17O and 63Cu NMR INVESTIGATION OF SPIN FLUCTUATIONS IN HIGH Tc
SUPERCONDUCTING OXIDES

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INTRODUCTION

Since the discovery of the high Tc superconducting oxides, the electronic structure of these compounds in the normal state (T > Tc) is still a matter of controversy. It was reported early on by Emery 1 that the holes introduced in these materials by doping were primarily going into the O(2p) orbitals, leaving exactly one d-hole at the Cu site (Cu2+) in the CuO2 plane. Neutron inelastic scattering 2 and La NQR 3 in La2−xSr xCuO4 as well as Cu NMR spectroscopy 4-6 and neutron inelastic scattering 7,8 in YBa2Cu3O6+x support this scheme. In YBa2Cu3O7 at least, however, the temperature dependence of the Nuclear Spin Lattice Relaxation Rate (NSLRR)9 and the Magnetic Hyperfine Shift (MHS) 10,11 of the Cu nuclei below Tc imply that these quasi-localized d-holes must be involved in the quasi-particles associated with superconductivity. Thus the nature of the coupling between these copper d-spins and the oxygen p-holes remains a central issue for the theoretical understanding of these high Tc materials 12-15. 17O NMR in these oxides is one of the most powerful tool to address this problem 16-23. In the framework of the so-called t-J model 12,14, this coupling is so strong that a knowledge of the Cu(2) spin dynamical susceptibility $\chi_{Cu}(\vec{q},\omega)$ should allow one to predict all NMR observables at O(2,3) and Y sites in the crystal. In contrast, two spin fluids models imply 15 or strongly suggest 13 the existence of a second spin susceptibility associated with the oxygen p-holes $\chi_{h}(\vec{q},\omega)$ which at least above some temperature $T^* > T_c$ should behave differently from $\chi_{Cu}(\vec{q},\omega)$.

In this paper we want to highlight two points: the first one is the dependence on the stoichiometry of the Cu(2) spin lattice relaxation rate and MHS tensor in YBa2Cu3O7 which support the description of localized d-holes and point out the peculiar behaviour of YBa2Cu3O7 as compared to its oxygen deficient parent compounds, whatever is their Tc value, 90 or 60 K. Secondly, we present the temperature dependence of the MHS tensor and the NSLRR of 17O nuclei in YBa2Cu3O6.65 (Tc = 60 K). The comparison of 17O NMR data (this paper and ref. 18-23) with those obtained for 89Y 24 shows that in this compound, the spins of the p-holes can have their own degree of freedom, at least above 120 K.

EXPERIMENTAL AND SAMPLES

All measurements were performed in a magnetic field H0 = 5.75 T. using pulsed NMR technique. As far as 63Cu NMR is concerned, three samples have been investigated: two "porous" single crystals25 of composition YBa2Cu3O6.9 (sample A) and YBa2Cu3O6.75 (sample B) and an
oriented powder sample YBa$_2$Cu$_3$O$_7$ (Sample C). This later was obtained by retreating under
Oxygen crushed single crystals from the same batch as sample A. The NQR linewidth of sample C
was found equal to 170 kHz (full width at mid height FWMH) which is among the best values
reported in the litterature. As discussed in Ref. 5-6, the distribution of oxygen vacancies in the
CuO$_2$ plane was concluded to be homogeneous in sample A, whereas in sample B, a strong tendency
to short range order has been observed. Details on the preparation of YBa$_2$Cu$_3$O$_6.65$ sample
enriched with $^{17}$O can be found in Ref. 18 and 23. Its oxygen composition was estimated from its
quenching temperature (700°C). Details on powder orientation, the NMR technique and the site
assignment can be found in Ref. 18.

RESULTS AND DISCUSSION

$^{63}$Cu NMR

We first would like to discuss our results on the Magnetic Hyperfine Shift tensor for the
Cu(2) site. We have found its component along the c-axis $K_{cc}$ to be independent of the temperature
(above and below $T_c$) and of the oxygen content: $K_{cc} = 1.28 \pm 0.03 \%$ for samples A and C and $K_{cc} =
1.31 \pm 0.05 \%$ for sample B. The absence of temperature dependence is a clear indication that
this shift is purely orbital, due to some accidental cancellation of the spin contribution for this
orientation of the magnetic field $H_0$. Calculation of the orbital shift in a metallic band picture
involve a summation over $\vec{k}$ of second order matrix elements of the type:

$$
\frac{\langle \vec{k},n| L_1 |\vec{k},n'\rangle \langle \vec{k},n'| L_2 |\vec{k},n\rangle}{E_{\vec{k},n} - E_{\vec{k},n'}} (1 - f_{\vec{k},n}^* f_{\vec{k},n'}^*)
$$

between Bloch states of same $\vec{k}$ and of different band index. In the present case, the $\vec{k},n$ states
belong to the $d_{x^2-y^2}$ band, and the $\vec{k}',n'$ to the other filled d-bands. This quantity should thus
directly reflect the number of holes in the $d_{x^2-y^2}$ band. So the absence of dependence of $K_{cc}$ on the
oxygen composition is a strong evidence that the number of d-holes stays constant at least in the
stoichiometry range $\delta = 0 - 0.35$ and finds its natural explanation in a description where the d-
holes are quasi-localized (Cu$^{2+}$) in which case the orbital shift is an atomic quantity.

Let us now discuss the Cu(2) NSLRR. Results for samples A, B, and C are reported in Fig.
1. A sharp transition is observed at 90 K for sample C. The results are in excellent agreement with

![Fig. 1](image_url)

Fig. 1 Nuclear spin-lattice relaxation rate of $^{63}$Cu(2) in $\delta = 0$ (+) oriented powder
(sample C) and $\delta = 0.1$ (□) and $\delta = 0.25$ (■) single crystals.