

Chapter 10: Superconductivity

References:

1. C. Kittel ; Introduction to solid state physics
2. M. Tinkham: Introduction to superconductivity
3. Paul Hansma, Tunneling Spectroscopy

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SUMMARY

*Experimental Survey of
Superconductivity Phenomenon*

WHAT IS A SUPERCONDUCTOR?

- 1. Zero resistance**
- 2. Complete expulsion of magnetic flux**

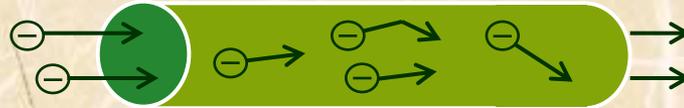
SUPERCONDUCTIVITY

Type of material

What happens in a wire?

Result

Conductor



Electrons flow easily
(like water through a
garden hose)

Collisions cause
dissipation (heat)

Insulator



Electrons are tightly bound no flow
(like a hose plugged with cement)

No current flow
at all

Superconductor



Electrons bind into pairs and
cannot collide
(a frictionless hose)

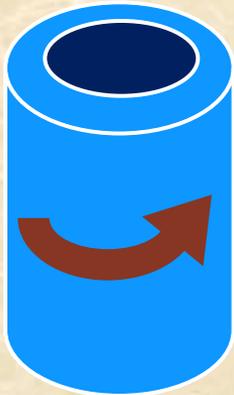
No collisions
No dissipation
No heat
No resistance

HOW SMALL IS THE RESISTANCE?



Copper Cylinder

- 1) Induce current
- 2) Current decays in about 1/1000 second



Superconducting Cylinder

- 1) Induce current
- 2) Current does not decay
(less than 0.1% in a year)
so, resistance is smaller than copper
by $\frac{1000 \text{ years}}{1/1000 \text{ second}}$
i.e., at least 1 trillion times!

Why Superconductivity is so fascinating ?

- ❖ Fundamental SC mechanism
- ❖ Novel collective phenomenon at low temp
- ❖ Applications

Bulk: - Persistent current, power storage
- Magnetic levitation
- High field magnet, MRI

Electronics:
- SQUID magnetometer
- Josephson junction electronics

POSSIBLE IMPACT OF SUPERCONDUCTIVITY

● Energy

- Superconductivity generators & motors
- Power transmission & distribution
- Energy storage systems
- Magnets for fusion power
- Magnets for magneto-hydrodynamic power

● Transportation

- Magnets for levitated trains
- Electro-magnetic powered ships
- Magnets for automobiles

● Health care

- Magnetic resonance imaging

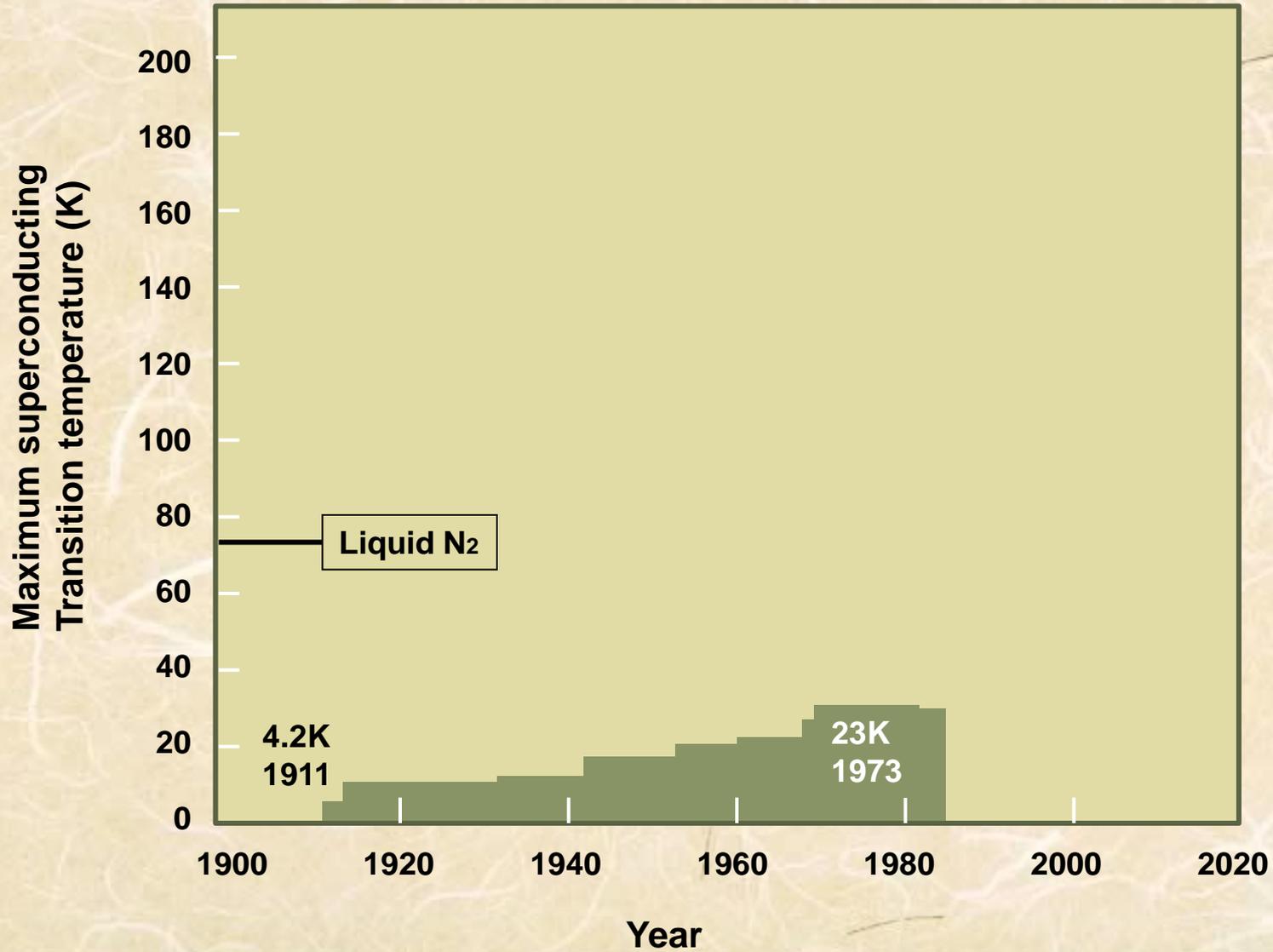
Low- T_c Superconductivity Mechanism



Electron phonon coupling



PROGRESS IN SUPERCONDUCTIVITY



A legacy of Superconductivity

Ted H. Geballe

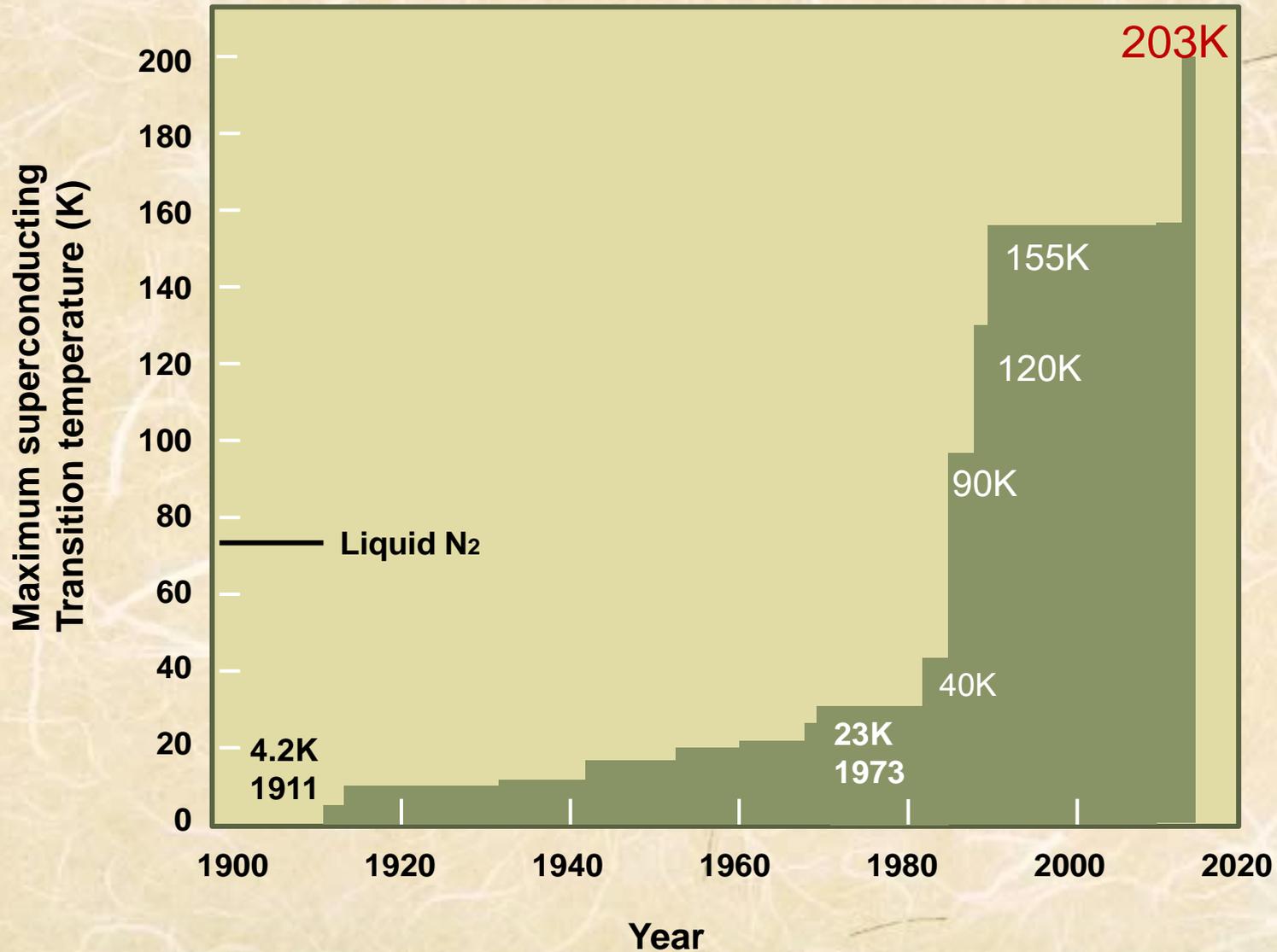


A legacy of Superconductivity



Bob Hammond

PROGRESS IN SUPERCONDUCTIVITY



- ❑ The results are the work of Mikhail Eremets, Alexander Drozdov and their colleagues at the Max Planck Institute for Chemistry in Mainz, Germany last year. They find that when they subject samples of **hydrogen sulfide** to extremely high pressures — around 1.5 million atmospheres (150 gigapascals) — and cool them below 203 K, the samples display the classic hallmarks of superconductivity: zero electrical resistance and a phenomenon known as the Meissner effect.
- ❑ Other hydrogen compounds may be good candidates for high-temperature superconductivity too. For instance, compounds that pair hydrogen with platinum, potassium, selenium or tellurium, instead of sulfur.
- ❑ Zhang in Dallas and Yugui Yao of the Beijing Institute of Technology in China predict that substituting 7.5% of the sulfur atoms in hydrogen sulfide with phosphorus and upping the pressure to 2.5 million atmospheres (250 GPa) could raise the superconducting transition temperature all the way to 280 K⁶, above water's freezing point.

