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Nuclear quadrupole resonance of Cu in hydrogenated $YBa_2Cu_3O_7$

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The ^{65}Cu and ^{63}Cu NQR lines were obtained at a temperature of 4.2 K for samples of $H_xYBa_2Cu_3O_7$, where $x = 0.021$, 0.058, 0.21, 0.60, and 1.00. New peaks appear upon the introduction of hydrogen. The amplitudes of the various peaks rise and fall but do not change their positions continuously as x is varied. The positions of the peaks are attributed to changes in the valency of the Cu atoms, which are thus seen to change in a discontinuous manner as x changes. The positions of the new lines that appear are the same as those obtained when oxygen is removed. The disappearance of the ^{63}Cu 31.5 MHz line for the nonsuperconducting material having $x = 1.00$, is attributed to antiferromagnetic order. The results confirm our previous assertion that adding hydrogen to $YBa_2Cu_3O_7$ changes many of the attributes of the material in a manner similar to removing oxygen. Possible evidence for magnetic interaction with chain Cu(1) atoms in the superconducting material is presented.

I. INTRODUCTION

The role of the basal oxygen atoms O(1) in $YBa_2Cu_3O_7$ has been found to be crucial in the superconducting or antiferromagnetic (AF) behavior of the material. Thus as oxygen is removed, T_c goes down, the crystal structure becomes more tetragonal, and at low enough oxygen concentration, the material becomes a nonsuperconductor and the Cu(2) atoms in the Cu–O plane take on an ordered AF structure.[1] We have found[2] that when hydrogen is introduced into $YBa_2Cu_3O_7$ many of the properties change in a manner similar to the removal of oxygen. Thus the crystal structure changes from orthorhombic to tetragonal, the ^{89}Y Knight shift moves from positive to negative values, and the ^{89}Y NMR linewidth jumps at the hydrogen concentration where the material becomes a nonsuperconductor. This is attributed to the appearance of long-range (AF) order. This latter property has been confirmed by muon-spin rotation[3] and Mössbauer measurements.[4] There are also some notable differences. Although in both cases the material changes from orthorhombic to tetragonal with oxygen depletion and hydrogen doping, the c axis expands in the former case and contracts in the latter. Also, whereas T_c decreases with a loss of oxygen until the material becomes AF, when the hydrogen concentration in $H_xYBa_2Cu_3O_7$ is increased, the onset T_c remains unchanged until $x \approx 0.8$ where it loses its superconducting property and becomes AF.

A number of investigators have obtained the Cu nuclear quadrupole resonance (NQR) spectrum as a function of oxygen depletion.[5–8] A change in oxygen concentration affects the Cu charge distribution, causing new NQR lines to appear. We have varied the hydrogen concentration in $H_xYBa_2Cu_3O_7$ and observed that the new NQR lines that appear are at the same frequencies as those obtained by oxygen depletion. We thus obtain information on the behavior of the Cu valency with the addition of electrons to the band.

II. EXPERIMENTAL METHOD

Samples of $YBa_2Cu_3O_7$ were prepared using standard techniques. Hydrogen was introduced in a closed system and the hydrogen concentration was determined from changes of the gas pressure in the known volume.

The nuclear quadrupole resonance of Cu was measured at 4.2 K over a frequency range of 21–33 MHz and in the case of $x = 0.21$ they extended down to 19 MHz. The echo of a two-pulse sequence P_A—τ—P_B—τ—detect was obtained using quadrature detection and the amplitude of the absorption line of the Fourier transform was recorded. P_A and P_B were rf pulses of 5 and 10 μsec duration, respectively.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Equivalence of hydrogen doping and oxygen removal

The NQR spectra of Cu in $H_xYBa_2Cu_3O_7$ for $x = 0.021$, 0.058, 0.21, 0.60, and 1.00 measured from 21 to 33 MHz at 4.2 K are shown in Fig. 1. The signal amplitude is given in arbitrary units. The signal amplitudes were normalized with respect to the masses of the different samples and the change in amplification factor of the amplifiers used for high and low frequencies. No attempt was made to compensate for the frequency-squared dependence expected in the amplitude. The relative amplitudes shown in the figure are only approximate. The amplitude scale for the 21–24.5 MHz region is five times that for the 24.5–33 MHz region (i.e., the low-frequency amplitude is one-fifth that of the high frequency). Lines have been drawn connecting the ^{63}Cu resonances with the lower frequency ^{65}Cu resonances for clarity in interpretation. The dots and crosses refer to measurements carried out at a repetition time of 1 and 20 sec, respectively, except for sample $x=1.00$, where the crosses refer to a 10 sec repetition time. The differences in the relaxation time for the plane Cu(2) and the chain Cu(1) are discussed in Refs. 6 and 7.

