^{89}Y NMR Probe of Zn Induced Local Moments in $YBa_2(Cu_{1-y}Zn_y)_3O_{6+x}$

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We report the observation of resolved ^{89}Y NMR lines due to Zn nearest neighbors (nn) in $YBa_2(Cu_{1-y}Zn_y)_3O_{6.64}$. Comparison of the Curie dependence of their frequency shifts with susceptibility data allows us to conclude that the Zn induced local moments reside on the nn Cu orbitals and to explain the absence of resolvable nn lines for $x = 1$. Analysis of the magnitude of the long-range spin-density oscillations monitored by the ^{89}Y NMR width indicates that the reduction of T_c might be connected with magnetic effects. For x=0.64, the low T increase of the spin-lattice relaxation rate of ^{89}Y nuclei near Zn is shown to be governed by the local moment dynamic susceptibility.

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Substitutions in cuprates present the opportunity for controlled study of impurity effects in the metallic correlated CuO_2 planes. To achieve this aim, NMR studies of near neighbor resonances of the impurity should be of considerable interest, as has been demonstrated in classical magnetic dilute alloys such as Cu-M (M : $3d$ element) [1]. Such studies have been crucial in answering fundamental questions related to the impurity: magnitude of its coupling with the carriers, Kondo effect, T dependence of local moment susceptibility, and fluctuation time, etc. Similar work in cuprates should also offer a novel insight on the magnetic properties of the metallic state, which are still poorly understood.

Zn substitution in $YBa_2(Cu_{1-y}Zn_y)_3O_{6+x}$ (O_{6+x}:Zn) is of particular interest, as it strongly modifies the phase diagram with varying oxygen content [2]. T_c is reduced by Zn and a "spin-glass-like" region of static magnetism [3] appears between the antiferromagnetic (AF) and the superconducting compositions. While the $\mathbf{q} = 0$ planar susceptibility χ_s far from the impurities is hardly affected [2], the magnetic pseudogap at the AF wave vector, $\mathbf{q}_{AF} = (\pi, \pi)$ disappears with Zn doping [4]. Previous ^{89}Y NMR data in O_{6+x}:Zn [2] and ^{89}Y and ^{63}Cu NMR data in O_7:Zn [5,6] indicate that Zn induces local moments in the CuO_2 planes, at variance with ^{63}Cu NMR in O_7:Zn by Ishida *et al.* [7]. From ^{63}Cu NMR in $YBa_2Cu_4O_8$:Zn, Zheng *et al.* [8] argue for the formation of local moments on orbitals orthogonal to Cu($d_{x^2-y^2}$)-O($2p_\sigma$).

In this Letter, we examine in detail the effect of Zn on ^{89}Y NMR, in oriented powders of O_{6+x}:Zn with $0.5\% \leq y \leq 4\%$, for $x = 0.64$ and 1. In the dilute samples, for $x = 0.64$, we detect Y near neighbor (nn) resonances, which enables us to study, for the first time, the magnetic modifications induced by Zn in its vicinity. Among various issues, we confirm the formation of local moments and show that they predominantly lie on the Cu($d_{x^2-y^2}$)-O($2p_\sigma$) orbitals. Finally, from an analysis of the long distance spin polarization for $x = 1$, we deduce that the coupling of the local moments with the conduction band might be sufficient to induce pair breaking of the superconducting carriers.

The samples were prepared by standard solid-state reaction techniques as described elsewhere [9]. The ^{89}Y NMR signal was observed in a field of 7.5 T ($\nu = 15.64$ MHz) by standard pulse NMR techniques. The ^{89}Y shift was measured with respect to a YCl_3 solution.

