^{89}Y NMR Study of the Anisotropy of the Static and Dynamic Susceptibilities in $YBa_2Cu_3O_{6+x}$

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We report ^{89}Y NMR shift (K) and spin-lattice relaxation (T_1) data on oriented $YBa_2Cu_3O_{6+x}$ powders, with $x=1$ and $x=0.64$. The anisotropy of K is shown to be dominated by that of the spin susceptibility on the oxygen sites $\chi_c^{(O)}/\chi_{ab}^{(O)}=1.2\pm0.05$, which agrees with that expected on the Cu sites, and with a single-spin fluid picture for the CuO_2 band. The anisotropy of T_1 is compatible with a nearly isotropic spin lifetime in the $q\sim0$ dynamic susceptibility. Deviations from $T_1TK\sim$const are found at high T for both the underdoped ($x=0.64$) and the overdoped sample ($x=1$).

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A great effort has been devoted these last few years to clarify with microscopic probes the magnetic behavior of 1:2:3 compounds in their normal state. The NMR shifts of ^{89}Y, ^{63}Cu, and ^{17}O provide direct measurements of the susceptibility associated with the CuO_2 planes [1]. The ^{63}Cu nuclear spin-lattice relaxation T_1 is dominated by the components of the dynamic susceptibility $\chi(\mathbf{q},\omega)$ at the antiferromagnetic (AF) wave vector $\mathbf{q}_{AF}=(\pi/a,\pi/a)$ [2,3]. The ^{89}Y [4–6] and ^{17}O [7–10] nuclei, which are located at symmetry centers of the AF unit cell, filter these AF components of $\chi(\mathbf{q},\omega)$ and mainly probe the contributions of the remaining part of the Brillouin zone. A phenomenological model (the MMP model) [11] has been proposed to analyze the NMR data. The lack of experimental results so far has led one to assume an *isotropic* T dependence of $\chi(\mathbf{q},\omega)$. (The anistropy of the T_1 of ^{63}Cu has been found to be fixed by that of the hyperfine coupling on the ^{63}Cu $3d_{x^2-y^2}$ orbitals [12].) Although some ^{89}Y data [13] allowed probing of the anisotropies of the NMR shifts, very few experiments have been performed so far to determine those of the dynamic responses, near $q\sim0$, although some recent results on ^{17}O [10,14] in single crystals reveal unusual behaviors.

In the present paper we report ^{89}Y NMR data taken on oriented powders for $x=1$ and for the $T_c\cong60$ K composition ($x=0.64$). For the former sample, $T_c=92$ K is 1.5 K smaller than for $x=0.95$, and therefore corresponds to a slightly *overdoped* composition. The complete set of data on the NMR shift and T_1 allow us to determine the anisotropy of the spin susceptibility on the oxygen sites. Further, the accurate results for $x=1$ allow us to conclude that $\chi(\mathbf{q},\omega)$, probed at the Y site around $q=0$ scales smoothly from the underdoped to the overdoped regime, a result which differs from recent data on ^{17}O [14].

The NMR data were taken in a field $H=7.5$ T, i.e., at a frequency of $\sim$15.64 MHz, using standard pulse NMR techniques, with a $\pi/2$ pulse width of about 15 μsec. The spectra were obtained as Fourier transforms of the spin-echo signal. The data for $x=1$ were taken on our best sample which, for **H**$\|$c, exhibits a linewidth $\Delta\nu_{1/2}<0.5$ kHz, down to 90 K, narrower than any reported data on $YBa_2Cu_3O_7$, which certifies the good stoichiometry of this sample [15]. For $x=0.64$, $\Delta\nu_{1/2}\sim1$ kHz was found nearly T independent for both directions.

