NMR and the BCS Theory of Superconductivity
Our NMR activities in the early 1950s
(Norberg, Holcomb, Carver, Schumacher)

Overhauser dynamic nuclear spin polarization
Conduction electron spin susceptibility (Pauli)

Measuring the nuclear spin-lattice relaxation time, $T_1$, of the alkali metals: The time for the nuclear magnetization of an unmagnetized sample to be established

<table>
<thead>
<tr>
<th>Energy</th>
<th>Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>spin up</td>
<td>unmagnetized</td>
</tr>
<tr>
<td>spin down</td>
<td>magnetized</td>
</tr>
</tbody>
</table>
Superconductivity: some milestones

*Discovery of the isotope effect* \( (T_c \sim M^{-1/2}) \) by Maxwell and by Reynolds, Serin, Wright, and Nesbitt (1950)

*Ginzburg-Landau theory* of superconductivity (1950)
(Ginzburg awarded Nobel Prize in 2003)

Pippard shows that the *superconducting wave function extends over long distance* \( (10^{-4} \text{ cm}) \) (1950)

Evidence develops for *a gap in the density of states* in energy (1954)

![Density of states diagram](image-url)
An energy gap in the density of states?

Evidence for a gap in the density of states in superconductors (Corak, Goodman, Satterthwaite, and Wexler, 1954)

The general features of the superconducting state are now well-established, although a good mathematical or detailed physical description is lacking. Pippard\(^1\) has shown that the wave functions (range-of-order) of the electrons in the superconducting state extend over relatively large distances (\(\sim 10^{-4}\) cm) and that the penetration depth does not vary much with magnetic field. The latter implies that a linear theory, in which only first-order changes of wave functions produced by the magnetic field are included, should be satisfactory. As pointed out particularly by Slater,\(^2\) wave functions extending over large areas are favorable for a large diamagnetism. While it is thought that the Meissner effect (\(B=0\)) follows rather generally from these considerations, it has been difficult to treat a specific model. One model, which is a modification of a degenerate free-electron gas, is discussed below.

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Fig. 1. Temperature dependence of the electronic specific heat of a superconductor.
Bardeen’s colloquium in 1954

Bardeen says that a *gap in the density of states at the Fermi energy*, *will probably explain the Meissner effect* and thus lead to an explanation of superconductivity.

Bardeen tried to explain *the origin of the gap using the electron-lattice interaction as suggested by the isotope effect*, but did not have a complete theory.

CPS realized that *nuclear relaxation in metals arose via the electrons close to the Fermi energy, so a gap should produce be a big change in $T_1$ in the superconducting state.*

We should *measure $T_1$ in a superconductor!!*
The crucial problem

Conventional NMR was done in large iron electromagnets or permanent magnets generating magnetic fields~7-10 kilogauss, with alternating magnetic fields operating at frequency~10MHz.

As a result of the Meissner effect (superconductors are perfect diamagnets), superconductors exclude the magnetic fields. **How can one do magnetic resonance in a superconductor?**
A solution to the experimental dilemma: Field Cycling

A strong magnetic field suppresses superconductivity.

Cycle between the normal and superconducting states, relaxing in the superconducting states, observing in the normal state.

Adiabatic remagnetization

Adiabatic demagnetization of the nuclei

Observe signal

Warm towards the lattice $T$
Which superconductor to study?

One must be able to cool below the superconducting transition.

One must be able to turn the magnetic field off and on in a time short compared to the nuclear spin-lattice relaxation time.

<table>
<thead>
<tr>
<th></th>
<th>$^{207}$Pb</th>
<th>$^{199}$Hg</th>
<th>$^{115}$In</th>
<th>$^{27}$Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C$ (K)</td>
<td>7.19</td>
<td>4.13</td>
<td>3.40</td>
<td>1.17</td>
</tr>
<tr>
<td>abundance</td>
<td>21%</td>
<td>16%</td>
<td>95%</td>
<td>100%</td>
</tr>
<tr>
<td>$\nu$ (MHz) at 1 T</td>
<td>8.9</td>
<td>7.6</td>
<td>9.3</td>
<td>11.1</td>
</tr>
<tr>
<td>$H_C$ (T=0) in gauss</td>
<td>803</td>
<td>412</td>
<td>293</td>
<td>105</td>
</tr>
<tr>
<td>$T_1$ at 1 K (msec)</td>
<td>$\approx$ 10 Too fast</td>
<td>$\approx$ 10 Too fast</td>
<td>$\approx$ 10 Too fast</td>
<td>450</td>
</tr>
</tbody>
</table>

$^{27}$Al is good except for the low $T_C$
Chuck Hebel (1952)
The properties of our apparatus

Cooling

Two choices to cool below 1.17 K:
- adiabatic demagnetization
- pump on $^4$He (Rollin film)

This was our first experiment at such low temperatures so we chose pumping

Three Dewar system
- (nitrogen, outer He, inner He) We could reach 0.94K ($T=0.8T_C$) by pumping
The properties of our apparatus

The magnet

Conventional NMR was done at about 10,000 gauss in large iron magnets.

