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NEUTRON SCATTERING INVESTIGATIONS OF LATTICE DYNAMICS AND STRUCTURE OF SUPERCONDUCTING CERAMICS $La_{2-x}Sr_xCuO_{4-\delta}$ AT DIFFERENT TEMPERATURES

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INTRODUCTION

The discovery of high temperature superconductivity (HTS) in metal-oxide compounds has challenged a great number of physicists, both experimentalists and theoreticians, to work on understanding of this phenomenon[1]. Despite the avalanche of papers published so far, we are still lacking a comprehensive explanation of the mechanism that leads to HTS. At the moment it seems that systematic investigations through purposefully planned experiments is one of the ways to achieve the goal.

Temperature dependence of the phonon density of states (DOS) is of decisive importance as to the role of phonons in the mechanism of superconductivity[2]. This is why a systematic study of the phonon DOS in lanthanum ceramics, with full information on the phase situation, is so important.

Such a study, via INS, in the $La_{2-x}Sr_xCuO_4$ system for $x = 0.0$, and $x = 0.15$, at temperatures ranging from 6 to 300 K, has already been reported[3-7]. Except for[3], all experiments reported were carried out on time-of-flight conventional geometry spectrometers and thus were subjected to their well-known restrictions: one had either to combine data obtained at different energies E_0 of incident neutrons or to accept a lower limit on temperatures accessible for the measurement[6,7].

On the contrary, the inverted geometry KDSOG-M spectrometer[8] is free from such limitations. For INS, it operates with the energy loss of incident neutrons. Hence the opportunity of covering a wide range of energy transfer at temperatures unlimited from below. This instrument has been applied to measure INS on samples of $La_2CuO_{4-\delta}$ as well as $La_{1.8}Sr_{0.2}CuO_{4-\delta}$. The magnetic excitation at about 6 meV could then be easily detected when examining the temperature dependence of the obtained spectra[9]. Possible existence of such an excitation in La_2CuO_4 (in the same energy region) has also been suggested in[5-7].

Here we report the results of systematic investigation of the INS spectra of $La_{2-x}Sr_xCuO_{4-\delta}$ ($x = 0.0$, 0.1, 0.2, 0.3) at 10, 77, and 290K. The phase diagram of the system under study, as a function of temperature (T) and Sr concentration (x)[10], comprises the regions of the following phases: tetragonal, orthorhombic, antiferromagnetic, and superconducting. We have chosen the values of x and T so as to represent all possible combinations from the phase diagram.

EXPERIMENTAL

It is well known that the quality of metal-oxide ceramics, and their superconducting properties, in particular, are extremely sensitive to the procedure of preparation. The samples used for the present study were synthesized in the following way: Stoichiometric amounts of powdered components: La_2O_3, $SrCO_3$, and CuO were carefully grinded, mixed together, and sintered at 1100°C. The specimens were then grinded again, cold-pressed into pellets, annealed at 1100°C, and finally quenched by means of fast pressing between massive copper slabs. Quenching was proved necessary for obtaining single-phased compounds.

During the whole manufacturing process the phase composition of the material was monitored with X-ray diffraction, using the DRON-3M diffractometer. The samples with x = 0.0, x = 0.1, and x = 0.2 were single-phased, while in that with x = 0.3 a small admixture of another phase has been detected. The neutron activation analysis[11] was applied to check the chemical composition of the compounds (except for oxygen). It was found that the total amount of impurities never exceeded 0.5 at. %, and the strontium concentration was within ±10% that of the assumed chemical formula.

Superconducting properties were examined by means of electrical resistivity and magnetic susceptibility measurements. The onset of the superconducting transition has been found at 16 and 20K for x = 0.1 and x = 0.2, respectively. Such low values of transition temperature point to the oxygen deficiency in the investigated materials[12]. For the samples with x=0.0 and x = 0.3 the temperature dependence of electrical resistivity was much like that for semiconductors (R steeply rises when T < 100K).

Neutron scattering experiments were carried out on KDSOG-M, the time-of-flight inverted geometry spectrometer at the high flux pulsed reactor IBR-2[13]. Here are the main characteristics of KDSOG-M: The reactor-scatterer flight path is 29.7m. The sample is irradiated with the full spectrum of neutrons as leaving the moderator. The incident neutron energy is fully determined by the reactor-detector time of flight since

the energy of scattered neutrons is selected by Bragg reflection from the pyrolytic graphite analysers, mounted behind the beryllium filters. In such an experimental setup one works with rather low energy of scattered neutrons (E_f = 4.82 meV), looking mainly at processes with the neutron energy loss, or with creation of elementary excitations. The opportunity of simultaneous recording the INS spectra and time-of-flight diffraction patterns is the unique facility of KDSOG-M.

