Properties of the electronic fluid of superconducting cuprates from \(^{63}\text{Cu}\) NMR shift and relaxation

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We use available \(^{63}\text{Cu}\) nuclear magnetic resonance (NMR) data of the high-temperature superconducting cuprates and show that one must resort to a coupled electronic spin scenario that leads to a suppression of the shifts, except for a few heavily overdoped systems where the coupling is weak. We uncover universal, Fermi liquid-like nuclear relaxation that is independent of material and doping in the normal state, and that is even in quantitative agreement with what one calculates from Korringa’s law for the maximum shifts. Contrary to the common interpretation of NMR that invokes enhanced electronic spin fluctuations we argue that suppressed shifts explain the lacking Korringa behavior. Shift and relaxation in the condensed state support this view, as well. A simple model of two coupled electronic spin components, one with \(3d(x^2 − y^2)\) orbital symmetry and the other with an isotropic \(s\)-like interaction can explain the data. The negative coupling between the two spins must be related to the pseudogap behavior of the cuprates. Its interplay with the spin components determines the dependence of the shifts as function of material and temperature. We can also explain the negative shift conundrum and the long-standing orbital shift discrepancy for NMR in the cuprates. We hint at consequences for other experiments and theory.

1. Introduction

Nuclear spins are powerful quantum sensors of their local electronic environment, so that the versatile methods of nuclear magnetic resonance (NMR) can be decisive for theories of condensed matter systems. However, deciphering the nuclear response is usually not a straightforward task if microscopic theory is missing, as is the case for high-temperature superconducting cuprates. Nevertheless, NMR contributed vital information for the understanding of these materials, e.g., concerning singlet pairing and the pseudogap [1].

Through magnetic shift and relaxation NMR can sense the field-induced electronic moments and local fluctuating fields, respectively, both related to the electronic susceptibilities. In addition, the electric quadrupole interaction, e.g., of Cu and O nuclei in the ubiquitous \(\text{CuO}_2\) plane, allows for the determination of the local charges [2–4].

For useful conclusions, however, the hyperfine interactions have to be known. For the electric interaction a convincing understanding could be achieved over the years [3–5], which led to, e.g., the correlation between the sharing of charge between planar Cu and O, and the maximum \(T_c\) [6], as well as the measurement of charge ordering [7]. However, the hitherto adopted magnetic hyperfine scenario was found to be flawed [8–12], and there is urgent need for the understanding of the implications of these findings.

In early experiments, predominantly on the \(\text{YBaCuO}\) family of materials, consequences of the apparent \(3d(x^2 − y^2)\) hole of Cu\(^{2+}\) were investigated, and indeed, the quadrupole splitting of Cu was found to be in qualitative agreement with such a hole [2]. However, and surprisingly, a related negative spin shift from that hole could not be observed [2, 13]. Rather, the total shift was found to be positive [13]. At lower doping, the shift was found to be temperature \((T)\) dependent even

\[ \text{Korringa relaxation} \]

\[ \frac{w}{T} = 20\text{Ks} \]

\[ T \sim 300\text{K} \]

\[ a + c = \text{const.} \]

\[ \frac{w(T)}{w(0)} = \text{const.} \]

\[ a + c < 0 \]

\[ b + c \ll 0 \]

\[ T \ll T_c \]

\[ w(0) = 0 \]

\[ T \sim \text{Ks} \]

\[ a + c = 0 \]

\[ b + c \ll 0 \]

\[ T \sim \text{Ks} \]

\[ w(0) = 0 \]

\[ T \ll T_c \]

\[ a + c = 0 \]

\[ b + c \ll 0 \]

\[ T \sim \text{Ks} \]

\[ w(0) = 0 \]

\[ T \ll T_c \]

\[ a + c = 0 \]

\[ b + c \ll 0 \]

\[ T \sim \text{Ks} \]

\[ w(0) = 0 \]

\[ T \ll T_c \]

