^{63}Cu NMR Evidence for Enhanced Antiferromagnetic Correlations around Zn Impurities in $YBa_2Cu_3O_{6.7}$

M.-H. Julien,[1,2] T. Fehér,[1,3] M. Horvatić,[1] C. Berthier,[1,2] O. N. Bakharev,[1,4] P. Ségransan,[2] G. Collin,[5] and J.-F. Marucco[6]

[1]*Grenoble High Magnetic Field Laboratory, CNRS and MPI-FKF,BP 166, F-38042 Grenoble Cedex 9, France*
[2]*Laboratoire de Spectrométrie Physique, Université J. Fourier, BP 87, F-38402 St. Martin d'Hères, France*
[3]*Physics Institute, Technical University of Budapest, H-1521, POB. 91, Budapest, Hungary*
[4]*Magnetic Resonance Laboratory, Kazan State University, 420008 Kazan, Russia*
[5]*Laboratoire Léon Brillouin, Centre d'Etudes de Saclay, CEA-CNRS, 91191 Gif-sur-Yvette, France*
[6]*Laboratoire des Composés non Stoechiométriques, Université Paris-Sud, 91405 Orsay, France*
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Doping the high-T_c superconductor $YBa_2Cu_3O_{6.7}$ with 1.5% of *nonmagnetic* Zn impurities in CuO_2 planes is shown to produce a considerable broadening of ^{63}Cu NMR spectra, as well as an increase of low-energy magnetic fluctuations detected in ^{63}Cu spin-lattice relaxation measurements. A model-independent analysis demonstrates that these effects are due to the development of staggered magnetic moments on many Cu sites around each Zn and that the Zn-induced moment in the bulk susceptibility might be explained by this staggered magnetization. Several implications of these *enhanced* antiferromagnetic correlations are discussed.

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The precise nature of antiferromagnetic (AF) correlations and how they influence electronic properties are the most puzzling aspects of high-T_c cuprate superconductors. A piece of this puzzle is the substitution of Cu^{2+} ions ($S = 1/2$) by dilute impurities, such as Zn, which is known to suppress spectacularly T_c (about 20 K/% of Zn in the underdoped regime) and to localize charges [1]. The most dramatic effects of Zn doping concern the magnetism of CuO_2 planes [2]: although Zn is nonmagnetic, the observation of specific EPR and NMR resonances have shown that the Curie term in the bulk susceptibility of Zn-doped samples [3] is due to a magnetic moment induced on Cu sites around Zn [4–7]. Furthermore, the broadening of ^{63}Cu [8,9] and ^{17}O NMR lines [10] reveals a distribution of moment magnitudes, which has been attributed to a spatially inhomogeneous spin polarization extending over several lattice sites around Zn. Both the symmetric character and the temperature (T) dependence of the line broadening can be accounted for by staggered spin density oscillations, as expected from the AF character of magnetic correlations [8,10,11]. Zn doping also has drastic effects on spin dynamics: low-energy AF fluctuations probed by neutron scattering are enhanced [12,13], and spin freezing eventually occurs [12–15]. From a general point of view, such clear manifestations of Cu^{2+} moments recall that metallic cuprates are primarily doped antiferromagnets. Nevertheless, a clear understanding of these effects, particularly the origin of the magnetic moment, remains elusive.

Here, we report on a ^{63}Cu NMR study of $YBa_2(Cu_{0.99}Zn_{0.01})_3O_{6.7}$. By exploiting the peculiarities of hyperfine interactions for Cu nuclei in CuO_2 planes, these measurements provide a model-independent demonstration which shows that the local magnetization becomes staggered around Zn impurities. The uncompensated sum of the staggered moments is found to be of the same order of magnitude as the moment detected in bulk measurements. Additional low-energy spin fluctuations from these staggered regions are identified within the pseudogap through measurements of the nuclear spin-lattice relaxation rate ($1/T_1$). The physical picture implied by these results is that AF correlations are *enhanced*, not destroyed, around impurities.

The measurements were performed on a single crystal of $YBa_2(Cu_{0.99}Zn_{0.01})_3O_{6.7}$ of ~400 mg weight. SQUID measurements have shown that $T_c = 38$ K, but it is reduced to ~20 K or less in magnetic fields (H) of 12–15 T used here. The T_c value is in agreement with published data [3] for 1% Zn/Cu [i.e., 1.5% Zn/Cu(2)].

