

## NMR evidence for localized spins on Cu(2) sites from Cu NMR in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ single crystals

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 (Received 11 August 1988; revised manuscript received 23 January 1989)

We report  $^{63,65}\text{Cu}$  NMR spectra and nuclear spin-lattice relaxation data for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c=91$  K) and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$  ( $T_c=57$  K) single crystals between 45 and 300 K. An analysis of the spin-lattice relaxation rates gives evidence for localized electronic spins on the planar Cu(2) sites. In  $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$  both fourfold and twofold oxygen-coordinated Cu(1) sites are observed; the latter experience the same quadrupolar coupling ( $\nu_Q \approx 31.5$  MHz) as the Cu(2) sites but a nearly zero magnetic hyperfine shift and a much slower relaxation rate ( $d^{10}$  configuration).

Very soon after the discovery of the high- $T_c$  superconducting oxide  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,<sup>1</sup> with  $\delta \approx 0$ , nuclear quadrupole resonance (NQR) studies of the  $^{63,65}\text{Cu}$  nuclei have revealed that one of the two Cu sites present in the structure [fivefold coordinated "in the plane" Cu(2) site and fourfold coordinated "in the chains" Cu(1,  $\text{O}_4$ ) site] was more strongly coupled than the other to the excitations of the superconducting ground state.<sup>2</sup> However, the assignment of the two  $^{63}\text{Cu}$  NQR lines ( $\nu_{\text{NQR}} = 31.5$  and 22 MHz) to the different sites has been subjected to a big controversy,<sup>3</sup> bearing some doubt on the respective influence of the Cu-O planes and chains on the high  $T_c$  of this compound. Recent NMR investigation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  single crystals (Ref. 4 and this work) and NQR in  $\text{Gd}(\text{Sm})\text{Ba}_2\text{Cu}_3\text{O}_7$  powder samples<sup>5</sup> have now firmly established the assignment of the 31.5 MHz line to the Cu(2) site, confirming the major role of the CuO plane. On the other hand, it has been demonstrated<sup>6</sup> that the  $^{63}\text{Cu}$  NQR line observed at  $\nu_{\text{NQR}} = 30$  MHz in the antiferromagnetic<sup>7</sup> (AF)  $\text{YBa}_2\text{Cu}_3\text{O}_6$  compound—in which all the oxygen from the O(4) sites have been removed<sup>8</sup>—had to be assigned to the oxygen twofold coordinated chain site Cu(1,  $\text{O}_2$ ). Due to this accidental similarity of the quadrupolar couplings experienced by the Cu(2) and Cu(1,  $\text{O}_2$ ), the assignment of the NQR lines for the intermediate oxygen concentration  $0 < \delta < 1$ , for which Cu(2) and Cu(1,  $\text{O}_n$ ) with  $n = 2, 3, 4$  are expected to be present, is fairly difficult. This is of particular importance for the interpretation of the nuclear spin-lattice relaxation rate (NSLRR) behavior of the Cu "31.5 MHz line" in the  $\delta = 0.3$  compound, which was found three orders of magnitude lower than in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>9</sup> Assigning this line to the Cu(2) site would indicate a tremendous change in the electronic structure of the CuO plane, in apparent contradiction with the yttrium Knight shift<sup>10</sup> which smoothly varies as a function of  $\delta$ .

In this Rapid Communication we report the NMR investigation of Cu in single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with  $\delta = 0$  and 0.25 ( $T_c = 91$  and 57 K, respectively). Three pairs of lines corresponding to Cu(2), Cu(1,  $\text{O}_2$ ), and Cu(1,  $\text{O}_4$ ) sites have been observed in a single  $\delta = 0.25$  sample. The relative intensities of these NMR lines clearly reveal a partial ordering of the oxygen vacancies in the 57-K compound. For the first time we show that instead of decreasing by three order of magnitude, the NSLRR for the Cu(2) stays the same for  $\delta = 0$  and  $\delta = 0.25$  in the temperature range 100–300 K, while the slowly relaxing line observed in the  $\delta = 0.25$  compound ( $\nu_{\text{NQR}} = 31.4$  MHz) actually corresponds to the Cu(1,  $\text{O}_2$ ) chain site. This lack of dependence of the Cu(2) NSLRR on the oxygen composition is interpreted as evidence for localized electronic spins on these sites, unaffected by the creation of holes in the oxygen  $p$  band.

