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### RAMAN SCATTERING IN SINGLE CRYSTAL $\text{La}_2\text{CuO}_4$

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#### Abstract

The results of a Raman scattering study of single crystal  $\text{La}_2\text{CuO}_4$  are reported. Three  $A_g$  symmetry modes are observed, rather than the two predicted by group theory. Mode assignments are discussed.

At present it is of great interest whether the mechanisms of superconductivity differ essentially for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ , or whether it is one mechanism with various parameters. Raman scattering (RS) is a powerful technique for investigations of phonon spectrum and electron-phonon coupling. Though the superconductivity in  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  was discovered earlier [1] than the 90 K superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [2], the latter compound has been studied more thoroughly by Raman spectroscopy [3-5] than  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ , for which the data, mainly obtained on ceramic samples, are inconsistent [6-10]. The investigation of single crystals makes it possible to define unambiguously the symmetry of Raman-active phonon modes and to classify them, taking into account the masses of vibrating atoms and the spacing between them.

The RS spectra were measured for different faces of  $\text{La}_2\text{CuO}_{4-\delta}$  crystals in back scattering configuration at  $T = 300$  K using a spectrometer with a microattachment. Laser radiation ( $\lambda = 4880 \text{ \AA}$  and  $5145 \text{ \AA}$ ) was focussed to a spot with a diameter  $\sim 3 \mu$ . To avoid the excited region overheating, the laser radiation power on the sample was less than 0.5 mW.

The RS experiments were performed using  $\text{La}_2\text{CuO}_{4-\delta}$  crystal plates ( $\sim 3 \times 4 \times 0.5 \text{ mm}^3$ ) with well-developed basal plane. The crystals were grown from a PbO-based flux. The superconducting transition for these crystals was found to be  $T_c \approx 14$  K. The single crystals had the orthorhombic symmetry (point group  $D_{2h}$ ) with  $a = 5.29 \pm 0.02 \text{ \AA}$ ,  $b = 5.34 \pm 0.02 \text{ \AA}$ ,  $c = 12.96 \pm 0.02 \text{ \AA}$  and contained twins with [110] twinning axis.

At high temperatures ( $T \gtrsim 530$  K)  $\text{La}_2\text{CuO}_4$  crystals belong to the tetragonal crystal structure of  $\text{K}_2\text{NiF}_4$  type ( $D_{4h}^{17}$ ,  $I_4/mmm$ ) with alternating Cu-O(2) and La-O(1) layers. A primitive cell contains 7 atoms (Fig. 1). The

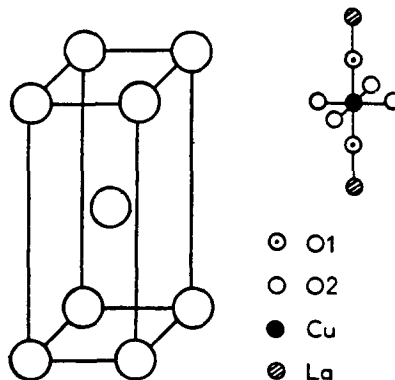


Fig. 1. The elementary cell and formula unit of  $\text{La}_2\text{CuO}_4$  crystal.

phonon spectrum includes 18 optic and 3 acoustic modes. The expansion in the types of symmetry at the  $\Gamma$ -point has the form:  $2A_{1g} + 2E_g + 4A_{2u} + B_{2u} + 5E_u$ . The atoms of La and oxygen O(1), located on the long axis of the distorted octahedra surrounding Cu atoms, have equal position symmetry and participate in  $(A_{1g} + E_g + A_{2u} + E_u)$  vibrations. The atoms of oxygen O(2) lying in the plane of Cu atoms take part in  $(A_2 + B_{2u} + 2E_u)$  vibrations, whereas Cu atoms with the position symmetry coinciding with that of an elementary cell give rise to an acoustic branch of  $(A_{2u} + E_u)$  vibrations. Since only even vibrations are Raman-active, one may expect that tetragonal crystals of  $\text{La}_2\text{CuO}_4$  will display two  $A_{1g}$  symmetry modes corresponding to axial vibrations of La and O(1) atoms, and two doubly degenerate  $E_g$  vibrations of the same atoms.

