PHYSICAL REVIEW B VOLUME 42, NUMBER 13 1 NOVEMBER 1990

Influence of hydrogen on the ^{89}Y NMR in $H_xYBa_2Cu_3O_7$

S. D. Goren, C. Korn, and V. Volterra
Department of Physics, Ben-Gurion University, Be'er Sheva, Israel

H. Riesemeier, E. Rössler, M. Schaefer, H. M. Vieth, and K. Lüders
Fachbereich Physik, Freie Universität, Berlin, Federal Republic of Germany

(Received 18 December 1989; revised manuscript received 23 May 1990)

The ambient-temperature ^{89}Y magnetic resonance line in $H_xYBa_2Cu_3O_7$ was measured at 14.707 MHz as a function of hydrogen concentration x. The Knight shift relative to an aqueous solution of YCl_3 increases from -100 ppm for $x=0$ to $+115$ ppm for $x=1.82$. The linewidth at half-amplitude is 1.2 kHz and increases slowly with x in the superconducting samples ($0<x<0.74$), then increases sharply in the normal samples. It was seen that, for a number of parameters, increasing the hydrogen content gives similar behavior to decreasing the oxygen concentration. Our ^{89}Y NMR data and those of other investigators are analyzed and are consistent with previous evidence for local antiferromagnetic correlations in the superconducting compound.

I. INTRODUCTION

We employed the nuclear magnetic resonance (NMR) technique and used hydrogen as a probe in the study of the electronic and superconducting behavior of the high-temperature superconductor $YBa_2Cu_3O_7$. A number of investigators have reported the effects of changing the oxygen concentration of the compound. While the oxygen concentration should influence the electron occupation of the energy bands, oxygen is also a building block of the material. Thus, the change from orthorhombic to tetragonal structure upon the removal of the O(1) (chain) atoms has been attributed to the removal of an asymmetry in the configuration along the **a** and **b** axes of the basal plane The antiferromagnetic (AF) properties have been attributed to oxygen-bonding bridges, and oxygen-hole pairing has been mentioned in connection with the superconducting properties. Hydrogen, on the other hand, enters the material interstitially, and, from its small size, can be expected to be crystallographically least intrusive. Its main influence should be on the electron occupation of the conduction band. The measurements show that the addition of hydrogen influences the above properties similarly to oxygen removal.

In a previous communication[1] we presented nuclear magnetic resonance data of the proton resonance in the hydrogen-doped superconducting material which showed evidence of local magnetic order. In this work we report on the ^{89}Y resonance. We compare the hydrogen concentration dependence of the Knight shift and linewidth found in the study with their behavior as a function of oxygen concentration in the undoped compound, as reported by Markert *et al.*,[2] Kramer *et al.*,[3] Alloul *et al.*,[4] and Balakrishnan *et al.*[5] We found that adding hydrogen or removing oxygen affects these parameters similarly. Our present results, and an analysis of the results of other investigators who measured the ^{89}Y resonance in the undoped material, are consistent with the hypothesis of local magnetic correlations put forward in our previous study.[1]

II. EXPERIMENTAL METHOD

Hydrogen was introduced into $YBa_2Cu_3O_7$ which had been prepared using standard techniques. The hydrogen concentration was determined from the change in gas pressure in a known closed volume.

The NMR measurements were performed on a Bruker CXP300 NMR spectrometer at a frequency of 14.707 MHz and temperature of 316 K. The frequency was set to the resonance frequency of ^{89}Y in an aqueous solution of YCl_3, the standard relative to which the Knight shifts were measured. The NMR absorption line shapes were obtained from the Fourier transform of the Hahn echo pulse sequence with phase cycling described by Kunwar *et al.*[6] which suppresses the free induction decay (FID) and ringing artifacts. Typically, each trace represents the average of about 5000 scans obtained at a repetition rate of 10 sec.

III. EXPERIMENTAL RESULTS

X-ray diffraction showed that the compounds became increasingly tetragonal from their original orthorhombic state as the hydrogen concentration increased, in agreement with Fujii *et al.*[7] Hydride formation was seen to occur for the samples $x=4.76$ and 5.74. The $x=1.82$ sample also showed some traces of other phases.

Some of the ^{89}Y NMR absorption curves are shown in Fig. 1 for the different hydrogen concentrations. Significantly, the line shapes are symmetric within experimental error for those samples where the hydrogen does not form a hydride phase. This is in agreement with other measurements performed on the hydrogen-free material.[3–5] The $x=4.76$ sample is a mixed-phase hydride. Its two peaks are probably due to different Knight shifts in

©1990 The American Physical Society

separate phases, with the Knight shift of one of them being much larger than the rest.

