Neutron study of the temperature dependence of the dynamics and structure of the superconducting ceramic compound $La_{2-x}Sr_xCuO_{4-y}$

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The spectra of inelastic scattering and diffraction of neutrons in the compounds La_2CuO_{4-y} and $La_{1.8}Sr_{0.2}CuO_{4-y}$ at temperatures 290 K, 77 K, and 10 K have been studied. The spectra of inelastic scattering at 77 K and 10 K revealed the presence of a ~6-meV line, whose temperature dependence of the intensity suggests that the excitation corresponding to it is magnetic in nature.

The first neutron studies of the dynamics of superconducting ceramics were published shortly after their discovery.[1] These studies determined the basic features of the phonon-state density and compared the results obtained for nonsuperconducting La_2CuO_4 and for superconducting $La_{1.85}Sr_{0.15}CuO_4$. The soft mode, which is responsible for the phase transition from the tetragonal phase to the orthorhombic phase at a temperature of about 500 K, has now been studied using La_2CuO_4 single crystals.[2] The behavior of the low-frequency part of the spectrum at low temperatures, however, has not yet been studied thoroughly. We have studied experimentally the scattering of neutrons by a family of $La_{2-x}Sr_xCuO_{4-y}$ compounds (for two values of x at temperatures between 290 K and 10 K). The measurements were carried out using a KDSOG-M spectrometer[3] which was installed near a pulsed high-flux-beam IBR-2 reactor.[4] The principal advantage of this spectrometer is that it can measure simultaneously the neutron diffraction and the inelastic neutron scattering. Here the inelastic neutron scattering is measured in a regime involving neutron energy release, making it possible to study the lattice dynamics at low temperatures.

The test samples were fabricated from La_2O_3, $SrCO_3$, and CuO following a standard procedure (see, e.g., Ref. 5). The chemical composition was monitored by neutron activation analysis.[6] The amount of impurity did not exceed 0.5 at.% and the strontium concentration in $La_{2-x}Sr_xCuO_{4-y}$ was $x = 0.2 \pm 0.02$. At room temperature the structure of the samples was examined using a DRON-3M x-ray diffractometer. The structure of La_2CuO_{4-y} is in complete agreement with the published data[7]: the sample was in the orthorhombic phase (*Bmab*), which was clearly evident from the splitting of the (200) and (020) peaks. The $La_{1.8}Sr_{0.2}CuO_{4-y}$ sample has a tetragonal structure (*I4/mmm*), whose unit cell parameters are in complete agreement with the published data.[8] The magnetic and resistive measurements of the superconducting transition temperature of $La_{1.8}Sr_{0.2}CuO_{4-y}$ showed that the transition begins near 20 K, suggesting that the sample is oxygen deficient.[9]

To conduct neutron measurements, we inserted the test samples, weighing approximately 100 g, into a helium cryostat. The neutron-diffraction spectra and inelastic-neutron-diffraction spectra were measured simultaneously. The experimental data were normalized to the monitor counts. The diffraction spectra, measured for the scattering angles $2\theta = 28°$, 48°, 68°, and 88°, were normalized to the incident-neutron spectrum. The inelastic-scattering spectra were measured at the scattering angles of 30°, 50°, 70°, and 90° in the transmission geometry and at the scattering angles of 80°,