The 100 K line shapes for O_{6+x}:Zn samples are shown in Fig. 1. Various facts allow us to ensure that the satellite resonances observed in $O_{6.64}$:Zn are not due to spurious phases: (i) Their position depends on the sample orientation with respect to the applied field, (ii) the relative intensity of the outer line increases with Zn content, while its position is unchanged, and (iii) no structure appears in the line shape of O_7:Zn at frequencies of the satellites in $O_{6.64}$:Zn, while this sample is obtained merely by vacuum reduction of O_7:Zn at low T (< 450 °C) . This further reveals a marked difference between the magnetic

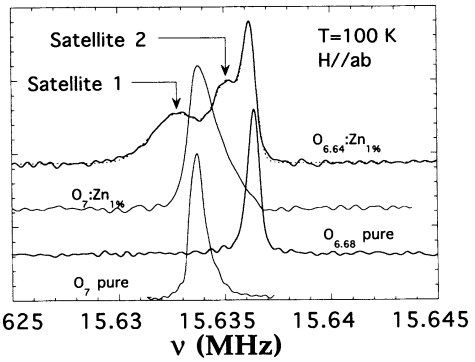

FIG. 1. Spectra for O_{6+x}:Zn (T=100 K, $H||ab$). Note that for $O_{6.64}$:Zn$_{1\%}$, the spectrum was obtained with a fast repetition rate, enhancing the satellites with respect to the main line due to their shorter T_1. The dotted line is a fit to three Gaussians.

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TABLE I. The experimental intensities (in % of total spectral intensity) of the satellites are compared with those expected from a statistical occupation of the Cu(2) sites by Zn, assuming full substitution on these sites, i.e., $c = 1.5y$.

y (%)	Sat. 1	Sat. 2	First/third nn	Second nn	Second+third (not first)
0.5	6±2	18±2	6	11	16
1	13±2	26±5	11	19	27
2	20±5	55±10	19	30	38
4	20±10	60±15	31	38	42

properties of the two sample compositions.

Experimental line shapes similar to that of Fig. 1 were fitted with a sum of three Gaussians. To make site assignments, data were taken for repetition times much longer than the spin-lattice relaxation times T_1. The intensities of the satellites were compared with that expected for statistical single occupancy of one neighboring shell by Zn for an in-plane concentration c [that is $8c(1-c)^7$ for the first shell, $16c(1-c)^{15}$ for the second, etc.]. The intensity (Table I) of the outer line is consistent with that of the first or the third nn shells assuming that all the Zn are substituted in the planes ($c = 1.5y$). We are inclined to believe that the outermost line is due to the first nn since, as we will show later, it experiences the strongest effect on the T variation of frequency shift ΔK and T_1. The situation for satellite 2 is less clear, but for dilute samples its intensity is consistent with the total occupancy of the second and third nn with the first nn unoccupied by Zn.

The variations of $\Delta K(T)$ for the various lines are plotted in Fig. 2. For the main line, $\Delta K(T)$ was found independent of Zn content confirming the absence of carrier density variation with Zn substitution [2], contrary to the arguments of Ref. [7,10,11]. ΔK of satellite 1 becomes more negative as T decreases, indicating a negative hyperfine coupling with the Curie susceptibility χ_c due to local moments, which will be analyzed shortly.

To measure T_1 on the satellites and the main line we took spectra for various repetition rates of the $\pi/2 - \pi$ pulse sequence. For $O_{6.64}$:Zn, the peak intensities of the fitted spectra (Fig. 1) allowed us to determine the T_1's of the individual lines (Fig. 3). We found that the outer line has the shortest T_1 while the main line T_1 is hardly affected both for O_7:Zn and $O_{6.64}$:Zn. This result contradicts that of Dupree *et al.* [5] who saw a sizable increase of the ^{89}Y relaxation rate in O_7:Zn at room temperature.

These data lead us naturally to point out that the Zn induced local moments reside in the immediate vicinity of the nonmagnetic Zn, that is on its four nn Cu or O orbitals. Further, we can discriminate between these possibilities via an analysis of the hyperfine couplings [12]. No sizable fraction of the local moment can reside on the $O(2p_\pi)$ orbital, as this should yield a positive, rather than the observed negative, Curie contribution to the first nn NMR line shift (Fig. 2). In undoped O_{6+x}, the Y spin polarization arises from its coupling with the small fraction of holes on the $O(2p_\sigma)$ orbitals due to their covalency with the $Cu(3d_{x^2-y^2})$ holes, while the spin polarization of the doped holes is negligible [12]. So, if the local moment holes were predominantly on the $O(2p_\sigma)$ orbitals, their hyperfine coupling should be about an order of magnitude larger than in the undoped material, contrary to the analysis performed below. For this we use here susceptibility data [3] on sintered pellets (grinding

