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NEUTRON SCATTERING STUDY OF $YBa_2Cu_3O_{6+\delta}$ ($0 < \delta < 0.8$) OXYDES

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Neutron scattering study of $YBa_2Cu_3O_{6+\delta}$ ($\delta = 0 \div 0.8$) compounds is performed. For $\delta = 0.08$ we observed tetragonal crystal structure with lattice parameters a=3.840 Å and c=11.737 Å and an additional diffractional peak which may be considered as (1/2 1/2 1) magnetic reflection. Any other magnetic reflections corresponding to AF structure suggested earlier have not been found within the limits of the experimental resolution and intensity.

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

Нейтронографическое исследование структуры $YBa_2Cu_3O_{6+\delta}$ при $0 < \delta < 0,8$

А.М.Балагуров и др.

Проведено нейтронографическое исследование структуры $YBa_2Cu_3O_{6+\delta}$ при $\delta = 0,08$, 0,36, 0,48 и 0,68. Только при $\delta = 0,08$ решетка кристалла является тетрагональной с a= 3,840 Å и c= =11,737 Å, и на нейтронограмме присутствует дополнительный пик, который можно интерпретировать как отражение (1/2 1/2 1) от антиферромагнитной структуры. Других магнитных пиков с интенсивностями, превышающими статистическую ошибку, не обнаружено.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

The possibility of the AF ordering in oxygen deficient $YBa_2Cu_3O_{6+\delta}$ compounds at temperatures $T < 500$ K has been recently confirmed in neutron scattering experiments [1,2]. Low intensity and very limited number of the magnetic reflections made impossible the reliable determination of magnetic structure, the effective Cu moment and even its orientation with respect to crystal structure. Measurements of magne-

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tic scattering in $YBa_2Cu_3O_{6+\delta}$ on polarized neutrons showed the presence of magnetic fluctuations up to $\delta = 0.59$ [3]. Taking into account the importance of the interconnection of magnetic and superconducting properties in $YBa_2Cu_3O_{6+\delta}$ compounds we need additional data to know exactly the magnetic structure.

In earlier experiments carried out with the help of crystal spectrometer one of the obstacles was connected with the strong higher harmonic contribution (mainly $\lambda/2$) into the measured integral intensity. We used the time-of-flight diffractometer where this contribution is absent and, therefore, we hoped to determine more correctly the magnetic reflection intensity. Also we aimed to check the absence of the long range antiferromagnetic order in $YBa_2Cu_3O_{6+\delta}$ compounds with $\delta > 0.2$.

Oxygen deficient $YBa_2Cu_3O_{6+\delta}$ samples were prepared by quenching them from different annealing temperatures T = 350 ÷ 950 C into liquid nitrogen [4]. The oxygen content was determined by the wet chemical analysis and also from Rietveld fitting of the diffraction patterns.

Time-of-flight diffractometer DN-2 [5] and pulsed reactor IBR-2 were used to register neutron diffraction patterns which were recorded by the position detector with the sensitive area of about 150 cm^2 and the angular resolution of 19′. The time-of-flight and interplane spacing relative resolution of DN-2 makes up 1% for d = 3 Å and $2\theta = 150°$. We looked for the magnetic reflections up to d = 20 Å for several scattering angles of 90, 40 and 30°.

The refinement of neutron diffraction patterns measured with high resolution at $2\theta = 150°$ was performed using the Rietveld method adapted to the DN-2 [6]. This diffractometer is designed for measurement of the medium and large d-spacing, so we cannot determine the thermal parameters of atoms independently. But including in the fitting the reflections with $d \gtrsim 1.4$ Å only makes the correlations between thermal parameters and occupancy more less.

Parameters derived from neutron scattering data are given in the Table. The oxygen content was found from the neutron diffraction pattern fitting in the range of 1.4 ÷ 3 Å (Fig.1). The δ value determined both by the wet chemical analysis and from neutron scattering data are in good agreement for samples No.2-4. For sample No.1 there is certain discrepancy between these two methods, δ_c is appreciably greater than δ_r and is not in accordance with low T_c. It may be caused by the existence of sharp dependence of T_c in the range $\delta = 0.7 \div 0.8$.

We do not show here the final results of Rietveld refinement as they agree well with the data from earlier neutron experiments [7], which showed that samples prepared in the above described manner

Table

Characteristics of the samples under study

Sample	T_a,K	T_c,K	δ Chem.	δRietv.	R,%	g1·10^2	g2·10^3
1	873	58	0,83	0.68(2)	5.4	4.1	7.8
2	923	40	0.51	0.48(2)	4.2	4.7	5.7
3	973	<20	0.41	0.37(2)	2.6	5.7	4.3
4	1213	0	<0.20	0.08(1)	7.3	7.2	0.0

T_a is the annealing temperature, T_c is the temperature of phase transition (the middle point of resistive curve), δ_c and δ_r are the 04 oxygen content determined by the chemical analysis and from Rietveld fitting. R – the profile R-factor, g1=c/3–(a+b)/2 and g2=(b–a)/(b+a) are the parameters of the deviation from the ideal perovskite structure and the orthorhombic distorsion of the tetragonal lattice.