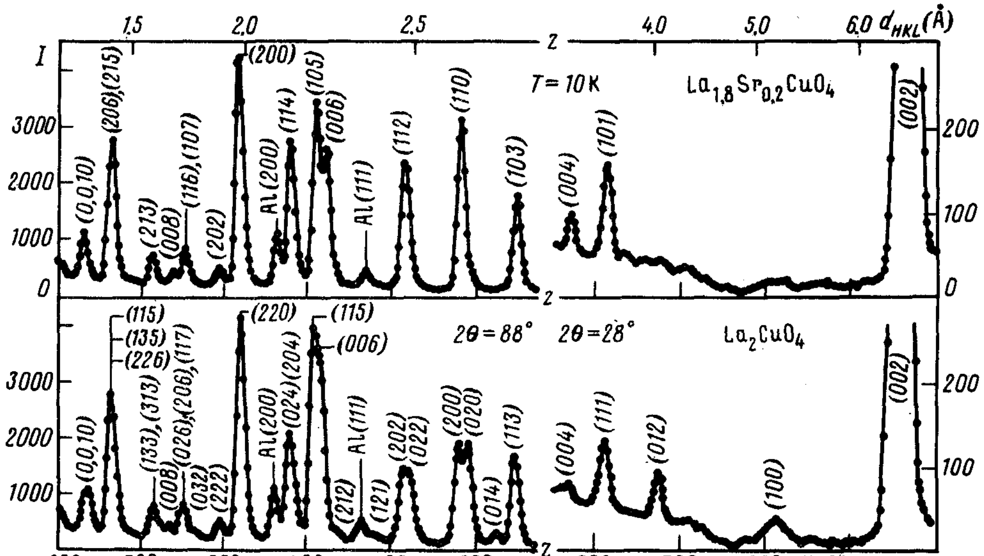

FIG. 1. Spectra of neutron diffraction at $T = 10$ K for the tetragonal phase $La_{1.8}Sr_{0.2}CuO_{4-y}$ and the orthorhombic phase La_2CuO_{4-y} for scattering angles $2\theta = 28°$ and 88°. N represents the number of the channel of width 64 μs.

100°, 120°, and 140° in the reflection geometry. The background of the cryostat without the sample was subtracted and the sum over the scattering angles was taken. The average measurement time was 1 day per spectrum.

At $T = 10$ K the neutron-diffraction spectra for the orthorhombic phase La_2CuO_{4-y} differ, as can be seen in Fig. 1, from the spectra of the tetragonal phase $La_{1.8}Sr_{0.2}CuO_{4-y}$ by the presence of (012) and (014) reflections, which are forbidden in the tetragonal phase, and by the fact that the (020), (200) and (022), (202) reflections are split.

At $T = 77$ K the diffraction pattern remains essentially the same and at 290 K the splitting of the (020), (200) and (022), (202) reflections is no longer observable because of the inadequate resolution of the spectrometer. The orthorhombic symmetry of the La_2CuO_{4-y} can, however, be clearly determined from the (012) and (014) reflections even at room temperature.

At 77 K the diffraction spectra of La_2CuO_{4-y} reveal a (100) peak, whose intensity increases as the temperature is lowered to 10 K (Fig. 1). The presence of this reflection suggests that there is antiferromagnetic ordering[10] and oxygen deficiency in the sample.[9]

The $La_{1.8}Sr_{0.2}CuO_{4-y}$ sample was in the tetragonal phase at all temperatures the measurements were conducted, consistent with the published data.[11] A lowering of the temperature from 290 K to 10 K causes only the position of the peaks to change, suggesting that the interplanar spacing changes by no more than 0.006 Å.

The spectra of inelastic scattering of neutrons by La_2CuO_{4-y} and $La_{1.8}Sr_{0.2}CuO_{4-y}$ at temperatures 10 K, 77 K, and 290 K are shown in Fig. 2, a and