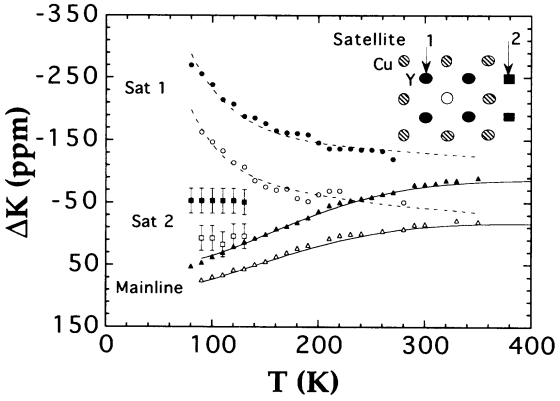

FIG. 2. Variation of ΔK of the satellites and the main line in $O_{6.64}$:$Zn_{1\%}$. Full (open) symbols represent data for $H||c$ ($H||ab$). Dotted lines for satellite 1 are fits with Eq. (1) (see text). The solid lines for the main line are the data for pure $O_{6.64}$ [15]. Inset: schematic of the neighbors of the Zn site with Y nuclei contributing to the satellites being indicated.

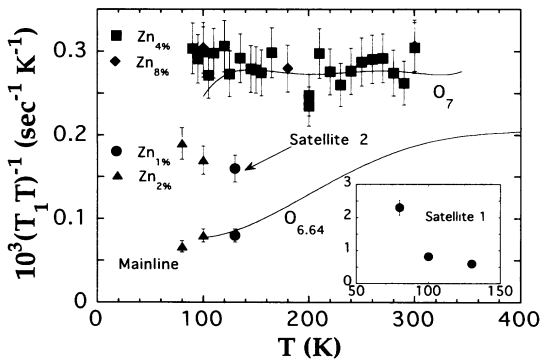

FIG. 3. $^{89}(T_1T)^{-1}$ versus T for the satellites and main line in O_7:Zn and $O_{6.64}$:Zn. The solid lines are the data for the pure samples [15]. Inset: data for satellite 1 which is seen to be enhanced with respect to that for the main line.

induces extrinsic Curie terms [13]) for which particular care was taken to get perfect reaction. These data report the lowest $\chi_c = C_m/T$ to date for full oxygenation. C_m was found to increase by a factor of 6 from $O_{6.92}$:$Zn_{4\%}$ to $O_{6.64}$:$Zn_{4\%}$. The values for C_m, 1.58 and 9.2 $\times 10^{-2}$ emu K/mole Zn, correspond to effective moments, $p_{\text{eff}} = g\mu_B[S(S+1)]^{1/2}$, of 0.36 and 0.86 μ_B/Zn.

The first nn Y site has five Cu nn which we assume are nearly unaffected by Zn, two Cu nn which exhibit Zn induced Curie magnetism and the nonmagnetic Zn neighbor. Its ^{89}Y shift can be written as

$$\Delta K_1^\alpha = (5/8)K_s^\alpha + K_c^\alpha + \delta_1^\alpha, \quad (1)$$

where index α refers to a principal direction, K_s^α is the spin shift of the main line, $K_c^\alpha = 2C_s^\alpha/T$ is the Curie contribution to the spin shift due to its two first nn Cu with a moment, and δ_1^α is the chemical shift. The least squares fit to the data in Fig. 2 allows us to deduce the two unknown parameters C_s^α and δ_1^α. The chemical shift values found δ_1^c (δ_1^{ab}) =100 (140) $\pm$ 10 ppm (parts per 10^6) are only slightly different from δ_1^c (δ_1^{ab}) =165 (150) ppm found in the pure material [14]. The values of C_s^α are 13 100 (11 600) $\pm$ 500 ppm K for H||c (H||ab) [15]. Using $\mu_B K_c = 2H_{\text{hf}}\chi_c/4$ where χ_c is the Curie susceptibility per Zn, we get the hyperfine field $H_{\text{hf}} \approx 3.2$ kG/Cu which is slightly larger than for the pure material (≈ 2 kG). Such an increase of H_{hf} could result from a small change of the Cu($3d_{x^2-y^2}$)-O($2p_\sigma$) hybridization due to a displacement of the first nn oxygen to Zn. This should not occur for more distant O orbitals, so that H_{hf} should be that of the bulk material, for the Y sites which contribute to satellite 2. Furthermore, the Y second nn to Zn has only one Cu nn local moment, so that the Curie contribution to its shift is expected to be about 2(3.2/2) times smaller than for satellite 1, in agreement with the data. However, a complete analysis would have to include the induced RKKY-like spin polarization on the second and further Cu nn to Zn. Finally, with the low value of C_m found for $x = 1$, the expected ^{89}Y shift for the first satellite is too small to be resolved. The tail in the high frequency side of the signal for O_7:$Zn_{1\%}$ in Fig. 1 should not be mistaken for a satellite resonance, as it was not found to scale with Zn content. This tail could often be seen even in pure samples when perfect oxygen stoichiometry is not achieved [12].