Figure 2(a) shows the ambient temperature Knight shift relative to YCl_3 as a function of hydrogen concentration. The shift is seen to increase from a negative value of -100 ppm for $x=0$, to $+115$ ppm at $x=1.82$. The three samples for which the shift was measured in the hydrogen-free samples are shown with the same symbol as the parent material. Figure 2(b) shows the Knight shift as a function of the oxygen deficiency δ ($YBa_2Cu_3O_{7-\delta}$), measured by Alloul *et al.*[4] and Balakrishnan *et al.*[5] We have also included the results of Fig. 2(a), where double the hydrogen concentration and the oxygen deficiency δ are drawn to the same scale. One can see that adding hydrogen has a similar effect on increasing the ^{89}Y Knight shift as removing oxygen.

Figure 3(a) shows the linewidth as a function of hydrogen concentration. It is seen to increase slightly with hydrogen concentration in the superconducting region, and to increase from $\Delta\nu_{1/2}\sim 1$ to 4 kHz near the superconducting-nonsuperconducting boundary. This increase is much too large to be attributed to nuclear dipole interaction with the hydrogen for any reasonable hydrogen site. In Fig. 3(b) we have plotted the linewidth as a function of oxygen deficiency δ obtained by Alloul *et al.*[4] together with the width as a function of hydrogen concentration obtained in this study. The values for $x=0$ and $\delta=0$ are in agreement, as is the magnitude of the jump. We obtain the jump to occur at $x\sim 0.8$, and Alloul *et al.* find it to occur at $\delta\sim 0.7$.

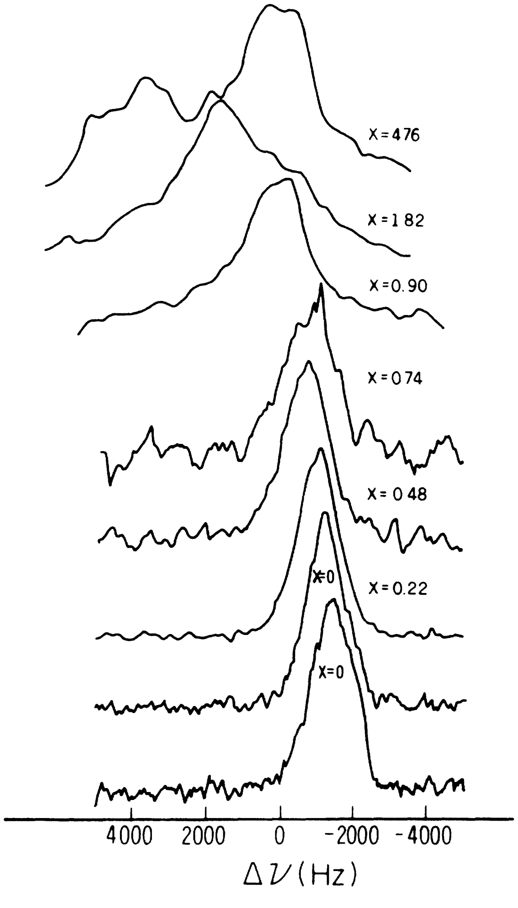

FIG. 1. ^{89}Y NMR absorption curves for $H_xYBa_2Cu_3O_7$ measured at a resonance frequency of 14.707 MHz and a temperature of 316 K.

