

THERMOGRAVIMETRY AND NEUTRON THERMODIFFRACTOMETRY STUDIES OF THE H-YBa₂Cu₃O₇ SYSTEM

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Summary

The high T_c superconducting oxide YBa₂Cu₃O_{7-x} reacts with hydrogen gas. Thermogravimetric, X-ray and neutron scattering experiments allow us to propose a two-step type of hydrogen bonding. Firstly, a few hydrogen atoms fill some oxygen vacancies and may favourably modify the electron state, giving rise to a slight increase in the critical temperature. Secondly, after a prolonged heating period, the collapse of the YBa₂Cu₃O_{7-x} type framework and of superconductivity were observed, and a new, highly hydrogenated material appeared.

1. Introduction

Since the discovery of superconductivity above liquid nitrogen temperature in YBa₂Cu₃O_{7-x} [1] there has been vigorous development in this field. Based on structural results, it was quickly recognized that the superconducting transition behaviour of this high T_c oxide is closely related to the existence of an orthorhombic phase in RBa₂Cu₃O_{7-x}. This finding has initiated the investigation of numerous chemical combinations in order either to understand better the chemical role of the constituting elements and/or to improve the superconducting characteristics.

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It is now well established that oxygen stoichiometry, *i.e.* the effect of oxygen atom disordering, governs the appearance of the superconducting state via a tetragonal ($P4/mmm$) to orthorhombic ($Pmmm$) transformation [2, 3]. Additional experiments have revealed a high sensitivity of T_c to copper-site substitutions by 3d metals, but the influence of R-site substitutions is in general only minor, even if the rare earth element is magnetic. All these facts enlighten the crucial role of copper through its intermediate valency state [4].

Recently, the effect of an additional light element — hydrogen — has been analysed. A significant influence on the structural and physical parameters has been noticed for the $H_zYBa_2Cu_3O_{7-x}$ series. Intrinsic or extrinsic parameters governing the superconductivity have been considered to be affected by hydrogenation [5 - 7].

As the material has a metal character, a metal hydride could be precipitated via the direct solid-gas reaction. Reilly *et al.* [6, 7] have noticed that up to $z \approx 0.5$ the superconducting temperature T_c increases slightly by 92 to 93.8 K. However, for larger hydrogen content T_c drops progressively and for $z > 2.5$ no superconducting transition is observed down to 4 K [7].

However, as the starting material is a non-stoichiometric oxide, hydrogen may be considered to be bonded to oxygen atoms in the same manner as observed in proton conductor materials.

These two types of possible chemical bonding H-M (M = metal) and H-O have to be considered and checked experimentally. Therefore, the role and the location of hydrogen atoms are of great importance irrespective of the electron state of the active superconducting bonds.

2. Hydrogen absorption in $YBa_2Cu_3O_7$

Both Nicolas *et al.* [5] and Reilly *et al.* [6 - 8], have measured direct H_2 gas absorption by the oxide using volumetric techniques. The absorption rate was generally recorded under low gas pressure at room temperature. In most cases, the reactivity process was initiated during a short activation time at $T_a \approx 400$ K, and is achieved in a few hours. Both groups have measured the increase in T_c for moderately hydrided compounds ($z < 0.5$). For larger absorbed hydrogen quantities, the proportion of superconducting material and its T_c drop drastically. Reilly *et al.* [6] have studied the impact of hydrogen on the structure using X-ray and neutron diffraction. They used deuterium instead of hydrogen-charged compounds in order to reduce neutron absorption. Dilatometric effects have been reported and a twinning mechanism has been proposed [7]. Again, mechanical implication of hydrogen absorption has been proposed to account for T_c improvements observed by Nicolas *et al.* [5]. The nature of the chemical bonds has been investigated by Yang *et al.* [8] using IR spectroscopy.

In the present study, we have performed hydrogen absorption measurements by continuously weighing the sample using a thermobalance designed

to operate under an H_2 gas atmosphere. The $YBa_2Cu_3O_{7-x}$ sample was prepared by the citrate synthesis route followed by pyrolysis in order to obtain a fine and homogeneous powder [9], containing significantly fewer impurities in comparison with those produced by the usual solid state reaction procedure. Moreover, this method allows us to synthesize homogeneous particle dimensions strictly distributed around $r = 2 - 3 \mu m$ and gathered as aggregates with a diameter of about $10 \mu m$. A homogeneous particle size is crucial in order to give a well defined solid-gas reaction. Prior to the experiments, the sample was controlled by using X-ray and neutron diffraction. It is a single, well crystallized phase, having the formula $YBa_2Cu_3O_{7-x}$ with $x < 0.025$. Measurements of the superconducting characteristics were achieved by $\chi_{a.c.}$ experiments [10], which show a sharp transition temperature $T_c = 91.2 \pm 0.5$ K.

