

# Specific Heat in Thermodynamics

Heat capacity:

$$C = \lim_{\Delta T \rightarrow 0} \left( \frac{\Delta Q}{\Delta T} \right)$$

Specific Heat:

$$c = \frac{C}{m} = \frac{dq}{dT}$$

Per mass or usually "per mole":  $C_p$  and  $C_v$

$$C_p = \left. \frac{dq}{dT} \right|_P \quad C_v = \left. \frac{dq}{dT} \right|_V$$

$$dQ = dU + dW = dU + PdV \Rightarrow C_v = \left( \frac{dU}{dT} \right)_V$$

neglect the volume expansion when solid is heated,  $dW \sim 0$

$$dQ = TdS \Rightarrow C_p = T \left( \frac{\partial S}{\partial T} \right)_P ; C_v = T \left( \frac{\partial S}{\partial T} \right)_V$$

reversible system in equilibrium with its environment

Free energy:

$$F = -k_B T \ln Z$$

$$Z = \sum_i e^{-\frac{E_i}{k_B T}}$$

sum over all possible states (i) with energies  $E_i$

$$dF = d(U - TS) = -SdT - PdV \Rightarrow C_v = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V$$

$$S(T_1) = \int_0^{T_1} \frac{C}{T} dT$$

Note lower boundary On integration

• Powerful method in materials characterization

• Modern time: high level of automatization (PPMS)

$$dH = TdS = dQ \Rightarrow C_p = \left( \frac{dQ}{dT} \right)_P = \left( \frac{\partial H}{\partial T} \right)_P$$

• Notice that what we calculate is  $C_v$  and what we measure is  $C_p$ .

For isobaric conditions

# Simplest Example: 1D Monoatomic Lattice

Chain of N identical atoms with M:  $x_n(t) = na + u_n(t), n \in N$

1  $M \ddot{u} = K(u_{n+1} - u_n) - K(u_n - u_{n-1}), n \in N$

Search for harmonic solution:  $u_n(t) = A_j e^{i(q_j na - \omega_j t)}$

Periodic boundary condition  $u_n(t) = u_{n+N}(t) \rightarrow \exp(iq_j Na) = 1$

$$q_j = \frac{2\pi j}{Na}, j \in N$$

2  $M\omega_j^2 A_j = KA_j(e^{iq_j a} + e^{-iq_j a} - 2)$

3  $\omega_j^2 = \frac{2K}{M}(1 - \cos q_j a) \Rightarrow \omega_j = 2\sqrt{\frac{K}{M}} \left| \sin \frac{q_j a}{2} \right|$

Extremal values:  $q_j = \pm \frac{\pi}{a}; (j = \frac{N}{2})$

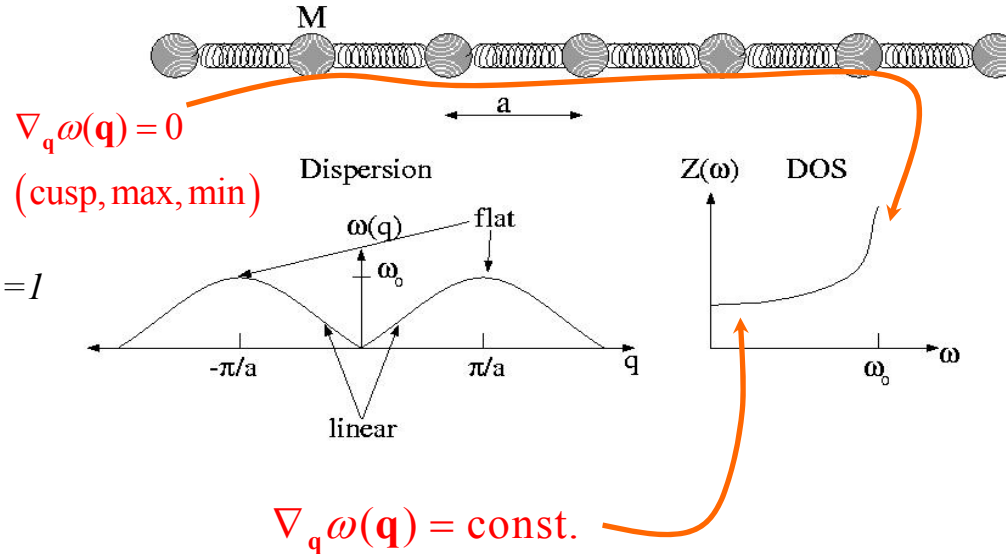
First Brillouin zone:  $q_j = \left( -\frac{\pi}{a}, \dots, \frac{\pi}{a} \right)$

