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Two-component behaviour of high-temperature superconductors from NMR

J Haase[1], **C P Slichter**[2] **and G V M Williams**[3]

[1] University of Leipzig, Faculty of Physics and Earth Science, 04103 Leipzig, Germany
[2] University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
[3] The MacDiarmid Institute, Industrial Research, PO Box 31310, Lower Hutt, New Zealand

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Abstract

Most NMR experiments on high-temperature superconductors, in particular spin shift measurements, have been interpreted in terms of a single component. New NMR experiments presented here on Cu and O in $La_{1.85}Sr_{0.15}CuO_4$, from which uncertainties from the Meissner effect have been removed experimentally by recording apical oxygen spectra, are in disagreement with single-component behaviour in the temperature dependence of the spin susceptibility. Instead, it can be explained within a two-component model that was used to explain early uniform susceptibility measurements. With this it is possible to determine the temperature dependences of the two susceptibilities, even below the transition temperature T_c, from NMR. It is found that one of the susceptibilities is constant above T_c and drops exponentially at lower temperatures, while the one that carries the pseudogap feature starts to decrease at much higher temperatures and continues to do so below T_c.

Hole doping of high-temperature superconductors [1] drives the parent Mott insulating material [2] away from antiferromagnetic order by creating holes in the CuO_2-planes. These holes predominantly enter [3–5] planar oxygen $2p_\sigma$ orbitals [6], while the Cu remains close to its parent $3d^9$ state with a single hole in the $d(x^2 - y^2)$ orbital that is hybridized with the O $2p_\sigma$ orbitals of the four surrounding, almost closed shell oxygen atoms in the $2p^6$ configuration. This may immediately suggest two-component behaviour [7–9], but as Zhang and Rice [10] showed, a single-band effective Hamiltonian may also be appropriate if the oxygen holes form stable singlets with the Cu spin. Since it was possible [11] to explain the planar Cu data in $YBa_2Cu_3O_{7-y}$ with Cu moments only, and since the Y NMR data [12] above T_c showed a doping-independent slope of shift versus temperature, it was believed [13] that this supported a single-fluid model (a doping-dependent, but temperature-independent shift contribution present in the data [12] was not discussed). Finally, a comprehensive NMR study [14] seemed to reveal that planar Cu and O shifts in $YBa_2Cu_3O_{6.63}$ are proportional to the uniform spin susceptibility. This account was taken by many [15] as the final proof for single-fluid behaviour of all high-temperature superconductors.

Several years ago, it was found with NMR linewidth analyses [16] that the Knight shifts in $La_{2-x}Sr_xCuO_4$, while in agreement with earlier work [17], seemed to contradict a single component's response. However, there was no firm experimental estimate for the Meissner-type diamagnetism that can influence the shifts [18] substantially. We have performed new measurements on magnetically aligned powder samples to remove these uncertainties. Our NMR results show that the uniform spin susceptibility cannot be explained by a linear response of a single electronic fluid, and in the usually adopted picture of hyperfine interactions it requires a two-component approach. Such a scenario was suggested by Johnston [19] many years ago and was later confirmed on a much larger set of samples [20]. Johnston showed that the uniform spin susceptibility (above T_c) can be explained in terms of two components: a temperature-independent, but doping-dependent contribution (that we show vanishes below T_c) and a second, temperature-dependent one that obeys a universal scaling behaviour. By relating Johnston's data directly to our two components we can deduce hyperfine coefficients and with them the temperature dependence of the two susceptibilities also below T_c. We find that the susceptibility that already decreases substantially above T_c reflects the pseudogap behaviour and continues to decrease below T_c. The second component, as already mentioned, is temperature independent above T_c and we find that it rapidly

decreases below T_c with a slope that cannot be distinguished within error bars from Yosida's prediction [21]. A possible scenario might be that of a spin liquid and Fermi liquid, as suggested by Barzykin and Pines [22].

