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^{89}Y NMR and Cu NQR of hydrogenated oxygen-deficient $YBa_2Cu_3O_{6.7}$

S. D. Goren and C. Korn
Department of Physics, Ben-Gurion University, Beer-Sheva, Israel 84105

C. Perrin
Laboratoire de Chimie du Solide et Inorganique Moléculaire, UA CNRS No. 1495, Université de Rennes-I, Avenue du General Leclerc, 35402 Rennes Cedex, France

W. Hoffmann, H. M. Vieth, and K. Lüders
Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

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The room-temperature ^{89}Y NMR line shift and line shape as well as the low-temperature Cu NQR lines were obtained as a function of hydrogen concentration for oxygen-depleted hydrogen-doped YBCO ($H_xYBa_2Cu_3O_{6.7}$) in order to investigate the interplay of the effect of hydrogen addition and oxygen removal on the electronic structure and superconducting-antiferromagnetic transition properties. The results seem to indicate that as far as filling the conduction band is concerned, hydrogen contributes twice as many electrons as the chain oxygen contributes holes. In contrast to this, the transition from a superconductor to an antiferromagnet is governed by other considerations which favor a 1:1 ratio. It is also seen that hydrogen enters into either an additional site or a new phase when enough hydrogen is added to oxygen-depleted YBCO.

I. INTRODUCTION

Previous NMR (Ref. 1) and NQR (Ref. 2) studies of $H_xYBa_2Cu_3O_7$ have shown that hydrogen affects many of the properties of YBCO in a manner similar to the removal of oxygen.[1-5] The ^{89}Y nuclear resonance frequency in $H_xYBa_2Cu_3O_7$ (Ref. 1) shifts continuously as a function of hydrogen concentration similarly to its shift as a function of oxygen concentration in the hydrogen-free material. The results indicate that the electronic structure behaves as if the addition of two hydrogens is equivalent to the removal of a single oxygen. In contrast, while both hydrogen addition and oxygen removal cause the material to transform from a superconductor to an antiferromagnetic nonsuperconductor, the indications were[1] that this occurs at a hydrogen concentration where the hydrogen addition–oxygen removal equivalency is closer to one-to-one, i.e., one hydrogen ≈ one oxygen. Hence there should be other factors working, rather than just the carrier concentration in the determination of whether the material is a superconductor or antiferromagnetic. Similar conclusions were reached for the case of fluorine doping of $YBa_2Cu_3O_y$.[6]

At the other extreme, we also studied the effect of hydrogen on the ^{89}Y NMR resonance in the nonsuperconductor $YBa_2Cu_3O_6$, where all the chain oxygen are missing.[7] Here the hydrogen does not cause the resonance line to shift continuously as a function of hydrogen concentration. Rather a new line is introduced at a higher frequency and this line increases in intensity as the hydrogen concentration is increased. The conclusions were that either the hydrogen enters a new site or, a new phase is produced.

In this study, we have investigated the intermediate case of $H_xYBa_2Cu_3O_{6.7}$ in order to clarify the interplay of oxygen removal and hydrogen addition. The results seem to confirm our previous findings of the contrasting ways that the hydrogen concentration affects the electronic structure and the transition from a superconductor to an antiferromagnetic material.

II. EXPERIMENTAL METHOD

Five samples of $H_xYBa_2Cu_3O_{6.7}$ ($x = 0$, 0.21, 0.50, 0.70, 1.04) were prepared by methods described previously.[4,8] Magnetic susceptibility measurements showed that the first three samples contained superconducting material having onset T_c's of 66, 60, and 40 K, respectively. This is in agreement with the finding that fully oxygenated YBCO, when doped with hydrogen, retains its onset T_c of 92 K,[3] while YBCO that has its T_c reduced by oxygen depletion or alloying, has its T_c reduced further upon hydrogen doping.[9,5]

The ^{89}Y NMR resonance was measured at room temperature at a resonance frequency of 14.707 MHz and the shift was relative to ^{89}Y in an aqueous solution of YCl_3. The NQR spectra[10] were obtained by measuring the echo intensity as a function of frequency at a stepwise frequency sweep. The spectra in the 20–35 MHz range were obtained at 4.7 K, while the measurements in the 90 MHz region were performed at 1.2 K.