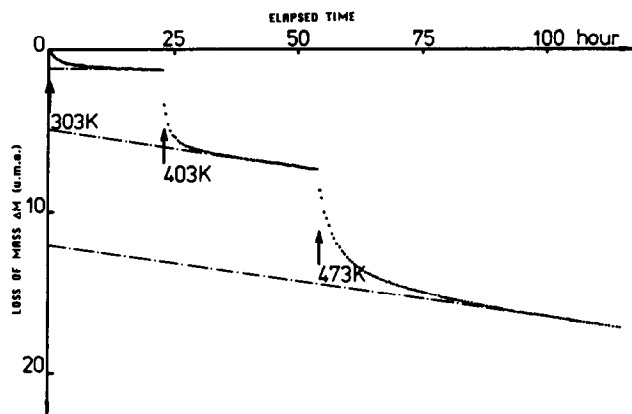
Samples of 0.5 g were used for the thermogravimetric analysis (TGA). A dried and purified H_2 gas flow (5N5 purity, pressure $p = 10^5$ Pa) was controlled at the rate of around $1000 \text{ cm}^3 \text{ h}^{-1}$ (around $3 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$). The sample temperature was monitored at different set points in the range 303 to 473 K. For a first series of experiments, the same sample was used at different temperatures. For a second series, a fresh sample was placed in the TGA apparatus and analysed at a unique temperature, this procedure was repeated at different temperatures.

In parallel, we have undertaken time resolved neutron scattering experiments using a D_{1b} spectrometer set up at the Institut Laue-Langevin, Grenoble. It is a position-sensitive detector with an 80° aperture and a fairly good statistic count. A sample of 4 g was loaded in a vanadium container and centred in a temperature-controlled furnace. The sample holder was connected via capillary tubing with a hydrogen tank through valves and manometers. In this experiment hydrogen samples were preferred to deuterated ones since the quantity of absorbed gas was relatively small, leading to a reasonable level of neutron absorption. If one considers that oxygen and deuterium have the same magnitude of neutron scattering lengths ($b_O = 5.805$ and $b_D = 6.674$ fermi respectively, as coherent cross-section), a better contrast effect will be obtained by using hydrogen itself ($b_H = -3.741$ fermi). Moreover, the high incoherent neutron cross-section of hydrogen allows us to record the gas absorption rate from the background level of the diffraction pattern.

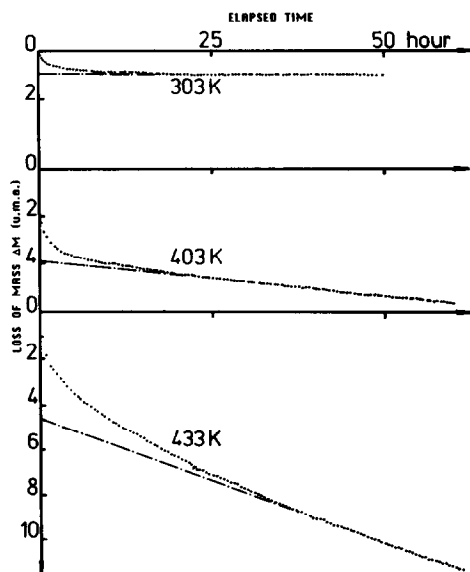
The applied H_2 pressure was $p = 5 \times 10^5$ Pa, and it was re-equilibrated when absorption took place. The neutron experiment was divided into several phases. First the sample was kept under pressure at room temperature for more than 7 h. Then it was heated step by step ($\Delta T \approx 7$ K) from room temperature to 358 K. At each step, the temperature was stabilized for 1.5 h. Finally a sample was heated at 358 K, then at 403 and 432 K for several hours. For some of these temperature cycles, the experiments were performed once more without the appearance of a significant difference in the results as compared with the previous ones.

