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Normal-state magnetic properties of Ni and Zn substituted in $YBa_2Cu_3O_{6+x}$: Hole-doping dependence

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Abstract. – We present SQUID susceptibility data on Zn and Ni substituted $YBa_2Cu_3O_{6+x}$. Cross-checks with NMR yield an unprecedented accuracy in the estimate of the magnetic susceptibility associated with the substituents, from the underdoped to the lightly overdoped case. This allows us to determine the Weiss temperature θ for YBCO: its value is very small for all hole dopings n_h. Since in conventional metals the Kondo temperature $T_K < \theta$, magnetic screening effects would not be expected for $T \gg \theta$; in contrast, increasing n_h produces a reduction of the small moment induced by Zn^{2+} and a nearly constant effective moment for Ni^{2+} corresponding to a spin 1/2 rather than to a spin 1.

There is widespread interest in the study of substitutions in correlated magnetic systems. It encompasses high-T_c cuprates, with the well-known depression of T_c, as well as cuprate-related materials such as spin ladders and even Cu chain materials. All of these systems share the features that the local magnetic environment around the defect differs from that of the bulk material and creates a long-range magnetic perturbation. For instance, a staggered static magnetization is induced by defects in chain compounds [1]; similarly in cuprates local moments appear around Zn substituted in the CuO_2 planes, as observed by ^{89}Y NMR [2]. Yet, the underlying theory is especially appealing for high-T_c cuprates since holes play a dominant role and require a different microscopic approach. In turn, in this context, the study of substitutions in the CuO_2 planes helps to achieve a more complete understanding of the normal state.

The differences between various substituents for Cu in cuprates, *e.g.*, Zn^{2+} ($3d^{10}$, $S = 0$) and Ni^{2+} ($3d^8$, $S = 1$), are still a matter of debate and probably lie not only in the magnetic properties of these 2 ions but also in the electronic structure of the defect centres,

which are responsible for the scattering of holes [3]. Theories clearly suggest that, around the impurities, the underlying antiferromagnetic correlations of the host are revealed [4]. Hole-doping dependence is thus expected and is already observed in T_c depression [5] and resistivity [6]. On the magnetic side, the focus of this letter, accurate determinations of the susceptibility associated with such defects have been, up to now, prevented by the existence of spurious magnetic phases [7, 8]. Thanks to special care in sample preparation, we present here, for the first time, a full study of the variation with hole-doping of the effects of Ni and Zn substitutions on the magnetism of the correlated CuO_2 planes. Our novel experimental determination of the Weiss temperature enables us to demonstrate that, for Zn, the weakness of the moment is not related to the classical Kondo effect. We present a possible explanation based on strong correlations.

Of all the cuprates, $YBa_2Cu_3O_{6+x}$ is the best suited for such a study, as the effect of doping on local magnetism can be followed by merely changing the oxygen content and does not require new synthesis. Our $YBa_2(Cu_{1-y}M_y)_3O_{6+x}$ (M = Zn, Ni) samples, hereafter noted O_{6+x}: My%, were prepared at 920 °C, using Zn and Ni oxides to introduce impurities, with $y < 4\%$. Above this limit, substantial amounts ($\sim$1%) of spurious phases were created. Deoxidizations have been performed under thermogravimetric control between 350 °C and 430 °C in a 0.1 mbar vacuum or with a 10 mbar partial pressure of oxygen for $0.85 < x < 1.0$ (accuracy $\Delta x = 0.01$). Magnetization data were taken using a SQUID magnetometer in 0.2–5 Tesla fields and T_c's were determined from ac susceptibility or SQUID measurements in low field.

The susceptibility χ can be divided into 3 contributions, $\chi = \chi_m + \chi_{YBCO} + \chi_{spur}$. The first one, of primary interest here, χ_m, is associated with local moments induced by substitution. It will be shown to follow accurately a Curie (or Curie-Weiss) law. The second one is similar to that of non-substituted YBCO and can be further split into 2 parts, $\chi_{YBCO} = \chi_{Cu(2)} + \chi_{ch}$, associated, respectively, with planar Cu far from the substitution site, and with CuO chains. NMR, as will be shown hereafter, allows one to contrast between $\chi_{Cu(2)}$ and χ_{ch}. Finally, Curie-like spurious terms due to extrinsic phases, χ_{spur}, are usually not easily separable from χ_m.