Figure 1(c) shows typical ^{63}Cu NMR spectra for $H \| c$ axis. Each spectrum consists of two broad lines, associated with the plane site Cu(2) and the chain sites Cu(1) (the various inequivalent Cu(1) sites are not resolved here). Spectra in Figs. 1(a) and 1(b) are obtained with a differential spin-echo pulse sequence designed to suppress the Cu(1) signal, which has longer spin-lattice (T_1) and spin-spin (T_2) relaxation times than Cu(2). The Cu(1) signal is not totally suppressed, but the mixing with the Cu(2) signal is largely reduced, allowing direct fits of the Cu(2) line shape. In Fig. 1, the amplitudes at the center of the Cu(2) line are normalized to a common value for all temperatures. This makes very apparent the huge broadening of the Cu(2) line as T is reduced. On the other hand, the width of the Cu(1) line is almost T independent. This shows that Zn substitutes only the planar Cu site, not the chain site.

Zn-induced magnetic broadening NMR spectra (already reported for ^{63}Cu in [8,9]) indicates a distribution of hyperfine fields h_i. The NMR spectrum simply corresponds to the histogram of this distribution. For $H \| \alpha = c, ab$ in the paramagnetic phase, h_i at a site (r_i) comes from an

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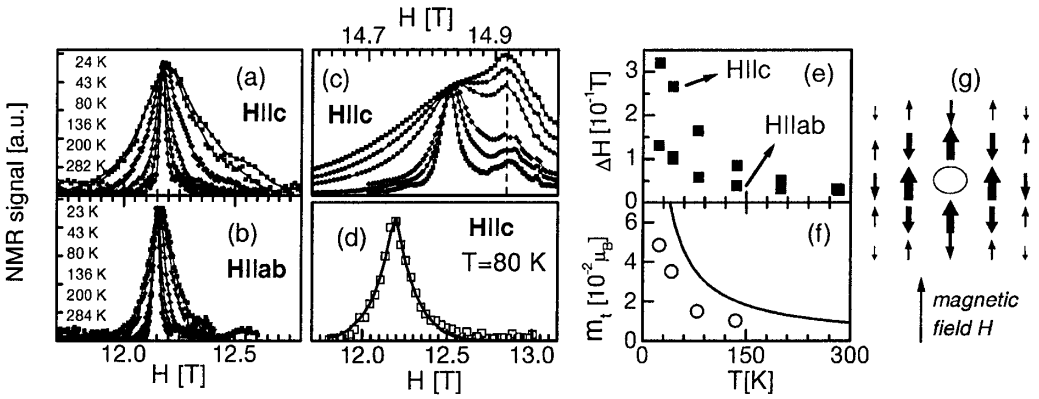

FIG. 1. (a) Normalized field swept ^{63}Cu(2) spectra with $H\|c$, the Cu(1) signal being suppressed by a differential spin-echo sequence. (b) ^{63}Cu(2) spectra obtained by the same method, but $H\|ab$. (c) ^{63}Cu spectra for $H\|c$ without the differential sequence (T = 26, 49, 83, 156, 203, and 285 K); the line shows the ^{63}Cu(1) signal; intensities are normalized at the Cu(2) peak position. (d) Fit of a ^{63}Cu(2) spectrum using the $\mathcal{I}$ function explained in the text. (e) Width at half maximum of the ^{63}Cu(2) spectra from plots (a) and (b). (f) Circles: total magnetization per Zn carried by staggered moments (see text); line: magnetization for an effective moment $p_{\rm eff} = 1\mu_B$ at 12.2 T. (g) Schematic drawing of staggered moments (arrows), induced on a characteristic length $\sim\xi$ around a single Zn impurity (circle). The size of each arrow represents the value of the moment.

orbital term, which is T independent, plus a spin term due to an anisotropic coupling ($A_\alpha^{\rm onsite}$) to the on-site Cu^{2+} moment and to an isotropic transferred coupling (B) to the four Cu^{2+} first neighbors (ϵ) [16]:

$$h_i = h_{\rm orb} + A_\alpha^{\rm onsite}\langle S_z^i\rangle + B\sum_{\epsilon=1,\ldots,4}\langle S_z^{i+\epsilon}\rangle. \quad (1)$$

