Thermal analysis – heat capacity

590B F08

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Detour – phase transitions of 2 ½ order

Heat capacity

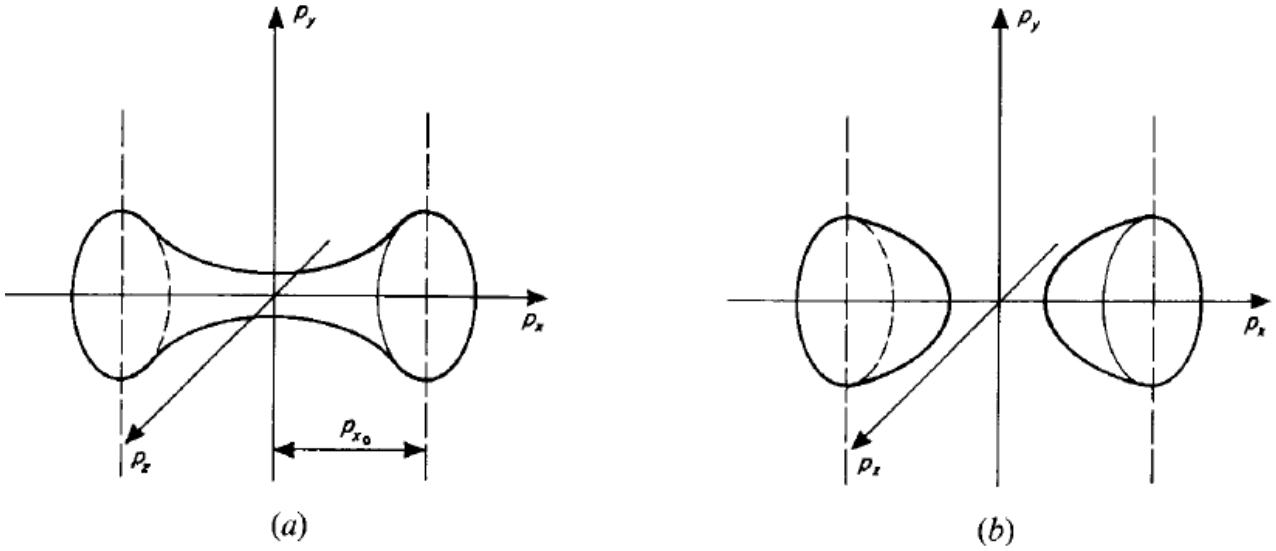
2 ½ order phase transition

aka: electronic topological transition (ETT), Lifshitz transition

LIFSHITZ, I. M., 1960, *Zh. éksp. teor. Fiz.*, **33,** 1569.

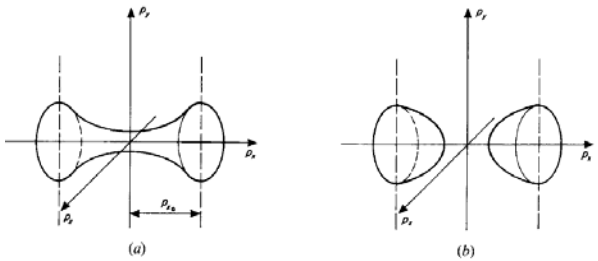
also:

MOTT, N. F., and JONES, 1936, *The Theory of the Properties of Metals and Alloys* (Oxford University Press), p. 326.
VAN HOVE, L., 1953, *Phys. Rev.*, **89,** 1189.
ZIMAN, J. M., 1956, *Proc. R. Soc.*, **252,** 63.



2 ½ order phase transition

electronic DOS $\varrho(\varepsilon) = \varrho_0(\varepsilon) + \delta\varrho$



$$\delta\varrho = \begin{cases} 0, & \text{region I,} \\ \alpha|\varepsilon - \varepsilon_c|^{1/2}, & \text{region II,} \end{cases}$$

$\alpha = N\varepsilon^{-1/2}$, and N is the electron concentration in the metal

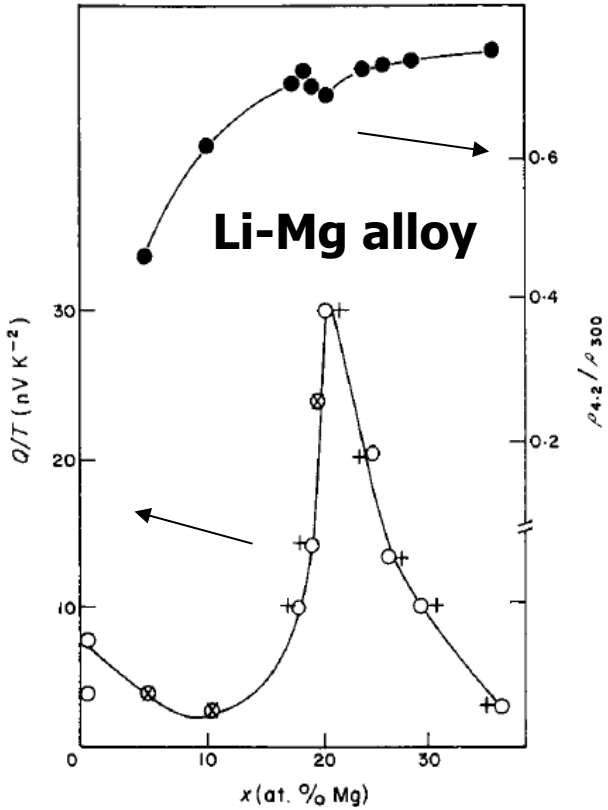
parameter: $Z = \varepsilon_F - \varepsilon_c$

