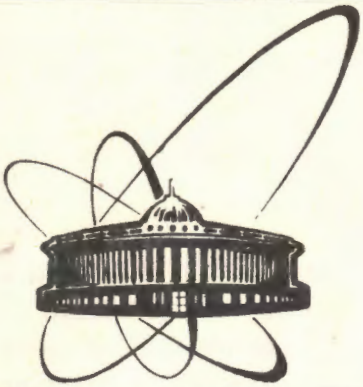

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TIME-RESOLVED NEUTRON DIFFRACTION INVESTIGATION OF EFFECT OF HYDROGEN ON THE HIGH-T_c SUPERCONDUCTOR $YBa_2Cu_3O_{7-\delta}$

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INTRODUCTION

The discovery of new superconductors has led to an intense research concerning the physical parameters which define or limit the T_c values. As to the potential use of these materials, one of the main drawbacks is their great reactivity versus various reagents. Several researches have pointed out that major degradation of $YBa_2Cu_3O_{7-\delta}$ oxides occurs in hydrogen atmosphere at elevated temperatures(1-6). However, the detailed description of early stages of this process and the true location of hydrogen atoms are still unknown. A recent neutron and x-ray diffraction work of D.Tran Qui et al(6) reports on samples under hydrogen pressure at temperatures up to 160 C a progressive reduction of orthorhombic ratio, (b-a)/(a+b), leading to an ortho-tetra transition before the decomposition of the initial product. This is in agreement with some other studies (5,7). On the contrary, in (2) no change of orthorhombicity was observed upon hydrogenation. In order to obtain additional experimental data we have undertaken a time-resolved neutron diffraction study of the process of effect of hydrogen on the $YBa_2Cu_3O_{7-\delta}$ in a wide region of d_{hkl}. This method was developed at the pulsed reactor IBR-2 on the time-of-flight diffractometer DN-2 and recently reported(8). Such technique makes it possible to investigate the solid state chemical reactions *in situ* with a temporal resolution of several seconds (9).

EXPERIMENTAL

Hydrogenation was performed with small pieces of sintered YBCO pellets (T_c=90 K) which were enclosed inside a quartz tube. The tube was placed into a furnace with windows incoming and

diffracted neutron beams. Two detectors, one at a high ($2\theta=170^{o}$) and second at a low ($2\theta=20^{o}$) scattering angles were used simultaneously, ranging the d_{hkl}-interval from 1 to 20A. Diffraction patterns were collected every 3 min. There were three stages of the experiment. First, the sample was kept under a hydrogen flow at room temperature (t=18-42 min). At the next stage the temperature was increased at approximately constant rate $\Delta T/\Delta t=$ 5 deg/min (Fig.1) up to 350 C (t=42-114 min).

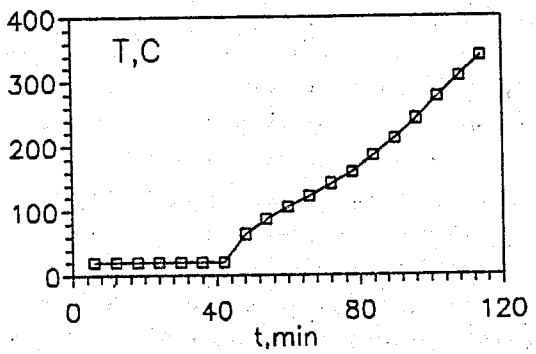

Fig.1. The temperature of the sample as a function of time.

Since drastic changes of a diffraction pattern occurred at this moment further increase of temperature was stopped and the hydrogen flow was changed on argon. At the last stage the sample was heated under argon flow up to 700 C.

RESULTS

Some of the diffraction patterns measured over the interval of 42-114 min are presented in Fig.2. First inspection clearly reveals a splitting of diffraction lines characteristic for an orthorhombic structure, practically independent on the temperature up to the moment of the decomposition evidenced by precipitation of a new phase marked by arrow. Processing of patterns by the Rietveld analysis yielded the evolution in time of cell parameters and population of the oxygen O4 site presented in Fig.3 and 4.

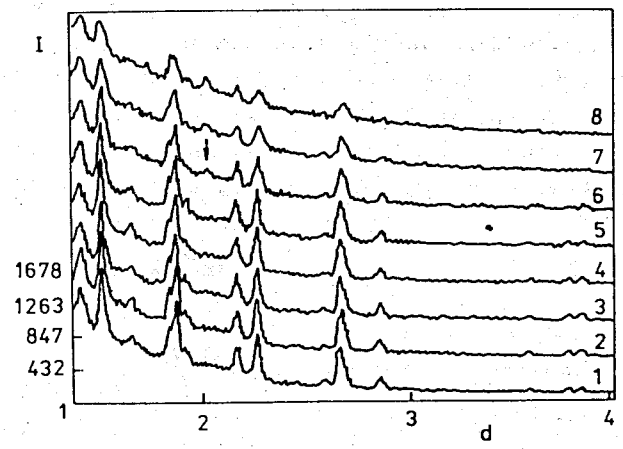

Fig.2. Diffraction patterns measured at $2\theta=170^{o}$ during the heating in the hydrogen atmosphere: 1 - 60 C, 2 - 100 C, 3 - 120 C, 4 - 150 C, 5 - 200 C, 6 - 250 C, 7 - 300 C, 8 - 320 C.

