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A neutron-spectroscopy study of the hydrogen vibrations in hydrogen-doped $\text{YBa}_2\text{Cu}_3\text{O}_x$

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Abstract. We studied the H vibrations in H-doped $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ ($y = 0.6$) by neutron spectroscopy. Neutron spectra were taken at 10 and 14 K from both orthorhombic ($x \simeq 6.9$) and tetragonal ($x \simeq 6.3$) samples. The spectra exhibit large H-induced intensities in the energy range between 40 and 130 meV. In comparison to orthorhombic samples, the H vibrations in tetragonal samples are shifted to lower energies by $\sim 11\%$. This shift is opposite to the spectral shift of the lattice vibrations between H-free orthorhombic and tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$, frequently attributed to differences in the electron–phonon coupling. Our results show that any such differences in the electron–phonon coupling are not apparent in the H vibrations. The results also support previous suggestions that the H occupies sites in the close neighbourhood of the Cu(1) atomic planes.

1. Introduction

Reilly *et al* [1] were the first to report that $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples absorb hydrogen in an H_2 gas atmosphere. The absorption process and the properties of the resulting compound $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ were subsequently investigated in numerous experimental studies (see [2]–[21] and references therein). In spite of these intensive experimental efforts, the present understanding of the absorption process and the physical properties of $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ is incomplete or even controversial. There exist no data for the solubility isotherms. The results reported for the influence of the H on the lattice parameters are contradictory, although most of the studies report that large amounts of absorbed H cause, for originally orthorhombic samples, a decrease of the orthorhombicity or even a transition to the tetragonal structure [1, 4, 8, 12, 13, 16, 20]. For oxygen concentrations close to $x = 7$, it was further found that the absorption of H leads to an initial increase of the superconducting transition temperature [1]. Both the reduction of orthorhombicity and the observed increase of the transition temperature result also from a decrease of the O concentration. In fact, similar effects of H absorption and a decreasing O concentration are observed for other physical quantities as well [4, 9, 13, 17]. Various experimental investigations make it reasonable to assume that the absorbed H occupies, at least preferentially, O vacancies in the Cu(1) (or CuO) atomic plane [1, 2, 5, 6, 10–12]. However, a convincing neutron-diffraction experiment confirming this assumption is still missing. A controversial question is the existence of a potential hydride phase at high H concentrations. Reilly *et al* [1] suggested a hydrogen solid solution up to a concentration $y \simeq 0.2$, and the precipitation

of a non-superconducting hydride phase at higher H concentrations. However, later studies [3–6, 11, 13, 16–18] could not confirm such a behaviour since their results demonstrated a continuous variation of a series of physical properties with increasing H content. These properties include the superconducting volume fraction [3–6], the lattice parameters [4, 11, 16], the ^{89}Y Knight shift [13] and the superconducting transition temperature of $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ films [17, 18]. According to the later studies, it seems unlikely that H precipitation occurs at least up to an H concentration $y = 0.6$ as investigated in the present study.

In this paper, we report the results of neutron-spectroscopy experiments investigating the vibrations of the hydrogen in $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ samples. The vibrational spectra are sensitive probes for the local environment of the hydrogen. Our experiments demonstrate a distinct spectral shift between the H vibrations in orthorhombic ($x \simeq 6.9$) and tetragonal ($x \simeq 6.3$) samples. An important result is that this shift is opposite to that found between the lattice vibrations of H-free $\text{YBa}_2\text{Cu}_3\text{O}_x$ in the case of the two structures [22, 23]. The observed spectral shift of the hydrogen vibrations further supports previous suggestions [1, 2, 5, 6, 10–12] according to which the H occupies sites in—or in the close neighbourhood of—the Cu(1) atomic planes.

The vibrational spectra of H in $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ have already been studied in two previous neutron spectroscopy experiments [7, 11]. Both experiments were carried out on orthorhombic samples ($x \simeq 6.95$, $y \leq 0.6$), so any differences between the orthorhombic and the tetragonal structure could not be investigated. The experiments allowed the identification of an intensity peak at a neutron-energy transfer of ~ 85 meV, but they did not yield any more detailed information on the shape of the neutron spectra.