We shall see that the addition of hydrogen gives results very similar to the removal of the basal oxygen. There is ample evidence that with proper care in the hydrogen doping process, oxygen does not actually leave the material. Such a removal of oxygen would be accompanied by an easily measured weight loss. Also, the *c* axis would expand instead of the contraction we observe and the onset T_c would be reduced instead of remaining constant. Yet the electron distribution is such as if oxygen were removed.[2]

We shall designate the hydrogen content by x and the oxygen content by y, i.e., we shall compare the ^{63}Cu NQR resonance lines of $H_xYBa_2Cu_3O_7$ with those of $YBa_2Cu_3O_y$.

The $x=0.021$ sample has very little hydrogen and we obtain the standard Cu(1)$_4$ line at 22.05 MHz and the Cu(2) line at 31.5 MHz. Cu(1) and Cu(2) refer to the chain and planar copper atoms, respectively. We designate the Cu(1) with a subscript according to the nomenclature of Yasuoka *et al.*[8] where, in the case of oxygen depletion, the subscript refers to the oxygen coordination of the Cu. When oxygen is removed from the basal plane, the Cu(1)$_4$ signal becomes weaker since there are fewer Cu(1) atoms having a coordination of 4. Instead, a Cu(1)$_3$ line appears at 24 MHz. Not all investigators obtain the 24 MHz line. This is because the equilibrium distribution of oxygen vacancies in the basal plane is not random but ordered near $y=6.5$, forming alternately full and empty chains along the *b* axis.[9,10] In that case the Cu(1) atoms have either 4 or 2 oxygen coordination. In our case, we assume that the hydrogen atoms enter their sites randomly. This would then be equivalent to producing an oxygen coordination of 3. Indeed we see for the case of $x=0.21$ a strong 24 MHz line which goes down in amplitude at both higher and lower x values, since at

