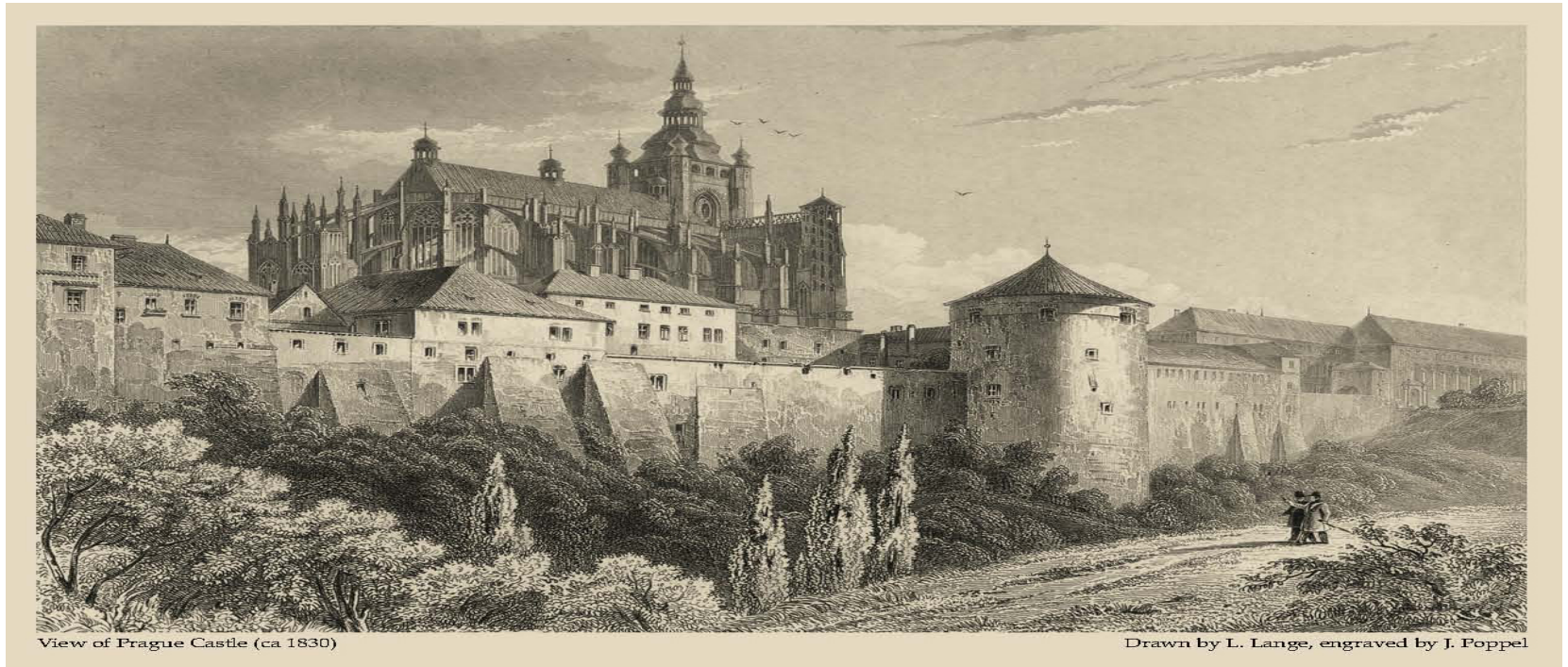


# ***Relaxation Phenomena in the Adiabatic Phase Transition of Type I Superconductor Particles***

**Peter D. Keefe**

**University of Detroit Mercy**



View of Prague Castle (ca 1830)

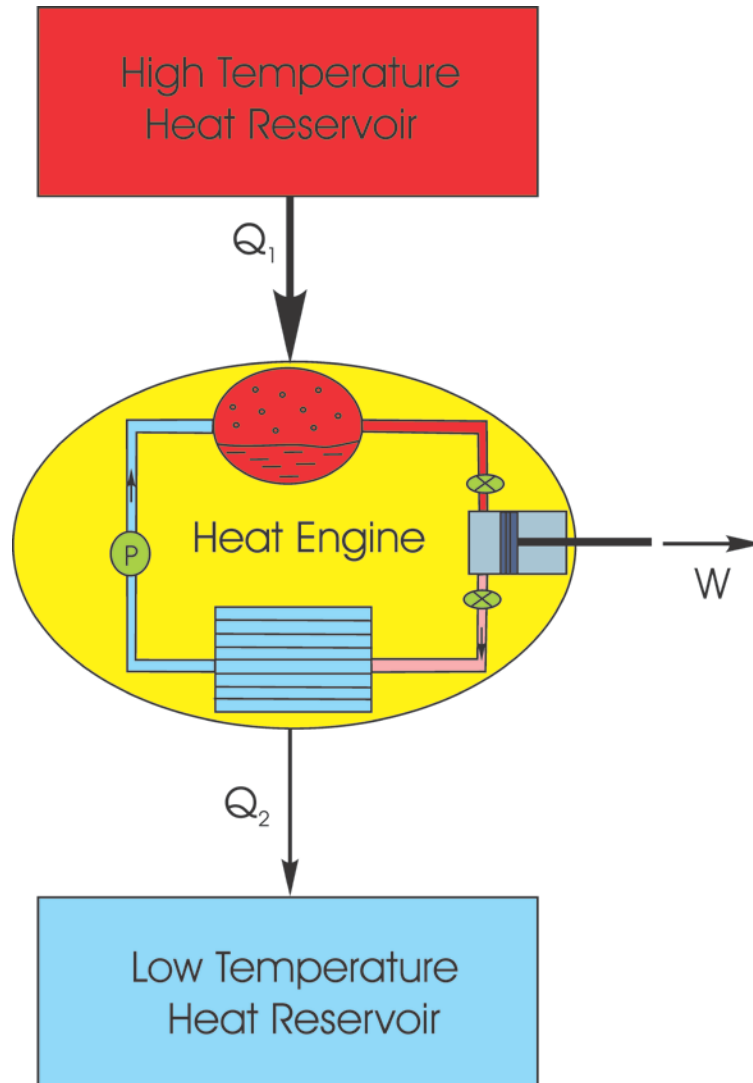
Drawn by L. Lange, engraved by J. Poppel

**Frontiers of Quantum and Mesoscopic Thermodynamics 2011**

**July 25-30, 2011**

**Prague, Czech Republic**

# Classical Heat Engine



Heat,  $Q_1$ , boils water in the boiler. Resulting steam actuates a piston of a valved cylinder, producing work,  $W$ . The cooled steam then passes through a condenser where heat,  $Q_2$ , is rejected to the atmosphere. Resulting water is then pumped back to the boiler.

$$Q_1 = Q_2 + W$$

# Properties of Type I Superconductors

- **Perfect electrical conductor**
- **Perfect diamagnet**
- **Entropy of the superconductive phase is less than the entropy of the normal phase**
- **First order phase transition**

A latent heat is absorbed at the phase transition from superconductive to normal phase because of the difference in entropy of the phases.

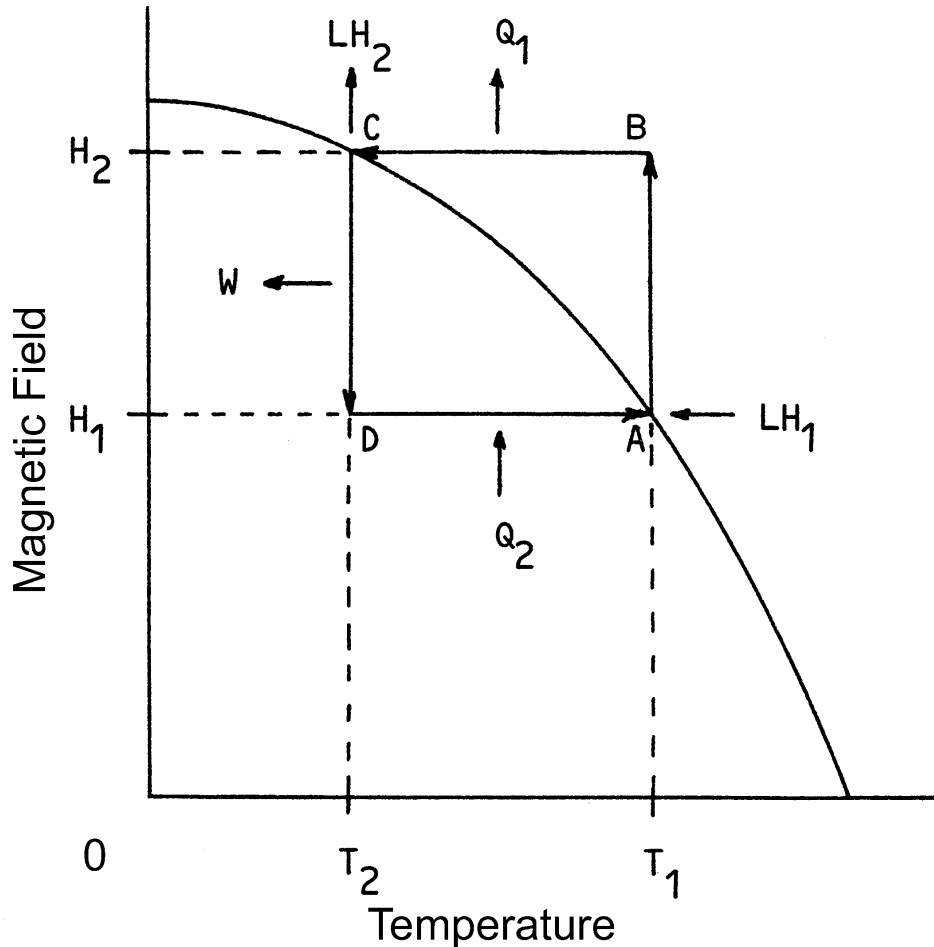
- **Magneto-Caloric Effect**

An adiabatically isolated superconductor driven normal by a magnetic field will self-cool because of the first order phase transition.

- **Meissner Effect**

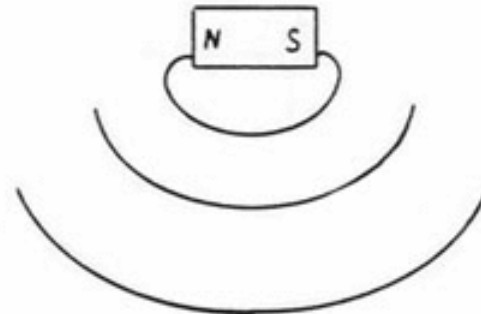
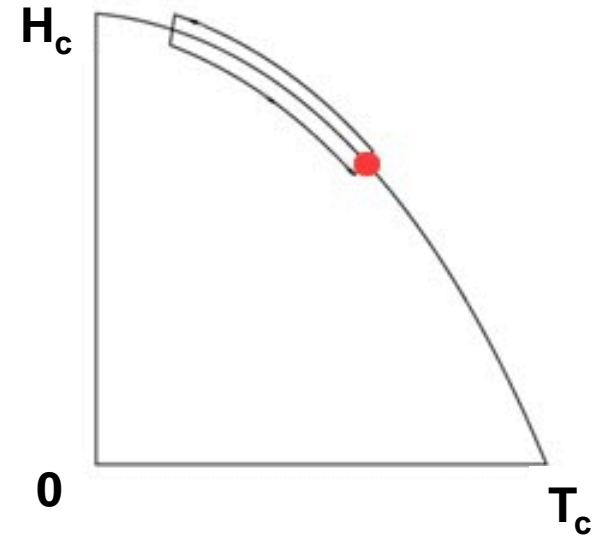
Expulsion of magnetic field occurs by merely lowering the temperature.

