NMR studies of the original magnetic properties of the cuprates: effect of impurities and defects

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Abstract. Substitutional impurities in the CuO$_2$ planes of the cuprates allow us to probe the electronic properties of the host material. The pseudo-gap in the underdoped regime is unmodified far from the impurities even though $T_c$ is greatly reduced. The spin polarisation induced by magnetic impurities has an oscillatory behaviour reflecting the existing AF correlations between the Cu spins. Its influence on the NMR spectra opens a way to determine the $q$ dependence of the static spin susceptibility and the $T$ dependence of the AF correlation length. NMR measurements demonstrate that non-magnetic impurities such as Zn induce a local moment behaviour on the neighbouring Cu sites. This magnetism revealed by spin-less sites can be understood on theoretical grounds in the case of undoped quantum spin systems, while here the carriers greatly complicate the situation. Susceptibility data show that the magnitude of the local moment decreases with increasing hole doping. This experimental evidence directly reflects the influence of AF correlations and the interference between the carriers and the Cu hole spins in the cuprates. The anomalously large scattering of the carriers on spinless defects is another indication of the originality of the electronic properties of the cuprates, which apparently extends even to the overdoped regime.

I INTRODUCTION: MAGNETIC PROPERTIES OF PURE MATERIALS

It is now experimentally well established that the CuO$_2$ planes display anomalous magnetic properties in the metallic normal state of the cuprates, at least in the underdoped and optimally doped states. The occurrence of magnetic correlations was first shown by the existence of an enhanced non-Korringa nuclear spin relaxation rate $1/T_1$ on $^{63}$Cu and not on $^{17}$O and $^{89}$Y [1,2]. In the recent past, considerable interest has been focused on the pseudo-gap in the excitation spectrum of the cuprates. It was detected first in microscopic NMR measurements of the susceptibility $\chi_p$ of the CuO$_2$ planes [2], which exhibit a large reduction in the homogeneous $q = 0$ excitations at low $T$ in underdoped materials, as shown in Fig.1. Similar low $T$ reductions of the imaginary part of the susceptibility at
FIGURE 1. The $^{89}$Y NMR shift data evidence the occurrence of pseudo-gaps from a large decrease of the susceptibility $\chi_p$ of the CuO$_2$ planes, in YBCO$_{6+x}$. The temperature at which the pseudo-gap begins to open, which corresponds to the $\chi_p$ maximum, increases markedly with decreasing $x$, that is decreasing hole doping (the original data [2] are less accurate than those displayed here).

the AF wave vector $\mathbf{q} = (\pi, \pi)$ were observed in $^{63}$Cu $1/T_1T$ data and inelastic neutron scattering experiments [3]. Presently, the pseudo-gap of the underdoped high-$T_c$ superconductors is also studied by many techniques such as transport and angle resolved photoemission, which yields its $\mathbf{k}$ dependence. Various explanations are proposed for the pseudo-gaps which are believed to be essential features of the physics of the normal state (and perhaps the superconducting state) of the cuprates.

Atomic substitutions in the planar Cu site have naturally been found the most detrimental to superconductivity. This has in parallel triggered a large effort, particularly in our research group, to use such impurities to reveal the original normal-state magnetic properties of the cuprates. We shall see that NMR, as a local magnetic probe, is an essential tool which lends weight to this approach. In section II we present the effect of impurities on the phase diagram and the pseudo-gaps. We will distinguish the average effect of impurities on the physical properties far from the impurity site from the local magnetic perturbations. The study of the distribution of the spin polarisation induced by magnetic impurities is shown in sec. III to be a direct probe of the non-local magnetic response $\chi'(\mathbf{r})$ of the pure system, a quantity which is hard to access by other experimental approaches. In section IV we consider the case of non-magnetic impurities like Zn ($3d^{10}$) which, upon substitution on the Cu site of the CuO$_2$ plane, strongly decreases the superconducting transition temperature $T_c$. It has been anticipated [4], and subsequently shown experimentally
[5], that, although Zn itself is non-magnetic, it induces a modification of the magnetic properties of the correlated spin system of the CuO$_2$ planes. We shall recall how $^{89}$Y NMR demonstrated [6] that local magnetic moments are induced on the Cu near neighbour (n.n.) of the Zn substituent in the CuO$_2$ plane. Experiments on La$_{2-x}$Sr$_x$CuO$_4$ have confirmed [7] that the occurrence of local moments induced by non-magnetic impurities on the Cu sites is a general property of cuprates. Recent measurements of the variation with hole doping of the effective magnetic moment associated with non magnetic impurities will be reviewed. Finally, we shall discuss briefly in sec.V the influence of impurities on transport properties.

