Suppression of the superconducting gap and the spin-fluctuation gap of $YBa_2Cu_3O_y$ ($y=7.0$ and 6.76) by Zn substitution as measured by Gd^{3+} electron-spin resonance

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The local susceptibility around Zn atoms in Gd-doped $YBa_2(Cu_{0.97}Zn_{0.03})_3O_y$ has been measured by the electron-spin-resonance Knight shift of Gd^{3+} at 245 GHz. The magnitude and distribution of the shifts are compared with the corresponding data for compounds with no Zn. For both $y=7.0$ and 6.76 the full density of states (corresponding to the high-temperature normal state of the pure $y=7.0$ compound) is restored at the first-neighbor sites of Zn atoms irrespective of whether the material is superconducting or not. This shows that both the superconducting gap and the spin-fluctuation gap are locally suppressed by Zn substitution.

The electronic structure of the high-temperature superconductor $YBa_2Cu_3O_y$ changes qualitatively[1,2] when the hole density on the CuO_2 planes is decreased from its optimum value by varying the oxygen content y. For $y>6.9$ it resembles a Fermi liquid above the superconducting transition temperature T_c with a temperature-independent density of states at the Fermi level (DOS). As the superconducting gap opens, the DOS decreases rapidly with temperature. In the underdoped material with $y<6.9$ a gap in the low-lying excitation spectrum persists well above T_c and the DOS measured by the static uniform spin susceptibility[1,2] χ_s or the coefficient of the electronic specific heat[3] γ changes continuously through T_c. The anomalous behavior of χ_s above T_c is related to a peak at the antiferromagnetic wave vector and finite energy in the spin-fluctuation spectrum.[4] The origin and nature of the gap in the electronic structure are still open questions,[5] in this paper we refer to it for clarity as a "spin-fluctuation gap." The substitution of Cu by a small concentration of Zn suppresses T_c strongly[6] without changing the hole density in the CuO_2 planes.[7] Loram, Mirza, and Freeman[8] concluded from specific-heat studies of Zn-doped $YBa_2Cu_3O_{7.0}$ that the DOS does not fall to zero as $T \rightarrow 0$ and suggested that pair breaking in regions around the Zn atoms may be the reason for the depression of T_c. ^{63}Cu NMR showed a finite DOS at $T=0$ in Zn-substituted samples.[9] Alloul et al.[10] interpreted ^{89}Y NMR above T_c by assuming that localized magnetic moments are formed around the Zn atoms substituted in the CuO_2 planes in both optimally doped and underdoped compounds. In *underdoped* compounds the presence of a Curie-like term in the static magnetic susceptibility measurements supports this suggestion,[11] however, neither NMR nor static susceptibility measurements above T_c show clear evidence for the formation of localized moments at $y=7.0$.

In this paper we report on the distribution of χ_s around Zn measured by Gd^{3+} electron-spin resonance (ESR) in 1% Gd-doped $YBa_2(Cu_{0.97}Zn_{0.03})_3O_y$ with $y=7.0$ (optimally or slightly overdoped) and 6.76 (underdoped). We compare results with χ_s measured on pure samples using the same technique.[12] Below 30 K and for both values of y, 3% Zn doping restores on average 50% of N_0, the DOS of the normal state of the Fermi-liquid-like pure compound. We show that in both cases χ_s is inhomogeneous, the full normal-state value of the susceptibility is restored at first neighbors to Zn atoms. We conclude that in regions around Zn both the superconducting and the spin excitation gaps are suppressed.

Sintered polycrystalline samples were prepared by standard solid-state reaction methods with 1% of Y substituted by Gd. Samples were lightly ground and the powder was aligned in epoxy resin along the crystallographic c direction in a magnetic field. X-ray diffraction showed that the samples were single phase, however, a small amount ($\approx 1\%$) of an impurity phase was detected in the Zn-doped compounds by Gd^{3+} ESR.