# Heat Engine Using a Bulk Superconductor as the Working Media



$$W_{\text{out}} = Q_{\text{in}} = (LH_1 - LH_2) + (Q_2 - Q_1)$$

$$\eta = [1 - (Q_1 + LH_2) / (Q_2 + LH_1)] \times 100$$



normal phase

superconductive phase

# The Magneto-Caloric Effect

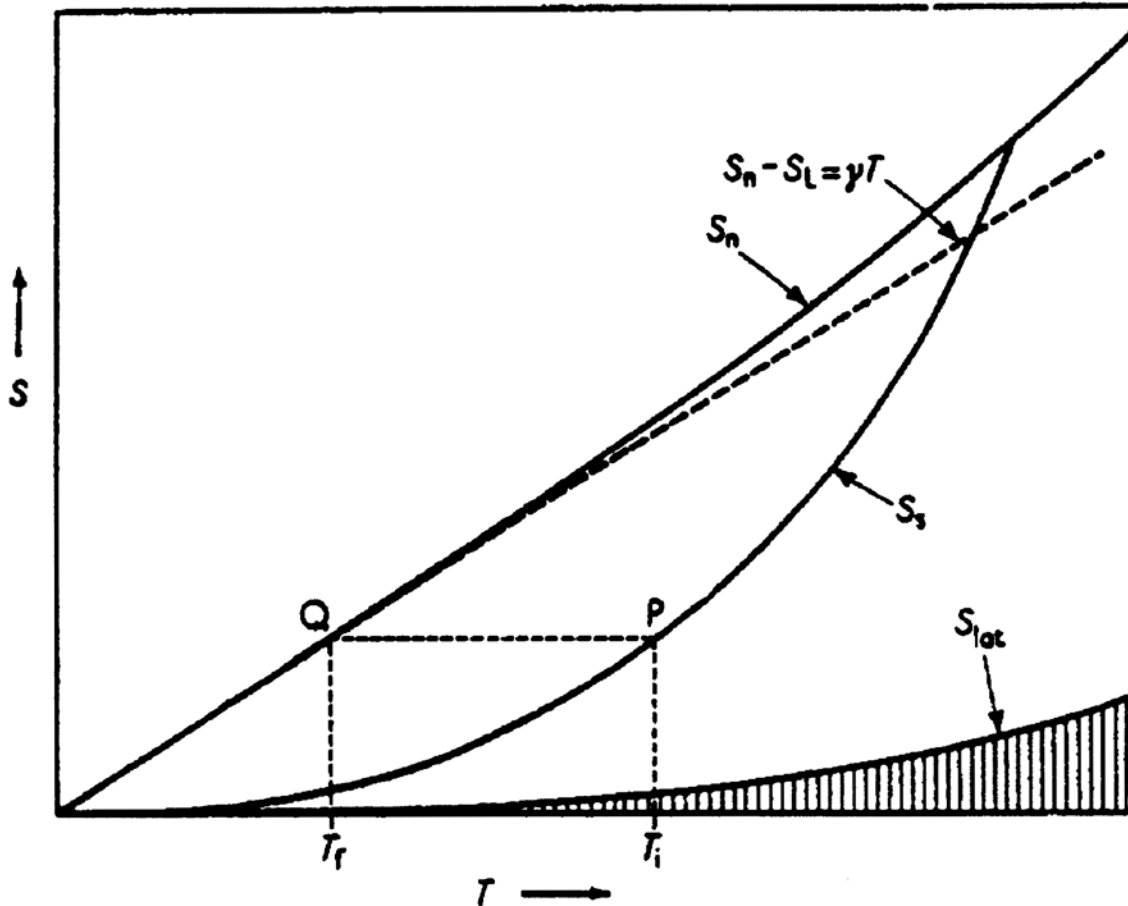


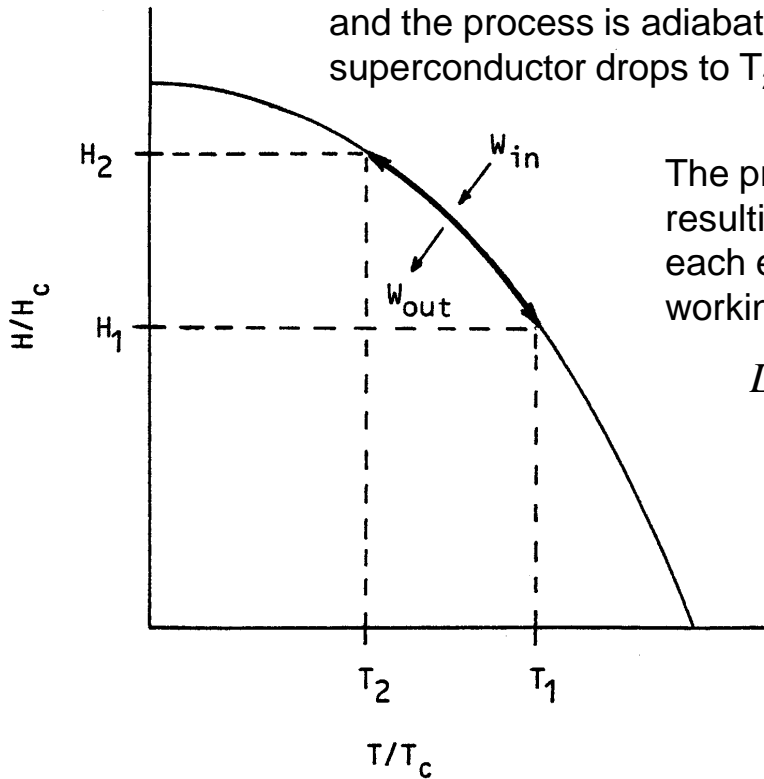
Figure 1. Diagram of entropy  $S$  versus temperature  $T$  curve

Taken from M. Yaqub, *Cryogenics*, December, 1960, 101

When a Type I Superconductor in the superconductive phase is driven normal by an increasing magnetic field, the phase transition is first order, and the temperature drops. The process is isentropic, and the final temperature is determined by the isentrop  $P$ - $Q$ .

# Adiabatic Phase Transition Process Performed on a Bulk Size ( $d \gg \lambda$ ) Superconductor Working Media

Beginning at  $T_1$  in the superconductive phase, the magnetic field is raised from  $H_1$  to  $H_2$ . Because the phase transition is first order and the process is adiabatic, the temperature of the superconductor drops to  $T_2$ .

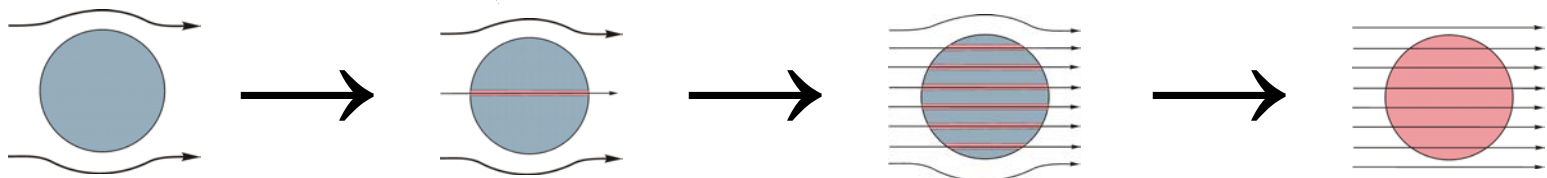


The process is performed infinitely slowly in increments of  $\Delta H$ , resulting in incremental phase volume changes,  $\Delta V$ , and for each elemental volume change, the latent heat cools the working medium by the relation:

$$LH_{\Delta V} = \int_{T_a}^{T_b} (C_n dT)(V_n + \Delta V) + \int_{T_a}^{T_b} (C_s dT)(V_s - \Delta V)$$

The process is reversed from  $T_2$  to  $T_1$ .

Magnetic work,  $W_{in}$ , is input and magnetic work,  $W_{out}$ , is output, where  $W_{in} = W_{out}$  due to the in-process presence of superconductive phase in the intermediate state.



Superconductive phase

Intermediate State

Normal phase

# The Magneto-Caloric Effect

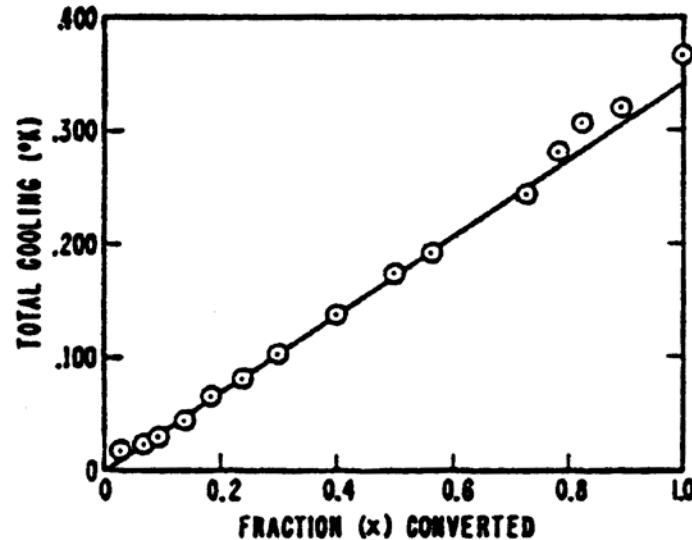
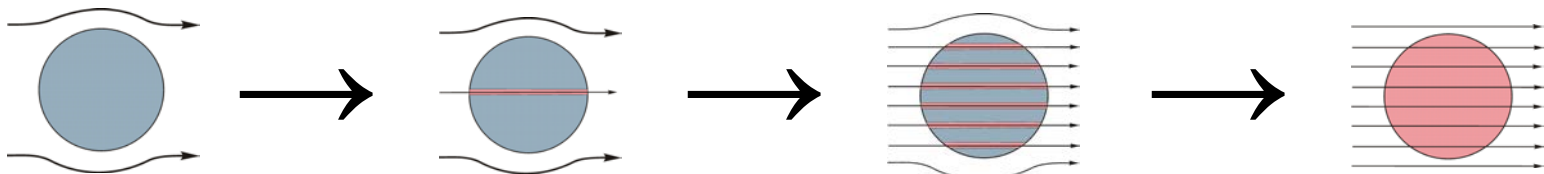


FIG. 2. Demonstration of the linear relationship between the applied magnetic field and the fraction of normal metal produced in the intermediate state. The straight line is drawn with a slope to fit best the data  $x \leq 0.6$  for which eddy-current corrections are small.

Taken from R. Dolecek, *Phy. Rev.* 96, 25 (1954)



Superconductive phase

Intermediate State

Normal phase



# Size Scale Regimes

- **Macroscopic Regime**

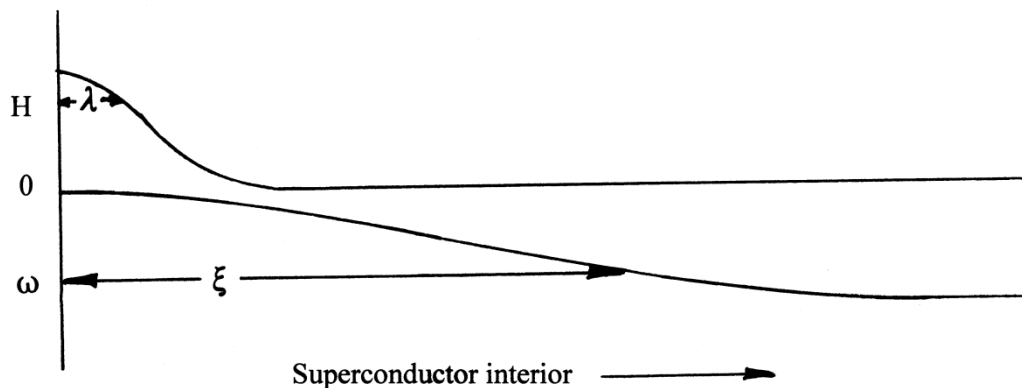
- The cross-section of the working media is much larger than the coherence length,  $\xi$ .
- Ensemble averaging results in relaxation time differences of the phase space variables being unobservable.

