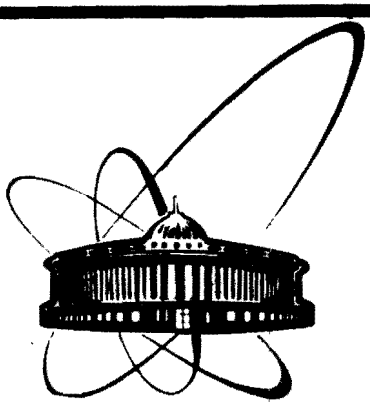

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PHONON DENSITY OF STATES OF $YBa_2Cu_3O_x$ IN DEPENDENCE ON OXYGEN CONTENT AND TEMPERATURE

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Soon after the discovery of superconductivity in a Y-Ba-Cu-O compound system[1], properties of such materials were found to be critically dependent on oxygen content. There was identified[2] as a superconducting phase at T_c = 90K the high temperature superconducting compound $YBa_2Cu_3O_{6.9}$, which can be described as an orthorhombic oxygen deficient perovskite. With a decrease of oxygen content to x = 6.8 in $YBa_2Cu_3O_x$, T_c drops to 60K and for x lower than 6.4 the samples do not show superconducting properties. With decreasing oxygen content, orthorhombic distortions become weaker, and for $x \lesssim 6.2$ $YBa_2Cu_3O_x$ undergoes phase transition from orthorhombic to tetragonal of the order-disorder type in oxygen subsystem (at T = 300K)[4,5].

In $YBa_2Cu_3O_x$ compound, Cu atoms occupy the sites: Cu1 and Cu2. Atoms Cu2 form Cu2-O2,O3 planes, and Cu1 Cu1-O1 chains in perovskite structure (the denotions are in accord with ref.[6]). It is known that under oxygen content reduction oxygen atoms leave only O1 sites[7]. The neutron diffraction experiments show three-dimensional antiferromagnetic long range ordering in $x < 6.15$ samples[8]. Our experiment was aimed at probing the phonon density of states of $YBa_2Cu_3O_x$ ceramics in order to study all possible states on the (x,T) phase diagram. The neutron scattering experiments performed thus far[9-13] did not give complete solution to the problem.

The sample $YBa_2Cu_3O_{6,95}$ was prepared from Y_2O_3, BaO_2 and Cu by firing with subsequent high temperature annealing in oxygen. Test measurements on susceptibility, resistivity, and X-ray diffraction have yielded the following results: T_c =92K, transition width ΔT_c = 2K, oxygen content x = 6.95±0.05, elementary cell parameters a = 3.824 Å, b = 3.892 Å, c = = 11.680 Å, space group Pmmm. Successive decrease of the oxygen content in the sample (down to x = 6.45 and 6.15), after performing INS measurements, was carried out by high temperature vacuum annealing. The test showed the $YBa_2Cu_3O_{6,45}$ sample to be single phased and have orthorhombic symmetry (Pmmm): a = 3.84 Å, b = 3.87 Å, c = 11.73 Å, with an onset temperature of T_c = 60K. A nonsuperconducting sample with x = 6.15 was of tetragonal symmetry (P4/mmm): a = b = 3.871 Å, c = = 11.818 Å. The lattice parameters and superconducting characteristics of our samples are in good agreement with the data reported in Refs.[3-5].

Neutron scattering experiments were performed using a time-of-flight inverted geometry spectrometer KDSOG-M[14] installed at the IBR-2 reactor. The spectrometer allows the inelastic neutron scattering (INS) and neutron diffraction (ND) measurements to be carried out simultaneously. We failed to make any conclusion about the presence or absence of antiferromagnetic ordering in our samples from the analysis of ND spectra. Their temperature dependence revealed no significant effects in evidence of structure changes with decreasing temperature.

The INS measurements were performed at scattering angles of 30, 50, 70 and 90° in transmission geometry and at scattering angles of 80, 100, 120 and 140° in reflection one. A measuring time per spectrum was about 30 hrs. Analogous measurements were undertaken on a cryostat without sample for the background subtraction. Summation of the data obtained at various angles was carried out providing satisfactory averaging over the momentum transfer Q. INS spectra taken for different oxygen concentrations were normalized to the same mass of the sample and transformed according to the one phonon scattering formula into the generalized density of states $G(\epsilon)$ (GDOS). No additional corrections for multiphonon scattering and multiple scattering were applied.

