Correlations between Magnetic and Superconducting Properties of Zn-Substituted $YBa_2Cu_3O_{6+x}$

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T_c and T_N (Néel) have been measured for a series of $YBa_2(Cu_{0.96}Zn_{0.04})_3O_{6+x}$ samples. The T variations of the homogeneous susceptibility χ_s of the CuO_2 planes, given by the shift of the ^{89}Y NMR line, are found to be nearly unchanged with respect to pure samples for $x > 0.5$, which implies that the charge transfer is negligibly modified by Zn, and that the magnetic pseudogap is not associated with superconducting pairing. Detection of an unusual Curie contribution to the ^{89}Y NMR width for $x \geq 0.5$ provides evidence that Zn induces magnetic moments in the CuO_2 planes, which play a role in the depression of T_c.

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The sizable reduction of T_c induced by Zn substitutions in cuprates has stimulated a large number of experimental studies [1] to try to understand the changes of the electronic properties induced by Zn. A major problem is to clarify whether the hole content of the conducting CuO_2 planes is modified in the presence of zinc. We insist here on the use of microscopic magnetic probes [2,3], such as the ^{89}Y NMR, which allows a separation of the modifications of the 1:2:3 phase from those associated with the existence of minute amounts of impurity phases. In the course of a detailed study on the phase diagram of pure $YBa_2Cu_3O_{6+x}$ we have evidenced that Zn does not induce an appreciable reduction of T_N in $YBa_2Cu_3O_6$ [2]. The present work is an attempt to compare the modifications of the magnetic properties over the whole range of oxygen content. We shall see here that both T_c and T_N are very sensitive to oxygen doping. This will allow us, among other things, to resolve an apparently conflicting experimental report from Mössbauer data [4] indicating that T_N is largely reduced by Zn substitution, in $YBa_2Cu_3O_6$. But the main concern of this Letter is to provide indications of the changes of the magnetic properties in the metallic state. We show here that the phase diagram versus oxygen content and the determination of the uniform susceptibility χ_s of the CuO_2 planes from ^{89}Y NMR data give direct evidence that the charge-transfer processes are not markedly modified by Zn in the metallic state. We rather clearly demonstrate for the first time on microscopic grounds that Zn induces local moments which are certainly responsible for a pair-breaking mechanism or an electronic localization. The fact that the moments are localized in the CuO_2 planes is demonstrated here by comparison with data taken on Co-substituted samples.

A large batch of $YBa_2(Cu_{0.96}Zn_{0.04})_3O_{6+x}$ has been synthesized with the standard solid-state reaction. The oxygen content has been modified systematically on a series of powder samples, by heat treatments under O_2 or mixtures of N_2+O_2, in order to control x as given by *in situ* thermogravimetric measurements, as detailed in Refs. [2] and [5]. The powdered samples have been directly used to perform NMR experiments after being fixed in Stycast 1066, which we found to be an efficient way to protect them during the thermal cycles. An ac-susceptibility mutual-inductance coil and a glass cryostat have been designed specifically to allow measurements of χ_{ac} on the NMR samples.

While a 60-K plateau for $x \approx 0.65$ is observed in $T_c(x)$ for pure samples, we surprisingly find a continuous sharp decrease of T_c with decreasing x for the Zn-substituted samples. We could not detect any trace of diamagnetism for $x < 0.7$, so that $-dT_c/dy$, where y is the Zn content, is even larger for $x \approx 0.65$ than for $x \approx 0.9$. Such results contradict the idea that Zn would induce a reduction of T_c in the most-oxygenated samples due to an excess hole doping of the CuO_2 planes [6]. In such a case an initial *increase* of T_c with decreasing x would be expected.

For samples with low x, we have similarly studied the variation of T_N versus oxygen content. As already detailed in Ref. [2], T_N has been deduced from the onset of line broadening of the ^{89}Y NMR for decreasing T. Here again, we surprisingly find that the antiferromagnetic (AF) state disappears more abruptly upon oxygen doping than in the pure samples. Such a reduction of T_N implies a more efficient charge doping to the planes for low x than in pure samples [2,3], which might be favored by the fraction of Zn substituted on the Cu(1) sites. Indeed, in the pure samples, for low x (< 0.2) an added oxygen atom introduces two holes in the structure, which are localized on the neighboring Cu sites in the chains (which become 2^+, and are linked in a singlet state, see Refs. [2] and [3]). For Zn-substituted samples, although we do not know exactly the atomic order around a Zn in the chains, we might consider that an oxygen atom introduced between a Zn 2^+ and a Cu(1) should free one hole, which can be transferred to the CuO_2 plane. The data also resolve the apparent experimental inconsistency between the results of Ref. [2] and those of Felner *et al.* [4], as these authors did not fully deoxidize their samples, so that $x \approx 0.2$ might explain the reported $T_N \approx 260$ K.