- **Mesoscopic Regime**

- The cross-section of the working media is about equal to the coherence length,  $\xi$ .
- Homogeneous coherence results in relaxation time differences of the phase space variables being observable.

- **Microscopic Regime**

- The cross-section of the working media is much smaller than the coherence length  $\xi$ .
- Vanishing dimensionality results in relaxation time differences of the phase space variables being unobservable.



$\delta$  represents the “*penetration depth*” of the applied magnetic field, H, at the surface of the superconductor.  $\delta$  is on the order of about  $10^{-5}$  cm.

$\xi$  represents the “*coherence length*” of the order parameter, T, of the superelectrons.  $\xi$  is on the order of about  $10^{-4}$  cm.



# Size and the Intermediate State

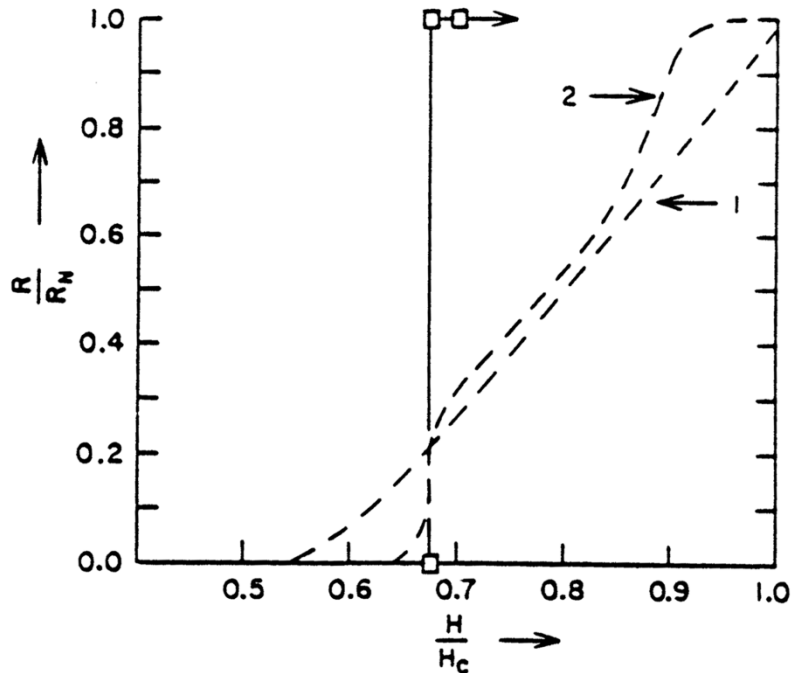
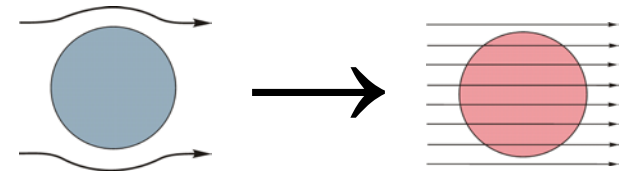


FIG. 2. Comparison of whisker transition with results of Andrew for larger wires. 1—Andrew,  $1.05 \times 10^{-1}$  cm diameter,  $1.66^\circ\text{K}$ . 2—Andrew,  $27 \times 10^{-4}$  cm diameter,  $1.66^\circ\text{K}$ .  $\square$ —whisker,  $1.2 \times 10^{-4}$  cm diameter,  $1.69^\circ\text{K}$ .

Taken from O. Lutes, E. Maxwell, *Phy. Rev.* 97, 1718 (1955)

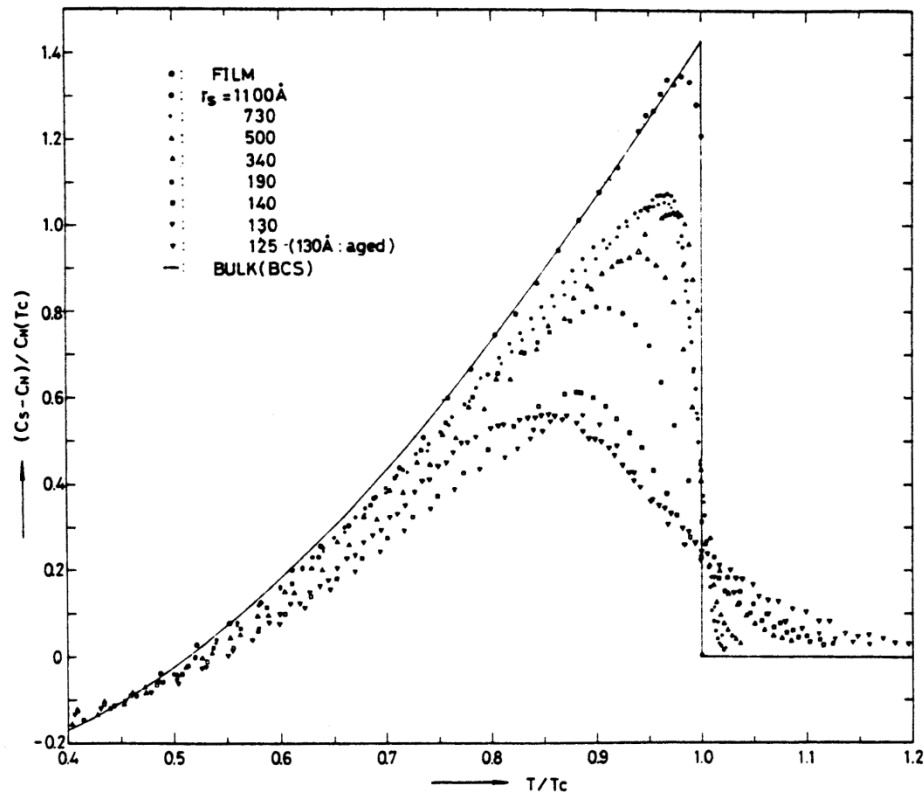
**Lutes and Maxwell discovered that for thin cylinders (whiskers) of tin having  $N=1/2$  and diameter near  $\lambda(T)$ , an intermediate state is not observed.**



Superconductive phase

Normal phase

# Size and Specific Heat



**Tsuboi and Suzuki report that for cross-sections in the range of about  $d = \lambda(T)$ , the specific heat function remains that applicable to bulk specimens.**

Fig. 5. Specific heat difference for Sn particles with different particle sizes as a function of the reduced temperature. The difference is normalized to  $C_N(T_c)$ , where  $C_N(T_c) = \gamma T_c$  with  $\gamma = 1.78 \text{ mJ} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}$ .

Taken from T. Tsuboi, T. Suzuki, J. Phy. Soc. Jap., 42, 437 (1977)

# Size and First Order Phase Transition

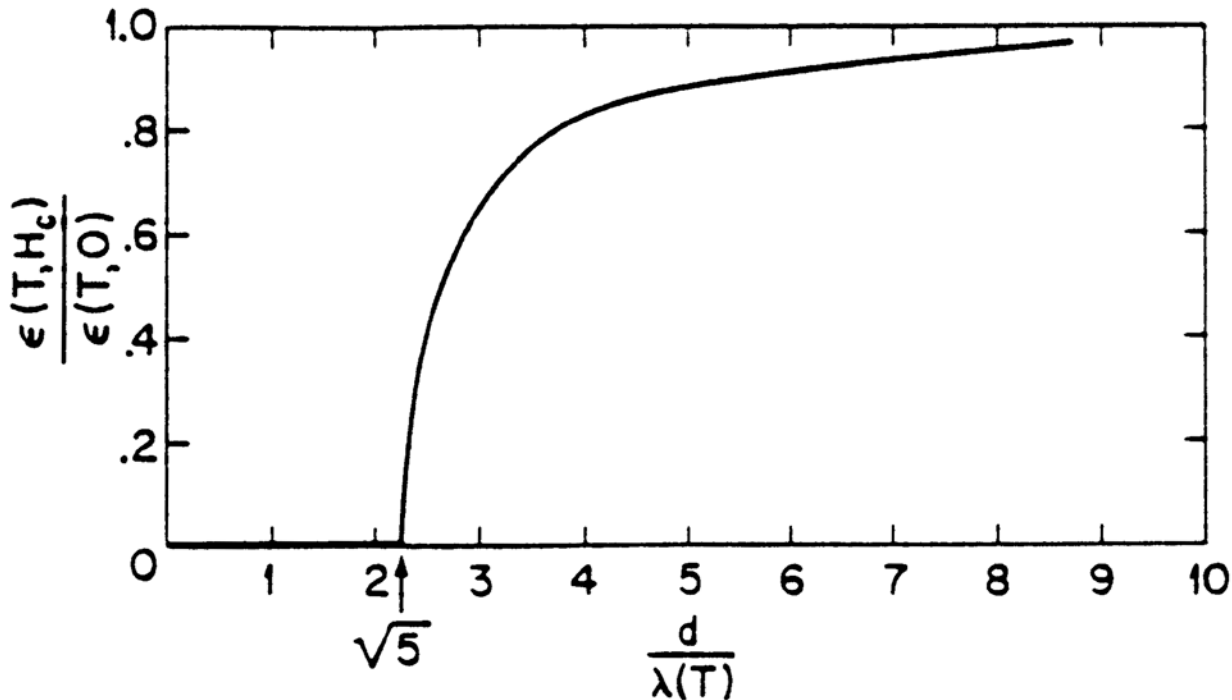


FIG. 1. Energy gap at the critical field vs thickness.

Taken from D. H. Douglass, *Phy. Rev. Lett.* 6, 346 (1961)

**Douglass predicts that upon application of  $H_c$ , the phase transition can be second order with no latent heat for cross-sections,  $d$ , of  $d < \sqrt{58}(T)$ , or be first order with a reduced latent heat for cross-sections of  $\sqrt{58}(T) < d < 58(T)$ .**

# Relaxation Times of the State Variables (T, H)

- **Thermal Relaxation (T)**

At very low temperature, heat transfer through the working media is mainly mediated by phonons through the lattice and minimally by the conduction electrons. In Al, an upper limit of phonon propagation<sup>1</sup> is about  $6.5 \times 10^3$  m/s, therefore requiring about  $10^{-8}$  seconds to travel a distance  $\lambda$ .

- **Electrodynamic Relaxation (H)**

The rate of magnetic flux movement is related to the speed of electromagnetic (E-M) waves through the working media. In Al, a lower limit of E-M wave propagation<sup>2</sup> is about  $1.5 \times 10^6$  m/s, therefore requiring about  $10^{-11}$  seconds to travel a distance  $\lambda$ .

For the macroscopic and microscopic regimes, where the phase transition is characterized by equilibrium processes, the thermal and electrodynamic relaxations are considered to be simultaneous and coupled, occurring<sup>3</sup> between about  $10^{-8}$  and  $10^{-11}$  seconds.

For the mesoscopic regime, where the phase transition is characterized by non-equilibrium processes, the thermal and electrodynamic relaxations are considered to be non-simultaneous and decoupled, where the electrodynamic relaxation time is several orders of magnitude faster than the thermal relaxation time.