4 Number of possible q values = N (number of unit cells in the system)

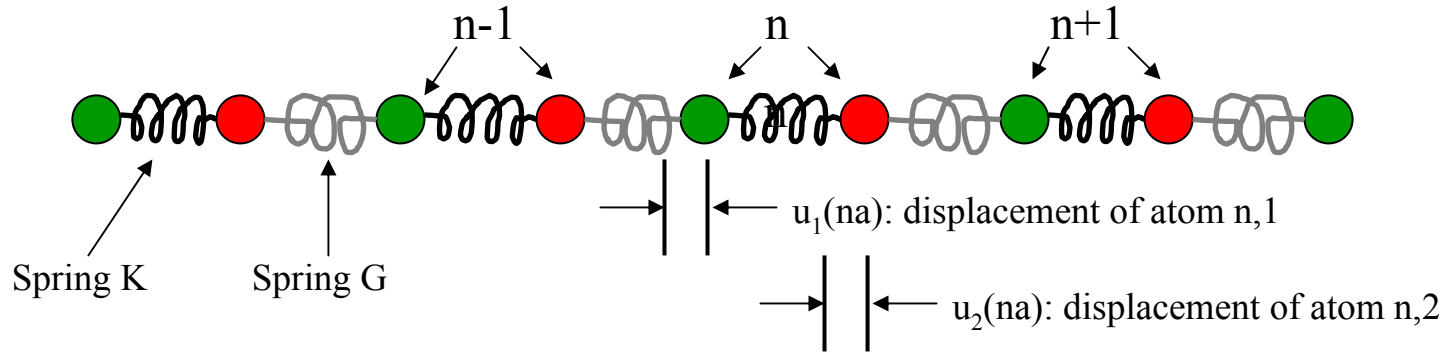
5 For low q  $\rightarrow \omega(q) \sim |q|c_s$   
( $c_s \sim$  speed of sound)

6 velocity of excitations in the chain (group velocity):  
 $c_g = \partial\omega/\partial q = c_s \cos(qa/2) \text{sgn}(q)$   
 $c_g = 0$  at the zone boundary  $|q| = \pi/a = 2\pi/\lambda$  (Bragg law)  
 $\rightarrow$  at the zone boundary lattice effects are strongest, atoms oscillate out of phase for  $|q| = \pi/a$

What is phonon density of states in 1D chain?



# Simple example: Diatomic chain in 1D



Coupled equations of motion:

See textbook, also Aschroft/Mermin "Solid State Physics"

$$M_1 \ddot{u}_1(na) = -K[u_1(na) - u_2(na)] - G[u_1(na) - u_2((n-1)a)]$$

$$M_2 \ddot{u}_2(na) = -K[u_2(na) - u_1(na)] - G[u_2(na) - u_1((n-1)a)]$$

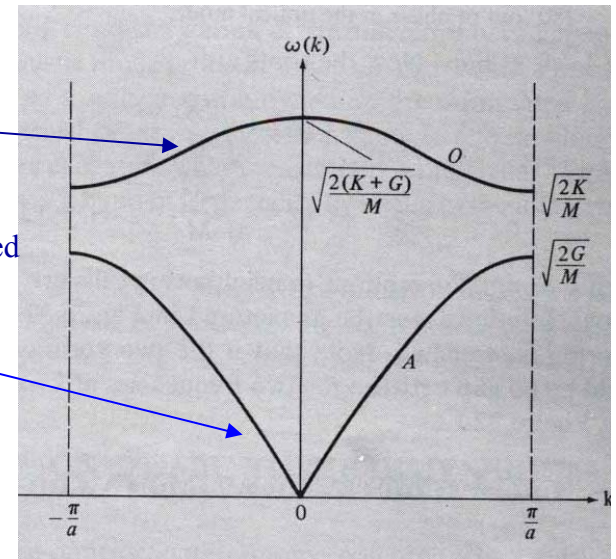
$$\omega^2(k) = \frac{K+G}{M_{eff}} \pm \frac{1}{M_{eff}} \sqrt{K^2 + G^2 + 2KG \cos qa}$$

Optical branch. Atoms vibrate against each other with their center of mass fixed

Long wavelength modes can interact with electromagnetic radiation (oppositely charged ions can be excited by E of the light wave)

Acoustic branch. Atoms and their center of mass move together as in acoustical vibration

$\omega \sim ck$  (sound waves)



There are  $N$  values of  $q$ ,  $N = \{1 \dots N\}$ :