Experimental Electrical Resistivity of Metals

The electrical resistivity of most metals is dominated at room temperature (300K) by collisions of the conduction electrons with lattice phonons and at liquid helium temperature (4K) by collisions with impurity atoms and mechanical imperfections in the lattice (Fig. 11).

$$\frac{1}{\tau} = \frac{1}{\tau_L} + \frac{1}{\tau_i} \quad (46)$$

Lattice phonons Imperfections

To a good approximation the rates are often independent.
And can be summed together

, where τ_L and τ_i are the collision times for scattering by phonons and by imperfections, respectively. The net resistivity is given by

$$\rho = \rho_L + \rho_i,$$

$$\text{Since } \rho \sim 1/\tau \quad (47)$$

Often ρ_L is independent of the number of defects when their concentration is small, and often ρ_i is independent of temperature.

This empirical observation expresses **Matthiessen's Rule**.

Different $\rho_i(0)$ but the same ρ_L

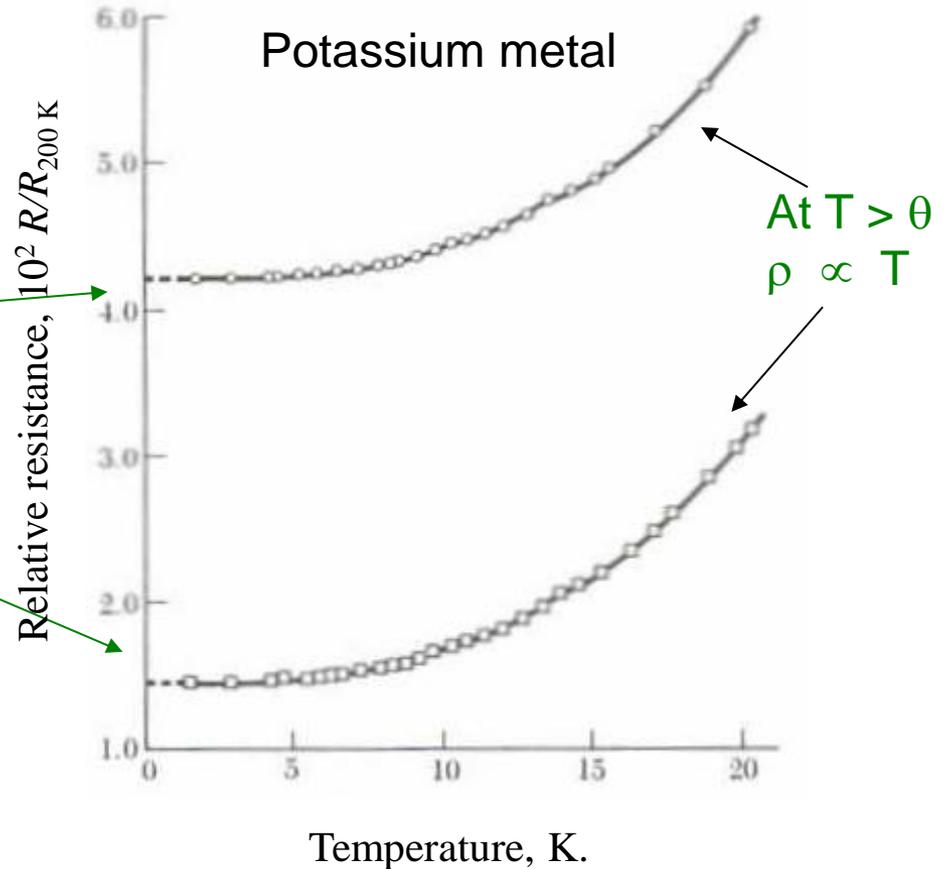


Figure 12 Resistance of potassium below 20 K, as measured on two specimens by D. MacDonald and K. Mendelssohn. The different intercepts at 0 K are attributed to different concentrations of impurities and static imperfections in the two specimens.

The temperature-dependent part of the electrical resistivity is proportional to the rate at which an electron collides with thermal phonons. One simple limit is at temperatures over the Debye temperature θ ; here the phonon concentration is proportional to the temperature T , so that $\rho \propto T$ for $T > \theta$.

$$N_{ph} \propto T, \text{ hence } \rho \propto 1/\tau \propto N_{ph} \propto T$$

The electrical resistivity of many metals and alloys drops **suddenly to zero** when the specimen is cooled to a sufficiently low temperature, often a temperature in the liquid helium range. This phenomenon, called superconductivity, was observed first by Kamerlingh Onnes in Leiden in 1911, three years after he first liquified helium.

First SC found in Hg by 1911 !

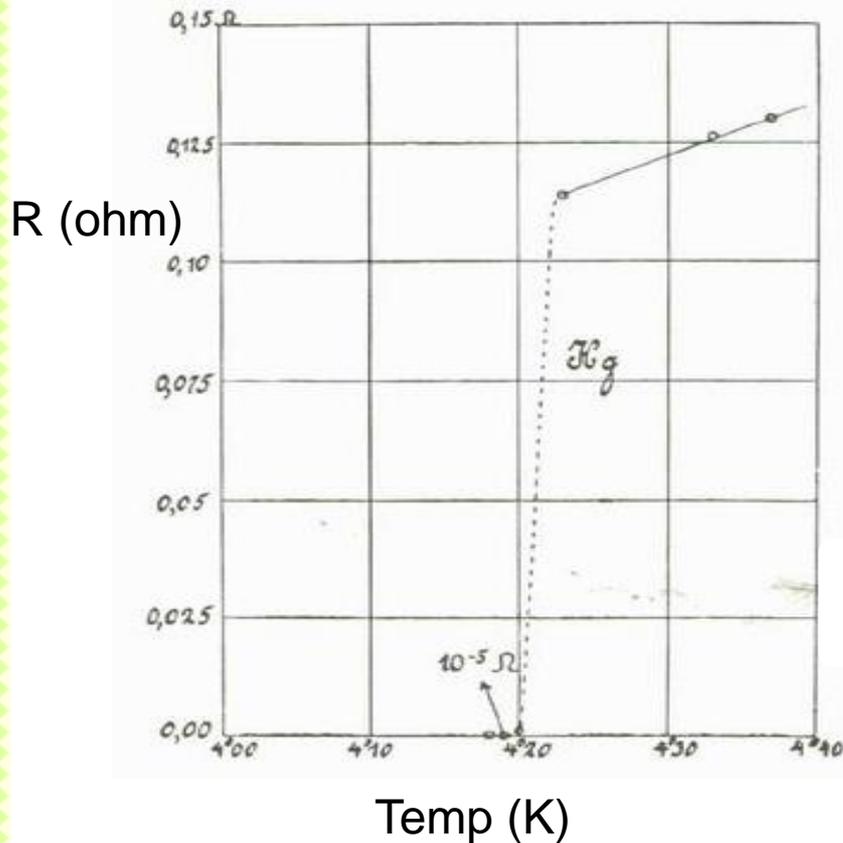


Figure 1 Resistance in ohms of a specimen of Mercury versus absolute temperature. The plot by Kamerlingh Onnes Marked the discovery of superconductivity.

Decay of persistent current from 1 year up to 10⁵ year

Meissner Effect

It is an experimental fact that a bulk superconductor in a weak magnetic field will act as a **perfect diamagnet**, with zero magnetic induction in the interior. When a specimen is placed in a magnetic field and is then cooled through the transition temperature for superconductivity, the magnetic flux originally present is ejected from the specimen. This is called the **Meissner effect**.

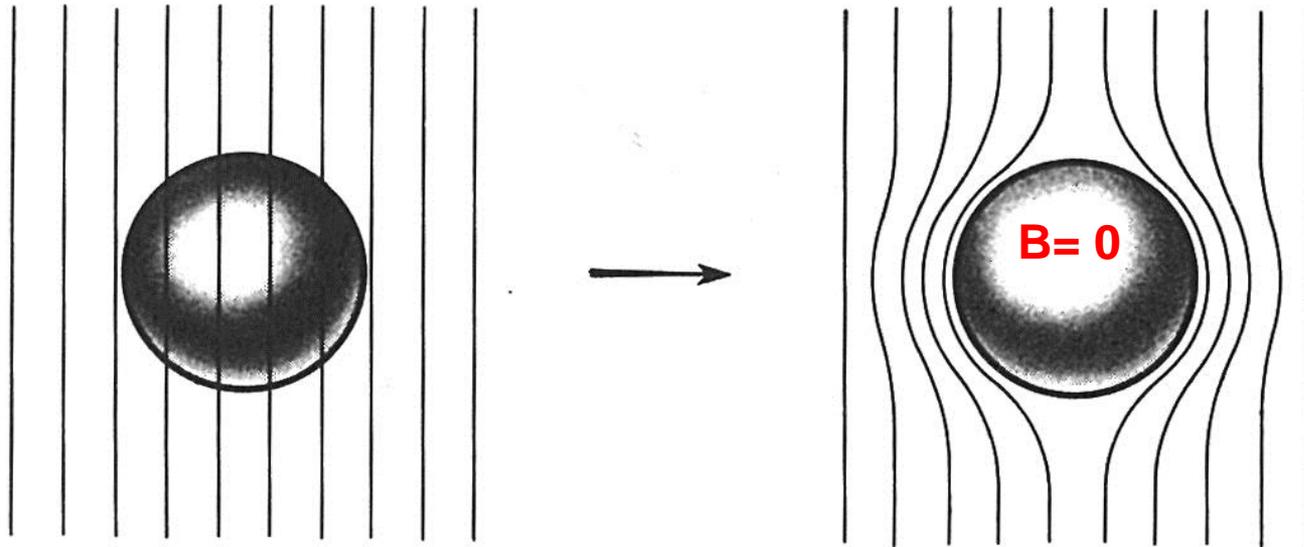


Figure 2 Meissner effect in a superconducting sphere cooled in a constant applied magnetic field; on passing below the transition temperature the lines of induction \mathbf{B} are ejected from the sphere.

Fundamental Mechanism

The superconducting state is an ordered state of the conduction electrons of the metal.

Electron-Phonon Coupling

Cooper Pair formed by two electrons k , and $-k$ with opposite spins near the Fermi level, as coupled through **phonons** of the lattice

The nature and origin of the ordering was explained by Bardeen, Cooper, and Schrieffer.³

BCS Theory, 1957

J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 162 (1957); **108**, 1175 (1957).

The Discovery of Superconductivity

- Early 90's -- elemental SP metals like Hg, Pb, Al, Sn, Ga, etc.
- Middle 90's -- transitional metals, alloys, and compounds like Nb, NbN, Nb₃Sn, etc.
- Late 90's -- perovskite oxides

Table 2 Superconductivity of selected compounds

Compound	T_c , in K	Compound	T_c , in K
Nb ₃ Sn	18.05	V ₃ Ga	16.5
Nb ₃ Ge	23.2	V ₃ Si	17.1
Nb ₃ Al	17.5	YBa ₂ Cu ₃ O _{6.9}	90.0
NbN	16.0	Rb ₂ CsC ₆₀	31.3
K ₃ C ₆ O	19.2	La ₃ In	10.4

A-15 compound A_3B , with $T_c = 15-23$ K

In the so called β -W structure

With three perpendicular linear chains of **A** atoms on the cubic face, and B atoms are at body centered cubic site

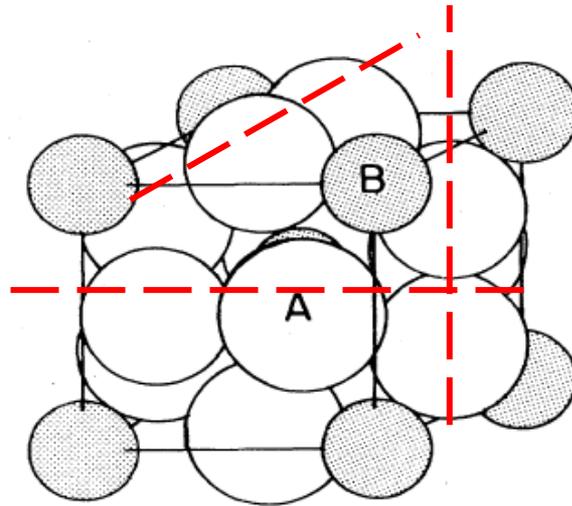


FIG. 1. The A-15 (or β -W) crystal structure for the compound formula A_3B . For the high T_c superconductors, A is a transition metal (usually V or Nb) and B is usually (but not always) a nontransition metal (e.g., Si, Ge, Sn, Al, Ga).

