Spinless Impurities in High-T_c Cuprates: Kondo-Like Behavior

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We compare the effects of in-plane nonmagnetic Li$^+$ and Zn^{2+} impurities on the normal state of high-T_c cuprates. ^{89}Y NMR shows that the extra hole introduced by Li is not localized in its vicinity. The T_c depression and induced moments on near neighbor Cu sites of Zn or Li are found to be identical. These effects of spinless impurities establish the major influence of the spin perturbation with respect to the charge defect. The susceptibility of the induced moment measured by ^{7}Li NMR displays a $1/(T + \Theta)$ behavior. Θ increases with doping up to about 200 K in the overdoped regime. We attribute this to a "Kondo-like" effect.

PACS numbers: 74.25.Nf, 74.62.Dh, 74.72.Bk

Increasingly, impurities are used to probe the magnetic properties of correlated systems. For instance, in cuprates, substitution of the Cu sites of the CuO$_2$ planes directly reveals the existence of magnetic correlations in the planes and probes their interplay with superconductivity. In particular, Zn^{2+} substitution has been studied thoroughly because it was unexpectedly found to strongly affect both the normal and superconducting states. Above T_c, in a metallic picture, Zn^{2+} should only weakly affect both magnetism and transport properties; the former because it is a spinless impurity and the latter because it has the same charge as Cu^{2+}. In contrast, Zn acts as a very strong scattering center [1]. The fact that T_c is depressed by this scattering is primarily a consequence of the now well established d-wave anisotropy of the superconducting order parameter [2]. Furthermore, Zn induces local magnetic moments on its near neighbor (n.n.) coppers, as shown by NMR [3] and macroscopic SQUID measurements [4]. Zn, as a spin vacancy, creates indeed a perturbation of the local antiferromagnetic correlations, as also observed in undoped low dimensional spin chains or ladders [5]. Such effects were anticipated on theoretical grounds [6,7]. However, until now no experiment could clearly expose the relation between the magnetic correlations and the scattering effects on T_c. Another interesting problem is the evolution of these anomalies with hole doping. Recent macroscopic experiments showed that the local moment susceptibility falls rapidly, though it still exists at optimal doping [4]. Such local moments have also been found in Al^{3+} substituted LaSrCuO at optimal doping, despite some qualitative differences with Zn [8]. In this later work, NMR of ^{27}Al itself was used to probe locally the susceptibility of its n.n. Cu sites. However, no experiment has yet been dedicated to probing the evolution of this moment into the overdoped regime. Such an experiment should help to clarify whether the cuprates exhibit an uncorrelated Fermi liquid behavior at high doping.

In order to address both problems, we have undertaken a study of Li in YBaCuO which substitutes within the CuO$_2$ planes [9]. Li$^+$ is not magnetic like Zn^{2+} but has a different valence. Comparing the local magnetism and the effect of T_c between Li$^+$ and Zn^{2+} will elucidate the respective roles of charge and spin in the impurity response of the cuprates. In particular, is the additional hole of Li$^+$ trapped in the vicinity of Li$^+$, as found in the undoped La$_2$CuO$_4$ [10]? We present here ^{89}Y NMR measurements which show that the local magnetic environment of Li is identical to that of Zn and establish both the presence of induced moments and the absence of localized hole. The effects on T_c are subsequently shown to be the same for Li and Zn. In the second part, we report ^{7}Li NMR measurements which enable us to make a detailed study of the doping dependence of these moments. Indeed, ^{7}Li, in contrast with ^{57}Zn, is a sensitive NMR probe which has already been detected in YBa$_2$Cu$_3$O$_7$ [9]. Like ^{27}Al NMR in La$_2$SrCuO$_4$, ^{7}Li NMR provides the opportunity to measure the susceptibility of the environment of Li with unprecedented accuracy. We present ^{7}Li NMR data for a wide range of concentrations and hole dopings, including, in particular, for the first time, the overdoped regime via simultaneous Ca substitution on the Y site. The local moment susceptibility is found to evolve from a Curie to a $1/(T + \Theta)$ law with increasing doping. Moreover, Θ is found to be independent of impurity concentration— behavior strongly reminiscent of the Kondo effect.