In the cuprates, the Cu and O nuclear spins' resonance frequencies are influenced by various effects that complicate the testing for one- versus two-component theories with NMR shift measurements. Fortunately, the electric quadrupole interaction that has been shown [6] to measure the hole doping at both nuclear sites is largely temperature independent and its influence on the NMR shift can be removed. The dominant magnetic shift effects are the following: the core diamagnetism shift, the van-Vleck paramagnetic shift, the electronic spin shift, and a term from Meissner diamagnetism in the mixed state. While the first two terms can be expected to be T-independent, the latter two are expected to show different T-dependences. In order to investigate the electronic spin response, the influence of the Meissner-type diamagnetism has to be removed. Since Meissner diamagnetism decreases the applied magnetic field B_0 in the material to ${}^{\alpha}B$, where α denotes the orientation of the external field with respect to the crystal axes, the anisotropic Meissner shift ${}^{\alpha}K_{\rm M}(T) = ({}^{\alpha}B - B_0)/B_0$ is the same for all nuclei for given α. Furthermore, for Cu, the van-Vleck shift ${}^{63}K_{\rm VV,ref}$ has been measured [23] for various reference compounds (e.g. ${}^{63}K_{\rm VV,ref}$(CuCl) $=$ 0.150%; for metallic copper ${}^{63}K_{\rm VV,ref}$(Cu-metal) $\approx$ 0, and the Knight shift ${}^{63}K_{\rm S}$(Cu-metal) $=$ 0.382% [23]), and ${}^{63}K_{\rm core}$ is close to 0.240% for Cu, Cu^{+}, and Cu^{2+} with negligible anisotropies [24]. Consequently, we can correct our experimentally observed shifts so that they measure

$$ {}^{63,\alpha}K = {}^{63,\alpha}K_{\rm VV} + {}^{63,\alpha}K_{\rm S}(T) + {}^{\alpha}K_{\rm M}(T) \qquad (1) $$

for the ^{63}Cu isotope, for example. For oxygen we can expect the orbital shifts to be small, due to the lack of excited states sufficiently close in energy. In particular for the water reference we can assume that ${}^{17}K_{\rm VV,ref}(H_2O) \approx 0$ for analysing the rather large shifts in the cuprates. Thus, we can correct the oxygen shift data so that they represent

$$ {}^{17,\sigma,\alpha}K = {}^{17,\sigma,\alpha}K_{\rm S}(T) + {}^{\alpha}K_{\rm M}(T), \qquad (2) $$

where we have added an additional label $\sigma \in [P, A]$ to differentiate between planar (P) and apical (A) oxygen. For our c-axis aligned powder samples we will only consider two orientations $\alpha \in [\parallel, \perp]$ with the external magnetic field B_0 parallel and perpendicular to the crystal's c-axis.

One typically assumes $K_{\rm S}(T = 0) = 0$ in the cuprates. This is a reasonable assumption since the spin shift decreases substantially with lowering the temperature, which indicates spin-singlet pairing that demands that the uniform electron spin susceptibility $\chi_{\rm S}$ vanishes at low temperatures, and with it

$$ {}^{n,\alpha}K_{\rm S}(T) = \frac{{}^{n,\alpha}A}{\gamma_{\rm n}\gamma_{\rm e}\hbar^2}\chi_{\rm S}(T). \qquad (3) $$

Here, $\gamma_{\rm n}$ and $\gamma_{\rm e}$ denote the gyromagnetic ratio of the nucleus and electron, respectively. The anisotropic hyperfine coupling constant is denoted by ${}^{n,\alpha}A$. In $La_{2-x}Sr_xCuO_4$ (and various other cuprates) one finds that ${}^{63,\parallel}K(T) \approx$ const. Since this is not true for the other shifts it is attributed to an accidental cancellation of ${}^{63,\parallel}A$, and ${}^{63,\parallel}K$ does not hold information about $\chi_{\rm S}$. On the other hand, due to spatial modulations [16] in these materials ${}^{63,\parallel}K$ shows a sizeable distribution of values, especially at lower T, and is thus not giving us a precise estimate of ${}^{\perp}K_{\rm M}(T)$. Due to distributions in the quadrupole splitting, ${}^{17,P,\perp}K$ cannot be analysed easily, as well. Therefore, in order to be able to determine the spin shift (3) from the experimentally corrected shifts in (1) and (2) without the disturbing Meissner term, we form the following two quantities,

$$ \begin{aligned} G_{\perp}(T) &= {}^{63,\perp}K(T) - {}^{17,A,\perp}K(T) \\ \text{and} \qquad G_{\parallel}(T) &= {}^{17,P,\parallel}K(T) - {}^{17,A,\parallel}K(T). \end{aligned} \qquad (4) $$

