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Doping effects in the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ -type structure: a Raman scattering study

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Abstract

Polarized micro-Raman spectra of different compounds belonging to the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ -type structure were studied. In the spectra with parallel polarization along the plane crystal axes of the insulating samples $\text{Sr}_9\text{R}_5\text{Cu}_{24}\text{O}_{41}$ ($\text{R} = \text{La}, \text{Y}$) a broad peak near 3000 cm^{-1} , similar to the well-known two-magnon peak in the layered cuprates, was observed. In addition to the Raman lines characteristic for this structure, we observed only in the spectra with polarization parallel to the chains numerous lines between 100 and 1200 cm^{-1} , probably originating from Raman-forbidden infrared-active only LO phonons and their combinations. In the spectra of the conducting compounds $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ ($x = 0, 7$) these features were very weak or disappeared. We interpret these results as Raman evidence for hole doping of the Cu_2O_3 “spin-ladder” planes and for a redistribution of holes between chains and planes through Ca substitution in the case of the rare-earth-free samples. © 1997 Elsevier Science B.V.

Keywords: Raman spectroscopy; Spin-ladder compounds

1. Introduction

The initial interest in the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ -type compounds was connected mainly to their identification as “impurity phases” in high- T_c superconducting ceramics [1]. Their structure is orthorhombic (space group Cccm or the lower Pcc2) and is described as consisting of two interpenetrating incommensurate substructures: planar $\text{Sr}_2\text{Cu}_2\text{O}_3$ layers (corner-sharing double Cu_2O_4 chains) and CuO_2 chains (edge-sharing CuO_4 squares) [2,3] (see Fig. 1). They have

identical a and b lattice parameters where $7c_{\text{plane}} \approx 10c_{\text{chain}}$, and this has as consequence the complicated formula describing the supercell $(\text{Sr}_2\text{Cu}_2\text{O}_3)_7(\text{CuO}_2)_{10}$.

This structure results in a possible partial occupation of different rare- and alkaline-earth atoms on the Sr-site. Different solid solutions were investigated: $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ [2,4,5], $\text{Sr}_{14-x}\text{Ba}_x\text{Cu}_{24}\text{O}_{41}$ [5,6], $\text{Sr}_{14-x}\text{R}_x\text{Cu}_{24}\text{O}_{41}$, $\text{R} = \text{Y}$ [6–8], La [9], and Sr-free $\text{Ca}_8\text{La}_6\text{Cu}_{24}\text{O}_{41}$ [3]. Due to the fact that the oxygen content of this structure is rather stable [1,10], the solubility x of rare earths is limited by the condition for the formal copper valence $v_{\text{Cu}} \geq 2$ (i.e. $x \leq 6$).

The transport properties of these compounds strongly depend on the substitutions of Sr by alka-

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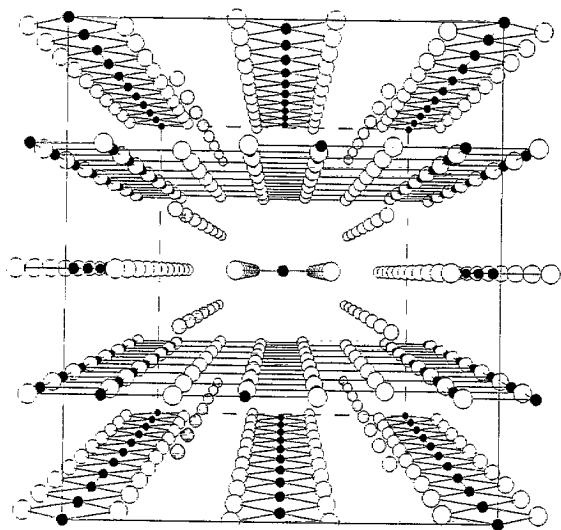


Fig. 1. The structure of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$. The small black circles are copper atoms, the large white circles are oxygen atoms, and the gray circles are strontium atoms. The a -axis is horizontal, the b -axis is vertical, the c -axis is along the chains.

