

Properties of the optical branch of the phonon spectrum of La_2CuO_4 single crystals

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X-Ray diffraction, acoustic, and thermal investigations of La_2CuO_4 single crystals were employed to determine the tetragonal-orthorhombic transition and anomalies in the temperature dependence of the absorption and velocity of longitudinal sound, which are governed by the interaction of the acoustic and optical branches of the phonon spectrum of La_2CuO_4 . The different values of the temperatures of these features are attributed to the deformation of the optical soft mode of the phonon spectrum due to the different atomic composition of the dopants added to the single crystals.

It is well known that the superconducting compound La_2CuO_4 undergoes a number of transformations, whose temperatures depend on the impurities in the material, in the temperature interval 4.2–535 K.^{1–6} For example, the temperature T_0 of the crystallographic tetragonal-orthorhombic transition in the compound $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ changes from 535 to 4.2 K as the Sr concentration is increased to 0.2.³ In the case of some impurities (Ba) different crystallographic transformations also occur at temperatures below 100 K.^{2,7}

The crystal structure of La_2CuO_4 is shown in Fig. 1. At high temperatures it is a body-centered tetragonal structure with the space group $14/mmm$ and the composition of the unit cell is described by the formula La_2CuO_4 . The CuO_6 octahedron, marked by the arrows in Fig. 1, can rotate around the 011 and $01\bar{1}$ axes. A second-order transition into the orthorhombic phase occurs as a result of this rotation. The transition is accompanied by doubling of the lattice and composition of the unit cell. Neutron-diffraction studies^{4,5,8} have shown that this transition is brought about by the softening of the optical phonon branch. The dispersion curves of this branch are presented in Fig. 2. The properties of this optical phonon mode are the subject of this paper.

In previous work,¹⁰ while studying the acoustic characteristics of a La_2CuO_4 single crystal, grown in $\text{Li}_4\text{B}_2\text{O}_5$ flux, we discovered anomalies in the temperature dependence of the absorption and velocity of longitudinal sound at 100–150 K (low-temperature feature). The dependences obtained were determined more accurately in Ref. 11, and it was conjectured there that the appearance of these features is associated with possible instability of the soft mode. It was subsequently shown in Ref. 12 that the observed features of the acoustic characteristics can be explained by taking into account the interaction of the optical soft mode with the acoustic mode in the region where these branches of the phonon spectrum intersect. Analysis of the form of the acoustic features then makes it possible to determine more accurately the type of optical-mode vibrations with which the acoustic vibrations mainly interact.

In this paper we present in detail all of the results of the investigation performed, including those obtained for a single crystal grown by a different technique. It was established that not only the temperature T_0 of the tetragonal-orthorhombic transition but also the temperature of the low-tem-

perature feature depends significantly on the presence of impurities in the sample. If the temperature T_0 increases when the impurity concentration decreases, then the temperature of the low-temperature feature T_{lf} decreases. This indicates that a nontrivial deformation of the low-lying optical mode occurs as a result of the presence of foreign atoms in the crystal lattice.

Experimental procedure

The objects of investigation were La_2CuO_4 single crystals grown in $\text{Li}_4\text{B}_2\text{O}_5$ or CuO melt. These samples are designated below as LCO(Li) and LCO(Cu), respectively. Single crystals of LCO(Li) were grown by A. P. Voronov at the Khar'kov Physicotechnical Institute of the Academy of Sciences of the Ukrainian SSR. The crystals were grown in a platinum crucible by drawing the crystal out of the melt on a platinum wire. The obtained crystals had dimensions of $3 \times 3 \times 5 \text{ mm}^3$. In this work we employed two samples, cut from the grown crystal. A $10 \times 5 \times 5 \text{ mm}^3$ LCO(Cu) single crystal was grown by the procedure of Ref. 13 in the laboratory of S. N. Barilo.

Samples machined into ellipsoids with semiaxes of 0.145, 0.181, and 0.185 mm were used for structural x-ray diffraction studies on an automated Enraf-Nonius CAD4F diffractometer (Ag $K\alpha$ radiation, $\lambda = 0.5609 \text{ \AA}$, graphite monochromator) in the temperature interval 100–480 K.

Measurements of the heat capacity were performed in a vacuum calorimeter with an inertial heat screen with a heater. The working heater and thermocouple were mounted directly on the sample, which had a mass of $\sim 40 \text{ mg}$.