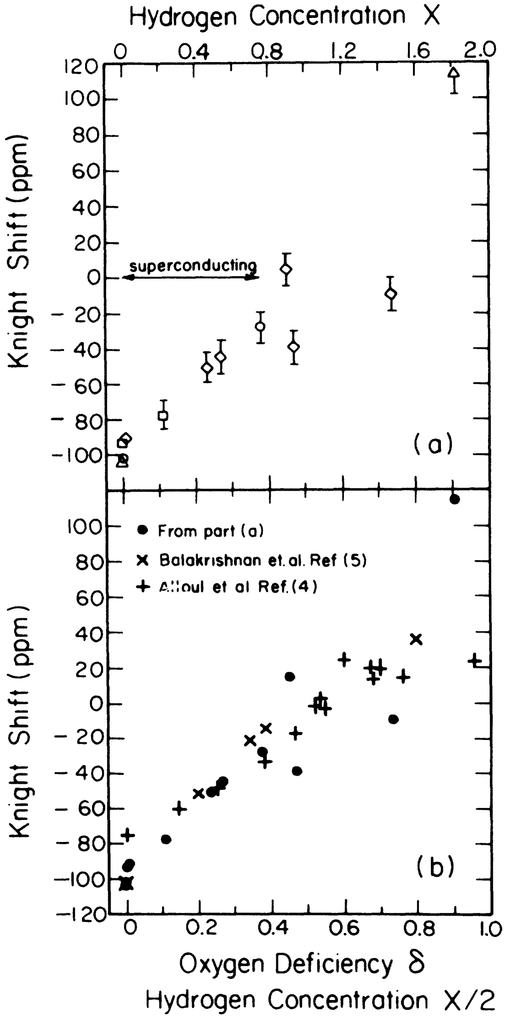

FIG. 2. (a) The ambient temperature Knight shift of ^{89}Y in $H_xYBa_2Cu_3O_7$ as a function of hydrogen concentration x. Symbols identical to those for which $x=0$ refers to the same parent compound. (b) The ambient temperature Knight shift of ^{89}Y in $YBa_2Cu_3O_{7-\delta}$ as a function of oxygen deficiency δ, obtained from Refs. 4 and 5. We have superimposed the points shown in (a). Note change of scale in (a) and (b).

Our ac susceptibility measurements showed superconducting behavior up to a maximum x of 0.8. The superconductivity onset temperature was independent of x in this region. Similar results were obtained by Fuji *et al.*[7] In our case, the concentration at which high-temperature superconductivity ceases is accompanied by a line broadening of a factor of ~ 4 (Fig. 3).

IV. DISCUSSION

Figure 2(b) shows that adding hydrogen has a similar effect on increasing the ^{89}Y Knight shift as oxygen remo-

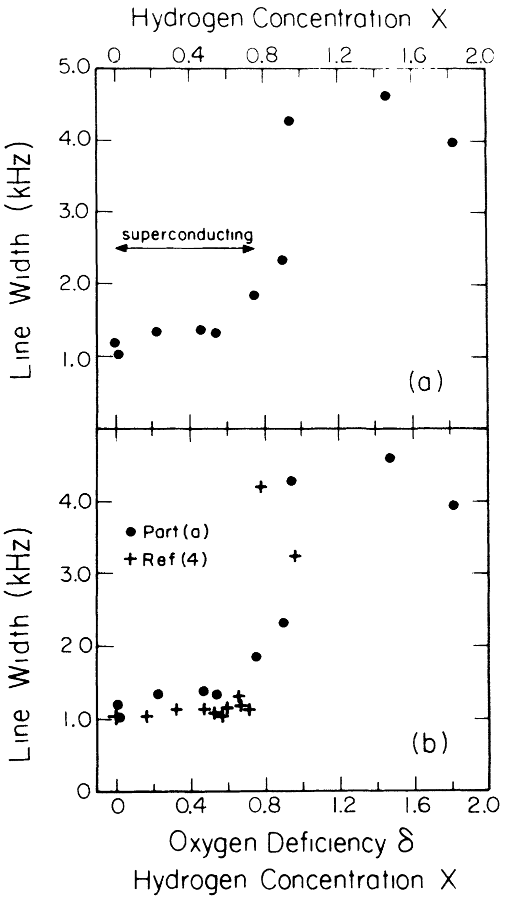

FIG. 3. (a) The hydrogen concentration dependence of the ambient temperature linewidth of the ^{89}Y resonance in $H_xYBa_2Cu_3O_7$ measured at one-half maximum amplitude. (b) The linewidth as a function of the oxygen deficiency δ obtained by Alloul *et al.* (Ref. 4). We have superimposed our points of (a) to the same scale.

val. This is reasonable since the Knight shift is a reflection of the density of states at the Fermi level and oxygen is assumed to be a donor of holes while hydrogen is usually a donor of electrons (e.g., in metal hydrides). Figure 3 shows that the addition of hydrogen also causes a destruction of the superconducting phase and is accompanied by a jump in the linewidth of the same order as that occurring upon the removal of oxygen. Alloul *et al.*[4] attributed the jump to the long-range antiferromagnetic arrangement occurring in the nonsuperconducting phase.