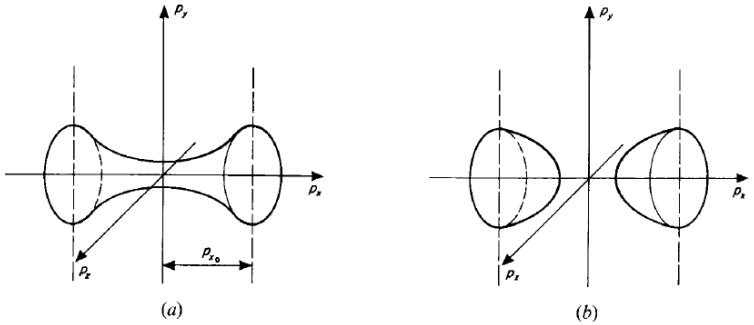
thermodynamic potential

$$\delta\Omega_e = \begin{cases} 0, & \text{region I,} \\ -(4/15)\alpha|Z|^{5/2}, & \text{region II.} \end{cases}$$

T=0, no scattering

2 ½ order phase transition



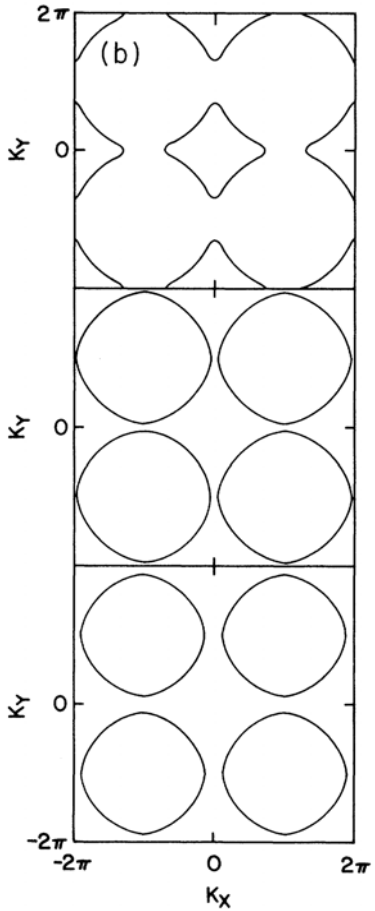


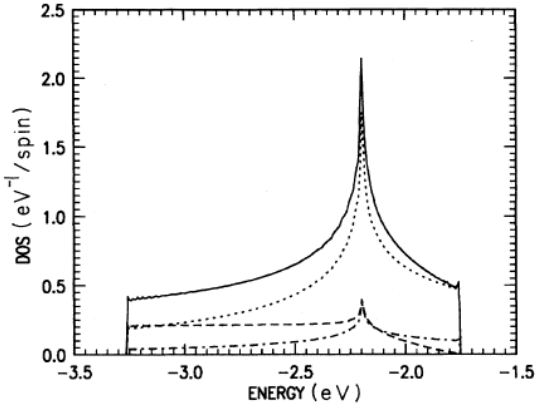
$$\delta\Omega_e = \begin{cases} -\left(\frac{\pi}{2}\right)^{1/2} \alpha T^{5/2} \exp\left(-\frac{|Z|}{T}\right), & \text{region I,} \\ -\frac{4}{15}\alpha\,|Z|^{5/2} - \frac{\pi^2}{6}\alpha T^2 |Z|^{1/2}, & \text{region II.} \end{cases}$$