Li substituted samples YBa$_2$(Cu$_{1-x_n}$Li$_{x_n}$)$_3$O$_{6+y}$ were prepared by solid state reaction of Y$_2$O$_3$, BaO$_2$, CuO, and Li$_2$CO$_3$ with nominal Li concentration x_n. The samples were annealed and ground many times to eliminate spurious phases. X-ray diffraction was performed to ensure their quality and purity. Deoxidation was performed at fixed temperatures ranging from 340 °C to 450 °C under vacuum. As explained later, we used ^{89}Y NMR to obtain a reliable evaluation of the doping level. The superconducting transition was measured in a SQUID magnetometer in field cooled experiments. T_c was determined by extrapolation to $\chi = 0$ of the Meissner transition (not as the onset of diamagnetism).

The powdered crystallites were c-axis aligned in an epoxy matrix in a ~ 7 T magnetic field. NMR measurements were performed in a homemade spectrometer with a field $H_0 = 7.5$ T using Fourier transform spectroscopy. Spin echoes were obtained using a $\pi/2$-τ-π sequence. The frequency shifts for ^{89}Y and ^{7}Li were taken with respect to the reference frequencies of aqueous YCl$_3$ and LiCl solutions at $\nu = 15\,634.15$ kHz and $\nu = 123\,994.0$ kHz.

Let us first compare the effects of Li and Zn on the magnetism of the doped CuO$_2$ planes. In the underdoped regime, ^{89}Y NMR established that Zn induces local moments on its four near neighbor Cu sites [3]. We have performed similar experiments on deoxidized Li substituted samples. A typical spectrum is presented in the inset of Fig. 1. As in the Zn case (Fig. 1 of Ref. [3]), three lines are resolved. The low frequency line is attributed to the Y n.n. sites, the second line to further shells of neighbors, and the main line to more distant Y sites. The temperature dependence of the shifts of these lines is reported in Fig. 1 for both Li, Zn, and the pure compound. The Y NMR shift is proportional to the magnetic susceptibility of the eight surrounding Cu sites of the two adjacent CuO$_2$ planes. The striking similarity of the spectra and the T dependences of the three lines for Zn and Li must result from a common local magnetic perturbation, which is likely characteristic of all closed shell spinless ion substitutions. In particular, the first n.n. shift exhibits a $1/T$ contribution in both cases, providing local evidence for the presence of nearby moments. The strong similarity between Zn and Li would not be expected if the extra hole given by Li$^+$ were localized on the n.n. oxygen orbitals (as suggested in [7] or [11]). Such a hole would carry a spin and make a markedly different contribution to the Y n.n. shift. The hyperfine coupling of the Y nucleus to the oxygen orbitals is considerably larger than the Cu orbitals; thus the shift would be much
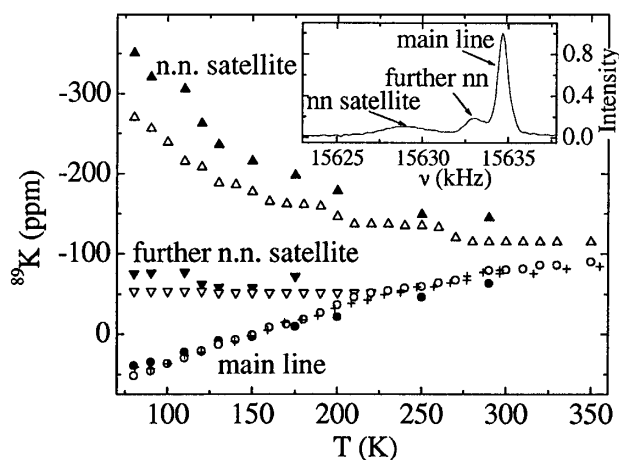
larger than observed. Our data suggest that any additional hole delocalizes in the band of carriers of the CuO$_2$ planes. Also, there are some indications that the introduction of Li is accompanied by an oxygen loss to maintain overall electroneutrality, as shown by iodometric titration [9]. In our dilute samples, these effects are not large enough to be detected. The delocalization of the Li hole contrasts with results in Li-doped antiferromagnet La$_2$CuO$_4$ which remains insulator [12], underlining the fact that the metallic and the antiferromagnetic regimes respond differently to the presence of an in-plane hole. In Fig. 1, the small difference between the amplitude of the n.n. Y shift for Zn and Li corresponds to a Li induced moment with $p_{\rm eff}$ 20% larger than for Zn. This could be due to a difference of doping level between the Zn and Li samples [13]. In all, these results show that Li$^+$ and Zn^{2+} have the same effect on local magnetism in the CuO$_2$ planes.