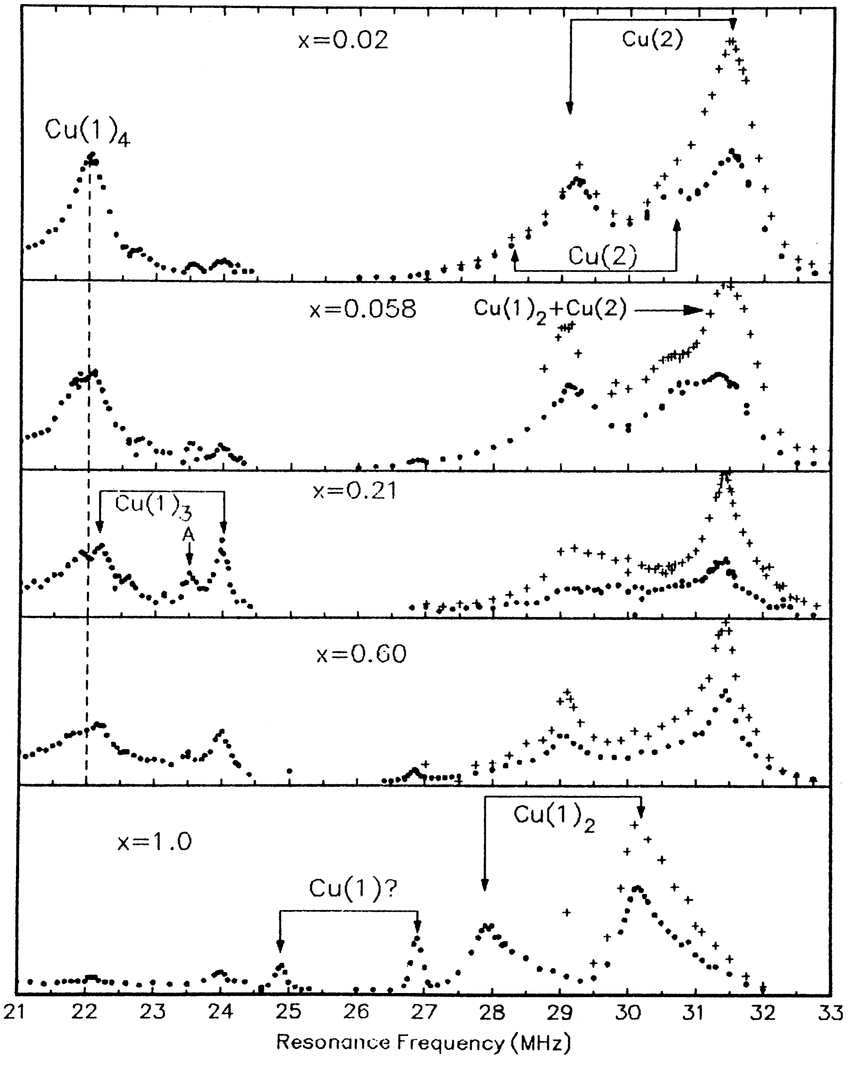

FIG. 1. NQR spectra of Cu in $H_xYBa_2Cu_3O_7$ for various values of x. The ^{63}Cu and ^{65}Cu resonances are connected by arrows.

low x and high x most of the Cu(1) atoms have either 4 or 2 oxygen coordination.

When all the basal oxygen is removed ($y=6.0$), no $\mathrm{Cu(1)_4}$ atoms are left. The Cu(1) are now all $\mathrm{Cu(1)_2}$, giving an NQR line at 30.2 MHz. We see in our case when the hydrogen concentration goes from $x=0.6$ to $x=1.0$, the $\mathrm{Cu(1)_4}$ 22.05 MHz line disappears and instead, the $\mathrm{Cu(1)_2}$ line at 30.2 MHz becomes prominent. Also at $y<6.4$ the internal magnetic field at the planar Cu(2) due to antiferromagnetism causes a Zeeman splitting and removes the Cu(2) line from its 31.5 MHz value to above 90 MHz (Ref. 8) (outside the region of our measurements). Indeed, when x goes from 0.60 to 1.00, $\mathrm{H_xYBa_2Cu_3O_7}$ changes from a superconductor to AF (Ref. 2) and the 31.5 MHz Cu(2) line disappears. In the case of oxygen depletion, the 30.2 MHz $\mathrm{Cu(1)_2}$ line does not appear until the AF region is reached.[8] Comparing the trace of $x=0.6$ (superconductor) with that of $x=1.00$ (AF), we see that here too the 30.2 MHz line is missing in the superconducting material and makes a strong appearance in the AF material.

In the $x=0.021$ sample there is a hint of a ^{63}Cu line at 30.7 MHz, which becomes more prominent for the $x=0.058$ sample. Yasuoka *et al.*[8] also show a small shoulder at this frequency in their Fig. 7(c) for a sample having $y=6.9$. As the oxygen becomes more depleted, the Cu(2) line splits into up to three lines. This is attributed by Yasuoka *et al.* to the influence of the coupling of $\mathrm{Cu(1)_4}$, $\mathrm{Cu(1)_3}$, and $\mathrm{Cu(1)_2}$ to the Cu(2) atoms via the O(4) oxygen bridge.

The spin-lattice relaxation rate of the nuclei of the conducting Cu(2) atoms is much greater than for the nonconducting Cu(1) atoms. This led Warren *et al.*[11,12] to the discovery of a Cu(1) line in oxygen-depleted material ($y\approx 6.7$) at almost the same frequency as the Cu(2) line at 31.5 MHz. They assigned this line to $\mathrm{Cu(1)_2}$, whereby the $\mathrm{Cu(1)_2}$ line is at 31.5 MHz when the material is a superconductor, and at 30.1 MHz when the material is AF. We observe the same thing when hydrogen addition takes the place of oxygen depletion. The $\mathrm{Cu(1)_2}$ line at 30.15 MHz for the $x=1.00$ AF material has already been discussed previously. In the case of $x=0.058$, the signal between 30.7 MHz and 31.6 MHz is almost flat when a repetition time of 1 sec is used, while at a repetition time of 20 sec, the relative magnitudes of the 30.7 MHz and 31.5 MHz peaks are quite different. We thus see that for $x=0.058$, the line at 31.5 MHz is composed of two components, one relaxing much faster than the other, similarly to the case described by Warren *et al.* in the case of O depletion.