1973 Nb_3Ge , 23K !
 Nb_3Si ??

3. The penetration depth and the coherence length emerge as natural consequence of the BCS theory. The London equation is obtained for magnetic fields that vary slowly in space. Thus, the central phenomenon in superconductivity, the Meissner effect, is obtained in a natural way.

penetration depth (λ) ; coherence length (ξ)

4. The electron density of orbitals $D(E_F)$ of one spin at the Fermi level, and the electron –lattice interaction U . For $UD(E_F) \ll 1$, the BCS theory predicts:

$$T_c = 1.14\theta \exp[-1/UD(\epsilon_F)] , \quad 2\Delta /k_B T_c = 3.52$$

Where θ is the Debye temperature and U is an attractive interaction (electron-phonon interaction).

For dirty metal (a poor conductor) $\rightarrow \rho(300)\uparrow, U\uparrow, T_c\uparrow$ (a good SC)

5. Magnetic flux through a superconducting ring is quantized and the effective unit of charge is $2e$ rather than e .

Evidence of pairing of electrons

Low temperature Superconductors

- Mediated by Electron phonon coupling
- McMillian formula for T_c

$$T_c = \frac{\Theta_D}{1.45} \exp \left\{ - \left[\frac{(1 + \lambda_{ep})}{\lambda_{ep} - \mu^*(1 + 0.62\lambda_{ep})} \right] \right\}$$

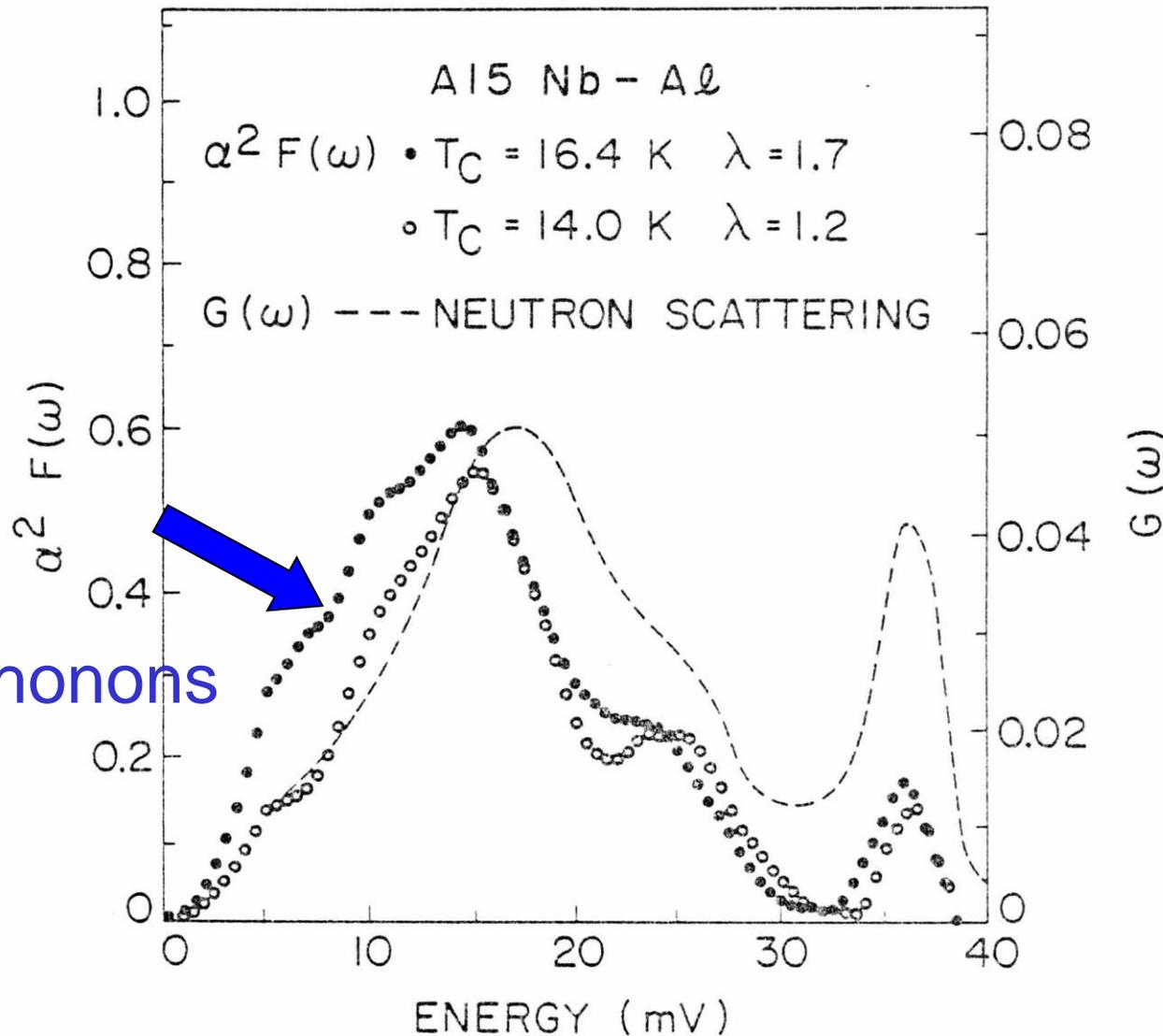
λ : electron phonon coupling constant

μ^* : Coulomb repulsion of electrons

$$\lambda \propto N(0) \langle I^2 \rangle / \omega^2$$

Are electrons or phonons more important?

The Phonon Spectrum of the low T_c A-15 compound Nb_3Al



Soft Phonons

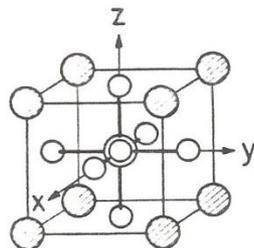
*Can we raise the T_c higher
than 30K?*

*Are we reaching the limitation
of the BCS Theory ?*

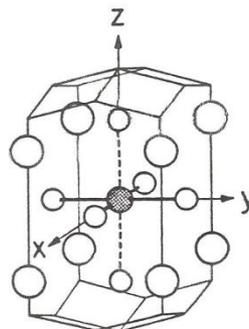
*Breakthrough in late 1986
By Bednorz and Muller*

Start the HTSC Era !