Let us now consider the long-range effects of these local moments, which are reflected by a distribution of ΔK for the Y sites, dependent on their position relative to the local moments. As evidenced for O_{6+x}:$Zn_{4\%}$ [2], the induced line-broadening ΔH of the main Y line also has a Curie T dependence. For O_7:Zn, we used for ΔH twice the half width on the low frequency side of the line, to avoid the influence of the uncontrolled high frequency tail in the spectra. In order to quantify the long-range effects, we looked at the Zn concentration dependence of $T\Delta H/H_0$. As displayed in Fig. 4, it initially increases abruptly and the overall y dependence is rather sublinear.

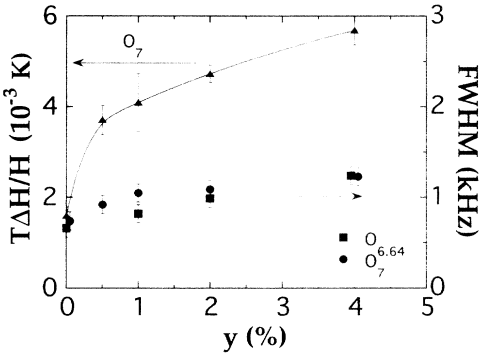

FIG. 4. Curie constants in the NMR linewidth (left axis) versus Zn content y in O_7. The solid line is a guide to the eye. Average linewidth (main line) for 120 K $< T <$ 200 K (right axis) as a function of y in O_7 and $O_{6.64}$.

In a 2D electron gas a local moment perturbation $\langle S_z \rangle$ induces at large distances r a spin polarization

$$n(r) = Ar^{-2}\cos(2k_F r)\langle S_z \rangle, \quad (2)$$

where A involves the coupling to the carriers. Following Ref. [16], the full width at half maximum of the NMR signal, for a concentration c of local moments per unit area, is given by

$$\Delta H = 4\pi c A H_{hf}\langle S_z \rangle. \quad (3)$$

Deviations from linearity should occur at large c when the field distribution reflects the weight of the nn shells, for which the asymptotic limit does not apply.

In a recent experiment on O_7:$Zn_{3\%}$, Walstedt *et al.* [6] also detected a broadening ($T\Delta H/H_0 = 0.27$ K) of the planar site ^{63}Cu NMR line for $H_0||c$. In view of the large difference in the hyperfine fields for ^{89}Y and ^{63}Cu, these data are consistent with our result for ^{89}Y ($T\Delta H/H_0 =$ 0.003 K per plane) in O_7:$Zn_{4\%}$ [17]. If we assume that the local moment spin S couples to the Cu hole spins on its first nn through an effective exchange interaction J_{eff}, in a noncorrelated electron gas picture, we expect $A = a^2 J_{\text{eff}}\rho(\epsilon_F)/\pi$, where a^2 is the unit cell area, and $\rho(\epsilon_F)$ is the Fermi level density of states per unit cell per spin direction. Using the data for χ_c and Eq. (3) for the Curie contribution to the ^{89}Y NMR width, we determine $J_{\text{eff}}\rho(\epsilon_F) = 0.45 \pm 0.2$ for a CuO_2 plane [18]. For $\rho(\epsilon_F) =$ 1.5 states/eV-Cu-spin direction, we get $J_{\text{eff}} = 0.3 \pm 0.15$ eV. In the Abrikosov-Gorkov pair-breaking theory [19], the change in T_c is $\Delta T_c = 0.14\pi^2 c\rho(\epsilon_F)J_{\text{eff}}^2 S(S+1)/k_B$. This yields $\Delta T_c/c \approx 100$ K which, considering our crude analysis, is in fair agreement with our experimental value of 800 K. Walstedt *et al.* [6] reached opposite conclusions mainly as their value for χ_c, apparently dominated by extrinsic phases, is 30 times larger than that of Ref. [3].