line- or rare-earth atoms. Whereas the maximally rare-earth-substituted $\text{Sr}_{14-x}\text{R}_x\text{Cu}_{24}\text{O}_{41}$ ($x \approx 6$) samples are insulators, the conductivity of the parent compound $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ is several orders higher [8,11]. The substitution of Sr by Ca leads to an additional increase in the conductivity [5]. There is a report of superconductivity near 12 K at 3 GPa in $\text{Sr}_{0.4}\text{Ca}_{13.6}\text{Cu}_{24}\text{O}_{41}$ [12]. Analysing the temperature dependence of the electrical resistivity in $(\text{Sr}_{0.4}\text{Ca}_{0.6})_{14}\text{Cu}_{24-x}\text{Co}_x\text{O}_{41-8}$ samples Akimitsu et al. [13] concluded that the conductivity of the Cu_2O_3 planes is one-dimensional along the c -axis. As was originally proposed by Kato et al. [14] the increase of the conductivity through the Ca substitution is due to the increase of hole carriers in the Cu_2O_3 plane by the redistribution of carriers between the CuO_2 chains and Cu_2O_3 planes. Two recent studies, analysing the optical reflectivity spectra of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ single crystals [15] and Cu NMR and NQR spectra of $\text{Sr}_{14-x}\text{A}_x\text{Cu}_{24}\text{O}_{41}$ ($\text{A} = \text{Ca}, \text{Y}, \text{La}$) [16], support the above mentioned hypothesis for hole doping of the Cu_2O_3 planes. However, based on both resistivity and magnetic susceptibility measurements, Carter et al. [11] came to the opposite conclusion: the Cu_2O_3 planes remain undoped and the mobile holes are in the CuO_2 chains.

Raman spectroscopy is a powerful tool for the investigation of the electronic structure of the layered high- T_c superconductors and their insulating analogs. In the Raman spectra of several types of insulating layered tetragonal cuprates Raman-forbidden phonons as well as two-magnon scattering signals were observed [17]. In conducting cuprates these spectral features disappear. Herein we show that the Raman spectra of insulating and conducting $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ -type compounds have the same differences.

2. Experimental

The following $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ -type compounds were synthesized: $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, $\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$, $\text{Sr}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ and $\text{Sr}_9\text{Y}_5\text{Cu}_{24}\text{O}_{41}$. The samples were prepared using a standard solid state reaction technique. Appropriate amounts of SrCO_3 , CaCO_3 , La_2O_3 , Y_2O_3 and CuO for the nominal ratios were mixed and heated in air at 850°C for 24 h, ground and again heated at 900°C for 24 h. The as-obtained materials were pressed into 1 g pellets and sintered at 950°C (1000°C for $\text{Sr}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$) for 24 h and then furnace cooled to room temperature. The pellets were polished using 5μ and 1μ diamond pastes and then ultrasonically cleaned in an ethanol bath.

The lattice parameters were determined from X-ray powder diffractograms, obtained with a URD-6 powder diffractometer ($\text{CuK}\alpha$ radiation). They are given in Table 1. The $\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$ ceramics contains small amounts of CuO and $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{CuO}_2$. The other samples studied are single phase.

The Raman spectra were obtained using a single spectrometer LABRAM, equipped with a microscope, a CCD multichannel detector and appropriate notch filters. An $100\times$ objective was used to both focus the incident laser beam into a spot of 1–2 μm

Table 1
Crystal lattice parameters of the compounds investigated

Compound	a (Å)	b (Å)	$c/7$ (Å)
$\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$	11.494	13.422	3.940
$\text{Sr}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$	11.432	13.234	3.983
$\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$	11.380	12.971	3.910
$\text{Sr}_9\text{Y}_5\text{Cu}_{24}\text{O}_{41}$	11.326	12.935	3.950

diameter and collect the scattered light in backward scattering geometry. A 600 and an 1800 grooves/mm grating was used for the different investigated spectral ranges. The 632.8 nm He–Ne and 514.5 nm Ar⁺ laser lines were used for excitation. All spectra were recorded at room temperature.

The crystal directions in the observed microcrystal surfaces were determined using the following facts: the microcrystals, consisting of ceramics, have elongated plate-like shape (from crystallographic considerations identifying the *xz*-plane as well as the *z*-direction in it) and strong optical anisotropy. The polarization behaviour of the Raman lines observed in the one-phonon spectral region confirmed the as-determined surface orientation (a detailed analysis of the Raman-active phonons will be published elsewhere). Thus, six types of Raman spectra were obtained (three of them in parallel *xx*, *yy* and *zz* polarization along the three crystal axes and the other three in crossed *xy*, *xz* and *yz* polarization).

