Dependence of the phonon state density of the ceramic $YBa_2Cu_3O_x$ on the oxygen concentration and temperature

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The inelastic neutron scattering and neutron diffraction spectra of the compounds $YBa_2Cu_3O_x$ with oxygen concentrations $x = 6.95$, 6.45, and 6.15 at temperatures of 290, 80, and 10 K have been studied. The generalized phonon state density functions have been obtained. These functions change considerably over a broad energy range (10–90 meV) with increasing oxygen deficiency. As the temperature is lowered, the superconducting samples ($x = 6.95$ and 6.45) exhibit an anomalous increase in the state density in the energy region 15–40 meV. This effect is absent in nonsuperconducting samples ($x = 6.15$).

Soon after the discovery of superconductivity in the system Y-Ba-Cu-O (Ref. 1) it was found that the properties of these materials depend strongly on the oxygen concentration. It was established[2] that the phase responsible for the superconductivity at the critical temperature $T_c \approx 90$ K is an orthorhombic oxygen-deficient perovskite of the composition $YBa_2Cu_3O_{6.9}$. Upon reduction of the oxygen content to that of the composition $YBa_2Cu_3O_x$ ($x = 6.8$), the critical temperature T_c decreases to 60 K and when $x < 6.4$, the sample loses its superconducting properties.[3,5] As the oxygen concentration is reduced, the orthorhombic distortions diminish, and when $x \lesssim 6.2$, a phase transition from the orthorhombic phase to the tetragonal phase of the order-disorder type occurs in the oxygen subsystem[4,5] (at $T = 300$ K).

In the structure $YBa_2Cu_3O_x$ there are two types of positions, Cu1 and Cu2, for copper atoms. The Cu2 atoms form Cu2–02,03 planes and the Cu1 atoms form Cu1–01 chains in the perovskite structure (the notation used for atoms is that of Ref. 6).

It has been established elsewhere[7] that as the oxygen concentration is reduced, the oxygen leaves only the 01 positions. Experiments on neutron diffraction have shown that at $x < 6.15$ the samples exhibit antiferromagnetic 3D long-range order.[8]

Our objective was to study the lattice dynamics of the ceramic $YBa_2Cu_3O_x$ in a wide range of x and temperatures with a view of realizing all the possible states on the x, T phase diagram of these compounds. The experiments on neutron scattering[9–13] carried out so far have not been able to solve this problem completely.

The sample of the composition $YBa_2Cu_3O_{6.95}$ was synthesized from a mixture of $Y_2O_3BaO_2$ and Cu by a method of self-combustion synthesis followed by a high-temperature annealing in oxygen. Based on the results of testing, which involved measuring the magnetic susceptibility, the resistance, and x-ray diffraction, the sample had the following characteristics: $T_c = 92$ K, transition width $\Delta T_c = 2$ K, oxygen content

$x = 6.95 \pm 0.05$, unit cell parameters $a = 3.824$ Å, $b = 3.892$ Å, and $c = 11.680$ Å, and space group P_{mmm}.

After the neutron diffraction measurements the oxygen concentration in the sample was reduced gradually to $x = 6.45$ and $x = 6.15$ by means of high-temperature annealing in a vacuum followed by a prolonged homogenization.

The testing results showed that the sample of the composition $YBa_2Cu_3O_{6.45}$ is a single-phase sample with an orthorhombic symmetry, lattice constants $a = 3.84$ Å, $b = 3.87$ Å, and $c = 11.73$ Å, space group P_{mmm}, and onset of the superconducting transition $T_c = 60$ K. The nonsuperconducting sample with $x = 6.15$ had a tetragonal structure: $a = b = 3.871$ Å, $c = 11.818$ Å, and space group $P4/mmm$.

The lattice constants and the superconducting properties of our samples are in good agreement with the data of Refs. 3–5.

The neutron scattering experiments were carried out at the IBR-2 reactor, using the KDSOG-*M* time-of-flight spectrometer[14] with an inverse geometry. The use of a spectrometer has made it possible to simultaneously study the inelastic neutron scattering and neutron diffraction. As to whether the samples studied by us had antiferromagnetic order could not be determined from the neutron-diffraction spectra. The temperature dependence of these spectra showed no evidence of the presence of relevant effects which would indicate a change in the structure as a result of lowering the temperature.