As a prerequisite to the determination of χ_m, studies of χ_{YBCO} were first performed on pure powdered or sintered samples prepared in the same manner. We succeeded in preparing nearly parasitic-phase–free samples ($\chi_{spur} \approx 0$) as evidenced by the absence of any detectable Curie behavior for $x = 1.0$ (fig. 1). Our accuracy allows a refined analysis of χ_{YBCO_7} beyond the (unjustified) usual assumption that χ is constant. The intrinsic spin susceptibility of the planes, measured by ^{89}Y NMR on our sample, *decreases* by about 7% ($\sim 2 \times 10^{-8}$ emu/g), from 150 to 300 K, as commonly observed by NMR [9,10]. Thus the observed $\sim$1% quasi-linear *increase* of χ_{YBCO_7} over this T range, fitted as $\delta\chi_{YBCO_7} = AT$, results from a near cancellation of the decreasing planar susceptibility with an increasing chain spin susceptibility (χ_{ch}), consistent with Cu(1) NMR shift measurements [11]. The susceptibility of our set of pure samples, all prepared from the same master batch, is also reported in the inset of fig. 1, for $0.55 < x < 1.0$. For the most depleted samples ($x \leqslant 0.65$), $\chi_{Cu(2)}$ is known from ^{17}O NMR to decrease monotonously at low T [12, 13]. Therefore, the flattening displayed in the inset of fig. 1 for $x = 0.66, 0.55$ and $T < 100$ K is not associated with χ_{spur}, as the low-T heat treatment performed in order to deoxidize our sample cannot create any new parasitic phases. It is the signature of a minor paramagnetic contribution due to χ_{ch}, very likely short chain segments. Finally, for $x = 1.0$, ^{89}Y NMR shift measurements at 100 K on our samples show that Zn substitution does not affect the level of hole doping in the planes, to within 0.02 in x [14]. We have therefore chosen to refer the x value to $x = 1.0$ taken for the maximum obtained oxygen content, whatever the substitution fraction, y.

