

## Superconducting $H_xYBa_2Cu_3O_7$ : The role of H

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The role of H in superconducting  $H_xYBa_2Cu_3O_7$  ( $0.14 < x < 5.0$ ) has been examined in infrared (ir) and x-ray absorption spectroscopy (XAS) measurements. The ir studies indicate the formation of Cu—H bonds and a hydride-phase precipitation. The XAS measurements of one of the samples,  $H_{1.0}YBa_2Cu_3O_7$ , show a partial reduction of the  $Cu^{2+}$  state to the  $Cu^{1+}$  state and deformation of both the Cu(1) and Cu(2) sites. The XAS results also confirm that H is located interstitially only near Cu sites.

Ever since the discovery of oxide high-temperature superconductors,<sup>1,2</sup> research on these materials has evoked a great deal of attention. Because structural changes can strongly affect the superconducting critical temperature  $T_c$  of these materials, recent major experimental and theoretical efforts have focused attention on the correlation between structure and superconducting properties. It is now evident that the structure of superconducting  $YBa_2Cu_3O_{7-\delta}$  is an orthorhombic phase<sup>3,4</sup> ( $\delta < 0.5$ ) and has a layered anisotropy. The basic units of this structure consist of the square planar configuration of Cu(1)—O layers forming a two-dimensional network and the ordered Cu(2)—O layers forming a one-dimensional linear chain along the  $b$  axis. The two Cu(1)—O layers per unit cell are separated by Y atoms. The Ba atoms are situated between the Cu(1)—O and Cu(2)—O layers.

In exploring the superconductivity of these materials, it is very unlikely that the three-dimensional arrangement of layers is important to the mechanism of superconductivity. There are two reasons. First, Y can be substituted with other chemically similar elements, including magnetic rare earths, without changing the superconductivity and, thus, it appears that the interaction *between* the layers is weak. Second, the transport properties associated with critical current are approximately isotropic in the basal plane, but are very much smaller for current perpendicular to the layers.<sup>5</sup> Thus, one may propose that the square Cu(1)—O planes appear to play a vital role in the high- $T_c$  superconductivity. In contrast to the orthorhombic phase, the tetragonal phase of  $YBa_2Cu_3O_{7-\delta}$  is not superconducting above 4.2 K.<sup>6</sup> Major differences between the orthorhombic and the tetragonal structure are due to the vacancies (unoccupied lattice sites) and disordering of O along the one-dimensional chain.<sup>3,4,6,7</sup> One may again expect that ordered linear Cu(2)—O chains are also crucial in determining the observed superconducting properties. Therefore, it is still an open question as to which types of Cu—O bonding, i.e., the square planes or the linear chains, play the dominant role in high- $T_c$  superconductivity. With this fact in mind, we decided to investigate our  $H_xYBa_2Cu_3O_7$ . It is well known that the presence of H in solids has a profound effect on the atomic structure as well as the vibrational and electronic properties.<sup>8</sup> Previously, we have reported the influence of H on

superconducting critical temperatures and crystal structures of  $H_xYBa_2Cu_3O_7$ ,<sup>9</sup> and in this work we particularly focus on the role of H with respect to the superconductivity and the atomic and the vibrational structures of these materials.

In this work the superconducting hydride  $H_xYBa_2Cu_3O_7$  presents a system in which two fundamental questions are addressed, including (1) what is the nature of the bonding configuration of H and (2) what is the change in electronic structure due to the presence of H in  $YBa_2Cu_3O_7$ ? To study these questions, we use ir and x-ray absorption spectroscopy (XAS) techniques to find out what is an interplay among the atomic structure, the electronic, and superconducting properties of these materials.