The acoustic characteristics of the crystals were measured at temperatures from 4.2 to 360 K at frequencies of 10, 20, 50, 60, and 150 MHz. Apparatus constructed according to the principle of a pulsed acoustic bridge, which has a measuring arm containing the sample with piezoelectric transducers and a signal comparison arm, including changeable attenuator and phase shifter, were used in the measurements. Pulses, cut from the continuous oscillations of an hf oscillator, appeared at the output detector approximately simultaneously. The pulses could be tuned so as to achieve complete cancellation at the receiver unit by adjusting the amplitude and phase in the comparison arm. The amplitude and phase were adjusted automatically in the comparison

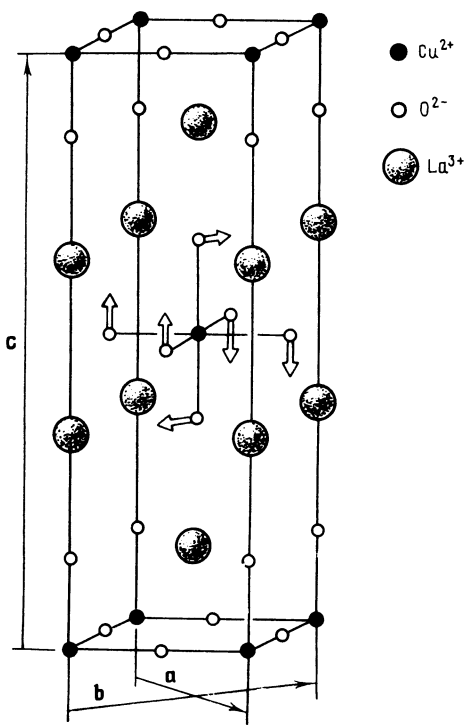


FIG. 1. The structure of La_2CuO_4 . The crystal structure changes as the CuO_6 octahedron (indicated by the arrows) rotates.

arm with the help of two servosystems. This made it possible to record at the same time during the experiment the change in the velocity and damping of the sound. The setup is described in detail in Ref. 14. Two devices were employed in

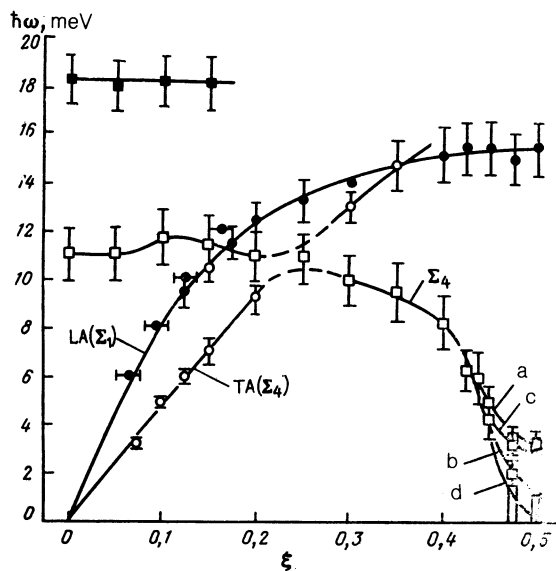


FIG. 2. The dispersion curves in the direction $(\xi\xi 0)$ in La_2CuO_4 from Ref. 4. The classification of the modes is taken from Ref. 9. The tetragonal-orthorhombic transition occurs with vanishing of the Σ_4 mode at the cell center $(1/2, 1/2, 0)$. The measurements were performed at the temperatures 295.78 K (a), 573 K (b), 473 K (c), and 423 K (d); $T_0 = 423$ K.

this work: one for performing measurements at 10 MHz and the other for performing measurements at 20–150 MHz. Plane-parallel slabs, whose planes were perpendicular to a selected crystallographic direction, were cut from the crystals for the measurements. Slabs of LiNbO_3 were used as emitter and detector.

Results

A preliminary x-ray diffraction analysis⁹ of the LCO(Li) crystal showed that at 300 K the lattice constants are equal to $a = 5.3845 \text{ \AA}$, $b = 5.35228 \text{ \AA}$, and $c = 13.1490 \text{ \AA}$ and the disorientation of the blocks was less than 5° . Analysis of the composition of LCO(Li),¹⁵ performed by the Rutherford-backscattering method and according to the yield of α particles produced in the reaction $\text{Li}(p, \alpha)$ caused by a beam of 650 keV channeling hydrogen atoms with a divergence of less than 0.01° , revealed the presence of Li atoms in an amount equal to 2 mass % in the La–Cu chains. These data were not sufficient to determine whether the Li atoms occupied interstitial positions or replaced Cu atoms.

