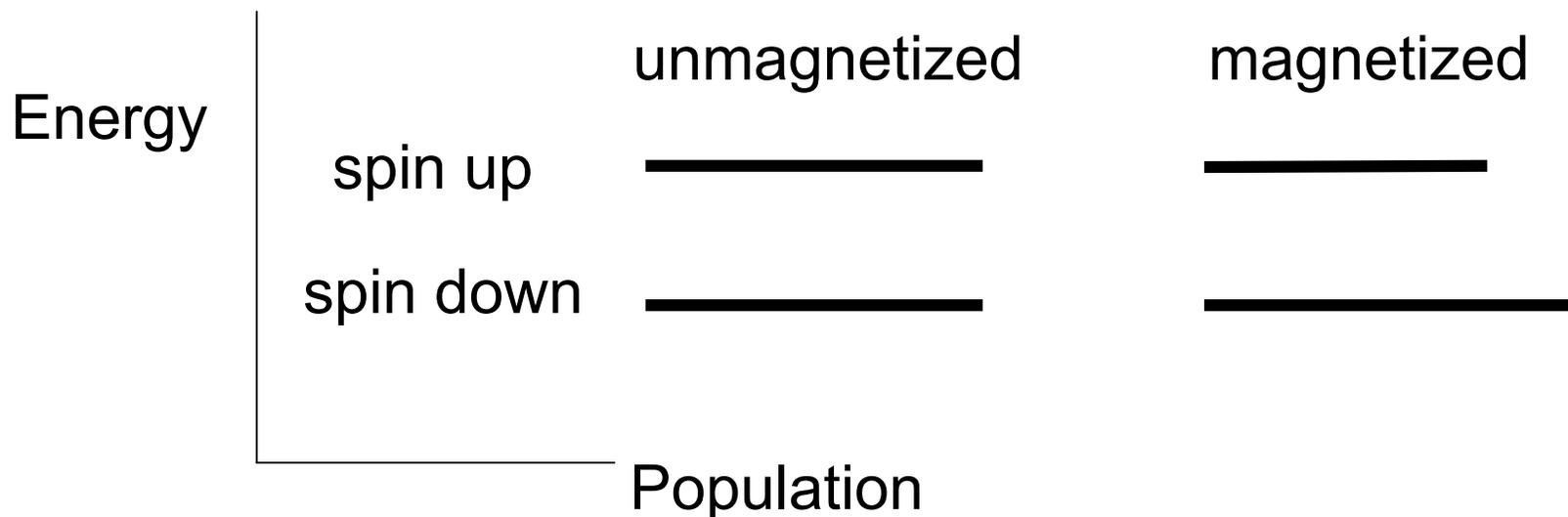


# NMR and the BCS Theory of Superconductivity

# 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**



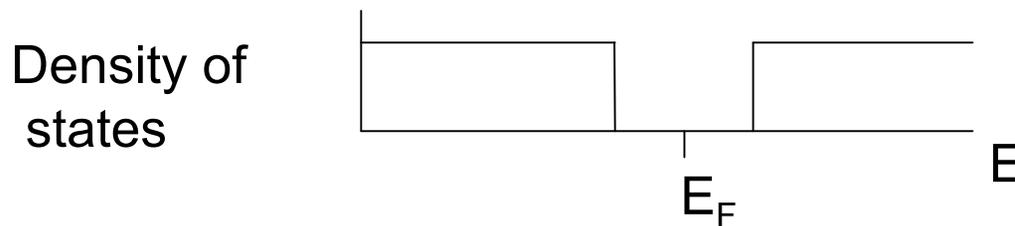
# Superconductivity: some milestones

**Discovery of the isotope effect ( $T_c \sim M^{-1/2}$ )** by Maxwell and 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** ( $10^{-4}$  cm) (1950)

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



# 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)

## Theory of the Meissner Effect in Superconductors

J. BARDEEN

University of Illinois, Urbana, Illinois

(Received January 3, 1955)

