Dynamics of the Local Moment Induced by Nonmagnetic Defects in Cuprates

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We present a study of the spin dynamics of magnetic defects induced by Li substitution of the plane Cu in the normal state of $YBa_2Cu_3O_{6+x}$. The fluctuations of the coupled Cu magnetic moments in the vicinity of Li are probed by near-neighbor ^{89}Y *and* ^7Li NMR spin lattice relaxation. The data indicate that the magnetic perturbation fluctuates as a single entity with a correlation time τ which scales with the local static susceptibility. This behavior is reminiscent of the low T Kondo state of magnetic impurities in conventional metals. Surprisingly it extends well above the "Kondo" temperature for the underdoped pseudogapped case.

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The substitution of the Cu^{2+} of metallic doped CuO_2 planes by spinless Zn^{2+} has been shown in the normal state of $YBa_2Cu_3O_{6+x}(YBCO_{6+x})$ to induce a local magnetic moment nearby [1,2]. The generality of this novel impurity response is supported by similar experiments on the *heterovalent* spinless substitutions: Al^{3+} in $La_{2-x}Sr_xCuO_4$ (LSCO) [3] and Li^+ in $YBCO_{6+x}$ [4]. Such induced magnetism does not occur in a simple Fermi liquid, but it does have parallels in other strongly correlated insulating spin systems [5] as well as nearly magnetic metals, e.g., Co or Ni in Pd [6]. In the cuprates, the induced magnetic defect is thought to consist of a strongly perturbed region in the immediate vicinity of the spinless site together with the associated intrinsic magnetic response of the CuO_2 plane at further distances. In the underdoped region, the nearby Cu moments are sufficiently decoupled from the strongly correlated CuO_2 band to make a Curie-like [7] contribution to the static susceptibility [in contrast to the intrinsic $\chi(T)$]. This model of the static local structure of the defect provides a reasonable explanation of the Y satellite NMR spectra [1,2] as well as the broadening of the host NMR by long range spin polarization [8]. Recently, we have shown that ^7Li NMR of Li substituted YBCO provides a very sensitive local probe of the surrounding induced magnetism [4]. Accurate measurements of the ^7Li NMR shift K revealed that the static susceptibility in the vicinity of the spinless defect follows a Curie Weiss $(T + \Theta)^{-1}$ temperature dependence, leading us to suggest that Θ might be associated with a Kondo-like crossover temperature.

An important way to study the depth of this analogy is through the spin dynamics of the induced moment. The correlation time τ of a local spin coupled to a metal is determined by spin-flip scattering with the conduction band electrons. In conventional systems, e.g., Cu:Fe, the Kondo effect results from the anomalous behavior of this scattering below a characteristic (Kondo) temperature $T_K \sim \Theta$, corresponding to a transition from weak to strong coupling in the sense of renormalization group theory [9]. For $T < T_K$, i.e., in the strong-coupling regime, both the local static magnetic susceptibility χ_0 and τ are determined by a single energy scale T_K. As a result, there is a well-established universal proportionality between them [10]. This scaling breaks down for $T > T_K$ (in the weak-coupling regime) [11], where τ follows a Korringa T^{-1} temperature dependence.

In correlated electronic systems very few attempts to study the dynamics of induced moments have been made so far. Theoretical investigations are also currently rather limited for the metallic cuprates [12] (though more advanced in insulators [13]). The fluctuations of the magnetic defect can often be investigated successfully through measurements of the spin lattice relaxation times T_1 of nearby nuclei [10]. In YBCO such measurements on ^{89}Y satellites corresponding to the near neighbors of Zn were limited to the underdoped state [1,2]. In LSCO the ^{27}Al NMR itself [3] was used, but the results were ambiguous because neither the defect concentration (z) nor the hole doping (n) dependence was investigated [3,14].