A more accurate structural analysis made it possible to find the parameters of the unit cell. They were determined from 25 distant reflections ($[\sin\vartheta]/\lambda = 0.7 \text{ \AA}^{-1}$): $a = 5.362(1)$, $b = 5.372(1)$, and $c = 13.124(3) \text{ \AA}$. Analysis of two-dimensional $\omega/2\vartheta$ scans of specially selected reflections showed that the crystal is divided into twins along the (110) and $(1\bar{1}0)$ planes. Approximately 3683 reflections were measured in the reciprocal-space hemisphere with radius 1.145 \AA^{-1} . Of these, 652 were independent with $I > 3\sigma(I)$. A correction for absorption was introduced by Gaussian quadrature ($\mu = 146.0 \text{ cm}^{-1}$, $R_{av} = 0.049$).

A detailed analysis of systematic extinctions in the diffraction data, taking into account twinning, made it possible to identify unequivocally the space group of symmetry $Abma$. The ratio of the volumes of the components of the twin was determined from the ratio of the intensities of reflections of the type $(2h + 1, 2k, 2l)$, $(2h, 2k + 1, 2l)$, $(2h, 2k + 1, 2l)$, and $(2h + 1, 2k, 2l + 1)$, since only separate components of the twin scatter at these sites (at other sites both components scatter simultaneously):

$$\begin{aligned} I(2n+1, 2m, 2l)/I(2m, 2n+1, 2l) \\ = -I(2n, 2m+1, 2l+1)/I(2m+1, 2n, 2l+1). \end{aligned}$$

For the LCO(Li) sample studied this ratio was equal to 0.69:0.31.

In order to refine the model of the structure, a definite value of the ratio of the volumes of the components of a twin was used to identify the contributions of separate components to reflections containing information about scattering from both components of the twin. The model of the structure was refined by the method of least squares using the crystallographic programs PROMETHEUS.¹⁶ The refinement of the model of the structure with 100% filling of the positions for all crystallographically independent atoms in the anisotropic approximation gave an R -factor = 0.023. From the data of Ref. 15 it was known that foreign Li atoms are present in the crystals. In order to determine the location of these atoms in the lattice the fill ratios for all atoms were refined. The results of the refinement showed that only the Cu atoms do not fill their positions completely

$[q = 0.92(1)]$, and the R -factor dropped from 0.023 to 0.017.

If the Li atoms occupied precisely the same positions as the Cu atoms, then it would be possible to recompute or refine the ratio of Cu and Li atoms in this position simply by recalculating or refining the model with a mixed scattering curve for the positions of the Cu atoms (recalculation gives the value $q = 0.91$, which is equal to, within a standard deviation, the value obtained above). However the Cu–O distances in the CuO_2 plane are equal to 1.9 Å, and they are short in the case when Cu atoms are replaced with Li atoms. It can be conjectured that the Li atoms are displaced from the CuO_2 plane in the direction of apical oxygen along the Cu–O–La chain by 0.3–0.4 Å, and thereby occupy positions in a semi-octahedron with the distance from the oxygen atoms equal to about two angstroms, which is characteristic for Li atoms.

Analysis of the map of difference syntheses of the electronic density near the proposed Li position did not give any additional arguments in support of this hypothesis; the Li atoms have only three electrons and they would have to occupy this position with a 4% probability (this is 0.12 electrons, which is at the noise level on the maps of the difference electron density). Since, however, we did not observe a copper deficit in any of the samples of lanthanum cuprates which we studied previously,¹⁶ we can assert quite confidently that in this crystal 9% of the Cu atoms are replaced with Li atoms and the latter atoms occupy a position shifted from the copper position in the direction of apical oxygen by 0.3–0.4 Å. The concentration of Li atoms which was obtained by the method of structural analysis, equal to $9 \pm 1\%$, satisfactorily agrees with the recalculation of the data of Ref. 15, which gives 10–11%.

At 273 K the LCO(Li) crystals belong to the orthorhombic system and are twinned along the (110) and (1 $\bar{1}$ 0) planes. The twinning effect can be clearly seen by recording the profiles of the diffraction reflections of the type $hh0$ ($\Delta\omega = 0.4$ between the extreme components in Fig. 3a). The profiles of the 440 reflection, which were recorded on a

CAD4 automated diffractometer (Mo $K\alpha$ radiation, pyrolytic graphite monochromator; the $K\alpha_1$ component was separated with an aperture detector) in the temperature interval 130–250 K and for the range 273–333 K, are presented in Fig. 3a. Figures 3b and c show the temperature dependence of the FWHH of the reflection 440. When the LCO(Li) crystal is heated up to 318 ± 2 K the splitting characteristic of twinning vanishes and the crystal transforms into the tetragonal phase at the temperature T_0 . When the temperature is lowered the splitting of the components of the twin is completely restored.