Figure 1. Shift and relaxation scenario in the cuprates: two coupled \((c(ζ))\) electronic spins \((a(ζ)\) and \(b(ζ))\) precess about the external magnetic field and determine the nuclear spin shift \((K(ζ))\). The parameter \(ζ\) is a material and doping dependent parameter (perhaps the true hole content). Near room temperature, \(c(ζ)\) is found to be temperature independent, causing isotropic changes in the NMR shifts. The largest shifts \((\sim 0.8\%)\) are observed for the largest \(ζ\), in agreement with Korringa-like relaxation \((\sim 20/\text{Ks})\). While the relaxation is hardly affected by the coupling (only the relaxation anisotropy \(W_x/W_y\) changes), the shifts become increasingly suppressed for smaller \(ζ\), thus appear to violate the Korringa law. The coupled spins possess \(a-\) and \(d(x^2−y^2)\)-like orbital symmetry, and with the corresponding hyperfine coefficients the negative coupling explains the unexpected spin shifts observed in the cuprates. Deep in the condensed state \(b + c = 0\) and relaxation disappears, but \(a + c\) can be finite. The changes in \(ζ\) must be related to the pseudogap.
Figure 2. Examples of $^{63}$Cu NMR shifts from Ref. [12]. $K_{\perp}(T)$ is plotted against $\hat{K}_0(T)$ (the hat denotes the total magnetic shifts, including orbital shifts). The plot origin coincides with the first-principle calculations of the orbital shifts of $K_{\perp,\text{L}} = 0.72\%$, $K_{\perp,\text{L}} = 0.3\%$ [17]. Nearly isotropic shift lines are indicated by dashed lines, the arrows indicate $T_c$ (OD: overdoped; OP: optimally doped; UN: underdoped materials, cf. Appendix). Inset: Materials with the highest $T_c$ depart from the isotropic shift line at the NMR pseudogap temperature far above $T_c$, unlike strongly overdoped systems in the main panel, for which $T_c$ determines the departure point.

above the superconducting transition temperature ($T_c$), which marked the discovery of a spin gap above $T_c$ [14]. Puzzling was also the finding that the shift for planar Cu was nearly temperature independent when the magnetic field is parallel to the crystal c-axis ($c \parallel B_0$). This was interpreted as an accidental cancellation of the spin shift due to the hyperfine coefficients, i.e., $A_0 + 4B' = 0$, where $A_0$ ($A_\perp$) is the anisotropic hyperfine coefficient for the 3d($x^2 - y^2$) electronic spins with orientation $c \parallel B_0$ ($c \perp B_0$). The term $B'$ is the isotropic transferred coefficient from the neighboring four Cu atoms in a single band scenario, which appeared to be supported by proportional shifts for Cu and O in early experiments [15, 16] ($B'$ is to distinguish it from another definition below).

In recent years, it was shown with a set of experiments on different materials that the adopted single spin component view does not hold, rather, two coupled spin components appear to be at play [9–11, 18]. Finally, by analyzing all available Cu NMR shifts (for which diamagnetic effects in the mixed state can be discarded) a quite different shift phenomenology of the cuprates was established, very recently, demanding a different hyperfine scenario [12].

This must have severe consequences for the understanding of nuclear relaxation that relies on the hyperfine scenario, as well. In fact, early analyses found the shifts to be too small to yield Korringa-like relaxation, demanding strong (non Fermi liquid-like) spin fluctuations (by using the shift-derived hyperfine scenario, $A + 4B' = 0$, antiferromagnetic fluctuations can invert the sign in this equation, which leads to enhanced relaxation).

Here, we show that this view cannot be sustained anymore. Rather, a negative coupling between two electronic spin components (a view that some of us established some time ago [8]) suppresses the shift, while hardly affecting a universal Fermi liquid-like relaxation that we show exists and is in agreement with the Korringa law for the largest shifts. This scenario is a paradigm shift in viewing cuprate electronic properties based on NMR.

2. Observations from shifts and relaxation
For the discussion of the results we will state important findings from earlier shift [12], and a new relaxation analyses for which details will be presented elsewhere [19].

2.A. Magnetic shifts
Reliable facts for understanding the shifts have been gathered previously [12]. Here we repeat what we believe are the most important phenomenological features. These can be conveniently followed in the shift-shift plot in Fig. 2.

2.A.1. There is a common low temperature shift for all cuprates for $c \perp B_0$, i.e., $K_{\perp}(T \rightarrow 0) \approx 0.35\%$. It agrees reasonably well with first-principle calculations that give $0.30\%$ [17].

2.A.2. At high temperatures (up to room temperature) changing the doping leads to nearly isotropic changes of the shifts. This generates lines with slopes of approximately 1 in Fig. 2, these will be called isotropic shift lines. Different materials appear to follow different such lines with only slightly different slopes.