$$q = \frac{2\pi n}{a N}$$

**For each  $q$ , there are 2 solutions, total of  $2N$  normal modes - phonons**

# General Case and Phonon Density of States

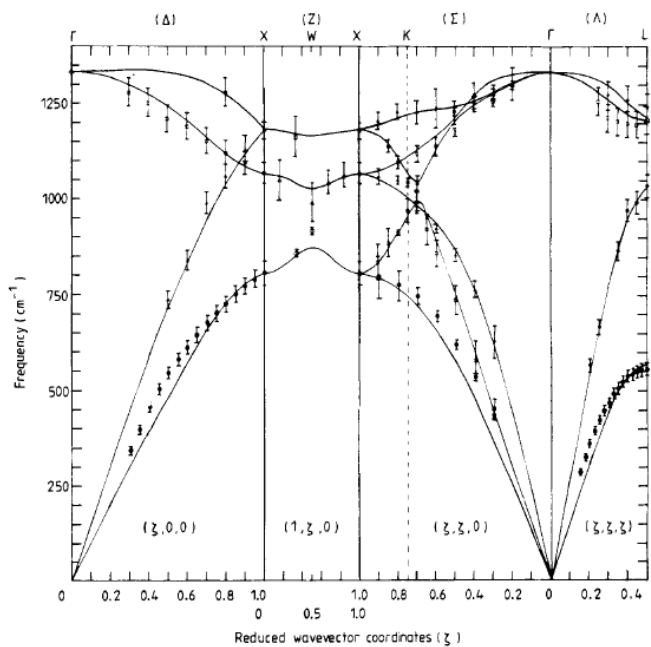
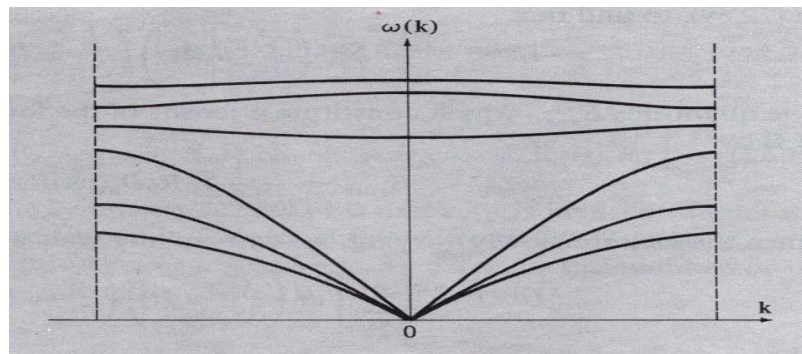
If there is  $s$  ions per unit cell and  $N$  cells, there will be  $3Ns$  degrees of freedom and  $3s$  normal modes for each  $\vec{q}$  **phonon**. The lowest 3 branches are acoustic. Remaining  $3(s-1)$  branches are optical.

**Each mode has its own polarization vector:**

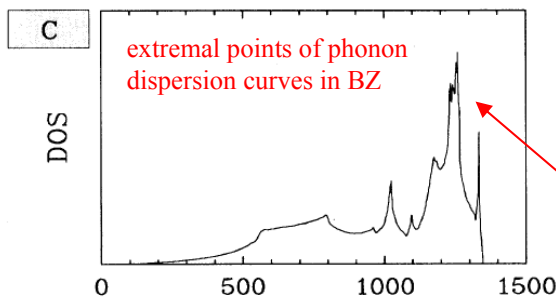
parallel to  $\vec{q}$  - **longitudinal mode**

perpendicular to  $\vec{q}$  - **transverse mode**

mixed excitations are of course possible



Phonon spectrum of real materials (diamond,  $s=2$ , 6 normal modes) include also interaction beyond nearest neighbors, electron – phonon coupling, anharmonicity...



Define phonon DOS: number of states per energy interval:

$$\rho(\omega) = \sum_{\mu} \int \delta(\omega - \omega_{\mu}(q)) \frac{V d\vec{k}}{(2\pi)^3}$$

$\rho(\omega)d\omega$  → total number of modes in infinitesimal range  $\omega+d\omega$  per total  $V$

If  $\omega_{\mu}(\vec{q}_0) = \omega$  then expand:

$$\omega_{\mu}(\vec{q}) = \omega_{\mu}(\vec{q}_0) + (\vec{q} - \vec{q}_0) \frac{\partial \omega_{\mu}}{\partial \vec{q}}$$

