Partial oscillation spectra of Cu, La, and O atoms in La$_2$CuO$_4$

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Using experimental data obtained by the isotopic-contrast technique in inelastic neutron scattering, and the results of shell-model calculations, we restore the partial oscillation spectra of Cu, La, and O atoms in the La$_2$CuO$_4$ lattice and construct the phonon spectrum of this system. The temperature dependences of the rms thermal displacements of different atoms and the heat capacity of the compound are calculated. The results are compared with theoretical calculations and independent experiments.

The interest in the high-T_c superconducting cuprate-crystal lattice dynamics is stimulated, on the one hand, by the possibility of phonons taking part in carrier pairing processes and, on the other hand, by peculiar dynamic properties of these complex compounds with a layered structure. It is not surprising, therefore, that many papers report studies of thermal excitations of the crystal lattice of high T_c superconducting cuprates and related compounds. In particular, the La$_2$CuO$_4$ crystal lattice oscillations are experimentally studied by means of neutron[1-4] and optical[5-7] spectroscopy. The results of inelastic neutron-scattering experiments giving information about phonon dispersion relations[4] or phonon spectral density[1-3] are usually interpreted in terms of collective oscillating excitations in each of which all the atoms take part. The information about the oscillations of individual atoms of the compound is thus lost.

Analysis of the literature shows that two approaches are used to get information about oscillating properties of single atoms of a complex compound. The first is based on model calculations of crystal-lattice dynamics, and the second on the analysis of indirect information about thermal atomic motions, obtained by neutron recoil spectroscopy for neutrons of energy ≈ 1 eV,[10] by resonance neutron absorption,[11] and by neutron diffraction.[12] All these methods suffer from an important shortcoming, namely the characteristics of thermal atomic motion are determined as fitting-procedure parameters, together with a lot of other parameters, which, in some cases, can substantially affect the final result. Moreover, neutron diffraction data do not allow to distinguish between static and dynamic atomic displacements from equilibrium in the crystal lattice. Apparently, these very difficulties account for a large spread in data concerning the mean oscillating energies of single atoms in La$_2$CuO$_4$ and their effective Debye temperatures. For example, Θ_D for copper atoms is 1500 K, according to Ref. 10, while in Ref. 12 it is 430 K.

The most reliable information about thermal motion of a definite type (i) of atoms in a complex compound can be obtained from the partial oscillating spectrum $g_i(E) = g(E)\langle|e_i|^2\rangle$, where e is the polarization vector of the ith atom when the latter oscillates with energy E.[13] Thus, the partial spectrum is determined by superposition of all normal modes with weight allowing for the ith atom

displacement in lattice oscillations with energy E.

As shown in Refs. 14 and 15, the method of isotopic contrast in inelastic neutron scattering makes it possible to experimentally restore the partial oscillating spectra of single atoms. In the present study this method was used to investigate the oscillations of Cu, La, and O atoms in La$_2$CuO$_4$.

EXPERIMENT

The samples, about 30 g each, were obtained by solid-phase synthesis from La$_2$O$_3$ and CuO. The degree to which the initial oxides are single-phase was monitored by x-ray analysis. The isotopic contrast technique is based upon the large difference between the cross sections for neutron scattering by the Cu^{65} and Cu^{63} isotopes (14.5 and 5.2 barns, respectively). Therefore we used for sample preparation copper oxide of the following isotopic composition: a) Cu^{65}—99%, Cu^{63}—1% and b) Cu^{63}—99.7%, Cu^{65}—0.3%. The mixture of copper and lanthanum oxides was milled for an hour in an electric ball mill and then pressed under a pressure of 100 kg/cm^2 into tablets of a diameter of 12 mm and a thickness of 3 mm. Sintering was carried out in several stages: 16 hours in air at $T = 850$ °C, milling and again pressing, 6 hours at $T = 1050$ °C, 10 hours at $T = 850$ °C, cooling to 500 °C with the oven, annealing at $T = 500$ °C in an oxygen stream for 10 hours and cooling in the oven down to the room temperature in an oxygen stream. According to the x-ray phase analysis, the samples were single-phase and had an orthorhombic cell with parameters $a = 5.393 \pm 0.004$ Å, $b = 5.338 \pm 0.004$ Å, and $c = 13.09 \pm 0.01$ Å.

