Raman effect in La$_{2-x}$Sr$_x$CuO$_4$

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The symmetry of the Raman-active vibrations in a tetragonal La$_{1.83}$Sr$_{0.17}$CuO$_4$ single crystal has been studied. A correlation is seen between the intensity of the A_{1g} modes at 221 cm^{-1} and 431 cm^{-1} and the superconducting transition temperature.

Research on the lattice dynamics of the high-temperature superconductor La$_{2-x}$Sr$_x$CuO$_4$ by the Raman-effect method has yielded extremely contradictory results.[1-7] Furthermore, the absence of comprehensive polarization measurements for single crystals makes it impossible to unambiguously identify the observed vibrations in various structural states.

In this letter we report measurements of the Raman spectra in a tetragonal single

crystal with the composition $La_{1.83}Sr_{0.17}CuO_4$ and also in ceramic samples with various strontium concentrations ($x = 0.05$–0.4), produced by solid-phase synthesis.[8] The spectra were excited by lines from an argon laser (4880 Å and 5145 Å) with a power up to 200 mW, focused to a spot $\sim 40 \times 150 \, \mu$m in size at grazing incidence on mechanically polished surfaces of the samples. The scattered light was detected by a DFS-24 spectral photometer with a photon counter at a resolution ~ 5 cm^{-1}. Observation of the surfaces of the samples in polarized light revealed some fairly large single crystals in some of the samples. For example, in a tablet with the composition $La_{1.83}Sr_{0.17}CuO_4$ with $T_c = 36$ K, crystals $\sim 1 \times 0.5$ mm in size exhibited a highly anisotropic reflection in measurements with an analyzer crossed with a polarizer. That result is evidence that the c axis of the crystal is oriented in the plane, so it becomes possible to measure all the components of the scattering tensor of the vibrations which are active for the K_2NiF_4 structure: $2A_{1g} + 2E_g$ (Ref. 9). The orientation of the c axis in the crystal was found by x-ray diffraction. The strontium concentration in the crystal was $x = 0.17 \pm 0.1$, according to x-ray spectral microanalysis. According to the selection rules, vibrations of oxygen atoms at the vertices of octahedra, $0(1)$, and of lanthanum (or strontium) atoms are active in the optical scattering. It is clear from the spectra of the single crystal shown in Fig. 1 that all three of the lines observed in ceramics,[10] 153, 221, and 431 cm^{-1}, correspond to symmetric vibrations of the A_{1g} type, associated with displacements of atoms along the c axis. As in $YBa_2Cu_3O_x$, we do not observe atomic vibrations of symmetry E_g, associated with displacements of atoms perpendicular to the c axis of the crystal. The high-frequency band at 431 cm^{-1},
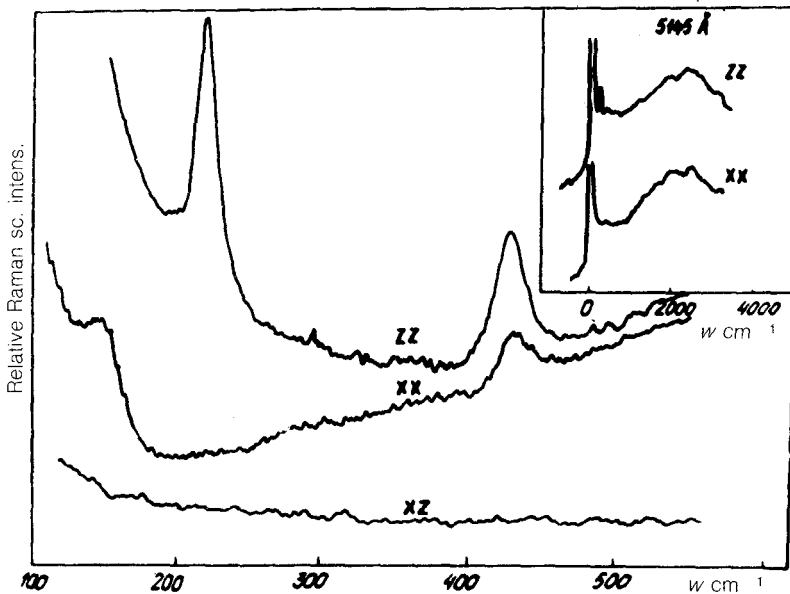

FIG. 1. Raman spectra of an $La_{1.83}Sr_{0.17}CuO_4$ single crystal for various components of the scattering tensor, XX, ZZ (A_{1g}), and XZ (E_g), at 300 K. The inset shows the electron scattering spectra.

which exhibits an isotopic shift[11], can be assigned in a natural way to vibrations of oxygen atoms (predominantly) with some admixture of out-of-phase displacements of lanthanum (or strontium) atoms. We do not rule out the possibility that the observation of three A_{1g} bands, instead of the two expected, is evidence of a two-mode behavior of the given mixed crystal. In this case, the lines at 153 and 221 cm^{-1} can be linked with lanthanum and strontium modes with an admixture of displacements in the phase of the oxygen atoms. For example, their frequency ratio, 1.44, is approximately equal to the square root of the ratio of atomic masses: $\sqrt{m_{La}/m_{Sr}} = 1.26$. It should also be noted that in the isostructural compound Sr_2TiO_4 (Ref. 12), which has an Sr–O bond length which is approximately the same (2.56 Å in comparison with the 2.35 Å in $La_{2-x}Sr_xCuO_4$), the band assigned to vibrations of strontium atoms has a frequency of 205 cm^{-1}. Although the lines at 220 cm^{-1} (Ref. 5) and 228 cm^{-1} (Ref. 6) have been attributed to La vibrations in several studies of lanthanum oxocuprate, the results of all of these studies[1,4-7] differ significantly in both the number of lines and their polarizations. Furthermore, the selection rules for the orthorhombic phase of La_2CuO_4 predict an activity of a far greater number of vibrations,[9] $5A_g + 3B_{1g} + 6B_{2g} + 4B_{3g}$[9]; obviously, the effect would be to hinder an interpretation of the observed spectrum.