2.A.3. New shift reference points are generated where $\hat{K}_{\perp}(T \rightarrow 0)$ intersects isotropic shift lines. While these are significantly smaller than $\hat{K}_0(T \rightarrow 0)$, they are still in strong disagreement with the calculated orbital shift of $0.72\%$ [17], cf. the figure origin in Fig. 2.

2.A.4. Basically all shift data fulfill the relation $\delta_T K_{\perp}(T) \leq \delta_T K_{\parallel}(T)$. This means that in the $\hat{K}_{\perp}$ vs. $\hat{K}_{\parallel}$ shift-shift plot, cf. Fig. 2, basically all shift data lie in the lower right triangle.

2.A.5. Whenever the shifts change as a function of temperature, their anisotropy changes, i.e., they depart from the isotropic shift line, maintaining for a given range of $T$ characteristic slopes. Characteristic slopes as a function of $T$ are: (1) $\delta_T K_{\perp}/\delta_T K_{\parallel} \approx 1$ (same slope as the isotropic shift lines, but here as function of $T$); (2) a rather steep slope $\delta_T K_{\perp}/\delta_T K_{\parallel} \geq 10$, and (3) $\delta_T K_{\perp}/\delta_T K_{\parallel} \approx 5/2$. 
2.B. Nuclear relaxation

Reliable facts from nuclear relaxation data the following, cf. Fig. 3.

2.B.1. The nuclear relaxation rates ($W_{\parallel,\perp}$) with the field parallel ($c \parallel B_0$) and perpendicular ($c \perp B_0$) to the crystal c-axis vanishes rapidly below $T_c$, even as $W_0/T$. Measured with the magnetic field perpendicular to the crystal c-axis ($W_{\perp}$) the relaxation just above $T_c$ is very similar for all (conducting) cuprates, i.e., it is material independent and it does not change very much across the phase diagram. Just above $T_c$ we have $W_{\perp}(T \gtrsim T_c)/T \approx 17$ to $25$ Ks.

2.B.2. The nuclear relaxation rate for $c \parallel B_0$ ($W_{\parallel}$), in the same range of temperatures, does change for different materials, but by less than a factor of about four compared to $W_{\perp}$. Importantly, for all materials and temperatures both rates are proportional to each other over the entire range of temperatures, $W_{\perp}(T) \propto W_{\parallel}(T)$, in particular for $T > T_c$, and the proportionality constants seems to be restricted to certain numbers that can be independent of doping, and have the tendency to increase on the underdoped side, cf. inset in Fig. 3.

3. Discussion

The fact that the nuclear spins are coupled to an electronic thermal bath with relaxation rates that are nearly independent on material and doping (even for one orientation of the field, $c \perp B_0$) points to a very robust property of the cuprates. This relaxation rate is already present at the highest doping levels for systems that must be rather close to a Fermi liquid. It appears to be out of question, then, that this liquid is present in all materials. This conclusion is not weakened by a doping or material dependent relaxation for the other direction of the field ($c \parallel B_0$) since both rates are proportional to each other. It rather points to an anisotropic coupling of the nuclear spins to a unique fluid. Note that for both directions of the field, the relaxation rates drop rapidly to zero below $T_c$ from basically the same high-$T$ value that is only weakly affected by electronic correlations.

Different from relaxation, both shifts vary significantly across the phase diagram and between different materials. We introduce a material and doping dependent parameter $\zeta$ that can describe the material and doping dependent shifts (it is probably related to the true hole distribution in the plane), in addition to temperature. The $\zeta$ and $T$ dependences of the shifts, cf. Fig. 2, must be explained by at least two spin components that are in general not proportional to each other [12]. If two spin components are present, a coupling term between them can bring complexity to the shifts while affecting relaxation in a very different way, and we believe that this coupling changes with $\zeta$, and at lower doping also with $T$.

3.A. Simple two-component description

In the most simple two-component model, the nuclear spin couples to two electronic spin components with the susceptibilities $\chi_A$ and $\chi_B$, and two different hyperfine coefficients (note that we need two different hyperfine coefficients to maintain a two-component description). These spin components will then have in general different $T$ dependences. We write,

$$K_{\parallel,\perp}(\zeta, T) = B_{\parallel,\perp} \cdot \chi_B(\zeta, T) + A_{\parallel,\perp} \cdot \chi_A(\zeta, T).$$  \hspace{1cm} (1)

With other words, the magnetic field ($B_0$) induces the two spin components ($S_A$ and $S_B$) ($\gamma_e h \langle S_j \rangle = \chi_j B_0$), which are not proportional to each other as a function of temperature. The Cu nucleus feels changes in the local field through the corresponding hyperfine coefficients $B_{\parallel,\perp}$ and $A_{\parallel,\perp}$.