The spin component can be expressed in q space as

$$h_i^{\rm spin} = \frac{1}{N}\sum_{\vec q} A(\vec q)\,\langle S_z(\vec q)\rangle \exp(i\vec q\cdot\vec r_i)\,, \quad (2)$$

where $A_\alpha(\vec q) = A_{c(ab)}^{\rm onsite} + 2B\cos(q_x a) + 2B\cos(q_y b)$. A well-established NMR result in $YBa_2Cu_3O_{6+x}$ (YBCO) is that $A_c(q=0) = A_c^{\rm onsite} + 4B \simeq 0$, which means that $h_i^{\rm spin} \simeq 0$ when the time averaged spin polarization is uniform in space, while A_c is maximum for $\vec q = \vec Q_{\rm AF} = (\pi/a, \pi/a)$. The huge ($T$ dependent) distribution of h_i observed here is thus a clear indication that the local magnetization is spatially strongly modulated $\langle S_z^i\rangle \not\approx \langle S_z^{i+\epsilon}\rangle$. Since it has to be so on the length of one lattice spacing, any nonmicroscopic modulation, such as induced by doping inhomogeneities, is ruled out. In addition, since $A_c^{\rm onsite}$ and B have opposite signs, large values of h_i are obtained when $\langle S_z^i\rangle$ and $\langle S_z^{i+\epsilon}\rangle$ have opposite signs, i.e., if the magnetization is *staggered*.

Further confirmation comes from measurements with $H\|ab$ plane. In this orientation, the ^{63}Cu(2) NMR spectrum also broadens on cooling, but, unexpectedly, its width becomes less than for $H\|c$ by a factor 2.6 ± 0.2 at low T [Fig. 1(e)]. Since the ratio $A_c(q)/A_{ab}(q)$ is close to 2.6 in the vicinity of $\vec Q_{\rm AF}$, this confirms without any detailed model that the staggered component of the magnetization is dominant.

This conclusion can be checked quantitatively by computer simulations of the line shape according to the following model (see also [8,10,11]). Any localized magnetic perturbation at a site $r_{\rm imp}$ is expected to polarize surrounding electrons r_i with a magnitude determined by the real-space spin susceptibility $\chi'(r_i - r_{\rm imp})$ [17]. This latter is the Fourier transform (FT) of the real part of $\chi(q)$, which in underdoped YBCO is well known to be peaked at, or near, $Q_{\rm AF}$ as a consequence of AF correlations. Around a single impurity, the spin polarization at a site r_i is given by $h_i^{\rm spin} = \frac{1}{N}\lambda\sum_q \chi'(q)A(q)\exp[i\vec q\cdot(\vec r_i - \vec r_{\rm imp})]$, in which we impose the absence of moment at the Zn site, and $\lambda = \chi'(Q_{\rm AF})V_{\rm eff}$, where $V_{\rm eff}$ stands for the local effective perturbating potential. Assuming that the response to the randomly distributed impurities are additive, the local field distribution in the plane $h_i^{\rm spin}$ is just given by the FT of $\lambda\chi'(q)\mathcal{D}(q)A(q)$, where $\mathcal{D}(\mathbf{q})$ is the inverse FT of a random distribution of impurity sites $\sum_{\vec r_{\rm imp}}\delta(\vec r - \vec r_{\rm imp})$, taken on a 256 × 256 lattice. The histogram of the $h_i^{\rm spin}$ convoluted with an intrinsic linewidth, which is small compared to the broadening, gives the NMR line shape.

Three different models for $\chi'(q)$ have been considered: a commensurate Lorentzian $\mathcal{L}(\xi,q) = 1/[1 + \xi^2(\vec q - \vec Q_{\rm AF})^2]$, a commensurate Gaussian $\mathcal{G}(\xi,q) = \exp[-\xi^2 \times (\vec q - \vec Q_{\rm AF})^2/2]$, and a four-peak incommensurate function $\mathcal{I}(\xi,\delta,q)$ corresponding to the functional form used to model recent neutron data in $YBa_2Cu_3O_{6.6}$ [18]. Spectra for $H \parallel c$ and $25 \le T \le 135$ K were first fitted using a nonlinear procedure letting λ and ξ free. For both $\mathcal{L}$ and $\mathcal{G}$ functions, the best fits are obtained for $\xi/a \simeq 2.5$–4. Using the values of λ and ξ obtained from these fits, and $g_c/g_{ab} = 1.15$ [19], one reproduces the observed anisotropy (~2.6) for the low-T linewidth [20]. The function $\mathcal{I}(\xi,\delta,q)$ gives similar results. If δ is also set as a fitting parameter, the best fit is obtained for $\delta = 0.26 \pm 0.01$ r.l.u. and $\xi/a = 5 \pm 1$, independent of