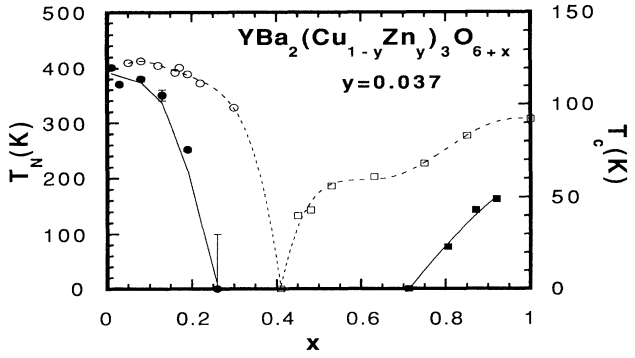

FIG. 1. Phase diagram of Zn-substituted (solid symbols) and pure $YBa_2Cu_3O_{6+x}$ (open symbols). In the former case an intermediate nonmagnetically ordered phase appears.

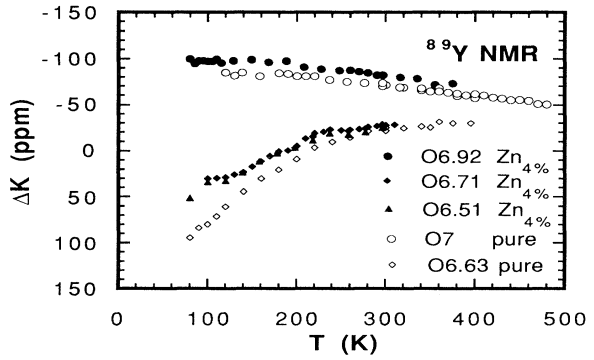

FIG. 2. ^{89}Y NMR shift for Zn-substituted and pure $YBa_2Cu_3O_{6+x}$ for various oxygen contents. The reduction of T_c occurs without any significant modification of the homogeneous susceptibility of the CuO_2 planes.

If we extrapolate the observed tendency for T_N vs x in Fig. 1, we can anticipate that, in a large region $0.25 < x < 0.7$ of the phase diagram, the samples are neither superconductors nor magnetically ordered. The phase diagram of Fig. 1 is rather comparable to that of $La_{2-x}Sr_xCuO_4$, with an intermediate phase in which frozen magnetic moments might occur at low T [7].

We have then studied in detail the spin susceptibility χ_s of the CuO_2 planes in the metallic range, by probing the T variation of the ^{89}Y NMR shift. The data for pure and Zn-substituted samples [8,9] are compared in Fig. 2. For maximum x they have quasi-identical nearly-T-independent normal-state χ_s, although T_c has been reduced to 60 K for the Zn sample. It has also been seen that, for $x \approx 1$, the T-linear term of the specific heat is independent of Zn content [10]. Further, ΔK for samples with $x \approx 0.70$, also show the sharp decrease with decreasing T initially reported by Alloul, Ohno, and Mendels [8] for similar oxygen content in pure samples. Such a variation of χ_s has been found in most lower-T_c cuprates [11], and is associated with a pseudogap which occurs in the magnetic excitations at low T. Indeed, another manifestation of these anomalous magnetic properties of cuprates is the large decrease in χ_s at all q values which occurs with decreasing T, as seen in the T dependence of the ^{63}Cu relaxation rate [12], found in depleted samples. This occurs altogether with a gap in the magnetic excitations at the AF wave vector detected by neutron scattering [13]. Within this interpretation of the NMR and neutron data, the present experimental results provide strong evidence that these magnetic anomalies are *not associated with precursive superconducting pairing, nor with manifestations of a superconducting gap* [13], as T_c is depressed below 1.5 K for our Zn-doped $x = 0.7$ sample.

It has been suggested, at least in $La_{2-x}Sr_xCuO_4$, that Zn doping induces the appearance of local moments with Curie contributions to the susceptibility [14]. However, this can hardly be deduced from ESR or macroscopic χ_m measurements, as spurious paramagnetic phases, which already are difficult to avoid in pure samples, are even more likely to be present for substituted samples, and may induce such signals. Cooper found, for instance [15], that the magnitude of the Curie term is much larger for samples synthesized with carbonates rather than oxalates.

