Using Ni Substitution and ^{17}O NMR to Probe the Susceptibility $\chi'(\mathbf{q})$ in Cuprates

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We present CuO_2 plane ^{17}O NMR measurements for Ni-substituted $YBa_2Cu_3O_{6+y}$. The Ni moment induces an oscillatory spin density responsible for the broadening of the NMR line. In slightly overdoped $y = 1$ compounds, this broadening scales with the Ni susceptibility. In contrast, such a scaling is not found in underdoped $y = 0.6$ samples. We associate it with the T dependence of the antiferromagnetic staggered spin susceptibility $\chi'(\mathbf{Q}_{\mathrm{AF}})$ intrinsic to the CuO_2 planes. Discussion with respect to ^{63}Cu NMR transverse relaxation (T_{2G}) and neutron scattering data shows that the AF correlation length ξ is T independent. [S0031-9007(97)03937-9]

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The normal state of high-T_c superconductors exhibits a peculiar magnetic behavior, distinct from that of a normal metal [1]. In the underdoped regime, well above T_c, the static susceptibility $\chi(\mathbf{q} = 0)$ shows an anomalous "pseudogap" decrease with decreasing temperature T [2]. Simultaneously, antiferromagnetic (AF) correlations occur within the CuO_2 planes, as evidenced by an enhancement of the imaginary part of the susceptibility χ'' near the AF wave vector seen both in neutron scattering [3] and ^{63}Cu NMR longitudinal relaxation time [4]. These AF correlations might play a crucial role in the mechanism of superconductivity in these materials [5]. Thus, the AF correlation length ξ and both the imaginary and the real part of the staggered susceptibility at $\mathbf{Q}_{\mathrm{AF}}$ are major parameters for any coherent description of the cuprates. No clear experimental agreement on the T dependence of ξ and $\chi'(\mathbf{q})$ is yet achieved. An integral information on $\chi'(\mathbf{q})$ is available through ^{63}Cu transverse relaxation data ($^{63}T_{2G}$) [6–9]. These data are usually analyzed as an increase of ξ at low T [10], whereas neutron experiments for χ'' suggest that ξ is T independent in $YBa_2Cu_3O_{6+y}$ [3]. No other technique has been used up to now to determine $\chi'(\mathbf{q})$ at $\mathbf{q} \neq 0$.

We propose here a new approach to probe $\chi'(\mathbf{q})$, using magnetic impurity substitution effects in the CuO_2 planes. The impurity magnetic moment $g\mu_B\langle S_Z\rangle$ acts as a local field $\mathbf{H}(\mathbf{r}) \propto \langle S_Z\rangle\delta(\mathbf{r})$, which induces an in-plane spin polarization $\mathbf{s}(\mathbf{r}) \propto \chi'(\mathbf{r})\langle S_Z\rangle$. This polarization may be probed by the NMR of nuclei coupled to the planes: at $\mathbf{r}$ from the impurity, the NMR frequency shift $\delta\nu \propto H_{\mathrm{hf}}\chi'(\mathbf{r})\langle S_Z\rangle$ is due to the hyperfine coupling H_{hf} with the spin density. Hence, the broadening due to the shift distribution among the nuclei yields information on $\chi'(\mathbf{r})$. We will show here that the use of the ^{17}O NMR probe allows us, for the first time, a thorough investigation of $\chi'(\mathbf{r})$. This approach contrasts with the usual impurity studies of the specific properties of the magnetic defects [11] and their influence on superconductivity [12]. We find an anomalously large T variation of the ^{17}O linewidth for the underdoped composition. The specific geometry of the ^{17}O nuclei within the planes allows us through extended numerical simulations to demonstrate that the ^{17}O linewidth probes the amplitude of $\chi'(\mathbf{Q}_{\mathrm{AF}})$ rather than ξ. Comparison with $^{63}T_{2G}$ shows that ξ is nearly T independent, in opposition with previous analyses. On the contrary, no anomalous variation of the ^{17}O linewidth is found for the slightly overdoped compounds. This difference contrasts with the similar relative T variations of $^{63}T_{2G}$ found for the overdoped and underdoped regime [8] and emphasizes the existence of a qualitative difference between these two regimes.