In the hydrogen-free material, the orthorhombic →tetragonal transformation and superconducting →long-range AF occurs at an oxygen deficiency of $\delta \approx 0.6$.[8] Alloul *et al.*[4] found the jump in linewidth to occur at $\delta \approx 0.7$. Fujii *et al.*[7] obtain the orthorhombic→tetragonal transformation and superconducting→nonsuperconducting transformation to occur at a hydrogen concentration of $x \approx 0.8$. We also obtain the superconducting-nonsuperconducting transition and a jump in the ^{89}Y linewidth to occur at $x \approx 0.8$. This would imply that, as far as these parameters are concerned, adding one hydrogen atom has a similar effect to removing one oxygen atom. Our Knight shift results, however, imply that two hydrogen atoms are necessary to compensate for the loss of each oxygen atom. This could be explained by assuming that a hydrogen atom donates its electron to the conduction band while each chain-site oxygen atom removes two electrons (contributes two holes). Niedermayer *et al.*[9] come to an identical conclusion from their muon-spin rotation measurements on the hydrogen-doped material. They, however, base their conclusions on the AF transformation, which is equivalent to our line-broadening results, for which we obtained two H atoms equal to one O atom equivalency. Matsunaga *et al.*[10] obtained an orthorhombic →tetragonal transformation and superconducting→nonsuperconducting transformation at a hydrogen concentration half that reported by Fujii *et al.* and half that which we obtained.

Tranquada *et al.*[11] showed that *long-range* antiferromagnetic order exists in tetragonal nonsuperconducting $YBa_2Cu_3O_{7-\delta}$, where $\delta > 0.6$. They speculate that antiferromagnetic correlations may survive in the orthorhombic superconducting phase; it is only the long-range order that is destroyed. Using neutron scattering, Petigrand *et al.*[12,13] reported antiferromagnetic order in an oxygen-deficient sample that retained enough oxygen to make it a superconductor below 55 K. Westerholt and Bach[4] interpret their magnetic susceptibility measurements by assuming that antiferromagnetic short-range order exists in superconducting $YBa_2Cu_3O_{6+x}$ with x up to at least 0.9. Vega *et al.*[15] also deduce antiferromagnetic interactions from their Cu nuclear quadrupole resonance (NQR) measurements in the superconducting material. Goren *et al.*[1] present direct evidence for local magnetic order from the hydrogen resonance in superconducting $H_{0.22}YBa_2Cu_3O_7$.

We believe that the ^{89}Y linewidth data confirm the existence of local magnetic order. The 1.2 kHz ^{89}Y linewidth in the orthorhombic superconducting phase found by Alloul *et al.*[4] and obtained in this study, is about an order of magnitude larger than what one would expect from dipolar broadening as calculated by Markert *et al.*[2] This linewidth is due to *inhomogeneous* broadening since Markert *et al.* measured the linewidth using the Hahn spin-echo decay technique which removes the inhomogeneous broadening contribution, and they obtained agreement with the theoretical nuclear dipolar broadening. Alloul *et al.*[4] attributed this large inhomogeneously broadened width to an anisotropy of the chemical shift tensor. But such an anisotropy should result in an asymmetric line shape. This is, within experimental error, contrary to our observation and those of Alloul *et al.*[4] and Balakrishnan *et al.*[5] It is also unlikely that the broadening is due to spatial inhomogeneity of the Knight shift which could be caused by intrinsic defects or oxygen depletion. It is improbable that the defect in our three hydrogen-free samples for which the Y line shape was measured, and the samples of Alloul *et al.*, would be such as to give the same large linewidth. As far as oxygen depletion is concerned, the Knight-shift dependence on the O concentration is such[4,5] that the sample would have to have a local O concentration distribution over almost the entire range from $\delta = 0$ to 0.6 in order to obtain the measured linewidth. This is impossible for our and Alloul's samples where the macroscopic δ is close to zero. Furthermore, Alloul *et al.* found that the linewidth is essentially independent of oxygen content in the superconducting region. In addition, Balakrishnan *et al.*[5] were able to narrow the line by sample spinning. If the width were due to a distribution of Knight shifts due to local inhomogeneities in the oxygen content, then the line should not be narrowed by spinning. On the other hand, the line *is* narrowed in the long-range AF $YBa_2Cu_3O_{6.2}$ as shown by Balakrishnan *et al.*[5] Here the nonspun linewidth is increased fourfold by the AF interaction.[4] We therefore propose that the inhomogeneous broadening is due to local magnetic order.

A somewhat bothersome feature that was indicated in Ref. 1 concerned the very small hydrogen line shift compared to that usually encountered (MHz) in antiferromagnetic materials. It is seen, however,[4] that when entering the phase where there is definitely long-range antiferromagnetism, the Y linewidth jumps to only about 4 kHz. Hence, the nuclei are probably located at magnetically symmetric sites and one should expect the shift to be small in this case.

It was speculated in Ref. 1 whether the hydrogen probes the internal local magnetic field or whether the stabilization of a magnetic field is due to the hydrogen itself. If the inhomogeneous broadening of the ^{89}Y line has its origins in the same local field detected by the split hydrogen lines, then we must conclude that the hydrogen acts as a probe of pure $YBa_2Cu_3O_7$ since the ^{89}Y inhomogeneous broadening also occurs in the hydrogen-free material.