II IMPURITIES AND PHASE DIAGRAMS

The main effect of impurities is to depress superconductivity, usually much faster in the underdoped regime than in the optimally doped case. Similarly the increase of resistivity is larger for underdoped materials. This results in a shift of the Insulator-Metal transition towards higher hole concentration in presence of impurities. So what happens then to the crossover pseudo-gap lines? There is a controversy which has arisen because of the differences between macroscopic and microscopic measurements of the pseudo-gap. NMR has the advantage that the sites in the vicinity of the impurity usually display well shifted resonance lines. Therefore, the main NMR line corresponds to sites far from the impurity. Its broadening, to be studied in section III, is associated with the oscillatory induced polarisation of the host. Its position measures then the average $\chi_p$ far from the impurities which reflects their influence on the homogeneous magnetic properties. The $T$ dependence of the shifts $\Delta K(T)$ of the $^{89}$Y or $^{17}$O NMR mainlines [5,6,8] are found to be unmodified by impurity substitutions, as can be seen in Fig. 2.

This demonstrates that, contrary to the Metal-Insulator transition, the pseudo-gap is unaffected by impurity substitutions at large distance from the impurities. Incidentally these data also ensure that the hole doping is not significantly modified. Conversely if hole doping is changed, i.e. by Pr substitution on the Y site [9], NMR shift data can be used to estimate its variation by comparison with calibrated curves for $\chi_p$ in the pure material (Fig 1).

Other experiments, which very often probe the macroscopic behaviour of the sample, have sometimes been interpreted differently, as they do not directly distinguish local from large distance properties. For instance, it was initially suggested [10] on the basis of neutron scattering experiments, that the pseudo-gap vanishes at $\mathbf{q} = (\pi, \pi)$ upon Zn substitution. However, the careful neutron data of Sidis et al. [11] indicate that the opening of the pseudo-gap still occurs at the same $T^*$ although new states appear in the pseudo-gap. Such states may be associated with local magnetic modifications induced around the Zn, which will be described in section IV. In any case, far from the impurities the pseudo-gap is quite robust upon impurity substitution. These results are quite natural if the pseudo-gaps are only
associated with the occurrence of AF correlation effects. However, in the scenario in which the pseudo-gaps are associated with the formation of local pairs below $T^*$, they indicate that impurities do not prevent the formation of local pairs except possibly in their vicinity.