1. CRC Handbook of Chem. and Phys., 51<sup>st</sup> Ed., pg. E-41.

2. Measurement Science Rev., V.4., Sec. 3 (2004).

3. Prog. in Low Temp. Phys., VI, 172 (1955).

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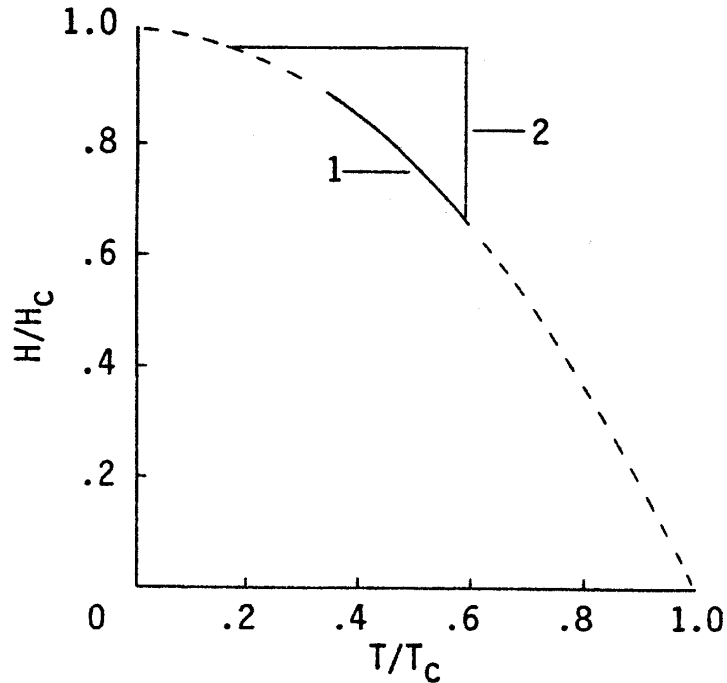
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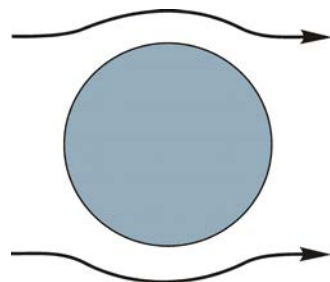
3. Prog. in Low Temp. Phys., VI, 172 (1955).

# Adiabatic Phase Transition Process Performed on a Particle Size ( $d = \gg$ ) Superconductor Working Media

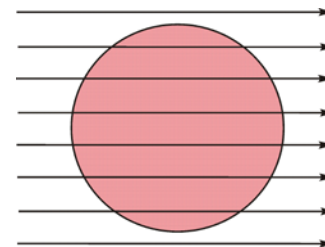


**Curve 1** represents the macroscopic adiabatic demagnetization process, performed at an infinitely slow rate so that the ensemble entropy remains constant.

**Curve 2** represents the mesoscopic adiabatic demagnetization process, performed at a maximal rate allowed by the difference in thermal and electrodynamic relaxation times.

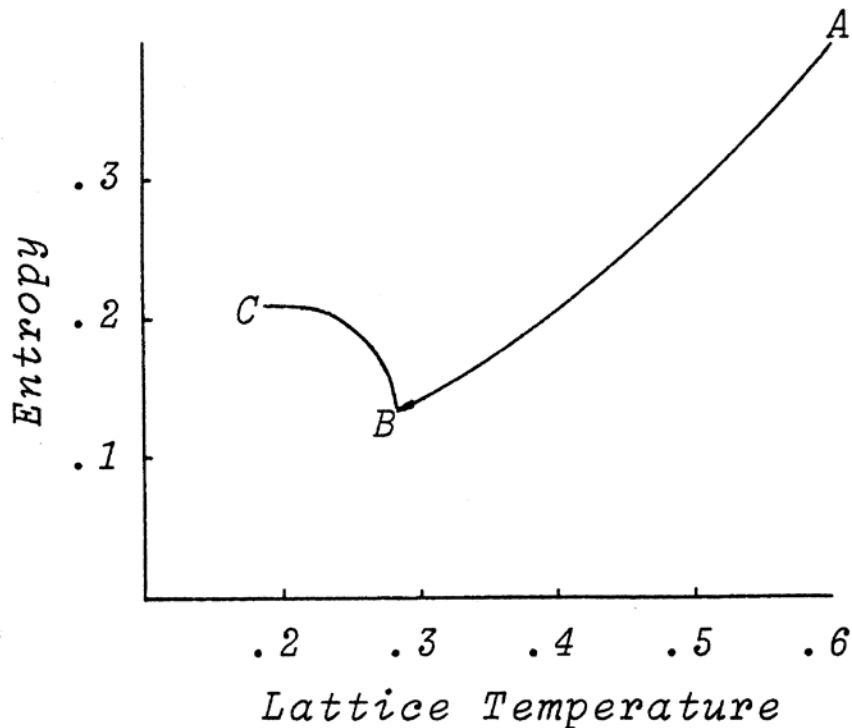


Superconductive phase



Normal phase

# Experiment Theory



**Point A:** Starting at  $T_1 = .6 T_c$ , in the superconductive phase.

**Point A to Point B:** Superelectrons below the Fermi sea gain entropy from the lattice and normal conduction electrons; overall entropy decreases.

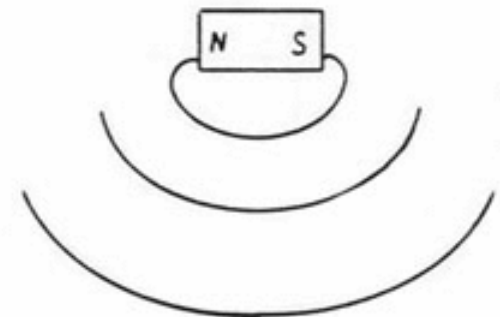
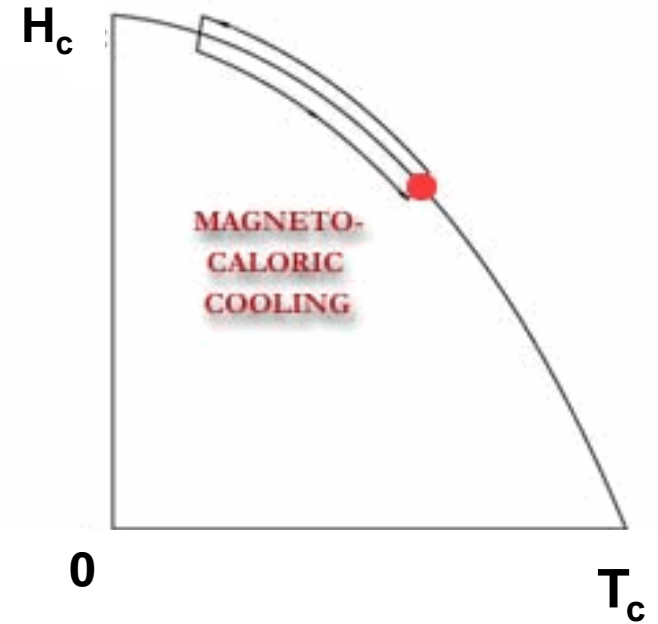
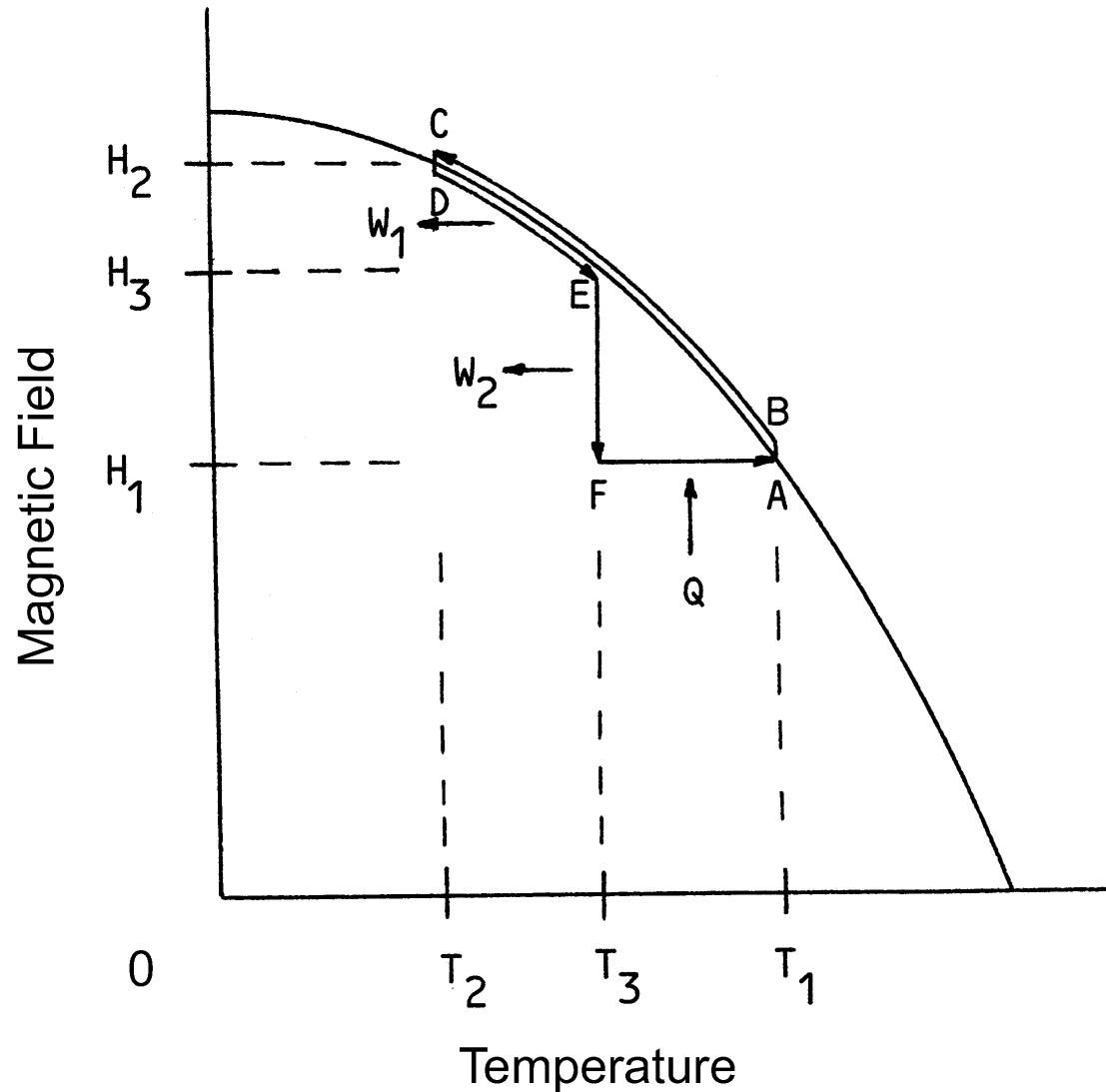
**Point B to Point C:** Superelectrons now above the Fermi sea continue to gain entropy from the lattice and normal conduction electrons; overall entropy increases.

**Point C:** Ending at  $T'_2 = .186 T_c$ , in the normal phase. The ending entropy is lower than the starting entropy, in violation of conventional formulations of the 2<sup>nd</sup> Law.

Temperature is in terms of  $T/T_c$  and entropy is in arbitrary units.



