Persistence of Li Induced Kondo Moments in the Superconducting State of Cuprates

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Using ^{7}Li NMR shift data, the anomalous local moment induced by spinless Li impurities persists below T_c in $YBa_2Cu_3O_{6+y}$. In the underdoped regime, the moments retain their Curie law below T_c. In contrast, near optimal doping, the large Kondo screening observed above T_c ($T_K = 135$ K) is strongly reduced below T_c as expected theoretically when the superconducting gap develops. The limited spatial extent of the induced moment (on first near neighbor Cu) is not drastically modified below T_c, which allows a comparison with STM determination of the local density of states. Our results constrain theoretical models of the impurity electronic properties.

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The influence of impurities on superconductors has always been used as an effective probe of their actual properties. For example, while magnetic impurities are the most prominent s-wave pair breakers, any type of scattering is detrimental to d-wave superconductivity. To our knowledge, experimental investigation of the modifications of the magnetic properties of an impurity below the superconducting transition T_c has never been performed. Macroscopic *bulk* magnetic experiments are unadapted since the various contributions to the susceptibility cannot easily be singled out below T_c. *Local* measurements of the susceptibility of these moments using hyperfine techniques are, in principle, possible, but are usually prohibited by technical limitations, such as strong spin lattice relaxation effects for the impurity NMR.

Despite this experimental void, an extensive theoretical work has been devoted to this question in classical Fermi liquids [1,2]. The behavior of the moment below T_c is predicted to depend both on the shape of the superconducting gap and on the Kondo temperature T_K of the moment in the normal state. T_K is a signature of the screening of the moment by the conduction electrons and is related to its coupling J to the carriers. The primary effect, anticipated, but not observed thus far, is a reduction of the Kondo screening due to the pairing of the carriers. For small J, this results in a complete restoration at low T of the Curie susceptibility of the moment.

In cuprate superconductors, which are correlated electronic systems, the magnetic properties of impurities are more intricate. In the normal state, spinless impurities such as Zn [3,4] or Li [5,6] substituted on the copper site of the CuO_2 planes induce a local moment in their vicinity. This moment extends essentially on the four Cu near neighbors (nn) of the impurity. Its static [5] and dynamic [6] susceptibilities exhibit a Kondo-like behavior with a large range of T_K values, which can be spanned by changing hole doping. The effect of superconductivity on this moment addresses two issues: the persistence of magnetic correlations in the superconducting state, and the influence of d-wave pairing on the Kondo screening.

We present here the first measurements of the induced moment properties below T_c. They are performed using ^{7}Li NMR since the transferred hyperfine couplings are weak enough that relaxation effects do not prohibit NMR spectroscopy of the moment. We propose a method to extract the susceptibility χ_{loc} probed at Li sites. This requires correcting the internal field seen by Li for screening and vortex effects due to superconductivity. It will then be shown that the Li induced moments survive below T_c and that T_K is strongly reduced. Furthermore, we will demonstrate that these induced moments remain confined primarily to the first nn coppers below T_c. Recent scanning tunneling microscopy (STM) experiments in the Zn substituted Bi2212 cuprate gave a measure of the local density of states (LDOS) in the superconducting state [7]. The STM data suggest the occurrence of a LDOS peak near the Fermi level on the Zn site and on the second nn Cu. This location contrasts with our finding of a magnetic state located dominantly on the first nn Cu. The discussion of this discrepancy will lead us to favor theoretical models which incorporate the magnetic character of the impurity.

The Li substituted samples $YBa_2(Cu_{1-x_n}Li_{x_n})_3O_{6+y}$ are those used in [5]. The two batches with Li nominal concentrations $x_n = 1\%$ and 2% had an effective in-plane Li concentration of 0.85% and 1.86% per CuO_2 layer. Two oxygen contents were obtained from each batch corresponding to optimally doped ($y = 0.97$) and underdoped ($y = 0.6$) regimes. Their T_c were found to be 85.3 and 79.5 K at optimal doping, and 41 and 25 K for the underdoped materials. The sample crystallites were aligned along the c crystallographic axis with an applied field. This allows accurate NMR measurements performed in fields parallel to c ranging from 3 to 7 T. Below T_c, NMR spectra are too broad for Fourier transform spectroscopy and were then measured point-per-point by sweeping the frequency over a few hundreds of kHz [8].

