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Muon-spin-rotation study of the effect of Zn substitution on magnetism in $YBa_2Cu_3O_x$

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The magnetic properties of $YBa_2(Cu_{0.96}Zn_{0.04})_3O_x$ were studied in detail by means of muon spin rotation and relaxation for $6.0 \leq x \leq 6.92$. The complete magnetic phase diagram was mapped out and a disordered magnetic state was found to persist between $x = 6.4$ and $x \cong 6.7$ (metallic transition), in contrast with pure $YBa_2Cu_3O_x$. The appearence of this magnetic state is attributed to the effect of Zn on the doped hole dynamics and might be associated with the freezing of local moments due to Zn ($6.43 \leq x \leq 6.88$), which were also detected here, in the paramagnetic state.

Many experimental studies have been made of the effects of Cu substitution on high-T_c cuprate superconductors. In $YBa_2Cu_3O_x$ ($YBCO_x$), trivalent ions such as Ga, Al, Fe, and Co substitute for the Cu(1) chain site and therefore reduce the charge transfer from chains to planes, which results in a slight decrease of T_c.[1] Much more appealing is the case of $YBa_2(Cu_{1-y}Zn_y)_3O_x$, as Zn^{2+} substitutes mainly for Cu ions in the key CuO_2 planes.[1] Previous ^{89}Y NMR measurements of the spin susceptibility have reliably shown at the microscopic level that neither the carrier concentration nor the homogeneity of the hole doping of CuO_2 planes were affected by a nominal $y = 4\%$ substitution of Zn for Cu.[2] This makes Zn a unique substituting element in YBCO as it creates in-plane disorder without affecting the density of carriers.

Beyond the original observation of a drastic and still debated depression of T_c in superconducting (SC) $YBCO_x$ (Ref. 3), Zn substitution also induces interesting changes in the magnetic properties of the CuO_2 planes. The usual abrupt crossover from antiferromagnetic (AF) to SC behavior observed in the pure compound around $x = 6.4$ spreads out, for $y = 0.04$, to a wide region between $x = 6.25$ and $x = 6.7$ where samples were found to be neither AF above 100 K nor SC.[2] Nothing is known of this intermediate phase and a part of the present paper emphasizes evidence for a magnetic ground state which persists up to the metallic threshold ($x \approx 6.7$), as detected in muon spin rotation and relaxation (μSR). Above the freezing temperature, we could also detect the Zn-induced local paramagnetic moments, already evident for $x \geq 6.5$ and $T > 80$ K in Y NMR experiments. The μSR study is complemented by a detailed comparison of the μSR data with macroscopic susceptibility measurements on the same samples (which proved to be as free of parasitic impurity phases as any ever reported). Furthermore, the unique ability of the muon to detect both the paramagnetic local moments and the frozen moments in the magnetic phase allows us to suggest that the latter might be due to the freezing of the former, much as in conventional spin glasses. These results represent a first step toward a better understanding of the specific magnetic properties created by Zn substitution, necessary for testing theories invoking magnetic pair breaking as the origin of the depression of T_c due to Zn.

All the 4% Zn pellets studied were prepared from the same original polycrystalline batch used for the ^{89}Y NMR measurements of Ref. 2, where further details regarding the synthesis and the deoxygenation processes can be found. The range of oxygen content that one can span for $y = 0.04$, namely $\Delta x \equiv x_{max} - x_{min} \cong 0.92$, is probably limited by the maximum achievable $x_{max} = 6.92$ for $y = 0.04$.[4] All x values are referred to this endpoint.