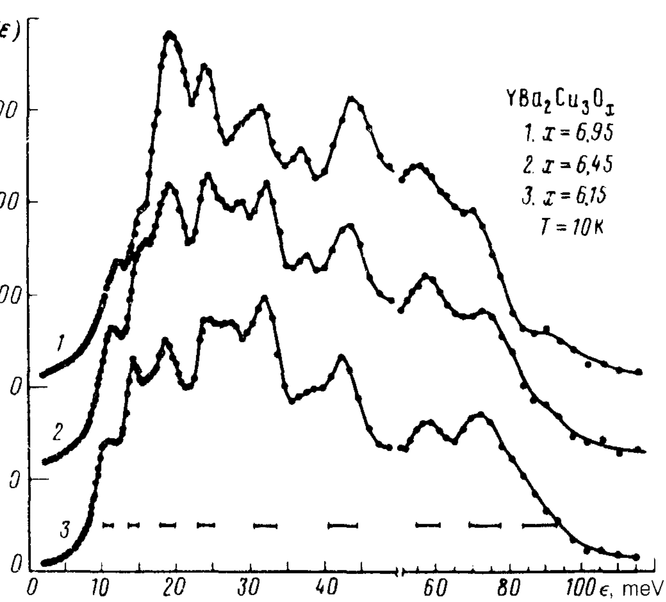

FIG. 1. Generalized state density $G(\epsilon)$ of the $YBa_2Cu_3O_x$ systems at $T = 10$ K and $x = 6.95$, 6.45, and 6.15. $G(\epsilon)$ is expressed in arbitrary units and ϵ is the energy transfer in meV. The horizontal bars above the energy scale denote the resolution of the spectrometer.

TABLE I. Comparison of the positions of the peaks on the $G(\epsilon)$ curve with the optical data.

$YBa_2Cu_3O_{6.95}$				$YBa_2Cu_3O_{6.15}$		
Our data	RS	IR data	Theory[13]	Our data	RS	IR (Ref. 19)
12.0				11,7		
15.0	14 (Ba) Ref. 15			14,2		
19,2	17,7 Ref. 13 18 (Cu2) Ref. 15	19,5 Ref. 13 18,5(Y,Ba,Cu)[13]	14,7 19,4 (Ag) 16,8 (B_{2g}) 17,3 (B_{3g}) 18,7 20,7 (B_{1u}) 18,4, 20,7 (B_{2u}) 20,4 (B_{3u})	18,7	Ref. 16 17,5	
23,7		24,2(Y,Ba,Cu)[17] 24 Ref. 13	22,2 (B_{1u}) 26,9 (B_{3u})	24,0		
	27,3 (O4) Ref. 15 28,1 Ref. 13		26,5 (B_{2g})	27,5	Ref. 16 27,3	
31,2				32,0		
36,5		36 Ref. 13 35(Y,Ba,Cu)[17] 39.2(Y,Ba,Cu)[17]	34,8 (B_{1u}) 32,4 (B_{2u}) 35,8 (B_{3u})			
43,5	42,3 Ref. 13 41,5 (O2,O3,O4) Ref. 15	40 Ref. 13	35,6 (B_{2g}) 34,9 (B_{3g}) 36,8 (B_{2u})	42,5	Ref. 16 41,5	
55	53,4 Ref. 13 62,5 Ref. 13 52.7 (O2,O3) Ref. 15 61,4 (O4) Ref. 15	58,8 (O) Ref. 17	48.4 (B_{3g}) 61,6, 62,8 (A_g)	58	53,9 Ref. 16 58,5 Ref. 16 56,2 Ref. 18 60,7 Ref. 18 58,3 Ref. 19	64,5 (O4)
70	72,5 Ref. 13 79,6 Ref. 13 72,5 (O2, O3)[15] Ref. 15	71 Ref. 13 71,2 76,6 (O) Ref. 17	74,4 (A_g) 82,8 (B_{2g}) 84,2 (B_{3g}) 79,3 (B_{1u}) 84,6 (B_{2u}) 83,1 (B_{3u})	72	72,5 Ref. 18 79,3 Ref. 18	73,4 (O2, O3) 78,8