Now, we denote with $B$ the apparently isotropic hyperfine coefficient that we know must be present (2.A.2) [12] (we do not invoke the factor of 4, as opposed to the old literature). Then, there must also be an anisotropic local field contribution. In a minimalistic model, we seek this component in terms of the partially unfilled $3d(x^2 - y^2)$
orbital. As in the early literature we denote this coefficient with $A_{\parallel}$. It is also known from reliable estimates, as well as experiment [2] that

$$A_{\parallel} \gtrsim 6 A_{\perp} \text{ and } A_{\parallel} = -|A_{\parallel}|,$$

(2)
i.e., the anisotropic hyperfine coefficient is negative and must lead to a negative shift for a positive spin moment. We will neglect the much smaller $A_{\perp}$, and have with (1),

$$K_{\perp} = B\langle S_{\parallel}\rangle, \quad K_{\parallel} = B\langle S_{\parallel}\rangle + A\langle S_{\perp}\rangle.$$

(3)
where we chose $A \equiv A_{\parallel}$. However, if two spin components are present we must allow for a coupling between them [8]. Thus, each spin component is the sum of two terms,

$$\langle S_{\parallel}\rangle \equiv b + c, \quad \langle S_{\perp}\rangle \equiv a + c,$$

(4)
where we simplified the notation by inducing the spin components $a, b$ and the coupling term $c_{\parallel}$. That is, we have to analyze the shifts in Fig. 2 with the following two equations,

$$K_{\perp}(\zeta, T) = B[b(\zeta, T) + c(\zeta, T)]$$

$$K_{\parallel}(\zeta, T) = A[a(\zeta, T) + c(\zeta, T)] + B[b(\zeta, T) + c(\zeta, T)],$$

(5)
where $T$ is the temperature, and $\zeta$ is a material related property (the chemical doping $x$ will be related to $\zeta$, but we expect that $x$ is not too useful to describe the material differences [6]).

3.B. Application of the model
We now investigate what we can conclude in this simple picture.

3.B.1. Low temperature shift $c_{\parallel}B_{0}$. We infer from (2.A.1) and with (5) that the spin shift goes to zero at low temperatures for this orientation, $K_{\perp}(T \to 0) \approx 0$. Since this low temperature line seems to fit all systems, agrees with first principle calculations [17], and follows the relaxation below $T_{C}$ (see later), we make a fundamental assumption that the sum $(b + c)$ vanishes at the lowest $T$, i.e.,

$$b(\zeta, T \to 0) + c(\zeta, T \to 0) \approx 0.$$  

(6)
One could also require that the sum accounts for the small difference to the first-principle calculations, but this is not of importance, now.

3.B.2. Isotropic shift lines. The isotropic shift lines in Fig. 2 demand to a good approximation that at high $T$ over a large part in Fig. 2, changes in the shifts induced by $\zeta$ are proportional to each other, i.e.,

$$\delta \zeta K_{\perp} \approx \delta \zeta K_{\parallel},$$

(7)
and it follows,

$$\delta \zeta (a + c) \approx 0.$$  

(8)
That means, the material related shift variations at high $T$ are given by $b_{\parallel}K_{\parallel} = B\delta \zeta (b + c)$, i.e., for both orientations of the field, and the changes in $a$ and $c$ are proportional to each other.

3.B.3. Orbital shifts. With our fundamental assumption (3.B.1) we demand that $K_{\perp}(T = 0) \approx 0.35\%$ is zero spin shift and thus equal to the orbital shift, $K_{\perp,\parallel}$, for $c_{\parallel}B_{0}$. Since an orbital shift anisotropy of 2.4 is a very reliable number [17], we conclude that $K_{\perp,\parallel} \approx 0.84\%$ is a rather reliable orbital shift value for $c_{\parallel}B_{0}$, as well.