The ability of the μ^+ to probe very sensitively internal fields and their distribution and dynamics[5–7] in zero external field (ZF), makes the present results unique. In contrast, the detection of magnetic freezing by ^{89}Y NMR in an external field[8] is hindered at low T by the Curie-like increase of the linewidth due to local moments.[2]

In Fig. 1 we present typical ZF μSR spectra for $y = 4\%$, in the x range $6.0 < x \leq 6.67$, where the magnetic ground state is found ($x \geq 6.4$). The damped 4 MHz oscillations seen for $x = 6.03$ [Fig. 1(a)] at low T are characteristic of long-range AF order, as in $YBCO_6$.[5,9] The oscillatory behavior of the μ^+ polarization at low T indicates that the $x = 6.28$ sample still exhibits AF order [Fig. 1(b)]. Its Néel temperature was determined to be $T_N = 16.5 \pm 1$ K both by means of the decrease of the local field magnitude with rising T and by the T dependence of the paramagnetic fraction in a weak transverse field of 14 G.[5] The large 1.35 MHz rms width, roughly twice that for unsubstituted samples of similar x, suggests a high degree of disorder in the AF structure. The low T_N value and the large distribution of local fields are comparable to those of $YBCO_{6.44}$.[6]

The $x = 6.43$ sample exhibits a clearly disordered magnetic ground state, as shown by the data at $T = 3$ K in Fig. 1(c). A fast relaxation (characteristic rate Λ), associated with the absence of any detectable oscillation, is the usual signature of either disordered static magnetism or strong dynamical effects. The two possibilities may be discriminated by means of longitudinal magnetic fields (LF) applied along the initial muon polarization. The response to LF of the order of Λ/γ_μ,[7] where γ_μ is the μ^+ gyromagnetic ratio, clearly establishes the static character of the local fields responsible for the μ^+ depolarization. This disordered magnetic ground state persists up to $x = 6.67$ [Fig. 1(d)], i.e., up to the metallic threshold. In contrast, undoped compounds are metallic and SC in this x range. The measured ZF μ^+ polarization $P_z(t)$ was modelled in detail by the phenomenological ansatz $P_z(t) = \exp[-(\Lambda t)^\alpha] G_{KT}(t)$, which describes well the main features of $P_z(t)$ at all temperatures. Here $G_{KT}(t)$ is a slow Kubo-Toyabe depolarization function,[7] Gaussian at early t, due to the contribution of Cu nuclear moments; $G_{KT}(t)$ is determined from data at high T, where it dominates $P_z(t)$. The parameter α varies sharply from 0 above the freezing temperature, T_f, to 0.4–0.5 below T_f, while Λ increases below T_f, which was defined as the intercept at $\Lambda = 0$ of a linear extrapolation of $\Lambda(T)$ (Fig. 2). In the frozen state, where the nuclear contribution is negligible, Λ^{-1} represents the time at which P_z has decreased by $1/e$ from its value at $t = 0$.

The complete magnetic phase diagram for $y = 4\%$ is presented as a semi-log plot in Fig. 3. The accuracy of the determination of T_N for $x = 6.28$–6.35 stresses the fact that Zn substitution deeply affects the AF order around $x = 6.3$, in contrast with the $x = 6.0$–6.1 range. An x-ray characterization shows that the $x = 6.35$ sample is tetragonal (T), while the parameters $a = 3.82$, $b = 3.89$, and $c = 11.68$ Å measured for $x = 6.43$, are characteristic of the orthorhombic (O) phase in the vicinity of the T-O transition, as for pure $YBCO_{6.43}$. This provides further evidence that the x reference is correct. Therefore, both the disorder in the AF state for $x = 6.28$ and the shift of the AF phase boundary in going from $y = 0$ to $y = 4\%$ are consistent manifestations of a cumulative effect of spinless Zn and doped holes on the pure AF order.