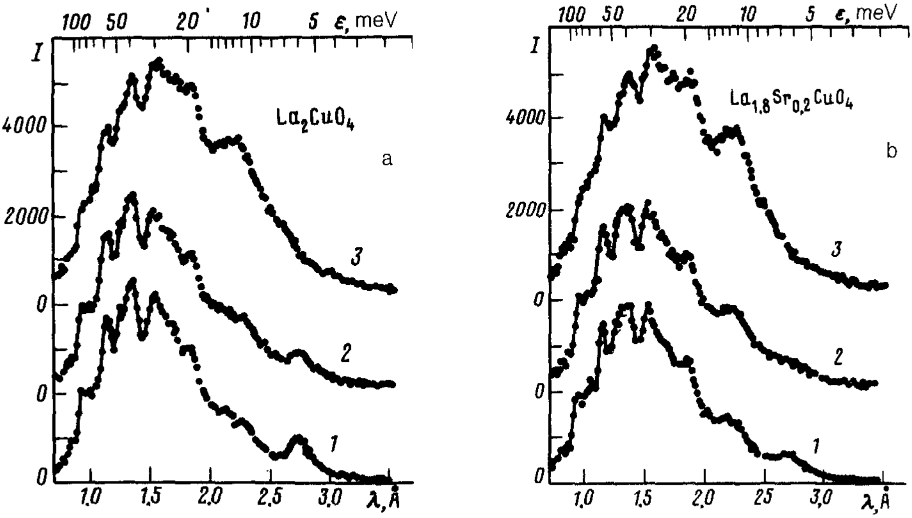

FIG. 2. (a) Spectra of inelastic scattering of neutrons by La_2CuO_{4-y}. 1—$T = 10$ K; 2—$T = 77$ K; 3—$T = 290$ K. Ordinate axis—The intensity $\times 10^7$ counts of the monitor; ϵ—energy transfer in meV. (b) Spectra of inelastic neutron scattering by $La_{1.8}Sr_{0.2}CuO_{4-y}$. 1—$T = 10$ K; 2—$T = 77$ K; 3—$T = 290$ K.

b. The positions of the structural features in the spectra at 290 K are fully consistent with the previously published data.[1] At 77 K and 10 K, however, an inelastic line is seen in the vicinity of 6-meV energy transfer, which was not seen previously. We see that the intensity of this line increases with decreasing temperature. A conversion of the experimental data into a generalized-frequency-spectrum function on the basis of the formula for single-phonon scattering gives a good agreement of the results obtained at various temperatures. These results also agree with the data published by Ramirez *et al.*[1] The only exception is the structural feature at 6 meV. Upon conversion, its intensity increases sharply as the temperature is lowered. This behavior and the angular dependence of the intensity of this feature suggest unambiguously that it is of a nonphonon nature.

To quantitatively analyze this structural feature at 6 meV, we used a simple model, according to which the scattering law was chosen in the form of a Gaussian curve on the Debye distribution ($\sim\omega^2$) and we convoluted it with the resolution function of the spectrometer. The results of an approximation of the experimental spectra by the method of least squares are shown in Fig. 3 and the parameter values of the Gaussian curve are given in Table I. We see that in the case of the two tested samples the intensity of the peak at 6 meV increases with decreasing temperature and its width remains essentially the same. Keeping in mind this circumstance and the fact that an increase in the scattering angle and hence the momentum transfer causes the intensity of this line to decrease, we conclude that the excitation corresponding to it is magnetic in nature. This feature is highly uncharacteristic of these compounds. Nominally magnetized electrons are the copper $3d$ electrons,[9] whose orbital moment is nearly completely quenched by the crystal field. If the excitation detected by us is caused by antiferromagnetic spin waves, the low-frequency part of the magnetic-excitation spectrum is characterized by the presence of a ~6-meV gap and by the absence of a marked dispersion, since the position of the peak, which is narrow in width, does

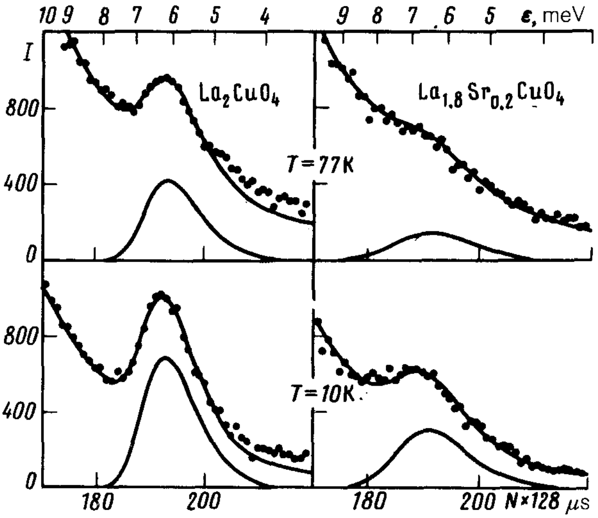

FIG. 3. The results of a model-based fit of the low-frequency part of the spectrum of inelastic neutron scattering at 77 K and 10 K. Lower solid curve—Peak at 6 meV without the use of a Debye substrate. N—The number of the channel of width 128 μs; ϵ—energy transfer in meV.

