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Phonons in $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$ ($x = 0, 0.2$ and 0.4): Raman and infrared spectroscopy, and lattice dynamics calculation

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Abstract. The polarized Raman spectra of Ca_2CuO_3 , $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{CuO}_3$ and $\text{Ca}_{1.6}\text{Sr}_{0.4}\text{CuO}_3$ single crystals and the IR transmission spectra of Ca_2CuO_3 and $\text{Ca}_{1.6}\text{Sr}_{0.4}\text{CuO}_3$ have been measured. The frequencies of all Γ -point phonons of Ca_2CuO_3 have been determined on the basis of assignment of the one-phonon Raman (A_g) and IR lines to definite normal modes and calculations of the lattice dynamics. The line assignment is consistent with earlier results for $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{CuO}_3$ as well as with the line shifts upon substitution of Sr for Ca. The intensive broad lines in the (bb)-polarized Raman spectra of both Sr-free and Sr-substituted samples (in addition to the two A_g lines already assigned) have been attributed to resonantly enhanced two-phonon scattering involving modes related to motions of Cu and/or O(2) atoms. A coincidence has been found between most of the line frequencies and half-widths in the (bb)-polarized Raman spectra and some of the maxima in the two-phonon density of states as obtained from lattice dynamics calculations.

1. Introduction

The compounds Ca_2CuO_3 and Sr_2CuO_3 are isostructural and form continuous solid solutions $(\text{Ca}_{1-x}\text{Sr}_x)_2\text{CuO}_3$ [1]. They belong to the orthorhombic system with space group $Immm$ (D_{2h}^{25}) [2, 3] and their unit cell is shown in figure 1. The Cu ions at the d sites (in Wyckoff notation) are coordinated with four coplanar oxygen ions (two O(1) at the f sites and two O(2) at the a sites), forming infinite Cu–O chains along the b axis, similarly to $\text{YBa}_2\text{Cu}_3\text{O}_7$ [9].

The solid solutions $(\text{Ca}, \text{Sr})_2\text{CuO}_3$ are often present as ‘impurity’ phases in the Bi-based superconducting ceramics, as confirmed by x-ray and SEM analysis [4, 5]. The first Raman spectra obtained from $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{CuO}_3$ microcrystals embedded in Bi–Ca–Sr–Cu–O ceramics have revealed a rather rich structure, pronounced only for parallel incident and scattered field polarizations, and characterized by lines at 201, 237, 300, 391, 439, 487, 525 and 700 cm^{-1} [5]. Similar spectra of $(\text{Ca}, \text{Sr})_2\text{CuO}_3$ have also been obtained by other groups [6].

Recently Yoshida *et al* [7] have reported polarized Raman and IR reflectance spectra from an oriented $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{CuO}_3$ single crystal. This has enabled experiments in exact scattering or reflectance geometries to be performed, and the spectra for light polarizations along the a, b and c directions to be compared. It was shown that Raman spectra exhibiting a rich structure are obtained only for parallel light polarization along the b axis (bb), whereas the spectra corresponding to (aa) or (cc) polarizations consist of only two sharp lines at 300 and 525 cm^{-1} . It is worth noting

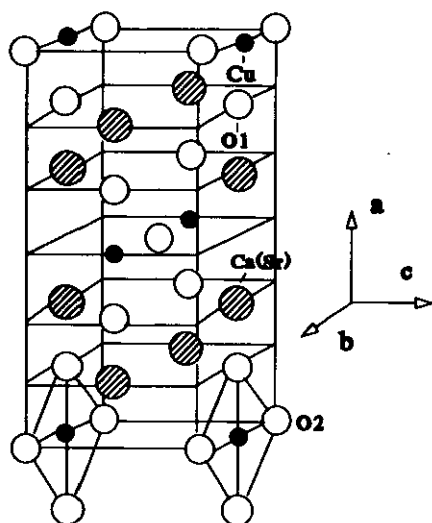


Figure 1. The unit cell of $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$.

that only two A_g of a total of six Raman allowed phonons ($2A_g + 2B_{1g} + 2B_{2g}$) are expected in the first-order Raman spectrum of $(\text{Ca}, \text{Sr})_2\text{CuO}_3$ with parallel polarization. The assignment of the additional lines in the (bb) -polarized spectra at 440, 500, 690, 880, 940, 1140, 1200 and 1330 cm^{-1} has been discussed in [7] in terms of two-phonon and Raman-forbidden disorder-induced scattering in close comparison with the Raman spectra of La_2CuO_4 .