3. Thermogravimetry analysis (TGA)

Figures 1(a) and (b) show the mass change ΔM of the samples. After a short heating time at a defined temperature, the sample temperature was maintained for a long period at this point. In a few hours a linear regime of the mass change *vs.* time $\Delta M/\Delta t$ is observed. In all cases the change of mass corresponds to a loss of matter, in apparent contradiction with volumetric



(a)



(b)

Fig. 1. (a) Thermogravimetry analysis under H_2 atmosphere of a unique $YBa_2Cu_3O_{7-x}$ sample, the temperature being stabilized at different points. (b) Thermogravimetry analysis under H_2 atmosphere of renewed samples at different temperatures. The loss of mass is expressed in a.m.u.

TABLE 1

Cell parameters of the samples treated under hydrogen in the TGA and the neutron experiments and measured by X-ray diffraction ($\lambda_{\text{CuK}\alpha}$)

	a (Å)	b (Å)	c (Å)	V (Å ³)
Initial	3.8212(2)	3.8839(2)	11.6848(6)	173.41(3)
TGA 303 K	3.829(3)	3.887(2)	11.673(7)	173.7(3)
TGA 403 K	3.825(3)	3.883(3)	11.670(9)	173.3(4)
TGA 433 K	3.855(3)	3.889(3)	11.676(9)	175.0(4)
Neutron (b)	3.837(5)	3.886(5)	11.650(15)	173.7(7)
Neutron (c)	3.880(3)	3.880(3)	11.640(10)	175.2(4)
Neutron (d)	3.855(5)	3.855(5)	11.610(10)	172.5(6)

The letters b, c and d refer to Section 4 (neutron scattering).

experiments indicating a hydrogen uptake, *i.e.* an increase of mass [5 - 7]. Even at 303 K, the sample reacts under pure hydrogen atmosphere, and loses a mass of about 1 g (mol g)^{-1} of compound. In fact the rate of the reaction depends on the applied temperature T , and also on the previous thermal treatment (fresh or already used samples). However, after a time $\Delta M/\Delta t$ remains constant (Figs. 1(a) and 1(b)) and then:

$$M(t) = M(0) - B(T) - \{A(T)t\} \quad (1)$$

$$\text{with } B(T) = e^{\alpha T + \beta}, \quad \alpha = 8.2 \cdot 10^{-3} \text{ K}^{-1}, \quad \beta = -202$$

Results recorded at 403, 433 and 473 K closely fit the activation law which holds for both types of experiments. Loss of matter (water) results in a single and temperature-activated phenomenon.

After each TGA experiment, the sample was immediately checked using X-ray diffraction. Table 1 presents the refined cell parameters of the phases after hydrogen treatment. A progressive increase of the width of the Bragg lines is observed and a reduction of the orthorhombicity ratio ($b - a$): ($b + a$) becomes progressively more pronounced with temperature. However, additional lines are perceptible on the pattern recorded at 433 K. Among them, some broad peaks are already visible on former patterns (403 K). They are probably due to some reactions on the sample surface, as reported for moist materials [11]. The hydrogen- and heat-treated compounds become very sensitive to the ambient atmosphere and they are destroyed (amorphized?) after a few hours.

4. Neutron scattering analysis

(a) H_2 pressure = 1, 5, 10×10^5 Pa; $T = 293$ K.

For several hours, no significant change is detected on the diffraction patterns, in agreement with refs. 6 and 7.

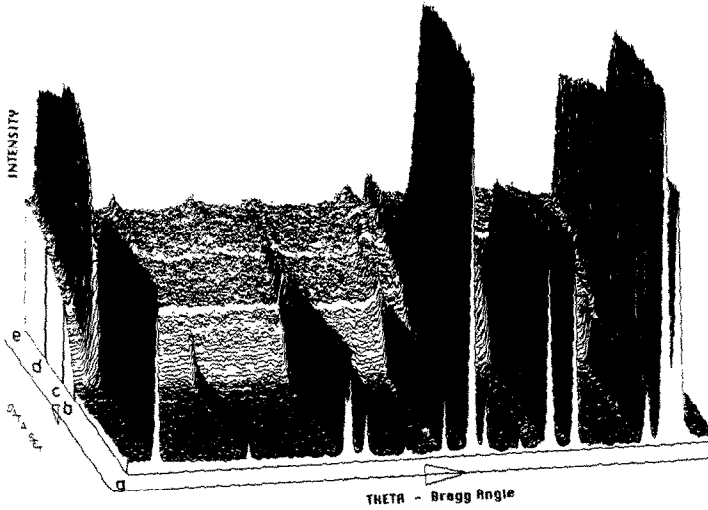


Fig. 2. Neutron diffraction time-resolved investigation of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sample under 5 bar H_2 gas atmosphere. The three-dimensional representation shows patterns recorded between 293 and 358 K (a-b), 358 and 403 K (b-c), at 403 K (c-d) and finally at 425 K (d-e).