If local moments occur at random in the structure, they should induce dipolar or RKKY local fields on the distant nuclear spins, which are orientation and distance dependent. Nuclear spins near local moments are usually largely shifted with respect to the NMR of the pure samples, while the superposition of the resonances for distant nuclei yields a broadening of the NMR line. The net effect is then a T-dependent broadening of the NMR for the various nuclear species. The ^{89}Y signal, being the narrowest in the cuprate family, is therefore the most sensitive probe of the existence of localized moments. In ^{89}Y NMR measurements, we have never detected, in pure samples, down to 100 K, any effect on the NMR linewidth which might be associated with paramagnetic sites in the structure. For instance, the local moments on the Cu(1) sites which might occur for low oxygen doping do not yield any detectable line broadening, in this temperature range. Apart from the AF samples, the only particular case for which we detected a significant change at low T of the NMR spectra is that of the highly oxidized samples with $0.9 < x < 1$. The NMR signals are then quite asymmetric for $T \approx 100$ K towards the low-susceptibility side, and can even split into two distinct lines, which indicates the occurrence of some local inhomogeneities in the oxygen ordering with an eventual phase separation. As will be discussed elsewhere [9], well-ordered samples show a narrow T-independent linewidth.

Here we surprisingly found that without particular care in the oxygen treatment, the metallic Zn-doped samples with maximum x exhibit symmetrical Y NMR line shapes, without any sign of inhomogeneity in the oxygen distribution [16]. However, *the linewidth is found to be T*

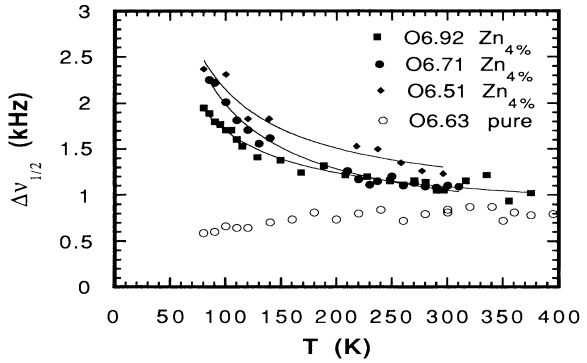

FIG. 3. ^{89}Y NMR full width at half intensity for Zn-substituted and pure $YBa_2Cu_3O_{6+x}$. For pure samples, such as for $x=0.63$, the linewidth is roughly T independent, while for Zn samples it increases at low T for all x. The curves are least-squares fits by Eq. (1).

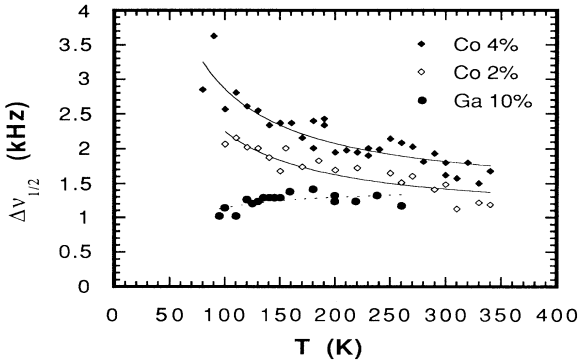

FIG. 4. ^{89}Y NMR full width at half intensity for Co- and Ga-substituted samples. Both substitute on the Cu(1) site, but for nonmagnetic Ga the linewidth slightly decreases at low T, while it increases for Co, which bears a local moment. The curves are least-squares fits by Eq. (1).

dependent, and increases progressively with decreasing T, as shown in Fig. 3. This is clear evidence that the linewidth is due to some paramagnetic broadening. This effect also occurs for Zn samples with $x=0.71$ or $x=0.51$. For such oxygen contents in pure samples [9], the NMR shifts are only slightly dependent on x at 100 K, so that oxygen disorder is not expected to induce any significant line broadening. Indeed, as displayed in Fig. 3 for comparison, for $x=0.63$, the linewidth is even found to decrease slightly at low T. Then the present results demonstrate unambiguously that the line broadening detected in all the Zn samples must be attributed to local moments which develop in the 1:2:3 phase.