The LCO(Cu) crystal transforms into the tetragonal phase at a higher temperature, which for samples cut from the same single crystal falls in the range 451–469 K. Hysteresis (~ 2 K) of the phase transition temperature is observed. When the samples are first heated appreciable redistribution of the intensities of the separate components of the twin occurs in them at temperatures $T < T_0$ below the phase-transition point. This redistribution is not recovered when the samples are cooled to room temperature. Subsequent heating and cooling cycles no longer change the pattern that emerged after the first cycle, if in so doing the temperature is not raised above the transition point T_0 .

Measurements of the heat capacity of LCO(Li) showed the presence not only of a Λ -like fluctuation maximum of the amplitude of about 1.5% at T_0 , but also that a systematic increase (by $\sim 1.4\%$) of the heat capacity after the sample transforms into the orthorhombic phase with the average heat capacity ~ 0.4 J/g·K is possible.

Measurements of the heat capacity of the LCO(Cu) sample performed after the sample has been repeatedly annealed up to 500 K, showed the presence of only a fluctuation maximum with an amplitude of about 3% at T_0 .

In the region of the tetragonal–orthorhombic transition at ~ 325 K clearly pronounced features of the acoustic characteristics, typical for second-order phase transitions, are observed in the LCO(Li) samples (Fig. 4). The significant anisotropy of the effect is interesting. The main changes of the velocity of sound occur for sound propagation directions

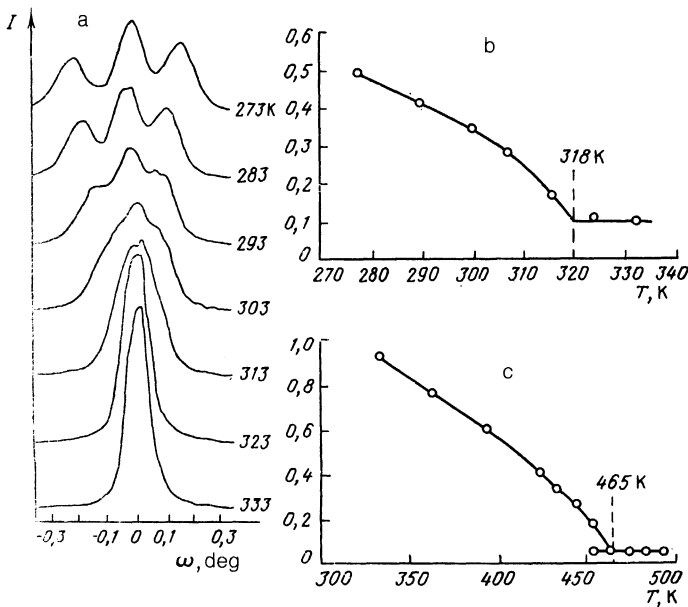


FIG. 3. a) Temperature dependence of the profile of the 440 reflection for LCO(Li); b, c) temperature dependence of the FWHH of the 440 reflection. b) LCO(Li) crystal; c) one of the samples of the LCO(Cu) crystal (heating). The vertical line is the temperature of the tetragonal–orthorhombic transition.

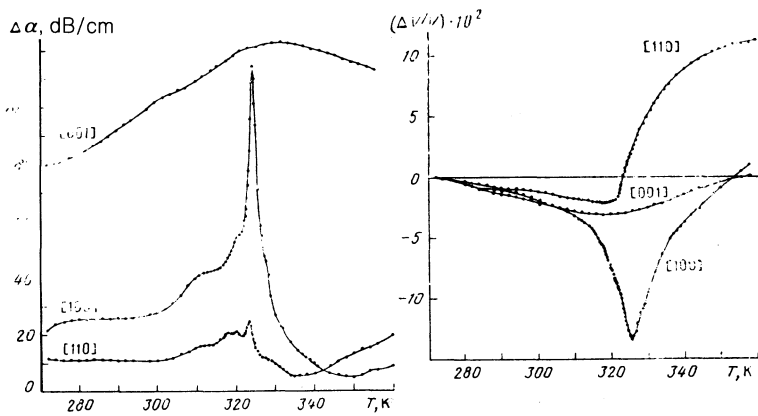


FIG. 4. Temperature dependence of the absorption α and velocity V of sound with frequency 50 MHz near the tetragonal-orthorhombic transition in the crystal LCO(Li). At 270 K V_{100} , V_{110} , and V_{001} are equal to, respectively, $(4.3 \pm 0.2) \cdot 10^5$, $(4.8 \pm 0.2) \cdot 10^5$, and $(5.7 \pm 0.2) \cdot 10^5$ cm/s.

lying in the ab plane, in which the lattice parameters change at the tetragonal-orthorhombic transition. A sharp λ -like feature, predicted in the theory of Ref. 18 for second-order phase transitions, can be seen on the absorption curves in the case of sound propagation along the 100 axis.