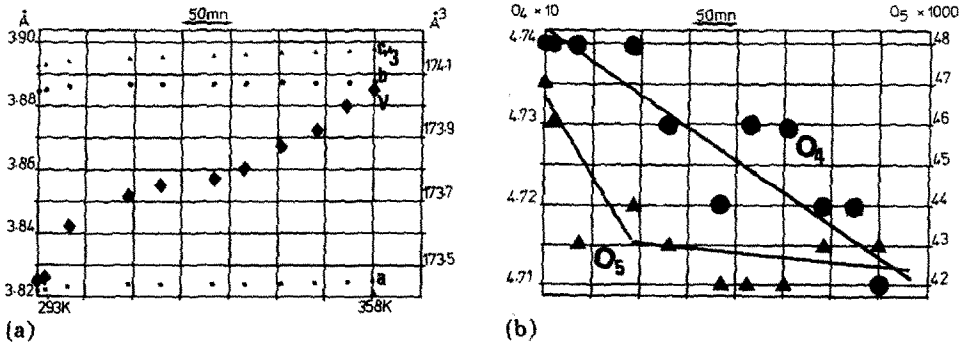


Fig. 3. (a) Thermal behaviour of the unit cell parameters from 293 to 358 K of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ under H_2 gas. (b) O_4 and O_5 relative populations (maximum equals 0.5) refined from the heat treatment data. The lines are for guidance.

(b) H_2 pressure = 5×10^5 Pa; T is increased steeply from 293 to 358 K.

Figure 2 shows the data recorded during all the time-resolved experiments as a three-dimensional representation. Apparently the structure transformations are continuous but weak (Fig. 2, first part). Refinements of the structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were performed on the basis of occupancy ratios of the O_4 and O_5 sites using the profile refinement technique. The refined cell parameters are given in Fig. 3(a). Very weak changes indicate a slight cell volume increase with temperature. However, the background measured apart from the Bragg peaks is only affected when the compound is heated near the highest temperature. A final 20% increase in the background is observed after cooling the sample to room temperature, indicating

substantial and permanent hydrogen uptake. The amount of hydrogen uptake is not, however, enough to account for the mass loss detected by TGA. The difference patterns analysed step by step (e.g. 300 - 293 K, 307 - 300 K, ...) show first a weak increase in background (293 - 314 K), then no significant change (321 - 351 K) and finally a noticeable increase in background (351 - 358 K). Furthermore, a weak profile distortion of the (001) line takes place at the low-Bragg-angle side. Refinements of the structure of the samples performed along the heating cycle show a weak decrease of the oxygen content both on the O₄ and O₅ sites (Fig. 3(b)).

(c) Time resolved experiment under 5×10^5 Pa H₂ pressure.

As the reactivity of hydrogen increases markedly with temperature, we have used a fresh sample in the same experimental conditions, but heated to and maintained at 403 K. Diffraction patterns have been recorded over periods of 300 s (Fig. 2, second part (b - e)). After an initial activation time, reaction with the hydrogen atmosphere starts again. The first one-third of the collected patterns have been successfully analysed on the basis of a dominant part of the mother phase (Fig. 4). Then a structure transformation is superimposed which makes neither profile nor integrated intensity refinements reliable. Figure 2 shows that a considerable background increase coexists with the structural transformations.

After these general trends are given, we report in more detail the 'high' temperature transformation in terms of crystal structure. The cell parameter behaviour *vs.* elapsed time resembles that observed at higher temperature when YBa₂Cu₃O_{7-x} re-equilibrates its O₄ and O₅ populations with a slight increase of *x* [12] (Fig. 5(a)). The $(b - a):(b + a)$ ratio and the cell volume show a similar progressive reduction of orthorhombicity (Fig. 5(b)). About