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In the superconducting state, the internal field B at any point in the sample may differ from the applied field B_{app} due to large screening effects. NMR measurements of the spin contribution to the NMR shift, which is proportional to χ_{loc}, are not straightforward. The spectral position ω^* of the NMR signal of a ^{7}Li nucleus is related to its NMR shift ^7K by

$$\omega^* = \gamma(B_{\text{app}} + \delta B)(1 + {}^7K), \qquad (1)$$

with $\delta B = B - B_{\text{app}}$, and γ the nuclear gyromagnetic factor. An independent determination of the distribution of δB at Li sites is needed. We can use the fact that the average of δB is almost independent of B_{app} in a large range of fields. Indeed, the magnetization $M \propto \delta B$ has been measured to be flat from $B_{\text{app}} = 2$ to 12 T in similar pure powder ceramics [10]. Measurements for two values of B_{app} yield both δB and K at the Li sites from Eq. (1) applied to the peak position of the NMR.

Let us specify first how ω^* has been extracted from the NMR spectra such as those plotted in Fig. 1. They consist of three lines at $\omega^* - \omega_c$, ω^*, and $\omega^* + \omega_c$, due to the quadrupolar splitting of the $I = \frac{3}{2}$ Zeeman transitions by the electric field gradient (EFG) at the Li site. The quadrupolar frequency ω_c is proportional to the EFG in the direction c of B_{app} [5]. Above T_c, the two outer lines are broader than the central one due to a small distribution of ω_c (typically $\delta\omega_c/\omega_c \sim 10\%$). The other source of broadening, common to the three lines, is the local distribution of hole content which induces a slight distribution of ^7K. It scales with ^7K and therefore increases with decreasing T. Below T_c, the presence of pinned vortices induces a distribution of δB among Li nuclei, leading to an additional asymmetric broadening [Eq. (1)], as observed in Fig. 1. The high frequency tail and the center peak of the line correspond, respectively, to Li sites in the vortex cores with $\delta B > 0$, and between vortices with $\delta B < 0$ [11]. We fitted the $T < T_c$ spectra using the $T > T_c$ shape convoluted by an asymmetric Gaussian representing the δB distribution. The resulting values of δB using two measurements of the central line peak position ω^* are plotted in Fig. 2 for optimal doping. The negative sign of δB confirms that the susceptibility probed by the peak position ω^* is associated to Li defects between vortices in the bulk superconducting state. At low T, the obtained $\delta B \simeq -30$ G is consistent with measurements by muon spin rotation (μSR) or ^{89}Y NMR in pure compounds [12]. The T dependence of δB originates from the T variation of the superconducting screening and of the field distribution in the vortex network. The data for $\delta B(T)$ has been fitted by a phenomenological power law corresponding, respectively, for $x_n = 1\%$ and 2% to $\delta B_{1\%} = -32[1 - (T/77)^2]$ and $\delta B_{2\%} = -26[1 - (T/60)^{1.5}]$ in Gaussian units. The decrease of δB with Li content can be explained by the concomitant increase of the penetration depth λ measured by μSR [13]. Above 77 and 60 K, respectively, we found $\delta B = 0$ within error bars (± 4 G). For optimally doped samples and applied fields of a few tesla, it has been shown that the vortices are in a liquid state in our range of temperatures below T_c [9,14]. Each vortex is then moving much faster than the NMR time scale, which averages out both the broadening and the screening effects, leading to $\delta B = 0$. The exact determination of the melting temperature, which depends on B_{app}, x_n as well as on the sample microstructure, is beyond the scope of this work. In the underdoped compound, for $B_{\text{app}} = 7$ T and $T > 10$ K, the vortices should always be in the liquid state [9,15]. Indeed, we find that $\delta B = 0$ within experimental accuracy, so that no correction to ω^* was needed for such conditions.