A number of additional features, whose location and amplitude changed when the sample was remounted in the acoustic holder, can be seen on the absorption curves. These additional features, like the deformation of the $\Delta V/V$ curves from one experiment to another, most likely indicate the appearance of mechanical stresses in the sample, which make the transition more complicated and lead to the appearance of twinning boundaries and additional features associated with the motion of these boundaries.

Acoustic investigations of the LCO(Li) single crystal in the interval 4.2–260 K led to the observation of sharp anomalies in the temperature dependence of the absorption and velocity of sound at 100–150 K (Fig. 5). These features differ from those observed in the region of the tetragonal-orthorhombic transition primarily by the fact that there is no sharp λ -like maximum on the absorption curve; in addition, the anisotropy of the change of the sound velocity has a different form. Sound absorption in this temperature range changes, to a first approximation, in proportion to the sound frequency and not the frequency squared, as is usually observed in crystals at low temperatures (Fig. 6).

For the LCO(Cu) single crystal the low-temperature anomaly in the acoustic characteristics, especially in the temperature dependence of the sound velocity, is several

times smaller. The anomalies are appreciably shifted in the direction of lower temperatures (Fig. 7). Thus in the case of the LCO(Li) single crystal the characteristic features (maximum of the sound velocity or minimum of the sound absorption in the 100 direction) occur at 120–130 K, whereas in the LCO(Cu) single crystal they are shifted into the region 60–75 K.

Laegreid *et al.*¹⁹ investigated the acoustic characteristics of a $\text{La}_{1.88}\text{Sr}_{0.12}\text{CuO}_4$ single crystal for longitudinal sound having the frequency 13 MHz and propagating along the 100 axis. They observed anomalies at 255 and 110 K. They identified the anomalies at 255 K with the tetragonal-orthorhombic transition. They did not determine the nature of the anomaly at 110 K, though a change in the intensity of the reflections of the orthorhombic lattice and a change of the characteristic frequency of an oscillator made from the crystal were observed in the same temperature range. It is very likely that this anomaly is of the same nature as the low-temperature anomalies that we observed at T_{lf} .

Discussion

We now examine the tetragonal-orthorhombic transition in La_2CuO_4 . The temperature of this transition, as follows from the data presented in Figs. 3 and 4, can differ somewhat, even if the samples were prepared from the same starting single crystal. Thus the temperature T_0 , determined from the acoustic and heat capacity measurements on the same single crystal, is virtually the same (325 K), but struc-

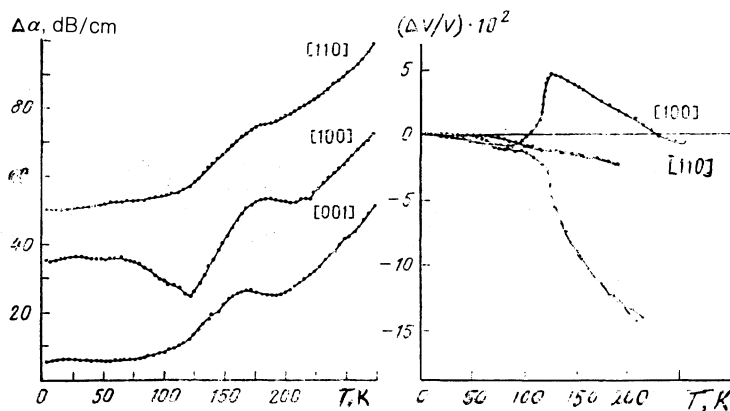


FIG. 5. The temperature dependence of the absorption α and velocity V of sound with frequency 50 MHz near the low-temperature feature in LCO(Li). The values of V_{100} , V_{110} , and V_{001} at 4.2 K are equal to, respectively, $(4.3 \pm 0.2) \cdot 10^5$, $(5.0 \pm 0.2) \cdot 10^5$, and $(6.8 \pm 0.2) \cdot 10^5$ cm/s.