The difference between optimally doped and underdoped systems is well illustrated by the resistivity (Fig. 1). For $y=7.0$, 3% Zn suppresses T_c from 92 to 55 K, and
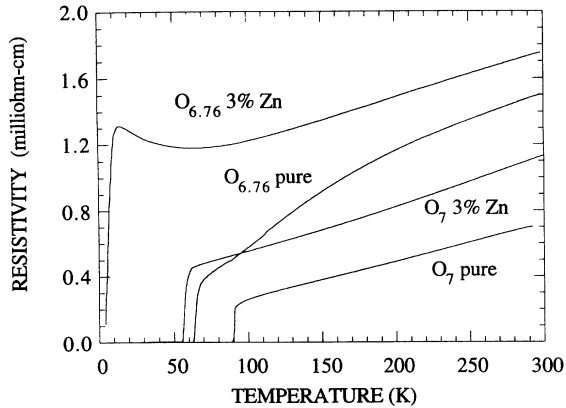
FIG. 1. Resistivity of pure and Zn-substituted YBa$_2$Cu$_3$O$_y$ samples (doped with 1% Gd) investigated by Gd^{3+} ESR. For $y=7.0$ Matthiessen's rule is followed above T_c, for $y=6.76$ Zn substitution has a stronger effect at lower T, where the resistivity of the pure material is suppressed by the spin gap.

in the normal state Zn substitution acts like a normal scattering center adding a constant term to the temperature dependence of the resistivity.[13] In the underdoped $y=6.76$ compound T_c is suppressed by 3% Zn from 63 to about 10 K. In this case Matthiessen's rule does not apply. In the pure $y=6.76$ sample the opening of the spin-fluctuation gap is accompanied by a decrease in resistivity below 200 K. This effect is no longer seen in the Zn-doped sample. Below 60 K the resistivity actually increases with decreasing T indicating a tendency toward electron localization.

Gd^{3+} electron-spin-resonance spectra were recorded at 245 GHz (8.8 T) and 9.1 GHz (0.3 T). The Gd^{3+} ESR in Gd:YBa$_2$Cu$_3$O$_y$ may be analyzed within the framework usually applied to NMR in metals.[12] The weak exchange interaction between electrons of the CuO$_2$ planes and the Gd^{3+} ($S=\frac{7}{2},L\cong0$) ions gives to a shift δH of the resonance field H_0, and a dynamic temperature-dependent line broadening ΔH. The local static homogeneous spin susceptibility is given by $\chi_s=(^{Gd}K-^{Gd}K_0)/^{Gd}A$, where $^{Gd}K=\delta H/H_0$ is the ESR Knight shift and ^{Gd}A is an isotropic "hyperfine" coupling constant proportional to the exchange integral and is independent of both T and y. The information obtained from Gd^{3+} ESR Knight shift is similar to that from ^{89}Y NMR, and $^{Gd}A\cong10(^{89}A)$. In this paper we discuss only the central transition between $-\frac{1}{2}\to+\frac{1}{2}$ Gd^{3+} Zeeman levels. For 245 GHz the perturbation of these levels by the crystalline field is negligible[14] for any orientation of H. For 9.1 GHz the $-\frac{1}{2}\to+\frac{1}{2}$ transition is unaffected by the crystalline field when $H\|c$. 245-GHz measurements are limited to $T\geq10$ K due to the loss of intensity caused by the depopulation of the Zeeman levels in the larger magnetic field. For the data presented here corrections of the Gd^{3+} Knight shift due to diamagnetism and flux pinning in the superconducting state or the paramagnetism of Gd^{3+} are negligible.[12]

As discussed in Ref. 12 there is some ambiguity in the value of $^{Gd}K_0$, i.e., the origin from which the Knight shift

is measured. In the superconducting YBa$_2$Cu$_3$O$_y$ compounds the ESR is anomalous at low temperatures when the external field H is in the (a,b) plane. It has been suggested that the anomaly arises from a very small magnetic moment on the plane Cu sites.[12] For the pure $y=7.0$ material at 245 GHz and for H in the (a,b) plane the origin of ^{Gd}K is shifted to lower fields by 950 ppm with respect to its value at any y for $H\|c$.

