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NMR investigation of single-crystal $YBa_2Cu_3O_{6+x}$ from the underdoped to the overdoped regime

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^{17}O and ^{63}Cu NMR results obtained in three single crystals of $YBa_2Cu_3O_{6+x}$, $YBa_{1.92}Sr_{0.08}Cu_3O_7$ ($T_c=89$ K) which is overdoped, and $YBa_{1.93}Sr_{0.07}Cu_3O_{6.92}$ ($T_c=91$ K) and $YBa_2Cu_3O_{6.52}$ ($T_c=59$ K) which are underdoped, show that the static spin susceptibility and $(T_1T)^{-1}$ for Cu(2) and O(2,3) have completely different temperature dependence according to the regime and irrespective of T_c. The principal characteristic of the underdoped regime is the opening of a pseudogap in the magnetic excitations well above T_c, supporting the phase diagram based on the spin-charge separation. The contribution of the antiferromagnetic fluctuations at the O(2,3) sites have been observed in $YBa_{1.92}Sr_{0.08}Cu_3O_7$, in good agreement with the inelastic-neutron-scattering results.

The possibility of describing the whole phase diagram, from antiferromagnetism to superconductivity, by simply changing the oxygen concentration in the CuO chains[1] has promoted $YBa_2Cu_3O_{6+x}$ to a model system for high-T_c superconducting oxides. Recently, a careful analysis of the phase diagram of $YBa_2Cu_3O_{6+x}$ by Graf, Triscone, and Muller[2] has revealed that close to the maximum concentration of oxygen, one moves from an underdoped regime (T_c increases with the number of holes) with a maximum of $T_c=94$ K for $x=0.94$, to an overdoped regime for $0.94<x<1$ with T_c decreasing on further doping down to 92 K. The existence of two distinct regimes in the so-called "90-K plateau" has been confirmed by several macroscopic techniques.[3,4] Theoretically, it has been predicted by Suzumura, Hasegawa, and Fukuyama[5] and Nagaosa and Lee[6] in the framework of the spin-charge separation[7] that the normal state in the underdoped and overdoped regimes should be quite different. For hole concentrations δ smaller than δ_c (which corresponds to the maximum of T_c), when lowering T, the system should first cross over from a "strange metal," in which holons and spinons are decoupled, into a resonating-valence-bond (RVB) state, and then undergo a Bose condensation at $T=T_c$. For overdoped compounds ($\delta>\delta_c$), there is a transition line below which holons condense and the system becomes a Fermi liquid, before undergoing a BCS-type transition at T_c. When the coupling between the spinons and holons by the gauge field is introduced, the phase diagram is modified;[6] there is a range of concentration close to the underdoped regime for which the precursor state to the superconductivity is a strange metal, instead of a Fermi liquid.

For the NMR point of view several authors[8,9] pointed out that overdoped and underdoped high-T_c superconductors exhibit different behaviors. In underdoped compounds, the magnetic hyperfine shifts (MHS's) for all nuclei of the CuO_2 plane (or within the sandwich made of neighboring CuO_2 planes) probe the same unique spin susceptibility χ_S which is decreasing with the temperature (T). For O(2,3) and Y sites, the nuclear spin-lattice relaxation rate (NSLRR) divided by $T(T_1T)^{-1}$ is proportional to χ_S, while for Cu(2) nuclei it passes through a maximum for a temperature T^* well above T_c. These features apply to $YBa_2Cu_3O_{6+x}$ ($x<0.94$),[10–15] $YBa_2Cu_4O_8$,[16] annealed $Bi_2Sr_2CaCu_2O_8$,[17] and to $La_{1-x}Sr_xCuO_4$,[18] although here the existence of a temperature T^* around 50 K is more controversial.

For overdoped compounds [$YBa_2Cu_3O_7$, $Tl_2Sr_2CaCu_2O_8$,[19] as-grown $Bi_2Sr_2CaCu_2O_8$ (Ref. 17)], the spin susceptibility is flat or rather increasing when T decreases from room temperature down to T_c. It has been claimed that for O(2,3) nuclei a Korringa law is obeyed;[20] whether this point is true or not will be discussed later. The striking difference with the underdoped compounds is that the Cu(2) $(^{63}T_1T)^{-1}$ continuously increases when T decreases from 300 K to T_c, and then drops abruptly. Indeed, a drastic difference in the temperature (T) dependence of the $(^{63}T_1T)^{-1}$ between $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{6.9}$ was first pointed out by Horvatić *et al.*[21] However, this difference was attributed to the disorder present in the substoichiometric phase, which induces a crossover from a metallic to nonmetallic conductivity along the c axis. Later, $(^{63}T_1T)^{-1}$ data in $YBa_2Cu_4O_8$ (Ref. 16) revealed the same behavior as for $YBa_2Cu_3O_{6.9}$, i.e., a maximum well above T_c, although the former is an ordered and stoichiometric compound, thus indicating that this behavior is related rather to the hole concentration in the CuO_2 planes.