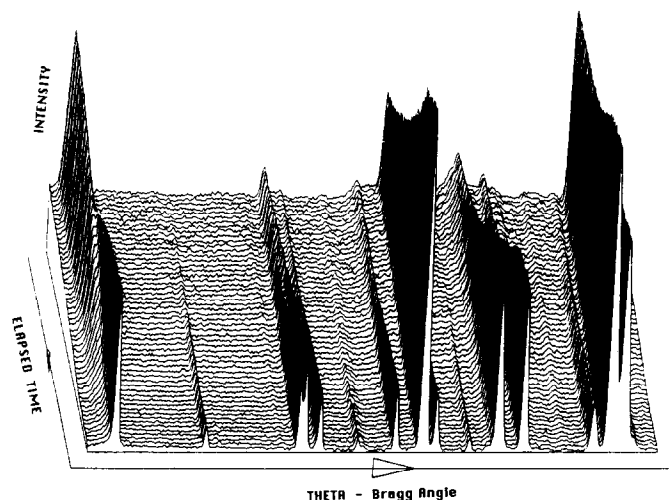


Fig. 4. Three-dimensional representation of the time-resolved neutron scattering experiment performed under 5 bar H₂ gas at 403 K on YBa₂Cu₃O_{7-x} details of the phase transformation.

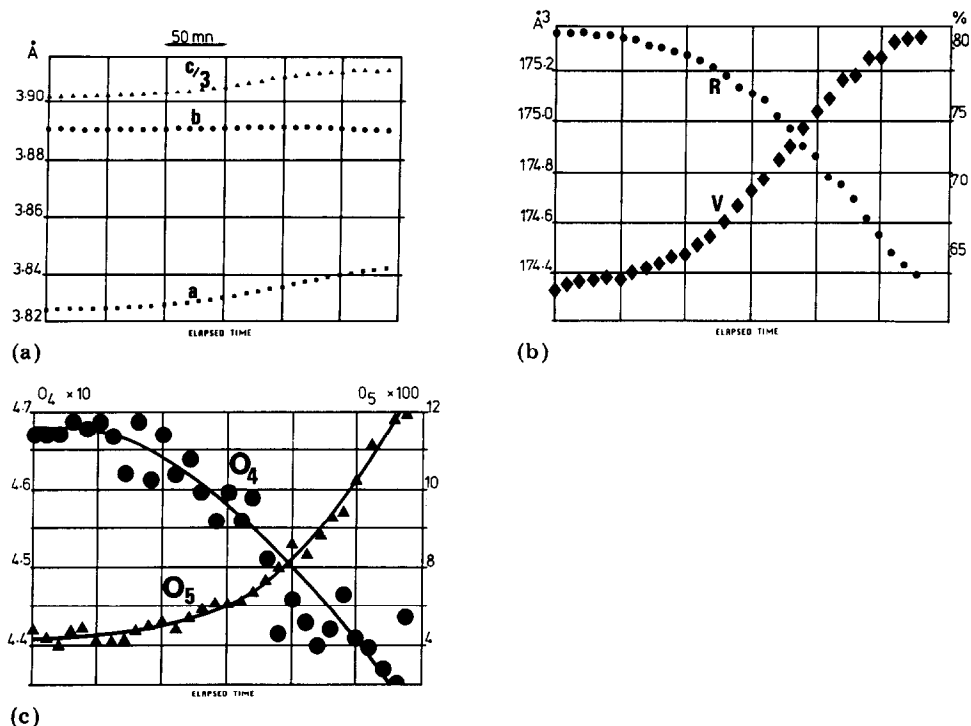


Fig. 5. (a) Time variation of the cell parameters recorded when the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sample was maintained at 403 K under H_2 gas pressure. (b) Time variation of the cell volume V and the distortion criterion $R = (b - a) : (b + a)$ under the same experimental conditions. (c) Time variation of the O_4 and O_5 relative occupancies. The lines are for guidance. Each of the points corresponds to a record of 300 s.

4 h later, the collapse to a tetragonal phase is reached, as indicated by the coalescence of the (103) and (013) lines, the extinction of Bragg peaks and a large reduction of the (001) line. Figures 2, 4 and 6 show the progressive disappearance of the (001) reflection at $2\theta \approx 11.8^\circ$ and the emergence of a new reflection at $2\theta \approx 10.5^\circ$. An irreversible structural (chemical) transformation has taken place with time.