In this paper, we carry out the first comprehensive study of the induced local magnetic dynamics using the lithium $^7T_1^{-1}$. We find predominantly single impurity behavior at low Li concentration and extract the T dependence of τ. Our analysis of the data is supported by measurements of the $^{89}T_1^{-1}$ of the yttrium NMR satellites in the underdoped region. The measured τ indicates that the induced moment is strongly coupled to the conduction band. Moreover, we find the universal low temperature relation between χ_0 and τ expected for a Kondo effect. Surprisingly, this

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correlation is maintained for all hole concentrations and all temperatures, even far above Θ, where the weak-coupling limit is expected.

The samples used for this study have nominal Li concentration z (used throughout) defined by $YBa_2(Cu_{1-z}Li_z)_3O_x$. However, the per plane Li concentration in our samples was found to be $\sim 0.85z$ [4]. Underdoping was accomplished by deoxidation and overdoping by Ca^{2+}/Y^{3+} substitution. Except for the Ca codoped sample, the powders were aligned in Stycast 1266 epoxy [15]. The spin lattice relaxation rate T_1^{-1} of the $I = 3/2$ ^{7}Li nucleus was measured, in the same spectrometer as Ref. [4], using a saturation recovery sequence with (for the aligned powders) the magnetic field parallel to the c axis. The resonance is sufficiently narrow that, using short (~ 1 μs) rf pulses, the entire spectrum was irradiated, and the resulting single exponential recovery yielded the rates shown in Fig. 1.

We can immediately make some important qualitative observations of the data: (i) In our relatively dilute samples, we find no Li concentration dependence of $^7T_1$ above 150 K, and only a relatively small z dependence below this. Thus for $z = 1\%$ the predominant nuclear relaxation mechanism is characteristic of the isolated magnetic defect interacting with the correlated metallic host. (ii) The spin lattice relaxation rates of the near neighbor ^{89}Y NMR satellites [4] in the underdoped state ($YBCO_{6.6}$) are quantitatively very similar to those of the Zn defect (Fig. 2), indicating the generality of the dynamics of the induced magnetic defect. (iii) The T and hole doping n dependence of T_1^{-1} is unrelated to that of the NMR of the pure material, e.g., Ref. [16]. Thus we conclude that the dominant relaxation mechanism for Li is the fluctuations of the magnetic defect and not the intrinsic magnetic dynamics, as was also apparent for Zn [1] and Al [3].

To extract the time scale for fluctuations of the local moment, we employ a relaxation model of the dynamic susceptibility, which is generally connected to $1/T_1$ via the Moriya expression [17]:

$$\frac{1}{T_1} = \left(\frac{\mu_n}{\hbar 2\mu_B}\right)^2 k_B T \sum_{\mathbf{q}} \bar{A}^2(\mathbf{q}) \chi''_{\perp}(\mathbf{q}, \omega_n)/\omega_n , \quad (1)$$

where μ_n is the nuclear magnetic moment, μ_B is the Bohr magneton, $\bar{A}$ is the (dominant) isotropic hyperfine coupling form factor, $\chi''_{\perp}$ is the imaginary part of the perpendicular spin susceptibility, and ω_n is the NMR frequency. In the superconducting state, inelastic neutron scattering finds an impurity response peaked at the antiferromagnetic wave vector with a characteristic energy of a few meV [18]. Thus at sufficiently low T, the defect will fluctuate as a single magnetic entity [14] as there will be negligible occupation of local internal fluctuation modes. Assuming this limit, the expression above is simply

$$\frac{1}{T_1} = 2\left(\frac{\mu_n}{\hbar \mu_B}\right)^2 k_B T A^2 \chi''_{\perp \mathrm{loc}}(\omega_n)/\omega_n , \quad (2)$$

where A is the local hyperfine coupling, with

$$\chi_{\perp \mathrm{loc}}(\omega) = \chi_0(T)\left\{\frac{i - \omega\tau}{i + (\omega - \omega_e)\tau}\right\}. \quad (3)$$