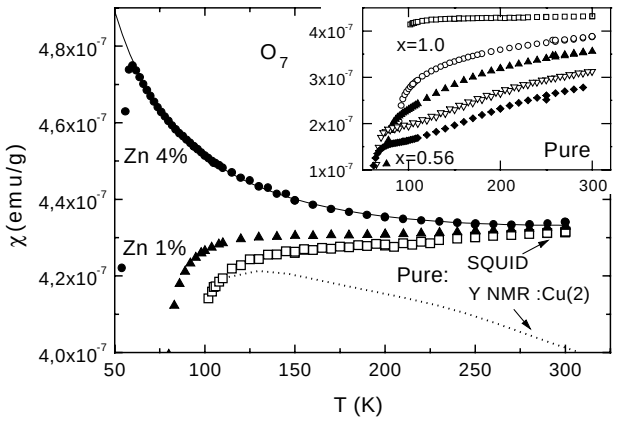

Fig. 1

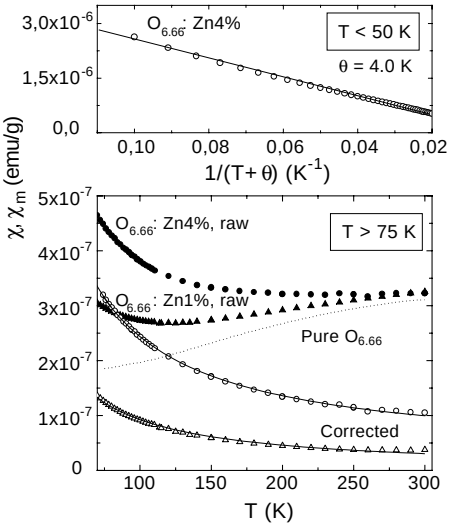

Fig. 2

Fig. 1. – Susceptibility of O_7 : Zn1% and 4% samples compared to pure O_7 (open squares). Notice, for the latter, the increase of χ with T; whereas the susceptibility of the CuO_2 planes (Y NMR, shifted up by 10^{-7} emu/g) decreases (dashed line). Inset $\chi_{\mathrm{YBCO}_{6+x}}$, for $x = 0.56, 0.65, 0.76, 0.85, 1.0$.

Fig. 2. – Lower panel: high-T plot of χ, χ_{m} for $O_{6.66}$: Zn1% and 4%. The closed symbols stand for raw data (χ), the open ones for χ_{m}, obtained after subtraction of χ_{YBCO} using i) (see text). The lines are Curie-Weiss fits described in the text. Upper panel: low-T plot of $\chi_{\mathrm{m}}(\mathrm{YBCO}_{6.66} : \mathrm{Zn4\%})$ *vs.* $1/(T+\theta)$ ($\theta = 4.0$ K). The line corresponds to the same value of C as determined in the lower panel.

The smallness of the value of the induced moment in the Zn case makes the analysis of the data far more difficult than for Ni. We first study a $y = 4\%$ Zn substitution for $x = 1.0$ or 0.66. Figure 1 shows our data for the $O_{7.0}$: Zn1% and 4% lightly overdoped samples in comparison with the corresponding pure sample. The contribution of χ_{m} can be extracted by a fit of the T-dependent part of the raw data to a $AT + C/T$ law, where the AT term accounts for the contribution of the non-magnetic Cu sites (chain + planes) similar to $\delta\chi_{\mathrm{YBCO}_7}$, as detailed in the previous paragraph [15]. There was no significant improvement in the quality of the fit if we took a Curie-Weiss $C/(T+\theta)$ behavior ($-5 < \theta < 10$ K). Figure 2 shows our results for $O_{6.66}$: Zn1% and 4% underdoped samples. We focus first on the latter for which data could be extended down to 5 K, since it is not superconducting. This makes the Curie increase of χ at low T more evident. However, the contribution of $\chi_{\mathrm{YBCO}}(T)$ to the total T-variation of χ_{m} is already quite sizeable above 60 K (much more than for $x = 1.0$). Various estimates of χ_{YBCO} were therefore performed,

i) using the susceptibility of the pure sample, $\chi_{\mathrm{YBCO}_{6.66}}$, presented in the inset of fig. 1 (dotted line), which limits the fit to the T-range $T > 75$ K,

ii) using the data from planar ^{17}O or ^{89}Y NMR measurements rescaled by the hyperfine constant and extrapolated linearly to zero spin shift at $T = 0$.

The main advantage of i) is to include contributions from the chains, (χ_{ch}), at low T [16] (see fig. 1), whereas in ii) χ_{ch} is completely neglected. The local moment contribution, $\chi_{\mathrm{m}} = \chi - (1-5c)\chi_{\mathrm{YBCO}}$ is then deduced, yielding the correct Curie-Weiss fit over the whole T-range. The factor $1-5c$ ($c = 1.5y$ is the concentration per plane) reflects the fact that the