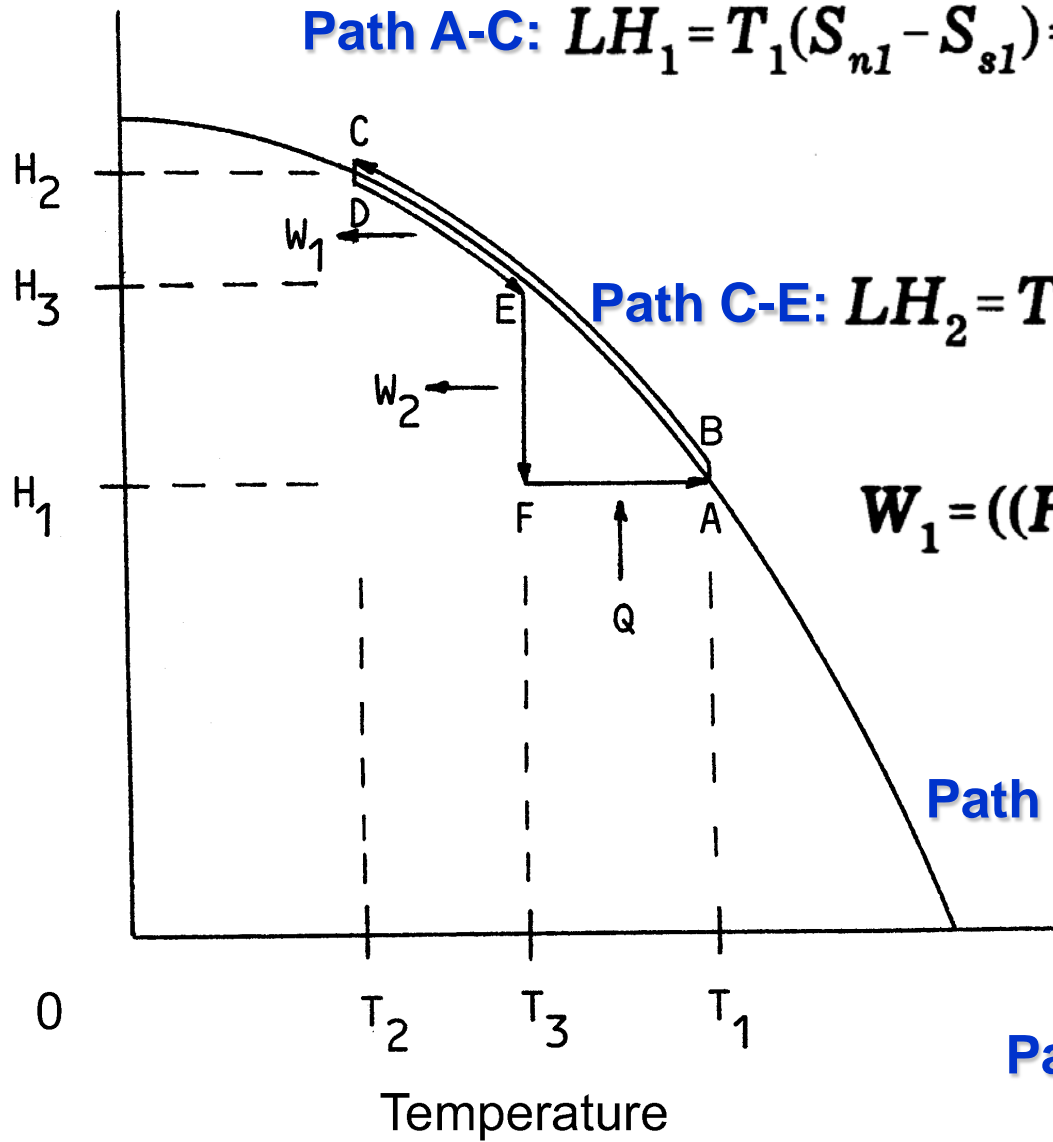
# Coherent Magneto-Caloric Effect Magnetization Process Cycle



normal phase

superconductive phase

Magnetic Field



**Path A-C:**  $LH_1 = T_1(S_{n1} - S_{s1}) = \left( \int_{T_1}^{T_2} C_n dT \right) \cdot V$

**Path C-E:**  $LH_2 = T_2(S_{n2} - S_{s2}) = \left( \int_{T_2}^{T_3} C_s dT \right) \cdot V$

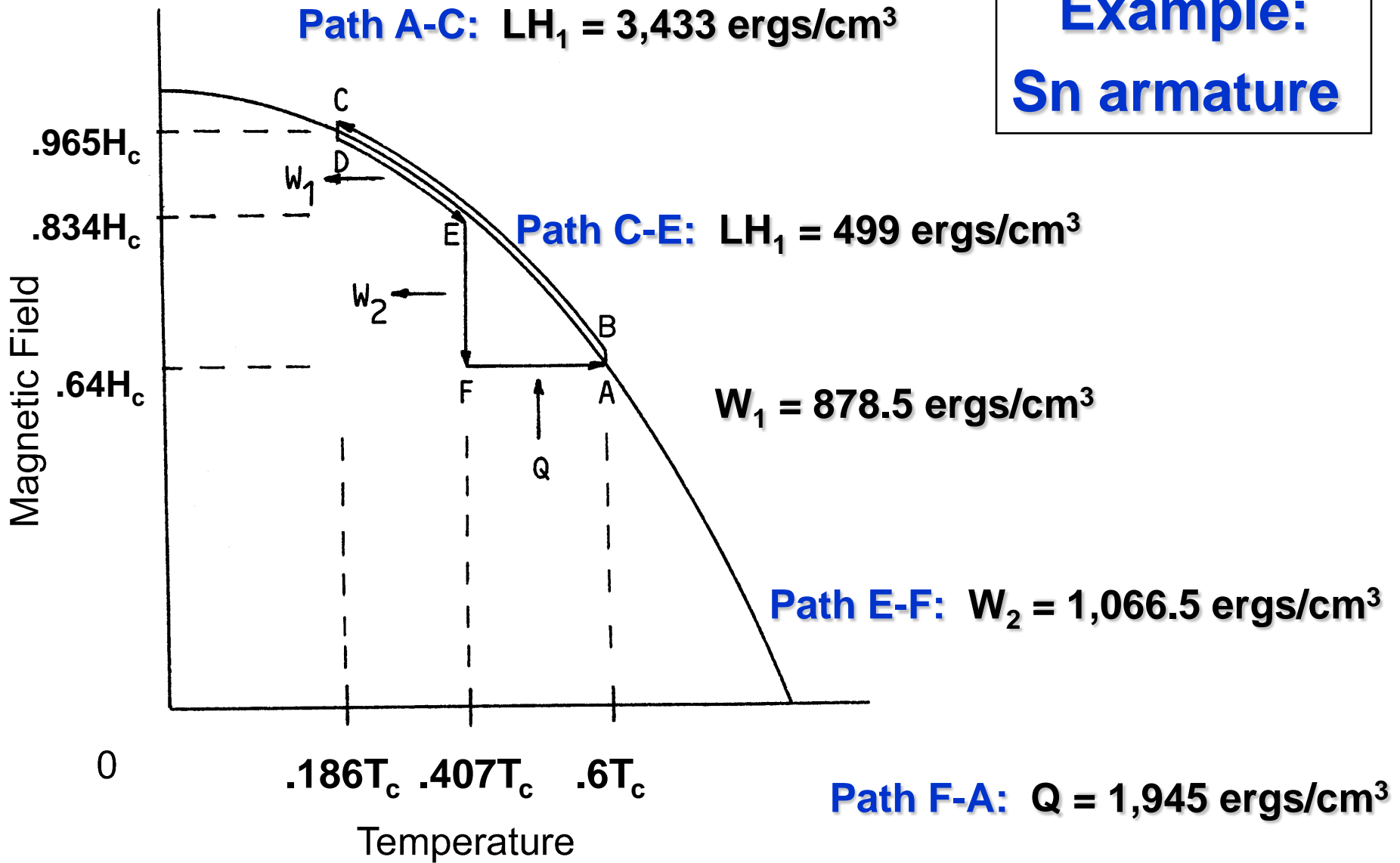
$W_1 = ((H_2^2 - H_3^2) / 8\pi) \cdot V$

**Path E-F:**  $W_2 = ((H_3^2 - H_1^2) / 8\pi) \cdot V$

**Path F-A:**  $Q = \left( \int_{T_3}^{T_1} C_s dT \right) \cdot V$

**$Q = W_1 + W_2$**

**Example:  
Sn armature**



$$Q = W_1 + W_2 = 1,945 \text{ ergs/cm}^3$$

An intermediate state is not possible if the cross-section of the armature,  $d$ , is such that  $\lambda(T) > d$ .

A first order phase transition requires  $d > \sqrt{58}(T)$ , preferably  $d > 58(T)$ .

Possible  $\lambda(T) > d > 58(T)$  superconductors:

**aluminum**, where  $\lambda/8 = 32$

**indium**, where  $\lambda/8 = 6.875$

**tin**, where  $\lambda/8 = 4.5$

University of Illinois  
at Urbana-Champaign

Department of Physics  
Loomis Laboratory of Physics  
1110 West Green Street  
Urbana  
Illinois 61801

March 25, 1987

Dr. Peter D. Keefe  
E. E. & Physics Faculty  
4001 West McNichols Road  
Detroit, MI 48221-9987

Dear Dr. Keefe:

At long last I have found a little time to study your proposal. The reprints of the earlier literature have been very helpful. However, I am puzzled by the cooling step that you say involves no work and no heat input. It should be possible to go from the superconducting phase at  $T_1, H_1$  to a normal phase at  $T_2$ , but then one would have to reduce the field at  $T_2$  to bring it into the superconducting phase. The adiabatic transition from  $T_1, H_1$  to  $T_2, H_2$  would require an input of work in the cooling step and there would be dissipation of heat in going from the normal to superconducting phases at  $T_2$ . The work input at the cooling step would be greater than the work output at the heating step, resulting in a net input of work going into heat.

Apparently you would like to have an adiabatic step from the superconducting phase at  $T_1, H_1$  to normal at  $T_2, H_2$ , but I don't see how this can happen without violating the laws of thermodynamics. Further the minimum applied field,  $H_a$ , must satisfy

$$F_s(T_1) + \frac{H_a^2}{8\pi} = F_n(T_2)$$

or

$$\frac{H_a^2}{8\pi} = F_n(T_2) - F_s(T_1)$$

with the condition  $S_s(T_1) = S_n(T_2)$ . Since  $F_s(T_1) < F_s(T_2)$ ,  $H_a$  must be greater than  $H_2$ . This implies that the transition cannot take place at  $H_1$ , but there must be considerable "superheating" to the higher field  $H_a$ . When at  $T_2$  the field must be reduced below  $H_2$  to make the transition to the superconducting phase. Heat is then released to the low temperature reservoir. Since the transition takes place at  $H_a$ , work that must be done on the system as  $H_1$  increases to  $H_a$ . This is more than the external work obtained as the system is heated.

Perhaps I have misinterpreted your ideas, but it seems to me that it is the assumption of no superheating that is at fault. It is a long time since I have thought about the thermodynamics of superconductors.

