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Muon-spin-rotation study of Zn-induced magnetic moments in cuprate high-T_c superconductors

C. Bernhard
Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany

Ch. Niedermayer and T. Blasius
Fakultät für Physik, Universität Konstanz, D-78434 Konstanz, Germany

G. V. M. Williams
The New Zealand Institute for Industrial Research, P.O. Box 31310, Lower Hutt, New Zealand

R. De Renzi and C. Bucci
Physics Department, University of Parma, I-43100 Parma, Italy

J. L. Tallon
The New Zealand Institute for Industrial Research, P.O. Box 31310, Lower Hutt, New Zealand

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Using muon spin rotation (μSR) we searched for evidence of Zn-induced magnetic moments in underdoped cuprates. We find that the moments, which in a previous μSR study were reported to be Zn induced, exist already in the pure underdoped compound and most likely arise from antiferromagnetic correlated Cu(2) spins. We obtain no evidence for additional Zn-induced moments. Nevertheless, we cannot exclude the possibility that Zn-induced magnetic moments exist in case they are very weakly coupled to the spin system and the mobile charge carriers of the CuO_2 planes. [S0163-1829(98)51438-5]

The magnetic properties of nominally nonmagnetic Zn^{2+} impurities in the CuO_2 planes of high-T_c superconducting (SC) cuprates have attracted considerable attention. The Zn^{2+} impurities not only rapidly suppress SC, apparently due to pair breaking, they also strongly affect the normal state ''pseudogap'' which appears in the underdoped cuprates as a depletion of the low energy spin and charge excitations (Refs. 1–4). ^{89}Y-NMR experiments indicate that the ''pseudogap'' in the static spin susceptibility is locally suppressed at the Zn site and the nearest neighboring Cu(2) sites while it is virtually unaffected at the next nearest neighbors and beyond.[1,2] The NMR spectra from the probe nuclei adjacent to the Zn^{2+} impurities exhibits a Curie term in the Knight shift K_s and in the relaxation rate $1/^{89}T_1$ which has been attributed to Zn-induced paramagnetic moments.[1,2] It has been suggested that the nonmagnetic Zn^{2+} impurities disrupt the local antiferromagnetic (AF) correlation of the Cu(2) spins and thereby induce a localized paramagnetic moment which is shared by the four neighboring Cu(2) sites (Ref. 1). ^{63,65}Cu NQR (nuclear quadrupole resonance) experiments, which probe the AF correlation of the Cu(2) spins, seem to confirm this scenario and indicate a suppression of the AF correlation in the vicinity of the Zn impurities.[3] Alternatively, it has been suggested that the Curie-like behavior of the ^{89}Y-NMR Knight shift can be understood, without invoking Zn-induced magnetic moments, simply in terms of a random distribution of impurities and a concomitant random variation of the local hole concentration.[5]

The technique of muon spin rotation (μSR) provides yet another sensitive nuclear probe for the study of weak or dilute magnetic moments. The muons reside on low-symmetry interstitial lattice sites and therefore probe a k-space average of the magnetic response including the AF correlation of the Cu(2) spins. The preferred muon site in Y-123 and Y-124 is either within the chain layer [~1 Å away from the O(1) oxygen] or about 1 Å away from the apex oxygen slightly pointing towards the CuO chains.[6] The magnetic coupling of the muon spin is mainly dipolar. The contact hyperfine coupling is extremely weak as is indicated by the small μSR Knight shift.[7] This circumstance and the absence of a muon electrical quadrupole moment help to avoid excessive line broadening and make the μSR technique suitable for exploring the magnetic correlation of the Cu(2) spins[8–10] and subsequent Zn-induced effects. Previous μSR experiments on underdoped $YBa_2Cu_{2.88}Zn_{0.12}O_{6+x}$ were reported to provide evidence for Zn-induced paramagnetic moments.[11] These Zn-induced moments were argued to undergo a freezing transition at low temperature.[11] Only Zn-substituted samples have been investigated, however, while the claim that the observed magnetic moments are Zn-induced was not confirmed by measurements on Zn-free samples.

Here we present a normal-state μSR study on underdoped Y-124 and Y-123 samples with variable Zn and Ni content. We show that, irrespective of the presence of Zn or Ni impurities, the previously observed magnetic moments exist already in the pure compound and most likely arise from the AF-correlated Cu(2) spins of the pure underdoped CuO_2 planes.

