^{89}Y NMR Evidence for a Fermi-Liquid Behavior in $YBa_2Cu_3O_{6+x}$

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We report NMR shift ΔK and T_1 data of ^{89}Y taken from 77 to 300 K in $YBa_2Cu_3O_{6+x}$ for $0.35 < x < 1$, from the insulating to the metallic state. A Korringa law and therefore a Fermi-liquid picture is found to apply for the spin part K_s of ΔK. The spin contribution $\chi_s(x,T)$ to χ_m is singled out, as the T variation of ΔK scales linearly with the macroscopic susceptibility χ_m. This implies that Cu(3d) and O(2p) holes do not have independent degrees of freedom. Their hybridization, which has a σ character, hardly varies with doping. These results put severe constraints on theoretical models of high-T_c cuprates.

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The interplay between the magnetic properties of Cu(3d) holes and the charge transport mediated by the O(2p) holes is still a highly controversial question in high-T_c materials. While T_1 nuclear-spin-lattice relaxation data on ^{89}Y and ^{63}Cu at the superconducting transition[1,2] indicate that both hole systems are involved in the superconducting pairing, some authors suggest that the persistence of 2D antiferromagnetic spin fluctuations[3] above T_c indicates that the Cu(3d) spins could somehow be decoupled from the charge transport mediated by the O(2p) holes.[4] This could result for instance from weak Cu(3d)-O(2p) π bonding at the Fermi level.[5] Such ideas have recently led Johnston[6] to attempt a partition of the macroscopic susceptibility χ_m in high-T_c materials into a T-dependent part attributed to the lattice of Cu^{2+} spins and a Pauli term associated with charge carriers. In order to gain local insight on these properties, NMR measurements are highly desirable. ^{89}Y nuclei are direct probes[7,8] of the susceptibility of the CuO_2 planes. We report here[9] an extensive experimental study of both the NMR shift K_s and the nuclear relaxation rate T_1^{-1} of ^{89}Y, which allows for the first time a direct comparison of the static and dynamic susceptibilities in these materials from the metallic to the semiconducting state. These results provide evidence that both K_s and $(T_1T)^{-1}$ are T dependent in the metallic state as soon as x departs from unity. A Korringa relation between T_1T and K_s is established and indicates that a Fermi-liquid picture holds. Our data suggest that this behavior might extend as well into the semiconducting state. Further, K_s, which probes the T dependence of χ on the oxygen sites,[7,8] is found to scale with χ_m, which is dominated by χ on the copper sites.[10] Therefore the T variation of χ_m should in no case be attributed solely to the Cu^{2+} spins and Cu(3d) and O(2p) holes do not have independent degrees of freedom.

NMR data have taken on the same powdered ceramic samples as in Ref. 7, which had been deoxygenated at low T ($\sim$500 °C) and immediately sealed in Pyrex vials *in a* ^{4}He atmosphere. Our initial $x=1$ sample (now labeled $x=1-\epsilon$) had been left about two weeks in air before being sealed and has probably lost some oxygen. Samples kept now for more than one year in such vials did not show any change in their properties. The positions ΔK of the NMR line relative to a YCl_3 reference, determined as in Ref. 7, are summarized in Fig. 1 for samples with $x > 0.35$ which are not antiferromagnetic above 100 K. It can be seen that ΔK is nearly T independent above T_c only for $x=1$, in good agreement with ^{63}Cu NMR data,[10] while a large-T variation of ΔK is detected already for $x=1-\epsilon$. Except for $x=1$, earlier data reported above 150 K[11] agree with the present results.

Let us recall here that the shift tensor $\Delta\mathbf{K}(x)=\sigma(x)+\mathbf{K}_s(x)$ involves a chemical-shift contribution $\sigma(x)$ due to filled electronic shells and a spin contribution $\mathbf{K}_s(x)$ due to the susceptibility on the O(2p) holes. Data on oriented powders, to be reported elsewhere,[12] confirm that σ is T independent, as might be expected from the negligible T variation of the lattice parameters, and that $\mathbf{K}_s(x)$ is purely isotropic, as obtained indirectly from