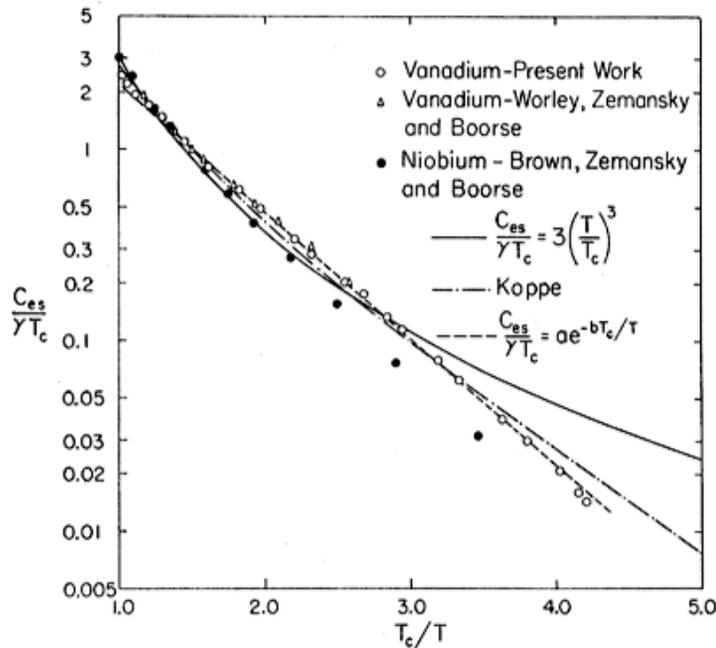


FIG. 1. Temperature dependence of the electronic specific heat of a superconductor.

**T**HE general features of the superconducting state are now well-established, although a good mathematical or detailed physical description is lacking. Pippard<sup>1</sup> 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,<sup>2</sup> wave functions extending over large areas are favorable for a large diamagnetism. While it is thought that the Meissner effect ( $\mathbf{B}=0$ ) 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.

## 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 !!***

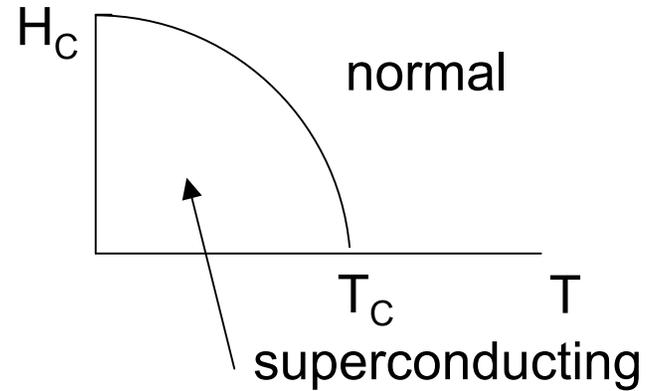
# The crucial problem

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.

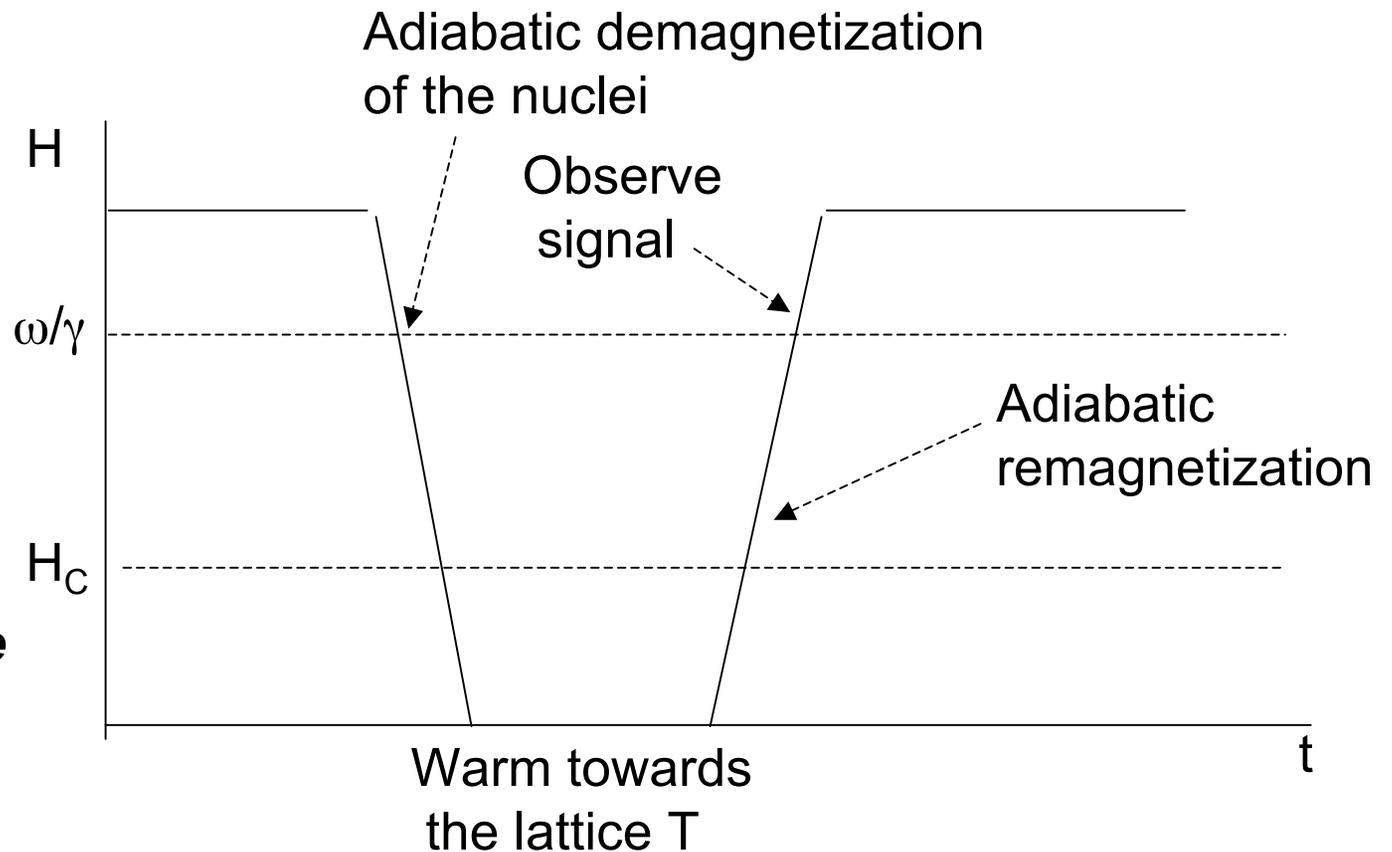
As a result of the Meissner effect (superconductors are perfect diamagnets) ,superconductors exclude the magnetic fields. **How can one do magnetic resonance in a superconductor?**