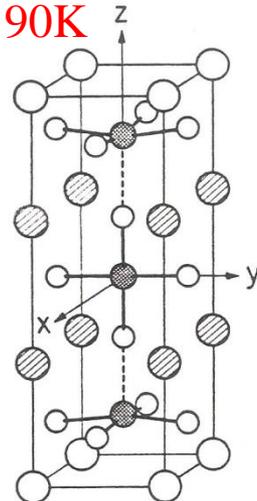
BaBiO₃
30K



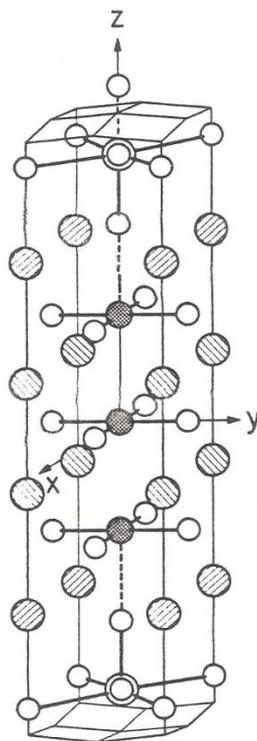
La₂CuO₄
40K



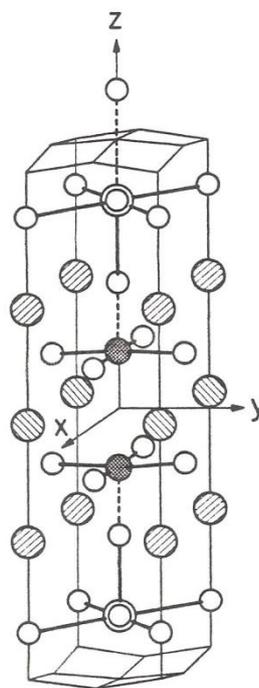
YBa₂Cu₃O₇
90K



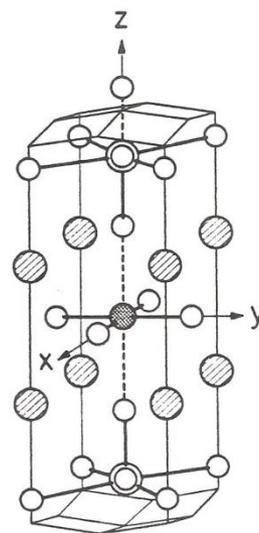
- La, Y
- Ba, Sr
- Ca
- Bi, Tl
- Cu
- O



Ca₂Ba₂Tl₂Cu₃O₁₀
120K



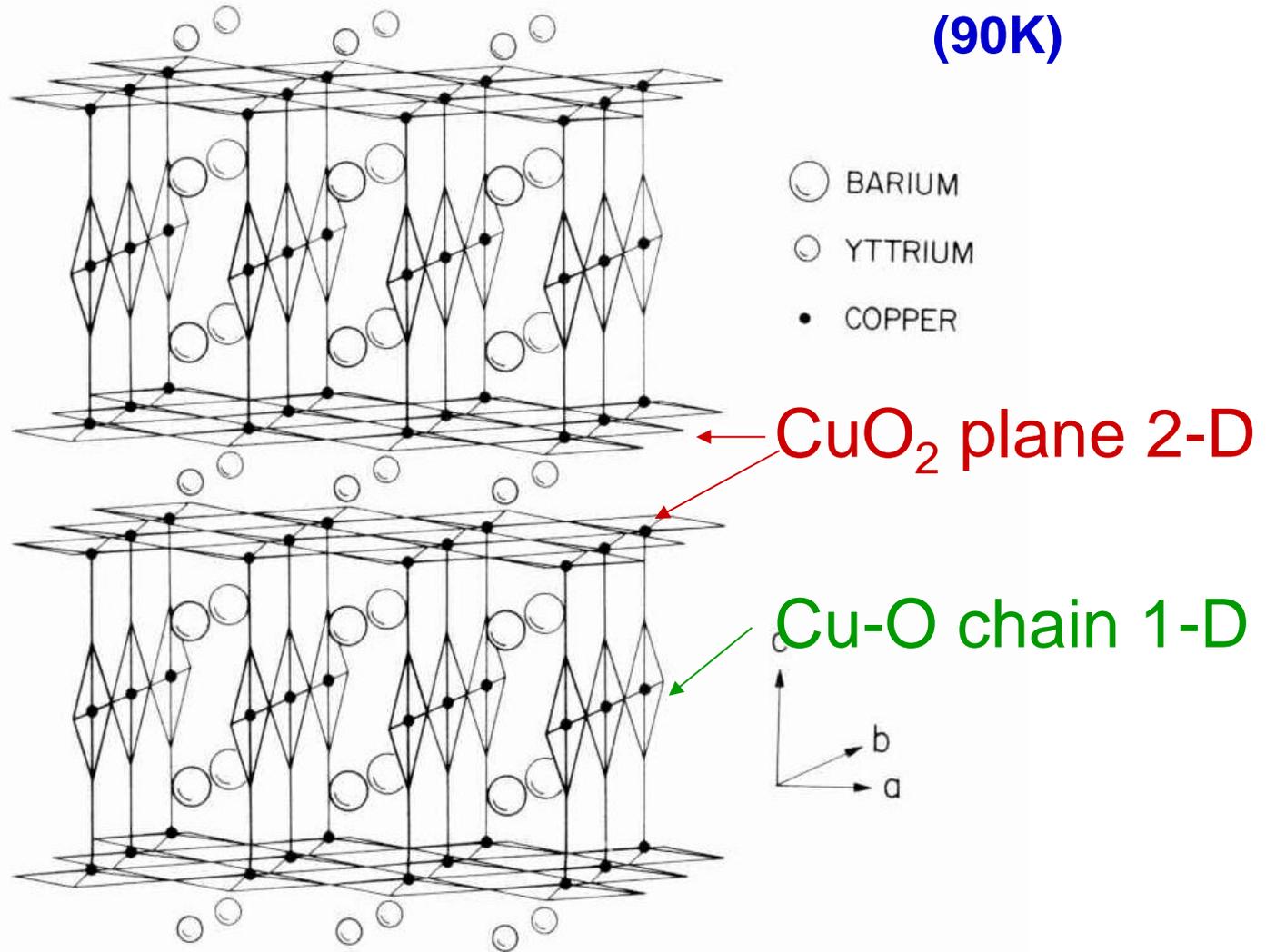
CaSr₂Bi₂Cu₂O₈
CaBa₂Tl₂Cu₂O₈
80K



Sr₂Bi₂CuO₆
Ba₂Tl₂CuO₆
40K

High Temperature Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$

(90K)



**Invention of Oxide Molecular Beam Epitaxy
For HTSC Single Crystal Films.**

Will all non magnetic metal become SC at low T?

(I) *Destruction of Superconductivity by Magnetic Impurities*

It is important to eliminate from the specimen even trace quantities of foreign paramagnetic elements

(II) *Destruction of Superconductivity by Magnetic fields*

At the critical temperature the critical field is zero: $H_c(T_c)=0$

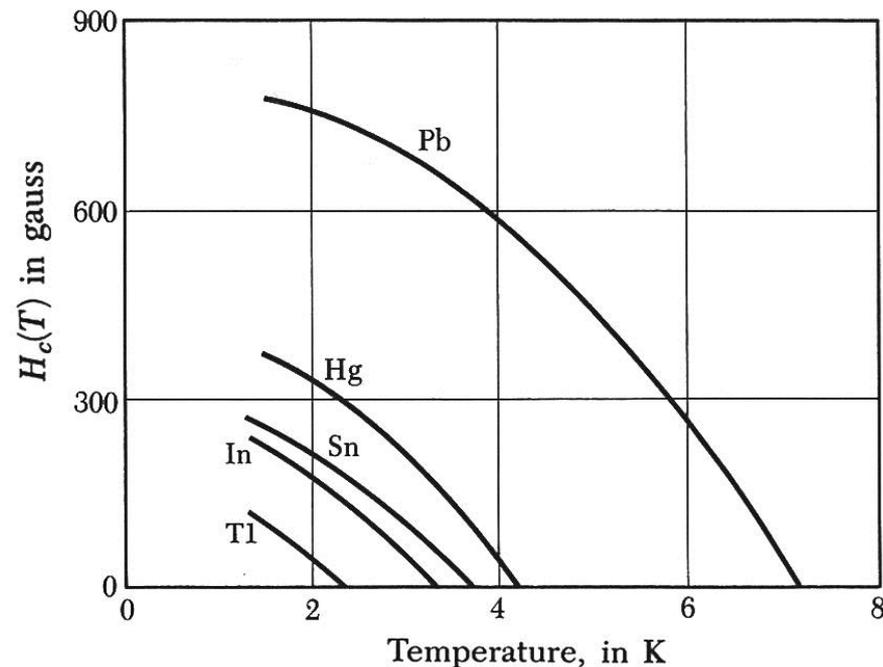


Figure 3 Experimental threshold curves of the critical field $H_c(T)$ versus temperature for several superconductors. A specimen is superconducting below the curve and normal above the curve.

Meissner Effect

It is an experimental fact that a bulk superconductor in a weak magnetic field will act as a perfect diamagnet, with zero magnetic induction in the interior. When a specimen is placed in a magnetic field, and is then cooled through the transition temperature for superconductivity, the magnetic flux originally present is ejected from the specimen. This is called the Meissner effect.

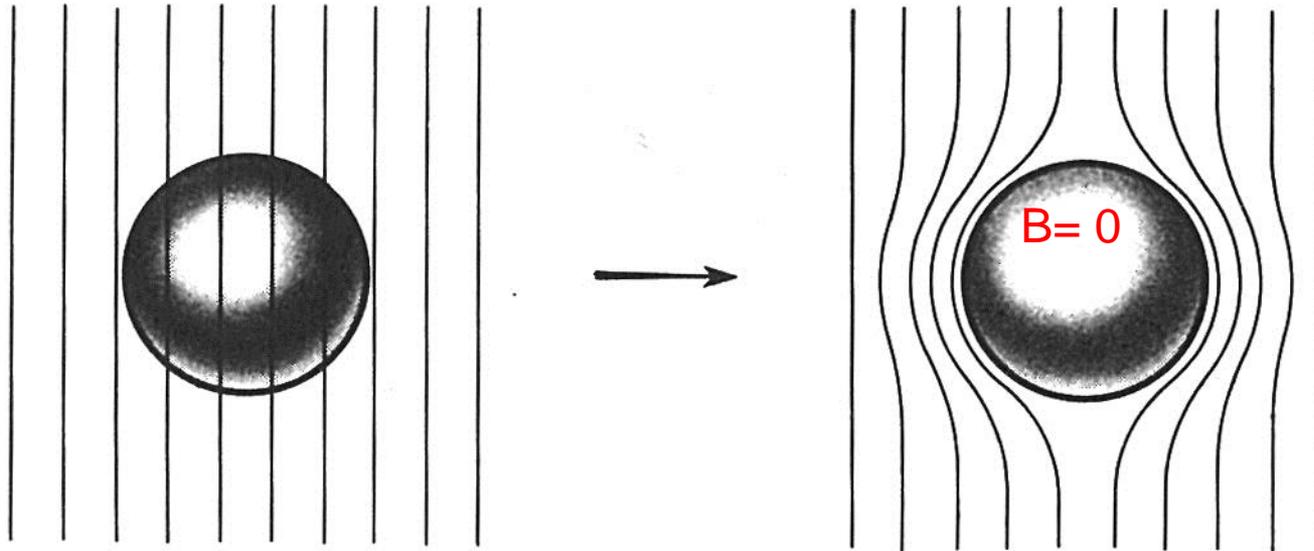


Figure 2 Meissner effect in a superconducting sphere cooled in a constant applied magnetic field; on passing below the transition temperature the lines of induction \mathbf{B} are ejected from the sphere.

Meissner Effect

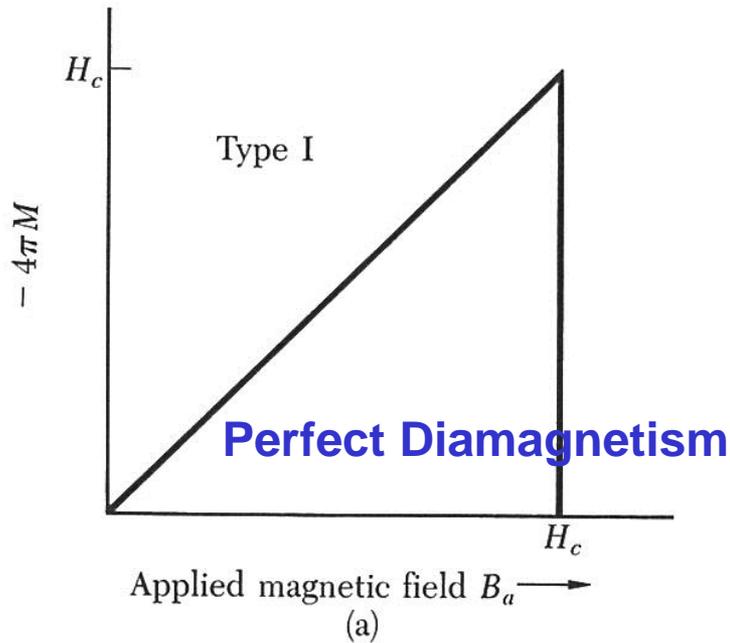
$$\boxed{B = Ba + 4\pi M = 0 ;} \quad \frac{M}{Ba} = -\frac{1}{4\pi} \quad \text{Eq.(1)}$$

Perfect Diamagnetism

The magnetic properties cannot be accounted for by the assumption that a superconductor is a normal conductor with zero electrical resistivity.

The result $B = 0$ cannot be derived from the characterization of a superconductor as a medium of zero resistivity. From Ohm's law, $\mathbf{E} = \rho \mathbf{j}$, we see that if the resistivity ρ goes to zero while \mathbf{j} is held finite, then \mathbf{E} must be zero. By a Maxwell equation $d\mathbf{B}/dt$ is proportional to curl \mathbf{E} , so that zero resistivity implies $d\mathbf{B}/dt = 0$. This argument is not entirely transparent, but the result predicts that the flux through the metal cannot change on cooling through the transition. **The Meissner effect contradicts this result** and suggests that perfect diamagnetism is an essential property of the superconducting state.

Type I superconductor



Type II superconductor

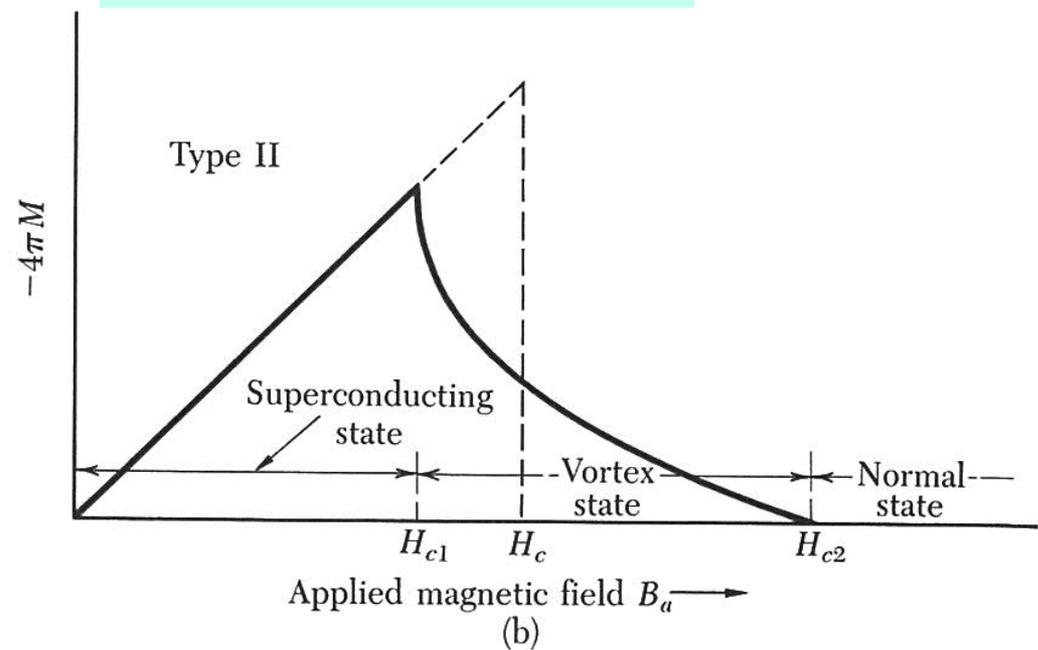


Figure 4 (a) Magnetization versus applied magnetic field for a bulk superconductor exhibiting a complete Meissner effect (perfect diamagnetism). A superconductor with this behavior is called a type I superconductor. Above the critical field H_c the specimen is a normal conductor and the magnetization is too small to be seen on this scale. Note that minus $4\pi M$ is plotted on the vertical scale: the negative value of M corresponds to diamagnetism. (b) Superconducting magnetization curve of a type II superconductor. The flux starts to penetrate the specimen at a field H_{c1} lower than the thermodynamic critical field H_c . The specimen is in a vortex state between H_{c1} and H_{c2} , and it has superconducting electrical properties up to H_{c2} . Above H_{c2} the specimen is a normal conductor in every respect, except for possible surface effects. For given H_c the area under the magnetization curve is the same for a type II superconductor as for a type I. (CGS units in all parts of this figure.)