The samples (about 100 g of the material) were put into a liquid helium cryostat. INS was measured for the scattering angles of 30°, 50°, 70°, 90° in transmission geometry and 80°, 100°, 120°, 140° in reflection. During each measurement data were being collected for about 20 hours. Analogous experiments were performed for the cryostat with an empty sample holder and the resulting background was subtracted from the corresponding data. The INS spectra were then summed up with respect to the scattering angles.

Time-of-flight diffraction patterns were simultaneously measured for scattering angles 2Θ = 28°, 48°, 68°, 88°. They were normalized with respect to the total incident flux (as given by the monitoring counter) and then with respect to the incident flux wavelength distribution (as obtained by elastic scattering using a standard vanadium scatterer).

RESULTS AND DISCUSSION

According to the X-rays (T = 300K) and neutron diffraction results (T = 290, 77, 10K), La_2CuO_4 remained in the orthorhombic phase (Bmab); and the strontium doped compounds with x = = 0.2 and x = 0.3, in tetragonal phase (I4/mmm). $La_{1.9}Sr_{0.1}CuO_{4-\delta}$ at a room temperature was in tetragonal phase; whereas at 77 and 10K, in orthorhombic one. The obtained unit cell constants were identical to those previously published[10,14].

Fig.1 shows ND spectra for all samples at 10K. The presence of the (100) peak in the ND spectrum of $La_2CuO_{4-\delta}$ at 77K and the fact that it gains intensity with decreasing temperature indicate that the sample developes antiferromagnetic properties[15], According to[12], this is connected with oxygen deficiency. Taking this into account as well as low superconducting transition temperatures for samples with x = 0.1 and x = = 0.2 one can infer that all samples under investigation exhibit similar oxygen deficiency δ. (All specimens were prepared in identical conditions). ND spectra of strontium doped compounds have shown no trace of antiferromagnetic ordering.

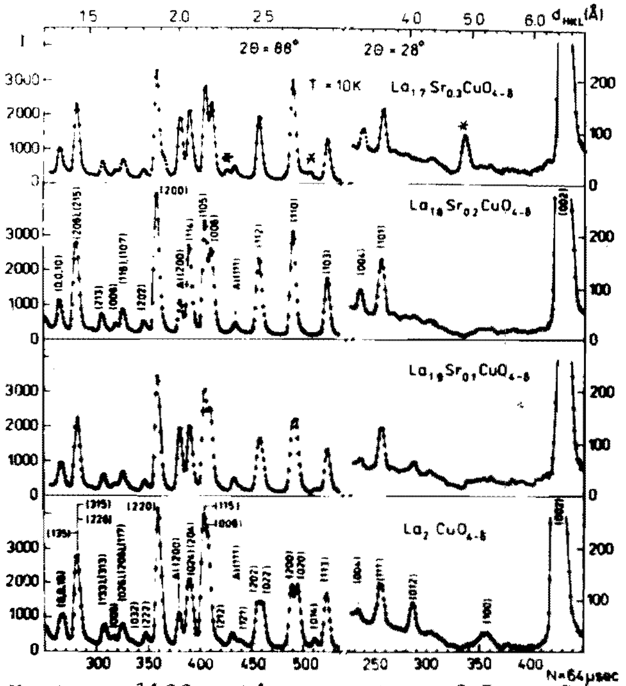

Fig.1. Neutron diffraction spectra of $La_{2-x}Sr_xCuO_{4-\delta}$ *at* T *= 10K for scattering angles* $2\Theta = 28^\circ$ *and* 88°. *N - channel number (its time width: 64 μsec).*

In the ND spectra measured at 10K (see Fig.1), orthorhombic phase of $La_2CuO_{4-\delta}$ can be easily distinguished from the tetragonal one of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$. In the former, the (020)-(200) and (022)-(202) peaks are apparently splitted and the (012) and (014) reflections appear, which are forbidden in the latter. With the increasing temperature or decreasing Sr concentration orthorhombic distortion becomes less pronounced so that the above splitting is no longer visible within the resolution of our instrument. However, the orthorhombic symmetry for x = = 0.0 at 290K and for x = 0.1 at 77K can still be easily detected due to the presence of (012) and (014) reflections. $La_{1.7}Sr_{0.3}CuO_{4-\delta}$ is tetragonal within the temperature range of 10K - 300K, but the sample is not single phased: in Fig.1 weak reflections due to the second phase are labelled with asterisks.