group velocity  $v_{\mu}(\vec{q}_0)$

$$N = \int \frac{V d\vec{q}}{(2\pi)^3} \sum_{\mu} 1 = 3s$$

van Hove singularity

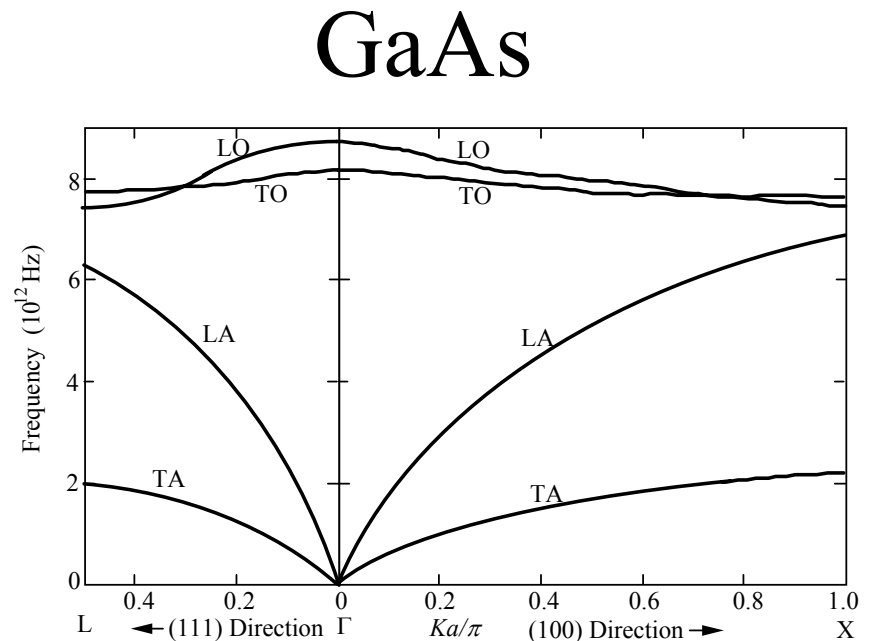
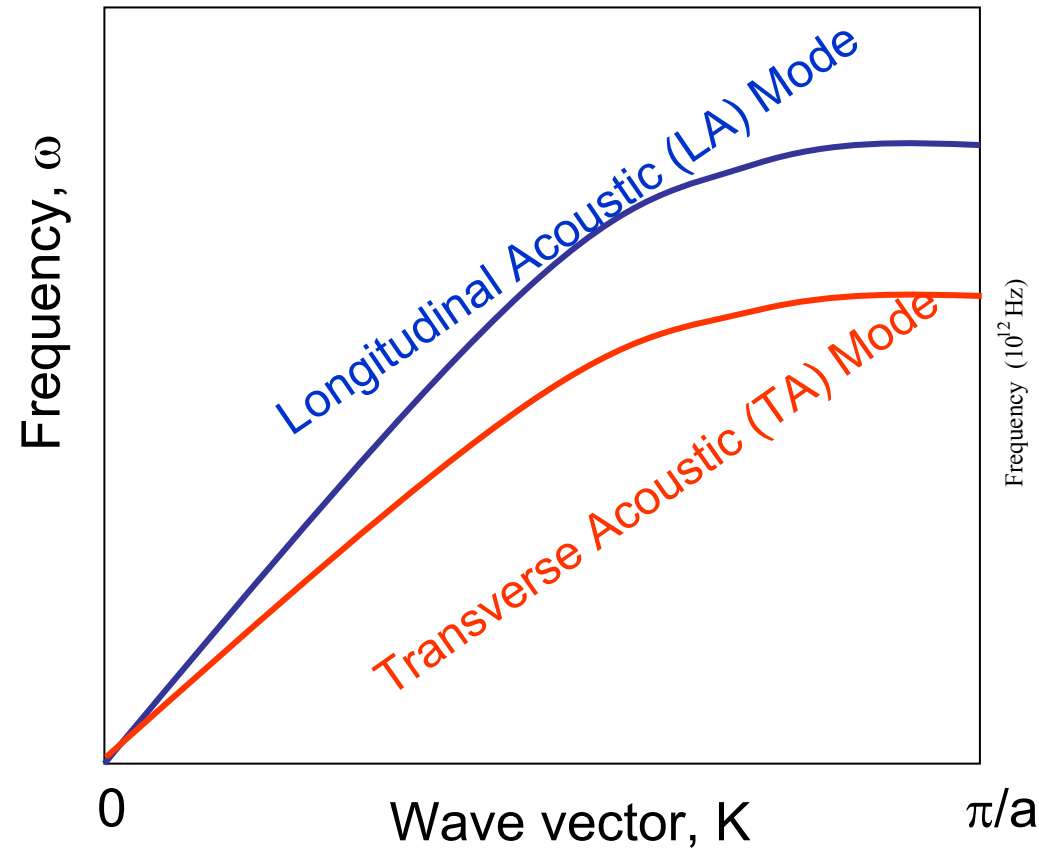
Phonon dispersion relation by INS:  $\lambda$ , E match

$$d\omega = \nabla_{\vec{q}} \omega_{\mu}(\vec{q}) d\vec{q}_{\perp} \Rightarrow d\vec{q} = \frac{dS_{\omega} d\omega}{\nabla_{\vec{q}} \omega_{\mu}(\vec{q})}$$

$$\rho(\omega)d\omega = \frac{V d\omega}{(2\pi)^3} \sum_{\mu} \int_{\omega=\omega_{\mu}(\vec{q})} \frac{dS_{\omega}}{\nabla_{\vec{q}} \omega_{\mu}(\vec{q})}$$

# Longitudinal and transverse modes

Group Velocity:  $v_g = \frac{d\omega}{dK}$



# Linear oscillator in quantum representation

Consider harmonic oscillator:  $V=(1/2)kx^2 = (1/2)m\omega^2x^2 \rightarrow H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 = \frac{1}{2m}[p^2 + (m\omega x)^2]$

Introduce raising and lowering operators:  $a^\dagger = \frac{1}{\sqrt{2\hbar m\omega}}(-ip + m\omega x), a = \frac{1}{\sqrt{2\hbar m\omega}}(ip + m\omega x)$