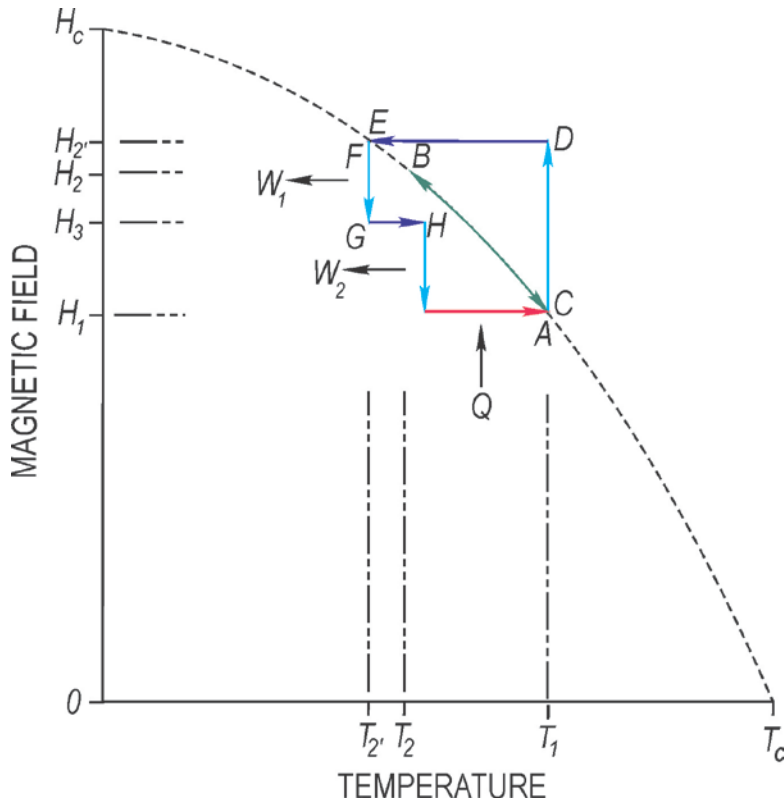
Sincerely,

*John Bardeen*  
John Bardeen

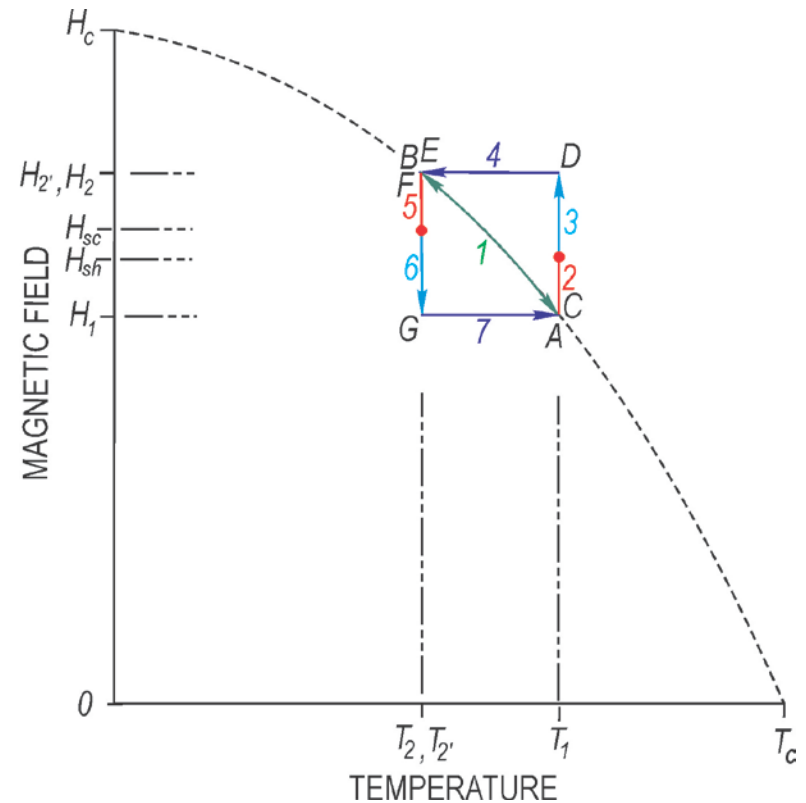
**John  
Bardeen**

Private communication  
to the Author, 03/25/1987

# Bardeen's Hypothesis of Superheating and Supercooling Fields



No Magnetic Hysteresis



Bardeen's Magnetic Hysteresis

# Magnetic Hysteresis in a Mesoscopic Type I Superconductor

XXI. *Magnetic Hysteresis in Superconducting Colloids*

By A. B. PIPPARD

Royal Society Mond Laboratory, Cambridge\*

[Received November 2, 1951]

## ABSTRACT

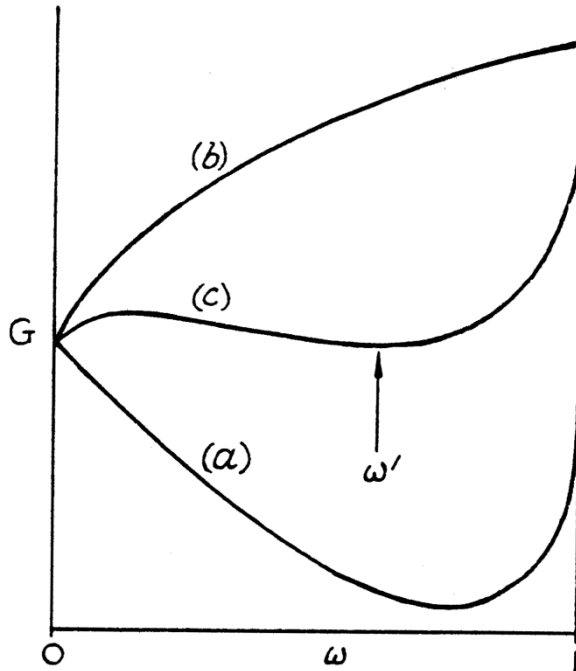
The irreversible effects exhibited in the magnetization cycle of a superconducting colloid are analysed in terms of a simple model of a superconductor. Expressions are derived relating various critical field strengths to temperature and radius of the particle ; there is fair agreement between experiment and theory.

Taken from A. B. Pippard, *Phil. Mag.*, 43, 273 (1952)



# Origin of Superheating in a Mesoscopic Type I Superconductor

Fig. 1



Gibbs function of small particle :

- (a) in absence of field,
- (b) field contribution,
- (c) resultant curve for  $G$ .

Taken from A. B. Pippard,  
Phil. Mag., 43, 273 (1952)

**Pippard suggests that the Gibbs function (curve c) is related to two contributions:**

- 1) The ordering of the electrons,  $\omega$ , (curve a) in absence of magnetic field; and**
- 2) The diamagnetic energy of the excluded magnetic field (curve b);**

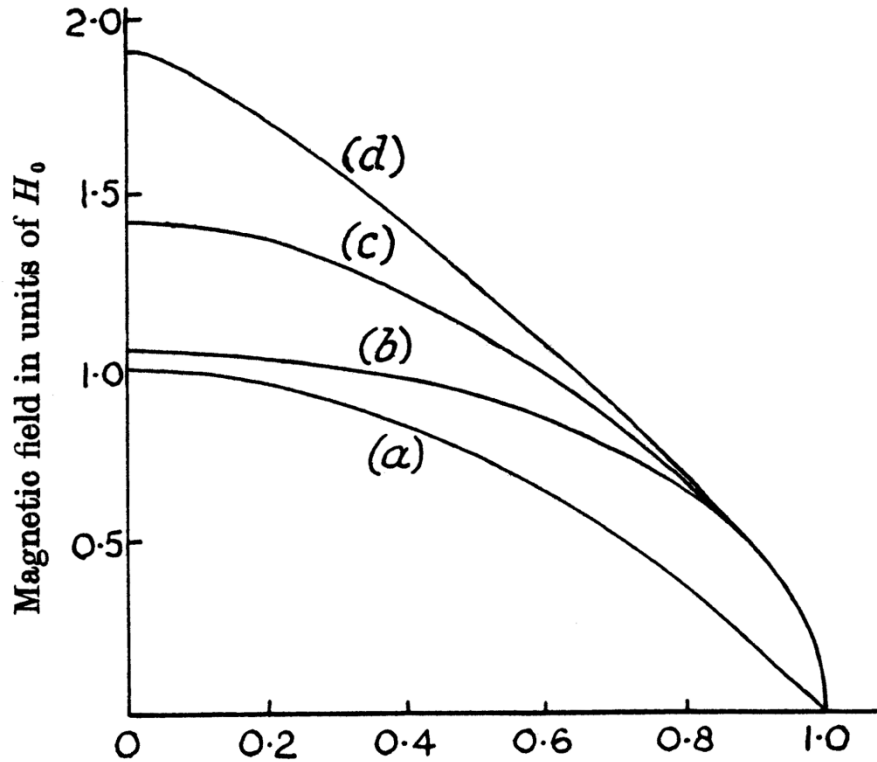
**wherein the Gibbs potential is the resultant curve c, and the minimum value  $\omega'$  is the Gibbs potential at  $H_c$ .**

**Magnetic hysteresis arises when there is an increase in free energy along curve c between 0 and  $\omega'$ , creating a potential barrier to the phase transition.**

# Superheating in a Mesoscopic Type I Superconductor

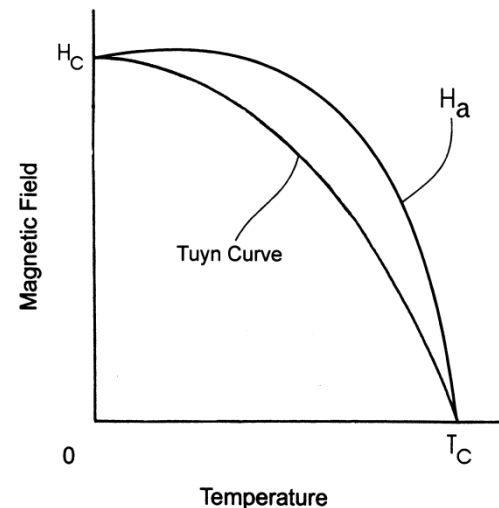
Fig. 6

Pippard predicts that critical field hysteresis is maximum at absolute zero, and disappears at finite temperature, well below  $T_c$ . This result is in fatal conflict with Bardeen's Hypothesis.



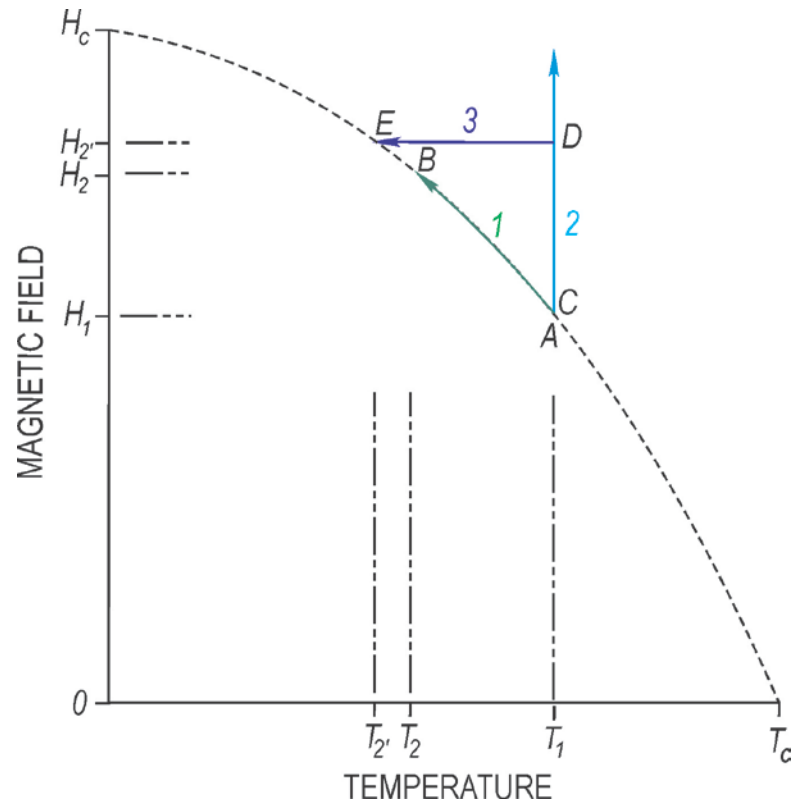
Critical fields versus reduced temperature :

- (a)  $H_c$  for bulk material,
- (b)  $H_{sc}$  for colloidal sphere of radius  $3\lambda_0$ ,
- (c)  $H_e$  for colloidal sphere of radius  $3\lambda_0$ ,
- (d)  $H_{sh}$  for colloidal sphere of radius  $3\lambda_0$ .