Before this transformation was achieved, it was observed that O_5 site occupancy increased perceptibly at the expense of the O_4 site, in agreement with the general trends of the orthorhombic-to-tetragonal transformation [13]. The oxygen atom number per formula unit remains close to 7 and the amount of hydrogen is $z \leq 0.05$ (within the e.s.d.), as long as it was possible to perform significant structure refinements. Simultaneously, the amount of orthorhombic phase decreased. Finally, the temperature was raised to 425 K for 3 h, making the chemical transformation more complete. The last diffraction patterns only contained a few parts of the 'initial' (probably tetragonal) material and both large and weak lines of (a) new system(s). Assuming that the first observable line is (001), it produces $d^{-1} = 0.065 \text{ \AA}^{-1}$ or $d \approx 15.3 \text{ \AA}$ as a main periodicity. On the basis of cell parameters $a, b \neq a,$

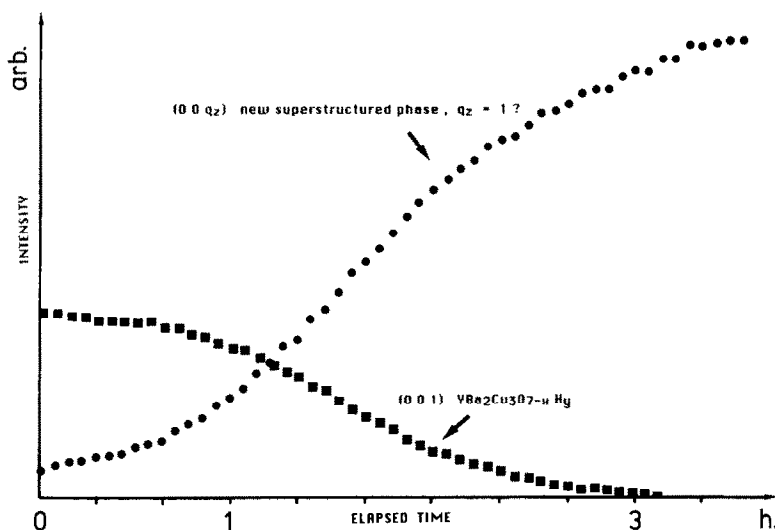


Fig. 6. The structure transformation initiated at 403 K as seen in the vicinity of the (001) Bragg peak: the intensity of the (001) for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ decreases, and that of the (001) for the new superstructured compound increases.

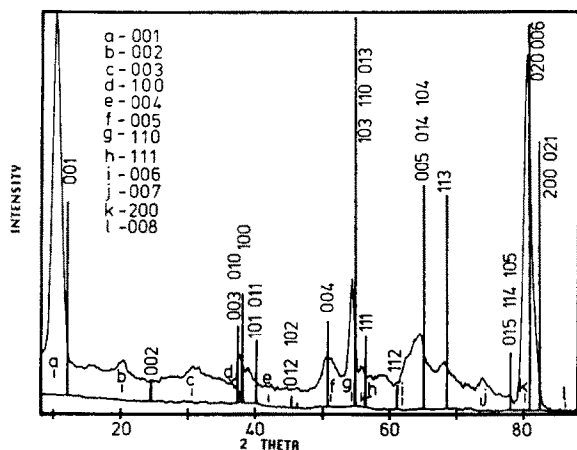


Fig. 7. Final neutron diffraction pattern recorded during the treatment at 425 K under hydrogen pressure. It shows the main peaks of the new superstructured phase discussed in Section 4(c) (continuous line) and is compared with the pattern of the fresh sample (shown by vertical bars).

$c \approx 4a$ with $a = 3.82 \text{ \AA}$, most of the observed lines of the final patterns can be indexed (Fig. 7). In the light of the breadth of the lines, crystal coherence in the (001) plane seems more established than that perpendicular to plane. However, a large incoherent scattering and modulations in the background, plus weak additional lines and the relatively poor crystallinity of the resulting phase, prevent any modelling of its crystal structure. More

probably, it could be a superstructure material (intercalated?) based on the simple perovskite frame.

(d) After the neutron experiments, all the samples were controlled using X-rays. They are very sensitive to the atmosphere and moisture; the black materials turn into green-brown ones. The superstructure lines described above quickly vanished. As already reported, decomposition materials [14] have been identified as BaCO_3 , $\text{Ba}_2\text{Cu}(\text{OH})_6$, etc., progressively more pronounced in successively recorded X-ray patterns. Part of the rest of the 'initial' phase could be indexed on the basis of a tetragonal or pseudo-cubic cell ($a \approx 3.86 \text{ \AA}$). After a few hours, the compounds appear amorphized (destroyed). Neither after the final TGA experiments nor after the neutron diffraction experiments did the residual materials (stored and protected against atmosphere contamination) exhibit superconducting properties. A strong increase in the normal state resistivity shows the non-conducting character of the transformed compounds, at both 77 and 300 K. If no EPR signal was obtained in the initial phase, the hydrogenated phase shows a noticeable resonance near $g = 2.2$, presumably due to Cu^{2+} ions. IR measurements show the presence of OH^- bonds: these experiments show that in the final state of the samples hydrogen is connected to the oxygen lattice mainly in the form of hydroxyl radicals.