III. EXPERIMENTAL RESULTS

The ^{89}Y NMR absorption spectra were obtained at room temperature for different hydrogen concentrations x. Three of the traces are shown in Fig. 1. The sample having a concentration of $x = 0.21$ has a shape similar to those of $x = 0$ and 0.50, while that of concentration

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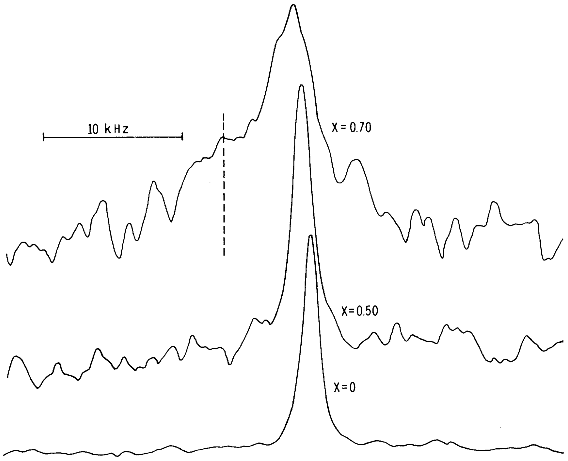

FIG. 1. The ^{89}Y NMR absorption traces of $H_xYBa_2Cu_3O_{6.7}$ where $x=0$, 0.50, and 0.70. The frequency increases toward the left. The broken line shows the position of the extra NMR line found for $H_xYBa_2Cu_3O_6$ (Ref. 7).

$x=1.04$ is similar to that of $x=0.70$. Both the $x=0.70$ sample and the $x=1.04$ sample show a hump at higher frequency. Its origin will be discussed later.

Figure 2(a) gives the line shift relative to YCl_3, and Fig. 3(b) the linewidth, as a function of x. The position of the lines was taken to be at the maximum of the resonance trace, and the linewidth was that at half-maximum amplitude. The jump in the linewidth by a factor of about 4 was determined to be an indication of the transition from a superconducting material to an antiferromagnetic one.[1,5,11] Magnetic susceptibility measurements confirmed that the samples having narrow lines were superconductors while those having a wide line showed no Meissner effect down to liquid helium temperature. The $x=0.5$ sample has a transition temperature of $T_c=40$ K and the NMR linewidth was that of a nonantiferromagnetic material. However, NQR measurements on this sample at 1.2 K showed an antiferromagnetic nuclear resonance (AFNR) signal in the 90 MHz region. Hence the sample is definitely a mixed phase at this low temperature. The nondetection of a wide NMR line at room temperature may be due to the fact that this temperature may be above the Néel temperature, or that it is buried in the noise.

The NQR spectra were obtained for hydrogen concentrations $x=0$, 0.21, 0.50, and 0.70 at 4.2 K in the range 20–35 MHz. The results are shown in Fig. 4. In addi-

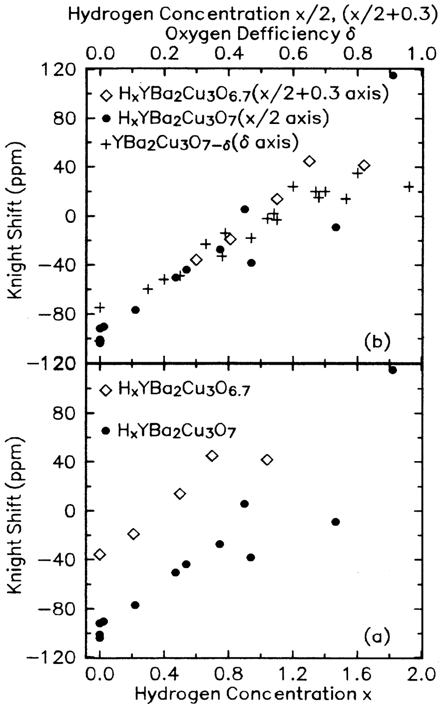

FIG. 2. (a) The room temperature ^{89}Y resonance shift of $H_xYBa_2Cu_3O_{6.7}$ as a function of hydrogen concentration x, compared to that of $H_xYBa_2Cu_3O_7$ (Ref. 1). (b) The same results as in (a) except that now the hydrogen concentration is plotted as a function of $x/2$ for $H_xYBa_2Cu_3O_7$, and as a function of $x/2+0.3$ for $H_xYBa_2Cu_3O_{6.7}$. In addition, the shift for undoped oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ is given as a function of δ (Refs. 12 and 13). It is seen that the three cases coincide within the scatter of the experimental points.

