Infrared-Active Phonons in $La_{2-x}Sr_xCaCu_2O_6$

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We report results of a far-infrared reflectivity investigation of double-layer $La_{2-x}Sr_xCaCu_2O_6$ ceramics with Sr content x between 0.2 and 0.4. The frequencies of infrared-active phonon modes were determined and found to be close to the known ones of superconducting compounds with similar crystal structures.

The study of phonons has been becoming of increasing importance in high-temperature superconductors, ever since the discovery that phonon-frequency and linewidth changes in the superconducting state compared to the normal state may be used to determine the gap, as reported for $RBa_2Cu_3O_{7-\delta}$ (R is a rare earth).[1,2] Furthermore, recent experiments indicate that phonons may indeed contribute significantly to the coupling mechanism of superconductivity.[3-5] It is thus important to know for a particular crystal structure the phonon eigenfrequencies and the assignment of their eigenvectors to the atomic motion in the unit cell. In the double-layer analogue of the Bednorz-Müller material, i.e., in $La_2CaCu_2O_6$, such a study has been performed at room temperature by Mateev *et al.*[6] for the Raman-active modes. The infrared-active modes, which are different from the Raman-active ones due to the presence of an inversion center in the crystal structure, have, to our knowledge, not yet been reported. It is the purpose of this paper to present the frequencies of these modes and to give a possible assignment to their eigenvectors.

Ceramic samples were synthesized according to the prescription of Cava *et al.*[7] with the starting materials Ln_2O_3, $Sr(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, and CuO (for more details, see Ref. 6). As the samples were not treated in oxygen under high pressure, they were not superconducting. An x-ray analysis of the ceramic pellets under investigation did not show any impurity phases. The lattice constants of the sample with $x = 0.2$ were $a = 3.824$ Å and $c = 19.51$ Å.

The far-infrared reflectivity measurements were carried out with a Bruker-113v Fourier-transform interferometer in the 40–650-cm^{-1} spectral range. The samples were mounted on a cold finger of a He cryostat. An aluminum mirror was used as a reference.

The crystal structure of the compound under investigation was recently studied in detail by a number of authors.[6,8-10] The undoped compound $La_2CaCu_2O_6$ belongs to the space group D_{4h}^{17} ($I4/mmm$) with two formula units in the crystallographic unit cell (Fig. 1). Note that some of the superconductor families with one CuO layer have the same space group D_{4h}^{17} (i.e., M_2CuO_4 with the so-called T and T' structures). The unit cell of La_2CuO_4 (T structure) is also shown in Fig. 1 for comparison. It is seen from this figure that $La_2CaCu_2O_6$ can be obtained from La_2CuO_4 by replacing every copper-oxygen layer with CuO_6 octahedra by two layers containing CuO_5 pyramids, separated by an additional layer of Ca ions. As a result, the lattice parameter in the c direction increases from 13.33 to 19.43 Å.[6] On the other hand, the presence of two CuO_5 pyramids in a primitive cell is known also for the T^*-structure $M_2M_2'Cu_2O_8$ materials[11,12] (space group D_{4h}^{7}), having metal ions M and M' in two positions with different local environments. With regard to the CuO_2 planes, the compound under investigation is thus structurally similar to the double-layer superconductors of the Bi or Tl families. The remaining structural elements resemble more the ones of the T^*-structure compound shown in Fig. 1.