The neutron inelastic scattering experiments were carried out with a spectrometer, using the transit time technique and a source of cold neutrons ($E_0 = 4.4$ meV).[16] The spectra measured at five scattering angles and at room temperature were processed in the incoherent approximation. In this case we can restore the generalized density $G(E)$ of oscillating states directly from the experimental data, without using any model.[15]

RESULTS AND DISCUSSION

The generalized oscillation spectra for isotopically enriched samples (Fig. 1) agree fully with respect to the
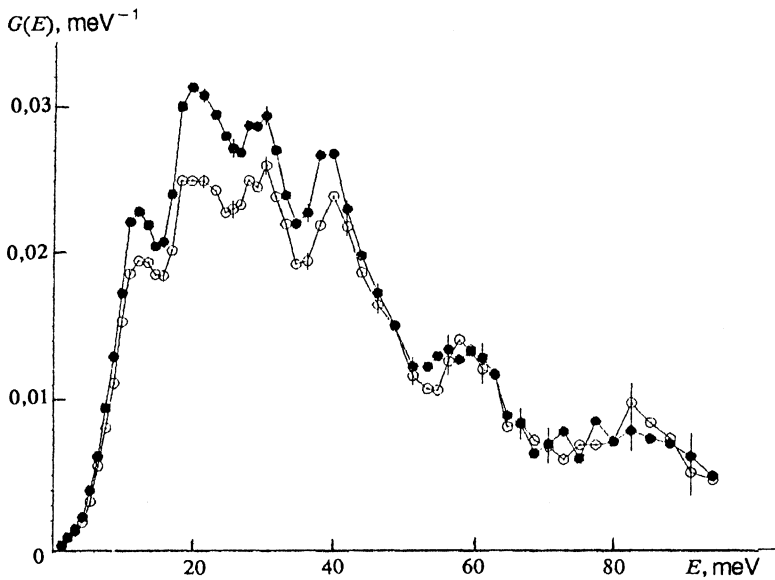
FIG. 1. Generalized oscillation spectra for $La_2Cu^{65}O_4$ (●) and $La_2Cu^{63}O_4$ (○).

positions of the maxima and the boundary energy with the data reported in Refs. 1–3 for La_2CuO_4 with a natural mixture of copper isotopes. For the energy $E \leqslant 40$ meV the values of $G(E)$ for $La_2Cu^{65}O_4$ are much larger than those for $La_2Cu^{63}O_4$. This excess corresponds to isotopic contrasting of copper atom oscillations. The partial oscillation spectrum of copper atoms is found as the difference between the generalized spectra shown in Fig. 1. We neglect the effect of the difference in copper isotope masses ($\approx 3\%$) on the oscillating spectrum of La_2CuO_4.

To restore the partial oscillation spectrum of lanthanum atoms $g_{La}(E)$ we used a procedure similar to that reported in Ref. 17. A correction factor found from the calculations of partial oscillation spectra of different atoms in La_2CuO_4 was introduced into the measured function $G(E)$. The procedure is based on the assumption that

$$\{g_{La}(E)/G(E)\}_{calc} = \{g_{La}(E)/G(E)\}_{exp}.$$

Then $g_{La}(E) = \{g_{La}(E)/G(E)\}_{calc} \cdot G(E)_{exp}.$

As the comparison of the functions $G(E)$ calculated in Refs. 8 and 9 with the measured one shows, the spectral distribution found in the framework of the shell model[8] agrees better with the experiment in the low energy range. Moreover, this model, in contrast to the model of hard unscreened ions,[9] gives a value of the oscillation spectrum boundary energy close to the experimental one. That is why the calculated functions $g_{La}(E)$ and $G(E)$ were taken from Ref. 8.