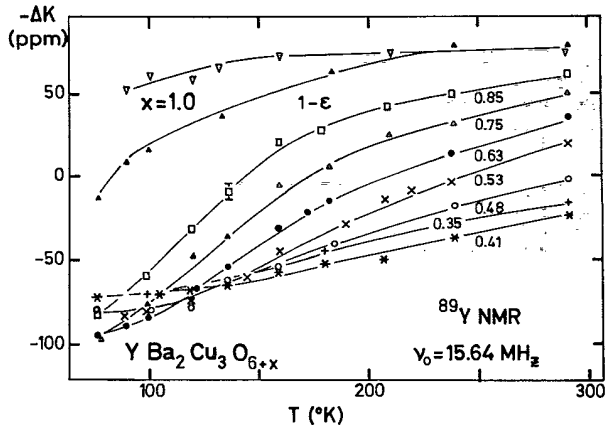

FIG. 1. The shift ΔK of the ^{89}Y line, referenced to YCl_3 plotted vs T, from 77 to 300 K. The lines are guides to the eye.

linewidth considerations in Ref. 7. In the present nonoriented powders the T variation of ΔK is then directly linked with $K_s(x)$. The unexpected decrease of ΔK with T, detected for $x=0.35$ and $x=0.41$, allows us to point out that σ is much larger than 22 ppm. This value was previously inferred[7] from the absence of variation of ΔK for $x<0.41$ at $T=293$ K, which appears now to be purely fortuitous (ΔK has been found to vary with x in the insulating state at 77 K[12]).

Before attempting further analysis of these results, let us consider the ^{89}Y relaxation data reported in Fig. 2. As for ΔK, one can see that $(T_1T)^{-1}$ varies with T (above T_c) except for $x=1$, in quantitative agreement with Ref. 1, for this latter case. For oxygen-deficient samples, some authors[11,13] reported $(T_1T)^{-1}$ values nearly independent of oxygen content even for $x\approx 0.2$, and always larger than the present results. This has to be ascribed either to technical difficulties in their T_1 measurements or to sample purity problems. On the contrary, a good overall agreement is found with the data reported by Warren *et al.*[14] for $x=0.70$. The efforts undertaken in order to improve the stability of our spectrometer might explain the increased accuracy of our data with respect to these previous works. Each T_1 point in Fig. 2 required, however, at least 24 h of data collection.

As the dominant coupling with O($2p$) holes is isotropic,[12] we expect a simple Korringa relation $T_1TK_s^2=\kappa\mathcal{S}$, where $\mathcal{S}=h(\gamma_e/\gamma_n)^2(4\pi k_B)^{-1}$, if a Fermi-liquid analysis applies. In elemental metals, κ is introduced in order to allow for deviations with respect to a free-electron case. κ might also differ from unity if various hyperfine relaxation channels coexist. As the value of $\sigma(x)$, hence of $K_s(x,T)$, is not yet determined, the best way to search for such a relation is to plot $(T_1T)^{-1/2}$ vs ΔK, as is done in Fig. 3. Linear relationships hold *with a sample-independent Korringa constant* $\kappa=5.3$ (given by the slope in Fig. 3), within experimental accuracy. Extrapolation to $(T_1T)^{-1/2}=0$, that is $K_s=0$, yields $\sigma=300(20)$ ppm for $x>0.6$. This is much larger than initially expected, but within the range of σ values observed in the usual Y oxides.[15] Further, the T variation of K_s for the $O_{6.63}$ sample is found to scale linearly with preliminary NMR shift data taken on ^{17}O by Butaud *et al.*[16] on a $O_{6.65}$ sample. From the zero of the ^{17}O shift, obtained for $T\ll T_c$, we deduce an independent estimate $\sigma\approx 300$ ppm, in excellent agreement with the value found above for $x>0.6$. The slightly different linear dependences in Fig. 3 can be safely ascribed to a small decrease of $\sigma(x)$ for low oxygen content.[17]