At room temperature the  $\text{La}_2\text{CuO}_4$  crystals are in the orthorhombic phase. In this case  $A_{1g}$  modes transfer to  $A_g$  ones, and  $E_g$  splits into  $B_{2g}$  and  $B_{3g}$ .

The experimental RS spectra in (zz) and (zx) polarizations are represented in Fig. 2a and 2b. All the three observed lines 220, 427 and  $527\text{ cm}^{-1}$  correspond to  $A_g$  symmetry modes, as can be concluded from their polarization properties. It was found that under excitation normal to the basal plane the intensities of these modes are much smaller. We have not succeeded in recording  $B_{2g}$  and  $B_{3g}$  compounds because of their low RS efficiency.

Therefore, in the Raman spectra of single  $\text{La}_2\text{CuO}_{4-\delta}$  crystals we observe three  $A_g$  symmetry vibrations, polarized along the c-axis. This fact is somewhat surprising, since the group-theory analysis suggests that only two modes of the  $A_g$  symmetry should be expected. These are connected with the vibrations of La and O(1) atoms along the axis, binding them with Cu atoms.

It would be natural to associate the low frequency  $220\text{ cm}^{-1}$  mode with the vibrations of the heavy La atoms, the frequency of the vibration being in good agreement with the calculated value [10]. The high-frequency 427 and  $527\text{ cm}^{-1}$  modes seem to be related to vibrations of oxygen. This is also confirmed by the fact that at high-densities of the excitation power, which causes severe overheating of the crystal and the subsequent loss of oxygen, one may observe the broadening of the high-frequency Raman modes and their slight softening by  $0.3\text{ cm}^{-1}$  (Fig. 2c).

An additional  $A_g$  symmetry oxygen mode, polarized along the c-axis, in the RS spectra may be due to a local breaking of symmetry in the basal plane. Such distortions can result from either spin correlations or the ordering of the oxygen vacancies, and they may lead to cell doubling in the (ab)-plane of the crystal. In this case the number of  $A_g$  symmetry vibrations should increase from 2 to 6.

The number of axial vibrations related with La and O(1) atoms will be doubled and, besides, there should appear two planar vibrations of oxygen O(2). The frequency splitting of the axial mode of O(1) atoms is due to the motion of

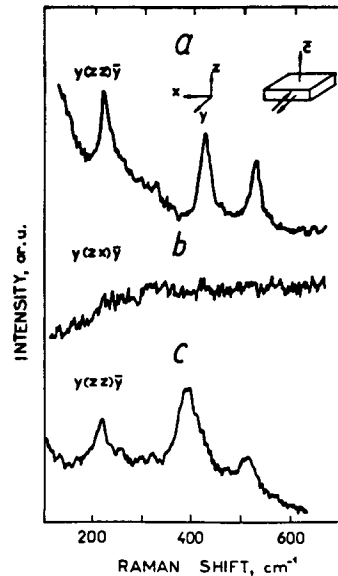


Fig. 2. (a,b) Raman spectra of  $\text{La}_2\text{CuO}_{4-\delta}$  crystals for two different polarizations of scattering light. (c) Raman spectrum in the case of overheating density of laser power (see text).

the two neighboring (ab) in-plane atoms (translationally non-equivalent) with respect to their Cu atoms which may occur now in antiphase. Such vibrations are believed to have higher frequencies than those with cophased motion of neighboring O(1) atoms. It would be desirable to observe the  $A_g$  symmetry planar vibrations to confirm the hypothesis of the doubling of the lattice period in the basal plane. However, no new bands of noticeable intensity appeared under excitation normal to the (ab)-plane. Therefore, we can now only speculate that the RS efficiency of planar modes is lower than that of axial modes.

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