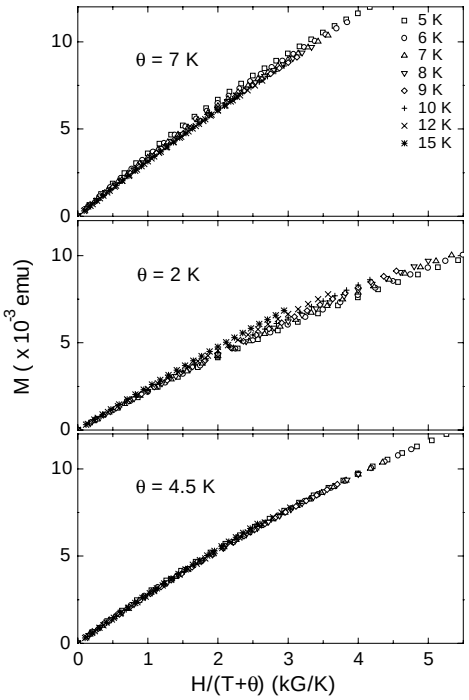

Fig. 3. – Plot of the magnetization *vs.* $H/(T+\theta)$ for various values of θ. The middle and upper panels show the deviations from the expected universality for a Brillouin function, for unappropriate values of θ ($\theta = 2$ and 7 K). The universality is only obtained for a narrow range of values of θ, $\theta = 4.5(5)$ K (bottom panel).

substituted Cu site and its four neighbors which carry the local moment are not expected to have the same susceptibility $\chi_{\mathrm{YBCO}_{6.66}}$, as the bulk Cu of the CuO_2 planes (as shown by Y NMR [2]). The high-T fit (procedure i)) yields $C = 2.3(2) \times 10^{-5}$ emu $\cdot$ K/g and $\theta = 5(3)$ K, whereas including the low-T data gives ii) $C = 2.5(2) \times 10^{-5}$ emu $\cdot$ K/g and $\theta = 4(1)$ K. C is modified by less than 15% if we extract χ_{m} by removing the contribution of the substituted site only, that is $(1-c)\chi_{\mathrm{YBCO}}$. The dominance of the Zn-induced contribution at low T ($T < 30$ K) makes the value of θ hardly dependent on the $T = 0$ extrapolation performed for χ_{YBCO} in approach ii). It is remarkable that all methods yield very similar results within a 15% error bar for a given sample. The value of θ was further checked by studying the variation of the magnetization M with the applied field H for $5 < T < 12$ K (fig. 3); indeed, one expects M to saturate for high fields and low T, according to the Brillouin function $M = B_J(\mu_{\mathrm{B}} H/k_{\mathrm{B}}(T+\theta))$. We find $\theta = 4.5(5)$ K, in good agreement with the previous values. Finally, it is interesting to note that θ is quite small and comparable to the transition temperature of the disordered magnetic state ($\simeq 2$ K) observed in μSR for the same $O_{6.66}$: Zn4% sample [17].

Determinations of C were also made along the same lines for lower Zn substitution rates but the occurrence of superconductivity prevented us from estimating θ as accurately as for $y = 4\%$. In any case the data plotted in fig. 4 clearly demonstrates that θ never exceeds a few K.

Our complete experimental data analysis for Zn and Ni, partially reported in fig. 1, 2 and 4, is summarized in the inset of fig. 4. We find that C increases linearly with y. The values of the local moment are deduced from a linear fit of $C(y) \sim y\mu_{\mathrm{eff}}^2$ and results are given in table I,