One significant difference in the spectrum between oxygen depletion and hydrogen doping has already been mentioned. This is the prominence of the $\mathrm{Cu(1)_3}$ line near 24 MHz seen for the $x=0.21$ and $x=0.60$ samples. Since the oxygen vacancy distribution is not random but the oxygen is aligned along alternating chains, one would not expect to have a significant number of Cu(1) atoms having an oxygen coordination of 3; the coordination should be limited to 2 and 4. Thus the presence of the 24 MHz line depends on sample preparation and should be absent in the equilibrium phase. In the case of hydrogen doping we expect the hydrogen to be randomly distributed at their lattice sites (to be discussed later) so that the above qualifications do not hold. Another significant difference is the presence of a ^{63}Cu line at 26.9 MHz in the $x=1.00$ AF material, which is not reported in the AF phase of oxygen depleted samples.[6,8] We speculate that the difference can be attributed to the hydrogen coordination of the Cu(1) atoms. Measurements of the quadrupolar coupling constant of deuterium in deuterium-doped $\mathrm{YBa_2Cu_3O_7}$ indicate that the probable site of the deuterium (hydrogen) is very near the bisector of the line joining the chain O(1) with O(4).[13] There are four such sites surrounding each Cu(1). While a contribution of one electron from each of two hydrogen atoms would be equivalent to the removal of two holes for each missing oxygen atom, at high enough hydrogen concentration, there may be as many as three or four hydrogen atoms surrounding the Cu(1), and these perhaps cause a charge distribution on the Cu(1) that gives rise to the 26.9 MHz line. (The question of the number of hydrogen atoms-oxygen atoms equivalency is discussed in Refs. 2, 3, and 14.)

The spectrum of $x=0.21$ gives a peak at 23.5 MHz (at A) with hints of this line in the other spectra (except $x=1.00$) as well. Neither Warren *et al.*,[7] nor Yasuoka *et al.*[8] report this line. Vega *et al.*,[6] on the other hand, observe a slow relaxation rate [implying Cu(1)] signal at 23.3 MHz. They attribute it to $\mathrm{Cu(1)_4}$ which moves from 22.0 MHz to 23.3 MHz upon oxygen removal. Perhaps this is our 23.5 MHz signal.

B. Possible evidence for magnetic interaction at the chain sites in the superconducting material

The ^{1}H NMR spectrum of $\mathrm{H_xYBa_2Cu_3O_7}$ shows a very wide line in addition to a narrow line even at hydrogen concentrations where the material is superconducting.[13,15,16] We have speculated[13] that the wide line is due to magnetic interactions in the basal plane. A possible splitting of the Cu(1) 22 MHz resonance indicated by the broken line across the superconducting samples in Fig. 1, may be due to such an interaction. While there is a peak at the $\mathrm{Cu(1)_4}$ line for the practically hydrogen-free material of $x=0.021$, there is a small dip for the other superconducting samples. A closer look at the data (especially that of $x=0.21$) reveals the possibility of an inner splitting of 0.3 MHz and outer splitting of 1.1 MHz. The peaks and shoulders are at the border of detection and one cannot say unequivocally that these are magnetic interactions.

If the shape of the 22.05 MHz line is indeed due to a magnetic interaction, then calculations along the lines of Ref. 17 indicate that the magnetic field seen by the Cu affected by the splitting is somewhere between 245 and 295 G, the exact value depending on the quadrupole asymmetry factor η and the direction of the magnetic field. Pennington *et al.*[18] obtained an asymmetry factor of $\eta=0.984$ for Cu(1) in the hydrogen-free material with the major principal axis along the b crystallographic direction. If we assume this to be the case for the hydrogen-doped material and if we assume that, similarly to the case of magnetism in Cu(2), the field is directed within the basal plane, then the magnitudes of the splitting here obtained yield a field of 251 G making an angle of 27° with the crystallographic *b* direction.

An argument against the reality of a magnetic splitting for the Cu(1) is that it is not detected at the $\mathrm{Cu(1)_3}$ line. One may, however, rationalize this by noting that there are superexchange interactions between the Cu(1) atoms and the Cu(2) atoms via the bridging O(4) atoms and these are different for the different Cu(1) coordination atoms. The relative movement of the Cu(2) lines as y changes, was attributed by Yasuoka *et al.*[8] to these different interactions with the variously coordinated Cu(1).

IV. CONCLUSIONS

Our measurements have confirmed that the addition of hydrogen to $\mathrm{YBa_2Cu_3O_7}$ has a similar effect on the quadrupole resonance of Cu, as the removal of oxygen.

There may also be evidence for a magnetic interaction at the Cu(1) sites in hydrogen-doped superconducting material, reinforcing this speculation adduced from a very wide ^{1}H NMR line.[13] The weakness of the resolution of the signal does not permit a positive conclusion. If the interaction is real, then the field seen by Cu(1) is about 250 G.

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