Let us now compare the data for ΔK with the macroscopic susceptibility χ_m. While most published results for χ_m exhibit Curie contributions from impurity phases, Parkin has reacted samples sufficiently to obtain a T-independent χ_m for $x=1$.[18] In Fig. 4, the plot of ΔK versus interpolations of χ_m from Parkin's data (taken by steps of 0.1 for x) demonstrates that ΔK is linear in χ_m for all samples. This implies that all the T variation of χ_m is sensed on the planar O($2p$) holes. Figure 4 allows us to write

$$\chi_m=\chi_0(x)+\chi_1(x,T), \tag{1}$$

and

$$\Delta K-\sigma(x)=a\chi_1(x,T)=K_s(x). \tag{2}$$

In Fig. 4, the negative coupling $a=-7.8$ kG/μ_B is independent of the concentration of O($2p$) holes, within experimental accuracy, while χ_0 has a slight x variation, as the ΔK vs χ_m plots do not coincide, even for $x>0.6$ for which σ is constant. With the values of $\sigma(x)$ obtained from Fig. 3 we deduced the values of χ_0 reported in the inset of Fig. 4. Let us focus on the results for the $O_{6.41}$ nonsuperconducting sample. For such oxygen contents χ_m has a small Curie contribution in Parkin's data.[18] Such Curie tails due to impurity phases in

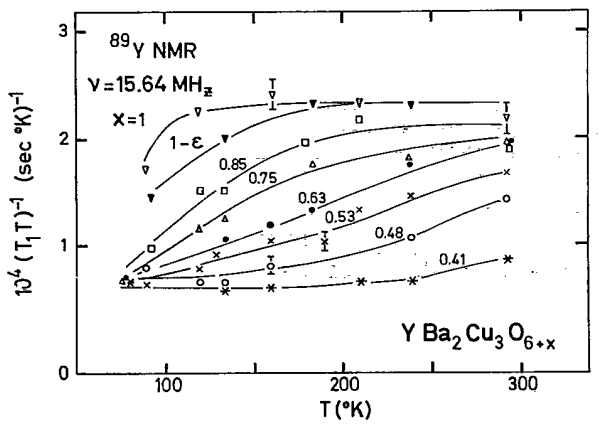

FIG. 2. $(T_1T)^{-1}$ data have a T dependence similar to that of Fig. 1 for ΔK. The lines are guides to the eye. Notice that $(T_1T)^{-1}$ is nearly constant below 200 K for sample $O_{6.41}$.

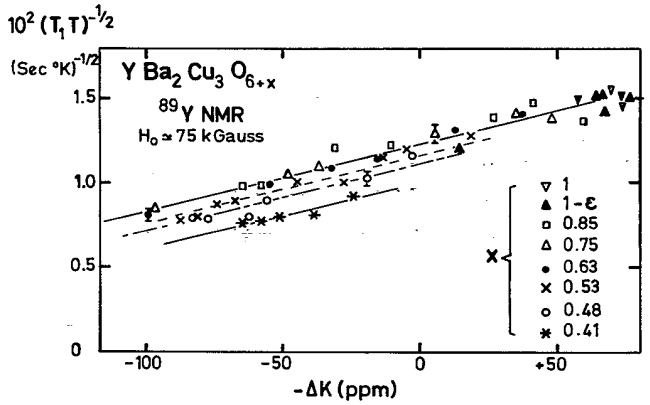

FIG. 3. The correlation between $(T_1T)^{-1/2}$ and ΔK. A linear least-squares fit is shown for $x>0.60$ (full line). Best fits with the same slope are displayed for $x=0.41$ (full line), $x=0.48$ (dash-dotted line), and $x=0.53$ (dashed line). Extrapolation to $(T_1T)^{-1/2}=0$ allows one to deduce $\sigma(x)$.