Type II Superconductors

1. A good type **I** superconductor excludes a magnetic field until superconductivity is destroyed suddenly, and then the field penetrates completely.
2. (a) A good type **II** superconductor excludes the field completely up to a field H_{c1} .
(b) Above H_{c1} the field is partially excluded, but the specimen remains electrically superconducting.
(c) At a much higher field, H_{c2} , the flux penetrates completely and superconductivity vanishes.
(d) An outer surface layer of the specimen may remain superconducting up to a still higher field H_{c3} .
3. An important difference in a type **I** and a type **II** superconductor is in **the mean free path** of the conduction electrons in the normal state. are type **I**, with $\kappa < 1$, will be type **II**. is the situation when $\kappa = \lambda / \xi > 1$.

1. A superconductor is type **I** if the surface energy is always positive as the magnetic field is increased, **For $H < H_c$**
2. And type **II** if the surface energy becomes negative as the magnetic field is increased. **For $H_{c1} < H < H_{c2}$**

The free energy of a bulk superconductor is increased when the magnetic field is expelled. However, a parallel field can penetrate a very thin film nearly uniformly (Fig. 17), only a part of the flux is expelled, and the energy of the superconducting film will increase only slowly as the external magnetic field is increased.

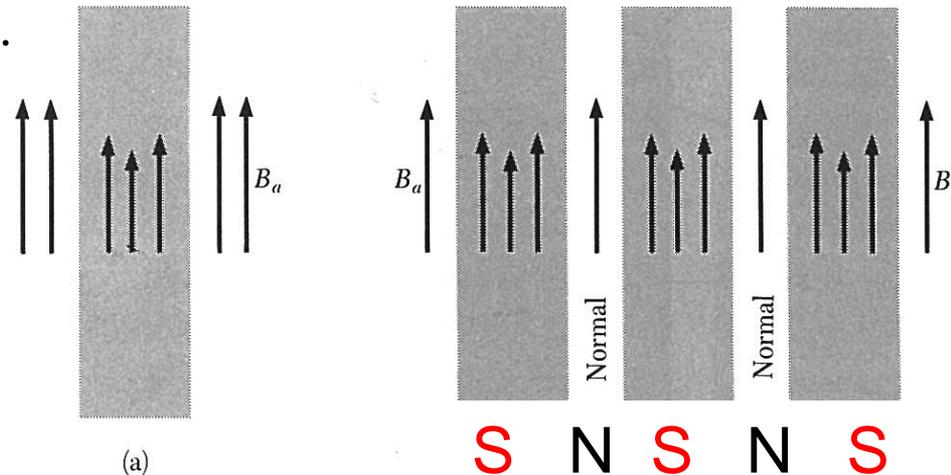


Figure 17 (a) Magnetic field penetration into a thin film of thickness equal to the penetration depth λ . The arrows indicate the intensity of the magnetic field. (b) Magnetic field penetration in a homogeneous bulk structure in the mixed or vortex state, with alternate layers in normal and superconducting states. The superconducting layers are thin in comparison with λ . The laminar structure is shown for convenience; the actual structure consists of rods of the normal state surrounded by the superconducting state. (The N regions in the vortex state are not exactly normal, but are described by low values of the stabilization energy density.)

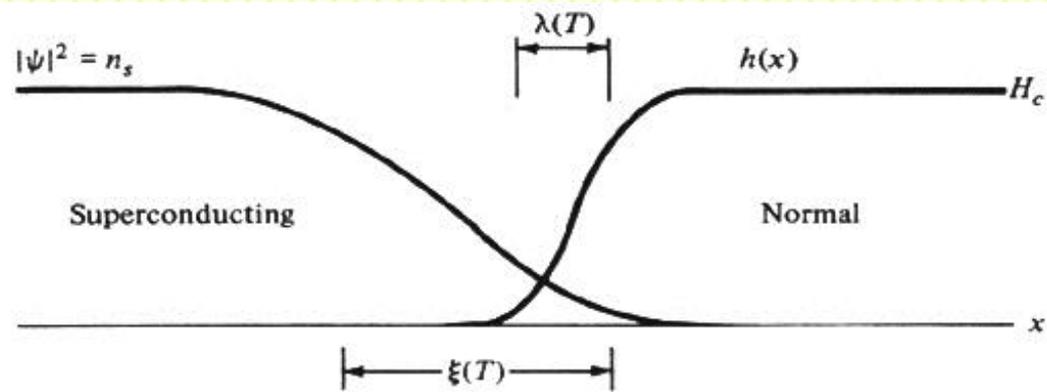


FIGURE 1-4
Interface between superconducting and normal domains in the intermediate state.

$$\kappa = \frac{\lambda_{\text{eff}}(T)}{\xi(T)} = \frac{2\sqrt{2}\pi H_c(T)\lambda_{\text{eff}}^2(T)}{\Phi_0}$$

Ginsburg Landau
Parameter

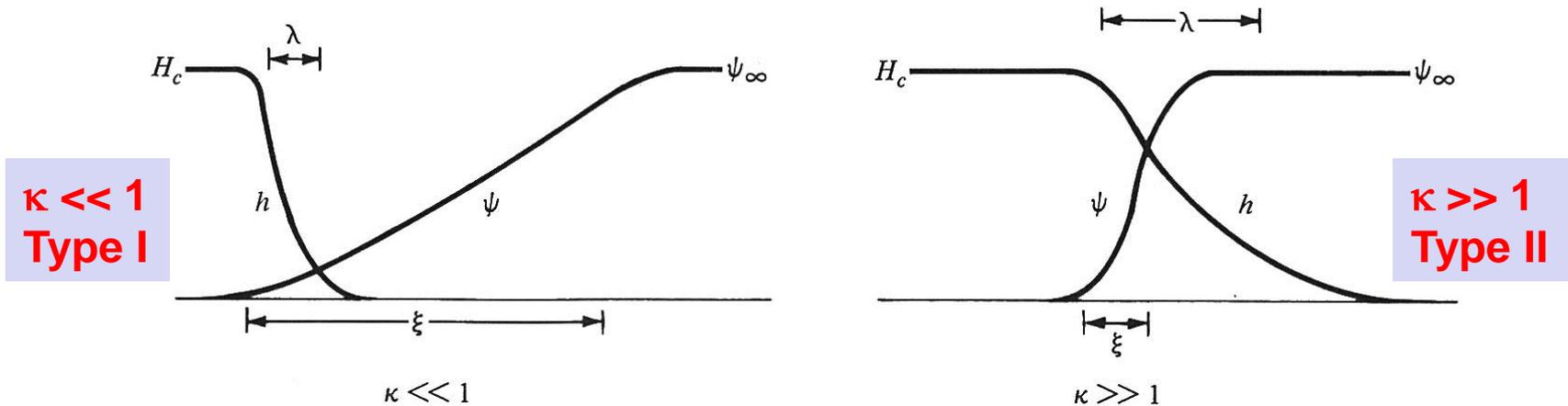


FIGURE 4-2

Schematic diagram of variation of h and ψ in a domain wall. The case $\kappa \ll 1$ refers to a type I superconductor (positive wall energy); the case $\kappa \gg 1$ refers to a type II superconductor (negative wall energy).

Vortex State

In such mixed state, called the vortex state, the external magnetic field will penetrate the thin normal regions uniformly, and the field will also penetrate somewhat into the surrounding superconducting materials

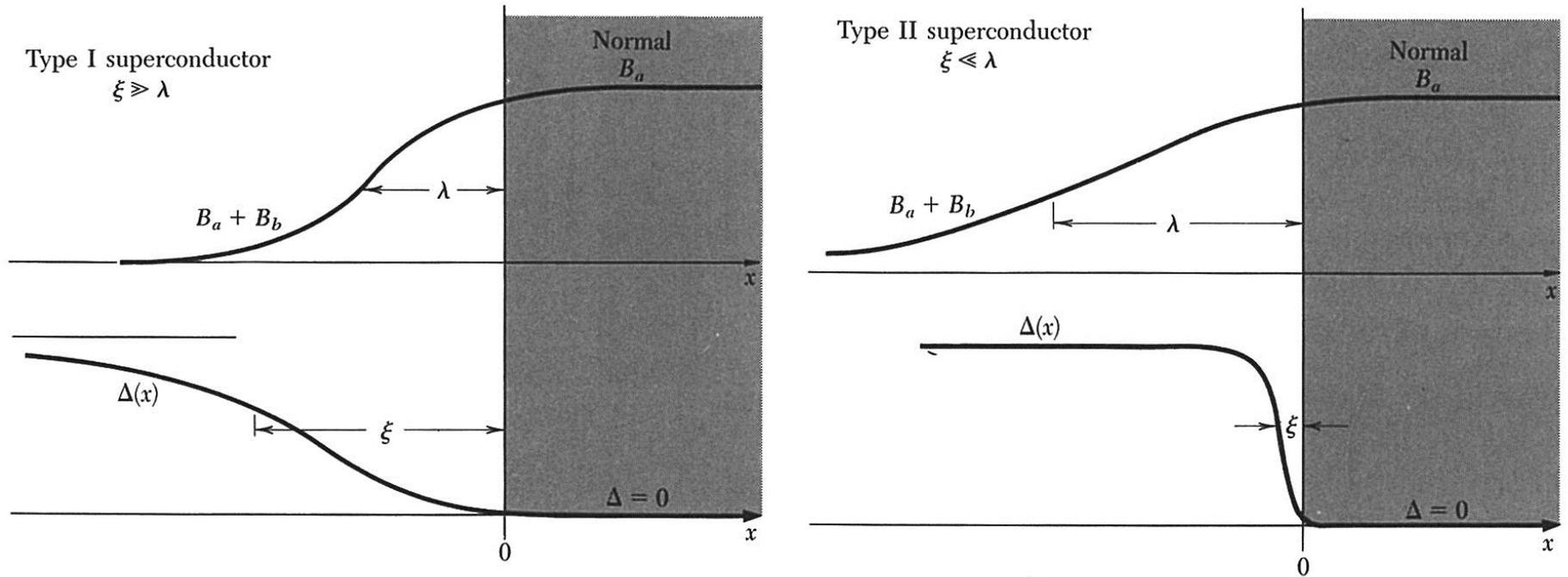
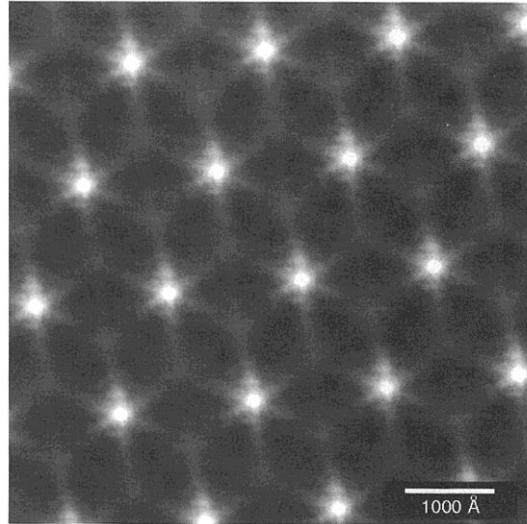


Figure 18 Variation of the magnetic field and energy gap parameter $\Delta(x)$ at the interface of superconducting and normal regions, for type I and type II superconductors. The energy gap parameter is a measure of the stabilization energy density of the superconducting state.