low temperature, no scattering

ALSO other control parameters

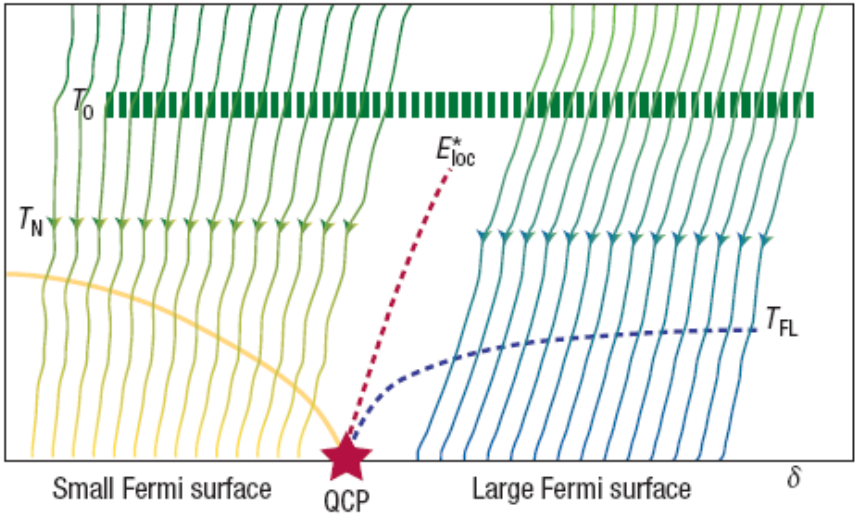
2 ½ order phase transition





New box – the same good old taste

QCP in heavy fermions



LSCO high-T_c SC

Heat capacity

$C_p = (dQ/dT)_p = T(\partial S/\partial T)_p$

$C_v = (dQ/dT)_v = T(\partial S/\partial T)_v$

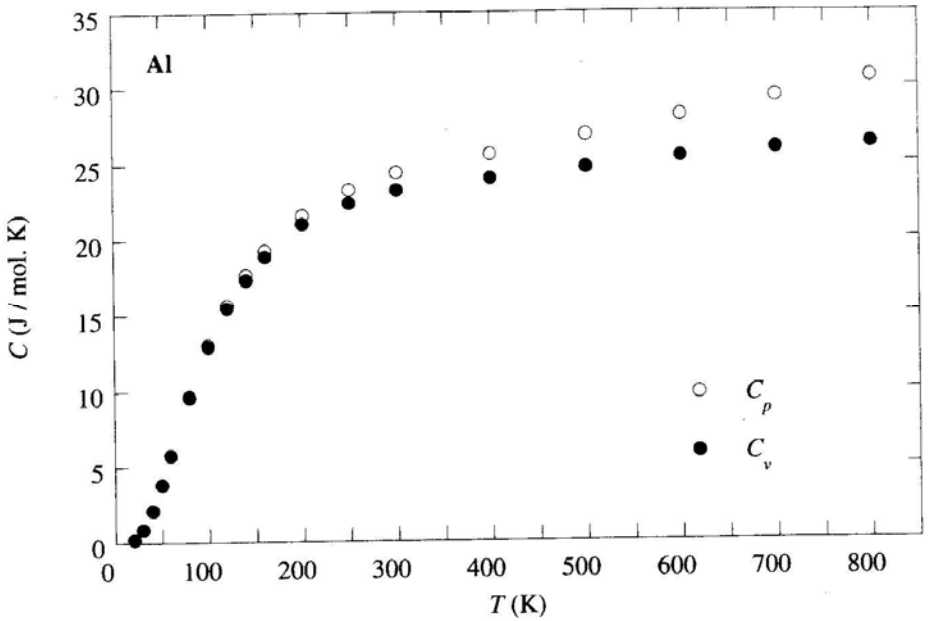
$C_p - C_v = TV\beta^2/k_T$

Q – heat, S - entropy

β – volume thermal expansion,
k_T – isothermal volume compressibility

For solids $C_p \sim C_v$

Usually we measure C_p



Heat capacity – WHY?

*** Useful knowledge for useful (structural) materials – how easy to cool down**

*** To learn something about electrons and phonons**

T -> 0: $C_p = \gamma T + \beta T^3$ (no magnetism)

$\gamma \sim N(0)(1 + \lambda)$ **- electronic density of states**

λ - measure of e-e (and e-ph) interactions, $m^*/m_0 = (1 + \lambda)$

$\gamma >$ 400 mJ/mol K^2 – "heavy fermions" – an enormous, separate research field that entertains number of us

$\Theta_D = (1944/\beta)^{1/3}$ **- Debye temperature** (use right units)

tells you something about stiffness of the lattice, helps to understand BCS superconductors [$T_c \sim \Theta_D \exp(-1/N(0)V)$]

Lattice heat capacity – Debye and Einstein

Einstein – single frequency

$$C_v\left(\frac{\Theta_E}{T}\right) = 3sR\left(\frac{\Theta_E}{T}\right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T)-1]^2}$$

$$C_v = 3sR\left(\frac{\Theta_E}{T}\right)^2 \exp\left(-\frac{\Theta_E}{T}\right) + \ldots \quad (T << \Theta_E)$$

$$C_v = 3sR\left[1 - \frac{1}{12}\left(\frac{\Theta_E}{T}\right)^2 + \ldots\right] \quad (T >> \Theta_E)$$

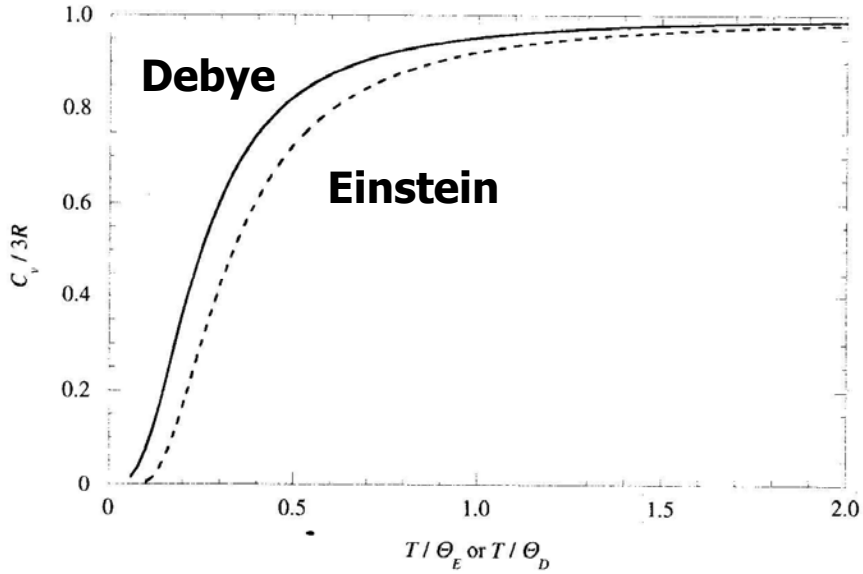
Debye – elastic continuum

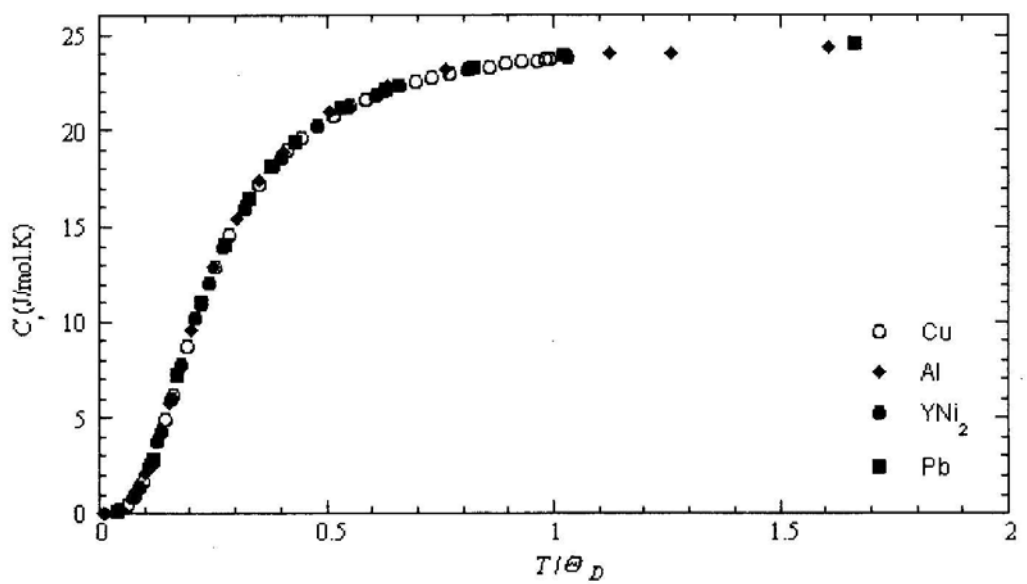
$$C_v = 9Rs\left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2} = 9Rs\,(T/\Theta_D)^3\, D(\Theta_D/T)$$

$$C_v = \frac{12\pi^4}{5}(Rs/\Theta_D^3)T^3 = \beta_3 T^3 \qquad (T << \Theta_D)$$

