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Journal

Physical Review B, 40(7)

ISSN

2469-9950

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Publication Date

1989-09-01

DOI

10.1103/physrevb.40.4413

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Peer reviewed

Infrared reflectivity spectra of single crystals of La$_2$CuO$_4$

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(Received 21 November 1988)

Infrared reflectivity spectra of a La$_2$CuO$_{4+x}$ single crystal have been studied over a spectral range of 50–5500 cm^{-1}. Anisotropy of the spectra has been observed, indicating a strong anisotropy of the high-frequency conductivity of the crystal. New lines have been found in the optical-phonon excitation spectra. A classification of lattice optical vibrations has been proposed. Spectral reconstruction has been observed in the phonon region of 370 and 445 cm^{-1} at $T_0 = 220 \pm 5$ K, which correlates with the antiferromagnetic transition.

I. INTRODUCTION

Until now infrared spectroscopic studies of the electronic properties and phonon spectrum of La$_2$CuO$_4$-based compounds were usually carried out for ceramic samples. In order to interpret such experimental results, assumptions were employed whose validity may only be established from investigations of single crystals. Some progress was achieved in Refs. 1–3, wherein the authors observed anisotropy of the infrared reflectivity spectra of La$_2$CuO$_4$ single crystals relative to the c axis, analogous to anisotropy of La$_2$NiO$_4$ spectra.[4] The spectra investigated in Refs. 1–3 demonstrated for different crystallographic orientations, behavior characteristic of the insulating state. At present it is customary to assume that stoichiometric La$_2$CuO$_4$ is an insulator (Mott-Hubbard insulator[5]) because of strong localization of carriers on interstitial sites. Doping with Sr, Ba,[5] and, also, deviations from stoichiometry of La and O increase the number of carriers per unit cell, and ultimately results in metallic-type conductivity. In view of this, it seemed interesting to study the behavior of the reflectivity spectra along different crystallographic directions and for different polarizations of light in La$_2$CuO$_4$ single crystals with deviating oxygen stoichiometry.

This work deals with studies of the reflectivity spectra of La$_2$CuO$_{4+x}$ single crystals within the 50–5500 cm^{-1} range (0.006–0.682 eV), of their anisotropy and, also, of the optical-phonon spectra and their transformation with varying the temperature from 77 to 300 K. It has been shown that the reflectivity of light with wave vector q⊥c (electric vector E∥c) demonstrated insulating behavior [conductivity $\sigma(0) \to 0$ as frequency $\omega \to 0$] whereas for the case q⊥c, E⊥c and q∥c, E⊥c a marked contribution of free carriers to the reflectivity spectrum was observed. It has also been found that for q∥c, E⊥c the overall structure of the reflectivity spectrum in the phonon excitation region is analogous to the spectrum of La$_2$NiO$_4$.[4] For La$_2$CuO$_4$,[3] however, detailed studies have made it possible to observe a number of new lines. On the basis of our experimental data and the results of a group-theoretical analysis, we discuss the nature of the reflectivity spectrum lines in the phonon excitation region. We have observed the reconstruction of the phonon spectra at $T_0 = 220$–250 K, which we attribute to the effect of the antiferromagnetic transition on the vibration spectrum.

II. EXPERIMENTAL TECHNIQUE

The reflectivity spectra of La$_2$CuO$_{4+x}$ were studied in near-normal reflection geometry using a Fourier-spectrometry method. To study the temperature dependence of the spectra, the samples were fixed to a cold finger in a vacuum cavity of a continuous-flow helium cryostat. X-ray measurements at 300 K show that the single crystals have orthorhombic symmetry (point group D_{2h}), the unit-cell parameters being $a = 5.29 \pm 0.02$ Å, $b = 5.34 \pm 0.02$ Å, $c = 12.96 \pm 0.02$ Å. The single crystals contained twins with twinning axis ⟨110⟩. The samples, with characteristic dimensions $2.0 \times 1.5 \times 0.5$ mm^3, had a developed basal plane (001). To measure the reflectivity spectra, corresponding to q⊥c, the as-grown crystal surface was studied. The measurements of the reflectivity spectra under the condition q⊥c were carried out from the freshly cleaved surface, parallel to the c axis. Inasmuch as the cleavage plane represented a chaotic set of terraces, with a characteristic size of the order of 100 μm, the spectra were investigated using an infrared microscope.