The partial oscillation spectrum of oxygen atoms was found as the difference of the function $G(E)$ and partial copper and lanthanum oscillation spectra taken with appropriate weight factors.[15] The finally restored copper, lanthanum and oxygen oscillation spectra are so normalized that the areas under them equal 1/7, 2/7, and 4/7, respectively (with respect to the number of atoms of each type per formula unit), and shown in Figs. 2a–c. The same figures show the results of shell model[8] and hard-ion model[9] calculations convoluted with the energy resolution function of the cold neutron spectrometer.

Clearly, neither the hard-ion nor the shell model adequately describes the partial oscillation spectra of copper and oxygen atoms, though it is not excluded that all the capabilities of the shell model have been covered in Ref. 8. It is worth noting that, though the two models differ greatly, they give a softer oscillation spectrum for oxygen in positions O2 than in positions O1. Hence we conclude that the spectral distribution of oscillations (Fig. 2c) for energies about 10 and 25 meV is governed mainly by the oxygen atoms in positions O2 and for energies about 60 and 80 meV by the atoms in positions O1.

The found Cu, La, and O partial oscillation spectra for the La_2CuO_4 lattice make possible straightforward calculations, for each atom, of such integral quantities as the spectrum average energy $\langle E \rangle$, the effective Debye temperature Θ_D, and the isotropic mean square displacement $\langle u^2 \rangle$. Since we cannot experimentally separate the oscillation spectra of oxygen atoms in positions O1 and O2, all the calculations are carried out for an "average" oxygen atom. To compare the results with the data of Ref. 12, we have assumed that Θ_D characterizes such a Debye distribution of oscillations of atoms of a given type which at $T = 300$ K gives an rms displacement equal to that calculated with the help of the partial oscillation spectrum (Table I).

Assuming that the partial oscillation spectra found at $T = 300$ K do not vary with temperature in the range 0–300 K, we have plotted the temperature dependences of $\langle u^2 \rangle$ for each type of atom (Fig. 3). It is seen that practically all the points (except $\langle u^2_{Cu} \rangle$ at $T = 300$ K) found from precision measurements of neutron diffraction[12] are higher than the curves calculated from the partial oscillation spectra. Such a result is quite natural, if we take it into account that the isotropic Debye–Waller factor $B = 8\pi^2 \langle u^2 \rangle$ affecting the diffraction maximum intensity is determined both by the dynamic and static displacements of atoms from the equilibrium in the crystal lattice: $\langle u^2 \rangle = \langle u^2 \rangle_{dyn} + + \langle u^2 \rangle_{stat}$, while the calculation from the oscillation spectrum gives only $\langle u^2 \rangle_{dyn}$.
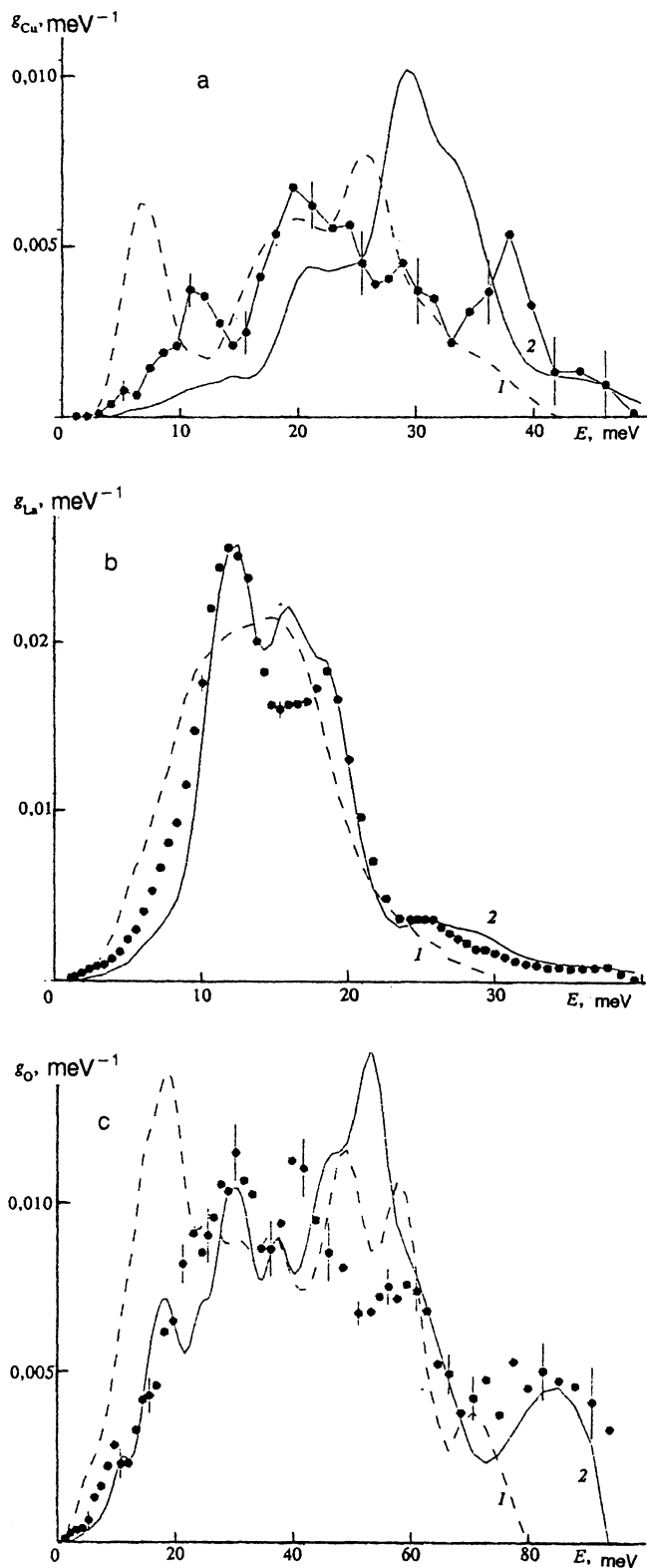
FIG. 2. Partial oscillation spectra of copper (a), lanthanum (b) and oxygen (c) atoms in La_2CuO_4: (●)—experiment; I—calculations;[9] 2—calculations.[8]