The crystal structure and the ion-site positions of $La_2CaCu_2O_6$ are available from x-ray studies. Therefore, a group-theoretical analysis of the long-wavelength lattice vibrations can be performed. Note that the compound under consideration has the point group D_{4h}, and thus obeys the same optical selection rules as the T^*- and T-structure compounds which have the same point group. These materials have, however, a different number of atoms in a primitive cell and thus a different number of optical vibrations. For the T-structure compounds[13,14] (7 atoms in a primitive cell) only $2A_{1g}(zz, xx + yy) + 2E_g(xz, yz)$ vibrations are Raman active, while for the T^*-structure compound[15] with a twice as large primitive cell, the $5A_{1g}(zz, xx + yy) + 2B_{1g}(xx - yy) + 7E_g(xz, yz)$ modes may be expected in a Raman spectrum. $La_2CaCu_2O_6$ has 11 atoms in a primitive cell, and the symmetry of the Raman-active phonons
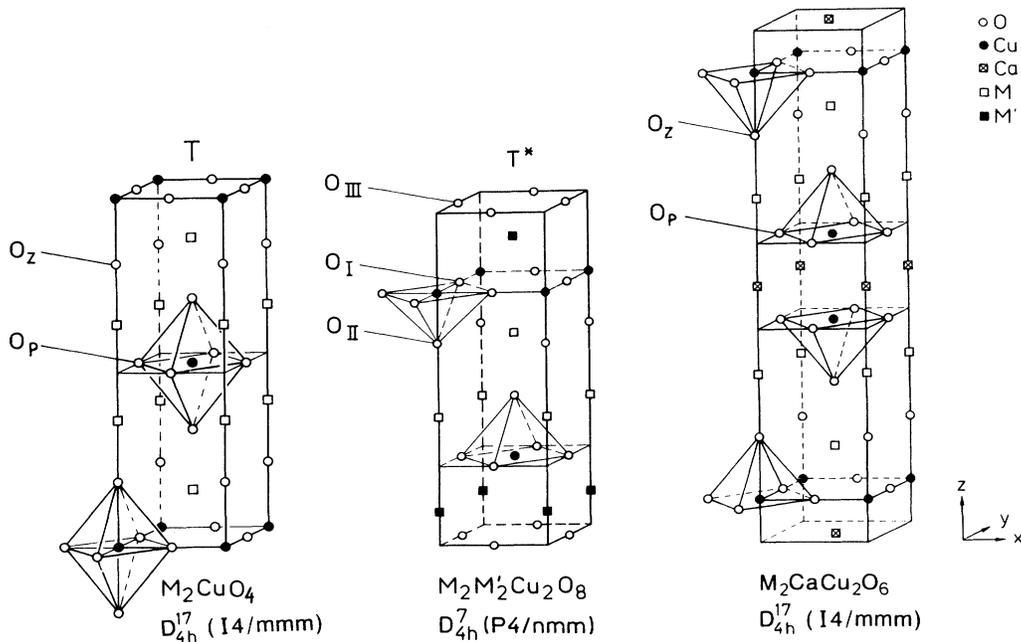
FIG. 1. The crystallographic unit cells of M_2CuO_4 (M = La), $M_2M_2'Cu_2O_8$ (M, M' = Nd, Ce, Sr) and $M_2CaCu_2O_6$ (M = La) compounds. Space groups of the materials are also listed. Note that the crystallographic unit cell is primitive only for the T^*-structure $M_2M_2'Cu_2O_8$. The other unit cells shown contain two primitive cells.

is $4A_{1g} + B_{1g} + 5E_g$. The frequencies of the nondegenerate out-of-plane modes ($4A_{1g}$ and B_{1g}) were determined experimentally by Mateev et al.[6] and found to be close to those of corresponding even vibrations in superconductors with similar structure.

The number of odd (infrared-active or silent) vibrations does not differ so drastically for the materials under consideration. In the T structure, $3A_{2u}(z) + 4E_u(x,y)$ phonon modes and, in the T^* structure, $5A_{2u}(z) + 6E_u(x,y)$ phonon modes are infrared active. For the $La_2CaCu_2O_6$ we expect four out-of-plane, z-polarized phonon modes (A_{2u}) and five in-plane modes (E_u). Note that the B_{2u} mode, involving vibrations of Cu-O plane-oxygen only (O_p in the T structure and $La_2CaCu_2O_6$, and O_I in the T^* structure), is silent in all material discussed.