2. Sample preparation and characterization

The experiments were carried out on $\text{YBa}_2\text{Cu}_3\text{O}_x$ powder samples with the two O concentrations $x \simeq 6.3$ and 6.9. The $\text{YBa}_2\text{Cu}_3\text{O}_x$ starting material was prepared by heating stoichiometric mixtures of Y_2O_3 , BaCO_3 and CuO powder in air at $\sim 950^\circ\text{C}$ for more than a day, followed by a slow cooling to room temperature and a subsequent pulverization in a mortar. The resulting $\text{YBa}_2\text{Cu}_3\text{O}_x$ powder was then again heated at $\sim 950^\circ\text{C}$ in air. The samples selected for the O concentration $x \simeq 6.3$ were subsequently quenched to room temperature, whereas the samples considered for the concentration $x \simeq 6.9$ were further annealed at $\sim 400^\circ\text{C}$ for several hours before they were also quenched to room temperature. The annealing temperature of ~ 400 and $\sim 950^\circ\text{C}$ before the final quenching were chosen according to literature data in order to establish the desired O concentrations [24, 25]. Since $\text{YBa}_2\text{Cu}_3\text{O}_x$ is known to absorb readily water molecules from the humidity of the air [25], it was extremely important to avoid any undesired water absorption processes of our samples. For this reason, the quenching was carried out in an argon atmosphere, and all our samples were continuously stored under Ar in sealed containers, except for the time during which they were being doped with H.

The H doping was performed in a vacuum system by exposing the samples to an H_2 gas atmosphere. The maximum doping temperatures were 180°C and the H_2 gas pressures were typically 800 mbar. The doping temperatures were well below those for which an H-induced decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_x$ is reported in [1]. The H concentration of the prepared $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ samples was $y = 0.6$, determined from the decrease of the H_2 gas pressure in the reaction chamber. The accuracy of this value is $\sim 15\%$. An aspect also worth mentioning is that all our doped samples were stored for at least one month at room temperature before the neutron spectroscopy experiments were carried out.

A fact to consider is the possibility of water formation due to a reaction between the H and the O in our $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples [1, 26]. We do not believe that substantial water formation occurred in our experiments since measurements of the sample weight, carried out before and after H doping, demonstrated that water did not desorb from our samples. Furthermore, recent proton NMR measurement [26] on identically prepared H-doped $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples yielded a spin-lattice relaxation time that was more than three orders of magnitude longer than the relaxation time measured on samples that were doped with water, showing that water was not present in the samples that were doped with H_2 gas. Therefore, the fact that neither a desorption of water from our samples nor the presence of water in our samples could be observed excludes a substantial reaction between the H and the O in terms of water formation.

We performed x-ray diffraction measurements on all our samples before and after the doping with H_2 gas. Depending on the O concentration ($x \simeq 6.9$ or 6.3), we observed the expected orthorhombic or tetragonal lattice structure and values for the lattice parameter which were in agreement with literature data [24, 25]. Within our experimental accuracy, we found further that the doping procedures did not cause any structural changes, new phases or variations of the lattice parameters.

3. Experimental results and discussion

Our inelastic neutron-scattering experiments were performed with the Be filter instruments IN1 (Cu(200) and (220) monochromator) at the Institut Laue-Langevin in Grenoble and BT4 (Cu(220) monochromator with 40'–40' collimators) at the National Institute of Standards and Technology in Gaithersburg. For the collimations and monochromators used, the energy resolution of the instruments varied from ~ 5 meV for a neutron energy loss of 50 meV up to ~ 22 meV (IN1) or ~ 14 meV (BT4) for an energy loss of 200 meV [24]. The investigated samples had transmissions of $\sim 80\%$. The samples were sealed either in Cu containers (IN1) or in Al containers (BT4). The data were taken at 10 K (IN1) or 14 K (BT4).

Figures 1 and 2 show the results of our measurements. The data of figure 1 were taken at 10 K with instrument IN1. They present a comparison of the spectra of orthorhombic and tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ samples ($x \simeq 6.9$ and 6.3) doped with the H concentration $y = 0.6$. For both O concentrations, the figure also shows the reference spectra of H-free $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples. Figure 2 presents the spectrum of an orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ sample with $x \simeq 6.9$ and $y = 0.6$, again together with the reference spectrum of an H-free sample. The spectra in figure 2 were taken at 14 K with instrument BT4.