In this paper, we compare the NMR properties—T dependence of the spin susceptibility and of the NSLRR for Cu(2) and O(2,3) sites—in $YBa_2Cu_3O_{6+x}$ single crystals of compositions belonging either to the overdoped ($x=1$) or to the underdoped ($x=0.92,0.52$) regime. To clarify the origin of the Cu(2) NSLRR temperature

dependence in both regimes, $(^{63}T_1T)^{-1}$ has been measured on the very same samples ($x=1,0.92$) as those studied by the inelastic neutron scattering (INS) by Rossat-Mignod *et al.*[22,23] We show that $(^{17}T_1T)^{-1}$ for the $x=1$ sample is increasing when T decreases from 300 K to T_c, a behavior which can be quantitatively explained as due to the antiferromagnetic fluctuations (AFF's), using the INS data. The overall data are in fair agreement with the phase diagram mentioned above, thus putting severe constraints to any comprehensive microscopic theory of these compounds.

The NMR measurements were carried out on four "porous" single crystals[24] corresponding to the following compositions: $YBa_{1.92}Sr_{0.08}Cu_3O_7$ (sample 1, $T_c=89$ K), $\approx YBa_{1.92}Sr_{0.08}Cu_3O_7$ (sample 1a, $T_c=91$ K), $YBa_{1.93}Sr_{0.07}Cu_3O_{6.92}$ (sample 2, $T_c=91$ K), and $YBa_2Cu_3O_{6.52}$ (sample 3, $T_c=59$ K). Samples 1 and 3 were enriched in ^{17}O whereas sample 1a and 2 are pieces of the single crystal used for neutron experiments by Rossat-Mignod *et al.*[22,23] As will be discussed below, samples 1, 1a, and 2 belong to the overdoped and underdoped regimes of the so-called "90-K phase," respectively. Details of the sample characterization and experimental setup can be found elsewhere.[9]

The Cu(2) $(T_1T)^{-1}$ data are plotted in Fig. 1, where we have also included the data from a $YBa_2Cu_3O_7$ oriented powder sample [with $T_c=92$ K (Ref. 21)], obtained by grinding porous single crystals. There are two clearly distinct behaviors: For the two O_7 samples ($T_c=92$ and 89 K), $(^{63}T_1T)^{-1}$ continuously increases when T decreases from 300 K to T_c, and then drops abruptly [Fig. 1(a)]. For samples 2 ($T_c=91$ K) and 3 ($T_c=59$ K), $(^{63}T_1T)^{-1}$ passes through a maximum around $T^*=130$ K, irrespective of the T_c value. Such behavior was first reported by Horvatić *et al.*,[14] and Warren *et al.*[15] for the 60-K phase.

These results are now fully corroborated by the inelastic neutron scattering; in Fig. 2(a) [2(b)] the T dependence of $(^{63}T_1T)^{-1}$ in sample 1a (sample 2) is compared to $\chi''[Q_{AF}, \hbar\omega=15\ (10)$ meV] (Refs. 22 and 23) as given by the INS. Remembering that $(T_1T)^{-1} \propto \sum_q |A_q|^2 \chi''(\mathbf{q},\omega_n)/\omega_n$, the fine agreement between the NMR and INS data means that the Cu(2) NSLRR is dominated by the contribution of the AFF to $\chi''(\mathbf{q},\omega)$. Neutron data[22,23] indicate that the decrease of $(^{63}T_1T)^{-1}$ below $T^* \cong 130$ K is due to the opening of a pseudogap in the magnetic excitations, i.e., due to a transfer from low energy to high energy in the spectral weight of magnetic excitations.

