2:1:1	La 2:1:1	Symmetry	Assignment
1	634	627	$A_{1g}+B_{2g}$	02 Davydov pair
2	572	554	E_g	02
3	436	418	E_g	02
4	410	375	$A_{1g}+B_{2g}$	02 Davydov pair
5	231	231	B_{2g}	R
6		196	B_{1g}	R
7	173	173	E_g	R
8	152	154	A_{1g}	R
	410–430	375–415	Defect band	
	384	389	Defect	
	139	133	Defect	

nounced much better for Nd 2:1:1 at 152 cm^{-1}) to the A_{1g} vibrations of La(Nd). This line is observed for parallel and absent in crossed polarizations of the incident and scattered light. The line at 231 cm^{-1} is assigned to the B_{2g} mode of La(Nd) as it is observed in xy and $x'x'$ polarizations. The B_{1g} mode should appear alternatively to B_{2g}, i.e., with $x'y'$ and xx polarizations. We do observe such a line at 196 cm^{-1} for La 2:1:1 but not for Nd 2:1:1. The line at 173 cm^{-1} in the spectra of both phases could be assigned to the E_g mode of La(Nd) as it is most intensive in the $x'z$ spectra.

We suppose that the frequencies of A_{1g} and B_{2g} modes of O2, which are Davydov's partners, nearly coincide. For scattering from xy plane, the A_{1g} mode has to be observed in the xx and $x'x'$, but not in the xy and $x'y'$ spectra. The B_{2g} mode has to be observed in $x'x'$ and xy, but not in xx and $x'y'$ spectra. Combining these selection rules one concludes that, if the A_{1g} and B_{2g} lines are superimposed, the line intensity should be the strongest one in the $z(x'x')\bar{z}$, of intermediate value in the $z(xx)\bar{z}$ and $z(xy)\bar{z}$, and the negligible one in the $z(x'y')\bar{z}$ spectra. Indeed, the relative intensities of the lines at 634 and 375 cm^{-1} (for La 2:1:1) and at 627 and 410 cm^{-1} (for Nd 2:1:1) in the bottom four spectra of Figs. 3 and 4 are consistent with these expectations.

The lines at 554 and 418 cm^{-1} (for La 2:1:1) and at 572 and 436 cm^{-1} (for Nd 2:1:1) are strong in the $y'(x'z)\bar{y}'$ spectra and we assign them to the E_g modes involving O2 vibrations. We suppose that the origin of the first E_g mode is internal B_{2g} molecular vibration whereas for the second E_g mode, it is rotational E_g molecular vibration.

The shape and intensity of the band observed at 410–430 cm^{-1} for Nd 2:1:1 in zz polarization and at 375–415 cm^{-1} for La 2:1:1 in xx, $x'x'$, and xy polarizations do not depend neither on laser line nor on annealing conditions of the samples (possible oxygen nonstoichiometry) and its origin remain unclear.

CONCLUSION

In conclusion we measured the polarized Raman spectra of tetragonal La_2BaCuO_5 and Nd_2BaCuO_5 and identified 10 from 12 Raman-active modes expected for the $P4/mbm$ structure of these compounds. It was found that the A_{1g} and B_{2g} modes, which are Davydov's partners arising from the vibrations of O2 atoms in the CuO_4 squares, have the same frequencies. This justifies the molecular-site group analysis used to assign the particular phonon lines to definite atomic vibrations.

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