III EXTENDED RESPONSE TO A LOCAL MAGNETIC EXCITATION

In noble metals hosts, any local charge perturbation is known to induce long distance charge density oscillations (also called Friedel oscillations). Similarly a local magnetic moment induces a long distance oscillatory spin polarisation (RKKY) which has an amplitude which scales with the magnetization of the local moment and with its coupling $J_{ex}$ with the conduction electrons. This oscillatory spin polarisation gives a contribution to the NMR shift of the nuclei which decreases with increasing distance from the impurity. In very dilute samples, if the experimental sensitivity is sufficient, the resonances of the different shells of neighbours of the impurity can be resolved [12]. These resonances merge together if the impurity concentration is too large, resulting in a net broadening $\Delta\nu_{imp}$ of the host nuclear resonance. For some impurities, like rare earths substituted on the $\text{Y}$ site, the hybridisation and therefore the exchange coupling $J_{ex}$ are extremely weak. The plane nuclear spins only sense the moment through its dipolar field. But for moments
located in the planes such as Ni, the induced spin polarisation dominates, especially for the $^{17}$O and $^{63}$Cu nuclei. The large $^{17}$O NMR broadening induced by Ni has been therefore studied in great detail by Bobroff et al [8]. It has been found that in underdoped YBCO, the linewidth increases much faster than $1/T$ at low temperature, contrary to what one might expect in a non-correlated metallic host (Fig.3). This fast increase is a signature of the anomalous magnetic response of the host which displays a peak in $\chi'(q)$ near the AF wavevector $(\pi, \pi)$, which can be characterized by a correlation length $\xi$. Therefore the $T$ variation of the NMR spectra yields a method to study the $T$ dependence of $\chi'(q)$ and $\xi$. The analysis of such data depends on the phenomenological shape given to the $q$ dependence of $\chi'(q)$, especially as the O site probes $\chi'(r)$ on its two neighbours, and therefore is governed somewhat by the gradient of $|\chi'(r)|$. Assuming a Gaussian shape for $\chi'(q)$, it is found that the linewidth is nearly insensitive to the $T$ dependence of $\xi$, in contrast to the case of a Lorentzian shape [13]. The experiment on a single nuclear site does not by itself allow deduction of $\xi(T)$. However comparison with spin-spin relaxation data, which also measures an integral quantity involving $\chi'(q)$ yields some complementary information. With a Gaussian shape we find that $\xi$ increases with $T$ while for a Lorentzian, it would decrease with increasing $T$. Similarly a comparison of the respective broadenings of the $^{17}$O, $^{89}$Y and $^{63}$Cu spectra, which probe differently $\chi'(r)$, lead us to conclude that the Lorentzian model is somewhat better, implying that $\xi$ increases at low $T$ as one might expect [14]. More accurate studies of the shape of the spectra as well as their concentration dependence are required to arrive at quantitative conclusions on the variation of $\xi(T)$. We should
point out here that, for YBCO, the $^{17}$O width varies roughly like $1/T$, while the Ni moment still displays a Curie law. This indicates that the $T$ dependence of $\chi'(q)$ is not as large in optimally doped systems. In such cases the detailed shape of $\chi'(q)$ could not be analysed up to now.

IV LOCAL MAGNETISM INDUCED BY NON-MAGNETIC ZN

Surprisingly it has been found that, as for Ni substitution, a $1/T$ broadening of the $^{89}$Y line occurs [5] in YBCO$_7$:Zn, even though Zn is expected to be in a non-magnetic 3d$^{10}$ state. This was the first experimental evidence for the occurrence of “local moment like” behaviour induced by Zn. A more refined picture of the response of the host to a non-magnetic substituent has been obtained in the case of underdoped YBCO$_{6.64}$, as distinct resonances of $^{89}$Y were observed and could be attributed to Y n.n. sites of the substituted Zn [6]. The measured Curie-like contribution to the NMR shift of the first n.n. line (Fig.4), and the shortening of its $T_1$ at low-$T$ are striking evidence which justify the denomination “local moment”, that we have been using throughout $^1$.

The Zn induced local moments are quite clearly located in the vicinity of the Zn. As is shown by analysis of the n.n. $^{89}$Y NMR intensity data, the Zn substitutes essentially on the plane copper site. Therefore, the Zn contribution $\chi_c$ to the macroscopic susceptibility could be inferred from SQUID data taken on samples free of parasitic impurity phases [18,19]. The hyperfine couplings deduced from the comparison of the $^{89}$Y NMR shift data to $\chi_c$ have the correct order of magnitude to demonstrate that the local moment resides mainly on the Cu n.n. to the Zn. Assuming that they are not modified with respect to pure YBCO, the data can be analysed consistently with a locally AF state extending over a few lattice sites. This might also explain the existence of a line corresponding to Y second n.n. to the Zn [16].