# 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***



# Which superconductor to study?

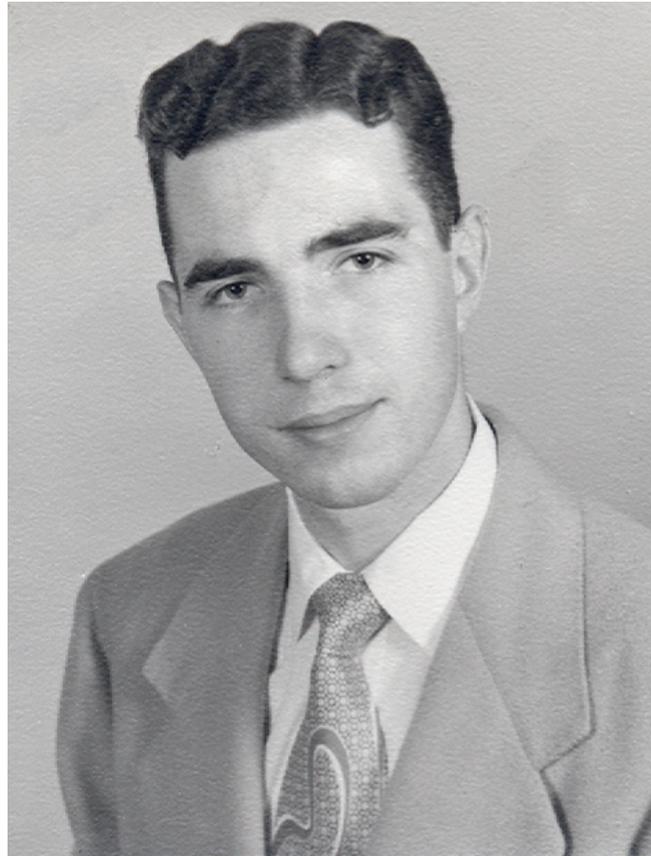
One must be able to cool below the superconducting transition.

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

	<sup>207</sup> Pb	<sup>199</sup> Hg	<sup>115</sup> In	<sup>27</sup> Al
T <sub>C</sub> (K)	7.19	4.13	3.40	1.17
abundance	21%	16%	95%	100%
ν(MHz) at 1 T	8.9	7.6	9.3	11.1
H <sub>C</sub> (T=0)in gauss	803	412	293	105
T <sub>1</sub> at 1 K (msec)	≈ 10 Too fast	≈ 10 Too fast	≈ 10 Too fast	<b>450</b>