5. Discussion

Coupled TGA and structural results (X-ray and neutron diffraction) provide a better understanding of $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ interactivity. Hydrogen absorption, detected by volumetric measurements, is confirmed as the activation process of the reaction by heating the sample [5]. However, a systematic loss of mass of the sample (TGA) corresponds to the observed gas pressure decrease (neutron experiments) even at the lowest temperature (303 K $\rightarrow \Delta M \approx 1 \text{ a.m.u.}$).

At the initial mass loss, drying of interstitial moisture might be invoked as a possible explanation. The general increase in background due to incoherent neutron scattering strongly suggests that additional hydrogen nuclei enter in the sample lattice. Simultaneously, a weak but significant decrease in both O_4 and O_5 site populations takes place (the last site being slightly occupied in the original sample). This could be interpreted either as an effective depletion of the two oxygen sites or as a weak occupancy of the vacancies by a few of the hydrogen atoms, accounting for the opposite sign of the scattering lengths (see Section 2). The second hypothesis seems to work better since Cu-H bonds have been shown in low hydrogen charged materials [7].

The cell parameters are markedly unaffected until a critical activation temperature is reached ($T_a \approx 400 \text{ K}$). At this point, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ structure is more dramatically perturbed if maintained up to T_a under H_2 gas. Hydrogen absorption is progressively larger (neutron incoherent scattering,

TGA) and the loss of mass extrapolated to $t = 0$ increases with T . From TGA experiments it is close to 3.5 a.m.u. (around 0.2 O atom f.u.⁻¹) at $T = 403$ K.

The cell parameters then behave in the same way as described earlier for the orthorhombic-tetragonal distortion accompanied by a net oxygen depletion [13]: here the O₄ sites are progressively less occupied in contrast to the refilling of the O₅ sites. The orthorhombicity criterion $(b - a):(b + a)$ is reduced and the cell volume increases with the amount of reacted hydrogen. Our structure refinements allow us to consider as significant only (within e.s.d.) a decrease in the Cu₂-O₁ distance from 2.28 to 2.22 Å before the transformation of the starting compound.

Finally, an increasing part of the sample becomes a larger stacking sequence of elemental perovskite blocks containing a large amount of 'protons' (incoherent scattering) probably intercalated as OH⁻ entities (IR data). This phase is formed and is stable under a reducing atmosphere only and it does not exhibit superconducting transitions. The reaction is not reversible and in ambient atmosphere the presumed perovskite superstructure cell is quickly destroyed.

5. Conclusion

Even at low temperature, hydrogen reacts with YBa₂Cu₃O_{7-x} with preliminary occupancy of some O₄ and O₅ holes (accounting for the respective sign of the scattering lengths of oxygen and hydrogen, the increase of the incoherent part of the background, etc.). It is necessary to initiate the process via a short time activation by heating the sample. For a low hydrogen charge, slight positive shifts of T_c [5 - 7] and Cu-H bonds have been reported [8], here corroborated by a weak occupancy of oxygen vacancies by hydrogen ($z \leq 0.05$). However, with temperature ($T > 400$ K) and time, the amount of the superconducting part of the sample decreases, with a tendency for both a re-equilibrium of the O₄ and O₅ populations. The unit cell of the YBa₂Cu₃O_{7-x} compound reduces in orthorhombicity; the volume increases with x . O-H bonds are formed as detected by IR spectroscopy in the final new 'superstructured' phase and by the large loss of mass directly measured by TGA. Such a type of bond makes unstable the already modified oxide (reduced in orthorhombicity) by a thermally activated reaction. This irreversibly transforms into a new, non superconducting compound, still unidentified.

In a recently published nuclear magnetic resonance (NMR) study [15], Y-H bonding is invoked. As for ref. 8, we suggest that Cu-H is the more realistic. Does the NMR line splitting attributed to (high) temperature AF correlations relate to a two-hydrogen-site model?

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