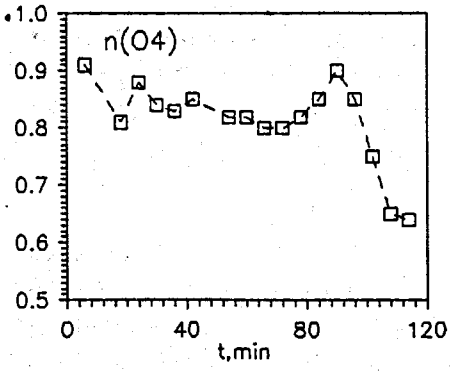

Fig.3. The evolution in time of the occupation of oxygen O4 site as determined by Rietveld analysis.

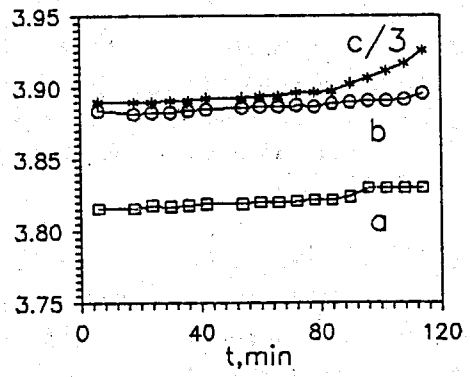

Fig.4. The lattice parameters of $YBa_2Cu_3O_{7-\delta}$ as a function of time during the heating in the hydrogen atmosphere.

It follows that the above mentioned reduction of orthorhombicity (6) does not take place in our experiment at least below the onset of decomposition. Below a temperature of about 220 C the only change in the specimen is gradual increase of incoherent background, occurring even at room temperature. As another example of the observed effect some data are shown in Fig.5.

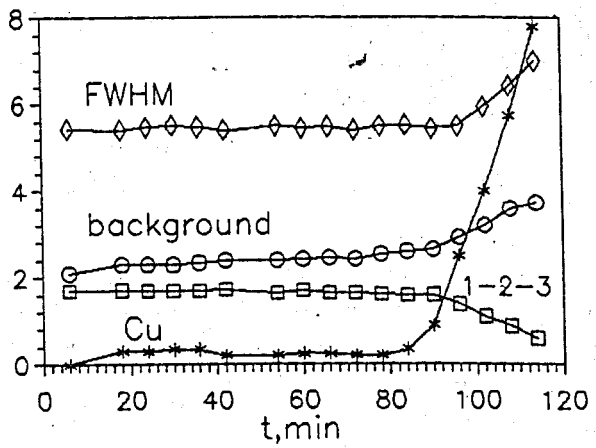

Fig.5. The content of the 1-2-3 phase, incoherent background, the width of diffraction peaks (FWHM) and content of the precipitated phase (metallic Cu) as a function of time.

Once the temperature 220C was reached all parameters represented in Fig.3, 4 and 5 evidenced drastic changes. The precipitated phase was identified as metallic copper. Fig. 6 shows a fit of one diffraction pattern measured at the end of second stage of the experiment and processed by a multi-phase Rietveld analysis. It appears that the localization of hydrogen in 1-2-3 structure is absent. At the last stage of the experiment hydrogen was removed from the specimen in the argon flow during the heating up to 700 C. The ortho-tetra transition was completed below 500 C. The remained 1-2-3 structure (< 20 % of initial amount) have not

been changed. On the contrary, the precipitated copper was transformed into other phases. The background dropped down almost to previous value. All the observations show that the presence of hydrogen in the specimen manifests itself only by an incoherent background.

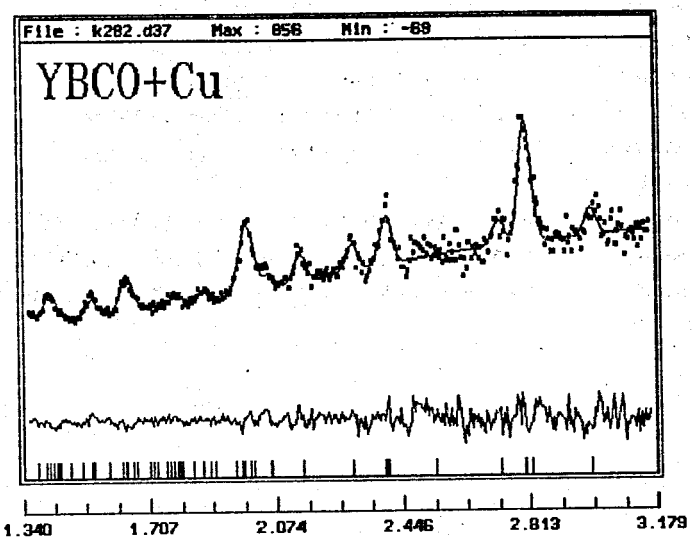

Fig.6. The normalized diffraction pattern (points) (2θ=170°, T=320 C), calculated one (line) and the difference between the measured and the calculated intensities. The peaks with d=2.09 A and 1.81 A are from metallic copper.

CONCLUSIONS

The data presented here, indicates that the reaction of $YBa_2Cu_3O_{7-\delta}$ with hydrogen, using the conditions described above, results in a partial amorphization of the 1-2-3 structure accompanied with the formation of significant amount of the metallic copper. Hydrogen does not make the solid solution with the 1-2-3 structure at any stage of the process (or the concentration is very small). It is adsorbed on the boundary of grains at lower temperatures, but it evidently attacks strongly the grains above 220 C increasing thus reacting surface.

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