T within error bars in the range $25 \leq T \leq 80$ K. Note that a roughly T independent ξ is not unexpected below $\sim$120 K [21], so our results do not conflict with the variation of ξ inferred at higher T [10,11].

The remarkable agreement between the above values and neutron data [12,18] demonstrates that the essential features of the response to Zn doping are included in the model (note that slight differences in line shapes are obtained with $\mathcal{L}$, $\mathcal{G}$, and $\mathcal{I}$ functions, but they are not sufficient to favor one model). It also gives us confidence that the obtained λ values are reasonable. This allows one, for the first time, to estimate the total magnetization carried by the staggered response: $m_{\text{tot}} = \sum_i \langle S_z^i \rangle$. Although one might naively expect $m_{\text{tot}} \sim 0$ for a staggered magnetization, not only is m_{tot} nonzero but it is comparable to the bulk magnetization $M_{\text{bulk}} = p_{\text{eff}}^2 H/3k_B T$ with $p_{\text{eff}} = 1\mu_B$ [3], in the case of $\mathcal{L}$ and $\mathcal{I}$ functions [Fig. 1(f)]. The $\mathcal{G}$ function, which is less likely [2,10,11], gives about 3 times smaller m_{tot}, because the amplitude on the nearest neighbors (nn) of the impurity is smaller than that obtained with $\mathcal{L}(q)$ models. The accuracy of the comparison between m_{tot} and M_{bulk} is further limited by several uncertainties: value of M_{bulk}, remaining Cu(1) signal, intensities possibly biased by inhomogeneous relaxation times, as well as a possible deviation from the asymptotic model on the four nn.

Despite these uncertainties, the results obtained with Lorentzian models of $\chi(q)$ suggest that the bulk magnetization (i.e., the "Zn-induced moment") may be explained as the sum of staggered moments only [22]. It is important to realize that this is conceptually different from an approach of Zn doping where the staggered response is attributed to the polarization of AF-correlated "band" electrons by a putative moment on the four Cu nn of a Zn. In our view, the staggered magnetization, which must occur in response to any kind of defect [23], naturally leads to a large moment on nn [22]. In other words, Zn only reveals already-existing moments, localized on Cu sites of the doped antiferromagnet (at least in the underdoped regime).

As a matter of fact, it must be emphasized that the enhanced staggered magnetization makes clear that, counterintuitively, AF correlations are not destroyed but *enhanced* by Zn.

It is interesting to make a connection with recent studies of nonmagnetic impurities in AF quantum spin chains. There, the staggered magnetization inferred from NMR is very well explained by the same type of model as used here, except for the appropriate $\chi(q)$ [24]. Such enhancement of AF correlations has attracted considerable theoretical interest because it was also shown to be a property of the "spin-liquid" ground state [25]. Enhanced moments around vacancies are also found in some approaches of the Heisenberg or t-J models in 2D [26]. However, the Zn-induced staggered magnetization, seen at relatively high T in a paramagnetic state, is expected from the general arguments used above. So, it is not by itself an indication of spin-liquid ground state.

It is natural to expect that staggered moments affect dynamical properties, at least locally. We have measured the ^{63}Cu spin-lattice relaxation rate $(1/T_1)$, which is a probe of the dynamical susceptibility at low energy:

$$\frac{1}{T_1} = k_B T \, {}^{63}\gamma^2 \sum_{q,\alpha \perp H} \frac{|A_\alpha(q)|^2}{(g_\alpha \mu_B)^2} \, \frac{\chi''(q,\omega_n)}{\omega_n} . \quad (3)$$

The recovery law of the nuclear magnetization $M_z(t)$ following an inversion pulse was fitted with two contributions at all temperatures: a short component due to ^{63}Cu(2) nuclei and a longer one from ^{63}Cu(1).