<sup>27</sup>Al is good except for the low T<sub>C</sub>

# Chuck Hebel (1952)



# The properties of our apparatus

## Cooling

***Two choices to cool below 1.17 K:***

adiabatic demagnetization

***or***

*pump on  $^4\text{He}$  (Rollin film)*

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

***Three Dewar system***

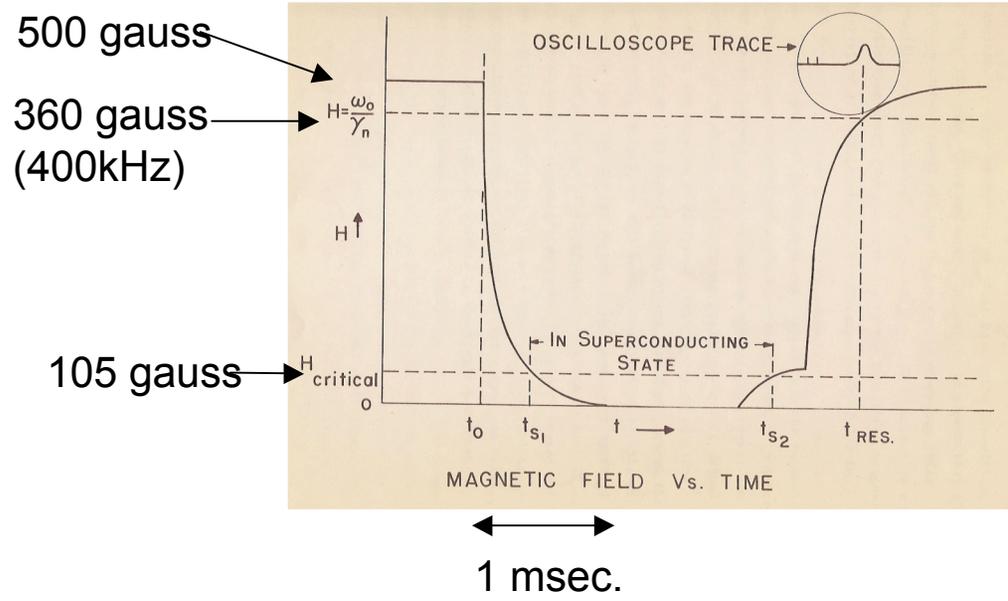
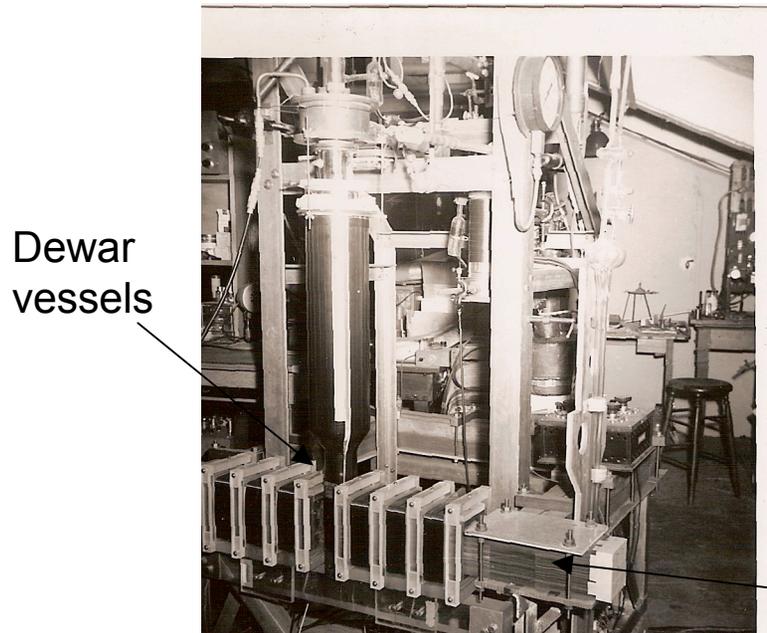
(nitrogen, ***outer He, inner He***) We could reach 0.94K ( $T=0.8T_c$ )  
by pumping

# 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)***

$$1/T_1 = C \int \underbrace{\left| \langle i | V_{en} | f \rangle \right|^2}_{\text{Fermi's Golden Rule}} \underbrace{\rho(E_f) [1 - f(E_f)]}_{\text{Final state Is empty}} \underbrace{f(E_i) \rho_i}_{\text{Sum over occupied initial states}} dE_i$$

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

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

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

C depends on the nuclear spin Hamiltonian and thus is field dependent.