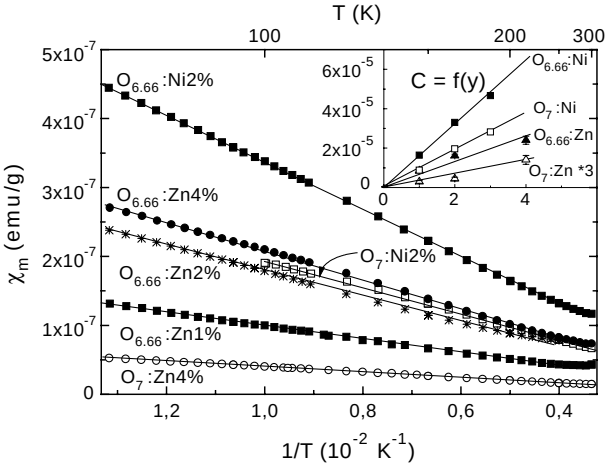

Fig. 4

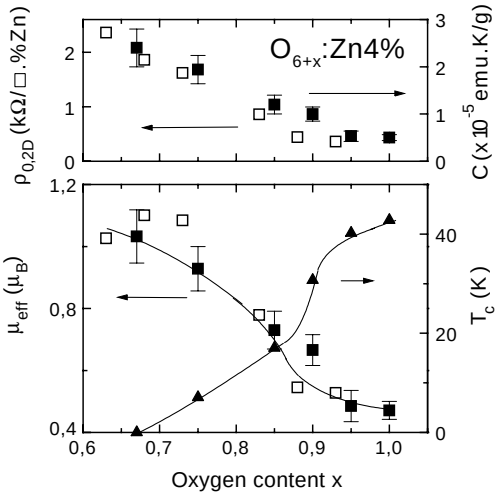

Fig. 5

Fig. 4. – $\chi_{\rm m}$ *vs.* $1/T$ for O_{6+x} : Zny%, Niy%. The lines are fits described in the text. Inset: Curie constant (in emu $\cdot$ K/g) *vs.* (%) impurity content for $x = 7.0$ and $x = 6.66$.

Fig. 5. – Top panel: evolution of C for $y = 4\%$ (closed squares), and $\rho_{0,2D}$ [6] (open squares) with oxygen content. Bottom panel: evolution of $\mu_{\rm eff}$ (closed squares) and $T_{\rm c}$ (triangles), for $y = 4\%$. The open squares are estimates for $\mu_{\rm eff}$ using eq. (2) for S.

along with the depression of $T_{\rm c}$. One of our important experimental conclusions is that the value of the Ni moment stays quasi-constant with hole doping and near a spin-(1/2) value ($\mu_{\rm eff} = 1.73\mu_{\rm B}$), far from the expected $S = 1$ for a Ni^{2+} ion ($\mu_{\rm eff} = 2.82\mu_{\rm B}$). In contrast, the moment induced by Zn is quite small. C decreases by a factor 5.8 from the under- to the lightly over-doped side of the YBCO phase diagram. One might wonder whether the reduction of the moment for Zn is due to a classical Kondo effect. In ordinary metals, such a reduction only occurs below θ, which is of the order of the Kondo temperature $T_{\rm K}$. On the contrary, here, for $T \gg \theta$, the moment is reduced, whereas $\chi_{\rm m}$ deviates only slightly from a Curie law (moreover θ is rather associated with long-range interactions between moments).

Finally, we monitored the decrease of the Curie constant, C, with hole doping for the 4% Zn concentration. In the upper panel of fig. 5, we evidence a strong correlation between C and the residual resistivity ρ_0 taken from [6]. This experimental finding suggests that local moments and scattering are closely related for cuprates, which, again, is at variance with the case of ordinary metals where non-magnetic impurities induce scattering without creation of any related magnetism. Accordingly, models should account not only for the scattering cross-section but also for the value of the moment induced by the substituting element. We

TABLE I. – $T_{\rm c}$ *depression and local moment for* Zn *and* Ni *substitutions in lightly overdoped and underdoped* YBCO.

	O_7 : Zn	O_7 : Ni	$O_{6.66}$: Zn	$O_{6.66}$: Ni
$-\delta T_{\rm c}$ (K/%)	11.0(1.5)	3.4(7)	21(2)	7.5(1)
$\mu_{\rm eff}$ ($\mu_{\rm B}$)	0.40 (5)	1.2(1)	1.0(1)	1.6(1)

next present a tentative theoretical interpretation, based on strong correlations, which relates these two quantities.