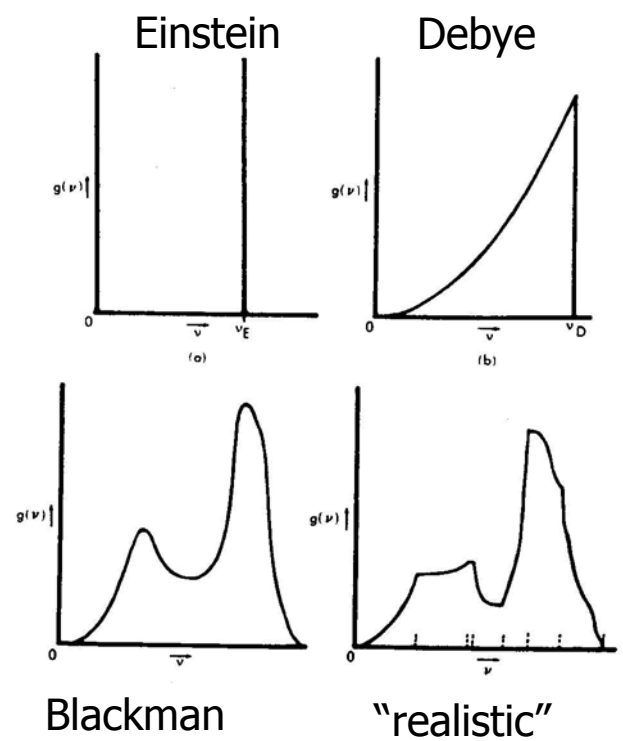
$$C_v = 3sR\left[1 - \frac{1}{20}\left(\frac{\Theta_D}{T}\right)^2 + \cdots\right] \qquad (T >> \Theta_D)$$

Lattice heat capacity – Debye and Einstein





One can also use realistic phonon DOS and calculate C_p



Heat capacity – WHY?

- **To learn something about magnons**

Ferro (ferri) magnets

isotropic

$$C_M = s_f R \left(\frac{k_B T}{2JS} \right)^{3/2}$$

anisotropic

$$C_M \sim T^{3/2} \exp(-E_g / k_B T)$$

Antiferromagnets

isotropic

$$C_M = s_{af} R \left(\frac{k_B T}{2J'S} \right)^{3}$$

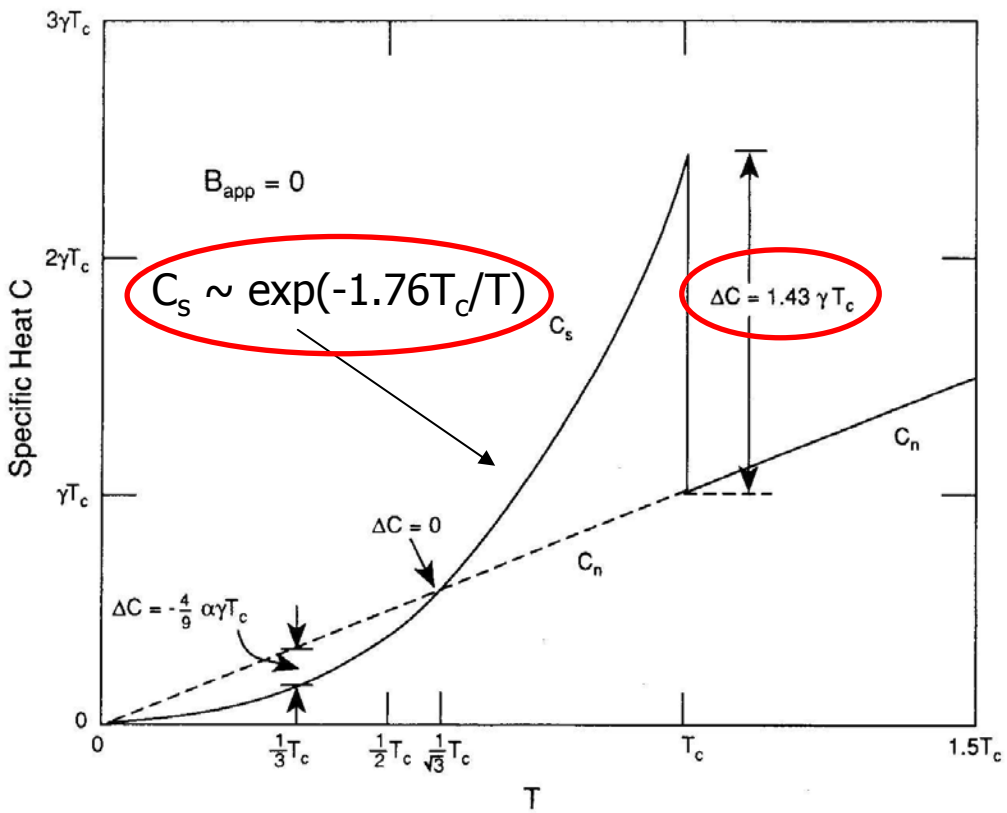
anisotropic

$$C_M \sim T^{3} \exp(-E_g / k_B T)$$

And need to remember contributions from electrons and phonons: $C_p = \gamma T + \beta T^3$

Heat capacity – WHY?