Polycrystalline samples of $YBa_2Cu_{4-z}Zn_zO_8$ with $z=0$ ($T_c=81$ K), 0.075 ($T_c=25$ K) and 0.13 ($T_c<4$ K) and $YBa_2Cu_{3.87}Ni_{0.13}O_8$ ($T_c<4$ K) have been prepared by solid-state reaction in 60 bar O_2 as described earlier.[2] T_c has been determined by ac-magnetic susceptibility measurements. The

Ni-substituted sample required repeated grinding and sintering in order to homogenize the Ni distribution. Once this was achieved, the T_c suppression was comparable to that of the Zn-substituted samples.[2] This contrasts the situation for Y-123 where the rate of suppression of T_c is much stronger for Zn than for Ni.[3] X-ray diffraction experiments show that all the Y-124 samples are phase pure. Also, Gd-ESR (electron spin resonance) experiments performed on a series of analogous series of 1% Gd-doped Y-124 give no indication for any traces of the magnetic impurity phases $Y_2Ba_2CuO_5$ and $BaCuO_2$. In addition, two strongly underdoped samples of $Y_{0.8}Ca_{0.2}Ba_2Cu_{3-z}Zn_zO_6$ with $z=0$ ($T_c=31$ K) and $z=0.15$ ($T_c<4$ K) have been prepared as described earlier.[12]

The μSR experiments were performed at the Paul-Scherrer-Institut (PSI) in Villigen, Switzerland, at the πM3 beamline which provides essentially 100% spin-polarized positive "surface muons." The muon spins precess in the local magnetic field B_μ with the Larmor frequency $\omega_\mu=\gamma_\mu B_\mu$, where $\gamma_\mu=851.4$ MHz/T is the gyromagnetic ratio of the muon. The dephasing (relaxation) of the muon spin polarisation $P(t)$, which is obtained from the time evolution of the asymmetry of the decay positron emission rate, provides a sensitive probe for the distribution (fluctuation) of the local magnetic field at the muon site.

First we discuss the result of the transverse field (TF) μSR experiments where an external magnetic field H^{ext} is applied in the direction perpendicular to $P(t)$. We have fitted our normal-state TF-μSR spectra with an exponential depolarization function:

$$P(t)=P(0)\exp(-\Lambda^{TF}t)\cos(\gamma_\mu\langle B_\mu\rangle t). \quad (1)$$

We found that the choice of the exponential damping function (which is appropriate for fluctuating moments or likewise for a dilute system of static magnetic moments) is not unique. Similarly good fits could be obtained using a Gaussian depolarization function (which typically applies for a dense system of static paramagnetic moments). From the TF-μSR data alone we hardly can differentiate between these two cases. In particular, we cannot conclusively decide whether the underlying magnetic moments are static or fluctuating. Our choice of an exponential damping function, nevertheless, is supported by the result of the zero field (ZF) μSR experiments (discussed below) which indicate that (probably) the same magnetic moments slow down at very low T and undergo a freezing transition.

Figure 1(a) shows the T dependence of the TF-μSR depolarization rate Λ^{TF} which measures the width of the internal field distribution, $\langle\Delta B_\mu^2\rangle$, at the muon site. Displayed are data at $H^{ext}=6$ kOe for $YBa_2(Cu_{1-z}Zn_z)_4O_8$ with $z=0$ and $T_c=81$ K (open circles), $z=0.075$ and $T_c=25$ K (open triangles) and $z=0.13$ and $T_c<4$ K (solid diamonds), for $YBa_2Cu_{3.85}Ni_{0.15}O_8$ with $T_c<4$ K (stars) and for strongly underdoped $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_6$ with $T_c=31$ K (open squares). Only normal-state data for $T>T_c$ are displayed in Fig. 1 since a flux-line lattice forms below T_c and dominates Λ^{TF}. Already for the pure Y-124 sample a small increase of Λ^{TF} towards low T is visible, even if the T regime for $T<T_c=81$ K is not accessible. The signature of the magnetic moments is clearer in the case of the strongly underdoped $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_6$ sample with $T_c=31$ K (open squares) for which Λ^{TF} exhibits a pronounced increase with decreasing T. Note that a similar result was obtained in Ref. 11 for a correspondingly strongly underdoped but Zn-substituted sample of $YBa_2Cu_{2.88}Zn_{0.12}O_{6.43}$ as indicated by the dashed line. It is evident from Fig. 1(a) that neither the Zn nor the Ni impurities introduce any extra enhancement of Λ^{TF}. Instead, a sizeable upturn in Λ^{TF} occurs only for moderately Zn-substituted Y-124 and Ni-substituted Y-124 while it is almost absent for heavily Zn-substituted Y-124. The inset of Fig. 1(a) shows the field dependence of Λ^{TF} in the Y-124 samples at $T=100$ K. It can be seen that Λ^{TF} increases almost linearly with H^{ext} irrespective of the Zn or Ni content. Note that the contribution of the nuclear moments to Λ^{TF} is field and T independent and that the muon diffusion is known to be negligible below 250 K.[6] We therefore conclude that the T and the field dependence of Λ^{TF} provide evidence for magnetic moments or magnetic correlations of electronic origin which exist already in the pure Y-124 and Y-123 compounds. No indication for additional Zn- or Ni-related mag-