The peak positions of the **H**$\|$c and **H**$\|$a-b lines have been measured over a large T range, for the two samples considered here. The two components of the NMR shift tensor ΔK_c and ΔK_{ab} are plotted in Fig. 1. These results agree with those reported on nonaligned powder samples [5], for which the peak position of the NMR spectrum occurs near the **H**$\|$a-b position. With the excellent accuracy of the present data for the $x=1$ sample, it is clear that for the two spatial directions, $|\Delta K|$ increases with increasing T and then goes through a maximum for $T_m\sim130$ K. The steady decrease of $|\Delta K|$ with increasing T has also been seen by Balakrishnan *et al.* [6] at high T, and the overall variation of $|\Delta K|$ agrees with that observed from 90 to 300 K on the ^{63}Cu NMR shift, for

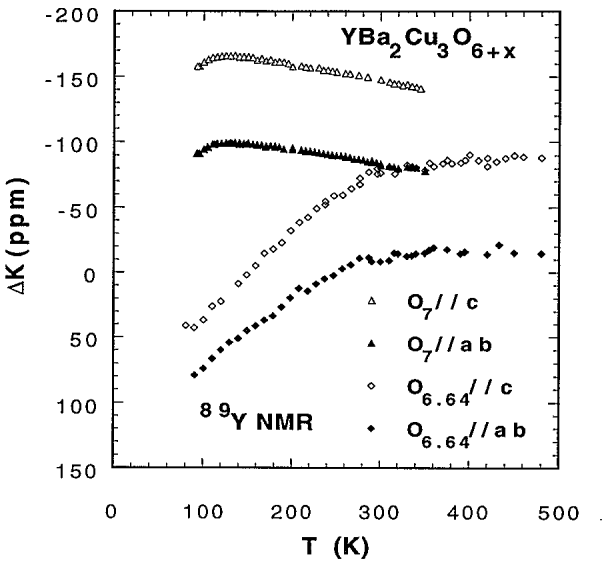

FIG. 1. ^{89}Y NMR shift ΔK, for $x=1$ and 0.64, for **H** parallel to the c axis and to the a-b planes, taken with respect to a reference YCl_3 solution. The origin for the spin contributions to ΔK_{ab} and ΔK_c are, respectively, near $\delta_{ab}=150$ and $\delta_c=135$ ppm (see text).

H||c, by Walstedt *et al.* [16]. For $x=0.64$, $|\Delta K|$ steadily increases and reaches a plateau around 400 K. Although T limitations did not allow us to probe whether $|\Delta K|$ decreases further with increasing T, these results are suggestive of a systematic increase of T_m with decreasing oxygen content from the overdoped to the underdoped regime ($x<0.95$). Indeed, T_m is found at 270 K for $x=0.91$ [15]. This T_m occurs well above the temperature at which a spin gap at $\mathbf{q}_{AF}$ is seen to open in neutron scattering experiments [17]. This might point to the existence of two different lines in the phase diagram. Theories [18] supporting the existence of spin charge separation yield a single crossover to a resonating-valence-bond state. Recently, Fukuyama has suggested that T_m might signal this crossover, while the Fermi-surface-dependent spin gap might occur below [19].

A small but definite $(T_1T)^{-1}$ anisotropy has been detected on both samples (Fig. 2). For $x=1$, $(T_1T)^{-1}$ is nearly constant for both directions, but is seen to decrease below 120 K, well above T_c. For $x=0.64$, it decreases continuously with decreasing T, as for nonoriented powders [5]. As can be easily seen, the $(T_1T)^{-1}$ anisotropy is too small, with respect to that of ΔK, to allow an explanation of the data by an anisotropic hyperfine coupling with a single-site isotropic $\chi(\mathbf{q},\omega)$, as done for the MMP model. A thorough analysis is therefore required.

The NMR shift tensor ΔK_ν (with $\nu=a,b,c$) is the sum of a usually T-independent orbital contribution δ_ν, the chemical shift, and a T-dependent term K_ν, associated with the spin susceptibility χ_ν of the CuO_2 planes. As a given nuclear spin is coupled to the different O and Cu hole spin neighbors j, with distinct hyperfine fields A_ν^j, the NMR shifts can be written as $\Delta K_\nu = K_\nu + \delta_\nu$, with