Here τ is the correlation time, and ω_e is the EPR frequency. We attribute the static macroscopic impurity susceptibility to the four near-neighbor sites per Li, i.e., $\chi_0 = 4\chi_{nn}$. The hyperfine coupling is obtained from its relation to the ^{7}Li NMR shift, $K = A\chi_0/\mu_B$ [4]. The contribution to the macroscopic χ_0 of more distant Cu sites, which possess negligible hyperfine coupling to Li, make this a (probably slight) overestimate of A. Assuming fast fluctuations, i.e., $\omega_e\tau \ll 1$, yields

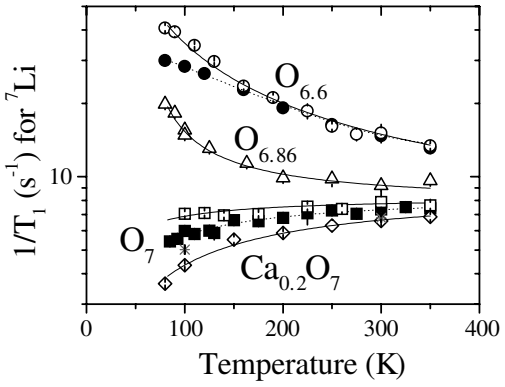

FIG. 1. The spin lattice relaxation rate of Li substituted on Cu(2) in YBCO as a function of doping for $z = 1\%$ (open symbols) and $z = 2\%$ (closed symbols) with $\mathbf{H} \parallel c$. The stars for $z = 2\%$ O_7 with $\mathbf{H} \perp c$ demonstrate the near isotropy of T_1.

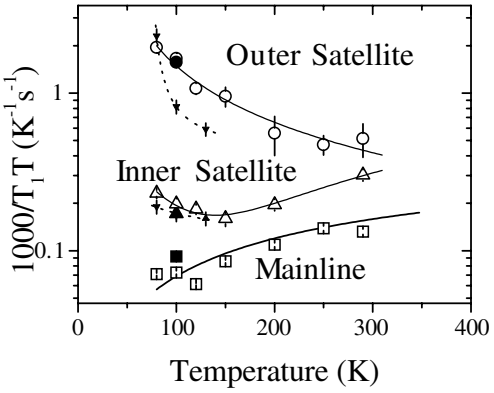

FIG. 2. $1/T_1T$ for the satellite Y NMR of $z = 1\%$ (open points) and $z = 2\%$ (large filled points) in $YBCO_{6.6}$. Also shown (small filled points) are the results for the Y satellite NMR of Zn doped samples from Ref. [2].

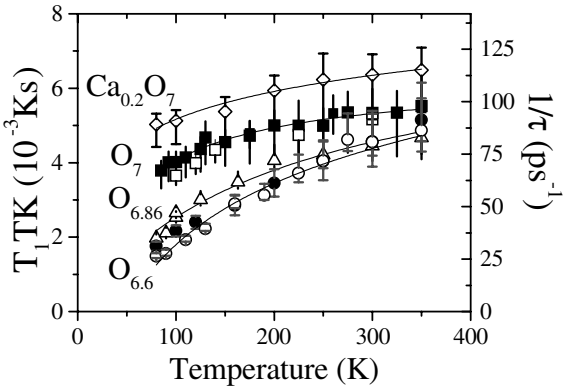

FIG. 3. T_1TK for Li in YBCO as a function of doping for $z = 1\%$ (open symbols) and $z = 2\%$ (closed symbols). K is the magnetic shift. The inverse correlation time for the local moment is given by the right scale.