The functions $G(\epsilon)$ obtained for different x at T=10K are compared in fig. 1. Significant changes in GDOS with decreasing x attract one's attention. A low frequency part of the spectrum is softening, and vice versa a high frequency one shifts towards higher frequencies. The cut-of-frequency of the GDOS is found at about 95 MeV and in the limit of our accuracy seems independent of the oxygen content. The energies of peculiarities seen in the $G(\epsilon)$ functions are compared in the Table with the optical data and model calculation results[13]. According to the optical data (see the Table) the

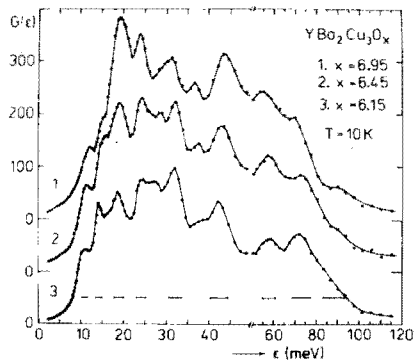

Fig. 1. The generalized density of states of $YBa_2Cu_3O_x$ *at T=10K and at x=6.95, 6.45, 6.15. $G(\epsilon)$ in arbitrary units. ϵ – energy transfer in meV. Horizontal dashes above energy scale are resolution of the spectrometer.*

Table

Comparison of peak positions in $G(\epsilon)$ with optical data

$YBa_2Cu_3O_{6.95}$				$YBa_2Cu_3O_{6.15}$		
our data	Raman data	IR data	Theory[13]	our data	Raman	IR [13]
12.0				11.7		
15.0	14 (Ba) [15]			14.2		
19.2	17.7 [13] 18 (Cu2) [13]	19.5 [13] 18.5(Y, Ba,Cu) [17]	14.7,19.4 (Ag) 16.8 (B2g) 17.3 (B3g) 18.7,20.7 (B1u) 18.4,20.7 (B2u) 20.4 (B3u)	18.7	17.4 [16]	
23.7		24.2(Y, Ba,Cu) [17] 24 [13]	22.2 (B1u) 26.9 (B2u)	24.0		
	27.3(04) [15] 28.1 [13]		26.5(B2g)	27.5	27.3 [16]	
31.2				32.0		
36.5		36 [13] 35(Y, Ba,Cu) [17] 39.2(Y, Ba,Cu) [17]	34.8 (B1u) 32.4 (B2u) 35.8 (B3u)			
43.5	42.3 [13] 41.5(02,03, 04) [15]	40 [13]	35.6 (B2g) 34.9 (B3g) 36.8 (B1u)	42.5	41.5 [16]	
55	53.4 [13] 62.5 [13] 52.7(02& 03) [15] 61.4(04) [15]	58.8(0) [17]	48.4 (B3g) 61.6,62.8 (Ag)	58	53.9 [16] 58.5 [16] 56.2 [16] 60.7 [16] 58.3 [19]	64.5(04)
70	72.5 [13] 79.6 [13] 72.5(02, 03) [15]	71 [13] 71.2, 76.6(0) [17]	74.4 (Ag) 82.8 (B2g) 84.2 (B3g) 79.3 (B1u) 84.6 (B2u) 83.1 (B3u)	72	72.5 [16] 79.3 [16]	73.4(02, 03) 78.8

main contribution is made by oxygen atoms at energies higher than 24 meV and an unambiguous conclusion about the contribution of O1 atoms to $G(\epsilon)$ is impossible.

However, the fact that with decreasing oxygen content the peculiarities in the vicinity of 20 meV, 24-30 meV, and 36 meV (for x=6.15 this is virtually not observed) experience drastical changes, indicates a significant contribution of O1 atoms to these regions of $G(\epsilon)$. This conclusion has also got confirmation in calculations [13]. The cardinal changes in $G(\epsilon)$ occurring over a wide energy range from 10 to 90 meV with increasing oxygen deficiency (see fig. 1) show that a decrease in concentration of O1 oxygen atoms on Cu1-O1 chains leads to the change of almost all the force constants.

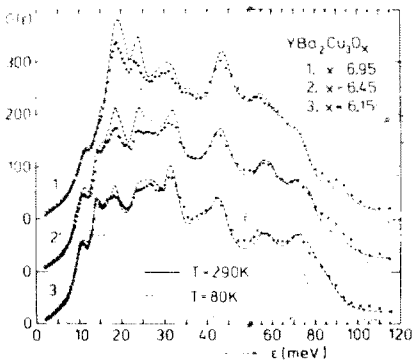

Fig. 2. The GDOS of $YBa_2Cu_3O_x$ at T=80K (dashed lines) and T=290K (points) for x=6.95, 6.45, and 6.15. Units on the axes are the same as in fig. 1.

Figure 2 illustrates the temperature dependence of $G(\epsilon)$. Slightly different GDOS for x=6.15 at T=290K and T=80K can be explained by weakening unharmonic and multiphonon scattering effects with decreasing temperature. The situation is different for x=6.45 and x=6.95. There is observed in the energy range from 15 to 40 meV an additional contribution to $G(\epsilon)$ at 80K as compared to that at T=290K. The comparison of INS spectra measured at different scattering angles points to the fact that the effect is stronger at low momentum transfer (at scattering angles 30, 50, 70°) and is virtually absent at high momentum transfer (at scattering angles 100, 120, 140°). This observation in combination with the temperature dependence of $G(\epsilon)$ for x=6.45 and 6.95 allows the assumption of the existence of the magnetic contribution to INS spectra of superconducting compounds in the energy transfer range from 15 to 40 meV. Today we lack a clear understanding of the nature of such effect occurrence in the studied materials. We would just like to note that the results obtained in Ref. [12] also by INS method are indicative of the existence of an excess density of states in Y-Ba-Cu-O compounds at low temperatures and our results [20] on lanthanum ceramics reveal an excitations at about 6 meV, which has a similar angular and temperature dependence.