Orthorhombic  $YBa_2Cu_3O_7$  was prepared from  $Y_2O_3$ ,  $BaCO_3$ , and  $CuO$ . A typical procedure<sup>10</sup> consisted of the following: the starting materials were mixed, pelletized, and fired in a Pt crucible at  $\sim 900^\circ C$  for 16 h in air. After the first firing, the sample was reground, pelletized, and refired under the same conditions. The sample was then reground, pelletized, and heated under flowing  $O_2$  at  $950^\circ C$  for about 16 h, followed by furnace cooling over several hours to  $200^\circ C$ . The sample was determined to be a single phase of orthorhombic  $YBa_2Cu_3O_7$  from x-ray diffraction. The tetragonal form of  $YBa_2Cu_3O_{7-x}$  was obtained by directly heating orthorhombic  $YBa_2Cu_3O_7$  to  $900^\circ C$  in air for 2 h, then subsequently quenching into liquid nitrogen before being returned to room temperature. The x-ray diffraction data of this sample showed  $\sim 95\%$  of it to have the tetragonal structure.  $H_xYBa_2Cu_3O_7$  was prepared by the direct reaction of the orthorhombic  $YBa_2Cu_3O_7$  with  $H_2$  gas as follows. A sample of 0.5 g of powdered  $YBa_2Cu_3O_7$  ( $-100$  mesh) was introduced into a Pyrex glass reactor of known volume and outgassed at room or slightly elevated temperature ( $\sim 400$  K) for a period of 30 min. After outgassing, a known quantity of  $H_2$  was introduced to give a pressure of 650 mm of Hg. In order to initiate the absorption reaction the reactor was briefly heated to 415 K after which the temperature was reduced to 385 K and kept constant. After a short period of time, which varied from sample to sample, apparently depending on its refractory character, the reaction began. The uptake of H by the sample was monitored by tracking the H pressure as a function of time.

The rate of H uptake is a function of temperature and pressure. The reaction was usually complete in a few hours. When the solids had attained the desired H content the reaction was terminated by quickly cooling to room temperature. The H content of the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  was calculated from the overall decrease in  $\text{H}_2$  pressure.

Superconducting critical temperature,<sup>9</sup>  $T_c$ , of the samples was measured by observing changes in voltage from a balanced pair of the secondary pickup coils as a function of temperature. Results are listed in Table I. The relation between the superconducting behavior of  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$  and H content has been described in Ref. 9. Briefly it is as follows: hydrogen will dissolve in the oxide up to a concentration of  $x \sim 0.2$ . This solid solution phase is superconducting with a  $T_c$  slightly higher than the original oxide. At higher H contents a hydride phase precipitates which is not superconducting; thus, the superconducting volume fraction is decreased at higher  $x$  values. Eventually the solid solution phase is completely converted to the hydride phase and no superconducting transition is observed.

The samples for the ir transmission measurement were ground into fine powders, having a particle size of 1–10  $\mu\text{m}$ . These powders were mixed with acetone and then deposited on a KBr disk. The transmission measurements were taken by a Mottson Cygnus 100 FTIR purged by nitrogen gas. One hundred scans were taken and averaged for each measurement. The results of the ir measurements are shown in Fig. 1 for the wave-number region 400–4000  $\text{cm}^{-1}$ . In terms of vibrational properties, the vibrational frequencies of Cu–O bands<sup>11</sup> occur in the wave-number region 400–600  $\text{cm}^{-1}$ . Therefore, for the orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  the ir absorption peaks located at 420 and 570  $\text{cm}^{-1}$  are probably due to the O stretching band associated with the Cu atom. In addition, a single broad band near 840  $\text{cm}^{-1}$  is believed to correspond to the first overtone of the 420  $\text{cm}^{-1}$  mode. For the tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , we found an absence of the absorption peaks at 420  $\text{cm}^{-1}$  as well as 840  $\text{cm}^{-1}$ . Two other distinct features clearly appear at 570 and 619  $\text{cm}^{-1}$  which are probably due to the different atomic configuration of the linear  $\text{Cu}(2)\text{—O}$  chain in the tetragonal structures. Of particular interest in the spectra for  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$  is that the peak at 570  $\text{cm}^{-1}$  (a tentative assignment of the