In the superconducting state, $^{63}$Cu NQR relaxation [20] and Mössbauer experiments [21] indicate the existence of states in the gap. In neutron scattering experiments [11], the local states induced by the Zn, both in the pseudo-gap and in the spin-gap detected below $T_c$, are found at the $(\pi, \pi)$ scattering vector, and correspond to a real state extension of about 7\AA. These thus constitute direct evidence for the persistence of AF correlations in the vicinity of the impurities [22].

$^1$ The validity of these observations has been periodically put into question, for instance as similar n.n. resonances were not detected [15] in ESR experiments on Gd (substituted on Y). From the $T_1$ data for $^{89}$Y NMR, we have shown that the large expected relaxation rate for Gd corresponds to a significant line broadening of the Gd ESR n.n. lines which prohibits their detection [16]. It has also been conjectured that substitution of Zn on Cu and Ca on Y yield similar disorder effects on the NMR [17]. This is not true as the line broadening does not exhibit a Curie-like $T$ variation for Ca substituted samples.
FIGURE 4. The n.n. $^{89}$Y NMR shift obtained in YBCO$_{6.64}$:Zn displays a paramagnetic Curie-like component in contrast to the decreasing (pseudo-gap) susceptibility of the host material [6].

It is clear that the observed local moment behaviour is original inasmuch as it is the magnetic response of the correlated electron system to the presence of a spinless site, as has been proposed from various theoretical arguments [4,23–26]. As complete understanding of the magnetic properties of pure cuprates is far from being achieved, it is no surprise that present theoretical descriptions of impurity induced magnetism are rather crude, and for example, do not address its microscopic extent. Our results also fit well in the context of recent theoretical work on undoped quantum spin systems. For instance Martins [27] predicts static local moments induced by doping $S = 1/2$ Heisenberg AF chains or ladders with non-magnetic impurities. NMR experiments on the $S = 1/2$ Heisenberg chain system Sr$_2$CuO$_3$ are consistent with the prediction of an induced local moment with a large spatial extent along the chain [28]. In this undoped insulating quantum liquid, the response is purely magnetic. Since AF correlations persist in the metallic cuprates, the appearance of a local moment near the Zn might be anticipated, but its properties could depend strongly on the density of charge carriers. Magnetisation data by Mendels et al. [18,19], shown in Fig. 5, demonstrate that the Curie constant decreases steadily from YBCO$_{6.64}$:Zn to YBCO$_{7}$:Zn. However existing experiments do not, at present, distinguish the respective roles of the AF correlation length and screening by the conduction holes in defining the local moment magnitude and spatial extent.

In the slightly overdoped YBCO$_{7}$, the occurrence of a local moment was confirmed from $^{17}$O NMR linewidth data [29]. The fact that we could not resolve the $^{89}$Y n.n. signal in YBCO$_{7}$ is consistent with the weak magnitude found for the Curie-like contribution to the local susceptibility. Furthermore, Ishida et al [7] showed that our observation extends to another cuprate family, as non-magnetic
FIGURE 5. The Curie constant for the local moment induced by Zn in YBCO$_{6+x}$, as measured by macroscopic magnetic susceptibility measurements is found to decrease markedly with hole doping [19].

Al exhibits a local moment behaviour in optimally doped La$_{2-x}$Sr$_x$CuO$_4$. A local signature of this fact was found in the shift of the $^{27}$Al NMR which exhibits a Curie-Weiss T dependence of $\chi_c$, with a sizable Weiss temperature ($\theta \approx 50K$). It is not very clear from these data whether such a high value of $\theta$ corresponds to a genuine single impurity effect or if it varies with Al content, thereby revealing a strong coupling between the local moments. By analogy with our results this observation is supposed to result from a local moment residing on the n.n. copper orbitals, which are coupled to the $^{27}$Al nuclear spin via transferred hyperfine couplings.