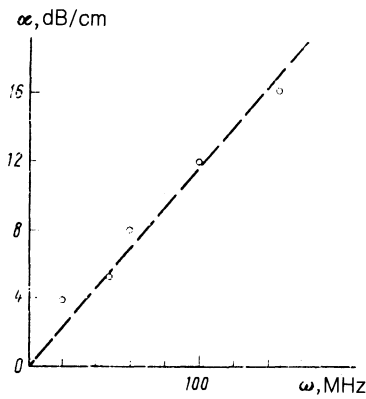


FIG. 6. The frequency dependence of sound absorption α in LCO(Li) at 120 K.

tural measurements on a grain of the same single crystal yield $T_0 = 318 \pm 2$ K. Analogously for the LCO(Cu) crystal the value of T_0 for two grains of the same crystal differed by 14 K. All this, and also experiments on the effect of heating on the details of the change in the structure of the sample with temperature, indicates the possible existence of additional factors (internal stress, nonuniform distribution of impurities, etc.), which complicate the details of the transition and make it impossible to compare these data with the results of the theory of second-order phase transitions. Measurements of the heat capacity showed that the possible difference between the heat capacities of the tetragonal (for $T > T_0$) and orthorhombic (for $T < T_0$) phases is, evidently, less than indicated previously in Ref. 6, if prior to the measurements the sample was made homogeneous by means of repeated annealings up to $T > T_0$.

The published data, obtained from comparison of experiments on ceramic samples,⁶ on the dependence of the temperature T_0 on the concentration x of foreign atoms in the La_2CuO_4 lattice do not make it possible to find a smooth dependence $T_0(x)$, even for the single impurity Sr. This reflects the uncertainty of the properties of the ceramic samples. If, however, the characteristics of only single-crystalline samples are studied, then, as one can see from Fig. 8, the dependence of T_0 on the concentration x of foreign atoms in the crystals does not depend on whether this atom is Sr, Ba, or Li. This reflects the fact that the decrease in T_0 is primar-

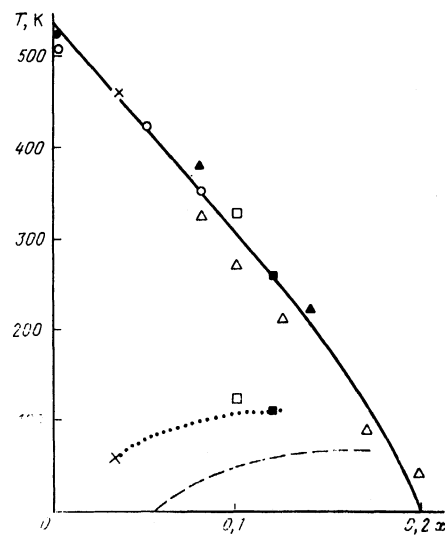


FIG. 8. Features of the characteristics of La_2CuO_4 with different foreign atoms introduced into the crystal. The solid curve represents the tetragonal-orthorhombic transition according to Ref. 3, the dotted curve is T_{1f} of the low-temperature feature, and the dashed curve represents the transition into the new tetragonal phase of samples with the impurity Ba (Ref. 7), Sr—● (Ref. 6), ▲ (Ref. 8), and ■ (Ref. 19); Li—○ (Ref. 5); × and □ are our data; Ba (polycrystal)—△ (Ref. 7).

ily associated with the weakening of the O-La bond, which can be caused both by the replacement of La atoms with Sr or Ba atoms and incorporation of Li into the chain La-O-Cu and, as a consequence, makes rotation of the CuO_6 octahedron easier. The dependence $T_0(x)$ can be used to determine, on the basis of the assumptions made, the concentration of defects in the LCO(Cu) sample also from the value of T_0 . The result of such an estimate shows that in this crystal $x = 0.035(5)$.

We now discuss the low-temperature acoustic features. As shown in Ref. 12, they could be associated with the interaction of the acoustic branch of the phonon spectrum with the optical branch. At $k = 0$ the optical modes of the La_2CuO_4 crystal form six one-dimensional and six doubly degenerate $E(2E_g + 4E_u)$ representations of the group D_{2h} . The energy spectrum of the phonons for small $k \neq 0$ for the E mode is given by

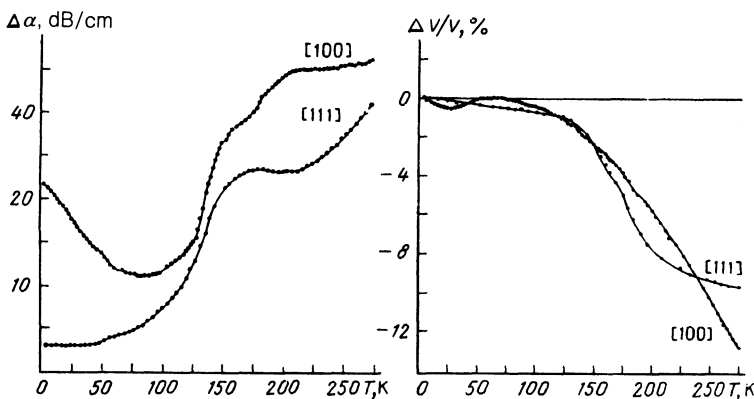


FIG. 7. Temperature dependence of the absorption α and velocity V of sound with frequency 50 MHz near the low-temperature feature in LCO(Cu). The values of V_{100} and V_{111} at 4.2 K are equal to, respectively, $(5.2 \pm 0.2) \cdot 10^3$ and $(5.5 \pm 0.2) \cdot 10^3$ cm/s.