3. Results and discussion

3.1. Two-magnon Raman scattering

The Raman spectra obtained in parallel polarization along the three crystal axes from the two insulating ($\text{Sr}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ and $\text{Sr}_9\text{Y}_5\text{Cu}_{24}\text{O}_{41}$) and the two conducting ($\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ and $\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$) samples with two laser excitations used are presented in Figs. 2–5. We can formally divide the spectral region investigated ($100\text{--}4000\text{ cm}^{-1}$) into three parts: the “one-phonon” region ($100\text{--}700\text{ cm}^{-1}$), the “two-phonon” region ($700\text{--}1400\text{ cm}^{-1}$) and a “non-phonon” region ($1400\text{--}4000\text{ cm}^{-1}$). Because of the fact that in the spectra with crossed *xy*, *xz* and *yz* polarization weak lines are present only in the one-phonon region (the analysis of which is out of the scope of this paper), they are not presented here.

At first we comment on the broad peak near 3000 cm^{-1} observed in the high-frequency “non-phonon” region. It has the following characteristics. (i) It has A_g symmetry and appears only in *zz* and *xx* polarization (i.e. parallel to the Cu_2O_3 planes). (ii) Its intensity is strong in the spectra of the insulating rare-earth-substituted samples, moderate in the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, and it practically disappears in the

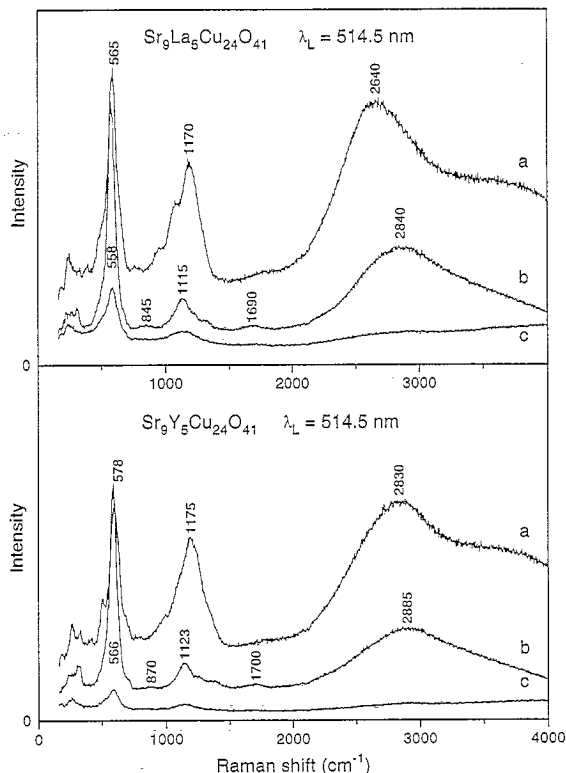


Fig. 2. Raman spectra in parallel polarization along the three crystal axes from $\text{Sr}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ (above) and $\text{Sr}_9\text{Y}_5\text{Cu}_{24}\text{O}_{41}$ (below). (a) *zz*, (b) *xx*, (c) *yy*. $\lambda_L = 514.5\text{ nm}$.

conductive $\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$. (iii) It is observable with 514.5 nm excitation, whereas in the *zz* and *xx* spectra obtained with 632.8 nm excitation a background decreasing monotonically with frequency is observed. (iv) The peak in *zz* spectra is asymmetric with a characteristic high-frequency tail. (v) For each of the samples the position of the peak in the *xx* spectra is centered at higher frequencies compared with the one in the *zz* spectra.

A comparison with the Raman spectra obtained from the tetragonal high- T_c cuprates and their insulating analogs (see Ref. [17] and references therein) leads immediately to the conclusion that the strong peak in the non-phonon region originates from two-magnon scattering. Based only on this comparison we can make several general conclusions. (i) The disappearance of the peak in $\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$ is Raman evidence for hole doping of the Cu_2O_3 planes in this compound. (ii) The differences between the