In this work we report the results of Raman studies in exact scattering geometries and of IR transmission experiments on $(\text{Ca}_{1-x}\text{Sr}_x)_2\text{CuO}_3$ for $x = 0$, $x = 0.1$ and $x = 0.2$. Except for the shifts of phonon frequencies, the spectra for various x are very similar and exhibit the same polarization properties as those reported in [7]. It is shown that Raman-forbidden structure in the (bb) polarization is present also for Sr-free Ca_2CuO_3 . The experimentally measured Raman and IR frequencies of Ca_2CuO_3 are compared with those obtained from calculations of the lattice dynamics [8]. A conclusion is drawn that the Raman structures in the (bb) spectra are related mainly to two-phonon processes and a correspondence is found between the frequencies and linewidths of these structures and those in the calculated two-phonon density of states (DOS).

2. Γ -point phonons in the $(\text{Ca}, \text{Sr})_2\text{CuO}_3$ structure

Table 1 summarizes the Wyckoff notations, site symmetries and irreducible representations for each set of atomic sites in the unit cell of $(\text{Ca}, \text{Sr})_2\text{CuO}_3$ (figure 1). Of the total of 18 phonon modes at the Γ point ($k = 0$), six ($2A_g + 2B_{1g} + 2B_{2g}$) are Raman active, nine ($3B_{1u} + 3B_{2u} + 3B_{3u}$) are IR active and three ($B_{1u} + B_{2u} + B_{3u}$) are acoustic modes. The A_g modes are due to displacements of Ca (or Sr) and O(1) along the a axis whereas the modes of B_{1g} and B_{2g} symmetry correspond to motions of the same atoms along the b and c axes, respectively. The A_g modes are allowed in $((aa))$, (bb) and (cc) polarizations of incident and scattered light, while B_{1g} and B_{2g} modes are allowed in (ab) and (ac) polarizations, respectively.

Table 1. Atomic sites, site symmetries and irreducible representations of Γ -point phonons in $(\text{Ca}, \text{Sr})_2\text{CuO}_3$.

Atom	Wyckoff notation	Multiplicity	Site symmetry	Irreducible representation
Ca(Sr)	f	4	C_{2v}^x	$A_g + B_{1g} + B_{1u} + B_{2g} + B_{2u} + B_{3u}$
Cu	d	2	D_{2h}	$B_{1u} + B_{2u} + B_{3u}$
O(1)	f	4	C_{2v}^x	$A_g + B_{1g} + B_{1u} + B_{2g} + B_{2u} + B_{3u}$
O(2)	a	2	D_{2h}	$B_{1u} + B_{2u} + B_{3u}$

3. Samples and experimental details

Ceramic samples of $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$ with $x = 0$ and $x = 0.4$ were prepared by a solid state reaction method. Appropriate amounts of CaCO_3 , SrCO_3 and CuO were mixed and calcined at 800°C (for 12 h) or 850°C (for 24 h) for Ca_2CuO_3 and $\text{Ca}_{1.6}\text{Sr}_{0.4}\text{CuO}_3$, respectively. After grinding, the powders were pressed into pellets and heated at 850°C for 8 d (Ca_2CuO_3) and at 950°C for 2 d ($\text{Ca}_{1.6}\text{Sr}_{0.4}\text{CuO}_3$). After the heat treatment the pellets were constituted of platelet-like microcrystals up to $10\text{--}20\ \mu\text{m}$ in the longest dimension. Most often the crystal surfaces coincide with the (100), (0 $\bar{1}$ 2), (021) or (011) planes as determined by TEM diffraction patterns. The x-ray powder diffraction performed by using a URD-6 diffractometer showed that the lattice parameters of Ca_2CuO_3 ($a = 12.23\ \text{\AA}$, $b = 3.78\ \text{\AA}$ and $c = 3.26\ \text{\AA}$) and $\text{Ca}_{1.6}\text{Sr}_{0.4}\text{CuO}_3$ ($a = 12.34\ \text{\AA}$, $b = 3.81\ \text{\AA}$ and $c = 3.31\ \text{\AA}$) are very close to those reported by Liang *et al* [1]. The Raman spectra of $\text{Ca}_{1.6}\text{Sr}_{0.4}\text{CuO}_3$ were obtained from relatively large ($50\text{--}100\ \mu\text{m}$) single microcrystals existing as 'impurity inclusions' in Bi-Ca-Sr-Cu-O ceramics. Details concerning its preparation have been given elsewhere [5]. The chemical compositions of all samples studied were also confirmed by SEM microanalysis.