In this framework, we have chosen Ni as a local perturbation nearly independent of the hole content. Indeed, SQUID measurements show that the Ni susceptibility follows a pure $1/T$ Curie law down to T_c, with an effective moment per impurity $p_{\mathrm{eff}} = 1.9\mu_B$ for $YBCO_{6.6}$ (hereafter $O_{6.6}$) and $p_{\mathrm{eff}} = 1.6\mu_B$ for $YBCO_7$ (hereafter O_7) [13]. It contrasts with the case of Zn, for which p_{eff} decreases by a factor of 2.4 from $O_{6.6}$ to O_7. Most NMR studies on impurity effects have been carried out with ^{89}Y or ^{63}Cu [11,12,14,15]. For ^{63}Cu nuclei, the large H_{hf} leads to NMR spectra too broad to allow standard NMR Fourier transform spectroscopy. By contrast, for the ^{89}Y nuclei, H_{hf} is so small that the dipolar and the indirect polarization broadenings are found comparable in the case of Ni [16]. These two contributions are therefore hard to separate. Intermediate between these two cases, the ^{17}O nuclei optimally probe only the induced spin polarization.

The single crystal grain powders were prepared by standard solid-state reaction techniques. We have performed $^{17}O(I = \frac{5}{2})$ exchange as ^{16}O does not carry any spin. The samples were annealed at 500 °C, for 48 h in a O_2 (50% ^{17}O) atmosphere, leading to an enrichment of 8% to 11% per oxygen site. The O_7 samples were obtained by oxidation at 300 °C in $^{16}O_2$ atmosphere. The reduction to the $O_{6.6}$ composition by heating under vacuum was controlled by thermogravimetric measurements. The powders mixed

with Stycast epoxy were then aligned by curing in a 7.5 T field ($\mathbf{c}\|\mathbf{H}$). The critical temperature T_c as determined by SQUID measurements was found to decrease linearly with nickel concentration [13]. The ^{17}O NMR spectra were obtained from a standard $\frac{\pi}{2} - \pi$ pulse sequence, in a field $\mathbf{H_0}\|\mathbf{c}$. The ^{17}O NMR shifts were measured with respect to the water frequency ($\nu_0 = 43.2524$ MHz). The quadrupolar second order shifts caused by electric field gradients on the $\frac{5}{2}$ spin of ^{17}O were taken into account using already known quadrupolar parameters [17]. In the central transition $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ of the NMR spectra, three lines are resolved. They correspond to the apical oxygen, the plane oxygen, and an unidentified one probably due to an intrinsic default (also seen in [18]). In our samples, the chain site could not be distinguished, probably because our enrichment procedure reduces the ^{17}O content of the chains.

With Ni substitution, we find that the ^{17}O planar NMR lines are symmetrically broadened for both $O_{6.6}$ and O_7. Their position, which represents the intrinsic average spin susceptibility of the CuO_2 planes, remains unchanged. As the latter is very sensitive to the doping, we conclude that the density of carriers is not affected by substitution of Ni. The pseudogap behavior at $\mathbf{q} = 0$, i.e., the decrease of the static susceptibility with decreasing temperature for $O_{6.6}$ compounds, is not modified either. This confirms that nickel creates only a local perturbation, as already pointed out for the case of zinc [11].

The observed widths of the planar oxygen line are plotted in Fig. 1 [19]. In comparison, the T-dependent broadening effects on the apical oxygen line are quite negligible. The dipolar couplings with the Ni moment are identical for both sites. The observed broadening of the planar line with respect to the linewidth of the pure material $\Delta\nu_{\text{pure}}$ is therefore only due to the indirect coupling with the nickel moment through the CuO_2 planes spin density [20]. Indeed, in presence of impurities, a spin polarization proportional to $\chi'(\mathbf{r})$ is induced. Since the NMR spectrum is a mere histogram of the local fields among all ^{17}O nuclear sites, its width represents the spatial distribution of $\chi'(\mathbf{r})$. In a free electron 2D metal, the susceptibility $\chi'(\mathbf{r}) \propto n(E_F)\cos(2k_F r)/r^2$ induces a broadening [21]

$$\Delta\nu_{\text{imp}} = (\Delta\nu_{\text{Ni}} - \Delta\nu_{\text{pure}}) \propto n(E_F)\langle S_Z\rangle x\,, \qquad (1)$$