Using this determination of δB in Eq. (1), the shift ^7K can then be safely extracted. As seen in Fig. 1, this shift and therefore χ_{loc} are increasing with decreasing T below T_c. This is confirmed by systematic measurements of ^7K for all concentrations of Li and oxygen dopings represented in Fig. 3. A more compelling representation of the variations of ^7K is obtained by plotting $1/({}^7K - {}^7K_0) \sim 1/\chi_{\text{loc}}$ versus T as done in Fig. 4. $^7K_0$ is the T independent part of the shift and is measured from high T data to be much smaller than the observed variations of ^7K. In this plot, the Curie-Weiss law ${}^7K - {}^7K_0 = C/(T + T_K)$,

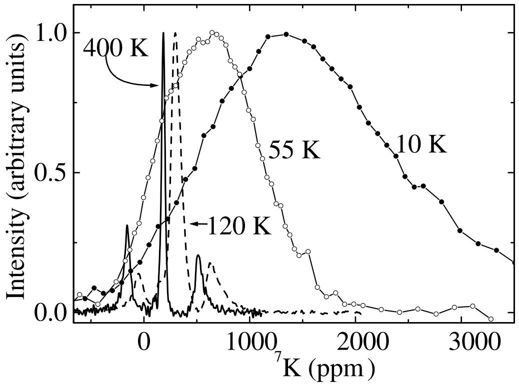

FIG. 1. ^{7}Li NMR spectra for $YBa_2Cu_3O_{6.97}$ with $x_n = 1\%$ obtained either by Fourier transform or point-by-point. In the superconducting state ^7K has been obtained after correction of demagnetization effects using Eq. (1).

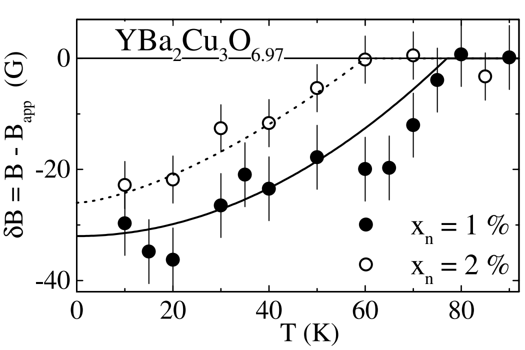

FIG. 2. Difference δB between applied and internal field on Li sites in optimally doped compounds deduced from measurements in $B_{\text{app}} = 3$ and 7 T. Full lines and dotted lines are phenomenological fits given in the text.

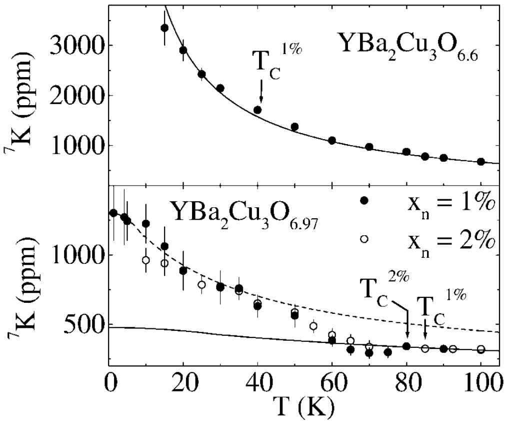

FIG. 3. T variation of the ^{7}Li NMR shift ^7K. The arrows indicate T_c in a 30 G applied field. For the underdoped $O_{6.6}$ sample, the full line is a Curie-Weiss fit with $C = 6.5 \times 10^4$ K ppm and $T_K = 2.8$ K. For the optimally doped $O_{6.97}$ samples, the prototype Kondo susceptibility of Fe in **Cu**Fe from Ref. [16] scaled to fit our data above (below) T_c is represented by a full (dashed) line.

which represents $\chi_{\rm loc}$ in the normal state is a straight line with slope C^{-1} which intercepts the horizontal axis at $-T_K$.