Measurements of the temperature dependence of the magnetic susceptibility $\chi(T)$ of the samples showed (see Fig. 1, curve 1) that χ increased monotonically with de-
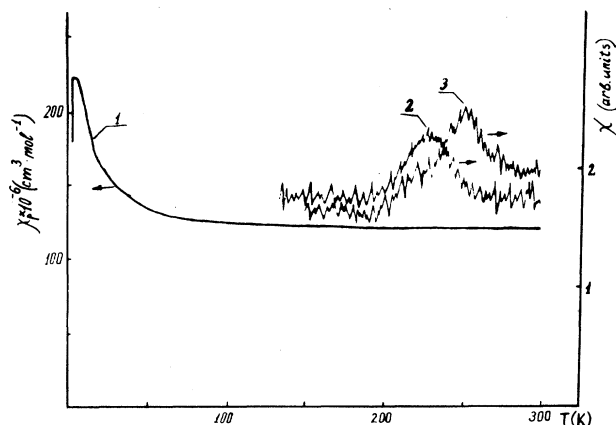
FIG. 1. Temperature dependence of the magnetic susceptibility of as-grown single crystal La_2CuO_{4+x} (curve 1: Faraday's method) and of annealed single crystal (curves 2 and 3: shielding method).

FIG. 2. Magnified image of the basal (001) plane of a La_2CuO_{4+x} sample.

creasing temperature (in the region $T < 300$ K), and at $T = 8$ K a maximum was observed. With further lowering of the temperature ($T < 8$ K) the magnetic susceptibility decreased drastically. Judging from the resistivity properties, no superconducting state arises during this procedure. Therefore the drastic decrease of $\chi(T)$ at low T is instead indicative of the transition to the antiferromagnetic state with the Néel temperature $T_N \approx 8$ K. In accordance with Refs. 6 and 7, in a stoichiometric La_2CuO_{4+x} ($x = 0$) $T_N \gtrsim 200$ K, and T_N monotonically decreases with increasing oxygen content ($x > 0$), approaching zero temperature at $x \approx 0.04$. So, on the basis of these results, one can assume that the as-grown single crystals of La_2CuO_{4+x} in our case have an increased oxygen content, $x \cong 0.04$.

As a result of a low-temperature annealing of single crystals at 300 K in a vacuum for several days (the annealing was followed by periodic cooling down to 77 K to measure the temperature dependence of the reflectivity spectra) there appeared in $\chi(T)$ a characteristic *additional* maximum, analogous to that in Refs. 8 and 9, at $T_N = 220 \pm 5$ K that shifted towards $T_N = 250 \pm 5$ K with increasing annealing time (curves 2 and 3 in Fig. 1). In accordance with Refs. 6–9, this can be attributed to a partial liberation of oxygen *from the surface layer of the sample* due to annealing, which increases T_N. The measurements of $\chi(T)$ were conducted by the Faraday method and a modified shielding method.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Anisotropy of the reflectivity spectra of La_2CuO_{4+x}

Figure 2 shows a magnified image of the basal plane (001) of the crystal. One can observe morphologic specific features in the form of round "plates" with a mean diameter of 150 μm, projecting over the mirror smooth surface. Using an infrared microscope, it was found that in the spectral range of 500–6000 cm^{-1} the reflectivity spectra of the smooth surface and those of the