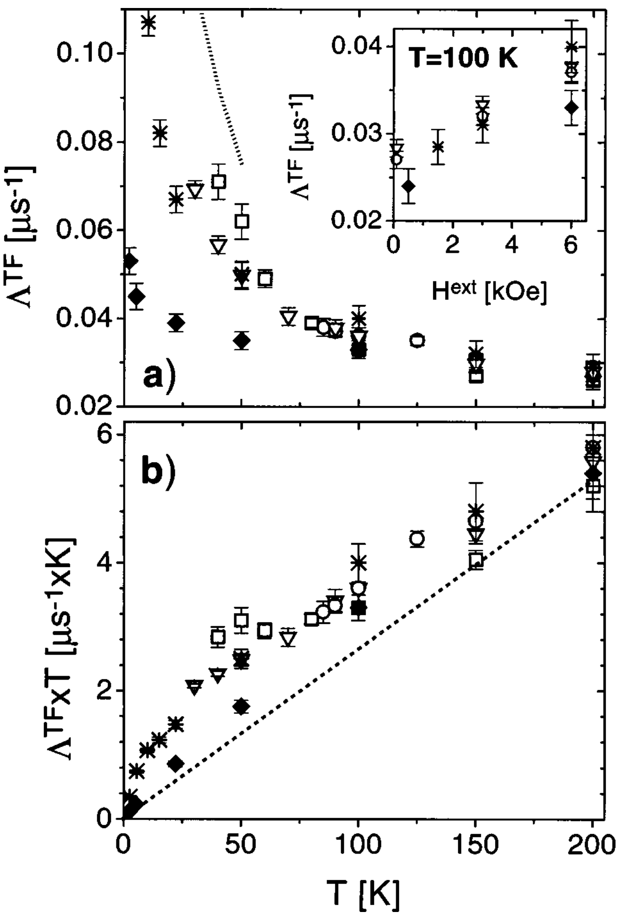

FIG. 1. (a) The TF-μSR depolarization rate Λ^{TF} vs T at $H^{ext}=6$ kOe for $YBa_2Cu_{4-z}Zn_zO_8$ with $z=0$ and $T_c=81$ K (open circles), $z=0.075$ and $T_c=25$ K (open triangles) and $z=0.13$ and $T_c<4$ K (solid diamonds), for $YBa_2Cu_{3.87}Ni_{0.13}O_8$ with $T_c<4$ K (stars) and for strongly underdoped $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_6$ with $T_c=31$ K (open squares). The dashed line sketches the result reported in Ref. 11 for $YBa_2Cu_{2.88}Zn_{0.12}O_{6.43}$. The inset shows the field dependence of Λ^{TF} in the Y-124 samples at $T=100$ K. (b) The same data as in (a) plotted for $\Lambda^{TF}T$ vs T. The dotted line indicates the approximate T-independent contribution of the nuclear magnetic moments.

netic moments is obtained. These may still exist but Λ^{TF} is dominated by the magnetic correlation of the pure system. Note that a sizeable contact hyperfine coupling was assumed in Ref. 11 in order to explain the broadening of Λ^{TF} in terms of the Zn-induced paramagnetic moments.