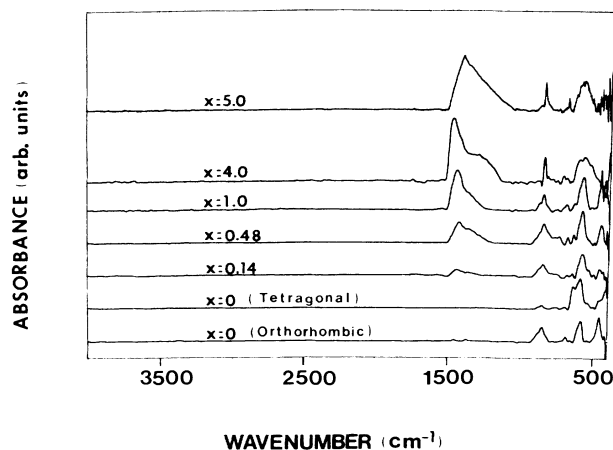


FIG. 1. ir transition spectra of  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$  as a function of  $x$ .

Cu–O band) is essentially the same as in orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , although its width increases at  $x > 4$ . It appears that the presence of H ( $x < 1.0$ ) in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has no effect on the O stretching bands.

Even though the  $\text{OH}^{-1}$  ion and  $\text{H}_2\text{O}$  are frequently reported in several hydrogen-containing solids, as shown in Fig. 1, no feature associated with the O–H bond in the 3000–4000 wave number ( $\text{cm}^{-1}$ ) region was observed for  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$ . This gives strong evidence that H is not located either interstitially near or substitutionally at any occupied O sites. The spectra of  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$  exhibit a strong absorption peak located at 1467  $\text{cm}^{-1}$ . Since Cu–H stretching modes typically occur in this region,<sup>12</sup> the ir spectra clearly indicate the formation of Cu–H bonds in  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$ . Detailed analysis of the absorption peak at 841  $\text{cm}^{-1}$  indicates existence of a very sharp feature for  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$ . This feature may be attributed to the Cu–H bending mode which usually accompanies the stretching mode. Thus, the H atom can execute<sup>13</sup> two independent motions associated with Cu atom.

It should be noted that the bond-stretching motion, in which the H atom is displaced in a direction parallel to the Cu–H bond, and the bond-bending modes, in which the

TABLE I.  $T_c$  of  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$ .

Sample	H concentration ( $x$ )	$T_c$ (K)	Superconducting fraction % <sup>a</sup>	Structure and comments
A	0	91.0	100	Orthorhombic
B	0	$N^b$	...	Tetragonal
C	0.14	92.5	100	Solid solution
D	0.48	93.6	70	...
E	1.0	93.2	30	Two phases <sup>c</sup>
F	4.0	$N^b$	...	Amorphous
G	5.0	$N^b$	...	Hydride phase(s)

<sup>a</sup>Relative to starting oxide.

<sup>b</sup> $N$ : Nonsuperconducting above 4.2 K.

<sup>c</sup> $\text{H} \sim 0.2\text{YBa}_2\text{Cu}_3\text{O}_7 + \text{hydride phase}$ .

H atom displacement is perpendicular to the direction of the Cu–H bond, are strongly enhanced by increasing the concentration  $x$  in  $H_xYBa_2Cu_3O_7$ . But, the Cu–H bending features do not broaden in comparison with the Cu–H stretching modes. Because of the symmetry, the Cu–H bending mode is doubly degenerate if the H is located at the Cu(1) site, while the Cu–H bending mode will, in principle, be split into a doublet at the Cu(2) site. Without a study of the polarization of ir spectra, the question as to which Cu atoms coordinate with H cannot be answered. However, the integrated intensities of the Cu–H stretching modes permit us to make an estimate of the total number of ions to account for the formation of Cu–H bonds. As a function of  $x$ , the relative total number of ions associated with Cu–H bonds in the region below  $x=1.0$  is drastically different from those in the region between  $x=1.0$  and  $x=5$ . In the second region, the integrated intensities do not significantly increase with the concentration of H. This indicates that the  $H_xYBa_2Cu_3O_7$  phase may undergo a phase precipitation between  $x=0.48$  and  $x=1.0$ . In this connection x-ray diffraction data indicate the precipitation of a hydride phase for  $x > 0.2$ .<sup>9</sup>

We also present the XAS spectra of orthorhombic  $YBa_2Cu_3O_7$  and  $H_{1.0}YBa_2Cu_3O_7$  which consists of a mixture of the solid solution and hydride phase. The XAS measurements were performed at the Cornell High Energy Synchrotron Source (CHESS). The samples were separately ground to fine powders and placed on Kapton tape. The energy scale was calibrated relative to a Cu foil. Transmission measurements on both samples were made at 300 K.