The INS spectra of $La_{2-x}Sr_xCuO_{4-\delta}$ measured at 290K and 10K are shown (as they change with x) in figures 2a and 2b, respectively. Positions of peculiarities within the room tempera-

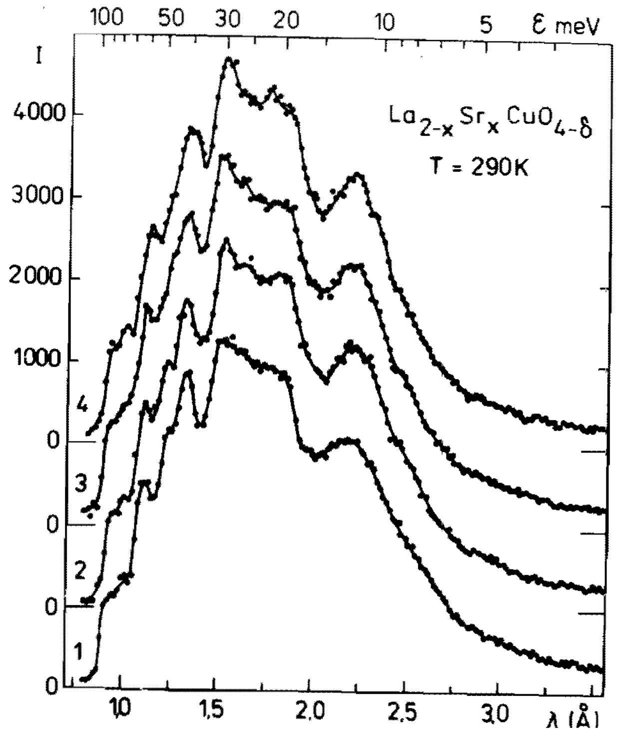

Fig.2a. INS spectra of $La_{2-x}Sr_xCuO_{4-\delta}$ *at* T *= 290K.1:* x*=0.0; 2:* x *= 0.1; 3:* x *= = 0.2; 4:* x *= 0.3. Abscissae: λ - neutrom wavelength [Å] ; ε - energy transfer [meV]. Ordinate: Scattering intensity normalized to monitoring detector counts of* 10^7 *(corresponds to about 10 hours).*

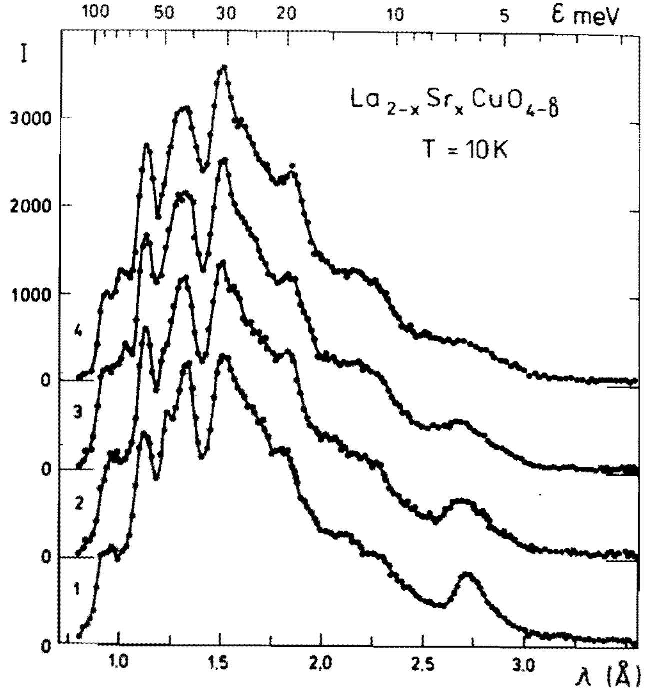

Fig.2b. INS spectra of $La_{2-x}Sr_xCuO_{4-\delta}$ *at* T *= 10K.*

ture (RT) spectra remain in good agreement with the other results[3-7] (x = 0.0, 0.15). They practically do not depend upon the strontium concentration.

On the contrary, as temperature decreases, the INS spectra become sensitive to x (cf. Fig.2b), especially in the low energy part (below 20 meV). A new line emerges for the energy transfer $\varepsilon \approx 6$ meV whose intensity decreases with the increasing dopant concentration. The peculiarity at $\varepsilon \approx 12$ meV apparently splits up for x = 0.0 and x = 0.1, i.e. for the orthorhombic phases.The shape of INS spectra in the region of high energy transfer remains almost insensitive to both temperature and x.