TABLE I. The parameters of a Gaussian distribution used for the description of the low-frequency part of the experimental spectrum.

Sample	Temperature K	Position of the peak, meV	Integrated intensity of the peak, arb. units	Intrinsic width at half-maximum, meV
La_2CuO_{4-y}	77	6.2 ± 0.1	11 ± 1	0.9 ± 0.1
	10	6.27 ± 0.03	18.1 ± 0.5	0.90 ± 0.05
$La_{1.8}Sr_{0.2}CuO_{4-y}$	77	6.6 ± 0.2	5 ± 2	1.5 ± 0.5
	10	6.57 ± 0.05	9.8 ± 0.5	1.5 ± 0.1

not depend on the momentum transfer. The gap might be the result of anisotropic exchange interaction. The corresponding strength of the internal molecular field, which acts on the $s = 1/2$ state of the copper $3d$ electrons, is ($g = 2$, $\Delta E = 6.2$ meV) approximately 54.4 T. In this interpretation, strontium doping may possibly destroy the long-range magnetic order but retain the short-range order, making it possible to see the magnetic excitation in $La_{1.8}Sr_{0.2}CuO_{4-y}$ at a lower intensity and greater width.

This is only a preliminary analysis of the results. At this point, it is difficult to describe unambiguously the physical nature of the structural feature that has been observed and how it is related to the superconducting properties. It is interesting to note, however, that the excitation energy is in order-of-magnitude agreement with the superconducting transition temperature of the La-Sr-Cu-O system.

We are accordingly planning further experimental studies of the properties of these systems as a function of strontium concentration in oxygen-deficient samples and in samples with good superconducting properties, annealed in oxygen atmosphere.

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[1] A. P. Ramirez, B. Batlogg, G. Aeppli *et al.*, Phys. Rev. **35**, 8833 (1987).
[2] B. N. Goshitskiĭ, S. A. Davydov, M. G. Zemlyanov *et al.*, Fiz. Met. Metalloved. (The Physics of Metals and Metallography) **64**, 188 (1987); B. Renker, F. Gompf, E. Gering *et al.*, Z. Phys. **B67**, 15 (1987); G. Balakrishnan, N. R. Bernhoeft, Z. A. Bowen *et al.*, Nature **327**, 45 (1987).
[3] G. Baluka, A. V. Belushkin, S. I. Bragin *et al.*, JINR P13-84-242, Dubna, 1984.
[4] V. D. Ananiev, V. A. Arkhipov, B. N. Bunin *et al.*, The Neutron and its Applications, 1982. Inst. Phys. Conf. Ser. **64**, 1983, p. 497.
[5] M. Decroux, A. Jinod, A. Bezinge *et al.*, Europhys. Lett. **3**, 1035 (1987).
[6] V. M. Nazarov, S. S. Pavlov, V. F. Peresedov, and M. V. Frontas'eva, Brief Commun JINR, No. 6–85, 1985, p. 37.
[7] V. B. Grande, Hk. Müller-Baschbaum, and M. Schweizer, Z. Anorg. Allg. Chem. **428**, 120 (1977).

[8] C. Politis, J. Geerk, M. Dietrich, and B. Obst, Z. Phys. **B66**, 141 (1987).

[9] D. C. Johnston, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, Phys. Rev. **B36**, 4007 (1987); P. Gutsmiedl, G. Wolff, and K. Andres, Phys. Rev. **B36**, 4043 (1987).

[10] D. Vaknin, S. K. Sinha, D. E. Monkton *et al.*, Phys. Rev. Lett. **58**, 2802 (1987); T. Freltoft, J. E. Fischer, G. Shirane *et al.*, Phys. Rev. **B36**, 826 (1987); G. Shirane, Y. Endoh, R. J. Birgeneau *et al.*, Phys. Rev. Lett. **59**, 1613 (1987).

[11] R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Rietman, Phys. Rev. **B35**, 7191 (1987).

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