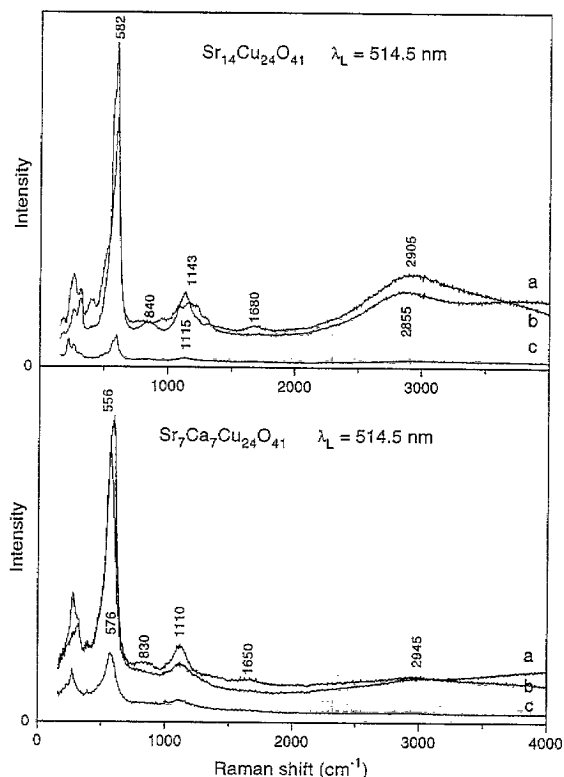


Fig. 3. Raman spectra in parallel polarization along the three crystal axes from $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ (above) and $\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$ (below). (a) zz , (b) xx , (c) yy . $\lambda_L = 514.5$ nm.

spectra of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ and isovalent substituted $\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$ support the hypothesis proposed for charge transfer of holes from the CuO_2 chains to the Cu_2O_3 planes through Ca substitution [14]. (iii) The disappearance of the two-magnon peak in the spectra of $\text{Sr}_9\text{R}_5\text{Cu}_{24}\text{O}_{41}$ ($\text{R} = \text{La}, \text{Y}$) obtained with the red excitation suggests that this peak has a similar resonance behaviour as in the tetragonal insulating cuprates [17,18].

At the same time there are essential differences between CuO_2 planes in the tetragonal layered cuprates and Cu_2O_3 planes in the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ -type compounds. The latter belong to the so-called “spin-ladder” materials with two legs [19]. The magnetic properties of these materials depend on the ratio J'/J , where J and J' are antiferromagnetic (AF) exchange couplings along the legs (the chains in the planes) and the rungs (perpendicular to the chains), respectively. This ratio was obtained to be

$J'/J \approx 0.8$ and $J \approx 1100$ K for the case of similar Cu_2O_3 planes in the more simple SrCu_2O_3 [20]. Whereas recently a theory of two-magnon resonant Raman scattering in AF tetragonal cuprates was proposed [21,22], explaining the existence of peaks near $3J$ and $4J$ in the Raman spectra of these materials, as well their polarization and resonant behaviour [18], for the case of ladder cuprates, to our knowledge, no such theory has been developed yet. Probably, the two-magnon peak in the “spin-ladder” materials is centered near $3J'$ in the zz spectra (parallel to the legs (chains)) and near $3J'$ in the xx spectra (parallel to the rungs). The change of its frequency in the zz and xx spectra of the different samples investigated correlates with the distances between two adjacent copper atoms along z and x directions, respectively. Note, that whereas the a and b lattice parameters correlate with the averaged ionic radius of the ions at the Sr-site, the c parameter is shorter

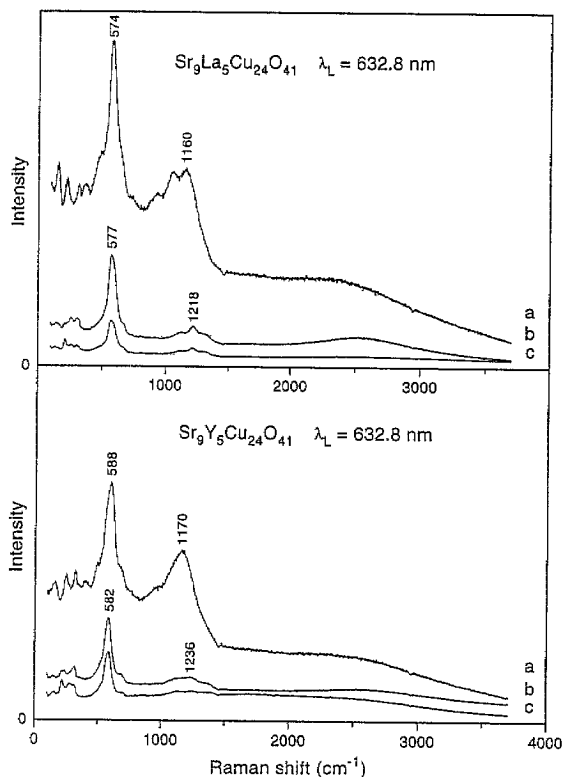


Fig. 4. Raman spectra in parallel polarization along the three crystal axes from $\text{Sr}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ (above) and $\text{Sr}_9\text{Y}_5\text{Cu}_{24}\text{O}_{41}$ (below). (a) zz , (b) xx , (c) yy . $\lambda_L = 632.8$ nm.