where $n(E_F)$ is the density of states at the Fermi level. As $\langle S_Z\rangle$ follows a $1/T$ Curie law for all the samples considered here, the variation of $T * \Delta\nu_{\text{imp}}$ versus T directly reflects the quantity $n(E_F)x$ in this approach. We find this quantity to be nearly constant with T within our experimental accuracy for O_7:Ni samples, as presented in Fig. 2 for $x = 2\%$, and already seen by ^{89}Y NMR for Zn substituted samples. The magnitude of $C = T\Delta\nu_{\text{imp}}$ mostly determined from the low-T data is plotted in Fig. 3(a). It scales linearly with concentration x, as expected from Eq. (1). In this formulation, the T variations of $T\Delta\nu_{\text{imp}}$ for $O_{6.6}$ should represent the variation of $n(E_F)$. In a Fermi-liquid picture, $n(E_F)$ should be proportional to $\chi'(\mathbf{q} = 0)$, and should therefore decrease at low T for $O_{6.6}$ because of the pseudogap. In contrast, we find a strong increase of $T\Delta\nu_{\text{imp}}$ at low T for all Ni concentrations, as shown in Fig. 2 for $x = 2\%$. This drastic change in the T dependence is a new strong evidence of *non-Fermi-liquid behavior* of underdoped compounds. Nevertheless, an oscillating spin polarization occurs within the planes as the line shapes are still symmetrical. In contrast, if the spin density was ferromagnetically polarized by the Ni, the ^{17}O line would be broadened only on the high frequency side. Therefore, any model for χ' must account for an oscillating spin polarization and for an increase of $\chi'(\mathbf{r})$ with decreasing T below 200 K.

Neutron scattering data in the underdoped compounds unambiguously show the existence of a peak at

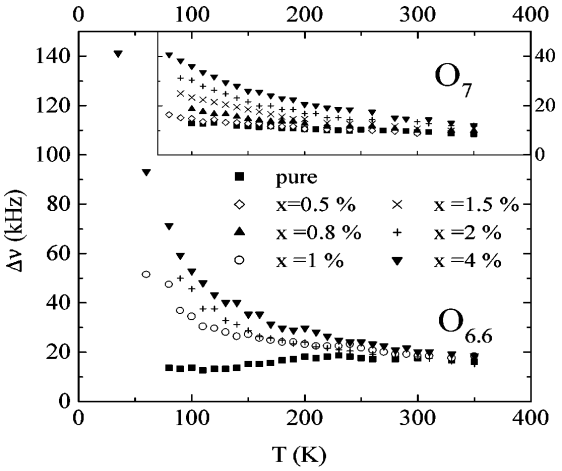

FIG. 1. Full width at half maximum of the CuO_2 plane ^{17}O NMR line for optimally doped $YBa_2(Cu_{1-x}Ni_x)_3O_7$ (right axis, upper curves) and $YBa_2(Cu_{1-x}Ni_x)_3O_{6.6}$ (left axis, lower curves).

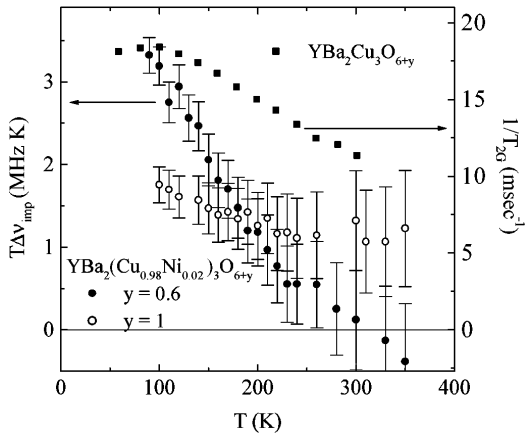

FIG. 2. Plot of $T\Delta\nu_{\text{imp}}$ for $x = 2\%$ where $\Delta\nu_{\text{imp}}$ is the Ni contribution to the width of the planar ^{17}O NMR line (left axis). The large T-variation found in $O_{6.6}$ contrasts with the nearly T independent values in O_7. The ^{63}Cu $1/T_{2G}$ data of Ref. [7] are reported for a pure $O_{6.6}$ compound (right axis).