That is, we subtract from the planar Cu shift with the field perpendicular to the c-axis that of the apical oxygen for the same orientation, and we subtract from the planar oxygen shift with the field parallel to the c-axis that of the corresponding apical signal. This experimental procedure ensures that the Meissner terms disappear and that we can write, cf (3),

$$ G_{\perp}(T) = {}^{63,\perp}K_{\rm S}(T) - {}^{17,A,\perp}K_{\rm S}(T) \equiv c_{\perp}\chi_{\rm S}(T) \qquad (5) $$

$$ G_{\parallel}(T) = {}^{17,P,\parallel}K_{\rm S}(T) - {}^{17,A,\parallel}K_{\rm S}(T) \equiv c_{\parallel}\chi_{\rm S}(T). \qquad (6) $$

Both quantities are plotted in figure 1 for $La_{1.85}Sr_{0.15}CuO_4$ and it is obvious from that plot that they do not follow the same temperature dependence dictated by a single $\chi_{\rm S}(T)$, cf (5) and (6). We must conclude that the single-component behaviour does not hold for all cuprates. We observe in figure 1 that the temperature dependences for $G_{\parallel,\perp}$ differ already at high temperatures, so that this is not just a peculiarity of the superconducting state. This fact also rules out that it can have to do with the distributions of shifts (linewidths) since they are much more pronounced at low temperatures [16].

Given that a description in terms of (5) and (6) fails, we make the two-component ansatz,

$$ G_{\perp}(T) = c_{11}\chi_1 + c_{12}\chi_2, \qquad G_{\parallel}(T) = c_{21}\chi_1 + c_{22}\chi_2, \quad (7) $$

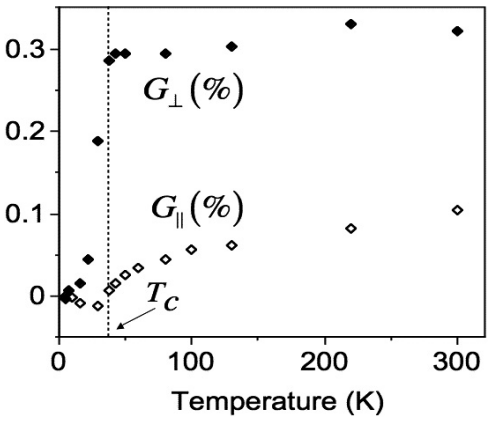

Figure 1. Temperature dependences of the generalized magnetic shifts $G_{\perp}$ and $G_{\parallel}$ (see the text) for which the diamagnetic Meissner term disappears.

with the two uniform susceptibilities χ_1, χ_2. If we plot $G_\perp$ versus $G_\parallel$ (not shown), we find a linear dependence above T_c from which we determine with

$$G_\perp(T) = \frac{c_{11}}{c_{21}} G_\parallel(T) + \left[c_{12} - \frac{c_{11}c_{22}}{c_{21}} \right] \chi_2, \tag{8}$$

where χ_1 has been substituted, that the ratio $c_{11}/c_{21} \approx 0.405$. As already mentioned in the introduction, this experimental observation is in agreement with Johnston's discovery [19] who found that the *normal state* uniform susceptibility $\chi(T, x)$ of $La_{2-x}Sr_xCuO_4$ could be explained in terms of two components, $\chi(T, x) = \chi_1(T, x) + \chi_2(x)$, i.e. a temperature-independent susceptibility $\chi_2(x)$ that is a function of doping only, and a temperature-dependent $\chi_1(T, x)$,

$$\chi_1(T, x) = [\chi_{\max}(T = T_{\max}, x) - \chi_2(x)]\, F(T/T_{\max}(x)), \tag{9}$$

that shows universal scaling given by $F(T/T_{\max})$, where $T_{\max}$ is the (doping-dependent) temperature at which the uniform susceptibility shows its maximum. In a most simple approach one can identify our two susceptibilities introduced in (7) with those of Johnston. He gives $T_{\max}(x = 0.15) \approx 410$ K, and from his universal function we find $\chi_1(300\text{ K})/\chi_1(50\text{ K}) \approx 2.42$. From our shift data we find $G_\perp(300\text{ K}) = 0.321\%$, $G_\perp(50\text{ K}) = 0.295\%$, $G_\parallel(300) = 0.105\%$, $G_\parallel(50\text{ K}) = 0.0264\%$, and we find $c_{12}/c_{22} = -9.34$. Near 300 K we estimate from Johnston's data that

$$\begin{aligned} \chi_1(T = 300\text{ K}, x = 0.15) &\equiv 6.8 \times 10^{-5}\text{ emu mol}^{-1}, \\ \chi_2(T > T_c, x = 0.15) &\equiv 10 \times 10^{-5}\text{ emu mol}^{-1}. \end{aligned} \tag{10}$$