"plates" are identical. This suggests that the observed peculiarities have the spectrum identical to that of the mirror smooth surface in the range of 50–5500 cm^{-1} too. Figure 3 shows the reflectivity spectrum from the basal plane of the sample (the region with characteristic dimensions of the order of several millimeters). The reflectivity spectrum from the (001) plane ($q\|c$, $E\perp c$) demonstrates the behavior corresponding to the reflectivity due to free carriers, namely for $\nu \rightarrow 0$, the reflectivity has a threshold value, corresponding to nonzero dc conductivity and, subsequently, with growing ν the reflectivity decreases monotonically. The reflectivity spectrum from the basal plane (Fig. 3) can be satisfactorily described in terms of Drude's model (reflectivity by free carriers) $\epsilon = \epsilon_\infty - \nu_p^2/\nu(\nu + i\gamma)$ with the following parameters: the plasma frequency $\nu_p = 12\,000$ cm^{-1}, the permeability $\epsilon_\infty \cong 6$, and the damping $\gamma \cong 9000$ cm^{-1}.

We investigated the angular dependence of the reflectivity spectra of the linearly polarized light within the spectral range of 500–5000 cm^{-1}. It has been found that the reflectivity spectra from the basal plane ($q\|c$, $E\perp c$, see labelings of Fig. 6) are analogous to the spectrum of Fig. 3 and are isotropic. Possibly this is associated with the presence of twins, providing for an effective averaging of possible anisotropy with respect to the a and b axes. At the same time, the reflectivity from the plane perpendicular to the basal one is anisotropic, as seen
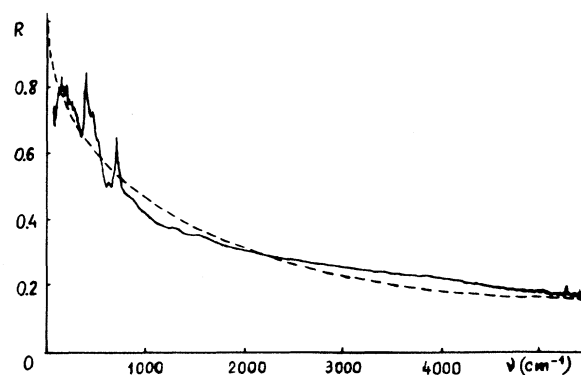

FIG. 3. Reflectivity spectrum measured from the basal (001) plane of La_2CuO_{4+x} at $T = 300$ K. The dashed curve is a Drude fit.
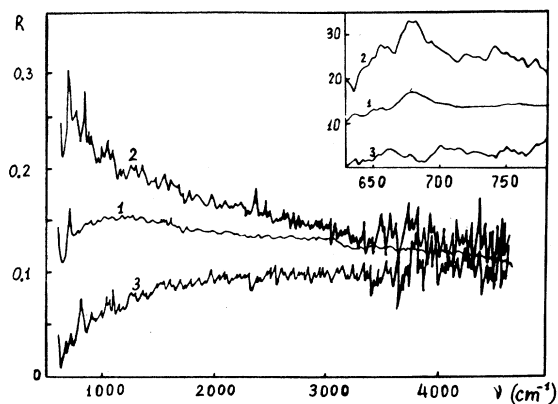
FIG. 4. Reflectivity spectra of linearly polarized light from the surface parallel to the c axis of a La_2CuO_{4+x} single crystal at $T = 300$ K: 1, reflectivity spectrum of unpolarized light (wave vector $q\perp c$); 2 and 3, $E\perp c$ and $E\|c$, respectively.

FIG. 5. Reflectivity spectra from the basal (001) plane: 1 and 2, spectra of La_2NiO_4 (Ref. 4) and La_2CuO_{4+x}, respectively, at $T = 300$ K; 3, spectrum of La_2CuO_{4+x} at $T = 77$ K.

from Fig. 4. Spectrum 3 ($q\perp c$, $E\|c$) demonstrates typical insulating behavior. On the other hand, a monotonic growth of the reflectance with decreasing of the wave number ν in spectrum 2 ($q\perp c$, $E\perp c$) is analogous to the reflectivity spectral behavior from the basal plane (Fig. 3) and indicates a greater high-frequency conductivity in the ab plane. The observed anisotropy qualitatively agrees with the results of theoretical calculations.[9] Moreover, taking into account the conclusions of Ref. 9, the high-frequency conductivity may be attributed to the preferential motion of free carriers in the cuprate plane $CuO_2(1,2)$ (see Fig. 6).

