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

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Using \textsuperscript{7}Li NMR shift data, the anomalous local moment induced by spinless Li impurities persists below \( T_c \) in YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{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 \( T_c \) \((T_K = 135 \text{ K})\) is strongly reduced below \( T_c \), as expected theoretically when the superconducting gap develops. The limited spatial extent of the induced moment \((\text{on } 1^{st} \text{ near neighbour Cu})\) 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.

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 before 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 \textsuperscript{[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 so 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 like Zn \textsuperscript{[3,4]} or Li \textsuperscript{[5,6]} substituted on the copper site of the CuO\textsubscript{2} planes induce a local moment in their vicinity. This moment extends essentially on the four Cu near neighbors \( (n.n.) \) of the impurity. Its static \textsuperscript{[5,6]} and dynamic \textsuperscript{[5]} 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 \textsuperscript{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 \( \chi_{loc} \) 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 \( 1^{st} \text{ n.n.} \) 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 \textsuperscript{[7]}. The STM data suggest the occurrence of a LDOS peak near the Fermi level on the Zn site and on the \( 2^{nd} \text{ n.n.} \) Cu. This location contrasts with our finding of a magnetic state located dominantly on the \( 1^{st} \text{ n.n.} \) 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\textsubscript{2}(Cu\textsubscript{1-x}Li\textsubscript{x})\textsubscript{3}O\textsubscript{6+y} are those used in \textsuperscript{[8]}. 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\textsubscript{2} layer. Two oxygen contents were obtained from each batch corresponding to optimally \((y = 0.97)\) and under- \((y = 0.6)\) doped regimes. Their \( T_c \) were found to be 85.3 K and 79.5 K at optimal doping, and 41 K 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 Tesla. 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 \textsuperscript{[8]}. 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 $\chi_{loc}$ are not straightforward. The spectral position $\omega^*$ of the NMR signal of a $^7$Li nucleus is related to its NMR shift $7K$ by

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

(1)

with $\delta B = B - B_{app}$, and $\gamma$ the nuclear gyromagnetic factor. An independent determination of the distribution of $\delta B$ at Li sites is needed. We can use the fact that the average of $\delta B$ 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 $B_{app} = 2$ to 12 Tesla in similar pure powder ceramics \[10\]. Measurements for two values of $B_{app}$ yield both $\delta B$ and $K$ at the Li sites from Eq.1 applied to the peak position of the NMR.

Let us specify first how $\omega^*$ has been extracted from the NMR spectra such as those plotted in Fig.1. They consist of three lines at $\omega^* - \omega_c$, $\omega^* + \omega_c$, due to the quadrupolar splitting of the $I = 3/2$ Zeeman transitions by the electric field gradient (EFG) at the Li site. The quadrupolar frequency $\omega_c$ is proportional to the EFG in the direction of $\gamma$ of $B_{app}$. Above $T_c$, the two outer lines are broader than the central one due to a small distribution of $\omega_c$ (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 $\delta B$ 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 \[3\]$. We fitted the $T < T_c$ spectra using the $T > T_c$ shape convoluted by an asymmetric gaussian representing the $\delta B$ distribution. The resulting values of $\delta B$ using two measurements of the central line peak position $\omega^*$ are plotted in Fig.2 for optimal doping. The negative sign of $\delta B$ confirms that the susceptibility probe by the peak position $\omega^*$ 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 $\mu$SR or $^{89}$Y NMR in pure compounds \[1\]. The $T$-dependence of $\delta B$ 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 $\delta B_{123} = -32(1 - (T/77)^2)$ and $\delta B_{2212} = -26(1 - (T/60)^{1.5})$ in Gauss units. The decrease of $\delta B$ with Li content can be explained by the concomitant increase of the penetration depth $\lambda$ measured by $\mu$SR \[4\]. Above 77 and 60K respectively, we found $\delta B = 0$ within error bars ($\pm 4$ 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 \[13\] \[14\]. Each vortex is then moving much faster than the NMR timescale, 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 $B_{app} = 7$ T and $T > 10$ K, the vortices should always be in the liquid state \[12\] \[13\]. Indeed we find that $\delta B = 0$ within experimental accuracy, so that no correction to $\omega^*$ was needed for such conditions.

Using this determination of $\delta B$ in Eq.1, the shift $7K$ can then be safely extracted. As seen in Fig.1, this shift and therefore $\chi_{loc}$ 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 $1/(7K - 7K_0) \sim 1/\chi_{loc}$ 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 $7K - 7K_0 = C/(T + 7K)$, which represents $\chi_{loc}$ in the normal state is a straight line with slope $C^{-1}$ which intercepts the horizontal axis at $-7K$.

In the underdoped regime, from both Fig.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 $7K = 2.8 \pm 1 K \[14\]$. To our knowledge, this is the first measurement of $\chi_{loc}$ in a superconductor for moments appreciably coupled to the carriers. In contrast we find a sharp increase of $\chi_{loc}$ 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 $\chi_{F\_Fe}$ of Fe impurities in the dilute alloy CuFe. We have scaled the $T$ variation of $\chi_{F\_Fe}$ measured in \[7\] by a factor $T_K(0)/T_K(CuFe) \simeq 135/27.6 \simeq 4.9$ to fit the normal state data. One can obviously see in Fig.3 and 4 that the rescaled $\chi_{F\_Fe}$ saturates at low $T$ like $\chi_{loc}$ but at a much lower value (of about a factor three). The data for $\chi_{loc}(T < T_c)$ is better fitted by another scaling of $\chi_{F\_Fe}$ also represented in Fig.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. \[15\] who attributed the absence of a Shottky anomaly below $T_c$ to Kondo screening of the Zn induced moments.