In our two-component analysis at the (virtual) intersection for $\zeta \equiv \zeta_{A}$ of an (high $T$) isotropic shift line with $K_{\perp}(T = 0) \equiv K_{\perp,\parallel}$ we have,

$$K_{\parallel}(\zeta_{A}, T_{h}) = A[a(\zeta_{A}, T_{h}) + c(\zeta_{A}, T_{h})],$$

(9)
where $T_{h}$ was introduced to denote a sufficiently high $T$, i.e., $T \gg T_{c}$. This is the material independent offset of the isotropic shift lines in Fig. 2. Near the intersection $\zeta_{A}$ we have with (5) that $K_{\parallel}(\zeta_{A}, T) = B[b(\zeta_{A}, T) + c(\zeta_{A}, T)]$, where $K_{\perp}(T)$ is very small even at high $T$. Thus, $c(\zeta_{A}) = -b(\zeta_{A})$ holds to a good approximation for all $T$. We thus have in addition to (9),

$$K_{\parallel}(\zeta_{A}, T_{h}) = A[a(\zeta_{A}, T_{h}) + c(\zeta_{A})]$$

$$K_{\parallel}(\zeta_{A}, T_{h}) = A[a(\zeta_{A}, T_{h}) - b(\zeta_{A})].$$

(10)
With $K_{\parallel,\perp} = 0.84\%$ we have,

$$K_{\parallel}(\zeta_{A}, T_{h}) = 0.21\%.$$  

(11)
Clearly, there could be differences between the materials in terms of $[a(\zeta) + c(\zeta)]$, but also the orbital shifts could vary slightly. In any case, it is predominantly the negative coupling term that we believe creates the positive offset in the spin shifts of the cuprates for $c_{\parallel}B_{0}$. With other words, there is an effective negative spin in the $3d(x^{2} - y^{2})$ orbital while component $a$ itself is positive (due to a dominating $b$ and negative coupling), and at high $T$ it does not change with $\zeta$.

We note that the maximum shift variation above the intersection defined by $\zeta_{A}$ is about 0.8%, and we conclude that

$$B \cdot (b(\zeta_{\text{max}}, T_{h}) - b(\zeta_{A}, T_{h})) \approx 0.8\%.$$  

(12)
Roughly, there is a factor of 4 between $K_{\parallel}(\zeta_{A}, T_{h})$ and the maximum $\zeta$-related shift change. Note that an isotropic shift of about 0.8% is in agreement with the observed universal relaxation rate just above $T_{C}$, i.e., it follows from Korringa’s law for a simple Fermi liquid. This is an important fact, as it says that the fluid is, also in terms of the maximum shifts, close to a simple Fermi liquid.
Based on the discussion we present in Fig. 4 a possible decomposition of the high-T shifts, and the ensuing shift-shift plot, inspired by a large b term from a robust Fermi liquid-like fluid, a negative coupling c that acts on positive spin components a and b.

3.B.4. Lower right triangle rule. The fact that basically all shift data lie below the isotropic shift lines in Fig. 2 tells us that as the shifts depart from the isotropic shift lines, \( \delta_T K_\perp \geq \delta_T K_\parallel \). Then, it follows with (5),

\[
\begin{align*}
\delta_T [A(a + c)] &\geq 0 \\
\delta_T (a + c) &\leq 0,
\end{align*}
\]

since A is negative. By lowering the temperature, \( A(a(T) + c(T)) \) becomes typically more positive so that \( K_\parallel \) stays to the right of the isotropic shift lines in Fig. 2. The nearly equal sign refers to points very near the isotropic shift line (high temperature values).

3.B.5. Special slopes. As noted above (2.A.5), as a function of T we observe certain slopes in Fig. 2.

First, we have \( \delta_T K_\perp / \delta_T K_\parallel \approx 1 \), an isotropic shift line, but now as a function of T, and we conclude \( \delta_T (a + c) \approx 0 \). This slope is observed, in particular, for overdoped systems where after an initial steep drop of \( K_\perp \) at \( T_c \), the system holds \( (a + c) = \text{const.} \) as \( T \) drops further, cf. Fig. 2. We do know that \( (b + c) \) varies in this range of \( T \) since \( K_\perp \) changes.

Second, we have \( \delta_T K_\perp / \delta_T K_\parallel \geq 10 \), the steep slope. It can be found for the strongly doped systems at \( T_c \) for a given range of \( T \), but also for other materials, e.g., YBa\(_2\)Cu\(_3\)O\(_y\) in the whole range of \( T \). This includes the variation in the NMR pseudogap region, but not for all materials as, e.g., HgBa\(_2\)Cu\(_2\)O\(_{4+\delta}\) takes on the slope of \( \approx 5/2 \) as it departs from the isotropic shift line at \( T_c \), or in the pseudogap region. With \( \delta_T K_\parallel \approx 0 \) we conclude that

\[
B \delta_T (b + c) \approx -A \delta_T (a + c).
\]

If only c became \( T \) dependent, \( A = -B \) would follow, the known argument in the old literature (our definition of \( B \) is that of \( 4B' \) in those papers).