The Raman spectra were measured at room temperature using a triple-multichannel spectrometer Microdil 28 (Dilor) equipped with an optical microscope (objective, $\times 100$) for focusing the incident laser beam ($\lambda_L = 488.0\ \text{nm}$; $P_L \leq 0.2\ \text{mW}$; focus spot diameter, about $1\text{--}2\ \mu\text{m}$) and collecting the scattered light in backward-scattering geometry.

The IR phonon frequencies of Ca_2CuO_3 and $\text{Ca}_{1.6}\text{Sr}_{0.4}\text{CuO}_3$ between 130 and $700\ \text{cm}^{-1}$ were obtained from IR transmission spectra of CsI pellets containing 0.5% of finely ground Ca_2CuO_3 or $\text{Ca}_{1.6}\text{Sr}_{0.4}\text{CuO}_3$ by means of a Fourier spectrometer (Bomem DA3).

4. Results

For the analyser crossed to the incident polarization the Raman signals were of negligible intensity. In all cases, for a parallel scattering configuration with light polarization parallel or perpendicular to a straight edge of the as-grown crystal surface, the Raman spectrum could be assigned to one of the three types shown in figures 2(a)–2(c). Taking into account that, following the TEM analysis, the crystal edges coincide mostly with the main crystallographic directions (a , b and c) and on the basis of our knowledge of the surfaces of easy cleavage, we conclude that these three types of spectrum correspond to the $z(aa)\bar{z}$, $a(bb)\bar{a}$ and $a(cc)\bar{a}$ scattering

configurations, where z is a direction in the b - c plane. A comparison between our work and that in [7] shows that our assignment is identical with that given by Yoshida *et al.*

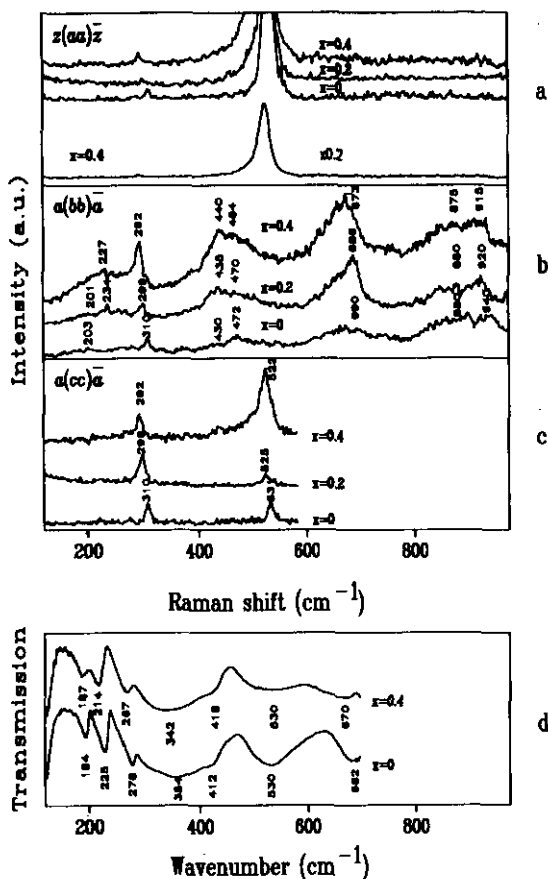


Figure 2. Raman spectra of $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$ ($x = 0, 0.2$ and 0.4) in (a) the $z(aa)z$, (b) the $a(bb)a$ and (c) the $a(cc)a$ scattering configurations (z is a direction in the b - c plane) and (d) IR transmission spectra for $x = 0$ and 0.4 (a.u., arbitrary units).

It follows from figures 2(a) and 2(c) that only two sharp lines near 300 and 525 cm^{-1} are observed in the (aa) and (cc) spectra, in the latter case the high-frequency line being much stronger. The variations in the line positions versus x are given in table 2.

The spectrum in the (bb) polarization is quite different (figure 2(b) and table 2). Broad bands peaking at 202 – 209 , 227 – 234 , 435 – 439 , 465 – 470 , 673 – 684 , 865 – 876 and 913 – 935 cm^{-1} are observed for both Sr-free and Sr-substituted samples. Although the line at 522 – 531 cm^{-1} is not seen, the sharp 293 – 311 cm^{-1} line is definitely present in the (bb) spectra. Most of the lines for the $x = 0.2$ samples appear at nearly the same positions as those reported by Yoshida *et al* [7]. The lines at 203 and 470 cm^{-1} , however, were not observed in the work in [7].