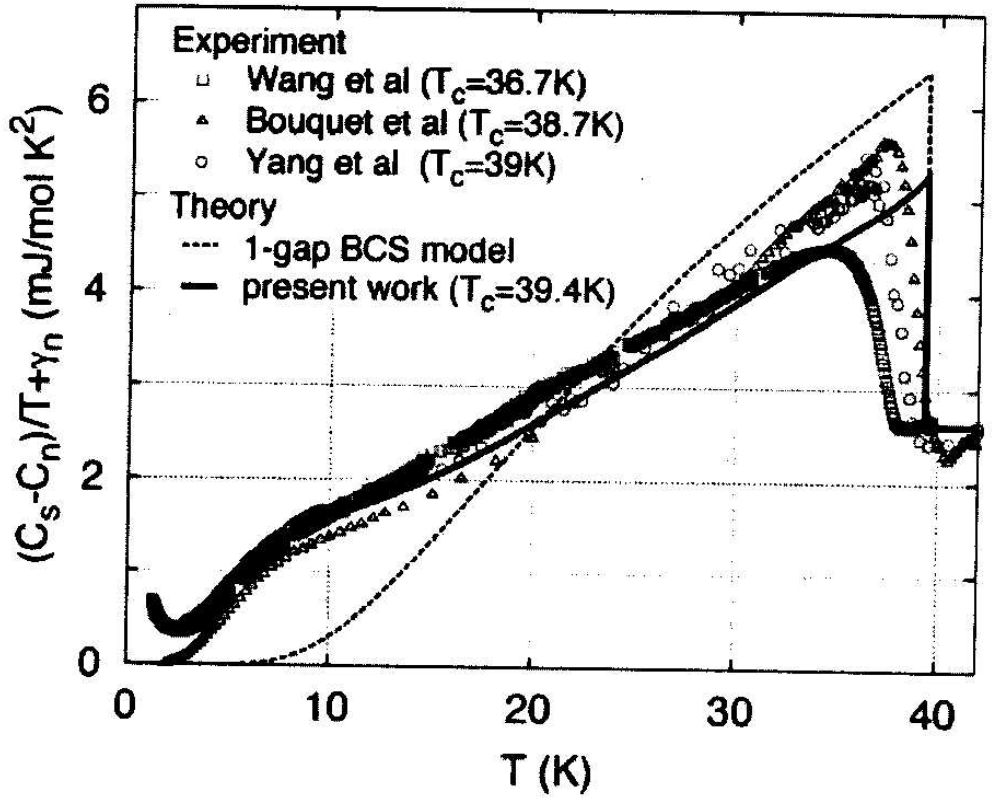
- **To learn something about superconductors**



BCS

Heat capacity – WHY?

- To learn something about superconductors



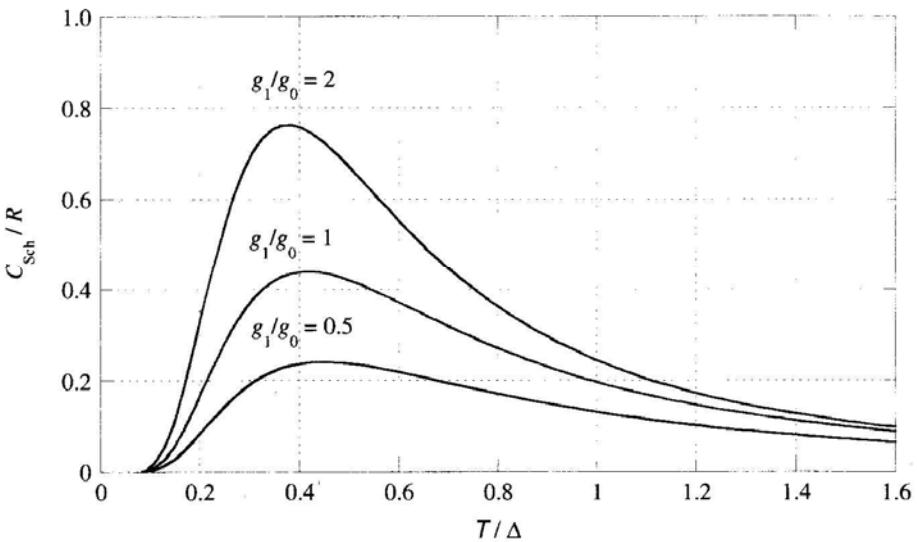
MgB_2

Two-gap superconductor

Heat capacity – WHY?

- **To learn something about crystal electric field (Schottky anomaly)**

$$C_{Sch} = R\left(\frac{\Delta}{T}\right)^2 \frac{(g_0/g_1)\exp(\Delta/T)}{[1+(g_0/g_1)\exp(\Delta/T)]^2}$$



$$C_{Sch} = R\left(\frac{g_1}{g_0}\right)\left(\frac{\Delta}{T}\right)^2 \exp\left(-\frac{\Delta}{T}\right) \qquad T << \Delta$$

$$C_{Sch} = R\frac{g_0 g_1}{(g_0+g_1)^2}\left(\frac{\Delta}{T}\right)^2 \qquad T >> \Delta$$

maximum:

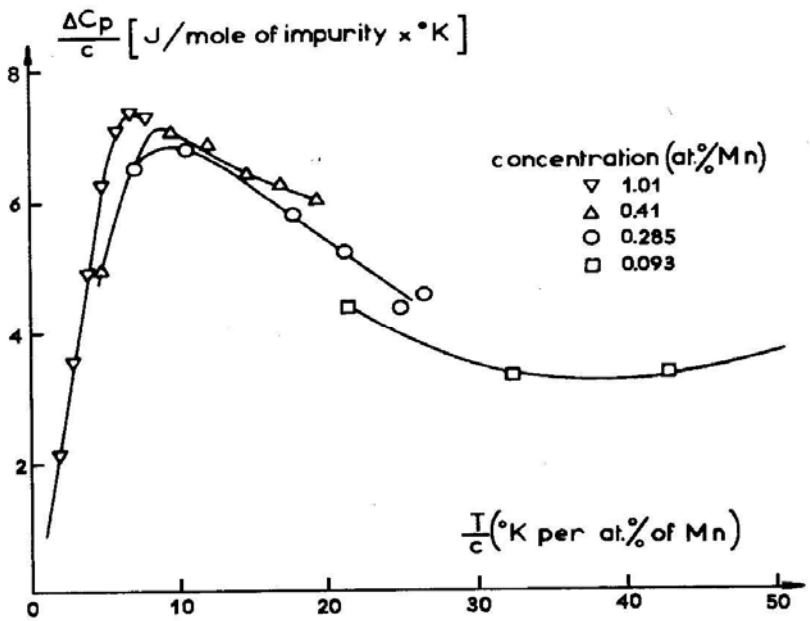
$$\exp\left(-\frac{\Delta}{T_m}\right) = \left(\frac{g_1}{g_0}\right)\frac{(\Delta/T_m)+2}{(\Delta/T_m)-2}$$