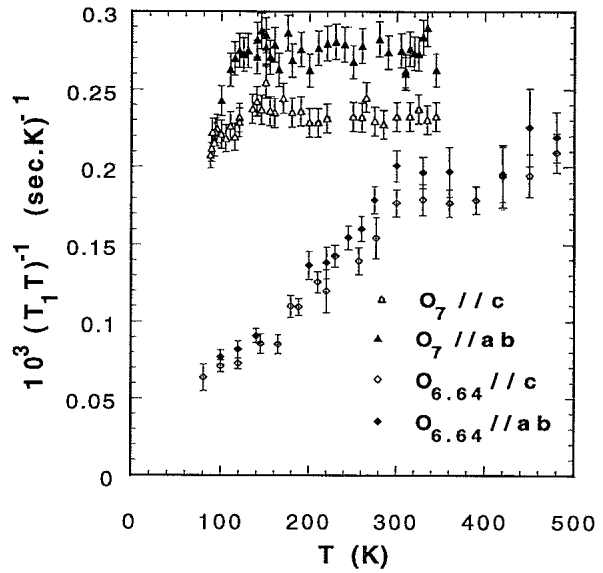

FIG. 2. $(T_1T)^{-1}$ for $x=1$ and 0.64 vs T, for **H** parallel to the c axis and to the a-b plane. The data for $x=1$ are nearly T independent down to 130 K, and slightly decrease below that.

$K_\nu=\sum_j A_\nu^j \chi_\nu^j(T)$. For ^{89}Y, the dominant contribution to $^{89}K_\nu$ is the isotropic negative hyperfine coupling $A^{(O)}$ with the O $2p\sigma$ orbital of the eight near-neighbor oxygens [20]. Anisotropic contributions do result from dipolar couplings A_d with the spins on the O and Cu hole orbitals, and therefore [21]

$$^{89}K_\nu\left(8A^{(O)}+\sum_j A_{d\nu}^j\right)\chi_\nu^{(O)}+\sum_k A_{d\nu}^k\chi_\nu^{(Cu)}, \quad (1)$$

where summations are on the O and Cu lattice sites (j and k, respectively). Previous comparisons of the ^{89}Y shifts on nonoriented powders with the macroscopic χ [5], and with the ^{17}O and ^{63}Cu NMR shifts [8], have allowed one to conclude that the T dependences of $\chi_\nu^{(Cu)}$ and $\chi_\nu^{(O)}$ are identical, and that the isotropic hyperfine fields were independent of doping. Here, we find that $^{89}\Delta K_c$ scales linearly with $^{89}\Delta K_{ab}$ (Fig. 3), and that this linear fit, for $x=0.64$, extends nearly through the data for $x=1$. The slight offset of the two T dependences might be due to a change of the chemical shifts. This absence of variation of the anisotropy shows that no detectable variation of the effective hyperfine field $A_\nu=8A^{(O)}+\sum_j A_\nu^j\chi_\nu^j/\chi_\nu^{(O)}$ occurs between the two samples. From the slope of Fig. 3 we deduce the anisotropy ratio $R=(^{89}K_c-{}^{89}K_{ab})/{}^{89}K_{ab}$, with

$$R=(A_c/A_{ab})(\chi_c^{(O)}/\chi_{ab}^{(O)})-1=0.29\pm0.03. \quad (2)$$

A comparison of the $x=0.64$ results for $^{89}K_{ab}$ with reported ^{63}Cu NMR data in similar samples, with a linear least-squares fit extrapolation to $\chi_\nu^{(Cu)}=0$ [i.e., $^{63}K_{ab}^{(s)}=0$] gives $^{89}\Delta K_{ab}={}^{89}\delta_{ab}\sim150$ ppm [22]. This implies, from Fig. 3, that $^{89}\delta_{ab}-{}^{89}\delta_c=15$ ppm, for $x=0.64$. Using $^{89}K_{ab}={}^{89}\Delta K_{ab}-{}^{89}\delta_{ab}\sim-240$ ppm, for $x=1$ at room temperature, Eq. (3) shows that the spin contribution to the anisotropy in $YBCO_7$, $^{89}K_c-{}^{89}K_{ab}\sim-72$ ppm, dominates over the chemical shift term.