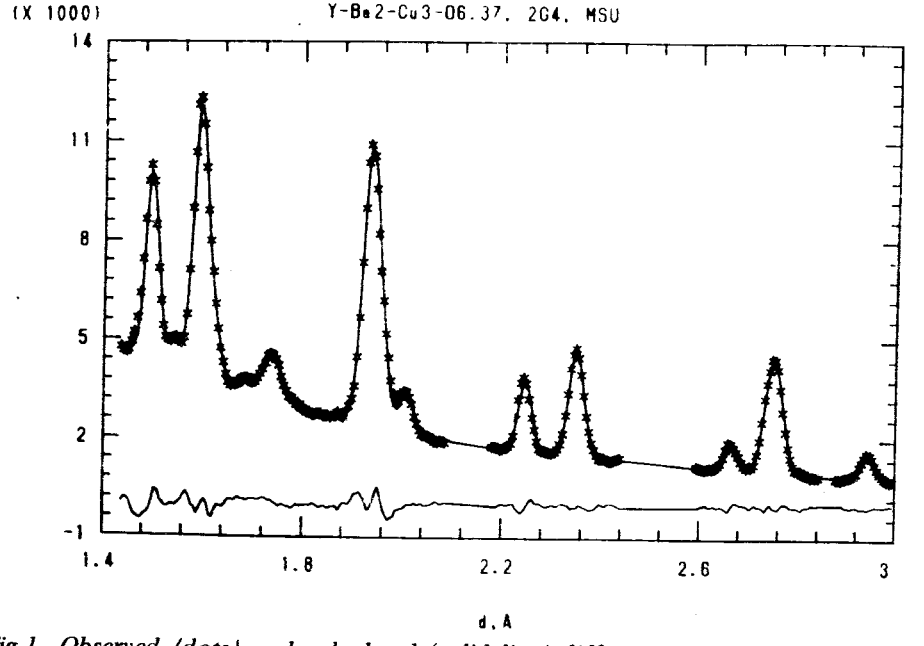

Fig.1. Observed (dots) and calculated (solid line) diffraction profile from sample No.3. The difference curve is shown in the bottom. The total of 245 experimental points were processed with R-factor over profile being 2.6%, weighted R_w-factor 3.4% and expected R_e =2.1%.

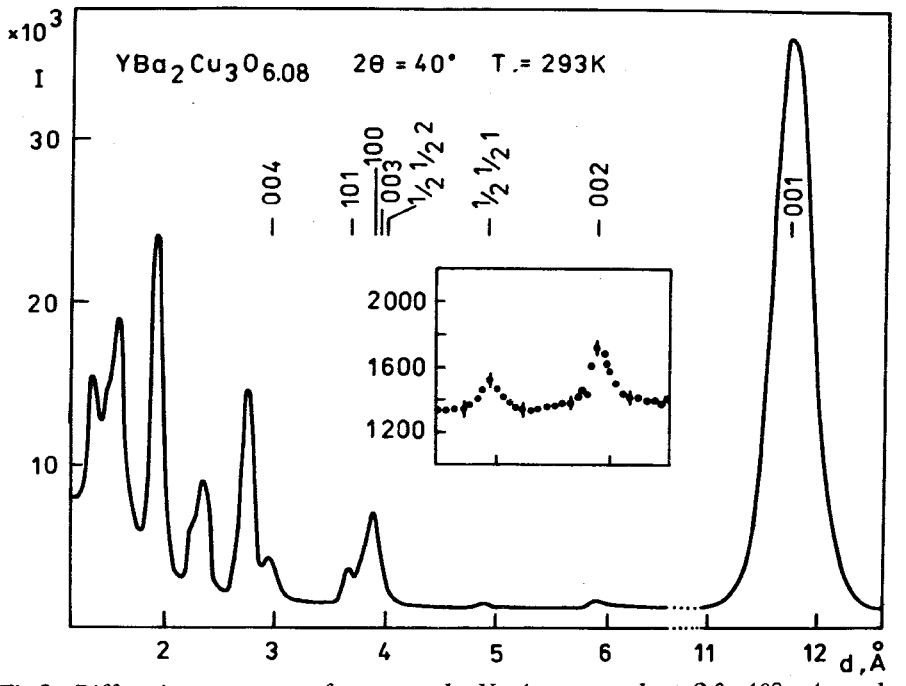

Fig.2. Diffraction spectrum from sample No.4 measured at $2\theta = 40°$. A peak at d= 4.93 Å is clearly observable. It may be considered as (1/2 1/2 1) magnetic reflection from the AF structure.

really become oxygen deficient and variation of δ correlates with the (b - a)/(b + a) value. After annealing at 970 K the diffraction pattern shows a pure single tetragonal phase with 04 removed from (1e) positions.