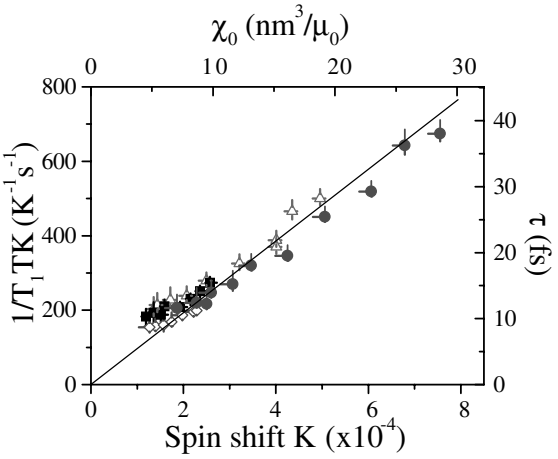

FIG. 4. $1/T_1TK$ vs K for $z = 1\%$ for various dopings: $x = 6.6$ (full circles), 6.86 (open triangles), 7 (full squares), and 7 $Ca_{0.2}$ (open diamonds). The proportionality of the static impurity susceptibility and the correlation time of the moment is characteristic of the $T < T_K$ Kondo regime.

$$\frac{1}{T_1TK} = \left(\frac{2k_B\mu_n^2A}{\hbar^2\mu_B}\right)\tau\,. \tag{4}$$

In Fig. 3 we plot T_1TK vs T for all the doping levels, using K from Ref. [4], and Eq. (4) is used to make the right scale for $1/\tau$. The fluctuations measured by τ become slower as n is reduced towards the insulating magnetic phase. Moreover, the value is always such that $\omega_e\tau \ll 1$ at the applied field of 7.5 T, as we assumed [19].

Conventional treatments of Kondo impurities start from the exchange Hamiltonian $-J\vec{S}\cdot\vec{s}$ between the local spin $\vec{S}$ and the band spins $\vec{s}$. In this case, the weak-coupling limit ($T > T_K$) corresponds to a Korringa regime for τ, i.e., $\hbar\tau^{-1} = \pi(J\rho)^2k_BT$, where ρ is the density of states at the Fermi level. YBCO is not a simple metal, so we do not expect simple Korringa behavior. However, $1/\tau$ for a weakly coupled magnetic moment should scale with the $1/T_1$ of the pure host nuclear spins, given the same hyperfine form factor. This is the case, for example, for Gd/Y substitution where the Gd ESR linewidth ($1/\tau_{\mathrm{Gd}}$) simply scales with the $1/T_1$ of yttrium [20]. It is clear that $1/\tau$ in Fig. 3 does not follow the Korringa law, nor does it in the ^{27}Al experiment [3]. Moreover, in the underdoped case, where $T \gg \Theta$ the observed $1/\tau$ displays none of the features of the pseudogap detected by the $1/T_1$ of the planar oxygen or copper nuclei [16]. In contrast to the Gd, this demonstrates that the conventional weak-coupling regime is never evident.

On the other hand, because the induced moment is composed of the same Cu atomic orbitals that normally participate in the band, we expect that it will have a large overlap with band states and couple strongly to the band excitations. In a conventional Kondo system, all the properties of the low temperature Kondo state, corresponding to the strong-coupling limit, are determined by T_K; in particular, τ is proportional to χ_0. This limit ($T < \Theta$) can be attained in the optimal and overdoped samples, where Θ exceeds 100 K. Figure 4 demonstrates such a correlation. There appears to be some small deviation at high T (low shift), which we consider in more detail below. Surprisingly, this scaling remains valid for all *n with the same slope*, even though Θ changes drastically, i.e., from less than 5 K in $O_{6.6}$ to more than 200 K in the overdoped regime [4]. Thus, the strong-coupling features of the Kondo state persist even far above Θ.