NMR measurements were performed at  $H_0 = 5.75$  T using standard pulsed NMR techniques. For the  $\delta = 0$  composition two types of crystals have been studied. Sample A was a flux-grown single crystal ( $\sim 4 \times 1.5 \times 0.05$  mm<sup>3</sup>) with a relatively wide superconducting transition from 86 to 82.5 K for 90–10% of the resistance. Sample B was a porous single crystal<sup>11</sup> ( $\sim 2 \times 1 \times 0.2$  mm<sup>3</sup>) with a well-defined transition at  $T_c = 91$  K with  $\Delta T_c = 0.4$  K as measured by the ac susceptibility with  $\mathbf{H}_{ac} \parallel a$ - $b$  plane. This method has proven to be very powerful for detecting the inhomogeneity in single crystals.<sup>12</sup> The  $\delta = 0.25$  sample C was of the same type and size as sample B, but with  $T_c = 57$  K and  $\Delta T_c = 3$  K.

A complete determination of the electric-field-gradient (EFG) and magnetic-hyperfine-shift (MHS) tensors have been carried out on the A and B ( $\delta = 0$ ) samples by measuring the position of the  $^{63,65}\text{Cu}$  ( $\frac{1}{2}, -\frac{1}{2}$ ) and ( $\frac{3}{2}, \frac{1}{2}$ ) transitions for the orientations  $\mathbf{H}_0 \parallel c$  and  $\mathbf{H}_0 \parallel a, b$  axis. A detailed account of these results will be reported else-

where<sup>13</sup> and in the following we shall restrict ourselves to a partial analysis of the spectra obtained for  $H_0 \parallel c$ . Two pairs of  $(\frac{1}{2}, -\frac{1}{2})$  transitions were observed. Two narrow lines (I) [80 kHz full width at half maximum (FWHM) at 100 K] corresponding to the Cu(2) site were found at frequencies the ratio of which corresponds to the ratio of the  $^{63,65}\text{Cu}$  gyromagnetic ratio ( $\gamma$ ) with a MHS  $K_{cc} = (1.28 \pm 0.03)\%$ . For the two broad lines (II) corresponding to the Cu(1, O<sub>4</sub>),  $K_{cc}$  was found equal to  $(0.2 \pm 0.1)\%$ . Due to its broadness ( $\approx 0.5$  MHz FWHM), this line overlaps with the corresponding line reported by Pennington *et al.*<sup>4</sup> although the position of the peak maxima differs. This difference, as well as the broadness of the  $(\frac{1}{2}, \frac{3}{2})$  transitions in our samples ( $\approx 2-3$  MHz FWHM)—in spite of the very sharp superconducting transition observed in sample B—are thought to be due to localized defects in the chains.<sup>11</sup> Their screening by the conduction electrons in the CuO plane may be responsible for a large distribution of EFG at the Cu(2) sites. Fortunately, this does not affect the width of the line I for the particular orientation  $H_0 \parallel c$  axis.

In sample C ( $\delta = 0.25$ ), in addition to lines I and II [ $K_{cc} = (1.31 \pm 0.05)\%$  and  $(0.2 \pm 0.1)\%$ , respectively, at 100 K], a new pair of narrow lines (III) was discovered (Fig. 1) with a much slower relaxation time and with positions in the ratio of the  $^{63,65}\text{Cu}$   $\gamma$ 's with  $K_{cc} = (-0.14 \pm 0.05)\%$ . Taking advantage of a much longer spin-spin relaxation rate, the satellite corresponding to the  $^{63}\text{Cu}$  line III was easily resolved from the broad ones due to Cu(2) site. The separation between the central line and the satellite was found equal to 31.4 MHz. A pure NQR measurement was carried out at frequency  $\nu_0 = 31.43$  MHz on the powder sample originating from the same batch as sample C for control purpose. A narrow line was observed (FWHM = 160 kHz at 100 K) with a slow relaxation rate in accordance with other authors.<sup>9</sup> However, a quickly re-

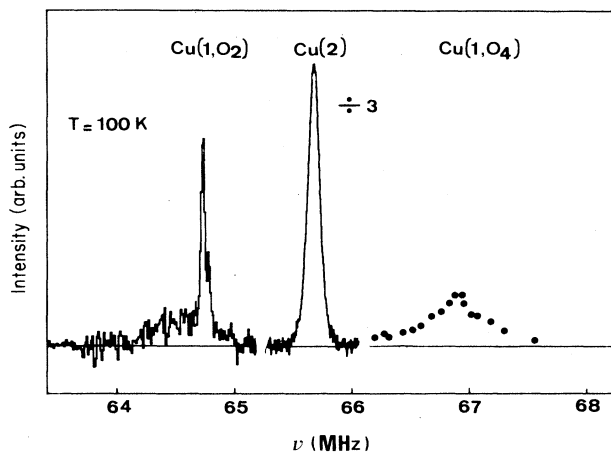


FIG. 1.  $^{63}\text{Cu}$  NMR spectrum corresponding to the  $(\frac{1}{2}, -\frac{1}{2})$  transitions in a  $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$  single crystal ( $H_0 = 5.7$  T and  $\parallel c$  axis). Intensities of the lines are approximately scaled [intensity of the Cu(2) line is reduced three times]. Underlying the line due to Cu(1, O<sub>2</sub>) is a broad line corresponding to the  $(\frac{1}{2}, \frac{3}{2})$  transitions due to the Cu(1, O<sub>4</sub>) nuclei.