TABLE I. Integral characteristics of atomic oscillations in La_2CuO_4 (Θ_D and $\langle u^2 \rangle$ are shown for $T = 300$ K).

Atom	$\langle E \rangle$, meV	$\langle u^2 \rangle$, 10^{-3} Å^2	Θ_D, K	Θ_D, K (Ref. 12)
La	15.4 ± 0.7	5.9 ± 0.3	221 ± 9	268 ± 3
Cu	25.3 ± 2.4	6.0 ± 0.7	334 ± 27	430 ± 7
O	45.2 ± 2.8	11.0 ± 0.7	524 ± 23	587 ± 7

Fig. 3, static atomic displacements in the La_2CuO_4 lattice grow with decreasing temperature rather than remain constant as was assumed in Ref. 12. Apparently, the difference between the effective Debye temperatures obtained in the present study and in Ref. 12 (Table I) is related just to this fact. It is not excluded that the result is indicative of the La_2CuO_4 crystal lattice predisposition to a structural phase transition with decreasing temperature, the more so as such transitions are observed in the system[18] when it is doped with Ba atoms or when the oxygen concentration is increased. The static displacement value is the greatest for La atoms and the smallest for Cu atoms. This result indicates that the lanthanum sublattice is "softer" and confirms the conclusion of Ref. 18 that the La_2CuO_4 lattice contraction in the temperature range 540–50 K is due to the decrease of the LaO_9 polyhedron, while the Cu–O distances practically do not change.

On the basis of the partial oscillation spectra of Cu, La, and O atoms we have constructed the phonon spectrum of the La_2CuO_4 crystal lattice (Fig. 4). It is seen that the restored spectrum differs both from shell model[8] and hard unscreened ion model[9] calculations. At the same time, the temperature dependence $C(T)$ of the heat capacity (Fig. 5) calculated with the help of the found phonon spectrum agrees well with the measured one,[19] though it lies somewhat higher.