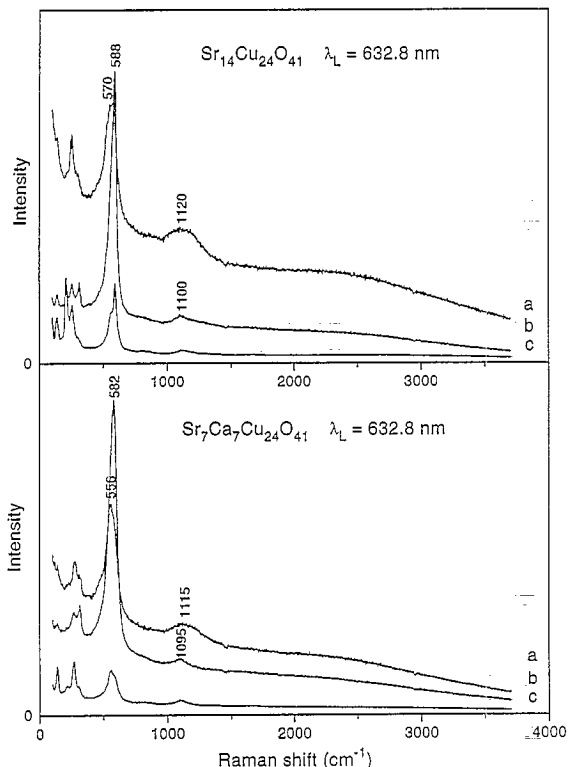


Fig. 5. Raman spectra in parallel polarization along the three crystal axes from $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ (above) and $\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$ (below). (a) zz , (b) xx , (c) yy . $\lambda_L = 632.8$ nm.

in the conducting samples. Such shortening of the interatomic distances in the CuO_2 planes upon hole doping is typical for the tetragonal layered cuprates, too.

The question arises as to what is the contribution to the scattering in the “non-phonon” region originating from the rest of the Cu–O sublattice (the CuO_2 chains). To our opinion it is negligible. We have prepared two additional samples $\text{Y}_2\text{Ca}_2\text{Cu}_5\text{O}_{10}$ ($\nu_{\text{Cu}} = 2$) and $\text{Y}_{1.2}\text{Ca}_{2.8}\text{Cu}_5\text{O}_{10}$ ($\nu_{\text{Cu}} = 2.16$), the structure of which contains only CuO_2 chains and is related to that of NaCuO_2 [1,23]. In the “non-phonon” region of their Raman spectra (not presented here) we did not observe any peaks. This result is expected, because the value of the nearly 90° Cu–O–Cu superexchange AF interaction in the CuO_2 chains is one order weaker compared to the nearly 180° one in Cu_2O_3 planes [24,25]. A possible scattering by magnetic excitations from the CuO_2 chains

should thus be observed in the “one-phonon” region of the Raman spectra of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ -type compounds.

3.2. Two-phonon and forbidden one-phonon Raman scattering

Previous Raman spectra (only in the one-phonon region and from surfaces with unidentified orientation) of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ -type phases were measured from multiphase Bi–Sr–Ca–Cu–O and Pb–(La, Sr)–Ca–Cu–O ceramics, containing this type “impurity” [26,27]. The analysis of the Raman-active phonons in this structure meets serious difficulties due to the large supercell, resulting in a large number of formally Raman-allowed modes. However, as was proposed in Ref. [27], one can consider the two Cu–O sublattices separately, each one having simple Fmmm structure with small $a \times b \times c_{\text{chain}}$ and $a \times b \times c_{\text{plane}}$ cells, respectively. Such an approach leads to the existence of only $4A_g + 4B_{1g} + 3B_{2g} + B_{3g}$ modes (only the A_g modes are allowed in the xx , yy and zz spectra). Two A_g modes correspond to the “breathing” oxygen vibrations (along the x -direction) of the CuO_2 chains and the double chains in Cu_2O_3 planes and they were assigned to the strongest double peak between 550 and 600 cm^{-1} [27].