Third, we have \( \delta_T K_\perp / \delta_T K_\parallel \approx 5/2 \). This leads to the equation,

\[
B \delta_T (b + c) \approx -\frac{5}{3} A \delta_T (a + c).
\]  

For example, if we assume that only c changes as a function of \( T \) for those slopes, we conclude that \( B \approx -5/3A \). This is perhaps a reasonable conclusion, and the \( T \) dependent NMR pseudogap feature is caused by \( c(\zeta) \) becoming \( T \) dependent. Then, in order to generate, e.g., the steep slope, we find \( 3\delta_T b = 2\delta_T a - \delta_T c \).

3.B.6. Highest \( \zeta \) liquid. The observed \( T \) independent shifts and the (universial) relaxation, both point to a simple Fermi liquid (Korringa relation works). The coupling is isotropic, as well. There is no condensate at lower \( T \).

3.B.7. Liquid at large \( \zeta \). Here, the shifts decrease isotropically with decreasing \( \zeta \), but remain \( T \) independent above \( T_c \). The relaxation remains similar, except the anisotropy takes on a certain value, \( W_\perp / W_\parallel \approx 1.5 \) \[19\]. By decreasing the temperature, \( T_c \) is encountered and the shifts can suddenly drop. First, \( K_\perp \) begins to change, the initial steep drop in Fig. 2. It is followed by a nearly proportional decrease of both shifts along isotropic shift lines as a function of \( T \). The implications of the involved slopes have been noted above.

This behavior is observed for a number of systems, cf. Fig. 2. The initial drop can be rather large, followed by a short isotropic shift line to reach \( K_\parallel (0) \approx 0.35\% \). Systems with a small initial drop have a longer isotropic shift line since it ends at \( K_{\perp,\parallel} \). Consequently, in the latter case a smaller shift \((K_\parallel(T = 0))\) remains at the lowest \( T \).

Figure 4. Left, possible decomposition of shifts as function of the material related parameter \( \zeta \) and the spin components \( a, b \) and the coupling \( c \), cf. (5). Right, resulting (high temperature) shift-shift plot according to (5) for \( B= 1 \) and \( A = -3/5B \).

Figure 5. Comparison of \( K_\perp \) and \( W_\perp / T \) below \( T_c \) for an underdoped and overdoped material. The relaxation rates for \( c \parallel B_0 \) (circles) and \( c \perp B_0 \) (diamonds) are plotted as a function of temperature for the YBa\(_2\)Cu\(_3\)O\(_y\) (\( T_c \approx 81 \) K) and TlSr\(_2\)CaCu\(_2\)O\(_{7-\delta} \) (\( T_c \approx 52 \) K); note that \( W_\parallel \) is multiplied by the proportionality constants above \( T_c \), as discussed earlier (2.B.2) (1.5 for TlSr\(_2\)CaCu\(_2\)O\(_{7-\delta} \) and 3.3 YBa\(_2\)Cu\(_4\)O\(_8\)). The original shifts shown in the inset are scaled in the main panel by a ratio of 15/4 to fit the relaxation curves.
3.B.8. Medium $\zeta$ - pseudogap region. As the magnitude of the coupling increases ($\zeta$ decreases), $T_c$ increases, as well. In this region of Fig. 2 many systems depart from the isotropic shift lines with a slope of about 5/2, like HgBa$_2$CuO$_{4+\delta}$, as discussed above (15). Systems with the highest $T_c$ appear to have the 5/2-slope when they initially depart form the isotropic shift line, cf. inset in Fig. 2.

3.B.9. Low temperature shifts. The behavior of the shifts at low temperatures is perhaps more complicated. One must also be aware of the fact that the measurements were not pursued with the appropriate rigor since such behavior was not suspected. In addition, the penetration depth of the r.f. decreases rapidly and signal-to-noise can become a limiting factor, certainly for single crystals. Perhaps, then, $K_\perp = 0.35\%$ is somewhat higher than the calculated $0.30\%$. We cannot be sure whether the values of $K_\parallel (T = 0)$ are indeed those plotted in Fig. 2, which clearly need negative spin $a + c$, i.e., $K_\parallel = +|A|(b - a)$ if $c = -b$. For example, the single layer HgBa$_2$CuO$_{4+\delta}$ [6] has a $T = 0$ shift of $K_\parallel = +0.6\%$, and we conclude that $A(a + c)$ increased 3-fold compared to the $\zeta_A$ value of 0.21\%.