V MAGNETISM AND TRANSPORT PROPERTIES

Let us now consider briefly the influence of impurities on transport properties. Most analyses of the resistivity data [30,31] suggest a large magnitude for the Zn scattering, not far from the unitary limit. Such results are generally observed for most local defects induced in the CuO$_2$ planes, such as irradiation defects [32]. It has occasionally been assumed [33] that strong scattering is due to potential scattering. In the present case, for which no charge difference occurs between Zn$^{2+}$ and Cu$^{2+}$, the scattering cannot be associated with charge difference, but rather is due indirectly to the fact that Zn is a spin-less defect. So, as for Kondo impurities in normal metal hosts, unitary scattering is associated with a magnetic effect. These remarks are of course included in most analyses of impurity scattering done in the strong correlation approaches [4,23–26]. Different behaviour of spinons and holons is at the root of the anomalous impurity scattering in such theories. However none
is at present sufficiently advanced to provide quantitative results which could be compared to experimental data.

As for the reduction of $T_c$ induced by “non-magnetic” impurities, the situation has evolved since our first report [6], since the d wave symmetry of the order parameter is now well established in most cuprates. In this case, any type of impurity scattering depresses $T_c$. This is exemplified by recent resistivity measurements performed on electron irradiated samples [34]. It is found that a universal law applies between the respective variations $\Delta T_c$ and $\Delta \rho$ of the superconducting temperature and of the resistivity induced by defects. The most remarkable feature detected in these experiments is that the universal relation extends to the overdoped regime, suggesting that the d wave symmetry of the order parameter is valid for the entire phase diagram, even in the doping range for which Fermi liquid behaviour seems to apply.

VI CONCLUSIONS

The studies presented above have allowed us to demonstrate that valuable information on the magnetic properties of the cuprates are obtained from the local study of their response to substitutional impurities in the CuO$_2$ planes. It could be anticipated, by analogy with RKKY effects in simple metals, that the large distance modifications of the host properties would directly reflect the non-local magnetic response of the host. This is indeed apparent in the NMR studies of the modifications of the central $^{89}$Y or $^{17}$O NMR lines, which give us some insight on the $q$ and $T$ dependence of the static susceptibility, i.e. of the AF correlation length. These studies also show that the pseudo-gap is unaffected by impurities and is therefore either a purely magnetic effect associated with AF fluctuations, or due to a local pairing which is not disrupted by impurities in contrast with the macroscopic superconducting condensate.

More surprising are the actual properties associated with spin-less impurities. The existence of magnetic correlations are responsible for the occurrence of local moment behaviour induced by non-magnetic impurities on the neighbouring Cu sites. While one might expect that the spin 1/2 moment which is released by such a defect in a magnetic quantum spin system should extend on a distance comparable to the AF correlation length, the measured decrease of the effective moment with increasing hole content is more likely to be associated with an interaction with charge carriers. As transport properties indicate that isovalent impurities produce a large scattering of the carriers, one can anticipate that this is due to the occurrence of a resonant state. But the actual Curie dependence of the susceptibility would not be expected then to extend to low T. However, the occurrence of superconductivity limits somewhat our experimental capability to investigate the magnetic properties of the metallic ground state. From SQUID data [19] it was concluded that in underdoped YBCO$_{6.6}$:Zn4%, for which $T_c$ is reduced to zero, the susceptibility follows a Curie-Weiss law down to 10K, with $\theta \approx 4K$. Does this correspond to a Kondo
like energy scale characteristic of the width of the impurity resonant state? Such a Kondo-like effect is a candidate mechanism [26] for the reduction of the magnitude of the local moment in YBCO$_2$:Zn. However in these systems, one does not a priori expect the physical properties to mimic those obtained for Kondo effect in noble metals in a classical sd exchange model. Such difficulties have already been pointed out by Hirschfeld [35] in view of our preliminary data [6]. Obviously further efforts are required to complete this approach both experimentally and theoretically in the context of a correlated electron system.

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