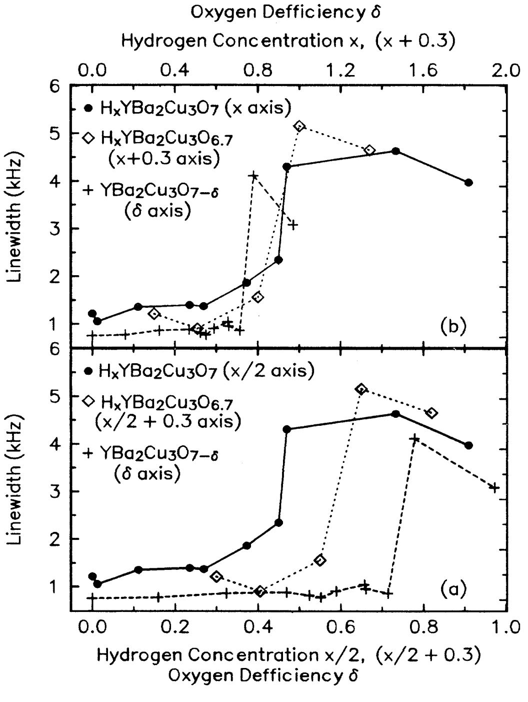

FIG. 3. (a) The room-temperature linewidth of the ^{89}Y resonance of $H_xYBa_2Cu_3O_7$ (Ref. 1) as a function of $x/2$, of $H_xYBa_2Cu_3O_{6.7}$ as a function of $x/2+0.3$, and of undoped $YBa_2Cu_3O_{7-\delta}$ (Ref. 11) as a function of oxygen deficiency δ. Connecting lines are aids to the eye. The jump in width indicates transition to the antiferromagnetic phase. (b) Same as in (a) except that the respective linewidths are plotted as functions of x, $x+0.3$, and δ.

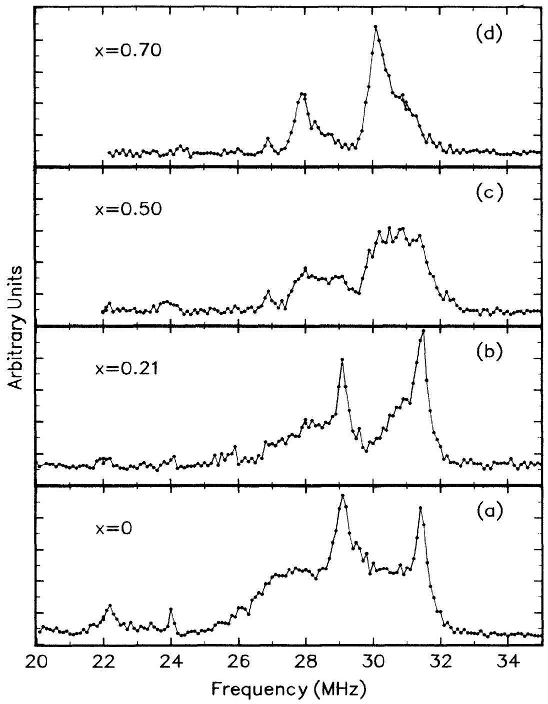

FIG. 4. The Cu NQR spectra of $H_xYBa_2Cu_3O_{6.7}$ in the 20–35 MHz range.

tion, an AFNR signal was detected at 1.2 K for sample $x=0.5$ in the 90 MHz region. The influence of hydrogen on the NQR spectra is readily apparent.