Before discussing the effects of the H on our spectra, we consider the reference spectra first. Figures 1 and 2 demonstrate that the reference spectra of the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples ($x \simeq 6.9$) measured with the two instruments IN1 and BT4 exhibit comparable characteristic features in the relevant energy range up to ~ 80 meV in which the lattice vibrations of the (H-free) samples are expected [22, 23]. Figure 1 shows further that the reference spectra of both the orthorhombic and the tetragonal sample have intensity peaks at 19 and 27 meV. These peaks can be attributed to the lattice vibrations of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples [22, 23, 25] and the Cu sample container [27]. Above 40 meV, the reference spectra of the orthorhombic and the tetragonal sample exhibit the striking differences already observed in previous neutron-scattering measurements [22, 23]. In agreement with these measurements, the intensity of the orthorhombic sample is higher in the energy range from 40 to 70 meV, whereas the tetragonal sample has a higher intensity above 75 meV. The

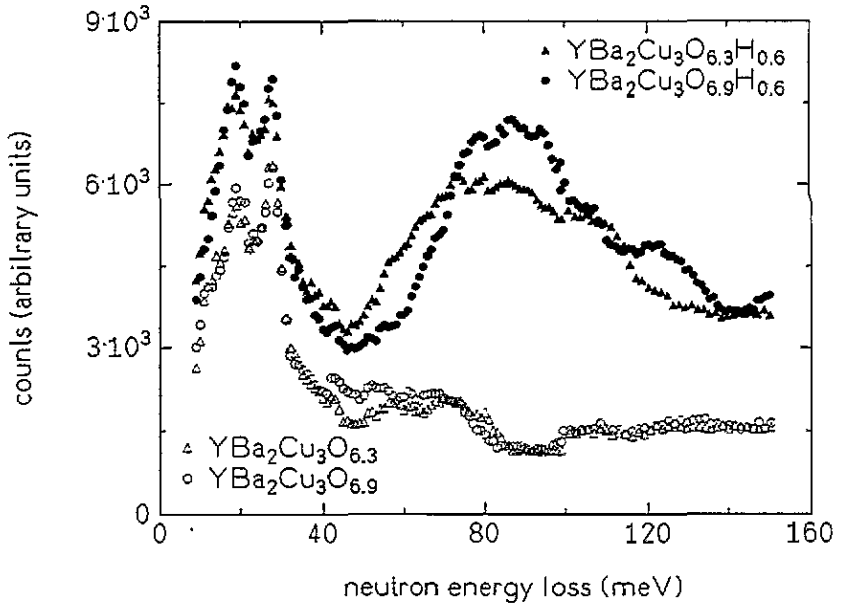


Figure 1. Neutron spectra of an orthorhombic ($x \approx 6.9$) and a tetragonal ($x \approx 6.3$) $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ sample with the H concentration $y = 0.6$. For both O concentrations, the figure also shows the reference spectra of H-free $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples. The data were taken at 10 K with instrument IN1.

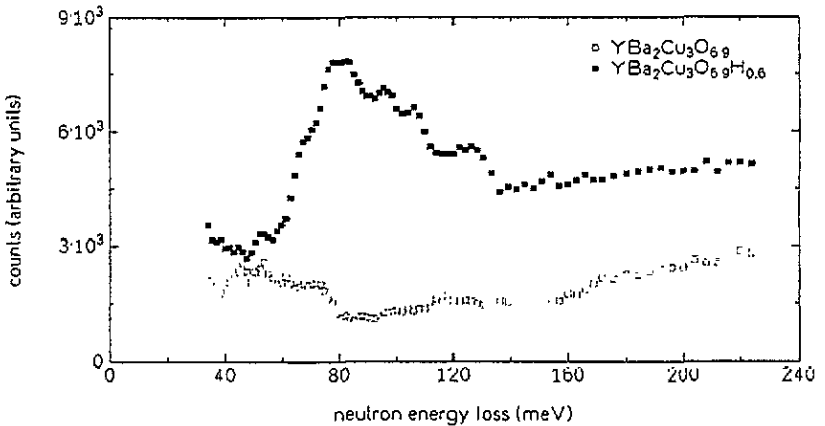


Figure 2. Neutron spectrum of an orthorhombic ($x \approx 6.9$) $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ sample with the H concentration $y = 0.6$. The figure also shows the reference spectrum of an H-free $\text{YBa}_2\text{Cu}_3\text{O}_x$ sample with the same O concentration. The data were taken at 14 K with instrument BT4.

vibrational energies of orthorhombic and tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$ range up to ~ 80 and ~ 90 meV, respectively [22, 23]. Above these energy values, the reference spectra represent the instrumental background.