3.C. Shift and Relaxation

As already mentioned, the shift data for the largest $\zeta$, non-superconducting samples show a perfect Fermi liquid-like behavior and give a $1/T_1T$ of about 20/$K_s$ if one uses the Korringa relation. For these systems $W_\perp/W_\parallel \approx 1$, as expected for relaxation dominated by fluctuations through $B$. As $\zeta$ decreases, one encounters superconducting systems with increasing $T_c$, but isotropically decreasing shifts that are still $T$ independent above $T_c$ (dense points on the isotropic shift lines in Fig. 2).

The relaxation rate just above $T_c$ remains very similar to that for the highest $\zeta$ materials. Below $T_c$, both relaxation rates disappear rapidly (even as $W_\alpha(T)$) nearly proportional to each other as function of $T$ ($W_\perp(T)/W_\parallel(T) = \text{const.}$). This is expected for singlet pairing (here as vanishing of $b + c$). However, the shifts show a different behavior, as they follow certain slopes for given ranges of $T$ in Fig. 2. Nevertheless, $K_\perp(T < T_c)$ does follow the $T$ dependence of the relaxation. This is demonstrated in Fig. 5 for an overdoped and underdoped system. It is obvious from Fig. 5 that $K_\perp$ is nearly proportional to $W_\perp/T$, however, while $W_\perp/T$ drops from about 17/$K_s$ and 25/$K_s$ to zero for both systems, respectively, the shifts have to be rescaled. For TiSr$_2$CaCu$_2$O$_{7-\delta}$ the shift drops from about 0.6% to zero, cf. inset in Fig. 5, and for YBa$_2$Cu$_4$O$_8$ from about 0.1%. From the Korringa relation one would expect $W_\perp/T$ of 9.6/$K_s$ and 0.26 $K_s$, respectively, very different values. The used scaling ratio between the two shifts in the main panel is 15/4, almost a factor of 4. We believe this confirms the increasing suppression of the $g = 0$ linear response as $\zeta$ decreases, given by $c(\zeta)$, the coupling term between both spin components.

In a classical scenario, one expects that the relaxation governing local field fluctuations are perpendicular to the orientation of the magnetic field. Thus, in-plane fluctuations set $W_\parallel$, while $W_\perp$ (measured with the field in the plane) is determined by both kinds of fluctuations, parallel and perpendicular to the plane. Of course, the mean values of the shifts (proportional to $\chi_0$) do not determine their r.m.s. averages (set by $\chi''$ at the nuclear frequency), but it might be a good first guess to seek a relation. For example, $K_\parallel$ is on average much larger than $K_\perp$, but there are exceptions to that rule, e.g., in terms of $W_\perp/W_\parallel$ [19]. In addition, we do not see a simple way to derive the special proportionality constants for $W_\perp/W_\parallel$, that hint at matrix element effects, so that we do not pursue this model any further.

There are very few systems that do not fit the general shift scenario, among them La$_{2-x}$Sr$_x$CuO$_4$ [12]. This is also true for the relaxation [19], where an additional mechanism increases the relaxation above $T_c$, but both rates stay proportional to each other. Therefore, we also do not pursue these few outlier systems here.

4. Conclusions

The drastic changes of the Cu NMR shifts, cf. Fig. 2, compared to the almost universal Cu NMR relaxation above and below $T_c$, cf. Fig. 1, are explained with a simple two-component model. One of the electronic spin components ($b(\zeta,T)$) has an isotropic hyperfine constant ($B$), while an anisotropic hyperfine constant ($A \equiv -|A| b$, $A \ll A_\perp$, as known for the 3$d(x^2 - y^2)$ orbital) sets the interaction of second component ($a(\zeta,T)$) with the nuclei. It is the negative coupling term ($c(\zeta,T)$) between both spin components that leads to the reduction of the shifts while allowing for a largely unchanged relaxation above $T_c$. This negative coupling can also resolve the long standing discrepancy between calculated and presumed experimental orbital shifts.