One can wonder whether their influence on scattering and superconductivity is also similar. The depression of T_c by Li is apparently much smaller than for Zn, if we consider the nominal Li concentration x_n. As the dominant effects on T_c originate only from in-plane substitutions, such a conclusion cannot be drawn because the actual distribution of Li in the compound is not known. One of the great advantages of the present experiments is to provide a quantitative estimate of the concentration $x_{\rm plane}$ of Li in the planes, through measurements of the intensities of ^{89}Y n.n. and ^{7}Li NMR lines which are proportional to the number of Y or Li contributing nuclei. The relative intensity of the first n.n. line to the whole ^{89}Y NMR spectrum scales with $4x_{\rm plane}$ in the dilute limit. While Zn was found to fully substitute in the planes ($x_{\rm plane} \simeq 1.5x_n$) [3], here we find that about half of the nominal Li substitutes in-plane [$x_{\rm plane} = 0.85(\pm 0.2)x_N$]. The ^{7}Li NMR intensity is another independent estimate of the relative number of in-plane Li which we used to compare samples, confirming the previous results from $x_N = 1$ to 8%. Using the experimentally determined plane Li concentration, we find that Li and Zn induce similar reductions of T_c versus $x_{\rm plane}$ (see Fig. 2). For optimal doping, the effects of Li (6 ± 1 K/%) and Zn (7.1 ± 0.5 K/%) are the same within error bars. In underdoped samples, the slight difference between Li and Zn might again originate from a slight doping difference [13]. So, we conclude that Li and Zn produce *quantitatively* the same effects both on T_c and on the local magnetic structure associated with the defect. The independence of these effects on the valence of the impurity indicates that the scattering cross section responsible for the decrease of T_c is dominated, not by the relative charge of the impurity but rather by the spinless perturbation created in the correlated magnetic system.

Having established the existence of induced moments in underdoped Li substituted compounds, we now proceed to study the evolution of these moments with doping and concentration. The ^{89}Y n.n. shift cannot be used at optimal doping because the corresponding NMR line can no longer be distinguished from the main line. In the case
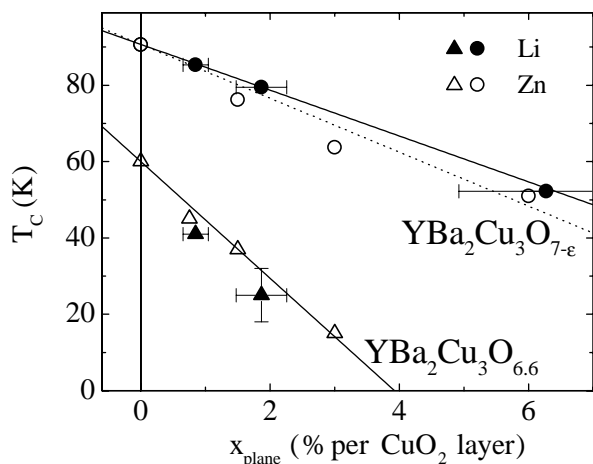

FIG. 1. ^{89}Y NMR shift for $H \perp c$, for pure (plusses), Zn $x_n = 0.5$ (open symbols, taken from Ref. [3]), and Li $x_n = 1\%$ (closed symbols) underdoped YBa$_2$Cu$_3$O$_{6.6}$ samples. The three data sets correspond to the shifts of the three lines of the spectrum. A typical one taken at 100 K for the Li sample is displayed in the inset.

FIG. 2. Variation of T_c versus the concentration x_{plane} of Zn or Li per CuO_2 layer, both for underdoped and optimally doped compounds. x_{plane} is deduced from the intensities of the n.n. [89]Y and ^{7}Li NMR lines.