The T dependence of $(T_1T)^{-1}$ is shown in Fig. 2, along with data from Ref. [27] in Zn-free $YBa_2Cu_3O_{6.63}$. Although similar in the range 300–150 K, the data show opposite trends below $\sim$100 K: $(T_1T)^{-1}$ decreases with T in Zn-free YBCO, this is the well-known pseudogap behavior, while $(T_1T)^{-1}$ increases in YBCO with Zn, signaling an enhancement of $\chi''(Q,\omega_n)$. Still, the plateau of $(T_1T)^{-1}$ at about 120 K for YBCO with Zn is strikingly reminiscent of the maximum at the characteristic temperature $T^* \simeq 140$ K, which is commonly used to define the pseudogap energy scale. Although some decrease of T^*, as found in [9], is not excluded by our data, the pseudogap (for AF excitations) appears to be filled in by Zn-induced excitations, rather than destroyed. This is in perfect agreement with the neutron scattering data at $q = Q$ plotted in the inset of Fig. 2 [13] (see also [12]). Most likely, the pseudogap remains intact far from Zn, where the magnetization is small. Note that this finding is complementary to, but different from, the fact that the decrease of $\chi'(q = 0, \omega = 0)$ between 300 and 100 K is unaffected by Zn at sites far from Zn [5]. Again there is an analogy with recent work in 1D: for example, the spin gap of the Zn-doped ladder $SrCu_2O_3$ coexists with low-energy AF fluctuations [28]. We also mention that our T_1 data are rather qualitative as they do not allow a quantitative

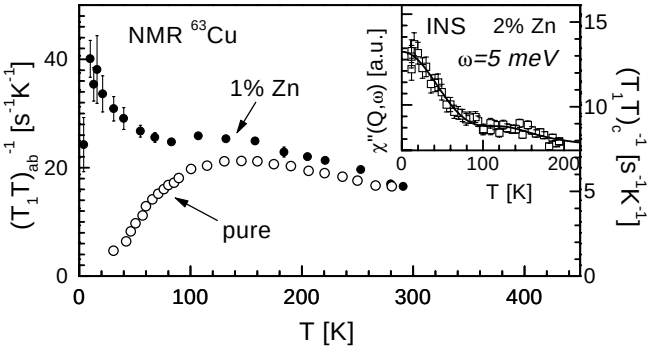

FIG. 2. $^{63}(T_1T)^{-1}$ data in $YBa_2(Cu_{0.99}Zn_{0.01})_3O_{6.7}$ ($H \| ab$, left scale) and in $YBa_2Cu_3O_{6.63}$ ($H \| c$, right scale, from Ref. [27]). Inset: neutron scattering data in $YBa_2(Cu_{0.99}Zn_{0.02})_3O_{6.7}$ from Ref. [13].

analysis of Zn-induced $^{63}T_1$ contributions. However, a recent extraction of these contributions for Ni doping led to conclusions similar to ours [29].

A remaining puzzle is why the bulk susceptibility obeys a pure Curie law [$\chi \sim (T + \theta)^{-1}, \theta \simeq 0$] [3], as if the moments were not interacting, even at concentrations where the mean distance between impurities is much less than 2ξ, the typical diameter of staggered areas. Most probably, individual spins in a staggered area are locked to each other, so each area behaves as a single moment, but negligible interaction between them is surprising. Actually, a pure Curie susceptibility is also found in the "cluster spin-glass" phase of $La_{2-x}Sr_xCuO_4$ [30], where staggered domains are thought to be encircled by doped holes [31]. We speculate that analogous hole segregation in regions of small staggered magnetization (i.e., far from Zn) may largely reduce interactions between "AF clusters." This is consistent with the suppression of the superfluid density in areas of characteristic length 2ξ [32,33]. Eventually, the tendency of doped holes to avoid AF regions around Zn, where their mobility would be reduced, could rationalize anomalous charge localization effects [1], including stripe pinning. Subsequent spin freezing is expected in most cases.

Finally, we stress that the Zn-induced staggered magnetization does *not* conflict with the possible presence of moments in impurity-free cuprates [15]: there are evidently staggered moments at low hole doping [31]. Moreover, the decrease of T_c when AF correlations are enhanced does not mean that antiferromagnetism and superconductivity are unrelated. Rather, the Zn-induced static character of AF correlations and/or randomness are presumably detrimental to high T_c.

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