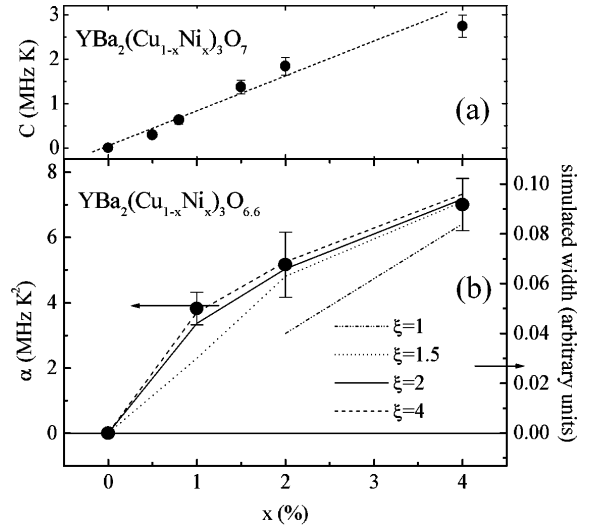

FIG. 3. (a) Concentration dependence of C obtained from fits with $\Delta\nu_{\rm imp} = C/T$ for $YBa_2(Cu_{1-x}Ni_x)_3O_7$. A linear fit to the data is shown. (b) Concentration dependence of α obtained from phenomenological fits with $\Delta\nu_{\rm imp} = \alpha/T^2$ for $YBa_2(Cu_{1-x}Ni_x)_3O_{6.6}$ (black circles, left axis). The different broken lines correspond to simulated NMR widths for the antiferromagnetic Gaussian model of $\chi'(\mathbf{r})$ given by Eq. (3) for different values of ξ.

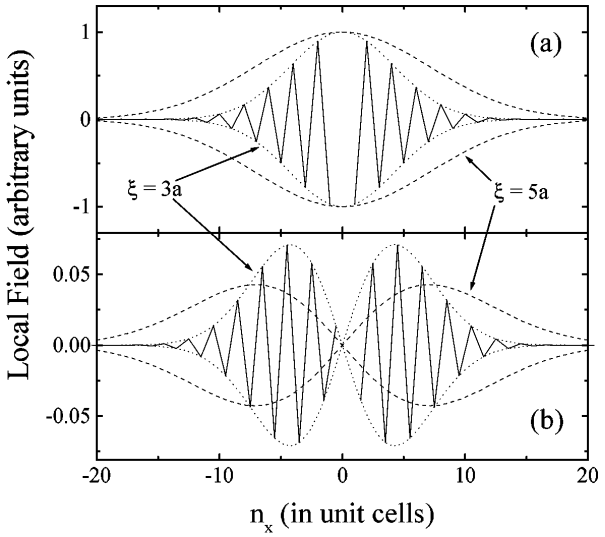

FIG. 4. Plot of the antiferromagnetic Gaussian polarization $\chi'(n_x\mathbf{a})$ from Eq. (3) along the x axis in the CuO_2 planes for $\chi^* = 1$. The local field due to the spin polarization occurring on copper positions is represented in (a). In (b) the local field on the ^{17}O nuclear site $(n_x + 1/2, n_y = 0)$ is seen to spatially extend when ξ increases, but decreases in magnitude.

$\mathbf{Q}_{\rm AF} = (\pi, \pi)$ in the imaginary part of the susceptibility $\chi''(\mathbf{q})$ [3], in agreement with the anomalous T dependence of the ^{63}Cu NMR longitudinal relaxation data. As for χ'', one might assume a response peaked at $\mathbf{Q}_{\rm AF}$ for χ' such as [14]:

$$\chi'(\mathbf{q}) = 4\pi\chi^*\left(\frac{\xi}{a}\right)^2 \exp[-(\mathbf{q} - \mathbf{Q}_{\rm AF})^2\xi^2], \quad (2)$$

where ξ is the AF correlation length, and a the CuO_2 unit cell. Then, by inverse Fourier transform,

$$\chi'(\mathbf{r}) = \chi^*(-1)^{n_x+n_y}\exp(-r^2/4\xi^2), \quad (3)$$

where $\mathbf{r} = n_x\mathbf{a} + n_y\mathbf{b}$ represents the position of the copper sites in the CuO_2 planes, and χ^* is the amplitude of the oscillation. The oscillatory behavior of the polarization due to the prefactor $(-1)^{n_x+n_y}$ can be seen in Fig. 4(a) where χ' is plotted along the **a** axis.

Using Eq. (3), we can perform numerical simulations of the NMR line shape. We used the formalism developed in Ref. [21], with 60×60 planar unit cells and randomly distributed magnetic moments. In order to test this model, we have first simulated NMR line shapes for a hypothetical probe coupled to the spin density occurring only on one copper site, without considering the specific case of ^{17}O. These simulations give nearly unshifted symmetrically broadened lines. Their line shape is intermediate between a Gaussian and a Lorentzian. The broadening is naturally found to scale linearly with ξ, which represents the spatial extension of the AF spin polarization in this model. This is seen in Fig. 4 when comparing $\xi = 3a$ and $\xi = 5a$. However, previous analyses of the hyperfine coupling of the planar ^{17}O nuclei have shown that these are dominantly coupled to the spin polarization of their two copper neighbors [17,22]. The AF spin polarizations on these two copper neighbors are nearly opposite. The resulting polarization on the ^{17}O site is the addition of these copper polarizations, and hence is strongly reduced and has a totally different **r** dependence. This is illustrated, for instance, for the oxygens on the x axis in Fig. 4(b). From this figure, the corresponding broadening of the ^{17}O line should be less sensitive to variations of ξ. Simulations indeed yield symmetric unshifted lines with a broadening almost independent of ξ, in a realistic range of ξ values between $1.5a$ and $4a$, as shown in Fig. 3(b). Thus, in this model, the broadening of the ^{17}O probe is not very sensitive to ξ [taking a Lorentzian shape for $\chi'(\mathbf{q})$ gives similar results]. Hence, the observed T variation of $T\Delta\nu_{\rm imp}$ represents only the T dependence of the prefactor χ^*. In Fig. 3, the concentration dependence of the experimental $T\Delta\nu_{\rm imp}$ is compared to that of the simulated width. The agreement is consistent with this AF model.