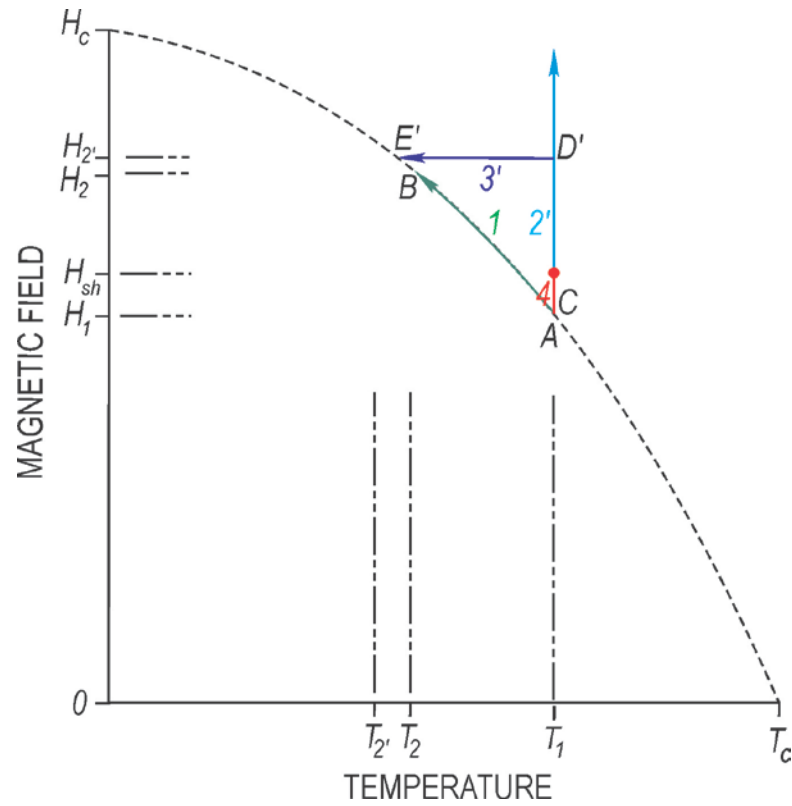


Taken from A. B. Pippard, Phil. Mag., 43, 273 (1952)

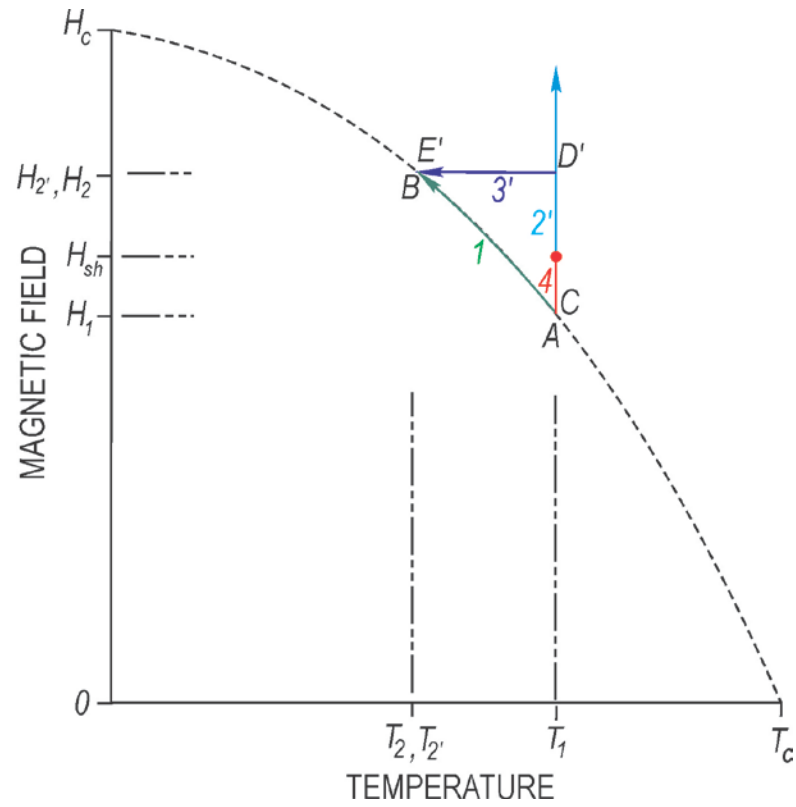
# Experiment Theory



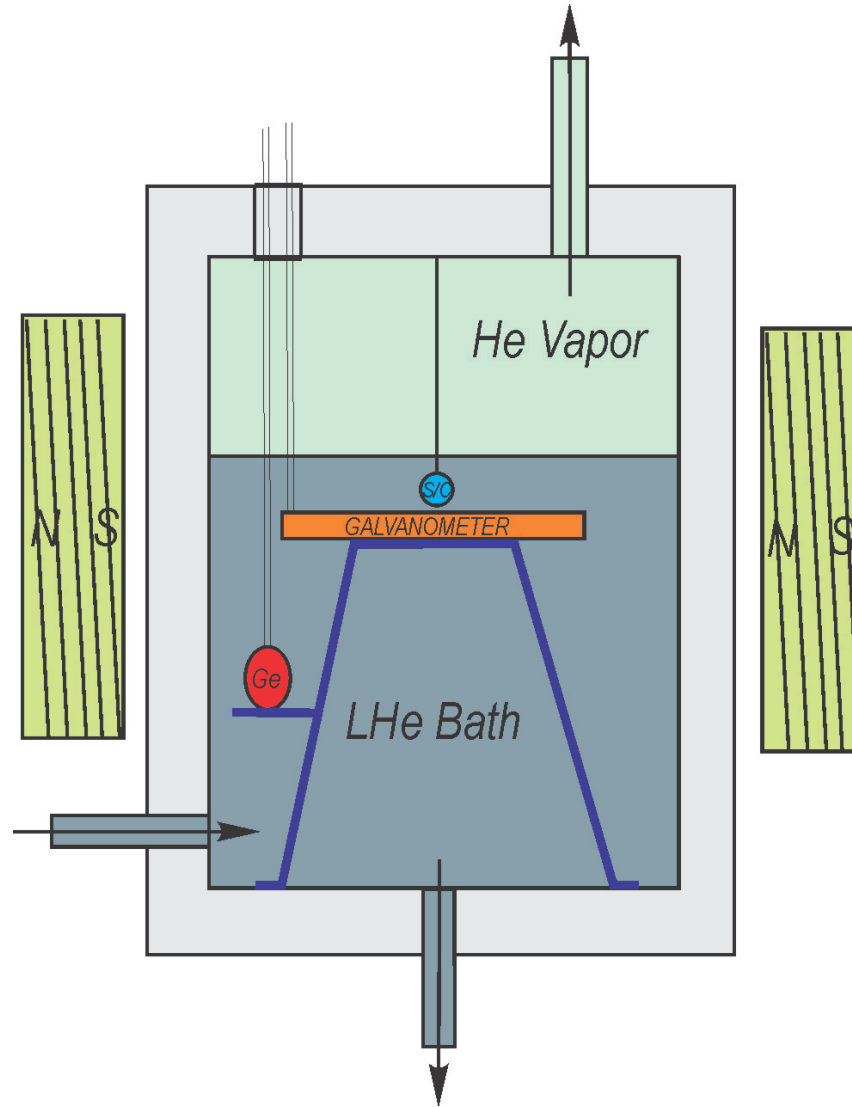
# Experiment Theory



# Experiment Theory



# Experimental Set-Up

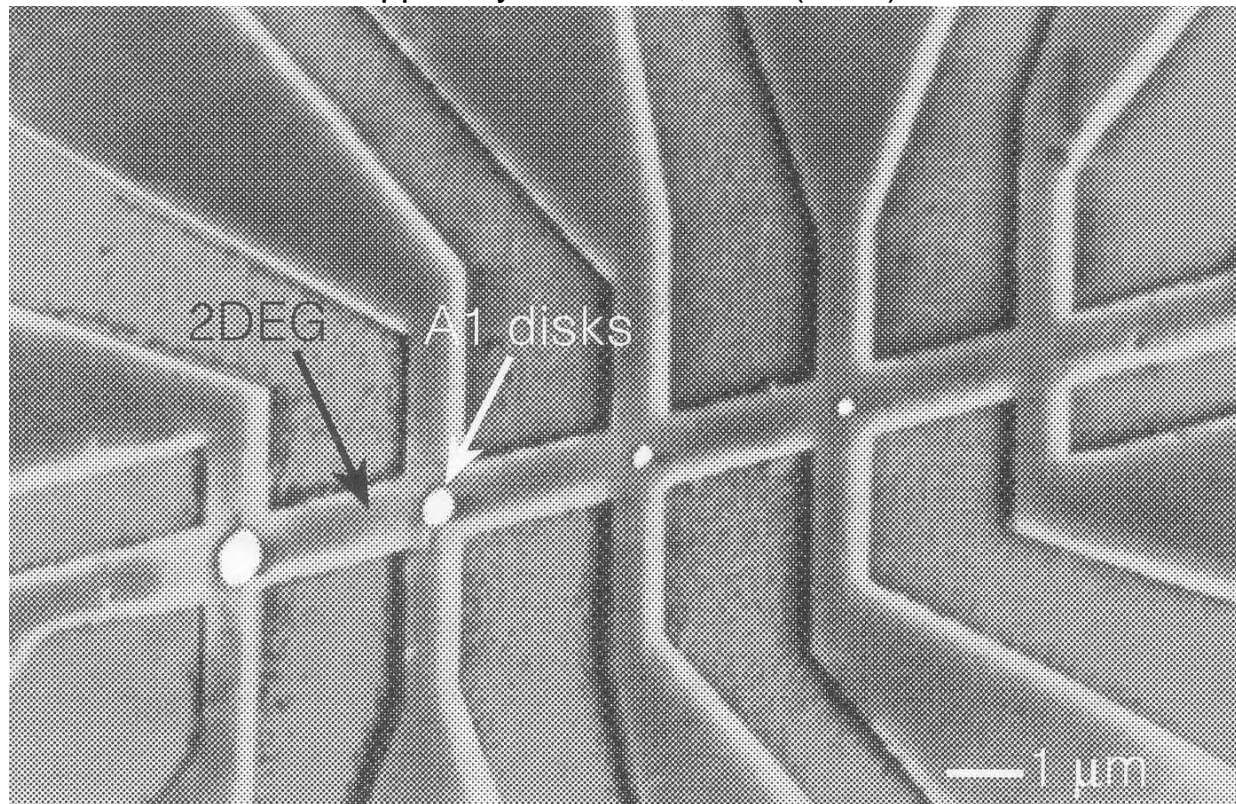




# Ballistic Hall Micromagnetometer

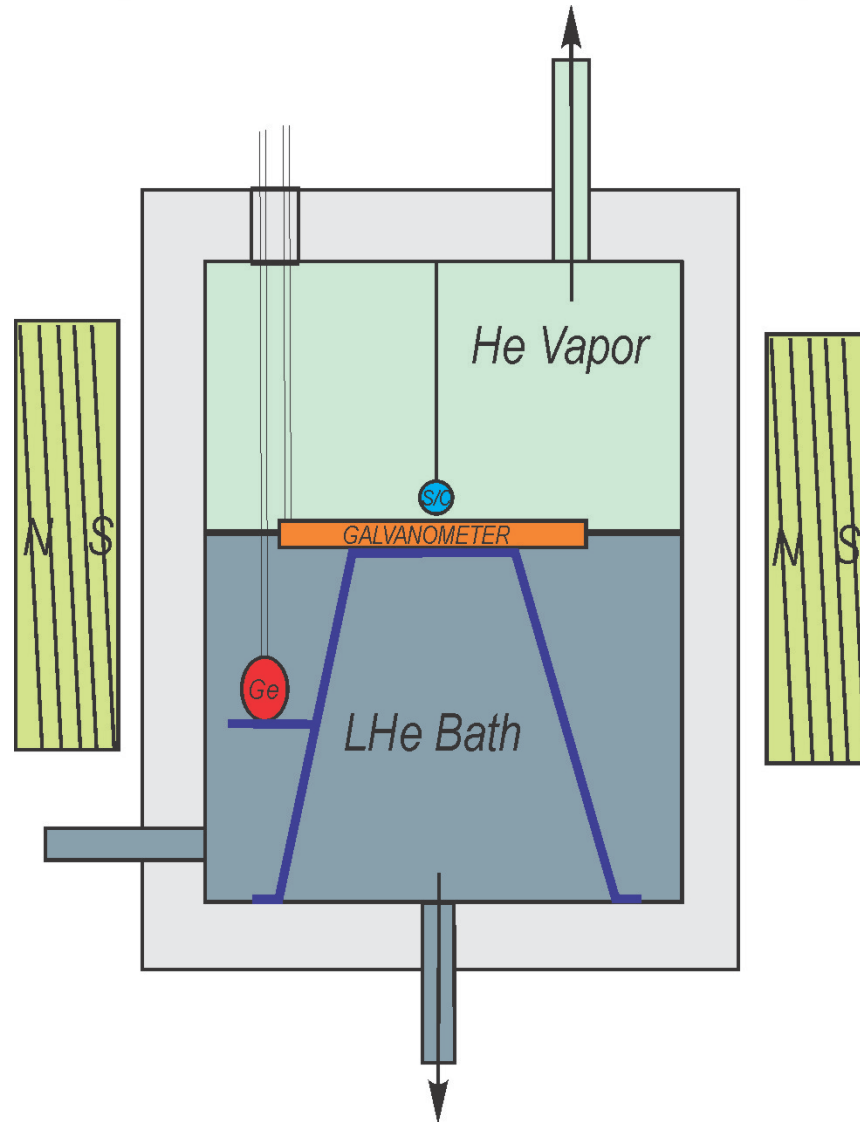
A magnetization measurement device which allows quantitative studies of thermodynamic properties of individual submicron superconducting particles fabricated on a GaAs/GaAlAs heterostructure with a high-mobility two-dimensional electron gas (2DEG) embedded 60 nm below the surface. A confined ballistic electron flow passes in close vicinity of a small magnetized object, deviations of the beam due to a stray magnetic field are detected. The signal depends on the filling factor at the junctions.