laxing component was also observed due to the overlap with a broad Cu(2) line. Due to the low values of its NSLRR and MHS, and because of the symmetry of the EFG ( $V_{zz} \parallel c$  and  $\eta \approx 0$ ), the line III was naturally assigned to Cu(1, O<sub>2</sub>) in the  $d^{10}$  configuration. The ratio of the intensities of line III to the line I was found equal to  $r = 0.08 \pm 0.01$ . This strongly supports the structural models in which vacancies are located preferentially on certain empty chains,<sup>14</sup> since a complete disorder of oxygen vacancies would lead to  $r = 0.03$  while full ordering would give  $r = 0.125$ .

NSLRR in samples B and C was measured for the Cu(2) site (line I), in the  $H_0 \parallel c$  axis configuration, for the  $^{63}\text{Cu}$   $(\frac{1}{2}, -\frac{1}{2})$  transition. For a spin  $I = \frac{3}{2}$  experiencing a large quadrupole coupling and a relaxation process of magnetic origin, the theoretical time dependence for the recovery of the magnetization corresponding to the transition  $(-\frac{1}{2}, \frac{1}{2})$ , is given by<sup>15</sup>

$$M(\infty) - M(t) \propto (9e^{-12Wt} + e^{-2Wt}), \quad (1)$$

which was found well in agreement with the experiment. Although the  $(\frac{1}{2}, \frac{3}{2})$  transitions were found very broad, the absence of a distribution of  $W$  is not surprising since Eq. (1) does not depend on the magnitude of  $\nu_Q$ . This also confirms that the distribution of EFG at the Cu(2) sites does not result from a distribution of the valence states in the plane, as suggested in Ref. 16, but rather from the screening of defects in the CuO chains, as mentioned above. In Fig. 2 the measured values of  $2W/T$  are compared to the ( $H_0 = 0$ ) NQR data<sup>2</sup> renormalized to  $2W$ . (In NQR a single exponential dependence is observed with  $1/T_1 = 6W$ ). The striking feature of our NMR data is that in the temperature range 100–300 K, the  $2W/T$  values are found to be the same for both com-

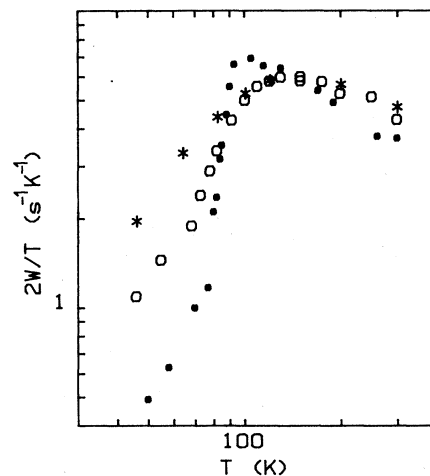


FIG. 2. The nuclear-spin lattice relaxation rate  $2W/T$  for the Cu(2) site as a function of the temperature, measured by NMR ( $H_0 \parallel c$ ,  $\nu_0 = 65.715$  MHz) in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (sample B—open circles) and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$  (sample C—stars) single crystals, and by NQR in a  $\text{YBa}_2\text{Cu}_3\text{O}_7$  powder sample ( $\nu_Q = 31.5$  MHz—closed circles). The NQR data are taken from the article of Imai *et al.* in Ref. 2.

positions, presenting a broad maximum around 120 K. Below 100 K, the NSLRR drops faster in the  $\delta=0$  than in the  $\delta=0.25$  compound. This, in addition to the ac susceptibility data, clearly shows that the Cu(2) nuclei observed in sample C do not belong to some  $\delta=0$  segregated phase. One also notices that in contrast to the NQR data the decrease of the NSLRR in our sample B ( $\delta=0$ ) starts well above  $T_c$ .<sup>17</sup> This difference might be due to the magnetic field, but because of the broadness of our ( $\frac{1}{2}, \frac{3}{2}$ ) transition, it is difficult to conclude.