As regards the NMR of O(2,3) nuclei, we first consider the T dependence of the spin susceptibility $\chi_S(T)$, which is directly related to the spin part of the MHS tensor $^{17}\mathbf{K}$ experienced by the O(2,3) nuclei by: $^{17}K_{\alpha\alpha} \propto {}^{17}C_{\alpha\alpha}\chi_S$, where α refers to the principal axis of the MHS and electric field gradient tensors (i.e., X parallel to the c axis, Y perpendicular, and Z parallel to the Cu-O-Cu bond in the a,b plane), and $^{17}C_{\alpha\alpha}$ is the hyperfine field. Figure 3(a) shows the $^{17}O(2,3)$ MHS results in sample 1. Note that $K_{\alpha\alpha}$ increases slightly with T decreasing from 300 K to T_c, which means that the spin susceptibility is not flat, but slightly increases as already noticed in Cu(2) (Ref. 25) and Y (Ref. 26) MHS. This could be compatible with the Pauli susceptibility of a Fermi liquid in a narrow band metal. Experimentally, it appears to be the signature of overdoped samples, which is the case of pure $YBa_2Cu_3O_7$.[2]

In contrast, the MHS of sample 3 corresponding to the underdoped regime [Fig. 3(b)] exhibits a strong T dependence as already reported in 60-K phase samples.[11,13,27,28] The relationship between K_{ZZ} and K_{YY} is linear[27] in agreement with the single spin-fluid model (sample 3). No definite theory is available yet to explain the strong continuous decrease of $\chi_S(T)$ with T, except recent quantum dynamical Monte Carlo calculations.[29]

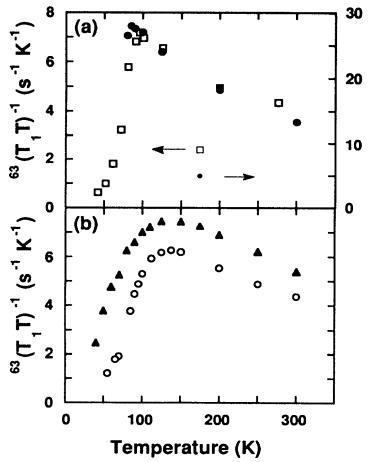

FIG. 1. Temperature dependence of $^{63}(T_1T)^{-1}$ in (a) the overdoped regime: □, $YBa_2Cu_3O_7$ (oriented powder, Ref. 3); ●, $YBa_{1.92}Sr_{0.08}Cu_3O_7$ (single crystal, $H_0 \| a,b$ plane); and (b) the underdoped regime: ○, $YBa_{1.93}Sr_{0.07}Cu_3O_{6.92}$ (single crystal, $H_0 \| c$ axis); ▲, $YBa_2Cu_3O_{6.52}$ (single crystal, $H_0 \| c$ axis).

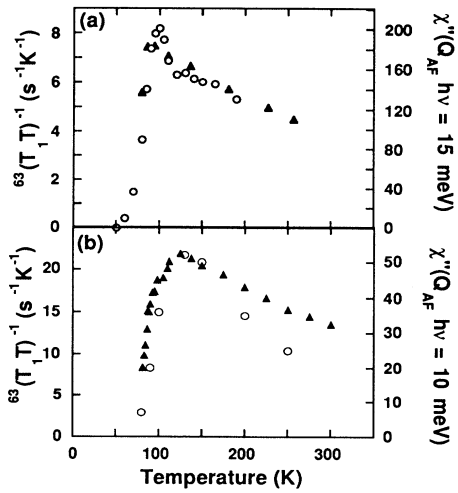

FIG. 2. Comparison between the temperature dependence of $^{63}(T_1T)^{-1}$ and $\chi''(Q_{AF},\omega)$ at a fixed small value of ω in (a) the $YBa_{1.93}Sr_{0.07}Cu_3O_7$ single crystal (overdoped regime): ▲, $^{63}(T_1T)^{-1}$ ($H_0=10.3$ $T \| c$ axis); ○, $\chi''(Q_{AF}, \omega=15$ meV); and in (b) the $YBa_{1.93}Sr_{0.07}Cu_3O_{6.92}$ single crystal (underdoped regime): ▲, $^{63}(T_1T)^{-1}$ ($H_0=5.7$ $T \| a,b$ plane); ○, $\chi''(Q_{AF}, \omega=10$ meV).

