NMR of Correlated Electron Superconductors

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  • NMR, classical superconductors, spin shift and relaxation

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Nuclear Spin Levels

NMR:
Induce transitions among the nuclear levels and measure the splitting and life-time.

\[ \omega_n = \gamma_n B_z \]

The chemical and electronic properties of the material influence the NMR parameters.

NMR is a bulk probe with atomic scale resolution.
Classical Superconductors

$^{27}\text{Al}$ spin shift and relaxation in Al-metal above and below $T_c$

![](image1.png)

$K_S(T)/K_S(0)$ vs $T/T_c$

The disappearance of the spin shift and $1/T_1T$ below $T_c$ are predicted by BCS theory for $S=0$ Cooper pairs (above $T_c$ Pauli susceptibility and Heitler-Teller relaxation).

NMR is a useful tool for studying superconductivity.
Cuprate Superconductors

Special circumstances:

- They are type II superconductors (partial diamagnetism below $T_c$ influences shift).
- We can investigate various nuclei (Cu, O, La, Y, Hg, ...).
- Most nuclei possess an electric quadrupole moment, so we have a competing interaction and various resonance lines.
- Inhomogeneities can cause substantial line broadening and overlapping lines.

Measurements can be very difficult.
NMR Spin Shift and Electronic Spin Susceptibility

\[ H = \mathbf{I} \cdot A_n \cdot \mathbf{S} \quad \text{spin hyperfine term} \]

\[ H_n = A_n I_z \langle S_z \rangle \]

\[ H_n = \gamma_n \hbar I_z B_z \frac{A_n}{\gamma_n \gamma_e \hbar^2} \chi_S \]

\[ H_{\text{total}} = \gamma_n \hbar I_z \left(1 + \frac{A_n}{\gamma_n \gamma_e \hbar^2} \chi_S \right) B_z \]

\[ \frac{\Delta \omega_n}{\omega_{n,0}} = K_{S,n} = \frac{A_n}{\gamma_n \gamma_e \hbar^2} \chi_S \]

NMR measures locally the electronic spin susceptibility.
If we compare the spin shift $K_S$ at different nuclear sites (1 and 2) they must be proportional to each other:

$$K_{S,1} = \frac{A_1}{\gamma_1 \gamma_e \hbar^2} \chi_S$$

$$K_{S,2} = \frac{A_2}{\gamma_2 \gamma_e \hbar^2} \chi_S$$

This proportionality is a critical test for single component behavior.
Early NMR: Discovery of Spin-Gap

Alloul, Ohno, and Mendels, PRL 63, 1700 (1989)

The spin shift is temperature-dependent above $T_c$. 

The spin shift is temperature-dependent above $T_c$. 

$\Delta K$ (ppm) vs. $T$ (°K) for different doping levels $x$. The plot shows the NMR shift for various doping concentrations, with $x = 1.0$ being the highest. The shift is seen to increase with decreasing temperature and is more pronounced at lower doping levels.
Early $^{17}\text{O}$ and $^{63}\text{Cu}$ Shift Results on YBa$_2$Cu$_3$O$_{6.63}$

Cu and O electronic spins seem to form a single component.

The single-fluid picture has dominated our view of the cuprates.

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Conflicting Evidence from NMR

- Pines et al. had to assume a revised hyperfine scenario to fit NMR data.
- Walstedt 1994 could not explain NMR relaxation in a single-component picture.
- We could not fit NMR linewidths data for LaSrCuO with the hitherto used hyperfine scenario (Haase et al. 2002).
- We found a break in the planar Cu vs. planar O spin shifts for LaSrCuO but did not know the Meissner contribution.

Related:
- Johnston (1989) and Nakano et al. (1994) found two uniform susceptibilities.

We set out to acquire a new set of data on La$_{1.85}$Sr$_{0.15}$CuO$_4$. 
The shifts at three nuclei in La$_{1.85}$Sr$_{0.15}$CuO$_4$

\[ K = K_{\text{Core Diamagn}} + K_L + K_Q + K_{\text{Meissner}}(T) + K_{S}(T) \]

T-independent

\[ K_{\text{Meissner}}(T) = \frac{\Delta B}{B} = \frac{\gamma_n \Delta B}{\gamma_n B} \] independent on $\gamma_n$

1. Measure all possible shifts (field parallel and perpendicular to crystal c-axis) at all temperatures.

2. This set of shifts allows us to remove the uncertainty from the Meissner effect and perform a complete

3. Test for single-component behavior.
1. \( \text{La}_{1.75}\text{Sr}_{0.15}\text{CuO}_4 \) Shifts vs. Temperature

- **Apical Oxygen** \( c \perp B \)
- **Apical Oxygen** \( c \parallel B \)
- **Planar Oxygen** \( c \parallel B \)
- **Copper** \( c \perp B \)

Here are the shifts.
2. Remove any Meissner Shielding

We allow for an anisotropic Meissner shielding by taking the appropriate differences:

\[ F_{\perp} = 63 K_s(T) - 17A K_s(T) \]
with \( c \perp B_0 \)

\[ F_{\parallel} = 17P K_s(T) - 17A K_s(T) \]
with \( c \parallel B_0 \)

Both quantities are obviously not proportional to each other:
3. The Test for Single-Component Behavior

This is not single-component behavior. We have to resort to a two-component scenario.

Based entirely on experimental data.

\[ F_\perp (\%) \not= \frac{\perp}{\parallel} F \parallel \]
Spin Shifts for Two Components

\[ K_k = a_k \cdot \chi_a (T) + b_k \cdot \chi_b (T) \]

Two electronic spins act on each nucleus.