IV. DISCUSSION

A. ^{89}Y resonance shift and linewidth

It is commonly accepted that the removal of chain oxygens from $YBa_2Cu_3O_7$ results in the loss of holes in the conduction band. We have previously[1] shown evidence that for the case of fully oxygenated $YBa_2Cu_3O_7$, the addition of hydrogen causes the resonance to shift in the same manner as the removal of the chain oxygen, where the addition of two hydrogens is equivalent to the removal of one oxygen. Since the shift is a reflection of the density of states at the Fermi level, this indicates that each hydrogen atom contributes half as many electrons to the conduction band as oxygen contributes holes. In contrast to this, the transition from a superconductor to an antiferromagnet seems to occur at a hydrogen to oxygen ratio closer to 1:1. This unexpected result is also confirmed in the present study. In Fig. 2(a), we again show the ^{89}Y shift as a function of hydrogen concentration obtained in the present study, compared with that obtained for the case of fully oxygenated $YBa_2Cu_3O_7$. We see that there is a displacement between the two results. Since $H_xYBa_2Cu_3O_{6.7}$ has a deficit of 0.3 oxygens as compared to $H_xYBa_2CuO_7$, if we shift the $O_{6.7}$ results by 0.3 we should get coincidence of the two if the equivalency of oxygen to hydrogen were 1:1. This does not occur. If, however, we plot the shift in $H_xYBa_2Cu_3O_7$ as a function of $x/2$ instead of x, and split the shift in $H_xYBa_2Cu_3O_{6.7}$ as a function of $x/2+0.3$ as was done in Fig. 2(b), we get very good coincidence. We have also included the ^{89}Y shift as a function of oxygen depletion δ in $YBa_2Cu_3O_{7-\delta}$ as obtained by Alloul *et al.*[11] and Balakrishnan *et al.*[12] The results bear out the contention of a ratio of 2:1 for H and O as far as the electron concentration in the conduction band is concerned.

As was originally shown by Alloul *et al.*,[11] the change from a superconductor to an antiferromagnetic material is reflected by an approximate quadrupling of the ^{89}Y linewidth due to the antiferromagnetic interaction. If we now try to do the same for the linewidth as was done for the resonance shift, i.e., we plot the linewidth as a function of $x/2$ for $H_xYBa_2Cu_3O_7$, as a function of $x/2+0.3$ for $H_xYBa_2Cu_3O_{6.7}$, and as a function of δ for the undoped $YBa_2Cu_3O_{7-\delta}$, then we get the result of Fig. 3(a). We see that there is no coincidence in the position of where the linewidth quadruples. If, however, we plot the respective cases as a function of x, $x+0.3$, and δ, as shown in Fig. 3(b), we get much closer to a coincidence of the position of the transition. This indicates that as far as the transition from superconductor to antiferromagnet is concerned, adding one hydrogen has the same effect as removing one oxygen.

B. Line shape of the high hydrogen concentration ^{89}Y resonances

The NMR absorption traces of the nonsuperconducting samples ($x=0.70$ and 1.04) shows a hump on the high-frequency side (Fig. 1). Approximating the trace as a sum of two Gaussians indicates that the extra peak occurs at the frequency where a second resonance was found for the case of $H_xYBa_2Cu_3O_6$.[7] ^{2}H NMR and measurements on deuterated, fully oxygenated $D_xYBa_2Cu_3O_7$ (Refs. 13 and 14) implied that the hydrogen probably resides between the bridging O(4) and chain O(1) oxygen. Thus it was reasoned in Ref. 7 that in the absence of chain oxygens, the hydrogen either sits at a different site, or a new amorphous phase is formed where the hydrogen enters. (The phase is deemed amorphous since it was not detected by x-ray diffraction.) The two ^{89}Y resonances found in $H_xYBa_2Cu_3O_6$ (whose frequencies were independent of hydrogen concentration), were attributed according to the first hypothesis to be due to Y having two different H environments; and according to the second hypothesis, to Y in the two different phases.