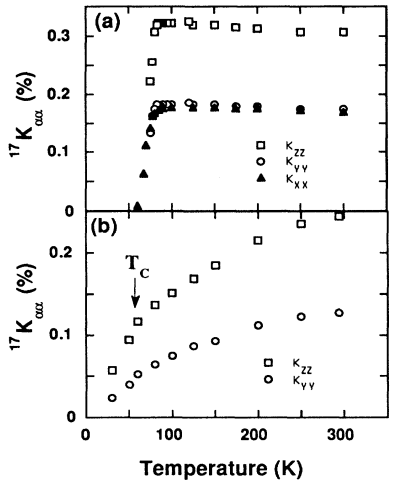

FIG. 3. Temperature dependence of the principal components of the MHS tensor for O(2,3) sites in (a) $YBa_{1.92}Sr_{0.08}Cu_3O_7$ and (b) $YBa_2Cu_3O_{6.52}$.

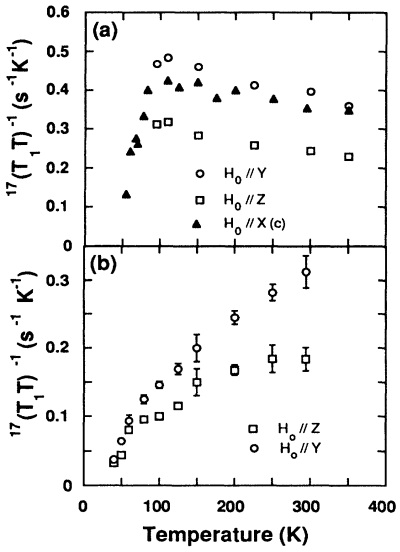

FIG. 4. Temperature dependence of $^{17}(T_1T)^{-1}$ for O(2,3) sites in (a) $YBa_{1.92}Sr_{0.08}Cu_3O_7$ and (b) $YBa_2Cu_3O_{6.52}$.

However, in the scenario proposed by Nagaosa and Lee,[6] this should be due to pairing of spinons. Experimentally, it is obviously related to the opening of a (pseudo-)gap.

Figure 4(a) shows the T dependence of the NSLRR for O(2,3) nuclei in sample 1 for the three orientations of the applied external magnetic field H_0.[30] The striking feature of these data is that $(^{17}T_1T)^{-1}$ also continuously increases on decreasing T from 350 K down to T_c,[27,30] although this increase is much less pronounced than that for the Cu(2) $(^{63}T_1T)^{-1}$. (As in the MHS data, the increase is more pronounced when H_0 is in the a,b plane.) Note that in $YBa_2Cu_3O_7$ only T-independent behavior has been reported so far[13,20] corresponding to the c-axis component of NSLRR measured on oriented powders. One possible explanation is that in these cases the T dependence has been masked by experimental errors, relatively limited temperature range, and by the fact that in these samples one actually observes a small "precursor decrease" of NSLRR somewhat above T_c—which flattens out the $(^{17}T_1T)^{-1}$ vs T dependence, which may be specific to the orientation of the magnetic field H_0 along the c axis.

The behavior of $(^{17}T_1T)^{-1}$ in $YBa_2Cu_3O_{6.52}$ is quite different, as is shown in Fig. 4(b). It continuously decreases with T, and at T_c only a small change in the slope can be noticed. Plotting $(^{17}T_1T)^{-1}$ versus K_{zz} demonstrates that for $H_0 \| Y$ the $(^{17}T_1T)^{-1}$ is accurately proportional to the spin part of the MHS.[27] Similar results have been reported in the 60-K phase for $H_0 \| X$ (c axis).[11,13] However, if we now turn to the data measured with $H_0 \| Z$, we see that such a relationship no longer holds, which has the important consequence that the NSLRR anisotropy is now T dependent,[27] in contrast to the behavior observed in $YBa_{1.92}Sr_{0.08}Cu_3O_7$.[27,30] Such a T dependence of the NSLRR anisotropy for H_0 in the a,b plane was reported by Barriquand, Odier, and Jérome[31] in a $YBa_2Cu_3O_{6.5}$ single crystal.

It is now widely recognized that the different T dependences of the NSLRR for Cu(2) and O(2,3) result from the filtering of the AFF's at the O(2,3) site, because of its symmetric position between its two Cu(2) first neighbors.[20] Since in substoichiometric samples $(^{17}T_{1_\alpha}T)^{-1}$ ($\alpha = X, Y$) depends linearly on $\chi_S(T)$,[13,27] a decomposition of the dynamic susceptibility has been proposed:[32] $\chi''(\mathbf{q},\omega) = \pi\omega\chi_S(T)/\Gamma + \chi''_{AF}(\mathbf{q},\omega)$.[33] Because of the filtering form factor, the contribution of $\chi''_{AF}(\mathbf{q},\omega)$, which is peaked around $Q=(\pi/a,\pi/a)$, vanishes and $(^{17}T_1T)^{-1} \propto \chi_S(T)$. We interpret the deviation from this behavior for $(^{17}T_{1_Z}T)^{-1}$ as the appearance (in addition to the spin mechanism) of an extra contribution which develops close to T_c, and could be due to spinless $2p$ holes.[34]