So that  $[a, a^\dagger]=1$  (easy to show since  $[x_i, p_j]=i\hbar\delta_{ij}$ )  $\rightarrow aa^\dagger=1+a^\dagger a$

$$a^\dagger|\psi_n\rangle = c_n|\psi_{n+1}\rangle \Rightarrow \langle\psi_n|aa^\dagger|\psi_n\rangle = \langle\psi_{n+1}|c_n^*c_n|\psi_{n+1}\rangle = |c_n|^2 = c_n^2 = \langle\psi_n|aa^\dagger + 1|\psi_n\rangle = n + 1 \rightarrow c_n = \sqrt{n+1}$$

$$a^\dagger|\psi_n\rangle = \sqrt{n+1}|\psi_{n+1}\rangle$$

$$a|\psi_n\rangle = d_n|\psi_{n-1}\rangle \Rightarrow \langle\psi_n|aa^\dagger|\psi_n\rangle = n = \langle\psi_{n-1}|d_n^*d_n|\psi_{n-1}\rangle = |d_n|^2 = d_n \Rightarrow d_n = \sqrt{n}$$

$$a|\psi_n\rangle = \sqrt{n}|\psi_{n-1}\rangle$$

Now we write Hamiltonian in terms of raising and lowering operators:

$$aa^\dagger = \frac{(-ip + m\omega x)(ip + m\omega x)}{2m\omega\hbar} = \frac{1}{2m\omega\hbar}[p^2 + (m\omega x)^2 + im\omega(xp - px)] = \frac{1}{\omega\hbar}\left(\frac{p^2}{2m} + \frac{m\omega^2x^2}{2} - \frac{m\omega\hbar}{2m}\right)$$

$$H = \hbar\omega\left(aa^\dagger + \frac{1}{2}\right) = \hbar\omega\left(aa^\dagger - \frac{1}{2}\right)$$

energy of linear harmonic oscillator of frequency  $\omega$  is quantized in  $\hbar\omega$

# Einstein Model of Lattice Specific Heat

Collection of uncoupled quantum oscillators, each vibrating with the same frequency  $\omega_E$   
 Number of oscillators is equal to number of degrees of freedom in the system

Average energy:

$\langle n \rangle =$  average quantum number for oscillator  $= [\exp(\beta\hbar\omega) - 1]^{-1}$  (Bose-Einstein distribution)

$$\langle E(T) \rangle = \frac{\sum_n \left( n + \frac{1}{2} \right) \hbar \omega e^{-\beta n \hbar \omega}}{\sum_n e^{-\beta n \hbar \omega}} = \frac{\hbar \omega}{2} + \frac{\sum_n n \hbar \omega e^{-\beta n \hbar \omega}}{\sum_n e^{-\beta n \hbar \omega}} = \frac{\hbar \omega}{2} - \frac{\partial}{\partial \beta} \ln \left( \sum_n e^{-\beta n \hbar \omega} \right) = \frac{\hbar \omega}{2} - \frac{\partial}{\partial \beta} \ln \frac{1}{1 - e^{-\beta \hbar \omega}} = \frac{\hbar \omega}{2} + \frac{\hbar \omega}{1 - e^{-\beta \hbar \omega}} = \left( \langle n \rangle + \frac{1}{2} \right) \hbar \omega$$

$$\sum_n x^n = (1-x)^{-1}$$

Specific heat in Einstein approximation:

$\Theta_E$  – Einstein temperature

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial}{\partial T} 3 N_A \langle E \rangle \right)_V = \left( \frac{\partial}{\partial T} 3 N_A \left( \langle n \rangle + \frac{1}{2} \right) \hbar \omega_E \right)_V = \frac{3 N_A k_B (\hbar \omega_E / k_B T)^2 e^{\hbar \omega_E / k_B T}}{\left( e^{\hbar \omega_E / k_B T} - 1 \right)^2}$$

High temperature limit ( $T \gg \Theta_E$ ) – exponents are replaced with expansions and we get Dulong – Petit result:

$$C_V = 3R \left[ 1 - \frac{1}{12} \left( \frac{\Theta_E}{T} \right)^2 + \dots \right] \approx 3R$$

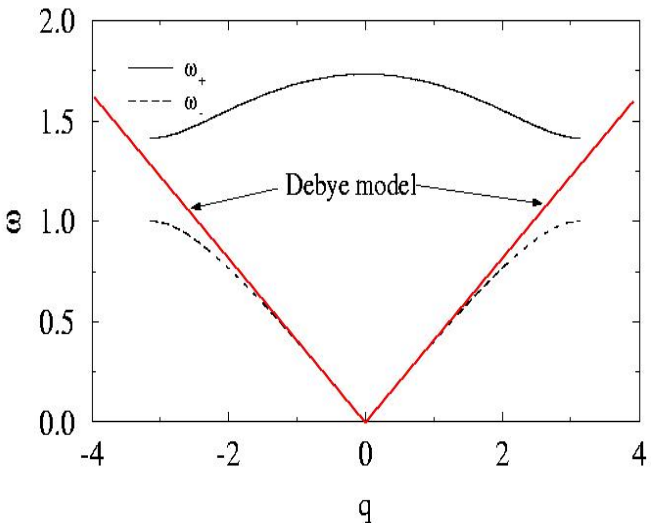
Low temperature limit ( $T \ll \Theta_E$ ) – predicts that specific heat should decrease to zero exponentially:

$$C_V = 3R \left( \Theta_E / T \right)^2 e^{-(\Theta_E / T)}$$

Real materials: atoms are coupled, vibrate collectively at many different  $\omega$