The extra peak in our higher concentration samples seems to indicate that the presence of chain oxygen vacancies creates an environment in which the hydrogen are either in an additional site, or form an additional phase. This is also supported by the fact that the Knight shift of the main ^{98}Y resonance does not continue to increase when x goes from 0.70 to 1.04 [Fig. 2(a)]; i.e., as more hydrogen is added to the material it does not go into the site that fills the conduction band. (We do not know whether the nonsuperconducting $H_{0.70}YBa_2Cu_3O_{6.7}$ and $H_{1.04}YBa_2Cu_3O_{6.7}$ samples are insulators. The resonance shift does seem to increase with x in $H_xYBa_2Cu_3O_7$ even after the nonsuperconducting region is reached.[1])

C. Cu NQR in $H_xYBa_2Cu_3O_{6.7}$

The NQR resonances of ^{63}Cu and ^{65}Cu in $H_xYBa_2Cu_3O_{6.7}$ are shown in Fig. 4. We will refer only to the higher ^{63}Cu resonance, the ^{65}Cu resonance being determined simply from the ratio of the quadrupole moments ($^{65}eq/^{63}eq=0.923$). As usual, we will refer to the chains coppers by Cu(1) and their oxygen coordination by a subscript, and the plains copper by Cu(2).

The NQR spectra of Cu in YBCO with various oxygen concentrations have been studied and interpreted by many investigators (see, e.g., Refs. 15–19). It has been shown[2] that when hydrogen is added to $YBa_2Cu_3O_7$, many of the same features show up in the NQR spectrum as when oxygen is removed. We now look at the effect of hydrogen doping on $YBa_2Cu_3O_{6.7}$.

Figure 4(a) shows the usual Cu NQR spectrum found for this oxygen concentration (see, e.g., Ref. 15). The sharp $Cu(1)_2$ line at 31.5 MHz is seen, superimposed on the broad Cu(2) line. Also the 22.1 and 24.0 MHz lines corresponding to $Cu(1)_4$ and $Cu(1)_3$ are observed.

When hydrogen is added [Fig. 4(b)], the Cu(2) line is considerably reduced, similarly to the case of hydrogen-free YBCO below the 60 K plateau. The latter was attributed by Heinmaa *et al.*,[15] to a slowing down of the spin fluctuations. Magnetic susceptibility measurements shows that the $x=0.21$ material has an onset T_c of 60 K. The remains of the 22.1 MHz $Cu(1)_4$ and 24.0 MHz $Cu(1)_3$ lines are essentially removed by the addition of $x=0.2$ of hydrogen. The $x=0.70$ material [Fig. 4(d)], is a nonsuperconductor and we see that the main contribution of the $Cu(1)_2$ line now appears at 30.2 MHz, just as for the case of oxygen-depleted nonsuperconducting hydrogen-free YBCO. The same occurs for fully oxygenated, hydrogen-doped YBCO.[2] The $x=0.5$ sample [Fig. 1(c)] shows both features: the 30.2 MHz line and the 31.5 MHz line. Such a spectrum is not observed for hydrogen-free, oxygen-depleted YBCO. The $x=0.5$ sample has been shown, by magnetic susceptibility measurements, to contain superconducting material having an onset T_c of 40 K. That it also contains an antiferromagnetic phase is proven by the presence of the Cu(2) AFNR signal around 90 MHz. Thus the $x=0.5$ sample must be a mixture of a superconducting and antiferromagnetic phase.

These measurements show again that the addition of hydrogen results in effects similar to the removal of oxygen. A significant difference is that for the case of oxygen depletion, the transition from superconductor to antiferromagnet is sharp, while in our case there is evidence of a mixed superconducting and antiferromagnetic phase.

V. CONCLUSIONS

By comparing the ^{89}Y resonance of hydrogen-doped oxygen-deficient $H_xYBa_2Cu_3O_{6.7}$ with the resonance in $H_xYBa_2Cu_3O_7$ and $YBa_2Cu_3O_{7-\delta}$, we conclude that as far as the electronic structure is concerned, the number of electrons contributed to the conduction band by each hydrogen is equal to 1/2 the holes contributed by each chain oxygen. On the other hand, the transition from a superconductor to an antiferromagnet is governed by other considerations, wherein the addition of one hydrogen is equivalent to the removal of one chain oxygen. The NQR results reconfirm that the addition of hydrogen changes the Cu valency in a manner similar to the removal of oxygen. It is also seen that when enough hydrogen is added to oxygen-depleted YBCO, the hydrogen enters in either two sites, or in an additional new phase.

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