The contribution of the dipolar couplings to the shift anisotropy at room temperature can be calculated, using the isotropic spin susceptibility value of the CuO_2 planes for the $YBCO_7$ composition [12,16] $\chi^{(Cu)}=2\times10^{-6}$ emu/cm^3. With the known atomic distances, the cou-

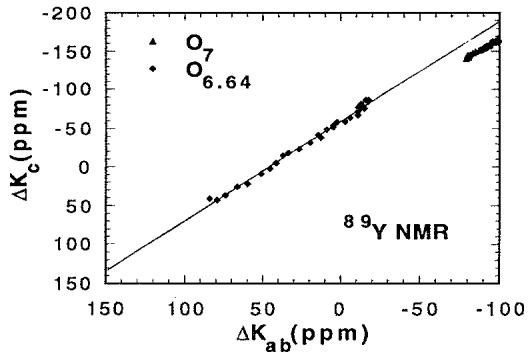

FIG. 3. The NMR shift for **H||c** vs that for **H||a-b**. The linear least-squares fit for $x=0.64$ nearly extends through the data for $x=1$.

pling with the eight near-neighbor Cu holes yields $^{89}(\Delta K_c - \Delta K_{ab})_{dip} = -6.3\chi^{(Cu)} = -12$ ppm, which does not exceed $\frac{1}{16}$ of the observed anisotropy. Summation on all Cu sites in a large sphere, including the Cu(1) sites, increases this number to $\frac{1}{3}$. The contribution of the oxygen sites, with $\chi^{(O)} = 0.15\chi^{(Cu)}$ [8,10], is smaller and of opposite sign, so that the total spin dipolar anisotropy is -20 ppm. With $^{89}K_{ab} = -240$ ppm, we obtain $A_c/A_{ab} = 1.08 \pm 0.02$. Therefore, from Eq. (2), the anisotropy of the ^{89}Y NMR shift is largely due to the anisotropy of $\chi^{(O)}$, with $\chi_c^{(O)}/\chi_{ab}^{(O)} = 1.2 \pm 0.05$.

An anisotropy of χ has not been measured on the Cu sites, but an estimate [16] of the Landé factors g_v, with the crystal field parameters used to describe the Van Vleck χ of the Cu^{2+} orbitals, gives $\chi_c^{T(CU)}/\chi_{ab}^{T(Cu)} = (g_c/g_{ab})^2 = 1.28$, where $\chi_v^{T(Cu)}$ is the total χ of the Cu ionic moment. Our data suggest that $\chi_c^{(Cu)}/\chi_{ab}^{(Cu)} = g_c/g_{ab}$, the anisotropy of spin polarization and spin susceptibility [16] on the Cu site, might be identical to that on the O, which is expected if the latter results from covalency between the Cu and O hole orbitals. This ratio might as well be deduced from the ^{17}O NMR shift data. Indeed, for **H**||c, and for **H** perpendicular to the CuO bond axis, the dominant O and Cu near-neighbor hyperfine fields for ^{17}O are identical, so that one expects $K_c/K_\perp = g_c/g_{ab}$. From the data of Yoshinari, Yasuoka, and Ueda [23], we deduce $K_c/K_\perp = 1.2 \pm 0.1$, which is further evidence that the $\chi^{(O)}$ anisotropy is compatible with Cu-O covalency.

As for T_1, it is dominated by transverse fluctuations of the local field sensed by the nuclear spins, which result from the transverse spin contributions to $\chi(\mathbf{q},\omega)$, and are therefore given by

$$(T_1T)_c^{-1} \propto 2\sum_{j,\mathbf{q}} f^j(q) A_{ab}^{j2} \mathrm{Im}\chi_{ab}^j(\mathbf{q},\omega)/\omega\,, \tag{3}$$

$$(T_1T)_{ab}^{-1} \propto \left\{\sum_{j,\mathbf{q}} f^j(q)[A_{ab}^{j2}\mathrm{Im}\chi_{ab}^j(\mathbf{q},\omega) + A_c^{j2}\mathrm{Im}\chi_c^j(\mathbf{q},\omega)]\right\}\Big/\omega\,, \tag{4}$$

where $f^j(q)$ is the form factor associated with the electronic orbitals j. Here, as the hyperfine couplings are squared, the Cu near-neighbor and macroscopic dipolar terms are now negligible with respect to the isotropic O contribution, and the only terms retained in Eqs. (3) and (4) are with $A_{ab}^{(O)} \approx A_c^{(O)} \approx A^{(O)}$.