We emphasize that the similarity of our phase diagram to that of $La_{2-x}Sr_xCuO_4$ (LSCO) (Ref. 10) is fortuitous. Indeed, the transfer of holes to the CuO_2 planes at the T-O transition,[11] responsible for the abrupt switch from AF to SC behavior in YBCO, still holds here, in contrast with the gradual doping either by Sr substitution for La in La_2CuO_4, in the intermediate disordered state, or by Ca substitution for Y in $YBa_2Cu_3O_6$.[12] This suggests a magnetic freezing induced by Zn doping in $YBCO_x$ with $6.4 \leq x \leq 6.7$, with low values of T_f (for LSCO, $T_f \approx 10$ K).[10]

High transverse field (TF) μ^+SR experiments were performed in the paramagnetic state for $x = 6.43$ ($H_{ext} =$

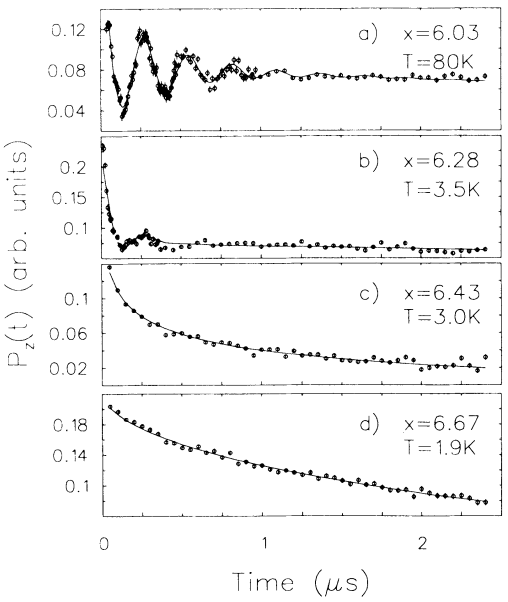

FIG. 1. Low-T ZF μSR spectra for $y = 0.04$ with various x. The solid lines are fits, see Refs. 5 and 6 (a),(b) or text (c),(d).

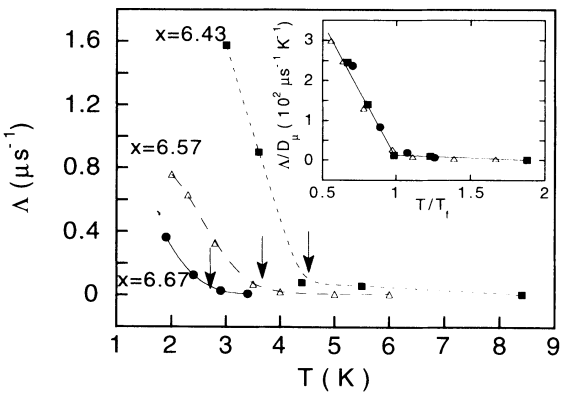

FIG. 2. Temperature dependence of the ZF depolarization rate Λ for $x \geq 6.43$. The arrows indicate T_f. Inset: T/T_f plot of Λ_{TF} normalized by D_μ, which measures the Curie-like effects due to local moments for $T > T_f$.

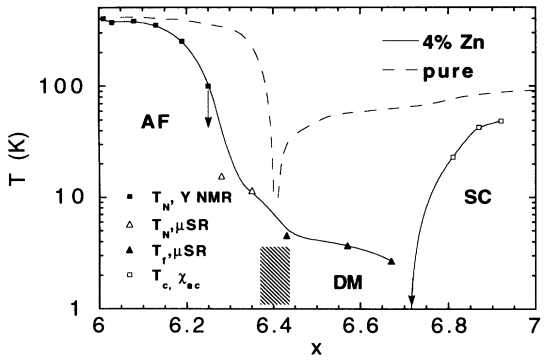

FIG. 3. Measured phase diagram for $y = 0.04$. The lines are only guides to the eye. The hatched area is the x range where the T-O transition occurs. The arrows indicate $T_N \leq 100$ K ($x = 6.25$), determined by ^{89}Y NMR, or $T_c \leq 1$ K ($x \leq 6.7$).