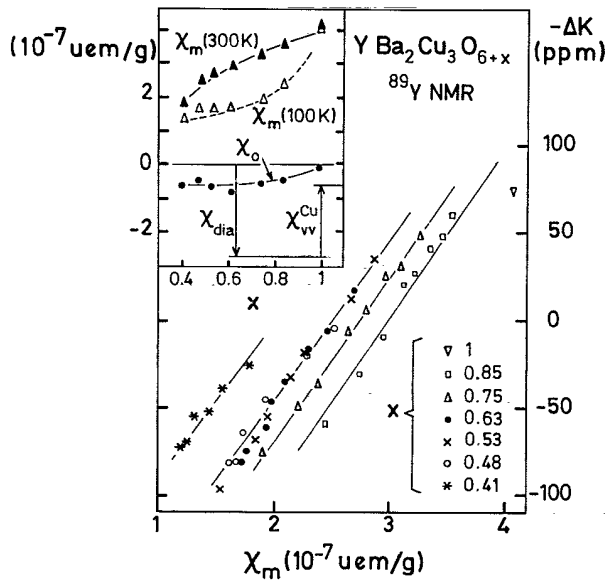

FIG. 4. Plot of ΔK vs the macroscopic susceptibility χ_m as measured by Parkin (Ref. 18). For $x=0.41$, χ_m has been corrected for a small Curie contribution at low T. The straight lines are least-squares fits to the data for $0.48<x<0.63$ and $x=0.75$ and best fits with the same slope for $x=0.41$ and 0.85. Inset: Estimates of $\sigma(x)$ deduced from Fig. 3 yield χ_0 from Eqs. (1) and (2), which is plotted together with χ_m (300 K) and χ_m (100 K). Values of χ_{dia} and χ_{VV} (Cu) (Refs. 10 and 19) are shown for comparison.

moderate amount or local moments, which might appear on Cu(1) sites, should not contribute to the ^{89}Y shift. We have therefore reported, in Fig. 4, ΔK vs χ_m, corrected for the Curie term, for this sample. Even without this correction we find that α does not change markedly from the metallic to the insulating state.

Theoretically χ_m can be written $\chi_m=\chi_{dia}+\chi_{VV}+\chi_s(T)$. Here, the diamagnetic term $\chi_{dia}=-2.65\times10^{-7}$emu/g has been calculated, and the dominant contribution to the Van Vleck term χ_{VV} associated with the Cu^{+2} sites $\chi_{VV}(Cu^{2+})=1.95\times10^{-7}$emu/g has been determined from ^{63}Cu residual NMR shifts measured below T_c,[10,19] for the O_7 compound. χ_{VV} should not be very dependent on x, if one assumes that the Cu(1) sites are still Cu^{2+} for $x\approx0.5$. As seen in the inset of Fig. 4, $\chi_{dia}+\chi_{VV}$ is not far from χ_0 and therefore χ_1 is directly linked with the spin term, which can be subdivided into chain and plane contributions, $\chi_s(T)=\chi_s^{ch}+\chi_s^{pl}$.

The ^{89}Y nuclear spin senses an internal field associated with the hole density magnetization located on the eight nearby O atoms. This yields a shift $K_s=8\alpha_0\chi_s^{pl}(O)$ of the ^{89}Y NMR, where α_0 is the hyperfine coupling given by the hybridization of an O hole wave function with the Y atomic orbitals. Here $\chi_s^{pl}(O)$ is the planar susceptibility on the oxygen site, that is, $\chi_s^{pl}=\chi_s^{pl}(Cu)+2\chi_s^{pl}(O)$. As $\chi_s(T)$ is dominated by the contribution of the copper sites, our finding of Fig. 4 implies that $\chi_s^{pl}(O)$ and $\chi_s^{pl}(Cu)$, and eventually χ_s^{ch}, have the same T dependence as χ_1. Although the three copper sites are supposed to be equivalent, that is, $\chi_s^{pl}=2\chi_s^{ch}$ is assumed in the analysis of the O_7 ^{63}Cu NMR data,[10,19] there is no experimental evidence yet favoring this partition of χ_s. Alternatively χ_s^{ch} might be small and could then rather contribute to χ_0, in which case $\chi_1=\chi_s^{pl}$ and $\chi_s^{ch}=\chi_0-(\chi_{dia}+\chi_{VV})$. NMR data on ^{63}Cu and ^{17}O for $x<1$ will certainly allow us to decide between these two possibilities. A major conclusion which can be drawn from the present results is that *$\chi_s(T)$ cannot be partitioned into two independent contributions associated with localized Cu(3d) holes and O(2p) change carriers.* Rather, the data of Fig. 4 allow us to demonstrate that $\alpha=8\alpha_0\chi_s^{pl}(O)/\chi_1$ is independent of x. As the atomic structure of the CuO_2-Y-CuO_2 sandwiches is quasi-invariable, this can indeed be expected for α_0. More surprising here is the absence of variation, within experimental accuracy, of $\chi_s^{pl}(O)/\chi_1$, that is, of $\chi_s^{pl}(O)/\chi_s^{pl}(Cu)$. *This, in fact, means that the degree of covalency of the Cu(3d)-O(2p) hole orbitals does not vary significantly from the metallic to the insulating state.* The symmetry for the Cu(3d)-O(2p) hole orbitals can be determined from the sign and magnitude of K_s as proposed initially by Adrian.[9] Let us recall that $\alpha<0$, and $|K_s|$ is much larger than initially expected, so that any positive contribution to K_s has to be negligible, in order to be compatible with the T_1 data.[20] The results therefore support the proposition that *$\chi_s^{pl}(O)$ is due to σ-bonded Cu(3d)-O(2p) hole orbitals* which, by symmetry, do not overlap with Y(5s) and therefore do not yield any positive contribution to K_s.[19,20] The anisotropy of the ^{17}O NMR shift of the planar sites[21] also favors this hybridization scheme, which is the starting point for most theoretical models of the electronic structure of the CuO_2 planes.