The independence of the NSLRR on the oxygen composition between 100 and 300 K clearly contrasts with the variation of the yttrium Knight shift ( $^{89}\text{K}$ ) which decreases by 30% from  $\delta=0$  to 0.25.<sup>10</sup> Assuming  $^{89}\text{K}$  proportional to the density of states at the Fermi level in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system, this should be reflected as a 60% drop of the relaxation rate of the Cu(2) if their  $3d$  wave function was present at the Fermi level. Although the Cu(2) NSLRR does not follow a Korringa behavior in the temperature range 100–300 K, one might try to explain the magnitude of the Cu(2) NSLRR in the framework of a metallic  $d_{x^2-y^2}$  band and to evaluate an enhanced density of states  $N_d(E_F)\Gamma(\alpha)$ , where  $\Gamma(\alpha)$  stands for the enhancement factor due to the electron-electron correlation.<sup>18</sup> Taking into account that the orbital contribution vanishes for symmetry reason in the orientation  $\mathbf{H}_0 \parallel c$  axis, the value is estimated between 2 and 4 states per  $\text{eV}^{-1}$  and spin direction which would require a large value of  $\Gamma(\alpha)$  according to band-structure calculations.<sup>19</sup> Although very strong electron-electron correlation has been invoked to explain the NQR data,<sup>20</sup> it is very unlikely that an increase in the correlation could exactly compensate the decrease of  $N_d(E_F)$  so that the NSLRR stays constant when  $\delta$  changes from 0 to 0.25.

The natural interpretation of our NSLRR data is that the removal of oxygen atoms in the chains changes the hole concentration in the oxygen  $p$  band without affecting the electronic structure of the Cu(2) sites. This absence of  $3d$  character in the density of states at the Fermi level leads us to describe the NSLRR in terms of localized spin fluctuations. Let us consider the Cu(2) as a planar set of localized  $\frac{1}{2}$  spins antiferromagnetically coupled by a first-neighbor exchange integral  $J$

$$\mathbf{H} = -J \sum_{i < j} S_i S_j. \quad (2)$$

In standard three dimensional (3D) AF above  $T_N$ , the NSLRR is given in the mean-field approximation by

$$(T_1)^{-1} \propto kT\chi_S \propto (T_{1\infty})^{-1} T/(T - T_N),$$

where  $\chi_S$  is the staggered susceptibility and  $T_{1\infty}$  the

high-temperature limit ( $kT \gg J$ )<sup>21</sup>

$$(T_{1\infty})^{-1} = (2\pi)^{1/2} (2\gamma H_{cp})^2 [S(S+1)/6z]^{1/2} \hbar/J, \quad (3)$$

where  $z$  is the number of nearest neighbors and  $H_{cp}$  the core-polarization field. (We have neglected the dipolar hyperfine field.) In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , we expect the NSLRR to deviate from this behavior for two reasons: (i) the magnetic scattering of the Cu(2) spins by the motion of the holes on the oxygen sites; (ii) the limitation of the correlation length  $\xi$  of the 2D AF correlations in the CuO plane to the mean distance  $d$  between the holes, as observed in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .<sup>22</sup> This stops the divergence of  $\chi_S$  below some temperature  $T^*$  as soon as  $\xi$  becomes limited by  $d$  and thus prevents 3D AF ordering even for  $kT \ll J$ . Let us rewrite the NSLRR as  $(T_1)^{-1} = (T_{1\infty})^{-1} K(\xi, T)$ , where  $K(\xi, T)$  accounts for all the effects of holes on the dynamic susceptibility of the Cu(2) spins. Taking  $J=0.1$  eV as inferred from light scattering experiments,<sup>23</sup>  $z=4$  and  $H_{cp}=-125$  kOe for a free  $\text{Cu}^{2+}$  ion, we obtain  $K(\xi, T) = \frac{1}{7}$  at 300 K. Although the dynamic scattering by the holes is expected to be the dominant reduction mechanism, the absence of divergence of  $\chi_S$  will also provide a factor of the order of  $T/T^*$ . (Because of the 2D character of the exchange, we expect  $T^*$  to be as large as a few times the Néel temperature observed in  $\text{YBa}_2\text{Cu}_3\text{O}_6$ ,  $T_N \approx 450$  K). The dependence of the NSLRR on  $\delta$  in this picture is hard to evaluate quantitatively but we expect it to be small since  $\xi$  should vary at most as the square root of the holes concentration. Further interpretation of the NSLRR data would require a full calculation of the dynamic susceptibility of the Cu(2) spins  $\chi(q, \omega)$  taking into account the motion of the oxygen holes.

However, one also has to explain how the localized spins on the Cu(2) couple to the carriers responsible for the superconductivity so that the relaxation rate decreases below  $T_c$ . Recently, Emery and Reiter<sup>24</sup> have proposed a model in which the charge carrier quasiparticles involve a strong coupling between the fixed Cu spins and the mobile oxygen holes which could provide a basis to solve this problem. Finally, we believe that joint NSLRR data for both Cu and oxygen<sup>25</sup> in the system  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for various values of  $\delta$  should provide a very valuable test for the theoretical description of these new superconducting oxides.

The authors gratefully acknowledge helpful discussion with K. Asayama, V. J. Emery, Y. Kitaoka, and R. E. Walstedt. Laboratoire de Spectrométrie Physique is Laboratoire associé au Centre National de la Recherche Scientifique.

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