Experiments on inelastic neutron scattering with polarization analysis may probably contribute to a better understanding of the nature of anomalies in INS spectra.

In conclusion it is our pleasure to express our gratitude to O.V.Zharikov and V.M.Prokopenko for their help in sample testing, to S.I.Bragin and E.Brankowski for their help in carrying out the INS measurements, to V.L.Aksenov and Yu.A.Osipian for stimulating discussions and encouragement.

REFERENCES

1. Wu M.K., Ashburn J.R., Torng C.J. et al. - Phys.Rev.Lett., 1987, v.58, p.908.
2. Cava R.J., Batlogg B., van Dover R.B. et al. - Phys.Rev. Lett., 1987, v.58, p.1676.
3. Tokumoto M., Ihara H., Hirabayashi M. et al. - Physica, 1987, v.148B, p.436.
4. Nakamura K., Ogawa K. - Jap.J.Appl.Phys., 1988,v.27,p.224.
5. Cava R.J., Batlogg B., Chen C.H. et al. - Phys.Rev.B, 1987, v.36, p.5719.
6. Beno M.A., Soderholm L., Capone D.W. et al. - Appl.Phys. Lett., 1987, v.51, p.57.
7. Roth G., Renker B., Heger G. et al. - Z.Phys.B, 1987, v.69, p.53.
8. Tranquada J.M., Cox D.E., Kunnmann W. et al. - Phys.Rev. Lett., 1988, v.60, p.156.
   Rossat-Mignod J., Burlet P., Jurgens M.J.G.M., Henry J.Y., Vettier C. - Physica C, 1988, v.152, p.19.
9. Mihály L., Rosta L., Coddens G. et al. - Phys.Rev.B., 1987, v.36, p.7137.
10. Tajima S., Masaki A., Rittaporn I. et al. - Physica, 1987, v.148B, p.423.
11. Rhyne J.J., Neumann D.A., Gotaas J.A. et al. - Phys.Rev.B, 1987, v.36, p.2294.
12. Jinghui R., Jizhou Li, Ansun Ju. et al. - Int.J.Mod.Phys., 1987, v.1, p.409.
13. Brüesch P., Bührer W. - Z.Phys.B., 1988, v.70, p.1.
14. Baluka G., Belushkin A.V., Bragin S.I. et al. JINR, P13-84-242, Dubna, 1984.
15. Kulakovsky V.D., Misochko O.V., Timofeev V.B., Emel'chenko G.A., Tatarchenko V.A. - ZhETF Lett., 1987, v.46,p.460.
16. Krol D.M., Stavola M., Weber W., Schneemeyer L.F., Waszczak J.V. - Phys.Rev.B, 1987, v.36, p.8325.
17. Sugai S. - Phys.Rev.B, 1987, v.36, p.7133.
18. Maskarenhas A., Geller S., Xu L.C. et al.- Appl.Phys.Lett., 1988, v.52, p.242.
19. Stavola M., Krol D.M., Weber W. et al. - Phys.Rev.B, 1987, v.36, p.850.

20. Belushkin A.V., Goremychkin E.A., Zajac V. et al. - ZhETF Lett., 1988, v.47, p.216.

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Зависимость плотности фононных состояний керамики $YBa_2Cu_3O_x$ от содержания кислорода и температуры

Исследованы спектры неупругого рассеяния и дифракции нейтронов от соединений $YBa_2Cu_3O_x$ для содержания кислорода x=6,95; 6,45 и 6,15 при температурах 290, 80 и 10 К. Получены обобщенные функции плотности фононных состояний, которые существенно изменяются в широком диапазоне энергий /10-90 мэВ/ с ростом дефицита кислорода. На сверхпроводящих образцах /x=6,95 и 6,45/ при понижении температуры наблюдался аномальный рост плотности состояний в диапазоне от 15 до 40 мэВ. Данный эффект отсутствует в несверхпроводящем образце /x=6,15/.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1988

Natkaniec I. et al. E14-88-430

Phonon Density of States of $YBa_2Cu_3O_x$ in Dependence on Oxygen Content and Temperature

Inelastic neutron scattering (INS) and neutron diffraction (ND) spectra of $YBa_2Cu_3O_x$ compounds for x=6.95, 6.45 and 6.15 at temperatures 290, 80 and 10 K were measured. Generalized functions of phonon density of states (GDOS) obtained from INS spectra change significantly in the wide energy range from 10 to 90 meV with increasing oxygen deficiency. An anomalous increase of the GDOS at energies from 15 to 40 meV with decreasing temperature was observed for superconducting samples (x=6.95 and 6.45), while in the non-superconducting sample (x=6.15) such effect was less pronounced.

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

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