In figure 2(d) are shown the IR transmission spectra of our samples with $x = 0$ and $x = 0.4$. In table 3 the frequencies of the IR absorption maxima, as derived from

Table 2. The frequencies of the Raman lines of $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$ ($x = 0, 0.2$ and 0.4) for parallel (aa), (cc) and (bb) scattering configurations.

Configuration	x	Raman frequencies (cm^{-1})								
(aa) and (cc)	0.0			311			531			
(aa) and (cc)	0.2			299			525			
(aa) and (cc)	0.4			292			522			
(bb)	0.0	203	—	310	430	472	—	690	880	940
(bb)	0.2	201	234	299	436	470	—	686	880	920
(bb)	0.4	—	227	292	440	464	—	673	875	915

figure 2(d), are compared with those obtained for $x = 0.2$ from Kramers–Krönig analysis of the IR reflectance of a single crystal with a well defined crystallographic orientation [7]. With few exceptions there is good agreement between our results and those of [7].

5. Discussion

In agreement with [7] the lines at 300 cm^{-1} in (aa), (bb) and (cc) polarizations and at 525 cm^{-1} in (aa) and (cc) polarizations can easily be assigned to the two A_g modes, involving mainly vibrations of Ca(Sr) and O(1) atoms along the a direction. The stronger softening of the mode near 300 cm^{-1} with increasing Sr content is an additional argument for its assignment to Ca(Sr) vibrations.

Searching for a proper assignment for the appearance of broad (bb)-polarized Raman lines, Yoshida *et al* [7] have outlined and discussed the possible reasons for additional Raman scattering. In close comparison with La_2CuO_4 it has been assumed that these lines may be due to zone-boundary phonons, in particular the point T with $k = (0.5, 0.5, 0)$. It has been suggested that the lines at $440, 500$ and 690 cm^{-1} correspond to first-order zone boundary phonons, activated in $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{CuO}_3$ by the partial substitution of Ca by Sr, which breaks the spatial symmetry and makes the T phonons Raman allowed. (In La_2CuO_4 the orthorhombic distortion doubles the volume of the unit cell and folds back the X-point phonons to zone-centre phonons.) The other lines have been assigned to two-phonon scattering processes, their intensity indicating strong coupling of the T-point phonons, associated with oxygen in the Cu–O bond, with the photoexcited electron–hole pair.

While the appearance of first-order X-point phonons in the spectra of La_2CuO_4 could tentatively be explained by phonon branch folding in the orthorhombic phase, it seems that no similar reason exists for $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$ and no special role is to be played in the latter case by the T-point phonons. Indeed, there are no indications for structural transformation or existence of superstructures in the Sr-doped materials. Moreover, the same additional spectral features are pronounced in the (bb)-polarized Raman spectra of both Sr-free and Sr-rich materials. In each of these cases, the number of experimentally observed IR lines does not exceed that expected for the Ca_2CuO_3 structure.

We suggest that all (bb)-polarized Raman peaks (except the peak near 300 cm^{-1}) are related solely to two-phonon scattering resonantly enhanced because of coincidence of the laser photon energy with the energy of certain electron transitions to bands (close above the Fermi level) extended along the b direction. At present there are no reports

available on experimental measurement of either the electronic band structure or the one-phonon and two-phonon DOSS of Ca_2CuO_3 or $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$. Nevertheless, it is plausible to assume that these electronic bands are not related to either Ca(Sr) or O(1) atoms as no enhancement of the phonon modes near 300 cm^{-1} and 525 cm^{-1} , involving mainly Ca(Sr) and O(1) motions, respectively, is observed in the (*bb*) spectra. One expects, therefore, that the electron band resonating is related to Cu, to O(2) or to both and, hence, strong electron-phonon coupling with phonons involving motions of mainly Cu and/or O(2) atoms (presumably along the *b* direction) is expected.