We consider now the spectra of the H-doped $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ samples. Both figures 1 and 2 show that the H doping causes an increase of scattering intensity in the energy range investigated. A very important result is that this H-induced intensity increase differs

distinctly between the orthorhombic and tetragonal samples. This is directly realized from the spectra in figure 1 which were taken from samples with both lattice structures. The spectra show that the tetragonal samples have a higher H-induced intensity increase in the energy range between 40 and 73 meV. In fact, the difference in the H-induced intensity increases is even larger than indicated by the two H-doped samples alone since, in this energy range, the reference spectrum for the tetragonal structure is below that for the orthorhombic structure. In the energy range between 73 and 104 meV and in the range between 115 and 137 meV, on the other hand, the H-induced intensity increase of the orthorhombic sample exceeds that of the tetragonal sample (the shoulders at ~ 100 meV are a background effect as evidenced by the reference spectra). Both figures demonstrate that the H-doped orthorhombic samples have a very high intensity between ~ 75 and ~ 100 meV and an additional large peak at ~ 125 meV. In comparison to these characteristics for the H-doped orthorhombic samples, the spectrum of the H-doped tetragonal sample in figure 1 has an H-induced scattering intensity that is shifted to lower energies by ~ 10 meV, or by about 11%. This is in striking contrast to the behaviour of the undoped reference samples where the spectra for the tetragonal samples are shifted to higher energies. It was suggested that the spectral shift between undoped orthorhombic and tetragonal samples is caused by differences in the electron-phonon coupling [22, 23]. We find it particularly worth mentioning that any such differences in the electron-phonon coupling are certainly not apparent in the vibrations of the H.

The H-induced intensity increase of the spectra does not only reflect localized vibrations of the H. It also results from the fact that the H participates in the vibrations of the YBa₂Cu₃O_x host lattice, a fact known from metal-H systems [28, 29]. These so-called band modes of the H are, for instance, well demonstrated in figure 1 by the H-induced increase of the intensity peaks at 19 and 27 meV. The band modes are expected to contribute to the neutron spectra up to the highest energies of the YBa₂Cu₃O_x vibrations (~ 80 meV for the orthorhombic and ~ 90 meV for the tetragonal structure). An immediate consequence of the occurrence of the band modes is that the localized H vibrations cause only a fraction of the total H-induced intensity increase which may be substantially smaller than the total intensity increase.

Previous neutron-spectroscopic experiments on H-doped YBa₂Cu₃O_xH_y were only performed for samples with an orthorhombic structure ($x \simeq 6.95$, $y \leq 0.6$) [7, 11]. The experiments show an intensity peak around 85 meV in agreement with the present result. However, the experiments do not provide any detailed information on the shape of the spectra, and, in particular, they do not indicate an intensity peak at ~ 125 meV as observed for the orthorhombic samples of our study. Infrared absorption measurements on H-doped orthorhombic YBa₂Cu₃O_xH_y samples demonstrated absorption peaks at 104 meV (841 cm^{-1}) and 182 meV (1467 cm^{-1}) [2]. The first peak may reflect the intensity found in the present study between ~ 75 and ~ 100 meV. However, the existence of the second peak is not supported by our data in figure 2. This negative result is, in fact, in agreement with the suggestion of [21] which explains the infrared absorption peak at 182 meV by vibrations of spurious C compounds.

It seems to indicate that the general $\sim 11\%$ energy shift of the H-induced scattering intensity between the orthorhombic and the tetragonal samples is attributed to the increased volume of the tetragonal unit cell (the cell volume increases by $\sim 1.2\%$ between $x = 6.9$ and $x = 6.3$ [24, 25]). However, a consideration of the cell volume alone would mean an unusually large Grüneisen constant of ~ 9 . What must further be accounted for in such a consideration is the lower O concentration of the tetragonal samples so that—depending on the site of the H—the distance of the H from its neighbouring atoms might additionally

be larger than in samples with orthorhombic structure. In fact, such a consideration would suggest that the H atoms are located in—or in close neighbourhood to—the Cu(1) atomic planes since it is in this plane that the O concentration is changing. This conclusion is in agreement with the suggestions of previous studies [1, 2, 5, 6, 10–12]. Finally, it also seems worth pointing out that the similar effects H-doping and decreasing O concentration have on a variety of physical quantities [4, 9, 13, 17] are also indicative of H sites in close neighbourhood to the Cu(1) atomic planes since, in the case of such sites, both modifications of stoichiometry take place in the same spatial region of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ unit cell.

4. Conclusions

The H vibrations in $\text{YBa}_2\text{Cu}_3\text{O}_x\text{H}_y$ were studied by neutron spectroscopy. Our most important result is that, in comparison to orthorhombic samples ($x = 6.9$), the H vibrations in tetragonal ($x = 6.3$) samples are distinctly shifted to lower energies. This is in striking contrast to the opposite shift of the lattice vibrations between H-free orthorhombic and tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$, commonly attributed to differences in the electron–phonon coupling. Our results show that any such differences in the electron–phonon coupling are not apparent in the vibrations of the H. The present results also support previous suggestions that the H occupies sites in close neighbourhood to the Cu(1) atomic plane.

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