First, we consider the Zn case where the impurity can be treated as a spin vacancy. Simulations for a weakly doped t-J model for cuprates yield a local moment for Zn [4], which agrees qualitatively with our findings but, for our experiments, the hole content is far larger. The extension to higher doping can be treated in the framework of gauge theories which advocate spinon-holon separation. Using this approach, Nagaosa and Lee [18] were able to account for resistivity data on O_{6+x}: Zn [6], in the two extreme cases $S = 0$ (overdoping) and $S = 1/2$ (underdoping). Following Gabay [19], a description covering the whole doping range can be obtained. Because Zn is in a $3d^{10}$ configuration, a singlet is always present on the substituted site. According to the t-J picture, this implies that both holons and spinons are scattered off this site. Their density is thus depleted within a typical radius, R_S, around Zn, or in mean-field theory within λ_{TF}, the Thomas-Fermi length; thus the spin 1/2 carried by those Cu surrounding the Zn impurity are not fully screened and a local moment S survives in the vicinity of Zn. For a hole fraction δ, the spinon number per unit cell is $1 - \delta$, far from the Zn site. Within a disk of radius a (the lattice constant) centered on Zn, it is reduced to $(1 - \delta)\rho_s(a)$ with, for a featureless Fermi surface,

$$\rho_s(a) = 1 - \left(\frac{a}{\lambda_{TF}}\right) K_1\left(\frac{a}{\lambda_{TF}}\right) \tag{1}$$

(K_1 is a Bessel function), leading to

$$S = \frac{1}{2}(1 - \delta)(1 - \rho_s(a))\,. \tag{2}$$

For scattering states in 2D characterized by a wave vector k_0, R_S is related to the planar resistivity, $\rho_{0,2D}$, by $R_S = e^2\delta/2k_0\hbar \times \rho_{0,2D}/c$. In the gauge picture, the main contribution to $\rho_{0,2D}$ comes from holons, that is, neglecting band effects, $k_0 = \sqrt{2\pi\delta/a^2}$. Connecting R_S to λ_{TF} gives the variation of the effective moment $\mu_{eff} = g\mu_B\sqrt{S(S+1)}$ with respect to doping. Standard scattering theory, when applied in 2D, gives that $R_S/\lambda_{TF} \sim \delta^{-3/2}$ [20] so that

$$\frac{a}{\lambda_{TF}} = \alpha\left(\frac{\rho_{0,2D}}{c}\right)^{-1}\delta^{-2}\,. \tag{3}$$

From the data of ref. [6] for $\rho_{0,2D}/c$ (expressed in $k\Omega/\square$.%Zn) and eq. (2), we find that $\alpha = 0.050(5)$ fits satisfactorily our data for $\mu_{eff}(x)$, in fig. 5. A more refined treatment (beyond the scope of this letter) would include taking into account the actual shape of the Fermi surface.

The case of a magnetic substitution (Ni) is quite different: no magnetic vacancy is introduced into the CuO_2 plane. A theoretical approach paralleling that for Zn impurity scattering also accounts for resistivity measurements in the case of Ni doping. In this latter case, scattering is due to the formation of a singlet bound state on the Ni site. In addition there remains a $3\,d_{3z^2-r^2}$ $S = 1/2$ spin on Ni, hardly coupled to the planes, in agreement with NMR experiments [21]. The magnitude of the moment is then expected to be independent of doping. Interplane coupling involving the $d_{3z^2-r^2}$ orbital may also help explain the experimental observation of a small variation of S with hole doping.

To conclude, we have found a strong contrast between the case of Ni and Zn substitutions in YBCO. Not only the depression of T_c and the value of S are drastically different but also the interplay of substitution with charge doping is now obvious in the case of Zn. This sets strong constraints on theoretical models by requiring them to link local moments and scattering by impurities, beyond the classical Kondo picture. We have addressed this point

using a model based on correlations but the problem is still open as, *e.g.*, the variation of the magnetic correlation length with doping could also play a role. Deviations from a Curie law are found negligible and more likely due to a very small spin freezing temperature linked with interaction between moments rather than classical Kondo behavior. The smallness of the moment observed in $O_7 : Zn$ raises the fundamental question: does it persist into the heavily overdoped phase of the cuprates?

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[15] A varies slightly from batch to batch in pure $YBCO_7$, so it was left free in the fit. The values found, $A = 3.5 - 5 \times 10^{-11}$ emu/K, for all our Zn samples are basically within the limits of data scatter for pure YBCO. The difference between our results and those of [7] lies in the presence of this T-linear term which was masked there by a Curie term due to parasitic phases.
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