Let us recall here that a correlation between $(T_1T)^{-1}$ and ΔK was first revealed in our ^{89}Y NMR measurements on nonoriented powders [5], which, after a correct $^{89}\delta_{ab}$ estimate, led [8,20] to the conclusion that T_1TK = const better describes the data. In Fig. 4, we have plotted $(T_1T)_c^{-1}$ and $(T_1T)_{ab}^{-1}$ vs ΔK_{ab} for both samples. Considering the data below room temperature for $x = 0.64$, as for previous experiments, a linear relation can be found between these quantities, and extends through the $x = 1$ data for both spatial directions. However, the high-T data for $x = 0.64$ departs from this linear fit, even

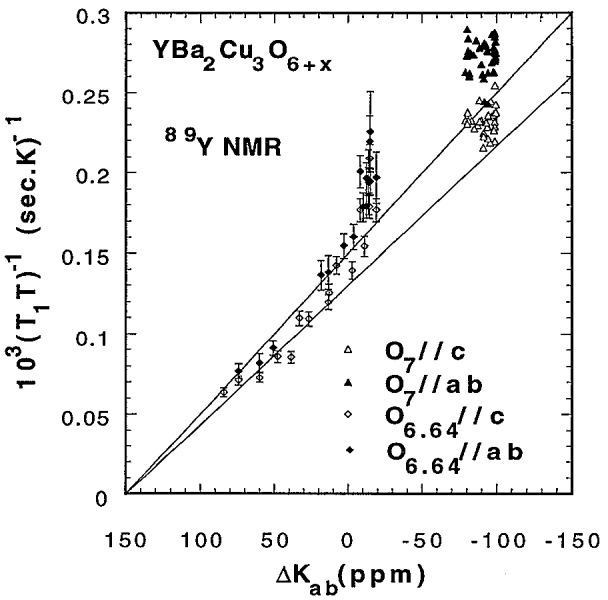

FIG. 4. The data for $(T_1T)^{-1}$ vs ΔK_{ab} for the two samples. Linear relations hold for the data for $T < 300$ K for the $x = 0.64$ sample and extend nearly through the results for $x = 1$. Those plotted here have been forced to extrapolate to zero for $K_{ab} = \delta_{ab} = 150$ ppm.

if we do not impose a vanishing of the relaxation rate for $^{89}\Delta K_{ab} = {}^{89}\delta_{ab} = 150$ ppm.

As for $x = 1$, the T variation of ΔK_{ab} detected here from 150 to 350 K is 7% of the total spin shift. With the poorer accuracy of the T_1 data, we can see in Fig. 3 that $(T_1T)_{ab}^{-1}$ is essentially constant above 150 K. Linear least-squares fits from 150 to 350 K give maximum relative decreases of $(T_1T)^{-1}$ of $2\% \pm 2\%$ and $4\% \pm 2\%$, respectively, for **H**||c and **H**||**a**-**b**. Therefore, T_1TK = const does not seem to hold above T_m for this sample as well. Further, the data differ significantly from those of Horvatic *et al.* on ^{17}O, in a well-oxidized $YBCO_7$ single crystal, with the Ba partly substituted by Sr [14]. If the 30% increase of $(T_1T)^{-1}$ for ^{17}O from 300 to 100 K found by these authors is not a sample artifact linked with the Sr substitution, it might be associated with the decrease of the AF correlation length (about 0.7 lattice constant) detected by neutron scattering [17] for $x = 1$. In such conditions the filtering of the AF fluctuations at the O site might become incomplete with respect to that on the Y site.

Finally, let us consider the anisotropy of the ^{89}Y relaxation rate, which is likely to originate from that of $\mathrm{Im}\chi^{(O)}(\mathbf{q},\omega)$, if $A_v^{(O)}$ is isotropic. If the spin shift anisotropy indeed results from Cu-O covalency, the g factor anisotropy should not appear as such in Eqs. (3) and (4), in a purely ionic picture [24]. However, the spin-orbit-coupling-induced admixture with higher energy levels of the Cu^{2+} ion might still result in an anisotropy of $\mathrm{Im}\chi^{(O)}(\mathbf{q},\omega)$, which is difficult to estimate as the microscopic origin of T_1TK = const is not well understood. An alternative might be to consider $\mathrm{Im}\chi^{(O)}(\mathbf{q},\omega)$ as isotropic,

and that the T_1 anisotropy results from that of $A_\nu^{(O)}$. We are inclined to favor the first possibility as we did not even find a hyperfine coupling giving rise to an anisotropy of the correct sing [20].