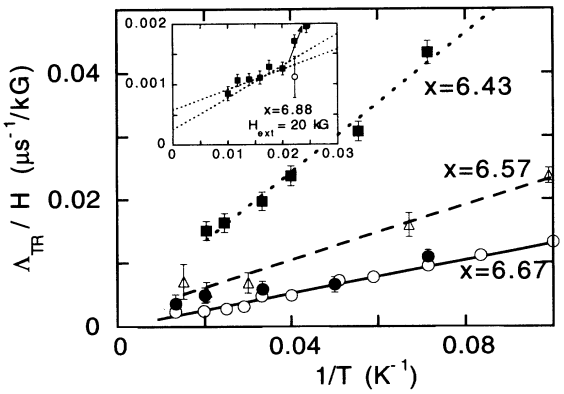

FIG. 4. Variation of Λ_{TF}/H_{ext} with inverse temperature for $T > T_f$ ($6.43 \leq x \leq 6.67$). For $x = 6.67$, open circles are for $H_{ext} = 3$ kG and full circles are for 1.5 kG. The lines are fits to the data (see text and Table I). Inset: the results for $x = 6.88$ ($T_c = 42$ K) suggest a Curie-like depolarization in the metallic state, but with lower accuracy than from ^{89}Y NMR. The arrow indicates the onset of fast depolarization due to vortices in the SC state below T_c.

1.7–2 kG), $x = 6.57$ ($H_{ext} = 2$ kG), $x = 6.67$ ($H_{ext} = 1.5$–3 kG), and $x = 6.88$ ($H_{ext} = 20$ kG). The TF depolarization rate, Λ_{TF}, was deduced from exponential fits (see below). An increase of Λ_{TF} is evident at low T where the nuclear contribution is negligible (Fig. 4). For the $x = 6.88$ sample (SC at $T_c = 42$ K) a stronger applied field (20 kG) was required to overwhelm the nuclear contribution at high T. At very low T, one might expect a dynamical (thus field-independent) origin of Λ_{TF} for T approaching T_f. On the contrary, above $2T_f$, we found that Λ_{TF} varies linearly with field in all our samples and therefore must have a static origin different from possible pretransitional fluctuations. The related inhomogeneity of the static local field at the μ^+ site implies a non-uniform susceptibility in the sample, analogous to what is observed by NMR in dilute magnetic alloys.[13] The Curie-like variation of Λ_{TF} (Fig. 4) is then due to random paramagnetic localized moments, in agreement with ^{89}Y NMR results.[14]

Above $2T_f$, for $x \leq 6.67$, and above T_c, for $x = 6.88$, one can fit the variation of Λ_{TF} with T and H_{ext} to the form $\Lambda_{TF} = D_\mu \gamma_\mu H_{ext}/T$. The resulting values of D_μ are reported in Table I. In order to perform a more quantitative analysis of these data, a dipolar coupling of the μ^+ with random moments is assumed first. Numerical simulations of the μSR line shape performed in the realistic case of YBCO with a stacking of bilayers [along the lines of the three-dimensional (3D) calculations[15]], yield the same $e^{-\Lambda_{TF}t}$ dependence for $P_z(t)$ in polycrystalline samples (powder average) as would be expected in an isotropic regular 3D lattice. The concentration of impurities was assumed to be $1.5y$ in each CuO_2 plane and no difference was found with the more realistic case where the four nearest neighbor (NN) Cu to a Zn atom share an equivalent moment. It was also checked that the various likely μ^+ sites give similar results in the considered x range.[16] Finally, the simulated linewidth is quite similar to that calculated analytically in the 3D dilute limit. One derives then that Λ_{TF}/H and the Curie constant, C_m, corresponding to local moments should be related by $\Lambda_{TF}/H = (4\pi^2/9\sqrt{3})\gamma_\mu C_m/T$,[15] assuming a dipolar coupling.

In order to check the plausibility of a dipolar coupling, we performed dc magnetization measurements on parts of the μSR samples. We found a susceptibility $\chi_m = (\chi_0 + C_m/T)$ for $T < 100$ K, where the intrinsic spin susceptibility of the unsubstituted CuO_2 planes, $\chi_0(x)$, is fairly T independent. The values of C_m are listed in Table I and are to our knowledge lower than any reported for $x \approx 6.9$.[3,17,18] A minor 3.3×10^{-6} emu K/cm^3 contribution from impurity phases was estimated by a quantitative electron spin resonance (ESR) search for Y_2BaCuO_5 and $BaCuO_2$ for $x = 6.88$. For lower x samples obtained from the same master batch by low-T deoxygenation, one does not expect any increase of the amount of impurity phases; this was also checked by ESR.