# Debye model of Lattice Specific Heat 1

**For thermodynamic properties optical modes are irrelevant (low T).  
We keep acoustic modes and replace them with purely linear mode with the same initial dispersion**



Enter discrete nature of the solid: total number of vibrational modes is normalized to  $3N_A$



$\exists$  maximum (cutoff) frequency  $\omega_D$

The number  $3N_A$  is large ( $10^{24}$ ), therefore we consider vibrational levels as continuous and write number of modes in  $\omega, \omega+d\omega$ :

Relation between  $\omega$  and wave vector  $q$  is defined by Debye approximation for sound waves: ~sound velocity

$$\int_0^{\omega_D} \rho(\omega) d\omega = 3N_A$$

$$\omega = c \frac{q}{2\pi} = \frac{c}{\lambda}$$

Periodic boundary conditions (L is the dimension of representative cube of continuum):

$$e^{i(xq_x + yq_y + zq_z)} = e^{i(x+L)q_x + (y+L)q_y + (z+L)q_z} \Rightarrow q_x, q_y, q_z = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots$$

Volume in reciprocal space for each wavevector is  $(2\pi L)^3 \rightarrow$  number of allowed values of  $\vec{q}$  per unit volume of  $\vec{q}$  space is  $(L/2\pi)^3 = V/8\pi^3$

Number of allowed  $\vec{q}$  values is large, so  $q \sim$  continuous variable  $\rightarrow$  number of modes with  $q$  or less is  $V/8\pi^3 \cdot$  volume of sphere with  $R = q$ :

$$N = \frac{V}{8\pi^3} \frac{4}{3} \pi q^3 \Rightarrow \rho(\omega) = \frac{dN}{d\omega} = \frac{4\pi V}{c^3} \omega^2$$

Real solid, elastic waves for each  $q$  have longitudinal component and 2 transverse:

$$\rho(\omega) = \frac{12\pi V}{\langle c \rangle^3} \omega^2$$

Total number of oscillators in interval  $\omega, \omega+d\omega$ :

$$\frac{12\pi V}{\langle c \rangle^3} \omega^2 d\omega = \frac{9N_A}{\omega_D^3} \omega^2 d\omega$$

Cutoff frequency for vibrational spectrum  $\rightarrow$

$$\omega_D = \langle c \rangle \left( \frac{3N_A}{4\pi V} \right)^{1/3}$$



# Debye model of Lattice Specific Heat 2

Specific heat in Debye model ( $x = \hbar\omega/k_B T$ ,  $\Theta_D = \hbar\omega_D/k_B$ ):

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \int_0^{\omega_D} \rho(\omega) \left( \langle n \rangle + \frac{1}{2} \right) \hbar \omega d\omega = \int_0^{\omega_D} k_B \left( \frac{\hbar \omega}{k_B T} \right) \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \frac{9N_A}{\omega_D^3} \omega^2 d\omega = 9R \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2}$$

$4\pi^4/15$



**High temperatures:**  $T \gg \Theta_D$  we replace exponential with series function and obtain Dulong Petit result

$$C_V = 3R \left[ 1 - \frac{1}{20} \left( \frac{\Theta_D}{T} \right)^2 + \dots \right]$$

**Low temperatures**  $T \ll \Theta_D$ , upper limit of integral is  $\infty$  and we get

$$C_V = \frac{12}{5} \pi^4 R \left( \frac{T}{\Theta_D} \right)^3 = \beta T^3 = 234 R \Theta_D^{-3} T^3$$

$$\Theta_D(N \text{ atoms}) = \sqrt[3]{\frac{N 234 R}{\beta}}$$

Note that it holds for 1 atom in unit cell = 3 phonon branches

Usually good for  $T < (\Theta_D/10 - \Theta_D/50)$ . For  $T >$  Debye region:

$$\rho(\omega) = \alpha_1 \omega^2 + \alpha_2 \omega^4 + \alpha_3 \omega^6 + \dots \Rightarrow C_V = \beta_1 T^3 + \beta_2 T^5 + \beta_3 T^7 + \dots$$

**Physical significance: Debye temperature is a measure of the stiffness of the crystal: above  $\Theta_D$  all modes are getting excited, and below  $\Theta_D$  modes begin to be “frozen out”, marking rapid reduction in  $C_V$  with decreasing temperature.**

Shortcoming of the model:  $\theta_D = \theta_D(T)$   
but at high T all vibrational modes are excited so  $\theta_D = \text{const.}$  (classical result)