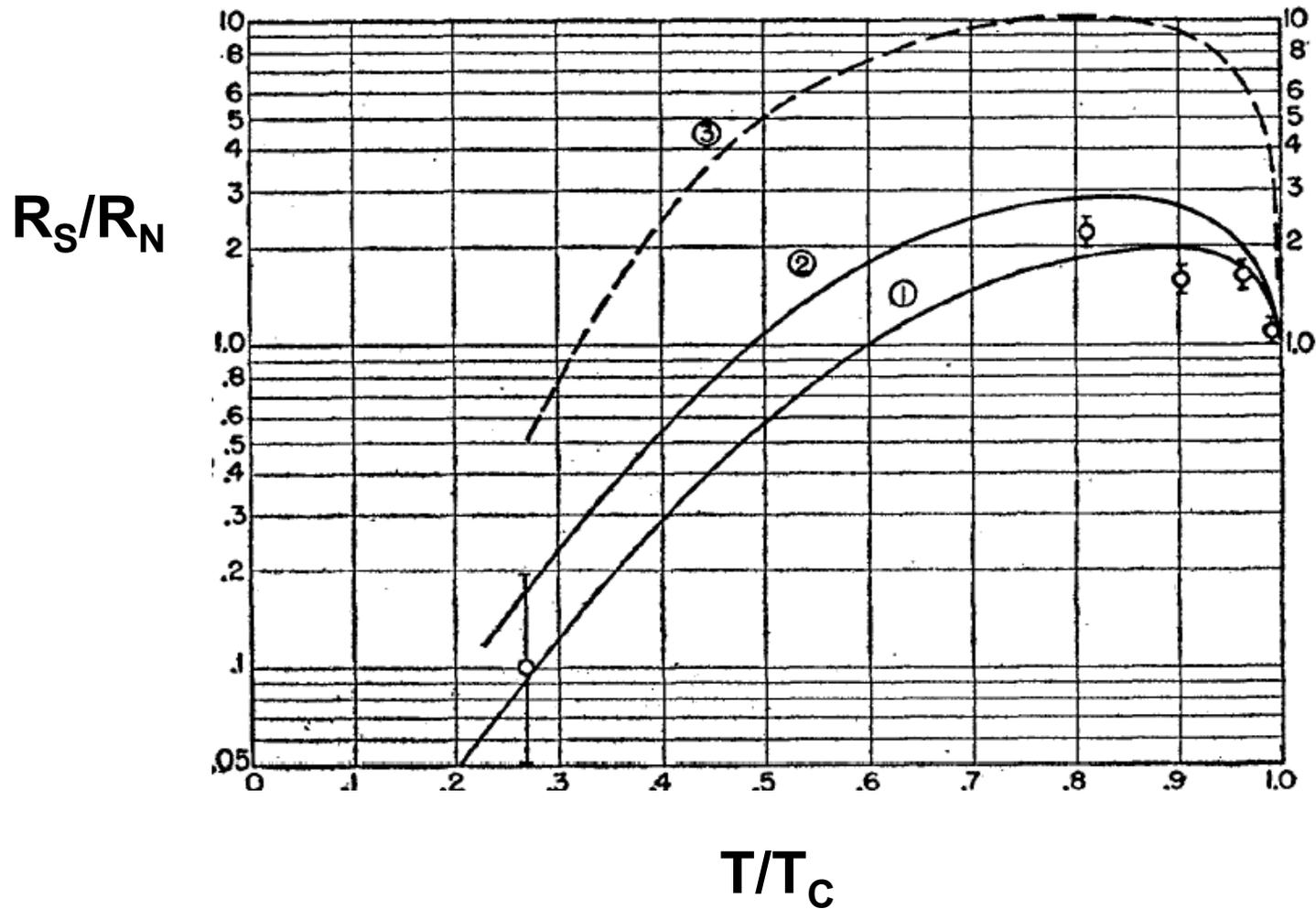
What did we expect?  ***$T_1$  should be slower!***

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) ( $R \equiv 1/T_1$ )

***$T_1$  is faster in the superconductor !***



# Direct observation of the energy gap (1956)

## 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)

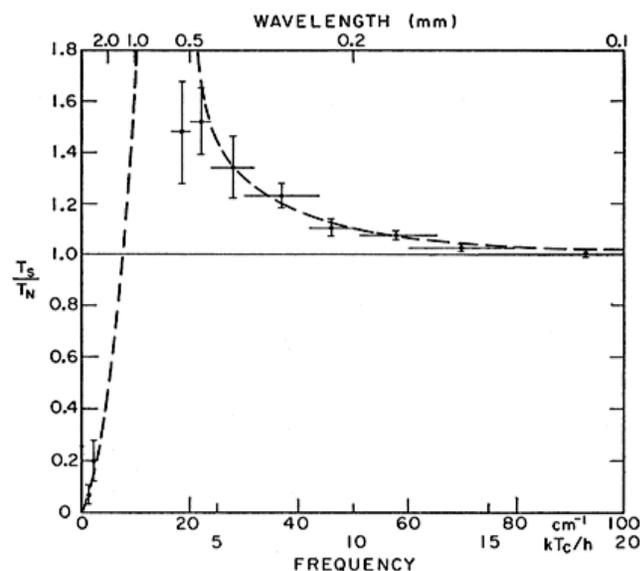
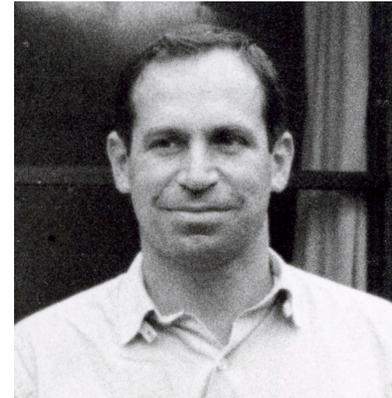


FIG. 1. Experimental transmission ratios of superconducting and normal states of a typical lead film (dc residual resistance 117 ohms; transmission in normal state =  $\frac{1}{4}$ ) at  $T/T_c = 0.67 \pm 0.03$ .