The 6 meV peculiarity has been examined with respect to its dependence upon the momentum transfer Q. This was accomplished by comparing the INS spectra measured at different scattering angles: 30° to 140°. For $\varepsilon \approx 6$ meV this covers the range of $1 Å^{-1} < Q < 4 Å^{-1}$. It has been established that the peak intensity monotonously decreases with the increasing Q. Now if we recall that it grows with the decreasing temperature[9] we are provided with clear evidence for the magnetic nature of the corresponding excitation.

For the quantitative analysis of a low energy part of the INS spectra ($\varepsilon < 10$ meV) we have applied the following formula for the neutron scattering law:

$$S(Q,\varepsilon, T) = A * [1 - \exp(-\frac{\varepsilon}{kT})]^{-1} * \varepsilon * \sum_{j=1}^{8} Q_j^2$$

$$+ B_T * \sqrt{\frac{2\ln 2}{\pi}} * \frac{1}{\gamma_T} * \exp[-4\ln 2\, (\frac{\varepsilon_T - \varepsilon}{\gamma_T})^2] . \qquad (1)$$

The first component of the sum is the Debye approximation of the phonon spectrum. An account is made for the temperature dependence of the phonon occupation number. The j index runs over the scattering angles. The second term is a normalized Gaussian, γ_T being its full width at half maximum (FWHM). A and B_T are multiplicative factors for the phonon and magnetic terms, respectively. The model (1) has therefore four free parameters: A, B_T, γ_T, and ε_T which were least-squares abjusted by fitting a convolution of (1) with the spectrometer resolution function[8,16] to the experimental data. The results are shown in Fig.3, and the best-fitting values of the Gaussians parameters are summarized in the Table.

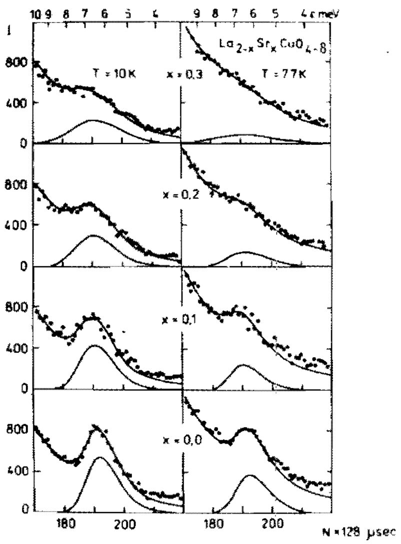

Fig.3. Results of fitting the model scattering law (1) to the INS data (T = 10K and 77K). Lower solid curve: the 6 meV line without the Debye background; N - time channel number (x 128 μsec); ε - energy transfer [meV].

The very presence of an inelastic peak of a magnetic origin was somewhat surprising in the spectra of these compounds. Its position (cf. the Table) is almost temperature-independent and does not change with the Sr concentration, while intensity strongly depends upon both variables. Less pronounced, althoug evident is the dependence of Gaussian's FWHM on x.

Table

Sample	T [K]	Peak pos. ε_T [meV]	Integral intensity [arb. un.]	FWHM γ_T [meV]
$La_2CuO_{4-\delta}$	10	6.42 ± 0.5	19.2 ± 0.5	1.13±0.05
	77	6.3 ± 0.1	13.6 ± 0.5	1.2 ± 0.1
$La_{1.9}Sr_{0.1}CuO_{4-\delta}$	10	5.6 ± 0.1	16.0 ± 0.5	1.3 ± 0.1
	77	6.6 ± 0.2	8.4 ± 1.0	1.1 ± 0.5
$La_{1.8}Sr_{0.2}CuO_{4-\delta}$	10	6.7 ± 0.2	13.0 ± 0.7	1.8 ± 0.1
	77	6.5 ± 0.2	6.0 ± 1.5	1.6 ± 0.5
$La_{1.7}Sr_{0.3}CuO_{4-\delta}$	10	6.7 ± 0.3	12.0 ± 1.0	2.0 ± 0.3
	77	6.7 ± 0.3	5.4 ± 1.5	3.0 ± 0.5

In the first study of phonon density of states in $La_{1.85}Sr_{0.15}CuO_4$ (carried out on the High Flux Reactor in Brookhaven)/3/ it was concluded that in order to reproduce the temperature dependence of the specific heat (known from calorimetric measurements) with that derived from the neutron scattering data, one had to assume the existence of an additional low frequency mode at about 4 meV. However, the resolution of the experiment was too poor to detect such a mode. Recently/7/, a careful examination of low frequency excitations in $La_{2-x}Sr_xCuO_4$ (x = 0.0, and 0.15) was carried out on the IN6 spectrometer at HFR-ILL, Grenoble (scattering with energy gain of the 3.07 meV incident neutrons).By comparing the results obtained for different Q values the authors have found a magnetic contribution to INS within the energy transfer range of 5-8 meV at 100K in La_2CuO_4. The effect vanished with the decreasing temperature, probably due to the fall of the occupation number of the excited state. Additional neutron scattering intensity below 8 meV for La_2CuO_4 has also been noticed in/5/.