Qualitatively, the effect of Zn substitution of the local spin susceptibility is clearly seen in Fig. 2 where we compare the Gd^{3+} ESR spectra of pure and Zn-substituted samples with $y=7.0$. The broadening and shift of the line at 24 K, i.e., well below T_c, by Zn substitution is in marked contrast with the lines at 100 K which are at the same position and have the same large widths. Above T_c Zn substitution only affects the crystalline field which does not shift or broaden the central transition, the other transitions (not shown) are of course broadened. In agreement with other studies,[8,10] at high T the DOS which determines the shift and the T-dependent part of the width is unaffected by Zn substitution. On the other hand the low-temperature shift shows that 3% Zn increases the average DOS to about 50% of N_0, the normal-state value. The 24 K line broadening is not of a dynamic origin (as shown below for $y=6.76$) but it is due to a spatially inhomogeneous Knight shift. This inhomogeneous shift extends approximately from the unshifted position to the position of the high-temperature line. We interpret the part of the low-temperature spectrum at the unshifted position as arising from Gd ions far away from any Zn impurities while the part with the full shifts corresponds to near neighbors of Zn where the superconducting gap is destroyed.

The temperature dependence of the Gd^{3+} shift for $y=7.0$ [Fig. 3(a)] shows clearly that Zn substitution only affects the spin susceptibility below T_c. Above T_c the shift is temperature independent and is the same for both the Zn-substituted and the pure $y=7.0$ samples. Below
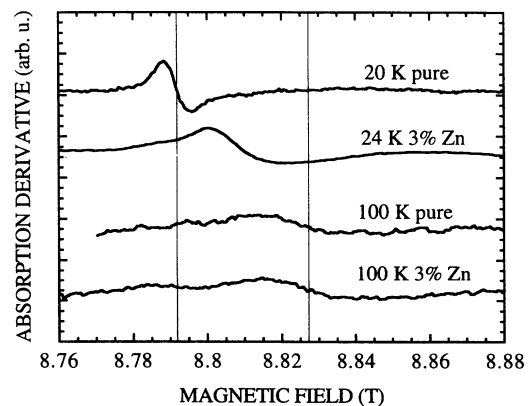

FIG. 2. Typical Gd^{3+} ESR spectra of Zn-substituted and pure Gd-doped YBa$_2$Cu$_3$O$_{7.0}$ at 245 GHz with $H\|c$. At $T\ll T_c$ the inhomogeneous increase of the local susceptibility χ_s around Zn atoms shifts and broadens the line. At 100 K Zn substitution has no effect. Vertical thin lines are at the ESR resonance fields for zero χ_s and in the normal state. The small ESR line in the Zn-substituted sample at 8.792 T is due to an insulating impurity phase. ESR amplitudes are arbitrary.
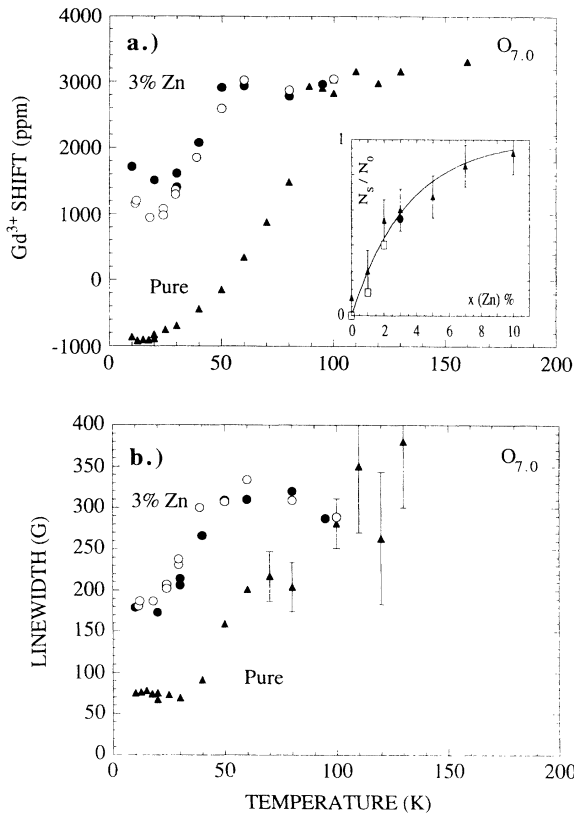
FIG. 3. Gd^{3+} ESR shift (a) and linewidth (b) vs temperature in optimally doped Zn-substituted [closed circles, $H\|c$; open circles, $H\|(a,b)$] and pure [closed triangles, $H\|(a,b)$] $YBa_2Cu_3O_{7.0}$. Note the strong inhomogeneous increase of χ_s at low T indicating the suppression of the superconducting gap around Zn atoms. Inset: N_s, the average DOS at $T \approx 0$, as a function of Zn concentration, relative to N_0 the DOS of the pure optimally doped material in the normal state. Open squares, ^{63}Cu NMR (Ref. 9); closed triangles, specific heat (Ref. 8); closed circle, present data.