A.K. Geim, S.V. Dubonos, J.G.S. Lok, I.V. Grigorieva, J.C. Maan, L. Theil Hansen and P.E. Lindelof, Appl. Phys. Lett. 71, 2379 (1997).

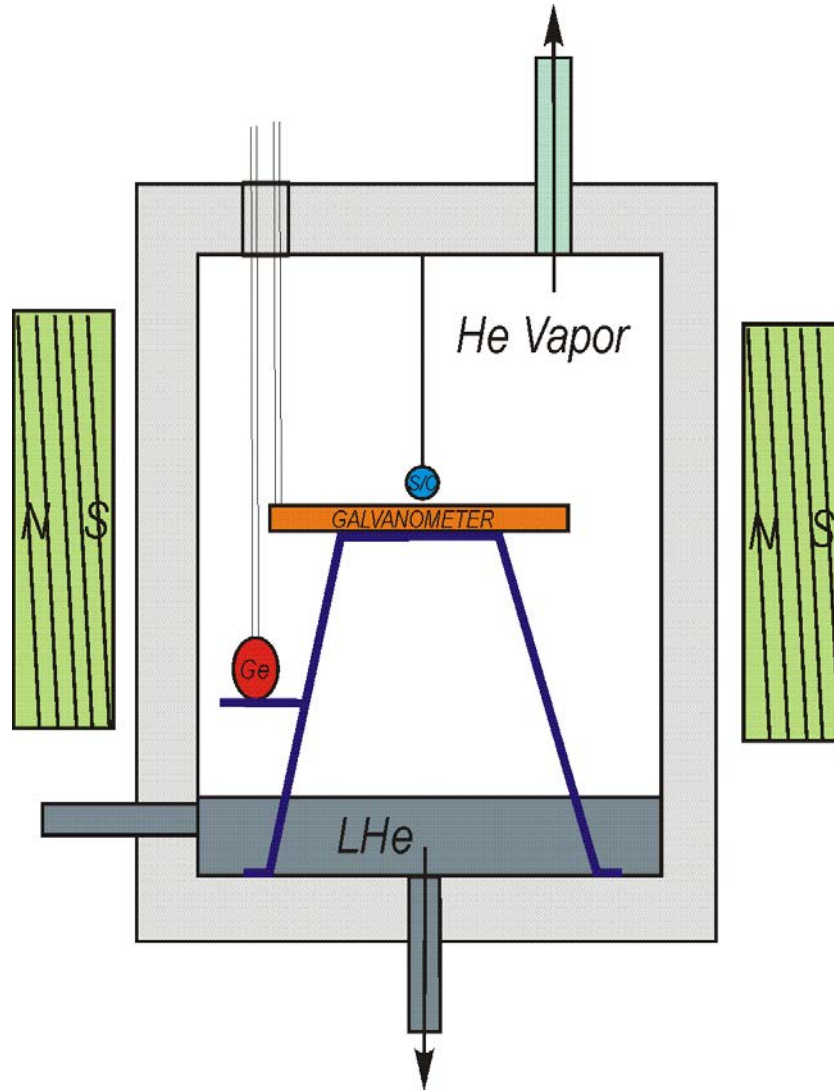




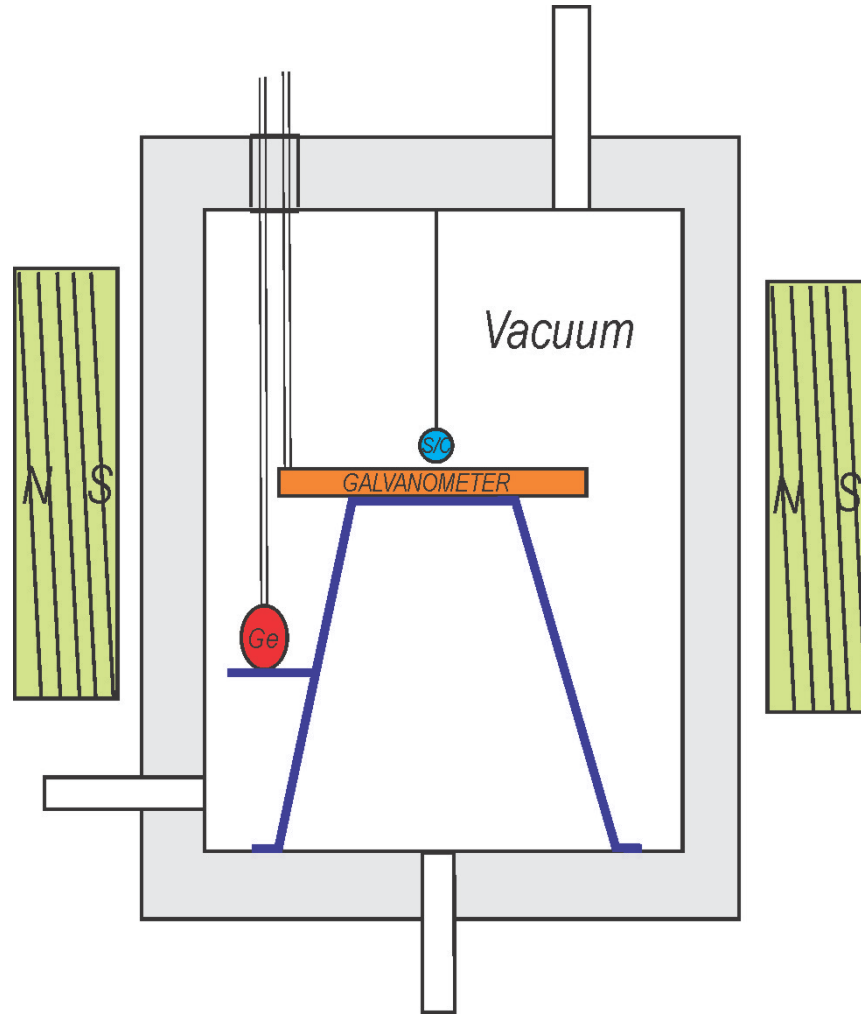
# Experimental Set-Up



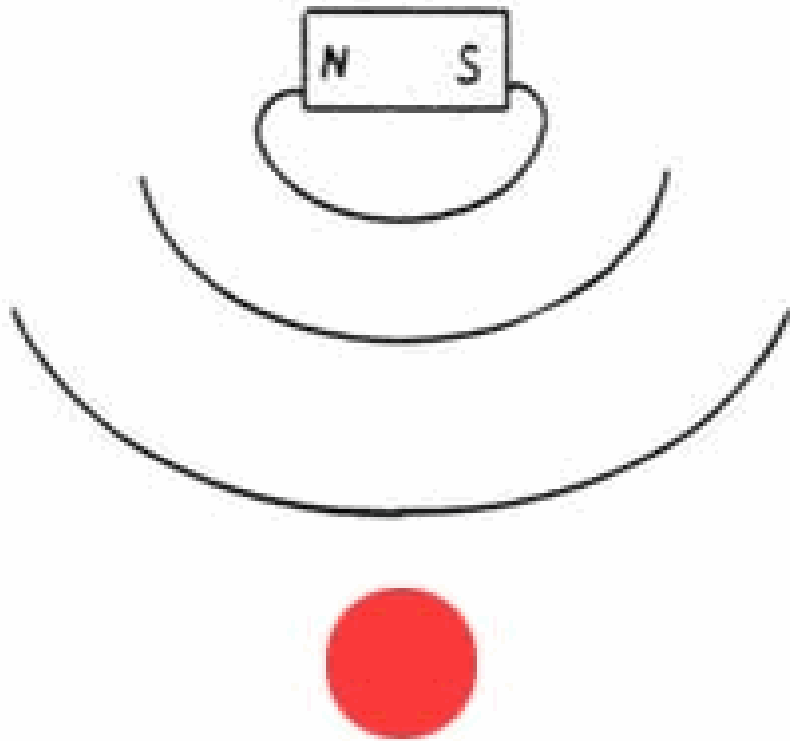
# Experimental Set-Up



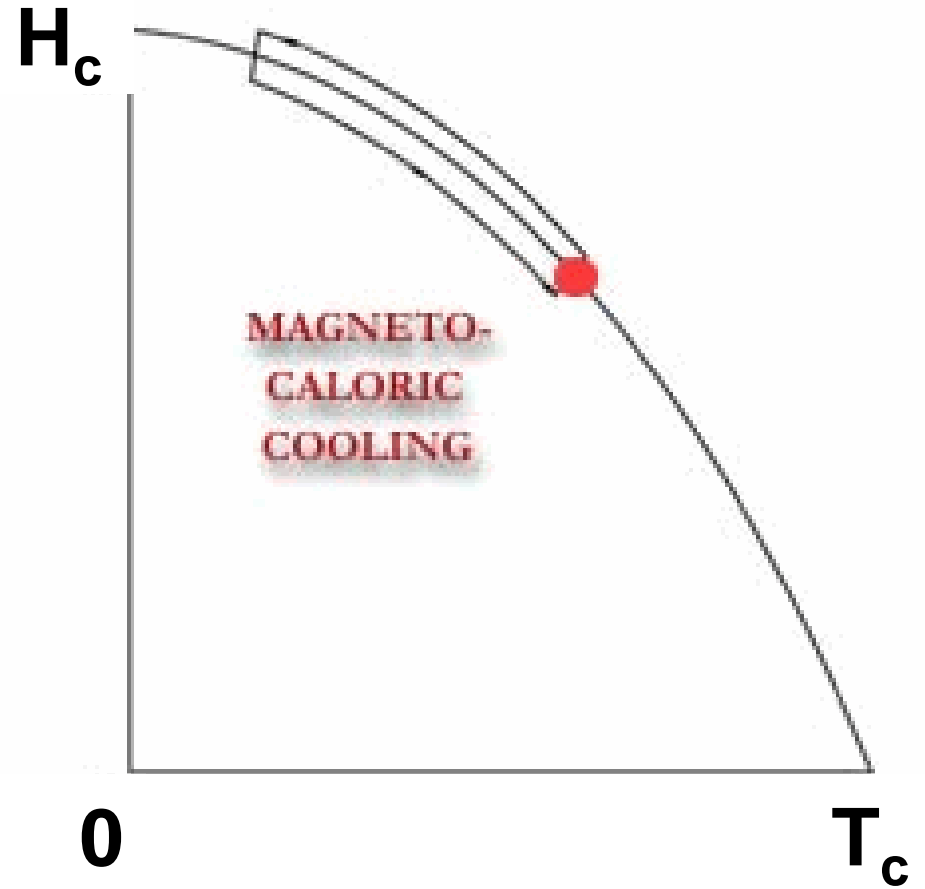
# Experimental Set-Up



**Thank You!**  
*Keefengine.com*



**Work Cycle**



**H-T Space Cycle**