Are these local moments playing any role in the destruction of the superconducting state? Certainly yes, if these moments occur in the CuO_2 planes. If they occur on the chain sites, the answer will be less obvious. Indeed, we know of local-moment substitutions which can be produced on the Cu(1) sites, such as Fe or Co. Those induce only slight reductions of T_c although they produce well-defined Curie terms [15], and line broadenings of the Y NMR [17]. We have therefore taken Y NMR data on Co-substituted samples to calibrate the ^{89}Y NMR broadening induced by local moments on the Cu(1) sites. The results are shown in Fig. 4, together with the data obtained for a Ga-substituted sample, with $y=0.1$, which is known to be a nonmagnetic Cu(1) substituent, for which no Curie-like contribution to the width is detected. Although our linewidth data are slightly smaller than that obtained by Webster *et al.* [17] (after normalization by a factor 1.5, which corresponds to the ratio of the field values in the two experiments), the results agree in both magnitude and T dependence. However, our low-T data, together with the comparison with the gallium-doped sample, allow us to conclude that the extra linewidth is due to the Co local moment. The line broadening is expected to scale with the local moment χ. Assuming that the latter follows a Curie law, as found by Cooper [15], we indeed find that the data can be fitted by

$$\Delta\nu_{1/2}=(\Delta\nu_{1/2})_0+D/T \quad (1)$$

for both Co- and Zn-substituted samples. The respective values of $D=124$ and 156 kHz K found respectively for the Co 2% and 4% samples do not scale linearly with the concentration y of local moments. Such a linear y dependence might be expected for the extreme dilute limit, for which the spatial distribution of the local moments might be approximated by a continuum. Similar fits for the data of Fig. 3 for the Zn samples are also found, and yield $D=90$, 145, and 130 kHz K respectively for $x=0.92$, 0.71, and 0.51. Therefore, if we compare the Zn- and Co-substituted samples with $y\approx 4\%$, we find that D is at most 1.5 times larger for Co than for Zn.

Cooper [15] has done some systematic measurements of χ_m for both Co- and Zn-substituted samples. Fits by

$$\chi_m=\chi_0+C/T \quad (2)$$

for Co samples indicate that both χ_0 and C increase with Co doping, with $C\approx 5y$ emu K/mole. For Zn-doped samples C is apparently 1 order of magnitude smaller for samples prepared with oxalates than for samples prepared with carbonates. In the latter case $C\approx 0.5y$ emu K/mole was found, which agrees with the value $C\approx 0.025$ emu K/mole measured at low T on our nonsuperconducting samples, also prepared with carbonates. In any case the Curie contributions to χ_m are at least 10 times larger for Co than for Zn, so that the weak susceptibility associated with the Zn substitution induces a broadening at least 6 times larger than for Co. This difference in the values of D/C can only be explained if the local moments developed in Zn-doped samples occur dominantly on the CuO_2 planes, which are nearer the Y than the Cu(1) planes, and for which indirect RKKY-type hyperfine cou-

plings might be large. These local moments might be associated with Cu^{2+} spins in the vicinity of the Zn dopants in the planes, as proposed by Finkelstein *et al.* [14], or with carrier orbitals, which might result from a localization process induced by disorder. Such a situation is known to occur near the metal-insulator transition in the metallic phase of *Si*-P, a classical case for which a metal-insulator transition occurs in presence of electronic correlations and disorder [18]. While in *Si*-P the disorder is intrinsic to the system, here the disorder might be associated with the fraction of Zn substituted in the CuO_2 planes.

In conclusion, the present results allowed us to demonstrate with a microscopic probe that the modifications of charge transfer induced by Zn are only perceptible for low oxygen content, in the AF state, and might be due to the fraction of Zn substituted on the Cu(1) chain site. For large oxygen content, the major effect [19] is the appearance of local moments in the CuO_2 planes associated with the disorder induced by the Zn substituted on the Cu(2) sites. We emphasize here that this qualitative conclusion is clearly established by the results presented here, but that more quantitative work, still required to determine the magnitude of the Curie contribution to χ_m and the fraction of Zn substituted on the Cu(2) sites, should help to clarify whether the moments are localized on Cu sites or result from disorder-induced carrier localization. Further, the rather weak modification of the T dependence of the homogeneous χ_s of the CuO_2 planes is proof that the anomalies of the magnetic properties of the cuprates are not direct precursors of the superconducting behavior. Rather, the localized magnetic states might induce pair breaking and could yield the increased relaxation rate and Cu NMR shift with respect to pure samples, observed below T_c by Ishida *et al.* [20] in Cu NMR experiments. The present results should stimulate further theoretical attempts to describe how nonmagnetic substituents can induce local magnetic behavior in correlated metals. A better knowledge of the electronic structure of the localized states will certainly provide further progress towards the clarification of the magnetic and superconducting properties of cuprates.

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