## Meanwhile, some other developments:

Theory of the ***effect of lattice vibrations on the electron-electron coupling***

(J. Bardeen and D. Pines,  
Phys. Rev **99**,1140 (1955).



Theory of the interaction of ***pairs of electrons above a filled Fermi sea, "Cooper pairs"***  
(L.N. Cooper, Phys. Rev **104**,1189 (1956).



Announcement that ***Bardeen, Brattain, and Shockley*** had won the ***Nobel Prize*** for Physics for invention of the transistor (October, 1956).

## John Bardeen in his office in Urbana

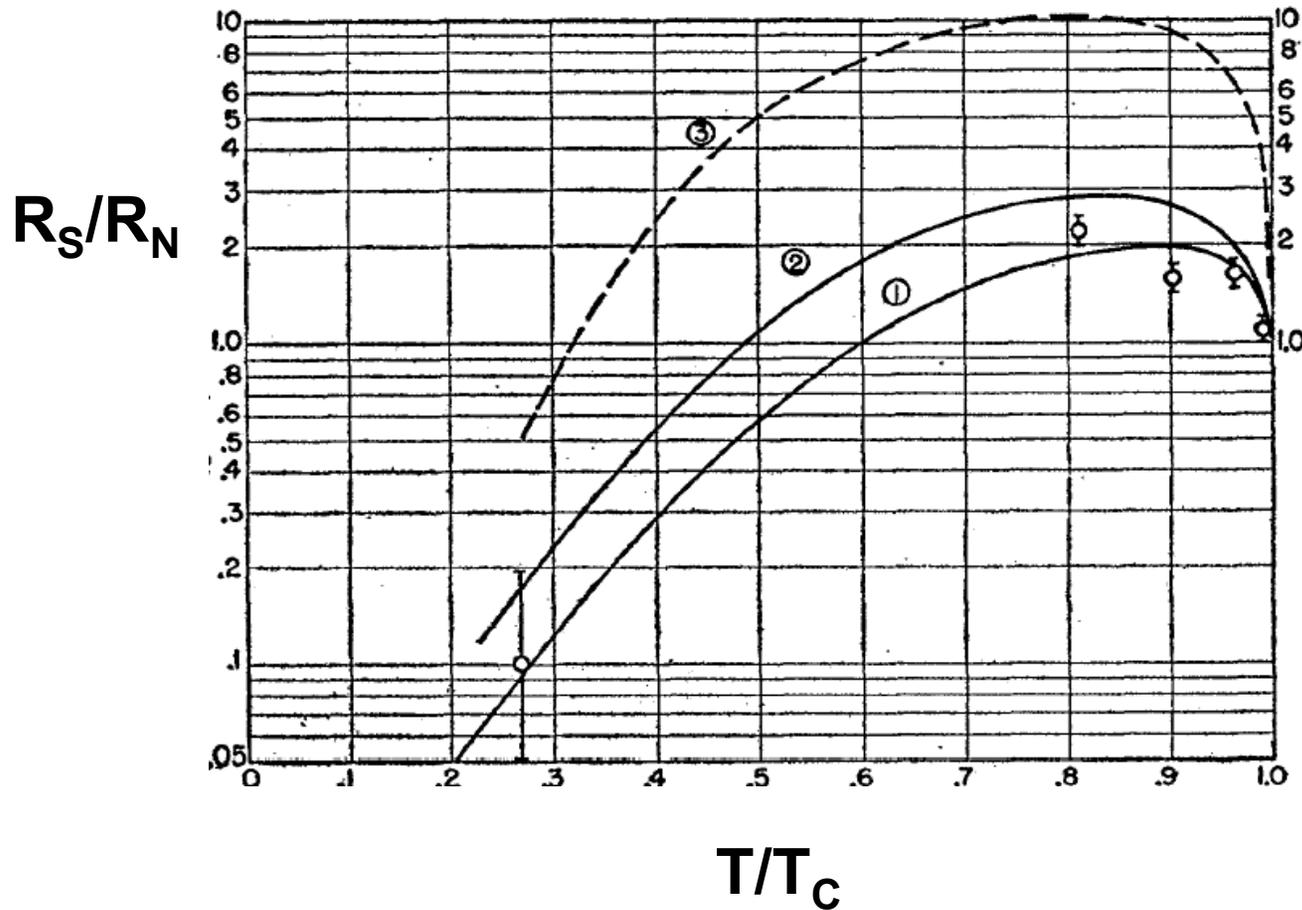


Bob Schrieffer (1954)