Coming back to Fig. 4, we note that within the investigated spectral range, spectrum 3 ($q\perp c$, $E\|c$) is identical to the corresponding spectrum of Ref. 3, which confirms the conclusion of the authors of this work about the presence of the electronic excitations at ~ 0.6 eV in La_2CuO_4.

B. The phonon spectrum

In the low-frequency range, $\nu < 750$ cm^{-1}, wherein the optical-phonon lines are located, the reflectivity spectrum of La_2CuO_{4+x} at $T = 300$ K (spectrum 2, Fig. 5), like the spectrum of La_2NiO_4 (Ref. 4) (spectrum 1, Fig. 5), consists of three intense lines, whose spectral positions are close in both type crystals. The analogous spectra have already been observed in single crystals of La_2CuO_4 in Ref. 3. However, the spectral range $350-650$ cm^{-1} exhibits an additional weak structure. With a temperature decrease down to 77 K (spectrum 3, Fig. 5) this structure becomes distinct, while the number of the lines in the reflectivity spectrum increase. The above-mentioned
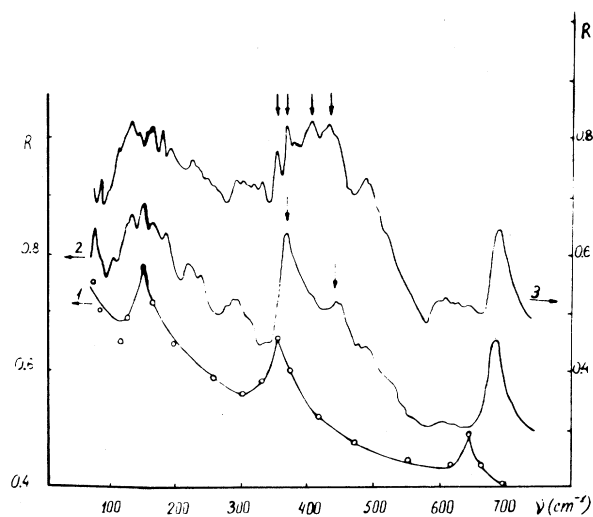
structure is a "true" intrinsic property of La_2CuO_4 single crystals because intensity of this structure is much higher than the noise level δR (over the spectral range $300-680$ cm^{-1} $\delta R = 0.005$). At the same time within the spectral range $50-300$ cm^{-1} the noise level is too high, $\delta R = 0.03$, so we cannot identify the real phonon lines with the structure, observed in that spectral range. Moreover, the structure observed in the spectral range $300-680$ cm^{-1} was reproduced on the series of La_2CuO_4 single crystals grown under slightly different conditions. Table I presents the spectral positions of the spectral lines of Fig. 5.

At $T > 530$ K, La_2CuO_4 is known to have the tetragonal crystal structure of the K_2NiF_4 type (D_{4h}^{17}, $I4/mmm$). At $36 < T < 480$ K, La_2CuO_4 has the orthorhombic structure (point group D_{2h}) (Refs. 10 and 11) that, in accord with Ref. 12, can transform to monoclinic at $T \lesssim 36$ K. Numerous x-ray and neutron-diffraction studies indicate a twofold increase of the unit-cell volume of La_2CuO_4 during its transition from the tetragonal to the orthorhombic structure. However, the real structure of the orthorhombic phase remains an open question.[11,13] At present the model of shearing of the ab plane as a result of inclination of the CuO_6 octahedra relative to the tetragonal b axis seems more reliable.[10,11] However, the other viewpoint based on variation of the angle between the tetragonal axes a and b cannot be excluded.[11,13] This complicates a theoretical group analysis of normal vibrations in the orthorhombic phase of La_2CuO_4. Several

TABLE I. Spectral position (cm^{-1}) of the reflectivity spectra lines maxima for single crystals of La_2NiO_4 ($T = 300$ K) (Ref. 4) and La_2CuO_{4-x} at $T = 300$ and 77 K.