Polarization measurements showed that all of the observed lines exhibit anisotropic scattering tensors. This is not the conclusion of a group-theory analysis. At the same time, the mode at the frequency of 153 cm^{-1} modulates the electron susceptibility only in the basal plane of the crystal ($\alpha_{XX} \gg \alpha_{ZZ}$), and the line at 221 cm^{-1} is observed only in the ZZ spectrum ($\alpha_{ZZ} \gg \alpha_{XX}$). The high-frequency band of oxygen vibrations is more nearly isotropic, with $\alpha_{ZZ} \approx 3\alpha_{XX}$.

The intensities of the lines also behave in different ways as x is varied. In contrast with the weak dependence of the line at 153 cm^{-1}, the intensity of the band at 221 cm^{-1} increases sharply with increasing x. It goes through a maximum at concentrations corresponding to the highest superconducting transition temperatures in this compound (see the inset in Fig. 2). The frequency of this band decreases from 230 cm^{-1} to 218 cm^{-1} as x is raised from 0.05 to 0.4. The intensity of the oxygen line at 431 cm^{-1} exhibits a similar, but smoother, behavior as a function of x, exhibiting no change in frequency.

Since we did not observe a strong dependence of the intensity of these lines on the excitation wavelength, these features of the behavior cannot be attributed to resonance effects. Since the intensification of these modes stems primarily from the ZZ component of the scattering tensor, one might suggest that a substantial increase in interlayer charge fluctuations, including Cud_{z}–Op_{z} orbitals, is responsible.[13]

As the temperature is lowered to 100 K, the Raman spectrum of the $La_{1.83}Sr_{0.17}CuO_4$ single crystal exhibits a narrowing of the lines at 221 cm^{-1} (from 20 to 11 cm^{-1}) and 431 cm^{-1} (from 26 to 14 cm^{-1}) and a slight shift of 2–3 cm^{-1} up the frequency scale. In the XX spectrum we see a slight structural feature at 370 cm^{-1}, which can be linked with a structural transition to an orthorhombic phase at ~120 K for this composition. This structural feature can be seen fairly clearly at 100 K for a sample with the composition $La_{1.9}Sr_{0.1}CuO_4$, which has a structural transition tem-
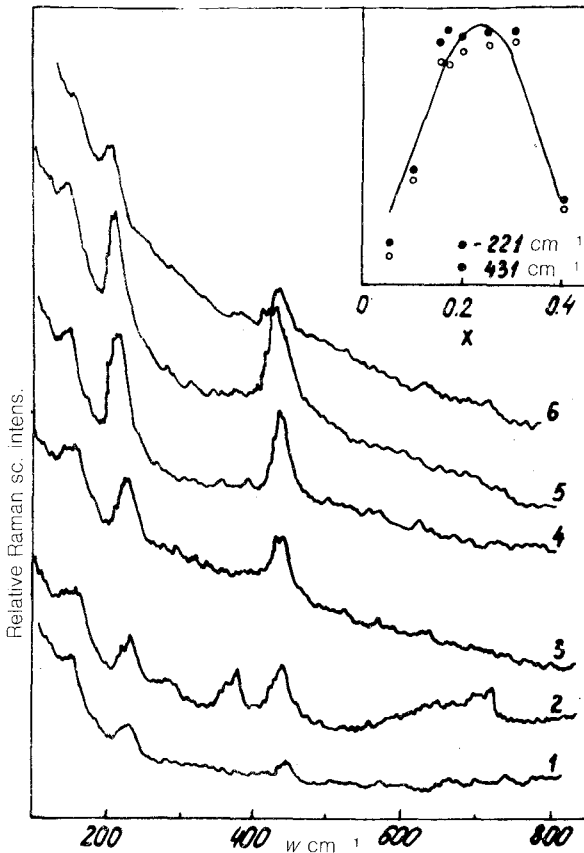
FIG. 2. Raman spectra of samples with various strontium concentrations at 300 K: $1-x = 0.05$; $3-x = 0.1$; $4-x = 0.17$; $5-x = 0.3$; $6-x = 0.4$. $2-x = 0.1$ at 100 K. The inset shows the x dependence of the intensities of the lines at 221 and 431 cm^{-1}.

perature ~ 300 K. The spectrum of this sample at 100 K also exhibits a broad band at 600–750 cm^{-1}, which can be attributed to breathing modes in copper-oxygen planes.[1] These lines were not observed in $La_{1.95}Sr_{0.05}CuO_4$ at 300 K. The reasons might be the very low intensity of the spectrum and a possible local heating at an elevated power of the exciting light.

As in $YBa_2Cu_3O_x$, the spectrum of the Raman scattering by phonons in $La_{2-x}Sr_xCuO_4$ in the Stokes region is superimposed on a strong background of electronic origin,[14] which forms a broad band peaking at 2500–3000 cm^{-1}. Determining the shape and position of this peak at our samples is hindered by the luminescence band observed at ~ 6600 Å, which intensifies with decreasing excitation energy. Nevertheless, the spectra found here permit the conclusion that this scattering is observed both in pure lanthanum oxocuprate and in samples doped with strontium. The XX and ZZ components are comparable in intensity in the $La_{1.83}Sr_{0.17}CuO_4$ single crystal (see the inset in Fig. 1). This result differs from that of Ref. 14: The ZZ spectrum should not be observed in the case of a scattering due to short-wavelength two-dimensional spin fluctuations.

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