XAS data reduction and analysis have been described previously.<sup>14</sup> Figure 2 shows a comparison of XAS for the Cu, Y, and Ba near edges between  $YBa_2Cu_3O_7$  (solid line) and  $H_{1.0}YBa_2Cu_3O_7$  (dashed line). The two spectra at the Y  $K$  edge (the edge shift is probably due to a drift in the energy calibration of the monochromator) and at the Ba  $L_{III}$  edges are very similar as shown in Figs. 2(b) and 2(c). The small differences between both  $YBa_2Cu_3O_7$  and  $H_{1.0}YBa_2Cu_3O_7$  at Y and Ba sites are attributed to the distortion of the lattice as indicated from x-ray diffraction results<sup>9</sup> of  $H_{1.0}YBa_2Cu_3O_7$ . A Fourier transform analysis on both edges also shows no gross structural change between  $YBa_2Cu_3O_7$  and  $H_{1.0}YBa_2Cu_3O_7$ . The presence of H has the strongest effect on the Cu  $K$  edge indicating a direct interaction of H with Cu. Therefore, we confine our discussion of the electronic and atomic structure to the Cu sites. Despite conflicting reports in the determination of the valence states of the Cu absorption edge in recent studies<sup>15–17</sup> of oxide superconducting materials, two distinct features allow us to clearly distinguish between  $Cu^{1+}$  and  $Cu^{2+}$ . First, because more energy is required to remove a core electron from a more positive ion, the absorption edge of  $Cu^{1+}$  lies 2–3 eV to the lower-energy side of the absorption edge of  $Cu^{2+}$  atom. Second, because of a completely filled  $d^{10}$  configuration of  $Cu^{1+}$ , there is no  $1s-3d$  transition for  $Cu^{1+}$  atom. As shown in Fig. 2(a), the onset of the Cu edge of  $H_{1.0}YBa_2Cu_3O_7$  is shifted to the lower-energy side in comparison with  $YBa_2Cu_3O_7$ . For  $H_{1.0}YBa_2Cu_3O_7$ , feature A (which is

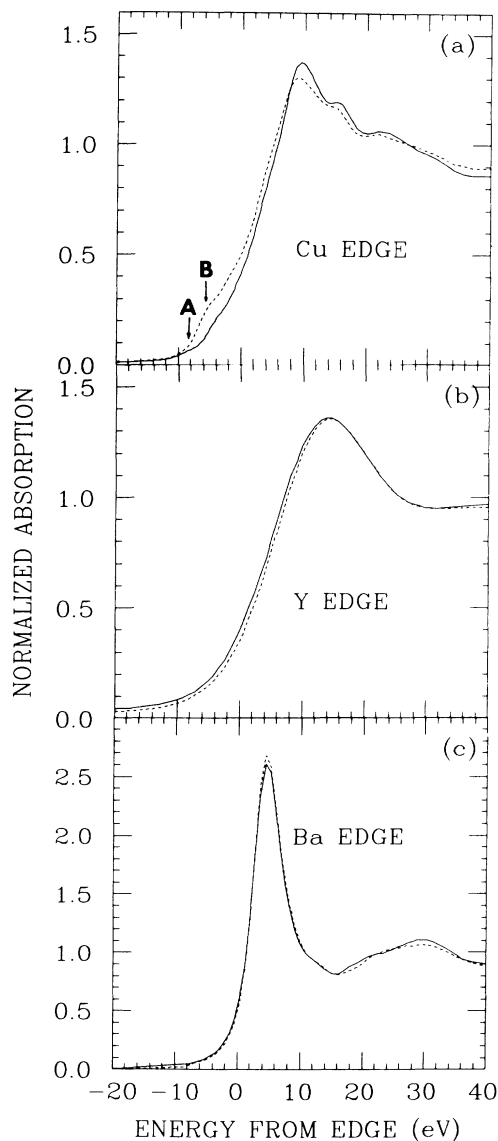


FIG. 2. XAS spectra of  $YBa_2Cu_3O_7$  (solid line) and  $H_{1.0}YBa_2Cu_3O_7$  (dashed line) at (a) Cu  $K$  edge, (b) Y  $K$  edge, and (c) Ba  $L_{III}$  edge. The zero of energy is arbitrarily taken at the half height of the main peak.