La_2NiO_4	300 K	646						356		146
La_2CuO_4	300 K	683	600	510	490	445		370		145
La_2CuO_4	77 K	691	600	510	490	432	405	369	354	145

workers[14,15] carried out a group-theoretical analysis of normal vibrations in the tetragonal La_2CuO_4. Allowing for the fact that at $T = 300$ K the most intensive lines of the reflectivity spectrum of the orthorhombic La_2CuO_4 are practically identical to the lines of the tetragonal structures of La_2NiO_4 and $La_{2-x}Sr_xCuO_4$, and that the orthorhombic structure is, in fact, a very weak distortion of the tetragonal phase (the ratio of the lattice parameters $a/b = 1.009$), the results of the group-theoretical analysis for the tetragonal phase may be used for classification of the main phonon lines in the orthorhombic La_2CuO_4. There are seven atoms in a unit cell of the tetragonal La_2CuO_4, therefore the vibrational spectrum contains 21 modes: three ($A_{2u} + E_u$) acoustic, which are determined by the motion of copper atoms, and 18 optic modes. According to the group-theoretical analysis,[15] the Raman scattering spectra may exhibit two fully symmetric A_{1g} modes and two twofold degenerate E_g modes. As the crystal is centrosymmetric, these vibrations do not have to be manifested in the infrared spectra. Allowing for the fact that the E_{2u} "silent" mode is also inactive in the infrared spectrum, one can presume that the infrared spectrum may exhibit three modes of the A_{2u} symmetry and four twofold degenerate E_u modes. A_{2u} modes are determined by atomic displacements along the c axis, E_u modes are planar vibrations in the (001) plane. Since we have investigated the normal reflection of light from the basal (001) plane, the reflectivity spectrum of the tetragonal La_2CuO_4 may exhibit four E_u modes, shown schematically in Fig. 6: one mode is connected with a planar vibration of La; one bending vibration is determined by the motion of oxygen O(3); the remaining two modes are attributed to the bending and stretching vibrations of O(1,2), respectively.

As a result of polarized reflectance measurements (see the inset of Fig. 4) it has been found that the 683 cm^{-1} line is excited only in the polarization E⊥c. Therefore, it corresponds to planar vibrations of the symmetry E_u. Inasmuch as this is the highest-frequency line, we believe that among possible normal vibrations, presented in Fig. 6, the 683 cm^{-1} line corresponds to the stretching vibration of oxygen atoms O(1,2) in the basal (001) plane, and the lowest-frequency 145 cm^{-1} line corresponds to the bending E_u vibrations of the heaviest atoms of La. The frequency of the bending vibrations is by a factor 1.5–2

FIG. 6. Schematic presentation of the E_u symmetry vibrations in the tetragonal La_2CuO_{4+x} and the corresponding frequencies at $T = 300$ K, in parentheses at $T = 77$ K.

lower than the stretching vibrations of the same atoms. Therefore the remaining two twofold degenerate vibrations of oxygen atoms (see Fig. 6) are naturally to be attributed to the 370 and 445 cm^{-1} lines. The 370 cm^{-1} line is determined by the bending vibrations of O(3), and the 445 cm^{-1} by the bending vibrations of O(1,2), since the Cu-O(3) bonds are 1.26 times longer than the Cu-O(1,2) bonds. This assignment of the vibrations is supported by the satisfactory agreement between the ratio of frequencies of these lines and the estimate based on the relationship $v \sim d^{-4}$, and also by that fact that, in accord with Ref. 15, the A_{2u} stretching vibration of O(3) atoms with a frequency 520 cm^{-1}, whereas the stretching vibration of O(1,2) is 683 cm^{-1}. As has been mentioned above, the cuprate plane $CuO_2(1,2)$ is likely to contain a high concentration of free carriers and, in accord with Ref. 16, the electronic and vibrational motions in this plane may be characterized by a strong electron-phonon coupling. Therefore, one can expect that, other conditions being equal, the reflectivity spectrum line, corresponding to the bending vibrations of O(1,2) atoms will have a greater width and a smaller intensity as compared with the line determined by the bending vibration of O(3) atoms. One can see from spectrum 2 of Fig. 4 that it is precisely this relationship that is observed for the 445 and 370 cm^{-1} lines.