We exclude oxygen-related defects within the CuO chain layer as a source of the magnetic moments[13] since Y-124 has stoichiometric CuO double chains which are structurally very stable. A similar argument holds for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_6$ which has a completely deoxygenated chain layer. We therefore conclude that the observed magnetic moments arise from the underdoped CuO_2 planes, most likely associated with the AF correlated Cu(2) spins. *We suspect that the observed magnetic moments are not static but rather fluctuate since the zero field* (ZF)-*μSR experiments (discussed below) indicate that most likely the same magnetic moments slow down and undergo a freezing transition at low T.* Also, a closer inspection of our data reveals that the increase of Λ^{TF} may not quite follow a Curie law. This is best seen in Fig. 1(b) where $\Lambda^{TF}\cdot T$ is plotted versus T. Here the T-independent contribution from the nuclear moments gives rise to a linear $\Lambda^{TF}T$ with zero intercept similar to that represented by the dotted line. An additional Curie-like contribution should show up as a T-independent offset. From Fig. 1(b) it appears that some magnetic moments are present at low T but they seem to melt away above 100 K, similarly as suggested by Cooper *et al.* from bulk susceptibility measurements.[14] This finding suggests that the increase in Λ^{TF} at low T may be related to the pseudogap which also shows up below a certain temperature $T^* > T_c$. Also, in analogy to the pseudogap,[2] the Curie-like behavior is suppressed by a large Zn content but not so much by a corresponding Ni content.

Next we turn to the magnetic freezing transition which is observable at low T in the zero-field (ZF) μSR experiments. It was reported early on from ZF-μSR studies that a magnetic freezing transition occurs at low T in strongly underdoped but yet SC samples of the pure La,Sr-214 and Y-123 systems.[8,9] Originally it was suspected that the related magnetic phase may arise from a poor sample quality or, especially in case of the partially oxygen reduced Y-123 system, from oxygen ordering effects which lead to an inhomogeneous hole distribution.[9] Very recently, however, it has been demonstrated that this freezing transition represents an intrinsic property of the spin and charge dynamics of the CuO_2 planes since it evolves systematically as a function of the average hole content.[10] It was found that the different kind of defects, which are introduced into the rocksalt layers in order to achieve the required hole doping, have a negligible influence on the magnetic phase diagram.[10] In the following we will show that, contrary to a previous paper,[11] neither is the magnetic transition fundamentally modified by the Zn impurities.

Figure 2(a) shows representative ZF-μSR spectra for the time evolution of the muon spin polarization $P(t)$ obtained at $T = 2.2$ K for the strongly underdoped and SC sample $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_6$ with $T_c = 31$ K (open squares; with an offset of 0.2) and for the corresponding Zn-substituted sample $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.85}Zn_{0.15}O_6$ with $T_c < 4$ K (solid squares). In both cases the spectra can be described with a Lorentzian damping function

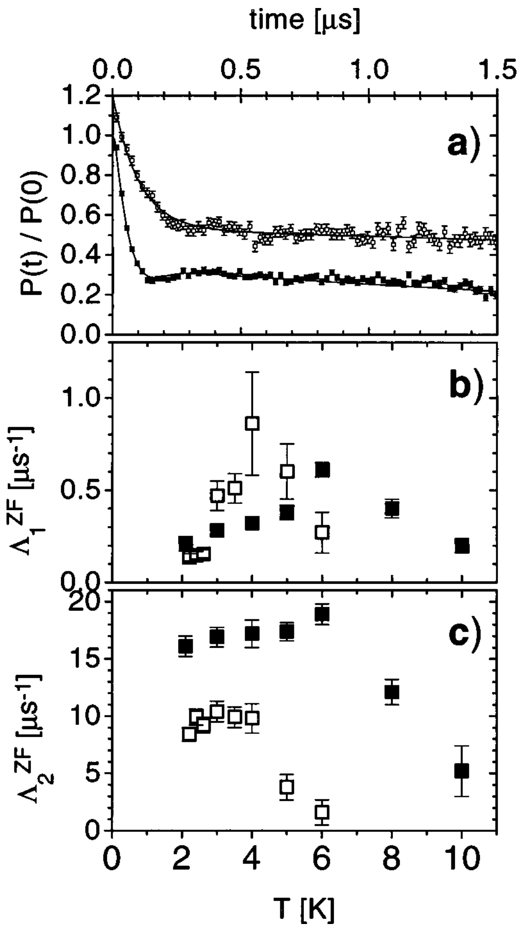

FIG. 2. (a) ZF-μSR spectra for $P(t)$ obtained at 2.2 K for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_6$ (open squares; with a vertical offset of 0.2) and for $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.85}Zn_{0.15}O_6$ (solid squares). (b) The longitudinal relaxation rate Λ_1^{ZF} vs T and (c) the transverse relaxation rate Λ_2^{ZF} as a function of T.