the transition of  $1s-3d$ ) is weaker, while feature B (which is tentatively assigned to the  $1s-4p$  transition) is enhanced. There are also some changes in the higher-energy side. Our results strongly indicate that a partial reduction of the  $Cu^{2+}$  state to the  $Cu^{1+}$  state results in going from  $YBa_2Cu_3O_7$  to  $H_{1.0}YBa_2Cu_3O_7$ . However, the  $Cu^{1+}$  state may be associated with the nonsuperconducting hydride phase. A further comparison of the Fourier transforms at the Cu edge is shown in Fig. 3. The positions of all major peaks in  $H_{1.0}YBa_2Cu_3O_7$  are systematically shifted toward higher R. This arises from increases of the lattice parameters in both the  $a$  and  $c$  axes in the solid solution phase.<sup>9</sup> The magnitude of Cu–O contributions in the first and fourth shells are very similar between

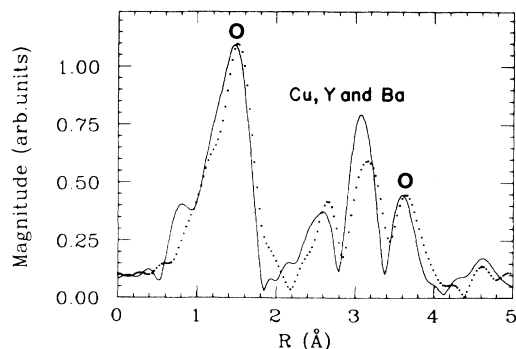


FIG. 3. Magnitudes of Fourier transforms at Cu edge for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (solid line) and  $\text{H}_{1.0}\text{YBa}_2\text{Cu}_3\text{O}_7$  (dashed line). The transforms of  $k^2$  EXAFS are taken over a range  $2.6\text{--}14.6 \text{ \AA}^{-1}$ . The assignment of each peak is based on the neutron-scattering-derived structure (Ref. 4).

$\text{YBa}_2\text{Cu}_3\text{O}_7$  (solid line) and  $\text{H}_{1.0}\text{YBa}_2\text{Cu}_3\text{O}_7$  (dashed line). This is consistent with the above ir results in which the presence of H has a very small effect on the O sites at the concentration  $x = 1$ . The third peak due to a combination of contributions from Cu, Y, and Ba atoms is drastically reduced for  $\text{H}_{1.0}\text{YBa}_2\text{Cu}_3\text{O}_7$ . A major component of the signal is due to the nearly linear Cu—O—Cu chains which have an enhancement due to multiple scattering.<sup>11</sup> The multiple scattering enhancement is very sensitive to

the degree of linearity of the chains. There is no significant change in the Ba and Y sites, and the above large effects may therefore be attributed to a rearrangement of the atomic configuration for both Cu(1) and Cu(2) sites because of the formation of Cu—H bonds, thereby introducing more structural disorder.

In conclusion, we note the significant role of H on the atomic structure, the electronic state, and superconducting properties in  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$ . The presence of H has the strongest effects on the Cu sites rather than the O, Y, or Ba sites. Our ir results indicate (1) the formation of Cu—H bond and (2) the existence of a second phase precipitate. On the other hand, our XAS results on  $\text{H}_{1.0}\text{YBa}_2\text{Cu}_3\text{O}_7$  show (1) a partial reduction of the  $\text{Cu}^{2+}$  state to the  $\text{Cu}^{1+}$  state which may be related to the unknown hydride nonsuperconducting phase and (2) the deformed atomic configuration of both Cu(1) and Cu(2) sites. A further study on the superconducting  $\text{H}_x\text{YBa}_2\text{Cu}_3\text{O}_7$  phase is currently underway.

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