$$\omega^2(k, \mu) = \omega_{0E}^2 + c_E^2 \gamma_{ik}^E(\mathbf{n}, \mu) k_i k_k, \quad \mathbf{n} = \mathbf{k}/|\mathbf{k}|, \quad \mu = \pm 1.$$

The tensors γ_{ik} and γ_{ik}^E determine the geometric properties of the isoenergetic surfaces $\gamma_{ik} k_i k_k = \text{const}$. It is convenient to classify the E modes, which have two mutually perpendicular polarization vectors, in terms of the properties of the geometric cross sections of the isoenergetic surfaces, lying in the basal plane. The cross sections form a figure with symmetry C_{2v} [$E(C_{2v})$ mode] or D_{2h} [$E(D_{2h})$ mode]. The symmetry axes for different $\mu = \pm 1$ are mutually perpendicular. For the $E(C_{2v})$ mode they are directed along the diagonals of the base of the unit cell and for the $E(D_{2h})$ mode they are directed along the edges of the base. A calculation leads to the following expression for the experimentally measured quantities:

$$A(T) = \frac{\Delta V(T)_{100}}{V(0)_{100}} + \frac{\Delta V(T)_{110}}{V(0)_{110}} = A_1(T) + A_2(T), \quad (1)$$

where $\Delta V(T) = V(T) - V(4, 2 \text{ K})$; for $T < \hbar\omega_{0E}$ (Ref. 12)

$$A_2(T) \propto T^4 (\hbar\omega_{0E}/T)^{1/2} \exp(-\hbar\omega_{0E}/T). \quad (2)$$

In the expression (1) A_1 is small in proportion to the parameter $(V_{110} - V_{100})/V_{110}$. This makes it possible to determine, by comparing theory with experiment, both to determine the type of E mode responsible for the observed anisotropy and to clarify the value of the parameters characterizing it. If $A_2 \gg A_1$ holds, then $A(T)$ is positive in the case of the interaction with the $E(C_{2v})$ mode and negative in the case of the interaction with the $E(D_{2h})$ mode in the temperature range $T > \hbar\omega_{0E}$. Figure 9 shows the results of a comparison of the experimentally obtained dependence $A(T)$ with calculations based on the relation (2), neglecting the contribution of A_1 . One can see that for the LCO(Li) sample the disagreement between experiment and calculation is small, whereas in the case of LCO(Cu), for which the magnitude of the features is an order of magnitude smaller, the disagreement between experiment and calculation is significant. This is probably attributable to the fact that in this case the term A_1 makes an appreciable contribution to the relation (1). The characteristic energies, obtained by fitting, of the optically soft phonons of the optical branches for LCO(Li) and LCO(Cu) are equal to 124 and 58 K, respectively.

As indicated above, the absorption of sound in the region of the low-temperature feature and possibly in the region of the tetragonal-orthorhombic transition changes, to a first approximation, in proportion to the sound frequency

and not in proportion to the frequency squared, even though for the phonon system the condition $\omega\tau_{ph} < 1$ is satisfied, where τ_{ph} is the characteristic relaxation time in the phonon system and is determined, for example, from the thermal conductivity.¹¹

The frequency dependence of sound absorption with an exponent less than two is usually associated to the presence of a multilevel system, as, for example, occurs in glasses. In this case such a system can be associated to defects of the crystal structure, which arise because of the Li atoms which evidently occupy positions other than the lattice sites. It is also possible that rotation of the CuO_6 octahedra play a significant role in the regions of softening of the optical mode near T_0 and T_{lf} .

In studying the position T_{lf} of the low-temperature feature for the system $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ for different impurities M we shall employ, aside from our results, the published data for the impurities Sr (Ref. 19) and Ba (Ref. 7). T_{lf} decreases as the impurity concentration x decreases (see Fig. 8) for all impurities $M = \text{Li, Sr, Ba}$. However, the amplitude of the low-temperature feature depends on the atomic composition of the dopants in the single crystal. Thus for $x = 0.1$ the change of the sound velocity near T_{lf} is equal to less than 1% for $M = \text{Sr}$ and about 5% for $M = \text{Li}$. In the case $M = \text{Ba}$ another tetragonal phase appears as a result of the new rotation of the CuO_6 octahedron. In Fig. 8 the new tetragonal phase exists in the region below the dashed line.⁷