Besides the considered lines, we have observed at $T = 300$ K comparatively weak 500, 520, and 600 cm^{-1} lines. The presence of these lines may be associated with the fact that in the investigated temperature range La_2CuO_4 has not the tetragonal but the orthorhombic structure. In accord with Refs. 1, 9, and 10, the transition from the tetragonal to the orthorhombic phase occurs via the rotation of CuO_6 octahedra against the pseudotetragonal b axis by an angle with the (001) direction of approximately 3° at 300 K. In this case, the unit-cell volume doubles, and apart from removal of degeneracy lifting of the E_u modes of the tetragonal phase, under the transition to the orthorhombic phase, additional lines in the infrared reflectivity spectra may appear, since the modes with Brillouin reflection in the case of the tetragonal phase can be excited at the Γ point (due to the doubling of the tetragonal unit cell). Therefore they can manifest themselves in the infrared spectra.

C. The temperature dependence of the reflectivity spectra in the range of 300–77 K

Figure 5 suggests that at $T = 77$ K instead of the 370 and 445 cm^{-1} lines ($T = 300$ K) there appear the 354 and 369 cm^{-1}, and 405 and 432 cm^{-1} lines. Such reconstruction of the phonon spectrum might be explained by an increase of an undetectable, at 300 K, splitting of the 370 and 445 cm^{-1} lines with lowering the temperature down to 77 K, since it is known that the degree of orthorhombicity of La_2CuO_4 increases monotonically during this event.[7] However, in such a case one may expect the appearance of the analogous structure in place of the remaining lines, for example, 683 cm^{-1}. But that line simply shifts to higher energy by approximately 8 cm^{-1} with decreasing temperature from 300 to 77 K. More-
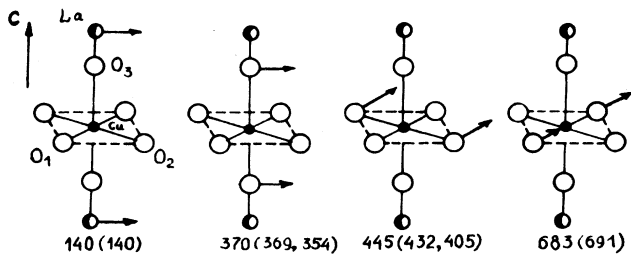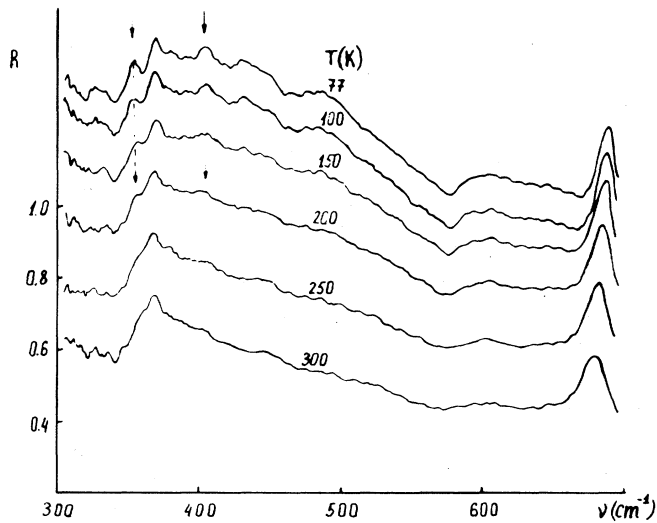
FIG. 7. Temperature dependence of the reflectivity spectrum from the basal plane of La_2CuO_{4+x}. The R axis corresponds to curve measured at 300 K. Other curves are shifted along R axis by step ~ 0.1.