In order to complete the assignment of all modes, we carried out lattice dynamics calculations for Ca_2CuO_3 using a shell model [8]. This model takes advantage of the predominant ionicity of the perovskite-like structures and describes the short-range interactions of the ion pairs by Born-Mayer potentials. Thus, a relatively small number of parameters is enough to obtain reasonable agreement with the experimental data. Moreover, these parameters are transferable from one structure to another. We implemented these ideas in the structurally similar compounds La_2CuO_4 and Ca_2CuO_3 . The Cu and O ionic charges, shell charges, ionic polarizabilities as well as the Born-Mayer potentials for the Cu-O interactions were taken from a fit to the experimentally determined Raman and IR frequencies of La_2CuO_4 . The remaining parameters referring to the Ca ion and Ca-O interaction were obtained from a fit to the frequencies of the two A_g Raman lines (seen in the (*aa*) and (*cc*) spectra) and three IR lines assigned to modes of B_{2u} symmetry in close comparison with the polarized reflectance data in [7].

The calculated phonon frequencies at the Γ point together with the measured values are presented in table 3. Apart from the agreement for the A_g and B_{2u} modes the calculation yields a prediction for the unobserved B_{1g} and B_{2g} modes and enables us to make the assignment of the rest of the experimentally obtained IR lines.

Table 3. Γ -point TO phonon frequencies of $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$ as obtained from experiments and from calculations of the lattice dynamics of Ca_2CuO_3 .

Mode	TO phonon frequency (cm^{-1})						Atomic vibrations
	Experimental results			Theoretical results			
	Yoshida <i>et al</i> [7], $x = 0.2$	This work			$x = 0$		
	$x = 0$	$x = 0.2$	$x = 0.4$	$x = 0$			
A_g	306	311	299	292	311	Ca(Sr)	
A_g	531	531	525	522	531	O(1)	
B_{1g}	—	—	—	—	157	Ca(Sr), O(1)	
B_{1g}	—	—	—	—	372	O(1)	
B_{2g}	—	—	—	—	206	Ca(Sr)	
B_{2g}	—	—	—	—	466	O(1)	
B_{1u}	260	278	—	267	291	Cu	
B_{1u}	410	412	—	418	400	O(1)	
B_{1u}	540–580	530	—	530	577	O(2)	
B_{2u}	215	225	—	214	201	Cu	
B_{2u}	340	354	—	342	371	O(1)	
B_{2u}	660	682	—	670	673	O(2)	
B_{3u}	—	194	—	187	155	Cu	
B_{3u}	350	354	—	342	337	O(1), O(2)	
B_{3u}	460	457	—	—	424	O(2)	

In addition, we calculated the two-phonon DOS of Ca_2CuO_3 in order to make a comparison between the frequencies and half-widths of the (bb)-polarized Raman structures and those of the maxima of the two-phonon DOS. It follows from figure 3 that the maxima of comparable half-width appear at 470–480, 880–890 and 930–940 cm^{-1} in both the two-phonon DOS and the (bb)-polarized Raman spectra whereas there is no Raman counterpart of the DOS maximum at 540 cm^{-1} . It is also not clear whether the DOS maximum at 690–750 cm^{-1} and the Raman maximum at 680–700 cm^{-1} are of the same origin. One should not expect, however, full coincidence between the two-phonon DOS and (bb) Raman lineshapes as in the latter case; of all the two-phonon processes, only those that are resonantly enhanced should contribute to the Raman intensity.

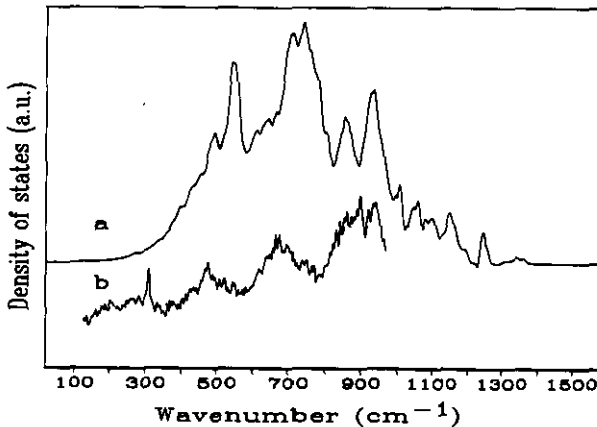


Figure 3. Calculated two-phonon DOS (curve a) and the (bb)-polarized Raman spectrum (curve b) of Ca_2CuO_3 (a.u., arbitrary units).

6. Conclusion

The polarized Raman spectra and the IR transmission of $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$ ($x = 0, 0.2$ and 0.4) have been measured and the observed spectral structures have been assigned to one- and two-phonon processes on the basis of phonon symmetry analysis and lattice dynamics calculations. A conclusion has been drawn that the unexpectedly rich structure in the (bb)-polarized Raman spectra is mainly due to resonantly enhanced two-phonon scattering.

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