From the experimental values of C_m, one can calculate the expected dipolar contribution to D_μ, D_m, which yields, surprisingly, $D_\mu > 5D_m$ for all x (Table I). This clearly suggests that the coupling of the muon with the local moments is not dipolar but is rather a hyperfine (HF) coupling with the NN Cu(2) which, in turn, couples to the local moments by RKKY-like interactions, as indicated by Y and Cu(2) NMR experiments.[2,18] The line broadening discussed here is then similar to those reported through NMR. By a mere scaling of D_μ with the Curie-like broadening of the Y NMR line for $x \approx 6.9$,[2,19] $T\Delta H/H = 1.5 \times 10^{-3}$ K, one gets a ratio of the HF constants for μ^+ and Y, $A_{\mu^+}/A_Y = 0.33(8)$. This would correspond then to a 75(18) ppm shift in pure $YBCO_7$,

TABLE I. Experimental values of D_μ and C_m. D_m is the calculated dipolar contribution to D_μ, deduced from C_m.

x	D_μ (K)	C_m (emu K/cm^3)	D_m (K)
6.92		1.9×10^{-5}	
6.88	$5.0(1.2)\times10^{-4}$	2.6×10^{-5}	6.5×10^{-5}
6.67	$1.5(1)\times10^{-3}$	1.1×10^{-4}	2.7×10^{-4}
6.57	$2.7(2)\times10^{-3}$	1.2×10^{-4}	2.8×10^{-4}
6.43	$6.7(3)\times10^{-3}$	1.4×10^{-4}	3.3×10^{-4}

consistent with early μSR data.[20] The absence of linear relationship between the variations of D_μ and C_m with x could be interpreted either as a variation of the μ^+ HF constant with x (slight changes in the μ^+ position) or as a dominant contribution of paramagnetic chain fragments to χ_m, consistent with the irregular variation of C_m with x for our deoxygenated samples.

Finally, the ZF depolarization rate, Λ, in the disordered magnetic phase, normalized by the value of D_μ found for $T > T_f$, has been plotted versus T/T_f ($x \leq 6.67$, inset of Fig. 2). The merging of all the points into a single line supports the important idea that the local moments detected at high temperatures are the same that freeze at T_f, usually associated with Cu(2) spins. This also indicates that the chains do not dominate the observed depolarization rate in the TF data. Another consequence of the latter plot is that the lower x, the broader the distribution of local fields for a given T/T_f, as D_μ increases with oxygen depletion. Then either the concentration or the magnitude of the moments increases with decreasing x, in agreement with ^{89}Y NMR results.[2,19]

We conclude that low-T magnetism persists in the $y = 0.04$ samples for x up to 6.67, as compared with 6.45 for $y = 0$. It is not surprising then to find that the magnetic excitation spectrum is affected by the presence of Zn for $x = 6.6$, as shown by the suppression of the pseudogap for $q = (\pi, \pi)$ evident in recent neutron and NMR experiments.[21,22] Such a pseudogap has never been detected for cuprates undergoing a magnetic transition at low T. Since the relationship between oxygen content and hole doping of the planes is hardly affected by Zn substitution, we are naturally led to correlate the persistence of the magnetic state with a definite decrease in the efficiency of the carriers at destroying magnetic correlations and yielding a metallic character. This could tentatively be understood in the picture of Zhang-Rice singlets,[23] as missing magnetic Cu ions limit the spatial extension of the wave function of the holes, leading to a damping of the carrier dynamics. This is consistent with the reported increase of the normal state resistivity,[24] since one might expect Zn-induced scattering of carriers propagating in an AF correlated background. The present results should stimulate further theoretical studies on the effect of Zn substitution in YBCO, not only in the metallic but also in the magnetic state.