$$P_z(t) = P(0)[2/3 \cos(\gamma_\mu B_\mu t)\exp(-\Lambda_2^{ZF}t) + 1/3 \exp(-\Lambda_1^{ZF}t)]. \quad (2)$$

The 2/3 (1/3) term accounts for the field component which, averaged over the randomly-oriented powder, is perpendicular (parallel) to $P(t)$. The longitudinal relaxation rate, Λ_1^{ZF}, measures the fluctuation of the magnetic field while the transverse one, Λ_2^{ZF}, is determined in addition by the static disorder. The considerably smaller relaxation process due to the nuclear Cu moments has been neglected in Eq. (2). The 2/3 component of the Zn-substituted sample exhibits an almost overdamped oscillation. The frequency of $\langle\omega_\mu\rangle \approx 2.4(2)$ MHz corresponds to an average magnetic field at the muon site of $\langle B_\mu\rangle \approx 18(1)$ mT. Such an oscillation indicates the presence of static magnetic order on the μSR-time scale of $\tau < 10^{-6}$ s. The rather large damping rate of $\Lambda_2^{ZF} \approx 17\ \mu s^{-1}$, however, implies that the magnetic order is not fully developed and/or spatially inhomogeneous. In contrast, no oscillation is observed for the Zn-free sample, despite its significantly smaller damping rate of $\Lambda_2^{ZF} \approx 9\ \mu s^{-1}$. This implies that $\langle B_\mu\rangle$ is considerably larger in the Zn-substituted samples than in the pure one. We emphasize that the observed behavior can be readily understood without invoking additional Zn-induced moments, simply by taking into account that the Zn impurities localize some of the mobile hole carriers[15] and thus reduce the effective carrier concentration in the Zn-free regions. It was previously shown for pure Y,Ca-123 and La,Sr-214 systems that $\langle B_\mu \rangle$ increases rather rapidly when the hole doping is reduced in the strongly underdoped regime.[8–10] As a result, B_μ is enhanced in the hole depleted Zn-free regions while it is reduced in the vicinity of the Zn impurities. Both effects, the increase of $\langle B_\mu \rangle$ and the enhancement of $\Lambda_2^{ZF} \sim \langle \Delta B^2 \rangle$, can be explained within this scenario. Also rather instructive is the T evolution of Λ_1^{ZF} which is displayed in Fig. 2(b). For both samples Λ_1^{ZF} can be seen to exhibit a cusplike structure which is indicative of a slowing down and a freezing transition (where the spin correlation time τ_c equals $10^{-6}-10^{-7}$ sec) of the magnetic moments. The cusp temperature is higher in the Zn-substituted sample with $T_g \approx 6$ K than in the pure sample with $T_g \approx 4$ K. Once more, a corresponding increase of T_g has also been observed in the pure system upon a reduction of the hole content.[10] We therefore conclude that the magnetic freezing transition at low temperature, as seen by ZF-μSR, is not fundamentally modified by the Zn impurities. In particular, no Zn-induced magnetic moments need to be invoked in order to explain the ZF-μSR data. We emphasize that the hole localization effect should be most efficient at low T (Ref. 15) while it should have a negligible effect on the TF-μSR data (reported above) at elevated T. Finally, we note that we believe that the nature of the magnetic ground state of the pure system is not fully understood yet. One possibility is that it is microscopically inhomogeneous, i.e., it may consist of a charge separated state where hole poor and AF correlated domains are separated by hole rich rivers. In that case, the ZF-μSR spectrum may consist of two components, (i) a moderately damped and oscillating Gaussian component due to the muons that reside within the AF correlated hole poor domains and (ii) a rapidly damped nonoscillating exponential function which accounts for the muons that stop in the vicinity of the hole rich stripes (which are only a few angstrom wide) where the Cu(2) spins are strongly disordered. Clearly, more detailed experiments are desirable in order to clarify this point which goes beyond the scope of the present paper.

In summary, from μSR experiments on Zn-substituted underdoped Y-124 and Y-123 polycrystalline samples we obtain no evidence for Zn-induced paramagnetic moments. Instead we find that the magnetic moments, which previously have been attributed to the Zn impurities,[11] are equally present in the pure underdoped compound and most likely are related to the AF correlation of the Cu(2) spins and/or the pseudogap. Nevertheless, we cannot exclude the possibility that Zn-induced magnetic moments exist, in case they are weakly coupled to the spin system and the mobile charge carriers of the CuO_2 planes.

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