FIG. 4. Gd^{3+} ESR shift (a) and linewidth (b) vs temperature in underdoped Zn-substituted and pure $YBa_2Cu_3O_{6.76}$. Note the inhomogeneous increase of χ_s at low T indicating the suppression of the spin-fluctuation gap around Zn atoms. The resonance magnetic field dependence of the increase of the linewidth in the Zn-substituted compound shows that linewidth increase is due to a distribution in χ_s and is not caused by increased spin lattice relaxation.

T_c the shift decreases in both samples but for the Zn-doped sample it levels off below 30 K at a much higher value than the low-temperature limit of the pure sample. The linewidth [Fig. 3(b)] shows a similar behavior to the shift, although at high temperatures spin-lattice relaxation broadening[12] limits the precision. Above T_c the linewidths are roughly equal, while at low T, Zn substitution increases the linewidth by 110 G corresponding to a width of about 1000 ppm in the distribution of the Knight shift. The shift of the Zn-substituted compound has an anomalous anisotropy, for $H\|(a,b)$ H_0 is about 45 G (500 ppm) lower than for $H\|c$. The anomaly is about half of that in the pure $y=7.0$ compounds.[12] The resulting ambiguity in the low T value of χ_s, i.e., N_s in the inset of Fig. 3(a), due to the uncertainty in $^{Gd}K_0$ is small, less than 15%.

Figures 4(a) and 4(b) show the temperature variation of the shift and linewidth for the underdoped $y=6.76$ system. In the pure material the temperature dependence of χ_s is dominated by the opening of the spin-fluctuation gap. χ_s is still suppressed at 200 K where it is about 20%
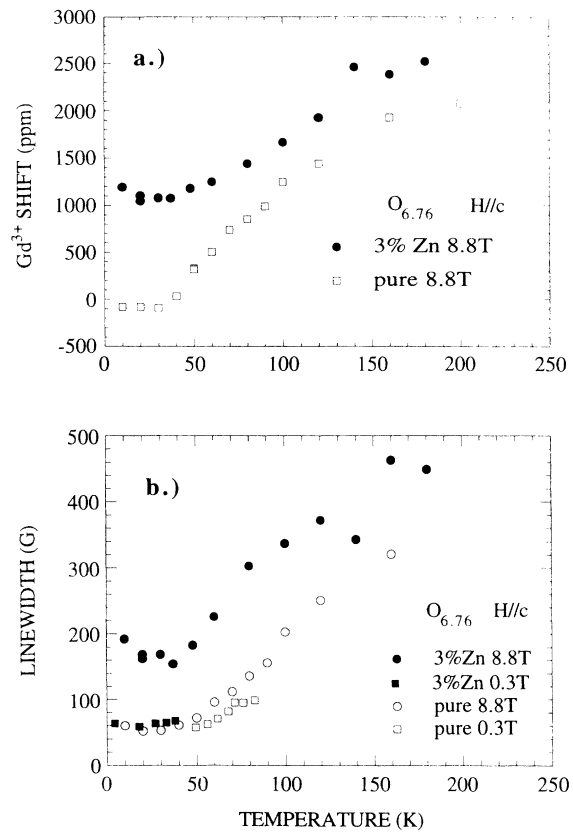
less than in the optimally doped sample. Also, there is no noticeable anomaly at $T_c=63$ K. The Zn-substituted material is not superconducting above 10 K. At low temperatures there is a large excess shift corresponding to about 40% of N_0. The difference between χ_s of the Zn-substituted and pure compounds decreases with increasing temperature, at 200 K this difference is zero within experimental error. As for the $y=7.0$ case the Knight shift in the Zn-substituted $y=6.76$ compounds is strongly inhomogeneous and this results in a large Gd^{3+} ESR linewidth.