With these two values for the susceptibilities we are able to calculate the hyperfine coefficients:

$$\begin{aligned} c_{11} \approx 8.0, \qquad c_{12} \approx 27.7, \qquad c_{21} \approx 19.7, \\ c_{22} \approx -2.9\text{ (all in mol emu}^{-1}\text{)}. \end{aligned} \tag{11}$$

In turn, these constants can now be used to deduce the full temperature dependence of the two susceptibilities in the whole temperature range studied by NMR, in particular also the region below T_c, by solving (7) for $\chi_1(T)$, $\chi_2(T)$ from the measured shifts. The corresponding plots are shown in figure 2.

By identifying our $\chi_1(T)$ with that of Johnston's very reliable scaling function at two temperatures, our data are found to be in very good agreement with its total temperature dependence above T_c and we find in addition that χ_1 continues to decrease below T_c. Since our data demand a second susceptibility that is T-independent above T_c we identify it with Johnston's χ_2. We find this component drops precipitously below T_c. Clearly, χ_1 carries the pseudogap feature first observed with NMR [12] while χ_2 behaves much like the Pauli susceptibility of a liquid going superconducting at T_c. While its T-dependence fits that of an s-wave Yosida function [21], we must say that given the uncertainties due to the NMR linewidths the small differences between different models [18] in this temperature range cannot prove a particular model.

To conclude, we have shown that the single-component behaviour of the cuprates is no longer upheld by NMR. Two susceptibilities suffice to explain the experimental findings that are in agreement with Johnston's [19] early analysis. By using his data we can convert the NMR shifts into temperature dependences of the two susceptibilities, also below T_c. We find that one component with a much larger spin-gap is responsible for the NMR pseudogap features while the second component resembles that of a Fermi liquid that undergoes a superconducting transition at T_c.

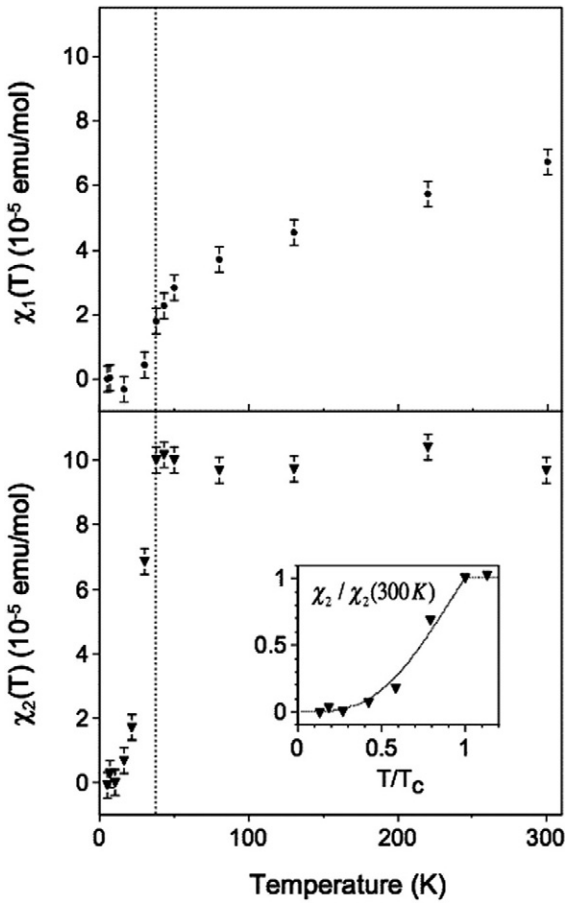

Figure 2. Temperature dependences of the two susceptibilities $\chi_1(T)$ and $\chi_2(T)$. The inset shows $\chi_2/\chi_2(300\text{ K})$ in comparison with Yosida's function [21].

Acknowledgments

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