There seems to be no clear idea as to the physical mechanism that would lead to the discussed peculiarity. One can for example assume that it is due to magnetic Rare Earth (RE) impurities in which INS can excite transitions between levels of the ground state split by interaction with the electric crystal field (CF). The neutron activation analysis, however, has not detected enough amount of magnetic RE impuruity. Moreover, if it were the right mechanism, the line intensity should decrease by 15% with x growing from 0.0 to 0.3. This is so because the cross section for scattering on transitions between CF sublevels is proportional to the number of scattering centers. It follows from the Table that at 10 K the intensity drops by as much as (38±9)% as x rises from 0.0 to 0.3.

Taking all that into account we can conclude that in a low frequency spectrum of elementary excitations in $La_{2-x}Sr_xCuO_{4-\delta}$, there exicts a band at about 6 meV, and that it corresponds to an excitation of a magnetic type. This appears to be a property of the investigated system. The peculiarity varies with both temperature and the dopant concentration, while other parts of the INS spectra do not exhibit such a pronounced dependence.

In the $La_{2-x}Sr_xCuO_{4-\delta}$ compounds only the copper $3d^9$ electrons can be considered magnetic. Their orbital moment however, appears to be almost fully frozen by the crystal field. Consequently, the 6 meV excitation cannot be ascribed to transitions between CF sublevels of $3d^9$ electrons.

Such excitation could also arise due to INS on antiferromagnetic spin waves. If it were the case the spectrum of magnetic excitations should have a gap of about 6 meV and a very small dispersion (about 1 meV), since the peak position is independent of Q and is pretty narrow. Such a spectrum for an antiferromagnet does not seem likely. The more so that it follows from the INS study of the La_2CuO_4 single crystal/17/ that the magnetic branch exhibits a very large dispersion.

In order to understand the origin of a low frequency magnetic excitation it seems necessary to measure INS on single crystal samples with the analysis of neutron polarization. For the nearest future we are planning to investigate the Q-dependence of low frequency dynamics of $La_{2-x}Sr_xCuO_4$ on materials with good superconducting properties, synthesized in oxygen atmosphere.

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Белушкин А.В. и др. E14-88-429
Нейтронные исследования температурной зависимости динамики и структуры сверхпроводящих керамик $La_{2-x}Sr_xCuO_{4-\delta}$

На времяпролетном спектрометре КДСОГ-М на реакторе ИБР-2 одновременно измерены спектры неупругого рассеяния нейтронов /НРН/ и дифракции нейтронов /с целью получения информации о структурных изменениях/ на образцах $La_{2-x}Sr_xCuO_{4-\delta}$ /x = 0,0; 0,1; 0,2; 0,3/ для температур 290, 77 и 10К. Новая особенность в спектрах НРН при переданной энергии 6 мэВ была обнаружена при 80 и 10К. Зависимость интенсивности этой линии от величины переданного импульса и от температуры указывает на магнитный характер соответствующего возбуждения. Интенсивность линии также зависит от концентрации стронция.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1988

Belushkin A.V. et al. E14-88-429
Neutron Scattering Investigations of Lattice Dynamics and Structure of Superconducting Ceramics $La_{2-x}Sr_xCuO_{4-\delta}$ at Different Temperatures

Inelastic neutron scattering (INS) together with neutron diffraction (simultaneous information on the structure behaviour) were measured for $La_{2-x}Sr_xCuO_{4-\delta}$ (x=0.0, 0.1, 0.2, 0.3) at temperatures: 290, 77, and 10 K using KDSOG-M - the time-of-flight spectrometer at the IBR-2 pulsed reactor. A new line near the energy transfer of 6 meV has been detected in the INS spectra at 77 and 10 K. The intensity of this line depends on both momentum transfer and temperature. That points to the magnetic nature of the corresponding excitation. It also veries with strontium concentration.

The investigation has been performed at the Laboratory of Neutron Physics, JINR.

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