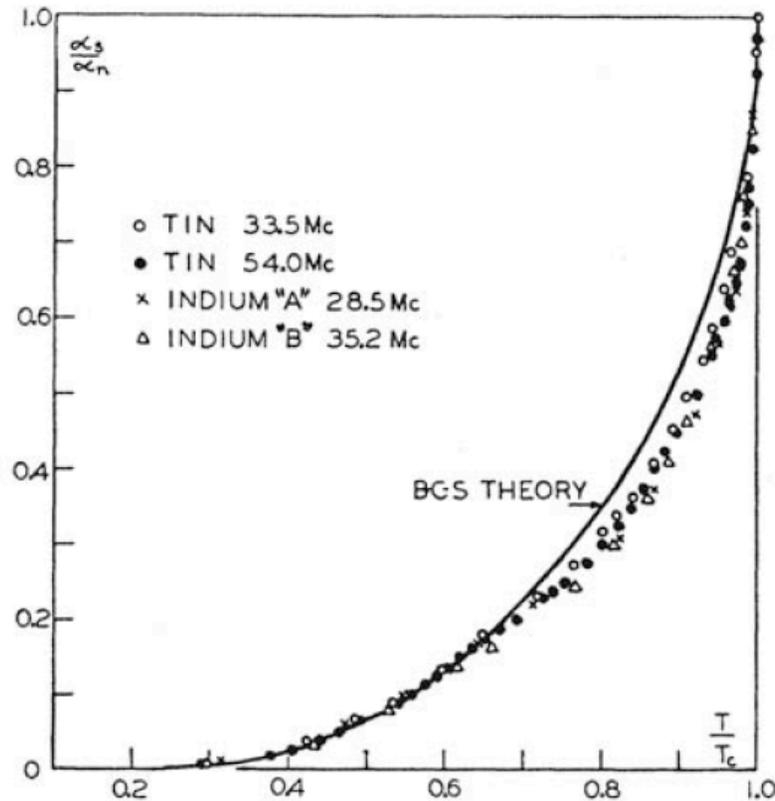
# Spring 1957: Our calculations using the BCS theory ( $R \equiv 1/T_1$ )

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



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

# 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  $E_i \cong E_f$ ,  $1/T_1 = C \int |V|^2 \rho^2 f(1-f) dE$

Winter of 1957

Reconciling the NMR and sound absorption data

$$1/T_1 = C \int \underbrace{\left| \langle i | V_{en} | f \rangle \right|^2}_{\text{Fermi's Golden Rule}} \underbrace{\rho(E_f)}_{\text{Final state Is empty}} [1 - \underbrace{f(E_f)}_{\text{Sum over occupied initial states}}] \underbrace{f(E_i)}_{\text{Sum over occupied initial states}} \rho_i dE_i$$