of Zn, only long range magnetic effects of the impurity or macroscopic measurements could be used to demonstrate the existence of local moments. A new possibility is offered here by ^{7}Li NMR [9]. Because [7]Li has a spin $I = 3/2$, the NMR transitions between Zeeman levels $-3/2 \leftrightarrow -1/2$, $-1/2 \leftrightarrow 1/2$, and $1/2 \leftrightarrow 3/2$ will be split by an electric field gradient (EFG) at the Li site. For our aligned samples, with $H \parallel c$, the quadrupolar spectrum of [7]Li is composed of three narrow lines separated by the quadrupolar frequency ν_c proportional to the EFG along c. This gradient parameter ν_c ranges from 40 to 57 kHz depending on the doping level [14], and similar quadrupolar frequencies are inferred from the powder pattern in the perpendicular orientation. Such small values of the quadrupolar frequencies relative to the Larmor frequency simplify significantly the analysis of the NMR spectrum. In particular, the position of the $-1/2 \leftrightarrow 1/2$ transition is determined only by the magnetic environment of Li. The shift of this transition is reported versus temperature for two dopings and two concentrations of Li in Fig. 3. In the underdoped compound, a clear $1/T$ behavior is observed as is found with the shift of the n.n. [89]Y line. Thus ^{7}Li NMR also senses the Curie behavior on its four n.n. Cu analogous to the ^{27}Al NMR in La_2SrCuO_4 [8]. The hyperfine coupling A_{hf} responsible for the Li shift is nearly isotropic, since the shift is almost identical for $H \parallel c$ and $H \perp c$. We use $K_c = 4A_{hf}\chi/N_A\mu_B$ with χ/N_A the atomic Curie susceptibility of one induced n.n. Cu moment. We can estimate this susceptibility by scaling the measured value $p_{eff} = 1\mu_B$ for Zn by the ratio 1.2 obtained above from the comparison of the n.n. [89]Y shifts. We obtain a value $A_{hf}^{iso} = 2.5$ kOe/μ_B which can be explained by a superexchange mechanism between Li nucleus and the four n.n. Cu $3d_{x^2-y^2}$. This mechanism is analogous to that proposed by Mila and Rice for the hyperfine couplings between n.n. Cu in CuO_2 planes [15]. In fact, using an LCAO computation as in [15], we find $A_{hf} = 1.6$

to 3.9 kOe/μ_B [14], which is compatible with the experimental value. It is apparent in Fig. 3 that the sensitivity of the Li probe is high enough to allow precise measurement of the temperature dependence of the n.n. susceptibility χ even in optimally doped samples. As already observed for Zn [3,4], this susceptibility falls off strongly with increased doping, but still has a significant T dependence at optimal doping. This motivated us to investigate an overdoped YBaCuO system obtained by Ca substitution for Y at maximal oxygen content [16]. The shift still varies substantially, increasing from 189 to 287 $\pm$ 4 ppm between 450 and 100 K, confirming that, *even in overdoped materials, there is still a substantial induced moment.* However, as can be seen in Fig. 3, the T dependence no longer follows a $1/T$ law at optimal doping. This is apparent in Fig. 4 where the shift is seen to progressively deviate from $1/T$ with increasing doping. Within experimental accuracy, all the data can be fitted with a $C/(T + \Theta)$ law. Similar T dependence was observed in optimally doped Al substituted LaSrCuO [8]. The present data permit us to study the x_{plane} and y dependence of C and Θ. For the dilute Li concentrations $x_{plane} < 2\%$ studied here, the susceptibility and therefore Θ are found to be independent of impurity concentration as seen in Fig. 3, implying that Θ is not due to interactions between induced moments of different Li sites. The variation of Θ with hole doping is represented in the inset of Fig. 4, where Θ increases markedly for $y > 6.8$ and reaches a value as high as 226 K for the Ca overdoped sample. It has been proposed that Θ originates from antiferromagnetic interaction between adjacent n.n. Cu sites of the impurity [17]. However, increased doping is known to reduce the strength of the magnetic correlations and should, in this scenario, also reduce Θ, in contrast to what we observe. Θ represents a new energy scale which evolves sharply with hole doping.
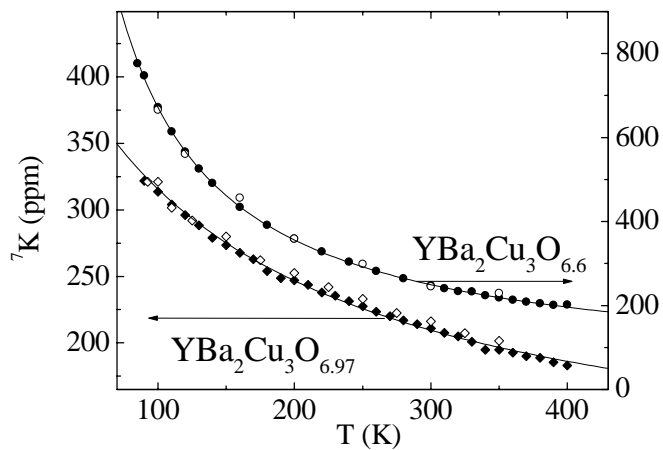