- \( K_k \) spin shift for particular nucleus and orientation
- \( \chi_a, \chi_b \) two susceptibilities
- \( a_k, b_k \) hyperfine coefficients for particular nucleus and orientation

Note that we expect:

\[ \chi_a = \chi_{AA} + \chi_{AB} \]
\[ \chi_b = \chi_{BB} + \chi_{AB} \]

With the uniform spin susceptibility

\[ \chi_0 = \chi_a + \chi_b = \chi_{AA} + 2\chi_{AB} + \chi_{BB} \]
Experimental Observation

Apical oxygen c\perp B

Apical oxygen c\parallel B

Planar oxygen c\parallel B

Copper c\perp B

Planar oxygen c\perp B

Copper c\parallel B

Apical oxygen c\parallel B

Apical oxygen c\perp B

Planar oxygen c\parallel B

Apical oxygen c\parallel B

Planar oxygen c\perp B
Every shifts is a linear function of any other shift \(( y = m x + n )\) at higher temperatures \( (T > T_c)\).
Conclusion from the shift-shift plots

Shift $k$: \[ K_k = a_k \cdot \chi_a(T) + b_k \cdot \chi_b(T) \]

Shift $l$: \[ K_l = a_l \cdot \chi_a(T) + b_l \cdot \chi_b(T) \]

substitute \( \chi_a(T) \)

\[ K_k(T) = \frac{a_k}{a_l} K_l(T) + \left\{ b_k - \frac{a_k}{a_l} b_l \right\} \chi_b(T) \]

\[ \chi_b(\overline{T}) = \chi_{AB} + \chi_{BB} \quad \text{not a function of } T \text{ for } T>T_c \]

Two susceptibilities \( \chi_{AB}, \chi_{BB} \) must be temperature independent above \( T_c \). The temperature dependence can only be in \( \chi_{AA} \).
Determining the Unknowns

\[ K_k(T) = \frac{a_k}{a_l} K_l(T) + \left\{ b_k - \frac{a_k}{a_l} b_l \right\} \chi_b \]

These two numbers can be read off the plots for \( T > T_c \).

We can solve for \( b_k \chi_b \) and thus calculate

\[ a_k \cdot \chi_a(T) = K_k(T) - b_k \cdot \chi_b. \]

We note that we can determine a universal function for \( T > T_c \):

\[ \frac{\chi_a(T)}{\chi_a(300K)} = \frac{K_k(T) - b_k \cdot \chi_b}{K_k(300K) - b_k \cdot \chi_b} \]
1. All shifts show the universal scaling down to $T_c$: $\frac{\chi_a(T)}{\chi_a(300K)}$.
2. Near $T_c$ this expression is strongly negative (is $\chi_{AB}$ negative?).
D.C. Johnston (1989) and later Nakano et al. (1994) showed that the uniform susceptibility (for LaSrCuO) could be decomposed into two contributions (for all doping levels):

$$\chi(T, x) = \chi_1(T, x) + \chi_2(x)$$

Since we can only have $\chi_{AA}$ as temperature-dependent susceptibility we must conclude that $\chi_{AA}(T) = \chi_1(T)$. 
Determination of $\chi_{AB}$

\[ \frac{\chi_a(T)}{\chi_a(300K)} = \frac{\chi_{AA}(T) + \chi_{AB}}{\chi_{AA}(300K) + \chi_{AB}} = \frac{\chi_1(T) + \chi_{AB}}{\chi_1(300K) + \chi_{AB}} \]

Temperature (K)

Use Johnston’s universal function

We can calculate $\chi_{AB}$.
Above $T_c$ we find the following numbers:

\[
\chi_{AA}(T) = \chi_1(T) \quad \chi_1(300K) = 6.8 \text{ emu / mol}
\]

\[
\chi_{BB} = 18.7 \text{ emu / mol}
\]

\[
\chi_{AB} = -4.2 \text{ emu / mol} \quad \text{(negative!)}
\]

With these values we can now determine the hyperfine coefficients.
Hyperfine Coefficients $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

|        | $\text{Cu} \ c \perp B$ | planar O c || $B$ | apical O c $\perp B$ | apical O c || $B$ |
|--------|--------------------------|------------------|----------------------|------------------|
| $\chi_a$ | 2.6          | 8.7             | 0.79                | 0.24             |
|        | 14.3         | 48.0            | 4.4                 | 1.3              |
| $\chi_b$ | 21.4         | 4.6             | 1.2                 | 0.38             |
|        | 120          | 26              | 6.9                 | 2.1              |

These are the coefficients that describe the coupling of each nucleus to the two electronic spin components (for two orientations).
Susceptibilities vs. Temperature

\[ \chi = \chi_{dd} + \chi_{pp} + \chi_{pd} \]

\[ \chi_{AA} = \chi_{dd} \] (copper d-contribution)
\[ \chi_{BB} = \chi_{pp} \] (oxygen p_\sigma -contribution)
\[ \chi_{AB} = \chi_{pd} \] (correlation d,p_\sigma)

These temperature-dependencies follow from
the NMR spin shift data!
Conclusions

- A single-component picture is not appropriate for the description of all cuprate superconductors.

- The spin shifts suggest a two-component scenario:
  - $\chi_{AA}(T)$ is temperature-dependent already above $T_c$ (pseudogap)
  - $\chi_{BB}(T>T_c)>0$ and temperature-independent
  - $\chi_{AB}(T>T_c)<0$ and temperature-independent
  - below $T_c$ all susceptibilities decrease to zero
  - each nucleus couples to two electronic spin components with the hyperfine couplings presented.
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