In the underdoped regime, from both Figs. 3 and 4, no significant change occurs at T_c, i.e., the almost perfect Curie law observed above $T = 80$ K is not affected by superconductivity and corresponds to $T_K = 2.8 \pm 1$ K [17]. To our knowledge, this is the first measurement of $\chi_{\rm loc}$ in a superconductor for moments appreciably coupled to the carriers. In contrast, we find a sharp increase of $\chi_{\rm loc}$ below T_c at optimal doping, as seen in the lower panel of Fig. 3. This increase is not expected for a usual Kondo impurity. This can be seen by comparing our data with a prototype of the Kondo susceptibility such as $\chi_{\rm Fe}$ of Fe impurities in the dilute alloy **Cu**Fe. We have scaled the T variation of $\chi_{\rm Fe}$ measured in [16] by a factor $T_K(O_7)/T_K(\mathbf{Cu}\mathrm{Fe}) \simeq 135/27.6 \simeq 4.9$ to fit the normal state data. One can obviously see in Figs. 3 and 4 that the rescaled $\chi_{\rm Fe}$ saturates at low T similar to $\chi_{\rm loc}$ but at a much lower value (of about a factor of 3). The data for $\chi_{\rm loc}(T < T_c)$ is better fitted by another scaling of $\chi_{\rm Fe}$ also represented in Figs. 3 and 4, leading to $T_K = 41 \pm 7$ K instead of 135 K above T_c. The moments survive below T_c even at optimal doping. They still display a Kondo-like susceptibility with a weaker screening than in the normal state. This value of T_K is consistent with the analysis of the specific heat measurements of Zn substituted YBaCuO$_7$ by Sisson *et al.* [18] who attributed the absence of a Schottky anomaly below T_c to Kondo screening of the Zn induced moments.

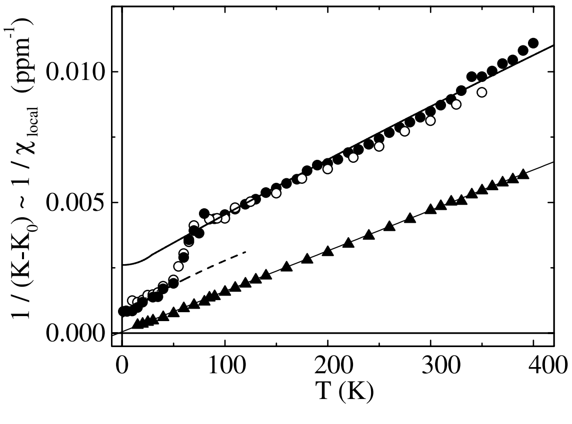

FIG. 4. T variation of the inverse of $^7K(T) - K_0$ which represents the inverse of the local susceptibility $\chi_{\rm loc}$ of the induced moments nearby Li. Solid triangles correspond to underdoped $x_n = 1\%$ YBa$_2$Cu$_3$O$_{6+y}$ while solid (empty) circles correspond to $x_n = 1\%$ (2%) at optimal doping. The fits with the **Cu**Fe Kondo susceptibility of Fig. 3 are plotted with the same symbols.

In the superconducting state of a Fermi liquid, the decrease of the DOS at the Fermi level prohibits the development of the Kondo divergence near or below a critical coupling J_c. This is also true for d-wave supercomputers for which the gap corresponds to a linear energy dependence of the DOS [1,2], except at low T in the presence of impurities. Qualitatively, this explains the reduction of Kondo screening and T_K at optimal doping below T_c. Renormalization group numerical studies using a realistic set of parameters may quantitatively account for the behavior observed in Fig. 4 at optimal doping [2].