The term vortex state describes the circulation of superconducting currents in vortices throughout the bulk specimen,

Flux lattice
at 0.2K of NbSe₂



Abrikosov triangular
lattice as imaged by
LT-STM, H. Hess et al

Figure 19 Flux lattice in NbSe₂ at 1,000 gauss at 0.2K, as viewed with a scanning tunneling microscope. The photo shows the density of states at the Fermi level, as in Figure 23. The vortex cores have a high density of states and are shaded white; the superconducting regions are dark, with no states at the Fermi level. The amplitude and spatial extent of these states is determined by a potential well formed by $\Delta(x)$ as in Figure 18 for a Type II superconductor. The potential well confines the core state wavefunctions in the image here. The star shape is a finer feature, a result special to NbSe₂ of the sixfold disturbance of the charge density at the Fermi surface. Photo courtesy of H. F. Hess, AT&T Bell Laboratories.

The vortex state is stable when the penetration of the applied field into the superconducting material causes the surface energy become negative. A type II superconductor is characterized by a vortex state stable over a certain range of magnetic field strength; namely, between H_{c1} and H_{c2} .

Doping *Pb* with some *In*

Type I SC becomes type II SC

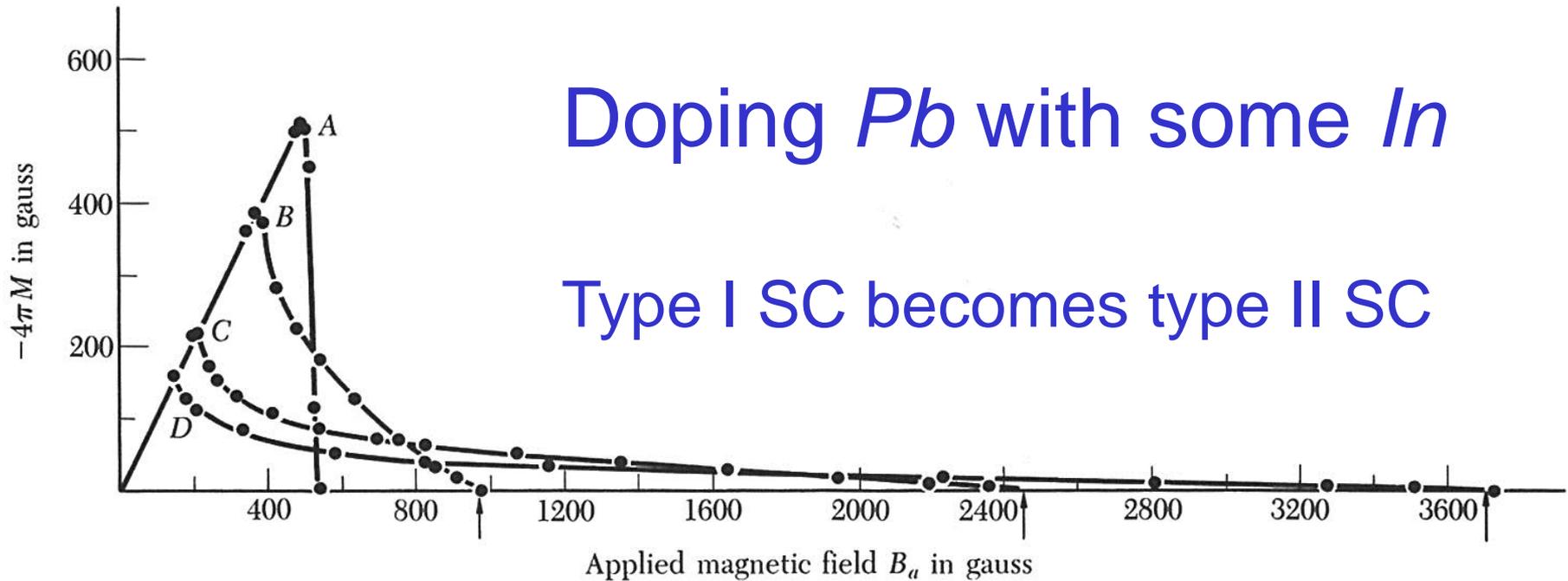


Figure 5a Superconducting magnetization curves of annealed polycrystalline lead and lead-indium alloys at 4.2 K. (A) lead; (B) lead-2.08 wt. percent indium; (C) lead-8.23 wt. percent indium; (D) lead-20.4 wt. percent indium. (After Livingston.)

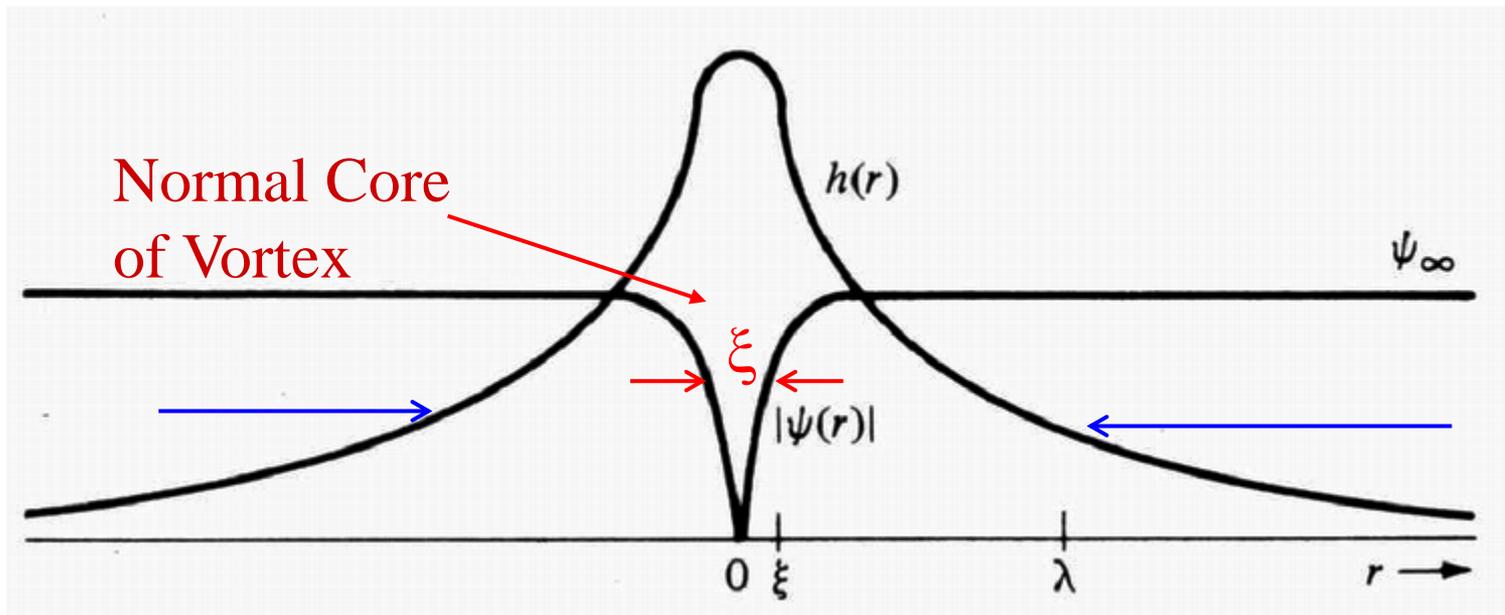


FIGURE 5-1

Structure of an isolated Abrikosov vortex in a material with $\kappa \approx 8$. The maximum value of $h(r)$ is approximately $2H_{c1}$.

$$\kappa = \lambda / \xi > 1$$

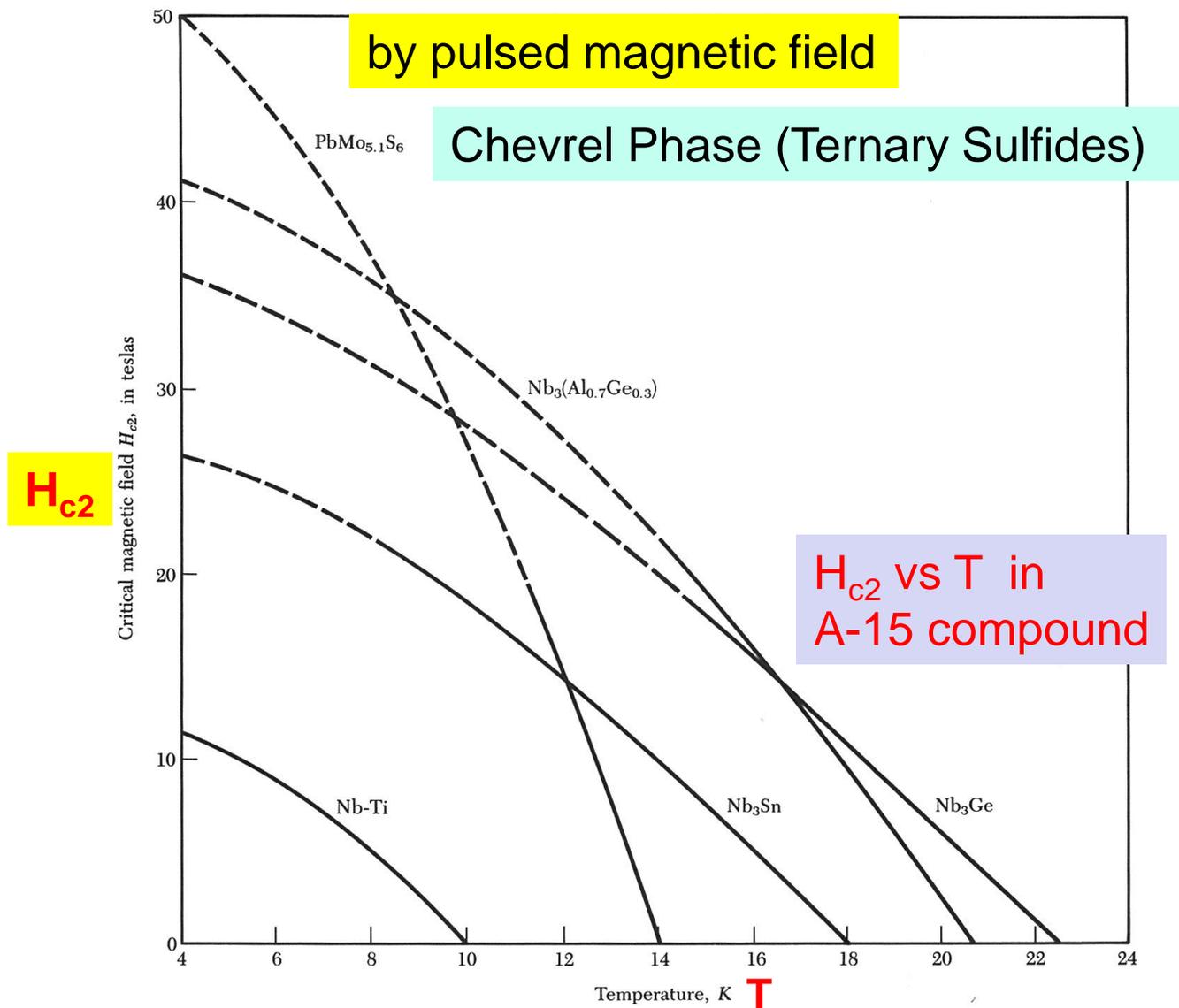


Figure 5b Stronger magnetic fields than any now contemplated in practical superconducting devices are within the capability of certain Type II materials. These materials cannot be exploited, however, until their critical current density can be raised and until they can be fabricated as finely divided conductors. (Magnetic fields of more than about 20 teslas can be generated only in pulses, and so portions of the curves shown as broken lines were measured in that way.)