For large $\zeta$ we find a Fermi liquid-like fluid with isotropic coupling to the nuclei, as given by the Korringa relation with shift $K(\zeta)$. As $\zeta$ decreases, $a(\zeta)$ increases, but the magnitude of the negative coupling $c(\zeta)$ suppresses the shifts while $T_c$ increases. Thus, $c(\zeta)$ must be related to the pseudogap. In a possible scenario $c(\zeta)$ becomes $T$ dependent above $T_c$ and causes the NMR pseudogap phenomenon, i.e., it suppresses the shifts as a function of $T$ already above $T_c$. In this case we can conclude for the hyperfine coefficients that $A \approx -3B$.

We think it is established with NMR, now, that there is a nearly universal fluid that is Fermi liquid-like in the cuprates. This was found with NMR in 2009 [8], but also with an increasing number of other probes, e.g., [20–22]. Then, the most simplistic scenario suggested by our data is that the electronic spin of this liquid is coupled to the
spin component in the $3d(x^2 - y^2)$ orbital. Of course, the latter spin could be part of the nearly universal liquid, as well. The term $b + c$ could be associated with quasiparticles in the nodal region of the Fermi surface [23–26], while the term $a + c$ represents the antinodal region with perhaps antiferromagnetic properties [27, 28]. For lower values of $\zeta$, antinodal regions could be large [29] and below $T_c$ antiferromagnetic correlations could exist with pairing. This could explain the reduction of shift being more gradual, in comparison to overdoped samples with a smaller $k$-space region. Then, $c$ is perhaps responsible for driving the $k$-space anisotropy, seen by ARPES and other techniques. Neutron scattering will mostly be determined by the $a$ component and its coupling to $b$, while the response from $b$ is likely to be distributed in reciprocal space and might escape detection.

Perhaps, a Fermi liquid could reside in a separate band and inter-band coupling is responsible for the high $T_c$ [30]. The residual shift (that may be moments [12]) could be related to time reversal symmetry breaking, but whether loop currents [31] could be involved in the suppression of the shifts has to be seen. A two-component model involving hidden fermions [32, 33] should relate to our findings.

Finally, we would like to mention from an NMR point of view that the evolution of the intra unit cell charge ordering that is now well documented also by NMR [7] could be connected to the coupling scenario.

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**Author contributions**

D.P. helped in relating the NMR findings to those obtained with other methods, discussing the contents and improving the manuscript. M.A. gathered the data, was instrumental in setting up the figures, discussing contents and improving the manuscript. J.H. supplied the main concepts, wrote the manuscript and had the overall project leadership.

**Appendix**

A collection of abbreviations used for the various compounds are given in Table I.

| Symbol       | System                  | Ref. |
|--------------|-------------------------|------|
| Y1248-UN-92K | YBa$_2$Cu$_4$O$_8$     | [16] |
| Y1212-OP-90K | YBa$_2$Cu$_{9.92}$O$_{19}$ | [34] |
| Tl1212-OV-10K,52K,-70K | Tl$_2$Sr$_2$CaCu$_2$O$_{7-\delta}$ | [35] |
| Ti201-0V,-19K,-72K | Tl$_2$Ba$_2$CuO$_{6+\delta}$ | [36, 37] |
| Ti2012-OP-112K | Tl$_2$Ba$_2$Cu$_2$O$_{6+\delta}$ | [38] |
| Hg1201-UN-45K,-74K | HgBa$_2$CuO$_{4+\delta}$ | [11] |
| Hg1201-OP-97K,-OV-85K | HgBa$_2$CuO$_{4+\delta}$ | [11] |
| Hg1223-OP-133K(IP) | HgBa$_2$Ca$_2$Cu$_2$O$_{6+\delta}$ | [39, 40] |
| Hg1212-OP-127K | HgBa$_2$Ca$_2$Cu$_2$O$_{6+\delta}$ | [41] |
| Ba$_2$Cu$_2$O$_2$(OP) | Ba$_2$CaCu$_2$O$_6$(F,O)$_2$ | [42] |
| Ba$_2$Cu$_2$O$_2$(OP) | Ba$_2$CaCu$_2$O$_6$(F,O)$_2$ | [42] |

1 For the corresponding shift corrections cf. [12]
2 OP or IP in parentheses refer to the outer and inner plane of the triple layer systems, respectively.
3 In Fig. 2 the orange curve corresponds to (IP) and the yellow curve to (OP), different from Ref. [42].

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