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[1] L.H. Greene and B.G. Bagley, in *Physical Properties of High T_c Superconductors II*, edited by D.M. Ginsberg (World Scientific, Singapore, 1990).
[2] H. Alloul *et al.*, Phys. Rev. Lett. **67**, 3140 (1991).
[3] G. Xiao *et al.*, Phys. Rev. Lett. **60**, 1446 (1988).
[4] C. Legros-Gledel *et al.*, Physica C **172**, 304 (1990).
[5] J.H. Brewer *et al.*, Phys. Rev. Lett. **60**, 1073 (1988).
[6] R.F. Kiefl *et al.*, Phys. Rev. Lett. **63**, 2136 (1989).
[7] R.S. Hayano *et al.*, Phys. Rev. B **20**, 850 (1979).
[8] H. Alloul *et al.*, Physica C **171**, 429 (1990).
[9] The rms frequency distribution σ was found intrinsic to Zn substitution for $80 < T < 200$ K and varies with y as σ [MHz] $\approx 0.12 + 9.3(1.1)y$. After subtracting the contribution from $1.5y$ randomly missing magnetic Cu ions in an otherwise perfect AF network, one can relate σ to spin disorder. This yields, for example, a rms deviation of 9.5(1.5)° from perfect AF alignment for $y = 4\%$, in agreement with the 7.7(6)° value deduced from an analysis of the ZF Cu(2) NMR experiments [as in P. Mendels *et al.*, Physica C **171**, 429 (1990)] on a sample from the same batch [X. Labouze (private communication)]. Then, the substitution of Zn in $YBCO_6$ induces a mild but progressive magnetic disorder, as expected for missing spins in an AF structure without any induced frustration.
[10] F.C. Chou *et al.*, Phys. Rev. Lett **71**, 2323 (1993).
[11] A. Tolentino *et al.*, Phys. Lett. A **139**, 474 (1989).
[12] H. Casalta, H. Alloul, and J.F. Marucco, Physica C **204**, 331 (1993).
[13] H. Alloul, J. Darville, and P. Bernier, J. Phys. F **4**, 2050 (1974).
[14] Our μSR data do not conflict with a previous negative ZF μSR search for local moments [J.L. Garcia-Munoz *et al.*, Physica C **185-189**, 270 (1991)]. We observe paramagnetic then *field-induced* electronic moments with typical fluctuation times likely smaller than 10^{-9} s, which would produce negligible line broadening effects in ZF.
[15] R.E. Walstedt and L.R. Walker, Phys. Rev. B **9**, 4857 (1974).
[16] W.K. Dawson *et al.*, J. Appl. Phys. **64**, 5809 (1988); N. Nishida and H. Miyatake, Hyperfine Interact. **63**, 183 (1990).
[17] J.R. Cooper, Supercond. Sci. Technol. **4**, 181 (1991).
[18] R.E. Walstedt *et al.*, Phys. Rev. B **48**, 10 646 (1993).
[19] A. Mahajan *et al.* (unpublished).
[20] F.N. Gygax *et al.*, Phys. Lett. A **127**, 448 (1988). The $-30(5)$ ppm T variation of the shift reported in that paper might be associated with the T decrease of the susceptibility of the CuO_2 planes for slightly depleted $YBCO_{7-\delta}$, corresponding to the -70 ppm variation of the ^{89}Y NMR shift detected later [H. Alloul, T. Ohno, and P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989)].
[21] K. Kakurai *et al.*, Phys. Rev. B **48**, 3485 (1993); G. Zheng *et al.*, J. Phys. Soc. Jpn. **62**, 2591 (1993).
[22] K. Ishida *et al.*, Physica C **179**, 29 (1991).
[23] F.C. Zhang and T.M. Rice, Phys. Rev. B **37**, 3759 (1988).
[24] T.R. Chien, Z.Z. Wang, and N.P. Ong, Phys. Rev. Lett. **67**, 2088 (1991).