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 superconductors for which the gap corresponds to a linear energy dependence of the DOS \[16\] \[17\], 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.

In the underdoped regime, the absence of detectable modification of $\chi_{loc}$ 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, 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 K and 2.8 K) in the superconducting regime remain to be understood.

Even though the above Fermi liquid picture explains the $T$ behavior of $\chi_{loc}$, 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 AF state which extends on many lattice sites, but resides predominantly on the impurity 1$^\text{st}$ n.n Cu sites. The present experiment demonstrates that this is still true below $T_c$. At optimal doping, scaling with $\chi_{Fxc}$ yields numerical values for the Curie term $C$ of 5.1 $10^4$ K/ppm and 4.8 $\pm$ 1.1 $10^4$ 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 1$^\text{st}$ n.n. but merely induces a modification of Kondo screening.

The measurements by STM on Zn substituted Bi2212 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. The absence of LDOS on the 1$^\text{st}$ n.n. found by STM contrasts with our observation of a d-wave gap. This reinforces the analogy of the magnetic behaviour with that of a classical Kondo effect.

We have found that the dominant magnetic contribution still resides on the 1$^\text{st}$ n.n. 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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[1] D. Withoff and E. Fradkin, Phys. Rev. Lett. 64, 1835 (1990); L. S. Borkowski and P.J. Hirschfeld, Phys. Rev. B 46, 9274 (1992); J. Low. Temp. Phys. 96, 185 (1994); C.R. Cassanello, E. Fradkin, Phys. Rev. B 56, 11246 (1997); M.E. Simon and C.M. Varma, Phys. Rev. B 60, 9744 (1999)

[2] C. Gonzalez-Buxton, K. Ingersent, Phys. Rev. B 57, 14254 (1998); K. Ingersent, private communication

[3] A.V. Mahajan et al., Phys. Rev. Lett. 72, 3100 (1994); Eur. Phys. J. B 13, 457 (2000)

[4] P. Mendels et al., Europhys. Lett. 46, 675 (1999)

[5] J. Bobroff et al., Phys. Rev. Lett. 83, 4381 (1999)

[6] W. A. MacFarlane et al., Phys. Rev. Lett. 85, 1108 (2000)

[7] S.H. Pan et al., Nature 403, 746 (2000)
The equivalent measurement by sweeping the applied field is not possible here since the presence of frozen vortices makes the internal field insensitive to a change of the applied field.

E.H. Brandt and A. Seeger, Advances in Physics 35, 189 (1986)

S. Senoussi et al., Phys. Rev. B 53, 12321 (1996) and private com.

S. E. Barrett et al., Phys. Rev. B 41, 6283 (1990); T.M. Riseman et al., Phys. Rev. B 52, 10569 (1995)

P. Mendels et al., to be published.

A.P. Reyes et al., Phys. Rev. B 55, R14737 (1997)

J.E. Sonier et al., Phys. Rev. B 61, R890 (2000) and private communication

M. Andersson et al., Physica Amsterdam C332, 86 (2000)

Measurements below T=15 K are not reported as the accuracy is reduced by the large broadening of the NMR line together with the overlap with a sharp line corresponding to Li near a chain site.

H. Alloul, Physica Amsterdam 86-88B, 449 (1977)

D.L. Sisson et al., Phys. Rev. B 61, 3604 (2000)

A.G. Loeser et al., Science 273, 325 (1996)

M. I. Salkola, A. V. Balatsky, D. J. Scalapino, Phys. Rev. Lett. 77, 1841 (1996); M. Flatté, Phys. Rev. B 61, R14920 (2000)

S. Haas and K. Maki, Phys. Rev. Lett. 85, 2172 (2000)

A. Polkovnikov, S. Sachdev, and M. Vojta, Phys. Rev. Lett. 86, 296 (2001)

After electronic diffusion of our preprint we have been directed towards recent independent propositions that the tunneling through the BiO layer could give in STM an erroneous image of the spatial distribution of the DOS.

See J-X. Zhu, C. S. Ting, Phys. Rev. B 62, 6027 (2000); I. Martin, A.V. Balatsky, J. Zaanen, cond-mat/0012446

FIG. 1. $^7$Li NMR spectra for YBa$_2$Cu$_3$O$_{6.97}$ 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.4

FIG. 2. Difference $\delta B$ between applied and internal field on Li sites in optimally doped compounds deduced from measurements in $B_{app} = 3$ and 7 Tesla. Straight and dot 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$_{6.5}$ sample, the full line is a Curie-Weiss fit with $C = 6.5 \times 10^4$ ppm.K and $T_K = 2.8$ K. For the optimally doped O$_{6.97}$ samples, the prototype Kondo susceptibility of Fe in CuFe from Ref. 3 scaled to fit our data above (below) $T_c$ is represented by a full (dashed) line.

FIG. 4. $T$ variation of the inverse of $^7K(T) - K_0$ which represents the inverse of the local susceptibility $\chi_{loc}$ 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 CuFe Kondo susceptibility of fig.3 are plotted with the same symbols.
Figure 1 (Bobroff et al.)
Figure 2  (Bobroff et al.)
Figure 3  (Bobroff et al.)
Figure 4 (Bobroff et al.)