The inelastic scattering of neutrons was measured at the scattering angles of 30°, 50°, 70°, and 90° in the transmission geometry and at the scattering angles of 80°, 100°, 120°, and 140° in the reflection geometry. The average measurement time of a single spectrum was approximately 30 h. Similar measurements were carried out using a cryostat containing a cassette without a sample, and the measured background was subtracted from the appropriate spectra. The data for the various scattering angles were summed, which allowed us to obtain a good average over the momentum transfer Q. The inelastic neutron scattering spectra for various oxygen concentrations were normalized to the same mass of the sample and were converted to a generalized state density $G(\epsilon)$ on the basis of a single-phonon scattering formula. Additional corrections for multiphonon scattering and multiple scattering were not made.

The functions $G(\epsilon)$ which we have obtained for various oxygen concentrations at $T = 10$ K are compared in Fig. 1. We see that the generalized density function changes dramatically as a result of a decrease in the oxygen concentration. The low-frequency part of the spectrum moderates, but its high-frequency part shifts toward higher frequencies. The positions of the $G(\epsilon)$ peaks are compared in Table I with the optical spectroscopy data and with the model-based calculations. As can be seen from the optical data, the principal contribution to the energy region above 24 meV comes from oxygen, but the contribution of the 01 atoms to $G(\epsilon)$ cannot be determined unambiguously.

Figure 1 shows that as the oxygen concentration decreases, the characteristic features in the energy regions of 19.2 meV, 24–30 meV, and 36.5 meV undergo par-

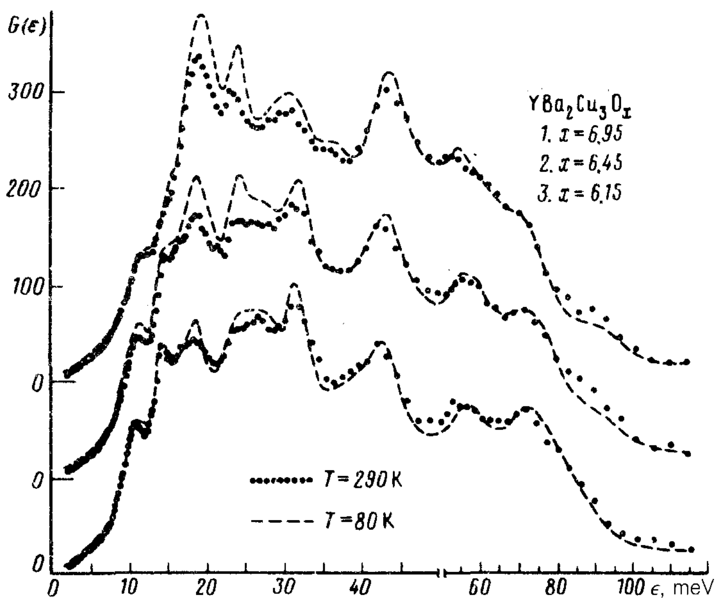

FIG. 2. Generalized state density $G(\epsilon)$ at $T = 80$ K (dashed curve) and $T = 290$ K (points) of $YBa_2Cu_3O_x$ for $x = 6.95$, 6.45, and 6.15. The units are the same as in Fig. 1.

ticularly strong changes (for $x = 6.15$ a structural feature was virtually observable), suggesting that the 01 atoms contribute significantly to these parts of $G(\epsilon)$. This conclusion has been confirmed indirectly by theoretical calculations.[13] A cardinal change in $G(\epsilon)$ over a broad energy range from 10 to 90 meV, in which the oxygen deficiency increases, shows, however, that a decrease in the oxygen concentration of 01 in the Cu1–01 chains causes virtually all force constants to change.