# Application of Debye Model

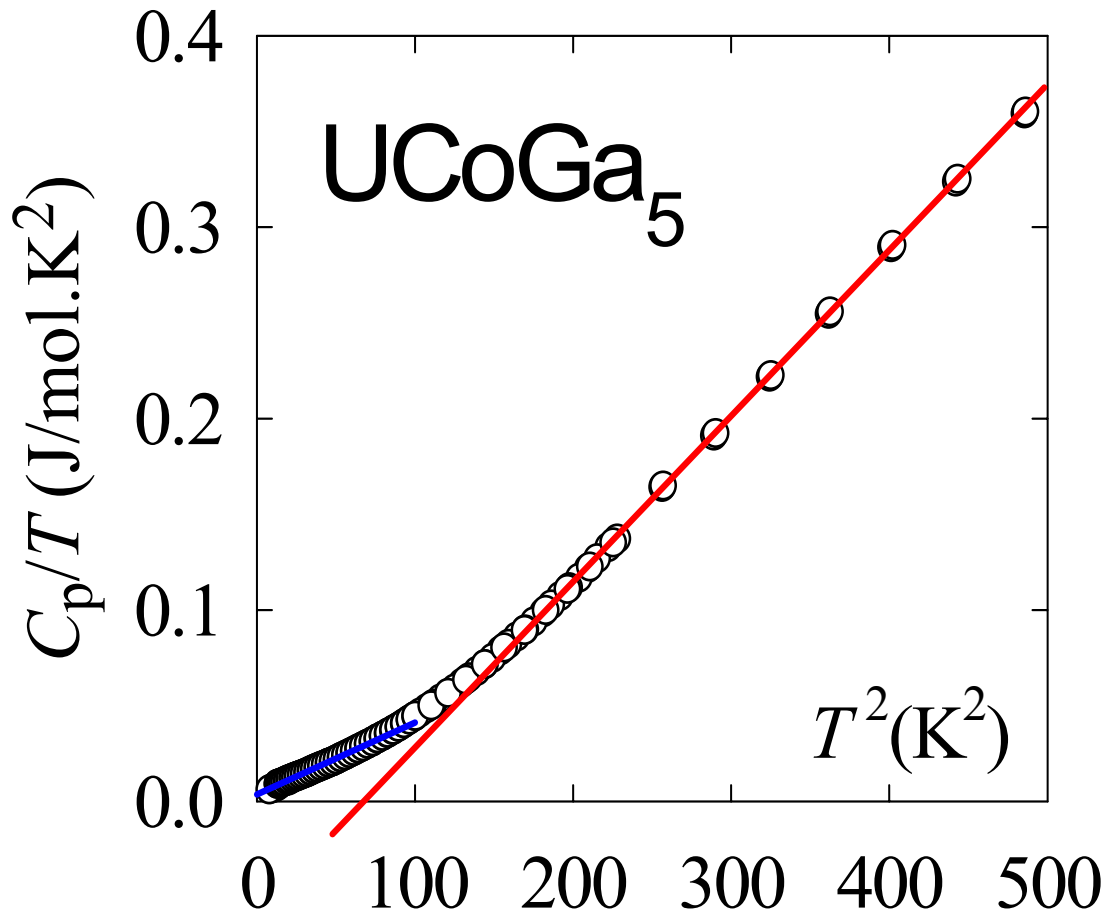
Debye model can be applied successfully to many materials with more than one atom in the unit cell.

Sometimes high temperature range can also have  $C_p \sim T^3$  which is unphysical.

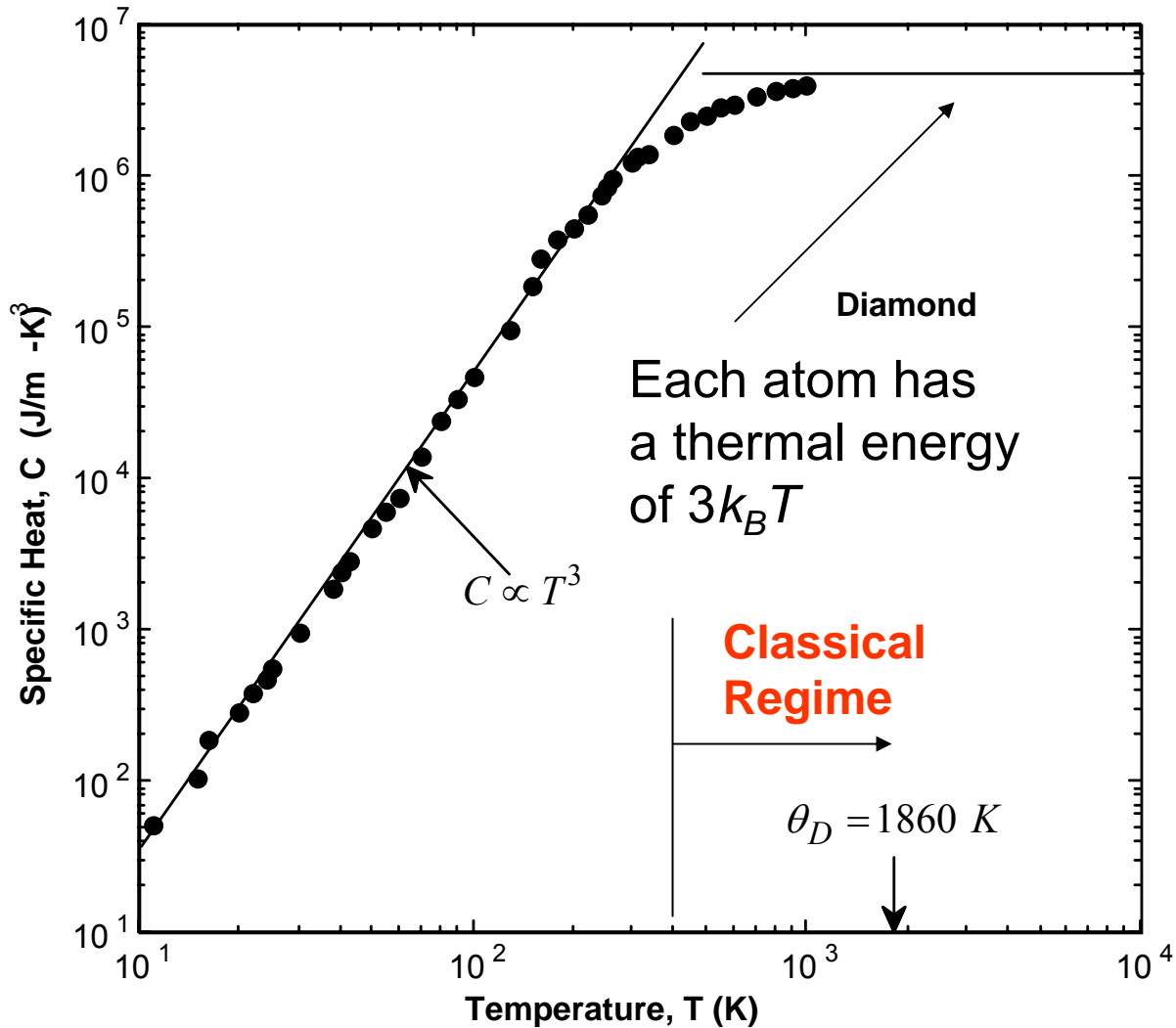
At  $T > \theta_D$  the model is not valid. Optical phonon mode contribution is not negligible. Thermal expansion may not be negligible