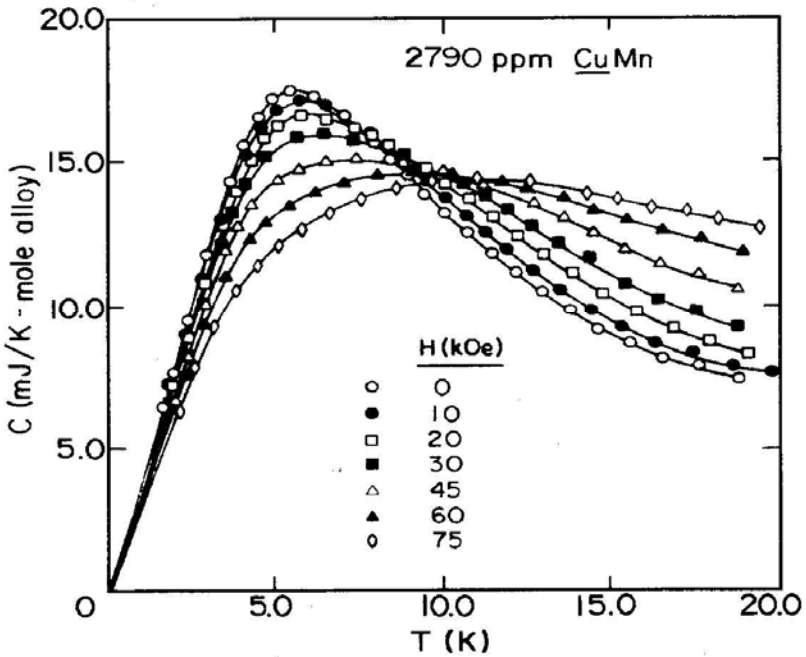
$$C_{Sch}(\max) = R\left[\left(\frac{\Delta}{2T_m}\right)^2 - 1\right]$$

Heat capacity – WHY?

- To learn something about spin glasses

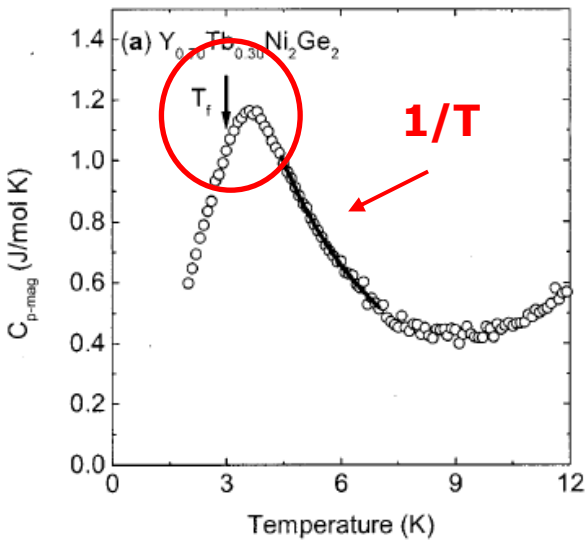
$$\frac{C_m}{c} = \Gamma\left(\frac{T}{c}\right)$$ **Scaling hypothesis**