Figure 2 is a plot of the temperature dependence of the function $G(\epsilon)$. The slight differences in $G(\epsilon)$ for $x = 6.15$ at $T = 290$ and 80 K can be explained by the decrease in the anharmonicity and multiphonon scattering upon lowering the temperature. At $x = 6.45$ and 6.95 the situation is entirely different. In this case an additional contribution to $G(\epsilon)$ occurs at $T = 80$ K, in contrast with that at $T = 290$ K in the energy region 15–40 meV. A comparison of the inelastic neutron scattering spectra measured at various scattering angles shows that this effect is clearly seen at a low momentum transfer (the scattering angles of 30°, 50°, and 70°) and that it is virtually absent at high momentum transfer (the scattering angles of 100°, 120°, and 140°). This circumstance in combination with the temperature dependence of $G(\epsilon)$ for $x = 6.45$ and 6.95 allows us to assume that the inelastic neutron scattering spectra of the superconducting compounds have a magnetic component in the energy transfer region of 15–40 meV. The nature of this effect in the compounds being studied is not clearly understood at present. We wish to point out that Jinghui *et al.*[12] also showed evidence, based on the use of the inelastic-neutron-scattering method, for the existence of excess state density in the compound Y-Ba-Cu-O at low temperatures and that we have observed[20] an excitation in the case of a lanthanum ceramic at an energy of about 6 meV, which had the same angular and temperature dependences.

Experiments on inelastic neutron scattering with an analysis of the polarization can, in our view, greatly clarify the nature of the anomalies observed in the inelastic neutron scattering spectra.

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[1]M. K. Wu, J. R. Ashburn, C. J. Torng *et al.*, Phys. Rev. Lett. **58**, 908 (1987).
[2]R. J. Cava, B. Batlogg, R. B. van Dover *et al.*, Phys. Rev. Lett. **58**, 1676 (1987).
[3]M. Yokumoto, H. Ihara, M. Hirabayashi *et al.*, Physica **B148**, 436 (1987).
[4]M. Tokumoto and K. Ogawa, Jpn. J. Appl. Phys. **27**, 224 (1988).
[5]R. J. Cava, B. Batlogg, C. H. Chen *et al.*, Phys. Rev. **B 36**, 5719 (1987).
[6]M. A. Beno, L. Soderholm, D. W. Capone *et al.*, Appl. Phys. Lett. **51**, 57 (1987).
[7]G. Roth, B. Renker, G. Heger *et al.*, Z. Phys. **B69**, 53 (1987).
[8]J. M. Tranquada, D. E. Cox, W. Kunnmann *et al.*, Phys. Rev. Lett. **60**, 156 (1988); J. Rossat-Mignod, P. Burlet, M. J. Jurgens *et al.*, Physica **C152**, 19 (1988).
[9]L. Mihaly, L. Rosta, G. Coddens *et al.*, Phys. Rev. **B 36**, 7137 (1987).
[10]S. Tajima, A. Masaki, I. Rittaporn *et al.*, Physica **B148**, 423 (1987).
[11]J. J. Rhyne, D. A. Neumann, J. A. Gotaas *et al.*, Phys. Rev. **B 36**, 2294 (1987).
[12]R. Jinghui, Li Jizhou, Ju Ansun *et al.*, Intern. J. Mod. Phys. **1**, 409 (1987).
[13]P. Brüesch and W. Bührer, Z. Phys. **B70**, 1 (1988).
[14]G. Baluka, A. V. Belushkin, S. I. Bragin *et al.*, JINR, P13-84-242, Dubna, 1984.

[15]V. D. Kulakovskiĭ, O. V. Misochko, V. B. Timofeev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 460 (1987) [JETP Lett. **46**, 580 (1987)].
[16]D. M. Krol, M. Stavola, W. Weber *et al.*, Phys. Rev. **B 36**, 7133 (1987).
[17]S. Sugai, Phys. Rev. **B 36**, 7133 (1987).
[18]A. Maskkarenhas, S. Geller, L. C. Xu *et al.*, Appl. Phys. Lett. **52**, 242 (1988).
[19]M. Stavola, D. M. Krol, W. Weber *et al.*, Phys. Rev. **B 36**, 850 (1987).
[20]A. V. Belushkin, E. A. Goremychkin, V. Zaĭonts *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 216 (1988) [JETP Lett. **47**, 262 (1988)].

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