CONCLUSIONS

Experimentally restored partial single atom oscillation spectra and the phonon spectrum of La_2CuO_4 are not described, on the whole, either by the unscreened hard ion model[9] or by the shell model.[8] The hard ion model does not even give the right value of the oscillation spectrum boundary energy. The temperature dependence of the heat capacity calculated from the phonon spectrum is in good agreement with the measured one.[19] We have found that the La_2CuO_4 crystal lattice is characterized by noticeable static atomic displacements from the crystallographic positions whose values grow with decreasing temperature. These displacements are larger for La atoms than for Cu and O atoms. This conclusion agrees with the notion of La sublattice "softness."[18]

Thus, using all the results of the present study and of Ref. 12, we can estimate the crystal lattice static distortions and draw a conclusion about the tendency of the temperature dependence of $\langle u^2 \rangle_{stat}$ for all atoms. As follows from
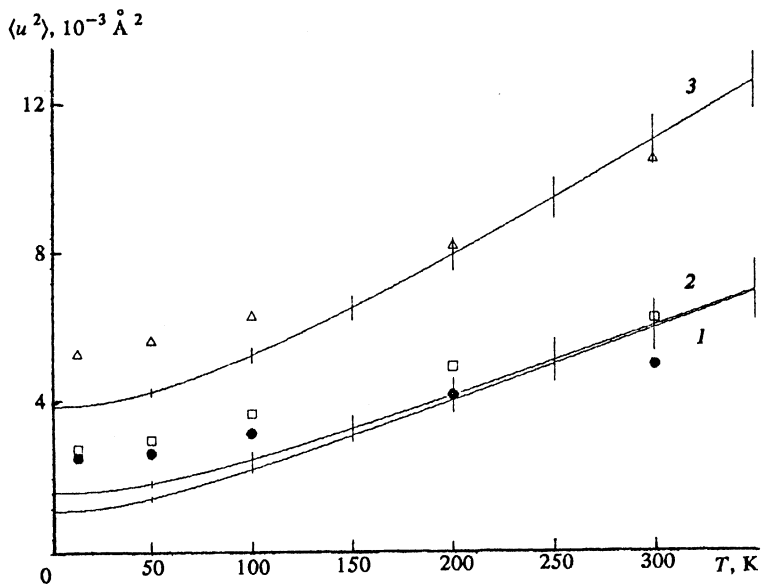
FIG. 3. Rms values of thermal atomic displacements in La$_2$CuO$_4$: *1*, *2*, and *3*—calculations, using partial oscillation spectra; □,●, and △—experiment[12] for La, Cu, and O, respectively.

FIG. 4. Phonon spectrum of La$_2$CuO$_4$: (●)—experiment; *1*—calculations;[9] *2*—calculations.[8]
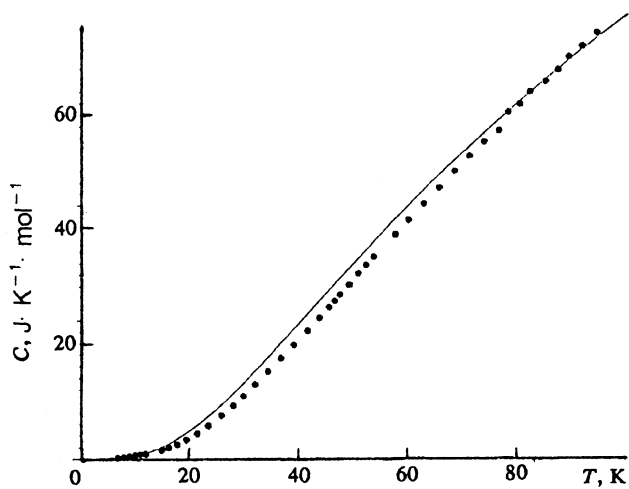
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FIG. 5. Temperature dependence of La$_2$CuO$_4$ specific heat: (●)—experiment;[19] (—)—calculations, using restored phonon spectrum.

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