FIG. 3. ^{7}Li NMR frequency for $H \parallel c$ in $YBa_2(Cu_{1-x}Li_x)_3O_{6+y}$ for $x_{plane} = 0.85\%$ (closed symbols) and $x_{plane} = 1.86$ (open symbols) for underdoped $y = 0.6$ (circles) and optimally doped (diamonds) compounds. Deoxidation is performed on samples from the same batch.
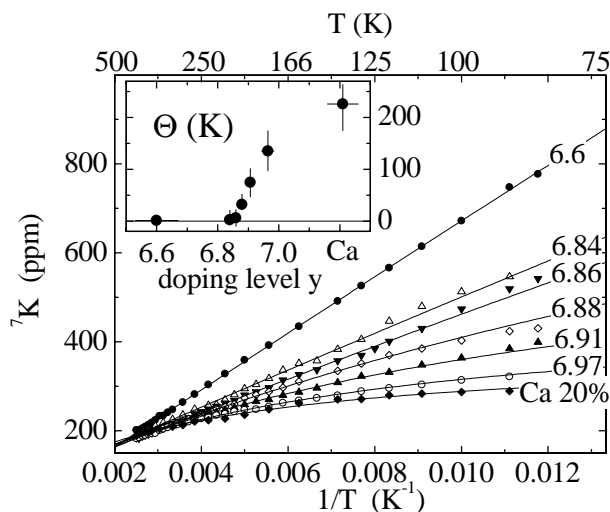
FIG. 4. ^{7}Li NMR frequency for $H \parallel c$ in YBa$_2$(Cu$_{99\%}$-Li$_{1\%}$)$_3$O$_{6+y}$ for $x_{\text{plane}} = 0.85\%$ and different oxygen contents y on samples taken from the same batch. The Y$_{80\%}$Ca$_{20\%}$Ba$_2$(Cu$_{99\%}$Li$_{1\%}$)$_3$O$_{6+y}$ compound corresponds to an overdoped $T_c = 63$ K sample. Black lines correspond to fit in $(T + \Theta)^{-1}$ which are also shown in Fig. 3. Θ is plotted versus oxygen content y in the inset. The doping level is determined through the main line ^{89}Y NMR shift calibrated with pure compounds with different doping levels.

This $1/(T + \Theta)$ susceptibility is analogous with the Kondo effect observed for dilute alloys with magnetic impurities. In these systems, the coupling of the impurity spin with the band induces a screening of the local moment below T_K, which yields $\chi \propto p_{\text{eff}}^2/(T + T_K)$. Though, here it is a nonmagnetic impurity which induces such a behavior in a correlated electronic band. Such a "Kondo" scenario has been proposed by Nagaosa and Lee to explain the effects of Zn on the resistivity [18]. They argue, as have others [19], that at high doping, the moment is screened, which is qualitatively consistent with our observed increase of Θ with doping. The value of C obtained from the fits is found to vary between 5000 and 8500 kHz K, ± 1500 kHz K. Thus, the moment value $p_{\text{eff}} \propto \sqrt{C}$ does not evolve strongly with hole doping in contrast with Θ, as also observed in the classical Kondo effect. This apparently contrasts with the strong decrease of p_{eff} with doping found in macroscopic susceptibility measurements on Zn substituted YBaCuO [4]. However, in such measurements, the magnetic contribution of Zn is so small at optimal doping that it can be extracted accurately only for large Zn concentrations ($x_{\text{plane}} = 6\%$). In this regime, $1/T$ behavior was apparent, and its reduced amplitude was attributed to a reduction in the net moment. The data on Zn and Li could be reconciled if Θ is progressively suppressed with increasing impurity concentration, as was observed in dilute alloys such as Cu:Fe [20], where at high impurity concentrations, interaction between the moments restores a $1/T$ behavior.

In conclusion, the influence of Li and Zn on the magnetic and T_c properties is governed by the presence of magnetic correlations. In particular, the strong impurity scattering appears to be connected with the absence of spin and is insensitive to charge. Such a spinless site induces moments in the correlated electronic system, which persist into the overdoped regime, clearly indicating that in-plane correlations are not suppressed and that pure uncorrelated Fermi liquid behavior has not yet developed. While these moments display a Curie law in the underdoped regime, a Kondo-like temperature Θ appears and increases sharply with doping. It is very interesting to consider possible connection of this magnetic screening energy to the pseudogap and T_c energy scales which both vary considerably in the same range of doping. The analogy with a Kondo effect is at the present stage phenomenological. Detailed experimental investigations of other normal state properties such as transport are needed to understand whether this analogy proves relevant.

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