Let us now consider the value of the proportionality constant between τ and χ_0 which is determined independently of the hyperfine coupling by

$$\mathcal{R} = \frac{1}{T_1TK^2S} = \frac{\mu_e^2}{2\pi\hbar}\,\frac{\tau}{\chi_0}\,, \tag{5}$$

where S is the conventional Korringa constant, $4\pi k_B/\hbar \times (\mu_n/2\mu_B)^2$. The values of $\mathcal{R}$ for Li are shown in Fig. 5. We also include the corrected values for the Y satellites of Li (Fig. 2) [21]. The accuracy for the satellites is not as good as for the ^{7}Li, but the values at low T are consistent. The deviation at high T in Fig. 4 appears as the slight increase of $\mathcal{R}$ with T. This may be the result of remnant impurity interactions yielding a slight decrease in $1/T_1$ from the isolated impurity value at low T, or it could signal the apparition of another relaxation process at high T possibly of quadrupolar origin. Assuming the defect consists of the four near-neighbor sites, because the Li is coupled to all four and each near-neighbor Y to only two, if the four moments fluctuate independently $^{89}\mathcal{R}$ should be twice as large as $^7\mathcal{R}$, whereas they should be equal if the moments are rigidly coupled. Despite the large error bars, the near equality at 100 K in Fig. 5 *favors the singly fluctuating model*. A relative increase of $^{89}\mathcal{R}$ over $^7\mathcal{R}$ at higher T could also be due to internal magnetic excitations.

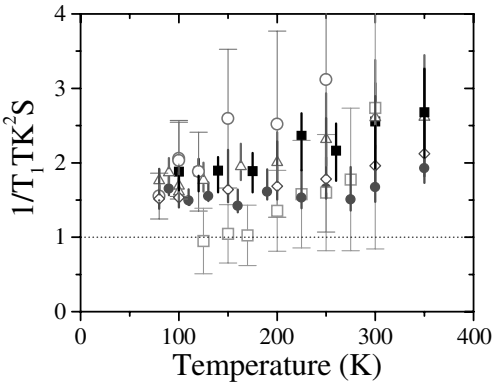

FIG. 5. $1/T_1TK^2S$ vs T for Li ($z = 1\%$) for $x = 6.6$ (full circles), 6.86 (open triangles), 7 (full squares), and 7 $Ca_{0.2}$ (open diamonds). Also shown are the values for the outer Y satellite of the Li at $x = 6.6$ (light open circles) and for Al [3] (light open squares).

For the induced moment in YBCO, $\mathcal{R}(T)$ is nearly constant, independent of n, confirming that the defect does not change in character from the underdoped far into the overdoped regime. We also include the data from the Al experiment [3], which possesses a remarkably similar T dependence with a smaller value. In conventional Kondo systems, the crossover expected at T_K should be reflected in a marked decrease of $\mathcal{R}(t = T/T_K)$ from the zero temperature value through $t = 1$ to a value determined by the parameter $(J\rho)^2$ for $t \gg 1$. In the only case where such measurements could be accomplished over a broad enough t range (Cu:Fe), the high t value turned out to be only slightly less than the low t limit [10]. In our case, T_K varies strongly with n, but $\mathcal{R}(t)$ is nearly constant for $t \approx 0.4$ to 100. This is further confirmation that the weak-coupling limit is never attained.

In summary, we have employed NMR as a powerful local probe of the dynamics of the magnetic defect that is created by a Cu spin vacancy in the CuO_2 plane of YBCO. We deduced the correlation time for the induced magnetic moment and concluded that it is strongly coupled to the band. As for a conventional Kondo impurity, we find that the correlation time is simply proportional to the static impurity susceptibility, making the case for Kondo-like behavior much more compelling than simply the behavior of $\chi_0(n, T)$ [4]. However, in contrast to expectations from conventional Kondo impurities, we find that this scaling extends far above T_K and persists from the pseudogap to the overdoped regime. Although the low T behavior mimics that of the conventional Kondo state, Θ does not appear to be a crossover from strong to weak coupling. Such simple general behavior of the defect response suggests the possibility of a straightforward theoretical explanation, and emphasizes the role of antiferromagnetic correlations in the cuprate metallic state, even at high T and far into the overdoped regime.

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