For zinc-substituted samples [23], we find similar T, x, and hole doping dependences of $T\Delta\nu_{\rm imp}$. The local electronic defect structure is known to be very different for the "magnetic" Ni and the "nonmagnetic" Zn. Thus, the ^{17}O linewidth is not sensitive to the microscopic electronic state of the defect and probes the *intrinsic* χ' for the pure compound.

The Gaussian transverse relaxation rate $1/T_{2G}$ of ^{63}Cu also probes $\chi'(\mathbf{r})$, as it is attributed to the indirect coupling between ^{63}Cu nuclear spins through the spin polarization within the planes [6]. In $O_{6.6}$, the values of $1/T_{2G}$ [7] are found to increase with decreasing T, as seen in Fig. 2. A computation for the same Gaussian shape of

χ' gives $1/T_{2G} \propto \chi^* \xi$. In most analyses, χ^* is supposed T independent, which implies that ξ increases with decreasing T [7,24]. Here, we experimentally showed that $\chi^*(T) \propto T\Delta\nu$ increases with decreasing T. It implies at least a much weaker T dependence for ξ than the previous T_{2G} analyses, which qualitatively agrees with neutron scattering data [3]. Trying a quantitative comparison between our data for χ^* (T) and T_{2G} data, we find in fact the contrary: a decrease of ξ of 50% from 200 to 100 K, which would be somewhat awkward [25]. However, recent measurements of ^{17}O T_{2G} data in O_7 [9] indicate that systematic errors are performed in the analysis of ^{63}Cu T_{2G}, as contributions from dynamic spin-spin effects have to be taken into account. Suggested corrections would reduce the relative increase of ξ in our analysis. In fact, taking ξ nearly T independent might reconcile $^{17}T_{2G}$, $^{63}T_{2G}$, neutron scattering data and our own experiment. Let us notice that both $^{63}T_{2G}$ and our experiment do not reveal the existence of the pseudo spin gap around $T = 150$ K detected by $^{63}T_1$. Both $\mathbf{q} = \mathbf{0}$ and $\mathbf{q} = \mathbf{Q}_{\mathrm{AF}}$ pseudogaps disappear with increasing doping. The present experiment allows us to stress that the marked change in behavior of $T\Delta\nu$ is a further qualitative difference between underdoped and overdoped materials (Fig. 2). In contrast, the relative T variations of $^{63}T_{2G}$ data are not found to change markedly with doping [8]. This might be associated with a significant modification in the spatial dependence of the spin polarization. In fact, photoemission data in Bi2212 report a complete change of the Fermi surface upon doping [26]. If a similar effect was to occur in YBCO, it should play a role in the evolution of $\chi'(\mathbf{r})$ with doping.

In conclusion, we have studied the spin polarization induced by a magnetic moment in CuO_2 planes. We found an anomalous T variation of $\chi'(\mathbf{r})$ in the underdoped case which confirms the correlated nature of the spin density at this doping content. Our analysis based on antiferromagnetic correlations shows that the amplitude of $\chi'(\mathbf{r})$ increases with decreasing temperature, while ξ is roughly T independent. These results are strong constraints for any theory of the correlated normal state of high-T_c cuprates. Furthermore, the novel method used here to probe $\chi'(\mathbf{r})$ opens new perspectives. Sensitivity improvements will certainly allow us, through spectrum shape analyses, to better characterize the spatial dependence of $\chi'(\mathbf{r})$ and its evolution with doping.

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[20] In fact, dipolar broadenings are computed in $O_{6.6}$ and O_7 to be $\Delta\nu^{\mathrm{dipolar}} \leq 4000x/T$ (kHz K). This is consistent with the maximum broadening observed for the apical site, at 35 K, which is less than 7 kHz. It is at least a factor of 20 smaller than the observed broadening of the plane oxygen line.

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