over, the investigation of the temperature dependence of the reflectivity spectra (Fig. 7) has shown that the annealing of the samples at 300 K in the vacuum cavity of a continuous-flow helium cryostat, used to measure the temperature dependence of the spectra, results in the appearance of weak 354 and 405 cm^{-1} lines at 300 K too, in contrast to the spectrum of the starting unannealed samples (spectrum 2, Fig. 5). The spectral position of the new lines with respect to the 370 and 445 cm^{-1} lines actually remains unchanged with decreasing temperature, whereas the ratio of the crystal lattice parameters a/b, characterizing the degree of orthorhombicity, grows from 1.009 to 1.016 with decreasing temperature from 300 to 77 K.[11] So the weak temperature dependence of the splitting of these lines cannot be simply explained in the approximation of degeneracy lifting in the orthorhombic phase. The reason for the spectrum reconstruction might be the alteration of the crystalline structure. It is, however, known that within 300–77 K no structural phase transition takes place in La_2CuO_4.[12]

Analysis of the temperature dependence reflectivity spectra suggests that the spectrum reconstruction may be associated with the phase transition in the electronic sys-

tem, namely with the transition to the antiferromagnetic state. Figure 7 shows that the 354 and 405 cm^{-1} amplitudes are practically unvarying for $T > 230$ K, and they strongly increase with decreasing temperature starting from $T_0 = 220 \pm 5$ K. The measurements of the magnetic susceptibility $\chi(T)$ in this crystal show the presence of a maximum, characteristic of the sample transition to the antiferromagnetic state, at $T_N = 220 \pm 5$ K (curve 2 in Fig. 1). Moreover, a subsequent anneal of the crystal in a vacuum at 300 K for several days leads to an increase of both T_0, at which the reconstruction of the reflectivity spectrum occurs, and T_N to 250 ± 5 K. So, the results of optical and magnetic measurements indicate the effect of the antiferromagnetic transition on the phonon spectrum.

As has been noted above, the 445 and 370 cm^{-1} lines ($T = 300$ K) are determined by the in-phase bending vibrations of oxygen atoms $O(1,2)$ and $O(3)$, respectively (Fig. 6). The 405 and 354 cm^{-1} lines, appearing on the long-wave side of the 445 and 370 cm^{-1} lines, are likely to be the analogous vibrations of the same atoms, and their appearance in the reflectivity spectrum is stipulated by the lifting of degeneracy due to the interaction of these vibrations with the ordered system of spins. A maximal splitting is observed for the bending vibrations of $O(1,2)$ (445 cm^{-1} at 300 K) and it amounts to 27 cm^{-1} at 77 K. Splitting of the 370 cm^{-1} is approximately two times smaller, i.e., 15 cm^{-1}. A smaller value of the splitting in this case is likely determined by a weaker overlapping of the wave functions of Cu and $O(3)$, compared to Cu-$O(1,2)$, due to the difference of the interatomic spacings (the ratio of these spacings is 1.28). In conclusion we note that the appearance of the 354 and 405 cm^{-1} lines at 300 K in the reflectivity spectra of the annealed crystals may be attributed to antiferromagnetic fluctuations at $T > T_N$, the probability of the appearance of which seems to be greater the closer T is to T_N. Therefore, the absence of these lines in the spectrum of the starting crystal at 300 K may be explained by the fact that in it $T_N = 8$ K, which is much lower than 300 K, as contrasted with the case of the annealed crystal ($T_N = 220$–250 K).

ACKNOWLEDGMENTS

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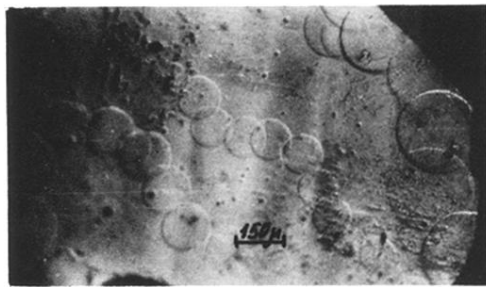
FIG. 2. Magnified image of the basal (001) plane of a La_2CuO_{4+x} sample.