In conclusion, we can say the following.

(1) Both the hydrogen and yttrium line structures can be explained by the presence of local magnetic order in superconducting compounds of Y-Ba-Cu-O.

(2) Increasing the hydrogen concentration in $H_xYBa_2Cu_3O_7$ causes (a) a shift from orthorhombicity toward tetragonality, (b) an increase of the ^{89}Y resonance shift from negative to positive value, (c) a destruction of the superconducting phase, and (d) a jump in linewidth when going from the superconducting to nonsuperconducting compounds.

A decrease of oxygen concentration in $YBa_2Cu_3O_{7-\delta}$ also exhibits all the above characteristics.

The crystal structure should be sensitive to the electronic structure, and the Knight shift depends on the density of state at the Fermi level. Hence, if one assumes that O acts as a hole donor and H as an electron donor, it is not surprising that increasing the hydrogen concentration gives similar results as decreasing the oxygen content. While both an increase in H concentration or a decrease of O content in the hydrogen-free material cause a disappearance of the superconducting phase, the former process retains the high onset T_c within the superconducting phase, while removing oxygen causes a continuous decrease in T_c until the superconducting phase disappears.

When enough oxygen is removed from $YBa_2Cu_3O_7$ to make it nonsuperconducting, the Cu II atoms have long-range antiferromagnetic order. The large rate of increase of linewidth when entering the nonsuperconducting region (Fig. 3) can be attributed to a possible increase towards longer-range magnetic order with increasing hydrogen concentration. The linewidth of the samples having hydrogen concentrations in the nonsuperconducting region is the same as that found by Alloul *et al.* for the ordered AF phase. They attribute this broadening to be a result of AF. Niedermayer *et al.*,[9] using the muon-spin rotation technique, found direct evidence for hydrogen-induced magnetic ordering. It would be interesting to see whether neutron diffraction would reveal long-range order in the nonsuperconducting $x > 0.8$ hydrogen-doped $H_xYBa_2C_3O_7$.

ACKNOWLEDGMENTS

We would like to thank Professor H. Stenschke for many enlightening discussions.

---

[1] S. D. Goren, C. Korn, V. Volterra, M. Schaefer, H. Riesemeier, E. Rössler, H. Stenschke, H. M. Vieth, and K. Lüders, Solid State Commun. **70**, 279 (1989).

[2] J. T. Markert, T. W. Noh, S. E. Russek, and R. M. Cotts, Solid State Commun. **63**, 847 (1987).

[3] G. J. Kramer, H. B. Brom, J. van den Berg, P. H. Kes, and D. J. W. Ijdo, Solid State Commun. **64**, 705 (1987).

[4] H. Alloul, P. Mendels, G. Collin, and P. Monod, Phys. Rev. Lett. **61**, 746 (1988).

[5] G. Balakrishnan, R. Dupree, I. Farnan, D. McK. Paul, and M. E. Smith, J. Phys. C **21**, L847 (1988).

[6] A. C. Kunwar, G. L. Turner, and E. Oldfield, J. Magn. Reson. **69**, 124 (1986).

[7] H. Fujii, H. Kawanaka, W. Ye. S. Orimo, and H. Fukuba, Jpn. J. Appl. Phys. **27**, L525 (1988).

[8] W. E. Farneth, R. K. Bordia, E. M. McCarron III, M. K. Crawford, and R. B. Flippen, Solid State Commun. **66**, 953 (1988).

[9] C. Niedermayer, H. Glückler, R. Simon, A. Golnik, M. Rauer, E. Recknagel, A. Weidinger, J. I. Budnick, W. Paulus, and R. Schöllhorn, Phys. Rev. B **40**, 11 386 (1989).

[10] T. Matzunaga, T. Kajitani, T. Kamiyama, M. Omori, S. Tomiyoshi, H. Yamauchi, and M. Hirabayashi (private communication).

[11] J. M. Tranquada *et al.*, Phys. Rev. Lett. **60**, 156 (1987).

[12] D. Petitgrand, G. Collin, P. Schweiss, S. Hadjoudi, and S. Senoussi, J. Phys. France **49**, 1815 (1988).

[13] D. Petitgrand and G. Collin, Physica B **156&157**, 858 (1989).

[14] K. Westerholt and H. Bach, Phys. Rev. B **39**, 858 (1989).

[15] A. J. Vega, W. E. Farneth, E. M. McCarron, and R. K. Bordia, Phys. Rev. B **39**, 2322 (1989).