To achieve rapid switching, we made a special magnet from leftover Betatron iron sheets and worked at low fields of a few hundred gauss.
Conventional theory of $T_1$ mechanism in a metal

the electron-nuclear hyperfine coupling scatters the electron, flipping the electron spin up (down) and the nuclear spin down (up)

$$1/T_1 = C \int \left| \langle i|V_{en}|f \rangle \right|^2 \rho(E_f)[1 - f(E_f)]f(E_i) \rho_i dE_i$$

Fermi's Golden Rule \underline{Final state is empty} \underline{Sum over occupied initial states}

$$|E_f - E_i| = \gamma_n \hbar H_o$$

$$V_{en} = \frac{8\pi}{3} \gamma_e \gamma_n \hbar^2 \delta(r) I \cdot S$$

$$I \cdot S = I_z S_z + \frac{I^+ S^- + I^- S^+}{2}$$

C depends on the nuclear spin Hamiltonian and thus is field dependent.
What did we expect? \( T_1 \textit{ should be slower!} \)

Two models:

- two fluid models: since only the “normal fluid” should be able to scatter, and since the normal fluid density drops with \( T \), \( T_1 \) should slow as \( T \) drops.

- A gap should inhibit excitations and thus \( T_1 \) should be slower below \( T_C \)
Experimental results (fall of 1956) \((R = 1/T_1)\)

\(T_1\) is faster in the superconductor!

\[
\begin{align*}
R_S / R_N & \quad T / T_C \\
\end{align*}
\]
Transmission of Superconducting Films at Millimeter-Microwave and Far Infrared Frequencies

R. E. Glover, III,† and M. Tinkham

Department of Physics, University of California,
Berkeley, California
(Received September 4, 1956)

Fig. 1. Experimental transmission ratios of superconducting and normal states of a typical lead film (dc residual resistance 117 ohms; transmission in normal state = ½) at $T/T_c = 0.67 \pm 0.03$. 

Direct observation of the energy gap (1956)
Meanwhile, some other developments:


Theory of the interaction of \textit{pairs of electrons above a filled Fermi sea}, “Cooper pairs” (L.N. Cooper, Phys. Rev \textbf{104}, 1189 (1956)).

Announcement that \textit{Bardeen, Brattain, and Shockley} had won the \textit{Nobel Prize} for Physics for invention of the transistor (October, 1956).
John Bardeen in his office in Urbana
Bob Schrieffer (1954)
Spring 1957: Our calculations using the BCS theory \((R \equiv 1/T_1)\)

Phys Rev 102, 901 (1957) and 113, 1504 (1959)

Three ways to deal with the Infinite density of states at the gap edge

\(R_S/R_N\)

\(T/T_C\)
Sound Absorption, Morse and Bohm (1957)

The precipitous drop in rate contrasts with the NMR rise. The two rates should have the same temperature dependence in a one electron theory.

Since $E_i \approx E_f$, $1/T_1 = \mathcal{C} \int |V|^2 \rho^2 f(1-f) dE$
Winter of 1957
Reconciling the NMR and sound absorption data

\[ \frac{1}{T_1} = C \int \left| \langle i | V_{en} | f \rangle \right|^2 \rho(E_f) [1 - f(E_f)] f(E_i) \rho_i dE_i \]

Fermi's Golden Rule
Final state is empty
Sum over occupied initial states

The peaking of the BCS density of states explains the rise in NMR rate just below \( T_c \).

For NMR we found that

\[ \left| \langle i | V_{en} | f \rangle \right|^2 = V_{if}^2 \left[ V_1^2 + V_2^2 \right] / 2, \]

\[ E^2 = \varepsilon^2 + \Delta^2, \quad V_1^2 = 1 + \frac{\varepsilon \varepsilon'}{E E'}, \quad V_2^2 = \frac{\Delta^2}{E E'}. \]

For sound absorption, BCS found that one needed

\[ \left| \langle i | V_{en} | f \rangle \right|^2 = V_{if}^2 \left[ V_1^2 - V_2^2 \right] / 2, \]

The distinction arose from the pair nature of the wave function and thus would not be present in a one electron theory! The combined data therefore confirm the pair nature of the wave function.
1958
A break-through in cooling($^3$He price drops tenfold!)

He$^3$ Cryostat for Measuring Specific Heat*

G. Seidel and P. H. Keesom
Purdue University, Lafayette, Indiana
(Received April 25, 1958)

An apparatus employing a bath of liquid He$^3$ as a coolant has been developed for measuring specific heats below 1°K. Temperatures as low as 0.30°K can be maintained for long periods of time. A description of a simple thermal switch is also included.
Al Redfield, when a post doc with Nico Bloembergen
1953-1955
The combined data shown in Cooper’s Nobel prize lecture

Solid dots: Hebel-Slichter  Crosses: Redfield-Anderson
The solid line is the prediction using the BCS theory with level broadening
Conclusion

The BCS theory gives a complete explanation of the nuclear relaxation time in a superconductor.

The contrasting behavior of NMR relaxation rate with ultrasound absorption is explained in a natural manner by the pair nature of BCS wave function, providing proof of this central concept of the BCS theory.