***The peaking of the BCS density of states explains the rise in NMR rate just below  $T_c$ .***

***For NMR*** we found that  $\left| \langle i | V_{en} | f \rangle \right|^2 = V_{if}^2 [V_1^2 + V_2^2] / 2$ ,

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

***For sound absorption***, BCS found that one needed

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

***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(<sup>3</sup>He price drops tenfold!)

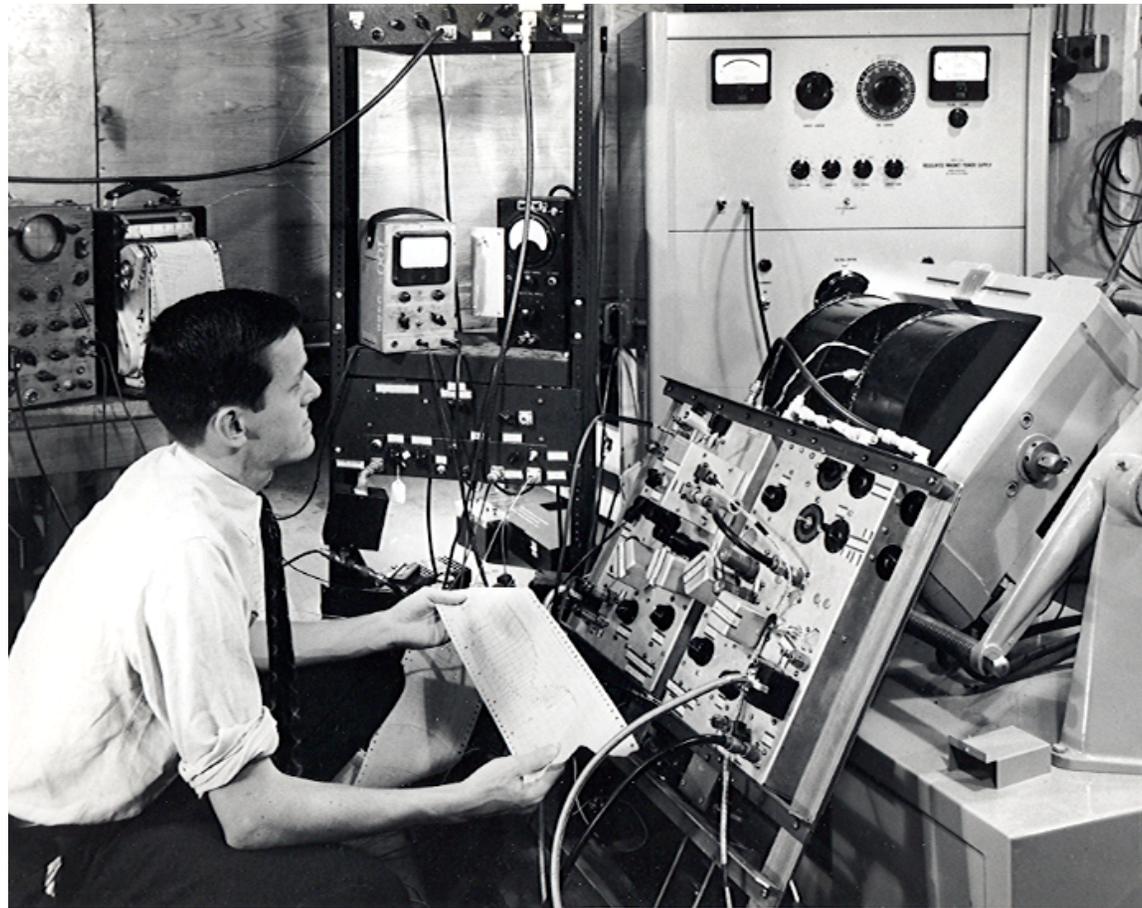
### **He<sup>3</sup> Cryostat for Measuring Specific Heat\***

G. SEIDEL AND P. H. KEESOM  
*Purdue University, Lafayette, Indiana*

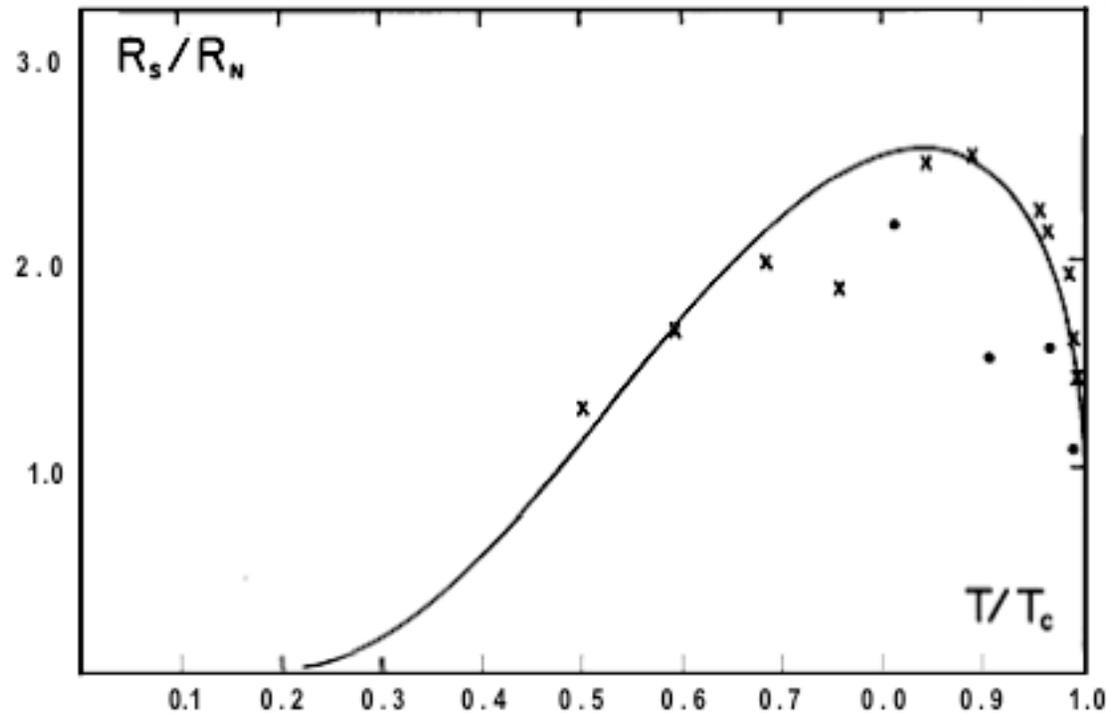
(Received April 25, 1958)

An apparatus employing a bath of liquid He<sup>3</sup> 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.