As is shown in Ref. [1,2] the AF ordering in $YBa_2Cu_3O_{6+\delta}$ for $\delta \leq 0.15$ leads to the unit cell doubling along a and b axes, i.e. permits the enhancement of magnetic peaks of the (1/2 1/2 ℓ) type (if Miller indices are used for nuclear cell). In experiments [1,2] the peaks (1/2 1/2 1) and (1/2 1/2 2) with d equal about 5Å and 4 Å, respectively, were observed to have approximately equal intensities.

A carefull check undertaken in the vicinity of d = 5 Å has revealed an additional weak reflection (d = 4.93 Å) in sample No.4 only (Fig.2). The lattice parameters for this sample were measured under good resolution ($2\theta = 90°$ and 150°), being a = b = 3.840 Å and c = 11.737 Å* and

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**In Ref.[1]: a = b = 3.857 Å and c = 11.855 Å, in Ref.[2]: a = b = 3.843 Å and c = 11.766 Å.*

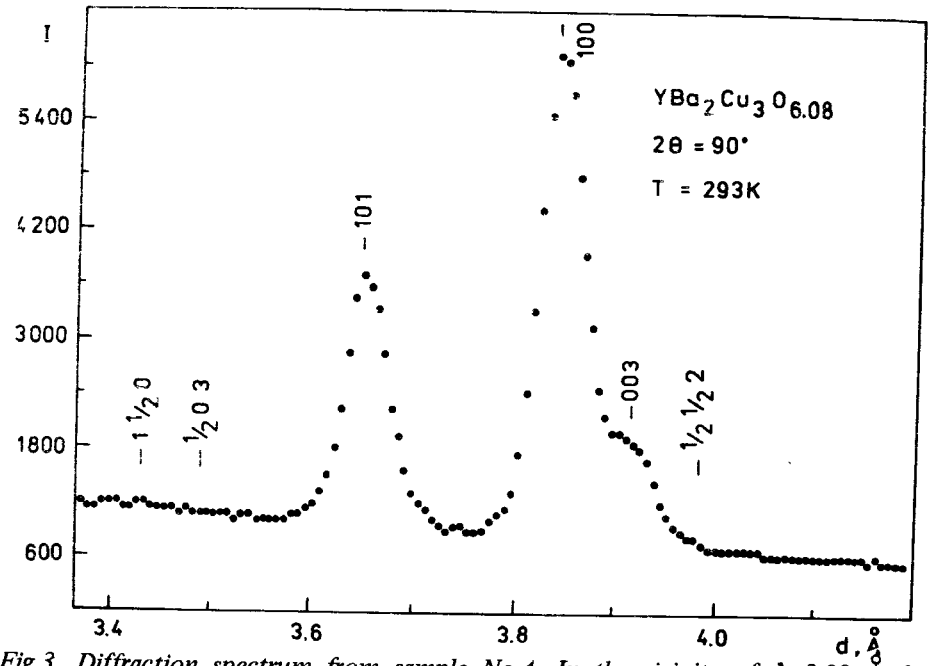

Fig.3. Diffraction spectrum from sample No.4. In the vicinity of d=*3.99 Å the (1/2 1/2 2) magnetic reflection must occur, but its intensity does not exceed the statistical error.*

corresponding to calculated (1/2 1/2 1) magnetic peak position. No other magnetic peaks were found within the limits of experimental resolution and intensity. Namely $I_{½\,½\,2}$ (d = 3.99 Å) = 38 ± 54 (fig.3), while $I_{½\,½\,1}$ (d = 4.93 Å) = 1053 ± 123. Corrections for the effective spectrum, Lorentz factor and absorption have small influence on the intensity ratio for these two peaks and so it appears to be equal to ~20 at least.

Rietveld profile refinement of the data from No.4 sample gave $\delta = 0.08$ (R = 7.3%) showing only a modest correspondence with the tetragonal P4/mmm structure. Many peaks especially those occurring in the range of d = 3 Å have some additional intensity.

Thus the performed experiments have not demonstrated any signs of AF long range ordering in $YBa_2Cu_3O_{6+\delta}$ compounds for $\delta \geq 0.36$. For $\delta = 0.08$ the additional peak appears and it may be considered as a magnetic reflection (1/2 1/2 1) from tetragonal AF lattice with doubled a and b. In contrast to Refs.[1,2] no other additional reflections have been observed in our experiments. Therefore, one should consider with care the models suggested in Refs.[1,2] and a new thorough search for magnetic peaks is necessary.

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