We return to the results in the overdoped regime. From Figs. 3(a) and 4(a) we see that $(^{17}T_1T)^{-1}$ increases faster than $^{17}K_{\alpha\alpha}$ when T decreases, so that these values are no longer proportional as in the 60-K phase. One possible explanation is that the filtering of the AFF's is no longer as perfect, due to a shortening of the AF correlation length.[30] Indeed, the variation of oxygen $(K^{spin}T_1T)^{-1}$ due to T dependence of AFF's [measured by copper $(^{63}T_1T)^{-1}$] can be very well accounted for[34] if from neutron data[23] we take the corresponding q width of χ''_{AF} ($\Delta q = 0.27$ r.l.u) and assume the Gaussian (or even better multi-Gaussian) shape of $\chi''_{AF}(\mathbf{q})$ corresponding to the minimization of the total width of $\chi''_{AF}(\mathbf{q})$. Note that the squared Lorentzian proposed by Millis, Monien, and Pines[32] is definitely too wide, and implies variations of $(K^{spin}T_1T)^{-1}$ which are much stronger than the observed ones.

It is interesting to remark that in fact the experimental data satisfy Korringa law $K^2T_1T = \text{const}$ quite well.[9] However, to view this behavior as a signature of a Fermi liquid, we have to suppose that AFF's of Cu(2) spins do not contribute to O(2,3) NSLRR at all, that the relaxation is due to a single process, and that for some reason

the corresponding density of states at the Fermi level is slightly T dependent. It is clear that at least the first condition is not fulfilled; for the given small T dependences of $^{17}\mathbf{K}$ and $(^{17}T_1T)^{-1}$, it is then impossible to make a reliable decomposition to different contributions and for the moment we are unable to distinguish the Fermi-liquid behavior evens if it exists. However, it must be noticed that according to the most recent phase diagram predicted by Lee and Nagaosa, one expects that our overdoped sample lies in the concentration range corresponding to a strange metal rather than to a Fermi liquid. We hope that ^{89}Y data (taken on the same sample) might help to reduce the ambiguity in the analysis.

In conclusion, we have shown in $YBa_2Cu_3O_{6+x}$ that depending on the hole concentration in the CuO_2 plane, the low-energy excitations around $\mathbf{Q}=(\pi/a,\pi/a)$ and $\mathbf{q}=\mathbf{0}$, as well as the static susceptibility, exhibit drastically different behaviors; in the underdoped regime ($x<0.94$), the decrease of the static susceptibility $\chi_S(T)$, the opening of a "gap" in the spin excitations at T well above T_c, the proportionality between $(^{17}T_1T)^{-1}$ and $\chi_S(T)$, and the T dependence of the O(2,3) NSLRR above T_c are signatures of a strange metal. For $x=1$, corresponding to a slightly overdoped compound (compared to the maximum value, T_c is decreased by only 2%), the gap for spin and charge excitations opens at the same temperature T_c and a pseudo-Korringa behavior is recovered. The crossover between the two regimes occurs in a very narrow range of oxygen concentration just *within* the so-called 90-K plateau in $YBa_2Cu_3O_{6+x}$. Such different behaviors for underdoped and overdoped compounds can also be recognized in other compounds, e.g., in $YBa_2Cu_4O_8$ (Ref. 16) and $Bi_2Sr_2CaCu_2O_8$ (Ref. 17), but for the moment, only the $YBa_2Cu_3O_{6+x}$ system offers the possibility to switch continuously from one regime to the other. These features, in particular the existence in the whole underdoped regime of two different temperatures, corresponding to the onset of the gaps for spin and charge excitations, which reduce to the same one in the overdoped case, strongly support the recent phase diagram based on the spin-charge separation[6] which for $T>T_c$ predicts a crossover from an RVB to a strange metal state when increasing the hole concentration. However, dimensionality effects, like a crossover from a two-dimensional to a three-dimensional electron gas, should also be considered.

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[33]Note that in a usual Fermi-liquid description, $\hbar\Gamma \propto N(E_F)^{-1}$ and should vary as $\chi_S(T)^{-1}$, while here Γ is constant.

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