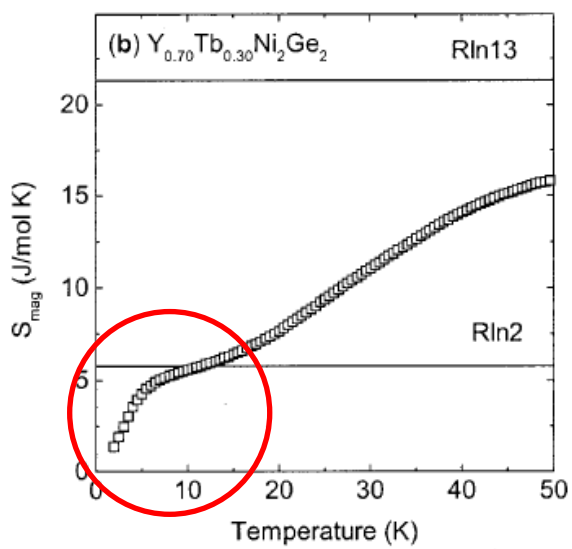


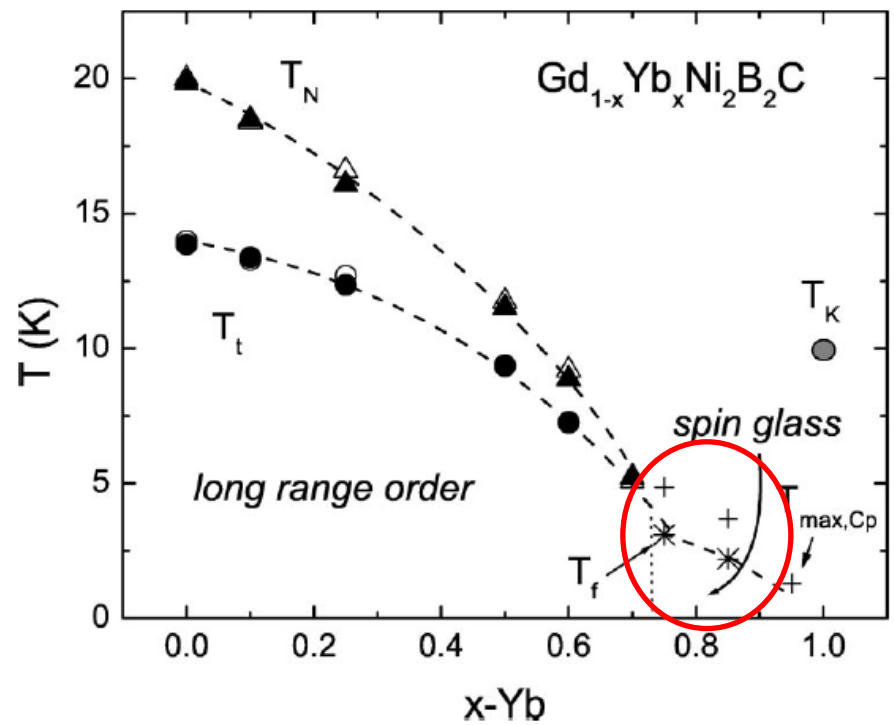


Heat capacity – WHY?

- **To learn something about spin glasses**



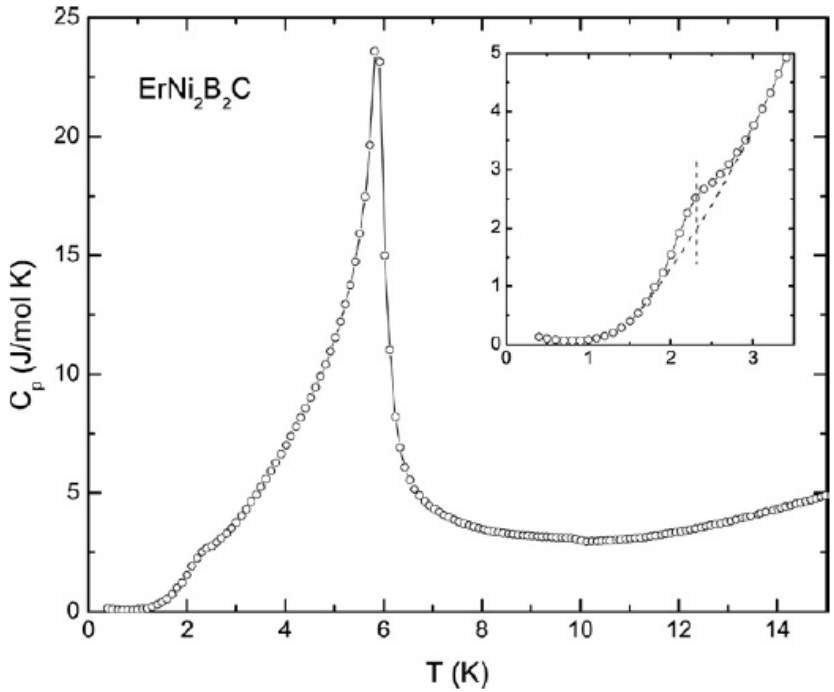


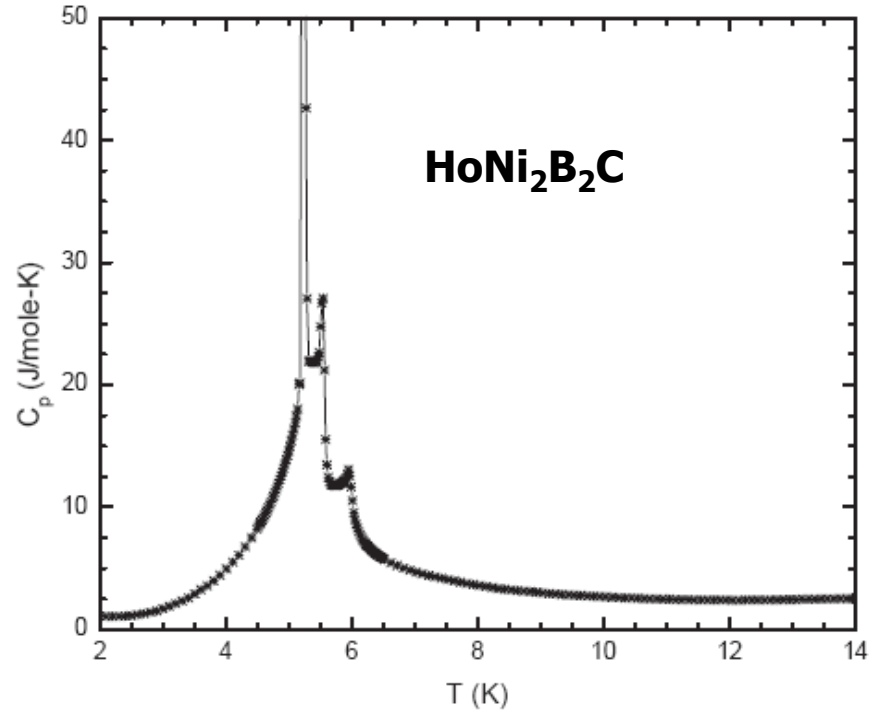


$T_{max} \sim 1.5\ T_f$

Heat capacity – WHY?