In Fig. 2(a) the reflection spectra of $La_{2-x}Sr_xCaCu_2O_6$ ceramics with different Sr contents (x) are presented. A number of phonon structures superimposed on a broad background can be clearly identified. The origin of the background is likely to be a high concentration of free charge carriers in the CuO planes due to doping with Sr (although this doping does not seem to suffice to make the material superconducting). As a consequence, only out-of-plane (A_{2u}) phonons are expected to be observed in infrared reflectivity measurements of the metallic oxides.[15-19] Thus, we believe that the strongest peaks in the spectra are due to $A_{2u}(z)$ phonons. To determine the frequencies of the infrared-active phonons precisely, a Kramers-Kronig transformation has been performed. The spectral dependence of the

real part of the conductivity obtained by the Kramers-Kronig transformation is shown in Fig. 2(b) for the three samples. The corresponding phonon parameters for $La_{2-x}Sr_xCuO_4$ (T structure) and $Nd_{2-x-y}Ce_xSr_yCuO_4$ (T^* structure) are listed in Table I for comparison. The values of longitudinal excitation frequencies (coupled plasmon-LO-phonon modes) for $La_{2-x}Sr_xCaCu_2O_6$ have been obtained from the $Im(-1/\epsilon)$ spectra, where ϵ is the dielectric function obtained in the Kramers-Kronig transform. Weak and broad structures at $\nu \sim 400$ and 460 cm^{-1} are found in all samples studied [see Fig. 2(b)]. These structures are probably due to incompletely screened in-plane $E_u(x,y)$ modes. It should be noted also that a band at $\nu = 292$ cm^{-1} appears in the $x = 0.3$ sample and its intensity increases for $x = 0.4$.

An assignment of the infrared-active phonon modes is more difficult than that of the Raman modes. This is because, contrary to even (Raman) modes, a single eigenmode of odd symmetry (ir modes) does not conserve the position of the center of mass of the unit cell. Out-of-phase motion equals symmetry of ions in inequivalent positions is thus always present for odd optical vibrations. The assignment can be best performed by a comparison to theoretical calculations of the normal modes in the compound under consideration or to assignments in compounds with similar crystal structures for which such an analysis has been performed.

One can see from Table I that the frequencies of the $A_{2u}(z)$ phonons observed in $La_{2-x}Sr_xCaCu_2O_6$ are very close to corresponding ones in the T- and T^*-structure materials. Incorporation of the Ca layers into the crys-
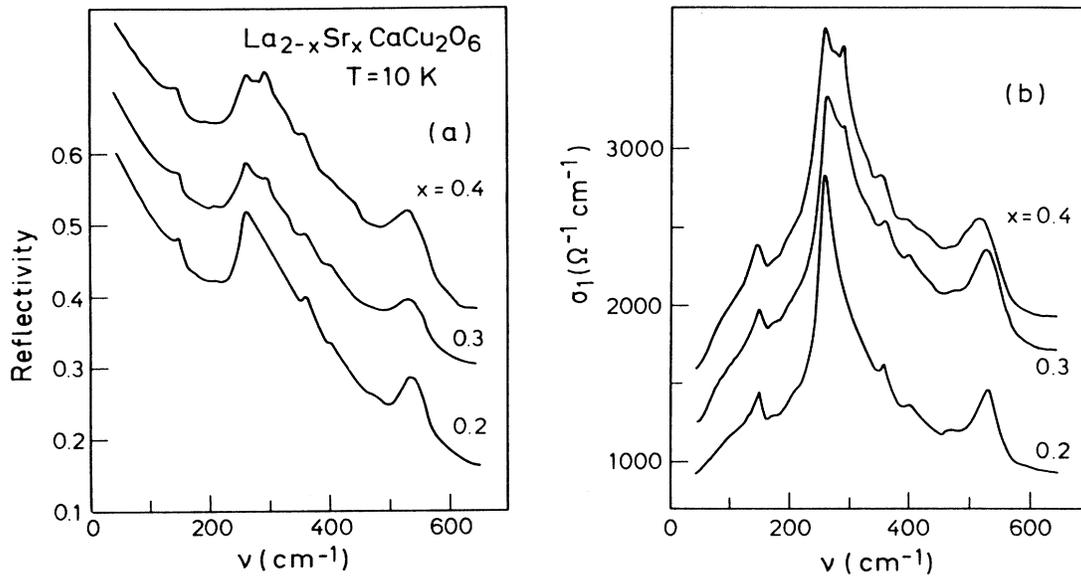
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FIG. 2. Reflectivity (a) and frequency-dependent conductivity (b) of $La_{2-x}Sr_xCaCu_2O_6$ ceramics for $x = 0.2$, 0.3, and 0.4 at $T = 10$ K. The curves have been shifted by (a) 0.1 and (b) 400 Ω^{-1} cm^{-1} along the vertical axis for clarity.