The careful observation of all type spectra obtained shows that only in the zz spectra of the insulating $\text{Sr}_9\text{R}_5\text{Cu}_{24}\text{O}_{41}$ ($R = \text{La}, \text{Y}$) samples obtained with the red excitation, several additional lines as well their frequency combinations appeared (see Fig. 6). The same phenomenon was observed in the Raman spectra of insulating layered cuprates when the polarization is parallel to the Cu–O planes and the incident laser energy is close to the charge-transfer gap energy (1.8–2 eV) [17,28,29]. Heyen et al. [29] explained their observation as Raman activation of infrared-only E_u LO phonons (vibrations parallel to the CuO_2 planes) via Fröhlich interaction. Recently Abrashev et al. [30] showed that similar forbidden scattering exists in the purely chained orthorhombic $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$ with the difference that due to the orthorhombicity in these compounds the activated phonons are B_{1u} LO modes (vibrations along the chains) and the scattering is observed only in polarization parallel to the chains. In our case the lines originating from such Raman-forbidden LO

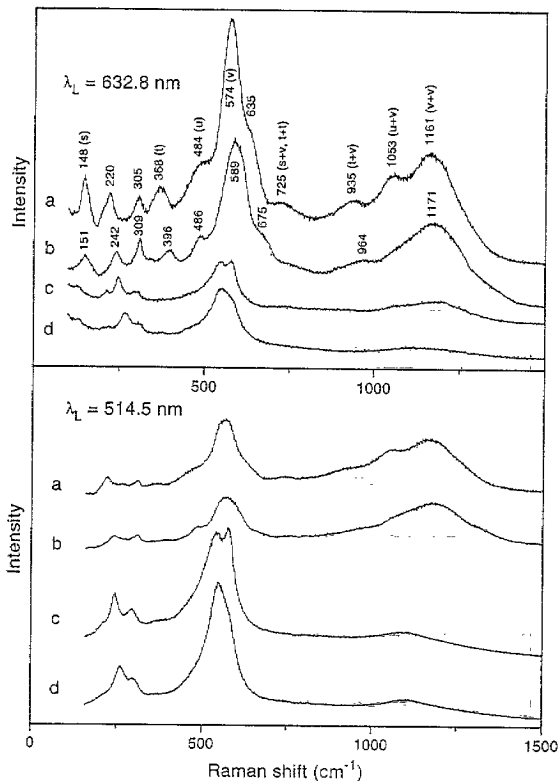


Fig. 6. Raman spectra in zz polarization from: (a) $\text{Sr}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$, (b) $\text{Sr}_9\text{Y}_5\text{Cu}_{24}\text{O}_{41}$, (c) $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, (d) $\text{Sr}_7\text{Ca}_7\text{Cu}_{24}\text{O}_{41}$. $\lambda_L = 632.8$ nm (above) and $\lambda_L = 514.5$ nm (below). For better comparison the spectra were shifted vertically.

phonons (here with B_{1u} symmetry, too) are likely to be at 148, 368, 484, and 574 cm^{-1} for $\text{Sr}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ and 151, 396, 486, and 589 cm^{-1} for $\text{Sr}_9\text{Y}_5\text{Cu}_{24}\text{O}_{41}$ (see Fig. 6). The last line overlaps with the double A_g peak. Three of these lines (indicated in Fig. 6 as (s), (t) and (v)) are very close to the three strongest reststrahlen bands in the infrared reflectivity spectrum ($E||c$, i.e. B_{1u} modes) of a $\text{Sr}_{11}\text{Y}_3\text{Cu}_{24}\text{O}_{41}$ single crystal (see inset of Fig. 1 in Ref. [15]) and to the observed B_{1u} LO modes at 154, 353 and 592 cm^{-1} in SrCuO_2 , containing similar double Cu–O chains (but isolated ones) as the Cu_2O_3 plane in the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ structure [30].

Two weak lines were observed near 850 and 1700 cm^{-1} in all samples (most pronounced in $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, see Figs. 2 and 3). They appear only in the xx spectra obtained using green excitation. If these two lines correspond to first and second-order

scattering by some excitation, this excitation cannot be a phonon (in all cuprates the frequencies of all phonons are below 700 cm^{-1}). The clarification of the origin of the two peaks needs additional measurements.

4. Conclusions

Polarized micro-Raman spectra of several $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ -type compounds were obtained. Systematic differences between the spectra of insulating $\text{Sr}_9\text{R}_5\text{Cu}_{24}\text{O}_{41}$ ($\text{R} = \text{La}, \text{Y}$) and conducting $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ ($x = 0, 7$) were found. Based on a comparison with the Raman spectra of the layered tetragonal cuprates, the additional features in the spectra of the insulating samples were explained as two-magnon scattering and as a scattering of Raman-forbidden infrared-active LO phonons, respectively. The lack of these features in the conducting samples is a Raman evidence for hole doping of the Cu_2O_3 planes in the structure. These results could be a base for a development of a theory of Raman scattering by magnetic excitations in the spin-ladder materials.

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