In the underdoped regime, the absence of detectable modification of $\chi_{\rm loc}$ below T_c could result from the already small value of T_K found in the normal state. In contrast with optimal doping, any reduction of T_K below T_c cannot be observed in our experimental conditions where $T \gg T_K$. The low value of T_K already in the normal state could be explained by the occurrence of the pseudogap, similar to the effect of the superconducting gap at optimal doping. Both gaps display the same d-wave symmetry [19], and should lead to a reduction of T_K. However, the significant difference between the optimal and underdoped regimes in the apparent T_K (respectively, 41 and 2.8 K) in the superconducting regime remain to be understood.

Even though the above Fermi liquid picture explains the T behavior of $\chi_{\rm loc}$, it cannot account for the very existence of the moment induced by spinless impurities. This moment is the result of electronic correlations intrinsic to the pure cuprate. From NMR experiments performed in the normal state, this moment consists of a staggered antiferromagnetic (AF) state which extends on many lattice sites, but resides predominantly on the impurity first nn Cu sites. The present experiment demonstrates that this is still true below T_c. At optimal doping, scaling with $\chi_{\rm Fe}$ yields numerical values for the Curie term C of 5.1×10^4 K ppm and $4.8 \pm 1.1 \times 10^4$ K ppm above and below T_c, respectively. These values are only 25% smaller than in the underdoped case. Hence, C is almost unaffected either by superconductivity or hole doping. Therefore the interaction with the charge carriers does not modify the effective moment on the first nn, but merely induces a modification of Kondo screening.

The measurements by STM on Zn substituted Bi2212 [7] also imply a small spatial extent of the impurity LDOS below T_c. This LDOS exhibits a narrow resonance peak at an energy of 1.5 meV ($\approx$18 K) below the Fermi level. This energy scale is close to our T_K value, suggesting a common origin for the two phenomena. But the absence of LDOS on the first nn found by STM contrasts with our finding. Most computations of the LDOS can reproduce the symmetry of the observed STM pattern, but did not consider the existence of an induced magnetism [20,21]. In order to explain altogether the magnetism and the STM experiments, we suggest two possible scenarios.

(i) For an on site potential, some interpretations [20] predict a weak LDOS on the impurity site, and an enhanced LDOS on the first nn, which might agree with NMR. If, as usually assumed, the tunneling is vertical from the Bi to the Zn site, this prediction would result in an observation of a large LDOS on the first nn, in contrast with STM data. We suggest that the tunneling occurring through a BiO layer could have a much larger matrix element to the nn sites than to the one on the vertical. This would yield an *apparent* LDOS on site and on the second nn in the STM experiments [23].

(ii) Let us assume that the perturbation induced by the impurity corresponds to a potential on its nn Cu. We can anticipate that calculations along the lines of [20], with a potential on a nn Cu, would induce an LDOS on the impurity and the second nn Cu sites. The total *actual* LDOS would then be consistent with STM for a vertical tunneling. Polkovnikov *et al.* have done such a computation [22], which is furthermore the first realistic attempt to account for the magnetic properties detected by NMR. They introduced an extended moment on the four Cu nn sites, exchange coupled to the quasiparticles of the superconductor, and could reproduce the spatial dependence of the LDOS observed by STM.

In conclusion, our measurements show that the moment induced by spinless Li in the normal state of cuprates still exists in the superconducting state. When the Kondo temperature T_K is comparable to T_c, the Kondo screening is strongly reduced below T_c. This is consistent with computations made in a classical Fermi liquid in the presence of a d-wave gap. This reinforces the analogy of the magnetic behavior with that of a classical Kondo effect.

We have found that the dominant magnetic contribution still resides on the first nn Cu of the impurity below T_c. Therefore the short range AF correlations remain in the superconducting state. The present work leads us to believe in a common understanding of the local magnetism and LDOS, in the spirit of [22]. Determination of the evolution of the LDOS with temperature and hole doping should help to establish the relationship between NMR and STM results. This would also constrain the theoretical models, which should in addition account for the low-T magnetic susceptibility using the energy dependence of the LDOS.

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