tal lattice leads to an additional infrared-active phonon mode (with respect to the T structure) with a frequency $\nu = 150$ cm^{-1}. This value is higher than the frequency of the infrared vibration involving mostly Cu ions in T'- (134 cm^{-1}) and T^*-structure (132 cm^{-1}) materials[15,17] a result expected from the fact that the mass of Ca is smaller than that of Cu. The square root of the ratio of the masses, $(m_{Cu}/m_{Ca})^{1/2} = 1.25$, is higher than the ratio of the frequencies (1.13) a fact that suggests that Cu ions also contribute (in phase) to the 150-cm^{-1} mode of $La_{2-x}Sr_xCaCu_2O_6$. The two high-frequency vibrations involve oxygen motion: the modes at 359 and 531 cm^{-1} are probably in-phase and out-of-phase displacements of O_p and O_z. The remaining peak at 261 cm^{-1} should then correspond to an out-of phase displacement of Cu and Ca, probably with an admixture of O_p and O_z as well as La. This assignment of oxygen-related modes agrees with that in the T and T' structures.[17,20]

We note, however, that from the proposed assignment

we might expect a large oscillator strength of the mode at 359 cm^{-1}. This is in contrast to what is found in the experiment. It is difficult though to estimate oscillator strengths without a precise knowledge of the eigenvectors, which have not yet been calculated for this structure.

Note that the frequencies of the infrared-active phonons in $La_{2-x}Sr_xCaCu_2O_6$ are only weakly influenced by the Sr concentration: the three low-frequency modes listed in Table I decrease by only 1 cm^{-1}, and the highest-frequency mode by about 10 cm^{-1} for x varying from 0.2 to 0.4. At the same time the half widths of all modes discussed increase by a factor of 1.2–1.7, probably due to disorder effects.

In conclusion, we have reported the far-infrared reflectivity spectra of $La_{2-x}Sr_xCaCu_2O_6$ materials for $0.2 \leq x \leq 0.4$. The frequencies of all four out-of-plane $A_{2u}(z)$ phonon modes predicted by the group-theoretical analysis have been determined and found to correspond well

TABLE I. TO (LO) frequencies and half widths of out-of-plane $A_{2u}(z)$ phonons in $La_{2-x}Sr_xCaCu_2O_6$ ($x = 0.2$) at 10 K. Data for the T-structure $La_{2-x}Sr_xCuO_4$ ($x = 0.08$, Ref. 20) and T^*-structure $Nd_{2-x-y}Ce_xSr_yCuO_4$ ($x = 0.25$, $y = 0.40$, Ref. 15) are also listed. Frequencies and half widths are given in cm^{-1}.

$La_{2-x}Sr_xCuO_4$	$Nd_{2-x-y}Ce_xSr_yCuO_4$			$La_{2-x}Sr_xCaCu_2O_6$			
ν_{TO}	ν_{TO}	(ν_{LO})	Γ_{TO}	ν_{TO}	(ν_{LO})	Γ_{TO}	Assignment
	132	(145)	8.5	150	(157)	14	Metals, in phase
	223	(232)	20				
242	273	(460)	51	261	(449)	48	metals, out of phase
342	321	(288)	66	359	(350)	14	O_p, O_z, in phase
501	524	(563)	45	531	(570)	35	O_p, O_z, out of phase

to the infrared vibrations reported for similar T- and T^*-structure superconductors.

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