In the MMP model, for $\omega \to 0$, $\mathrm{Im}\chi_\nu^{(O)}(\mathbf{q},\omega)/\omega = \mathrm{Im}\chi_\nu^{(O)}$ is assumed to be $\mathbf{q}$ independent, except for a narrow range of $\mathbf{q}$ values near $\mathbf{q}_{AF}$. If the form factor cancels the contributions of the AF correlations, then Eqs. (3) and (4) yield

$$(T_1)_{ab}^{-1}/(T_1)_c^{-1} - 1 = \tfrac{1}{2}\{(A_c^{(O)}/A_{ab}^{(O)})^2 \times (\mathrm{Im}\chi_c^{(O)}/\mathrm{Im}\chi_{ab}^{(O)}) - 1\}, \quad (5)$$

which equals 0.16 ± 0.02, from the data of Fig. 2 or Fig. 4. It is further customary to assume that $\mathrm{Im}\chi^{(O)}(\omega)/\omega = \chi^{(O)}\tau$, where τ is an electronic spin lifetime, so that the linearity of $(T_1T)^{-1}$ vs K implies a T- and doping-independent τ. Extending this phenomenology to anisotropic quantities $\chi_\nu^{(O)}$ and τ_ν, with $\chi_c^{(O)}/\chi_{ab}^{(O)} = 1.2 \pm 0.05$ and $A_c^{(O)}/A_{ab}^{(O)} = 1$, yields $\tau_c/\tau_{ab} = 1.08 \pm 0.09$, implying a nearly isotropic spin lifetime. One can as well conjecture that the scaling between $(T_1T)_\nu^{-1}$ and K_ν might be expressed as $(T_1T)_cK_{ab} = (T_1T)_{ab}(K_c + K_{ab})/2 = \text{const}$.

In conclusion, we emphasized here that, contrary to the case of Cu and O nuclei, the anisotropic couplings of the ^{89}Y spin with the O and Cu hole spins are much smaller than its isotropic coupling with the O holes. The Y nuclei therefore directly probe the anisotropic properties of $\chi(\mathbf{q},\omega)$ near $q = 0$ for the CuO_2 band, which have been deduced from the complete set of data presented here. Although they allow us to confirm that a $T_1TK = \text{const}$ law extends smoothly at low T from the underdoped to the overdoped sample, they lead us to question its validity in the high T range. This suggests a crossover in the physical properties at the temperature T_m of the maximum of the spin susceptibility. Whether T_m corresponds to a transition proposed by theories [18,19], suggesting spin charge separation, is a speculation which would require further experimental support.

Our results allow us to confirm that the anomalous increase of $(T_1T)^{-1}$ observed on ^{17}O at low T in an overdoped sample [14], if not of extrinsic origin, might be due to an incomplete screening of the AF fluctuations at the oxygen site. With the accuracy of the present ^{89}Y data, further quantitative comparison with relevant ^{17}O NMR data might help to refine the phenomenological MMP-like models for $\chi(\mathbf{q},\omega)$. In particular, it is not clear whether the $T_1TK = \text{const}$ law has any relation with that observed in nearly ferromagnetic itinerant systems [25], that is, whether $\chi(\mathbf{q},\omega)$ is peaked at $q = 0$ or is uniform over q space other than near $\mathbf{q}_{AF}$.

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[21] Here, a small eventual isotropic coupling with Cu holes has been neglected as it might be summed up with the isotropic contribution on the O without changing the discussion.
[22] This estimate slightly differs from the value $\sim$200 ppm obtained from earlier comparisons of the ^{63}Cu, ^{17}O, and ^{89}Y NMR data for the isotropic chemical shift $^{89}\delta$, for nonoriented powders, but using 200 ppm would even reduce the value of A_c/A_{ab} to 1.066.
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