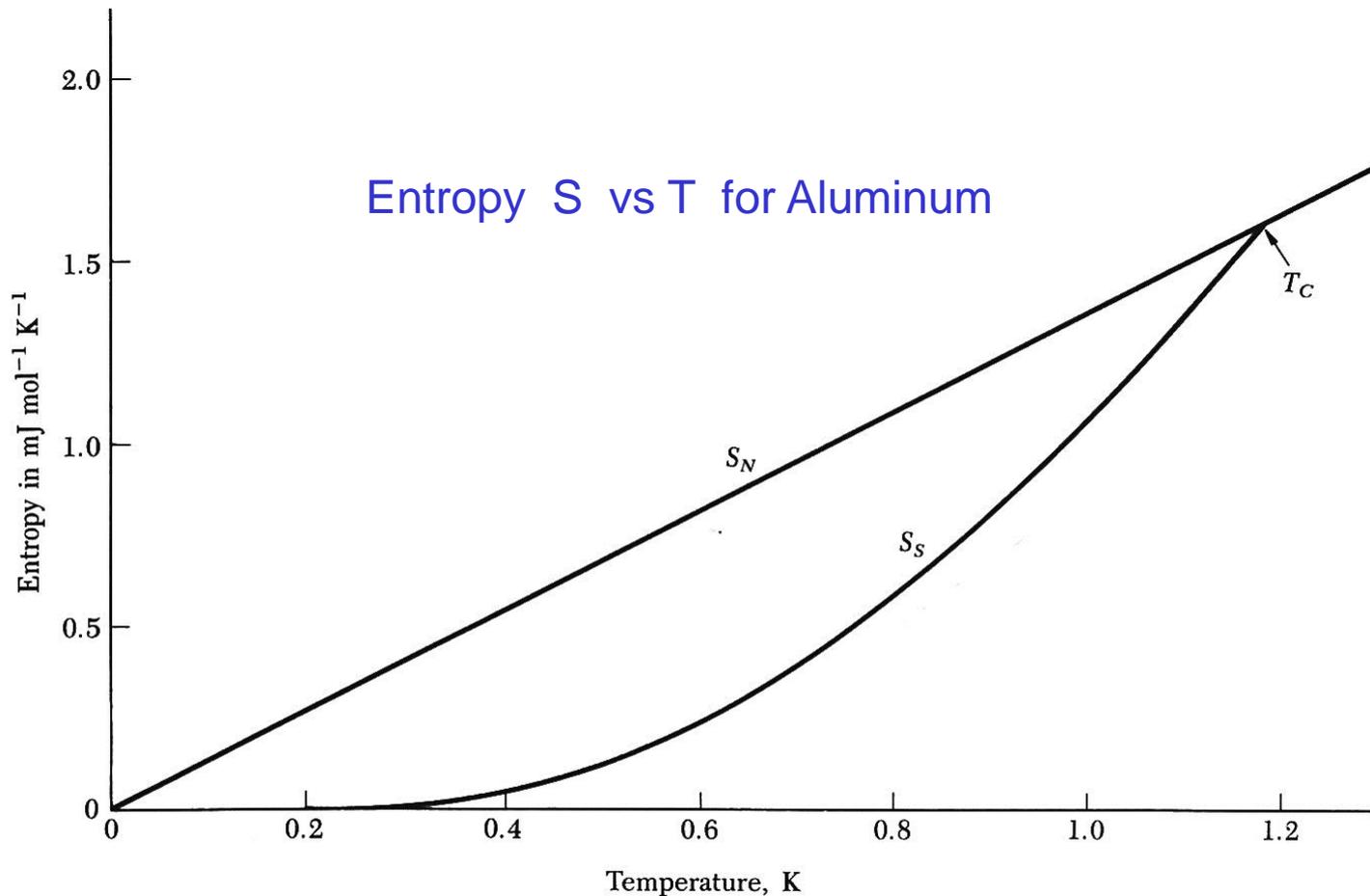
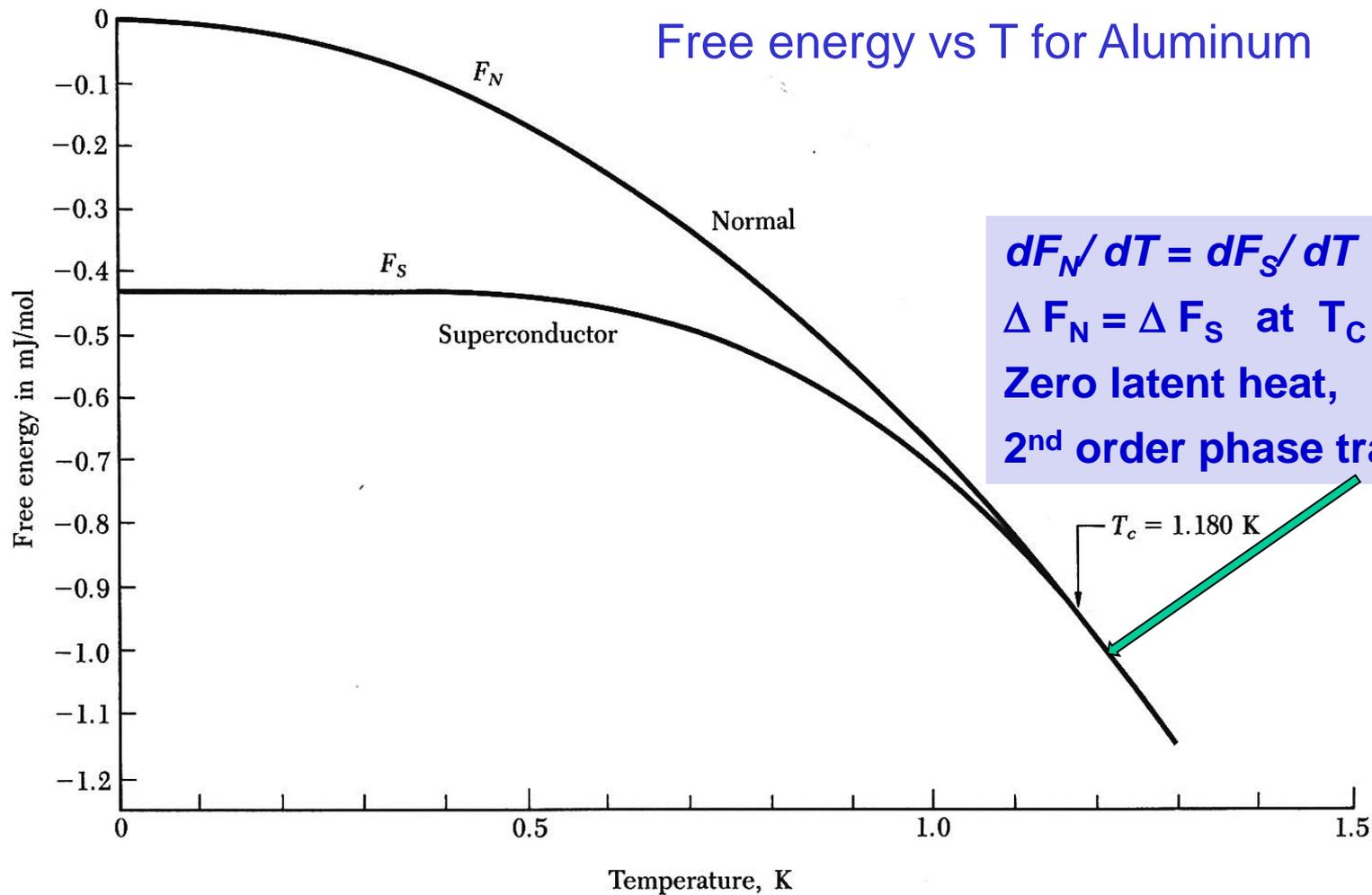


Figure 6 Entropy S of aluminum in the normal and superconducting states as a function of the temperature. The entropy is lower in the superconducting state because the electrons are more ordered here than in the normal state. At any temperature below the critical temperature T_c the specimen can be put in the normal state by application of a magnetic field stronger than the critical field.

The small entropy change must mean that only a small fraction (of the order of 10^{-4}) of the conduction electrons participate in the transition to the ordered superconducting state.

Free energy vs T for Aluminum



So that the phase transition is second order (there is no latent heat of transition at T_c).

heat capacity of an electron gas is

$$C_{el} = \frac{1}{3} \pi^2 D(\epsilon_F) k_B^2 T \quad (34)$$

$$D(\epsilon_F) = 3N/2\epsilon_F = 3N/2 k_B T_F \quad (35)$$

$$C_{el} = \frac{1}{2} \pi^2 N k_B T/T_F \quad (36)$$

Compare with $C_V = 2Nk_B T/T_F$

where $\epsilon_F = k_B T_F$

T_F is called the Fermi temperature,

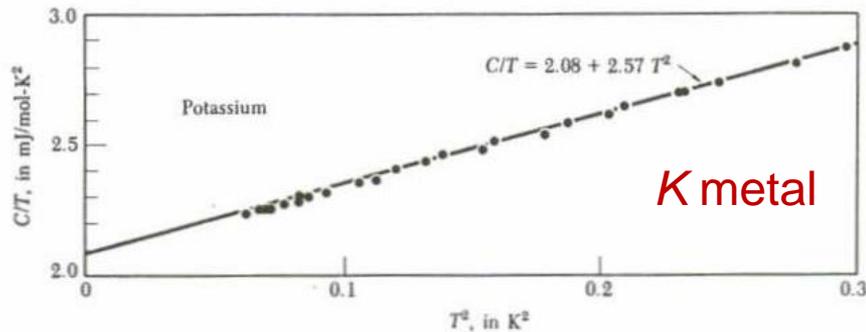


Figure 9 Experimental heat capacity values for potassium, plotted as C/T versus T^2 . (After W. H. Lien and N. E. Phillips.)

$$\gamma = \frac{1}{2} \pi^2 N k_B T/T_F \quad \text{Since } \epsilon_F \propto T_F \propto 1/m \quad \therefore \gamma \propto m \quad (\text{See Eq. 17})$$

At temperatures much below both the Debye temperature and the Fermi temperature, the heat capacity of metals may be written as the sum of electron and phonon contributions: $C = \gamma T + AT^3$

$$C/T = \gamma + AT^2 \quad (37)$$

γ , called the Sommerfeld parameter

At low T , the electronic term dominates.