Another major finding here is *the validity of a Korringa relation, which demonstrates that a Fermi-liquid picture applies, even in the presence of a large variation of $\chi_s(T)$.* Recent T_1 data on ^{17}O NMR of the planar sites[22] yield $T_1T=$const for the O_7 sample for which K_s is T independent. This gives a Korringa constant $\kappa(^{17}O)\approx0.7$, closer to unity than our result $\kappa(^{89}Y)\approx5.3$. Let us point out here that these two measurements are not equivalent. While ^{17}O relaxation occurs mainly through isotropic coupling with the on-site fluctuating spin density,[22] the ^{89}Y relaxation proceeds through fluctuations of the total field due to its eight O neighbors and is therefore sensitive to the correlation of their spin fluctuations. If these are totally incoherent, it is easily derived[23] that $\kappa(^{89}Y)=8\kappa(^{17}O)$ which seems to be the case here as the data yield $\kappa(^{89}Y)/\kappa(^{17}O)\approx7.6$.

Current theories for the electronic structure of the high-T_c cuprates have not been carried out far enough to calculate the local static and dynamic χ in the metallic state, so that only rough comparisons can be done at present. The Fermi-liquid behavior could be naturally

explained with a single band of weakly interacting fermions. The weak x dependence of χ_s at high T could even be taken as evidence for a constant density of states, as expected for free electrons in 2D. As suggested by neutron scattering,[3] antiferromagnetic (AF) correlations have to be considered. Although the static χ on the O and Cu sites do scale with each other, the same might not be true for the fluctuating components. The enhancement of the Cu NMR T_1 with respect to a Korringa law[2] could reflect a larger incidence of the AF fluctuations on the Cu than on the Y or O, which are symmetric sites for the AF lattice of the O_6 compound.[7] In the band picture, AF correlations might induce a pseudogap, as suggested by Friedel,[24] which could explain the reduction of χ_s at low T. However, it is less clear whether this approach is compatible with the smooth variation of χ_s and K_s from the metal to the insulating state.

The latter result might be better explained if one considers strong-correlation theories, assuming a Mott insulating state for $x=0$. In these models χ_s is essentially localized, and the charge degrees of freedom are ensured by quasiparticles which can propagate in the correlated-spin background. For instance in the single band t-J model,[25] hole doping induces singlet states involving one Cu and the four surrounding O atoms. Although the increase of χ_s with T, and x, might be attributed to a softening of the spin background, when injecting holes, the applicability of a Fermi-liquid picture and/or a Korringa relation is not demonstrated so far in such a framework. The crossover towards a local-moment regime would then only occur above 300 K. This could be possible if the exchange coupling $J\sim 1000$ K measured in the AF state keeps the same order of magnitude up to the O_7 composition as suggested by some experiments.[26]

In conclusion, the features revealed by these experiments confirm that the properties of the quantum spin fluid involved in the cuprates are rather intricate, as local and extended characters can hardly be untangled. This is further emphasized by the fact that a Korringa relation seems to apply as well for the $O_{6.41}$ sample (for which T_1T is nearly constant below 200 K in Fig. 2). This puzzling result would imply that a Fermi-liquid picture applies as well to excitations in the semiconducting state. We intend to check whether free Curie spins, as detected in χ_m, contribute to T_1^{-1} and then make the observed behavior of T_1T purely fortuitous for this sample. Although such experimental progress is required, we believe that the present results already put severe constraints on theories which intend to describe the actual properties of high-T_c cuprates.

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