Determination of the long range effects for $O_{6.64}$:Zn is somewhat more difficult, as the satellites influence the NMR spectra. However, a lower estimate of these effects could be obtained by considering the fitted value of ΔH for the main line, and comparing it to the data for O_7:Zn

in a range between 120 and 200 K. The main result (Fig. 4 right axis) is that the linewidths are quite similar for the two oxygen contents, which might be explained by the opposing variations of $\langle S_z \rangle$ and $\rho(\epsilon_F)$ [20].

Let us finally comment shortly on the spin-lattice relaxation rate, which is given by

$$1/(T_1T) \propto \sum_{\mathbf{q}} A^2(\mathbf{q})\chi''(\mathbf{q},\omega)/\omega, \quad (4)$$

where $A(\mathbf{q})$ is the coupling to the magnetic fluctuations at wave vector $\mathbf{q}$. The O and Y nuclei are at symmetry positions with respect to Cu so that $A(\mathbf{q}_{AF}) = 0$, and the fluctuations at $\mathbf{q}_{AF}$ are filtered at these two sites. Consequently, in O_{6+x} the T dependence of $(T_1T)^{-1}$ for Y and O is different from that of Cu which is dominated by the fluctuations at $\mathbf{q}_{AF}$ [21]. On adding Zn, the symmetry around the first nn Y is broken and, independently of any specific local moment effect, an increase in $^{89}(T_1T)^{-1}$ could occur on this Y site due to nonzero $A(\mathbf{q}_{AF})$. But as $\chi''(\mathbf{q} = \mathbf{q}_{AF}, \omega)$ is only weakly dependent on oxygen content at 100 K in the pure compounds, as shown from $(T_1T)^{-1}$ data for Cu(2) [21], we would expect similar T_1's for the first nn of Zn in O_7:Zn and $O_{6.64}$:Zn. This is contradicted by the data as we do not find any component with a short T_1 in the ^{89}Y spectrum for O_7:Zn. Moreover, the symmetry of the form factor is unlikely to be modified for the next nn but $(T_1T)^{-1}$ for satellite 2 in $O_{6.64}$:Zn is found to be increased with respect to the main line. These results imply that the enhancement of T_1^{-1} is not due to the local modification of the magnetic symmetry of the site, but that it is dominated by the local moment fluctuations. Such a contribution should be given as $(T_1T)^{-1} \propto \chi_c\tau$ where τ is the spin lifetime. We find that $(T_1T)^{-1}$ increases faster than T^{-1} in $O_{6.64}$:Zn, and therefore that the fluctuation rate τ^{-1} slows down at low T, as expected. One might as well deduce that for O_7:Zn the faster dynamics and weaker local moment might only be detected for $T \ll 100$ K.

In conclusion, we have presented here the most comprehensive set of data showing the magnetic modifications induced by Zn on its neighbors. We have demonstrated that the local moments do not result from holes trapped on the nn oxygen orbitals, but rather from modifications of the magnetic properties of the neighboring Cu holes. The absence of detectable satellite in O_7:Zn samples, in accord with the reduction of the Curie term, ensures that these modifications decrease with the AF correlation length of the host material. The use made here of a simple RKKY analysis of the long distance spin polarization, and of the pair-breaking formulation of Abrikosov-Gorkov might not seem appropriate for a correlated electronic system. However, the deduced exchange coupling J_{eff} between the local moment and the Cu holes has the order of magnitude of that between Cu spins in the pure material as might be expected on microscopic grounds. This allows us to conclude that the magnetic modifications are significant enough to play a role in the suppression of superconductivity. We think that the present results open wide a new direction on local studies of the magnetic properties of impurity states in cuprates which should help to test the reliability of microscopic theories of their metallic state.

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