For $y=6.76$ we could verify by 9.1 GHz ESR on the same sample that the additional width caused by Zn substitution is entirely due to a Knight shift distribution and is not caused by relaxational broadening. The dynamical broadening due to spin lattice relaxation is independent of the resonance field H_0 while any inhomogeneous broadening due to a distribution of the Knight shift is proportional to H_0. As shown in Fig. 4(b) for the pure $y=6.76$ compound the linewidths at the two frequencies are very similar and therefore the increase of the

linewidth with temperature is mostly due to an increase of the spin lattice relaxation rate. The close agreement between the linewidths at 9.1 GHz (0.3 T) and 245 GHz (8.8 T) shows that in the pure sample ESR lines are homogeneously broadened. On the other hand the low temperature increase in linewidth caused by Zn doping is only observable at high fields, at 0.3 T the estimated increase is only 4 G.

The low T shifts and inhomogeneous linewidths induced by Zn substitution in the $y = 7.0$ and 6.76 compounds are similar (Figs. 3 and 4) and in both cases the ESR lines overlap with the resonance position of the pure $y = 7.0$ compound in the normal state (Fig. 2). Thus as far as the first neighbor Cu sites of Zn atoms are concerned the full DOS is restored irrespective of whether it is suppressed in the pure samples by the superconducting gap or by the spin fluctuation gap. Not all Gd ions are perturbed by the Zn atoms since the ESR of the Zn-substituted compounds also overlaps with the low T resonance field of the pure systems where the DOS is zero. The probability that a given Gd ion will have a Zn neighbor in both of the adjacent CuO_2 planes within a circle of radius less than $3a_0$ (where $a = 3.82$ Å is the in-plane lattice constant) is nearly 100%. (We assume all Zn atoms are substituted in the CuO_2 planes.) Thus the region around Zn atoms in which the DOS falls from its normal-state value to zero is less than 3 lattice constants.

The above conclusions are in good agreement with the results of specific-heat[8] and ^{63}Cu NMR studies[9] in Zn-substituted optimally doped $YBa_2Cu_3O_{7.0}$. The average increase of the density of states at low T measured by these methods at various Zn concentrations x and our value for $x = 0.03$ are shown in the inset of Fig. 3(a). From the x dependence Loram, Mirza, and Freeman[8] deduced that the perturbation of the superconducting state becomes significant in a range of 6.5 Å around Zn atoms in agreement with our finding of a complete suppression of the gap at first neighbors and no significant perturbation at $3a_0$. Recent inelastic neutron-scattering studies[15] of a Zn-substituted underdoped crystal have provided direct evidence for the suppression of the gap in the spin-fluctuation spectrum.

We find (in agreement with the ^{89}Y studies of Alloul et al.[10]) that at high T the average Knight shift is not changed by Zn substitution in the optimally doped compound and is only slightly increased for the underdoped one. On the other hand our results are inconsistent with magnetic moments localized on the Cu plane sites surrounding the Zn atoms.[10] The magnetic susceptibility per Zn atom corresponding to the small increase of the shift observed between 20 and 10 K for both $y = 7.0$ and 6.76 [Figs. 3(a) and 4(a)] is very small, it is 100 times less than the average shift expected for a free $S = \frac{1}{2}$ paramagnetic moment formed on the Cu sites around Zn atoms. In this estimate we assumed that the Gd^{3+} shift arises from the exchange interaction with Cu plane sites having neighboring Zn atoms. We suggest that the apparent contradictions between the Curie-like ^{89}Y line broadening[10] and the large increase in the Curie-like susceptibility measured by static methods[11] (SQUID) and the lack of a Curie-like term in the Gd^{3+} shift and linewidth may be resolved if the moments created by Zn substitution are actually on Cu *chain* sites. For such moments the ^{89}Y and Gd^{3+} shifts are dipolar (and not contact or exchange) and even large moments give rise to small shifts only.

In conclusion it is extremely unlikely that T_c of Zn-doped high-temperature superconducting oxides is suppressed by the classical pair-breaking mechanism associated with impurity magnetic moments. Rather, the present work confirms that the partially filled Cu d shells play a crucial role in the superconductivity and the pair breaking is associated with the full d shells of the Zn atoms.

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