It is very likely that the specific nature of the soft optical mode of the phonon spectrum of La_2CuO_4 is responsible for all these features. At T_0 the mode vanishes and the samples transform from the tetragonal phase into the orthorhombic phase. The temperature T_{lf} corresponds to the energy at which the mode goes soft as a result of its intersection with the acoustic branch of the spectrum. This energy is close to $\omega_{0E}(k=0)$. If this point of view is adopted, then the data given in Fig. 9 indicate the existence of a nontrivial deformation of the optical mode as a result of the presence of dopants in the matrix of the crystal: as $\hbar\omega \approx T_{lf}$ increases (as x increases) the temperature T_0 at which the mode vanishes decreases. This question merits further study.

Softening of the phonon mode at T_{lf} can be accompanied by a change in the other characteristics of La_2CuO_4 crystals. In particular, the magnetic characteristics of these crystals can be expected to change. The data presented in Fig. 10, which were obtained with the help of a SQUID magnetometer, show that while the temperature dependence of

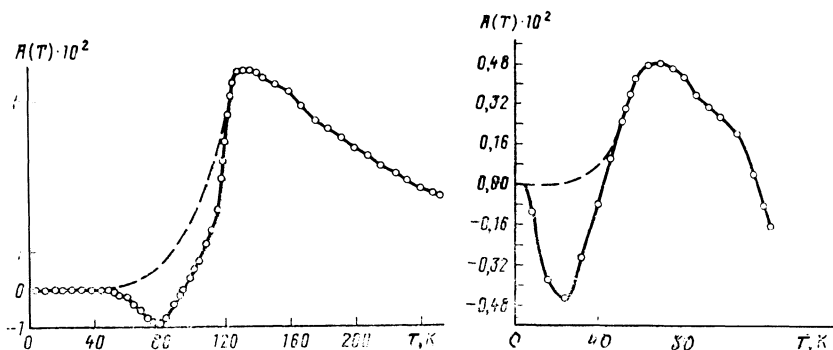


FIG. 9. Comparison of the experimental dependence $A(T)$ (solid curve) with the fit according to the relation (2) (dashed line). LCO(Li)—top and LCO(Cu)—bottom.

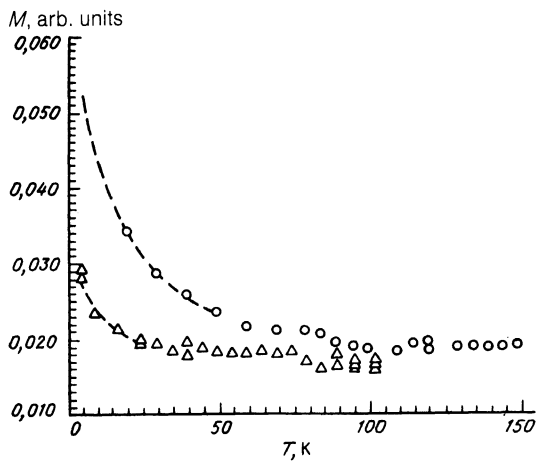


FIG. 10. The temperature dependence of the magnetization M of two samples in a magnetic field of 300 Oe. $\text{La}_2\text{CuO}_4(\text{Li})$ — \circ and $\text{La}_2\text{CuO}_4(\text{Cu})$ — Δ .

the magnetic moment of the LCO(Li) sample is qualitatively similar to that of the LCO(Cu) sample the temperature dependent part of the curve is shifted in the direction of low temperatures for the sample with the lower value of T_{lf} .

Conclusions

The comprehensive investigation of La_2CuO_4 single crystals performed in this work with different dopant elements and comparison with other investigations of single-crystalline samples have made it possible to show that both the temperature of the tetragonal–orthorhombic transition, associated with vanishing of the optical mode at T_0 , and the temperature T_{lf} of the low-temperature feature, associated with softening of the optical mode as it intersects with the acoustic branch of the phonon spectrum, are displaced, to a first approximation, identically for different elements (Sr, Li, Ba) introduced into the matrix of the crystal. The change in the properties of the crystal at T_{lf} depends on the dopant, and increases in the order of the elements presented above. In the case of Sr only a weak (less than 1%) change of the

sound velocity is observed; in the case of Li this change reaches 5%; and, in the case of Ba the crystal transforms into a new tetragonal modification.⁷ The deformation of the soft optical mode, with which all these changes are probably associated, is nontrivial: when foreign atoms are introduced into the crystal the temperature T_0 at which the mode vanishes decreases and the energy ω with $k \approx 0$ increases.

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