- **To learn something about magnetic transitions**



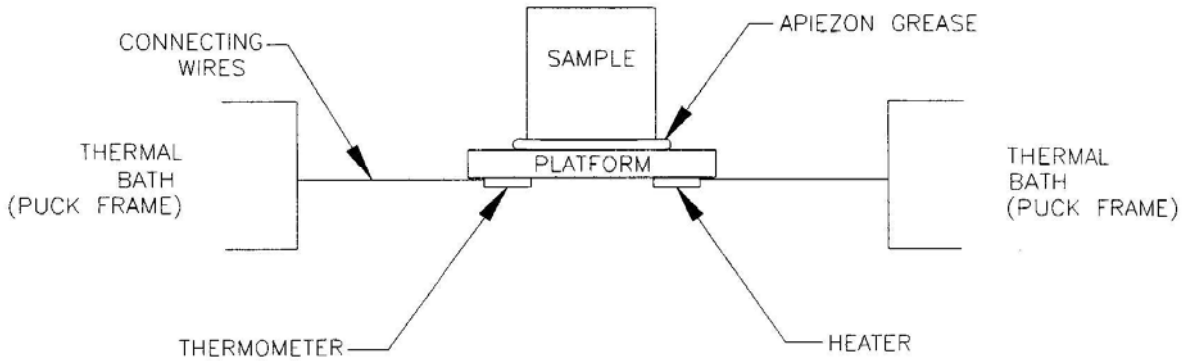


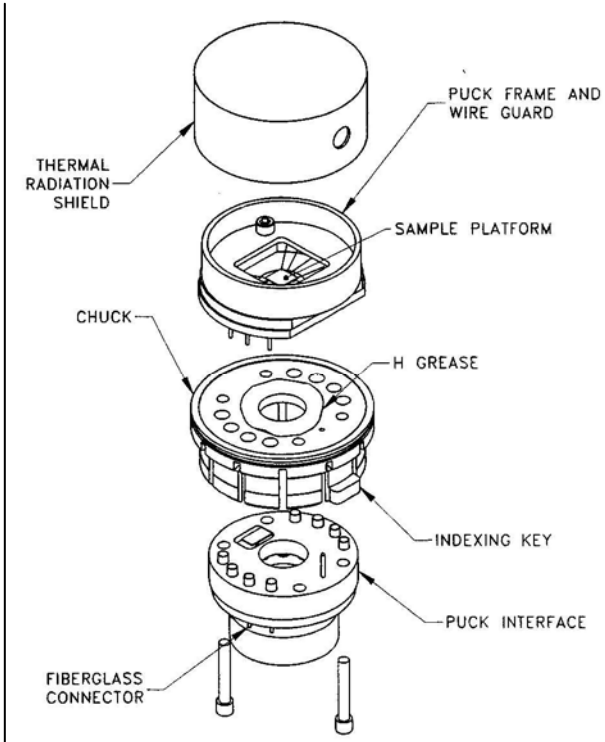
Also can play entropy game and evaluate degeneracy of the ground state

$\Delta S_m = R \ln N$

Heat capacity – HOW?

- **relaxation (QD PPMS)**





$$C_{\text{total}} \frac{dT}{dt} = -K_w (T - T_b) + P(t),$$

simple

$$C_{\text{platform}} \frac{dT_p}{dt} = P(t) - K_w \left(T_p(t) - T_b\right) + K_g \left(T_s(t) - T_p(t)\right)$$

$$C_{\text{sample}} \frac{dT_s}{dt} = -K_g \left(T_s(t) - T_p(t)\right),$$

more realistic

fit with two exponents

Heat capacity – HOW?

- relaxation (QD PPMS)

calibrated heater and thermometer

sophisticated temperature control and fitting software

need to measure addenda (platform + grease) every time

need to calibrate heater and thermometer in magnetic field

need to shape your sample

vertical 3He platform may oscillate in magnetic field

remember about torque

assembly is fragile

measurements take long time

not good for 1st order phase transitions

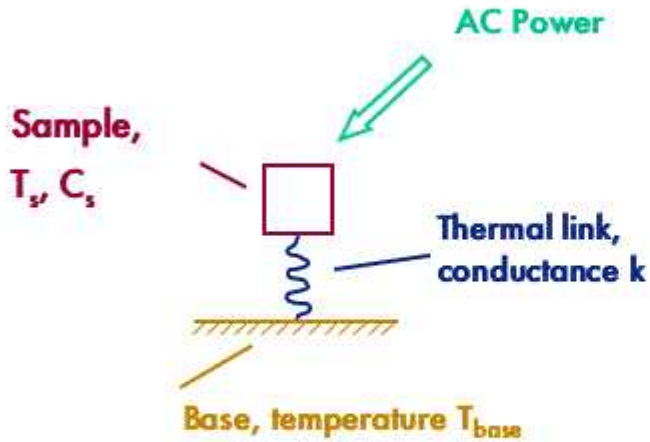
Heat capacity – HOW?

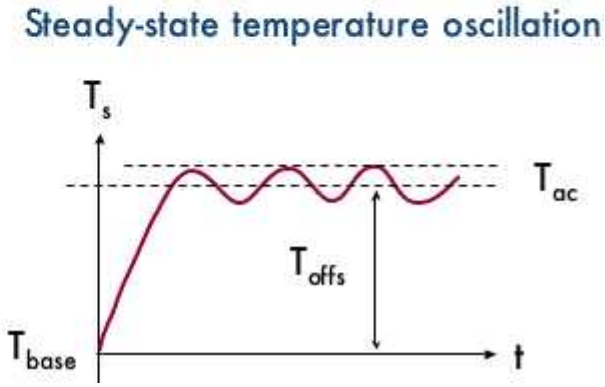
- **ac modulation**

P. F. Sullivan and G. Seidel, Phys. Rev. **173**, 679 (1968).

τ_1 – sample to bath;

τ_2 – response time of the sample





$$T_{ac} = \text{Power}/2\omega C(1 + 1/\omega^2\tau_1^2 + \omega^2\tau_2^2 + \text{const})^{1/2}$$

if $\tau_2 << 1/\omega << \tau_1$

$$C = \text{Power}/2\omega T_{ac}(1 + \text{const})^{1/2},$$

Heat capacity – HOW?

- ac modulation

fast

scalable, good for small sample

accurate (relative measurements)

can use e.g. in pressure cells

hard to get absolute values

Reading:

Quantum Design Manual and refs therein

E.S.R. Gopal, Specific heats at low temperatures.

A.Tari, Specific heat of matter at low temperatures.

T.H.K. Barron and G.K. White, Heat capacity and thermal expansion at low temperatures.