Heat Capacity of Ga at low T

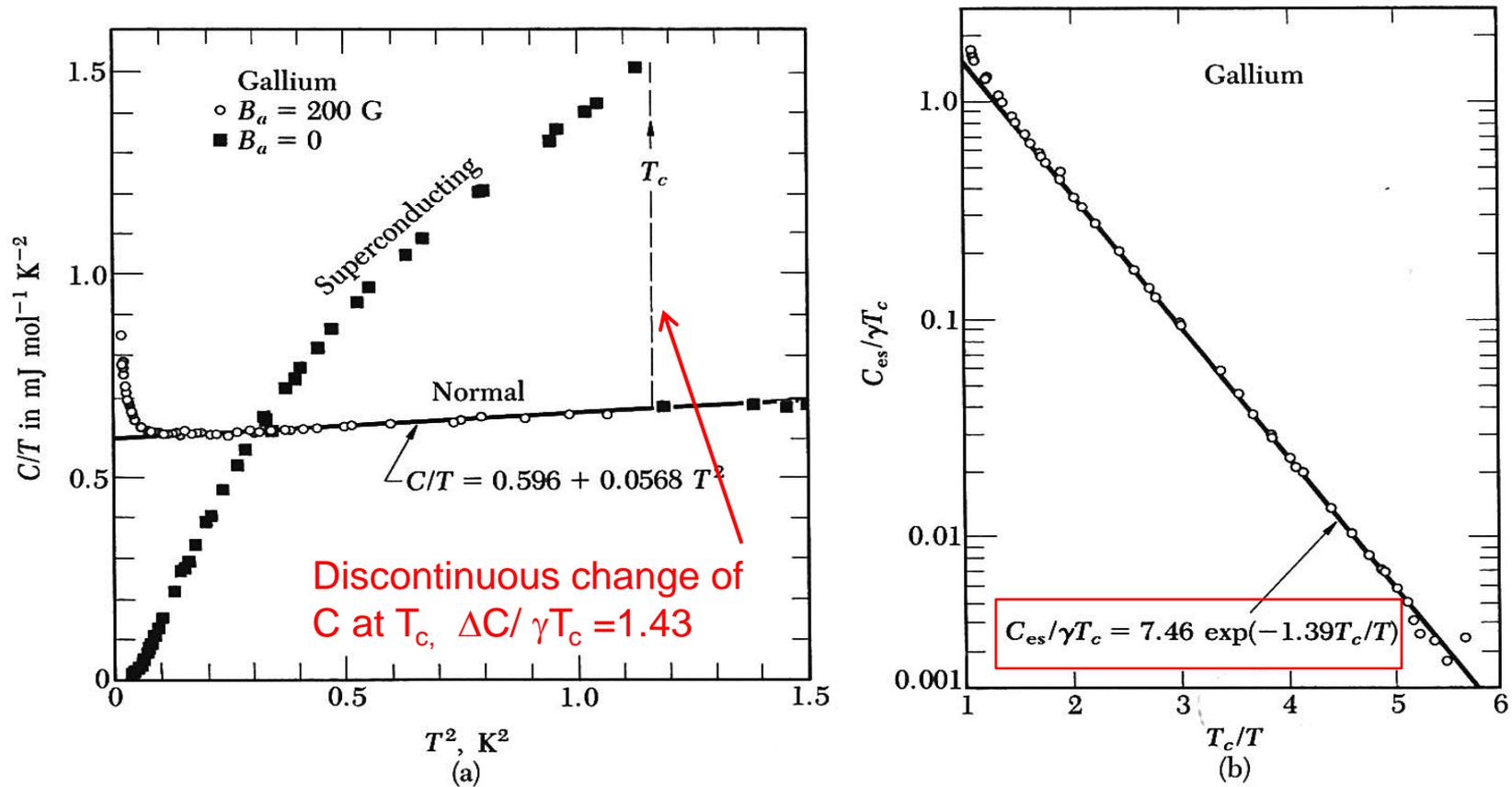


Figure 8 (a) The heat capacity of gallium in the normal and superconducting states. The normal state (which is restored by a 200 G field) has electronic, lattice, and (at low temperatures) nuclear quadrupole contributions. In (b) the electronic part C_{es} of the heat capacity in the superconducting state is plotted on a log scale versus T_c/T : the exponential dependence on $1/T$ is evident. Here $\gamma = 0.60 \text{ mJ mol}^{-1} \text{ deg}^{-2}$. (After N. E. Phillips.)

Electronic part of heat capacity in SC state: $C_{es} / \gamma T_c \propto \mathbf{a \exp(-b T_c / T)}$

proportional to $-1/T$, suggestive of excitation of electrons across an energy gap.

Energy Gap

In a superconductor the important interaction is the electron-electron interaction via phonons, which orders the electron in the k space with respect to the Fermi gas of electrons.

The exponential factor in the electron heat capacity of a superconductor is found to be $-E_g/2k_B T$

$$C_{es} = \gamma T_c \exp(-1.76 T_c/T)$$

The transition in zero magnetic field from the superconducting state to the normal state is observed to be a second-order phase transition.

Energy Gap of superconductors in **Table 3**

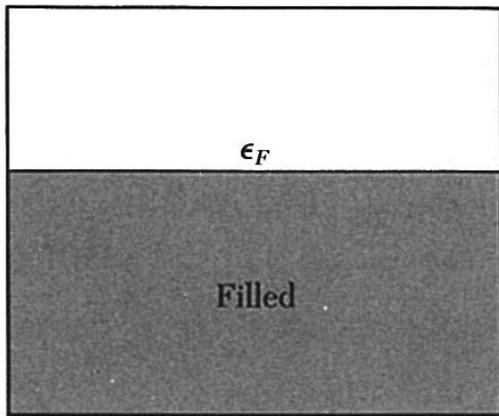
$E_g(0)/k_B T_c = 3.52$ **Weak electron-phonon coupling**

$E_g(0)/k_B T_c > 3.52$ **Strong electron-phonon coupling**

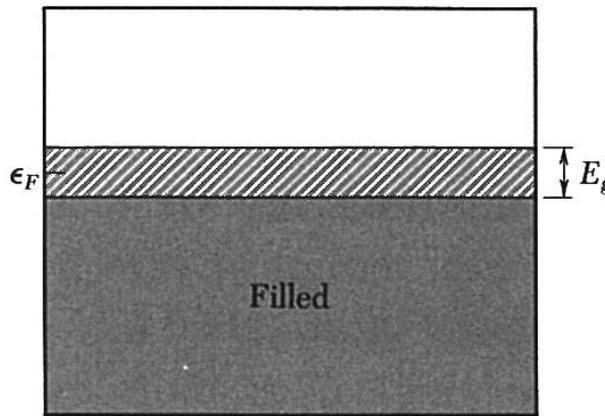
Table 3 Energy gaps in superconductors, at $T = 0$

$$\frac{E_g(0) \text{ in } 10^{-4} \text{ eV.}}{E_g(0)/k_B T_c} = 2\Delta$$

										Al	Si
										3.4	
										3.3	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
		16.							2.4	3.3	
		3.4							3.2	3.5	
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn ^(w)
		30.5	2.7						1.5	10.5	11.5
		3.80	3.4						3.2	3.6	3.5
La ^{fcc}	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg ⁽ⁿ⁾	Tl	Pb
19.		14.							16.5	7.35	27.3
3.7		3.60							4.6	3.57	4.38



Normal
(a)

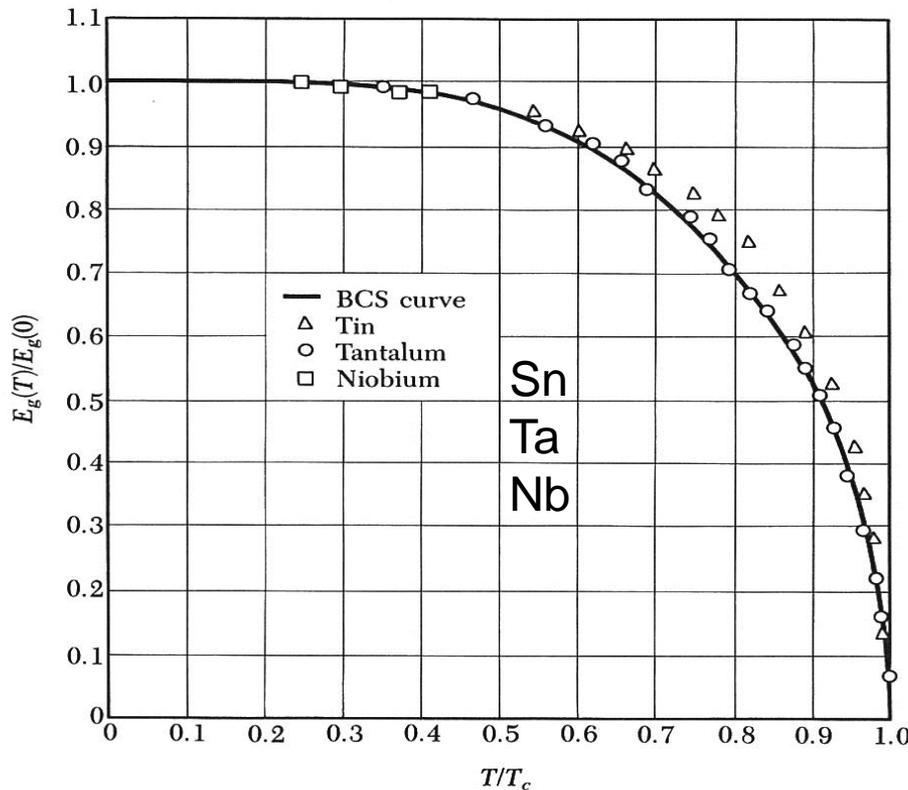


Superconductor
(b)

$$E_g \sim 10^{-4} \epsilon_F$$

1-5 meV

3-10 eV



$$\Delta(T)/\Delta(0) = (1 - T/T_c)^{1/2}$$

Mean field theory

Figure 10 Reduced values of the observed energy gap $E_g(T)/E_g(0)$ as a function of the reduced temperature T/T_c , after Townsend and Sutton. The solid curve is drawn for the BCS theory.

$E_g(T)$ as the order parameter, goes smoothly to zero at T_c

-- second order phase transition

Isotope Effect

It has been observed that the critical temperature of superconductors varies with isotopic mass.

The experimental results within each series of isotopes may be fitted by a relation of the form

$$M^{\alpha}T_c = \text{constant} \quad \alpha \sim 0.5$$

Table 4 Isotope effect in superconductors

Experimental values of α in $M^{\alpha}T_c = \text{constant}$, where M is the isotopic mass.

Substance	α	Substance	α
Zn	0.45 ± 0.05	Ru	0.00 ± 0.05
Cd	0.32 ± 0.07	Os	0.15 ± 0.05
Sn	0.47 ± 0.02	Mo	0.33
Hg	0.50 ± 0.03	Nb ₃ Sn	0.08 ± 0.02
Pb	0.49 ± 0.02	Zr	0.00 ± 0.05

From the dependence of T_c on the isotopic mass we learn that lattice vibrations and hence electron-lattice interactions are deeply involved in superconductivity.

$$\theta \propto \nu \propto M^{-1/2}$$

$$T_c \propto \theta_{\text{Debye}} \propto M^{-1/2}, \text{ so that } \alpha = \frac{1}{2}$$