Debye temperatures of solids:

Aluminum	426K	Platinum	240K
Cadmium	186K	Silicon	640K
Chromium	610K	Silver	225K
Copper	344.5K	Tin (white)	195K
Gold	165K	Titanium	420K
$\alpha$ -Iron	464K	Tungsten	405K
Lead	96K	Zinc	300K
$\alpha$ -Manganese	476K	Diamond	2200K
Nickel	440K	Ice	192K



# Specific Heat Dominated by $\sim T^3$ Phonon Contribution



# Electronic specific heat

Gas obeying Fermi-Dirac statistics. Fermi Dirac distribution function:  $f(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/k_B T} + 1}$

At  $T=0$  all energy levels with  $\epsilon < \epsilon_F$  ( $\sim T_F = \epsilon_F/k_B$ ) are occupied, rest are vacant. At  $T > 0$  electrons with  $\epsilon \sim k_B T$  of  $\epsilon_F$  have sufficient thermal energy to become excited to vacant levels.

At  $T < T_F$ , fraction of electrons with  $\epsilon \sim k_B T$  is of the order of  $T/T_F$ , contributing to  $U \sim N_A (T/T_F) k_B T$  and to  $C \sim 2RT/T_F$

Since  $T_F \sim (10^4 - 10^5)K \rightarrow C_e \sim 10^{-2}R$  which is  $\sim 1\%$  of lattice contribution (think Dulong Petit).

Internal energy of a system of  $N$  electrons is:  $U = \int_0^\infty \epsilon f(\epsilon) n(\epsilon) d\epsilon$  where  $N = \int_0^\infty f(\epsilon) n(\epsilon) d\epsilon$

Total density of states for both spin directions is  $n(\epsilon)$ , so that  $n(\epsilon)d\epsilon$  is the number of energy levels in interval  $\epsilon, \epsilon+d\epsilon$

At very low temperatures  $T \ll T_F$ , we can write  $0 = \epsilon_F \frac{\partial N}{\partial T} = \int_0^\infty \epsilon \frac{\partial f}{\partial T} n(\epsilon) d\epsilon$



Nonzero only in the vicinity of  $\epsilon_F$ .

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \int_0^\infty \epsilon f(\epsilon) n(\epsilon) d\epsilon = n(\epsilon_F) \int_0^\infty (\epsilon - \epsilon_F) \frac{\partial f}{\partial T} d\epsilon = k_B^2 T \int_{x_0}^\infty \frac{x^2 e^x dx}{(e^x + 1)^2}$$

For  $x_0 = -\infty$   
 $\sim \pi^2/3$



We introduce  $x = (\epsilon - \epsilon_F)/k_B T$  and  $x_0 = -T_F/T$

$$C_e = \frac{\pi^2}{3} n(\epsilon_F) k_B^2 T = \gamma T$$

Linear T dependence of electronic specific heat

# Free electron model

Simplest but rather useful approximation. Electrons move as free particles with dispersion:

$$\varepsilon = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} [k_x^2 + k_y^2 + k_z^2]$$

Periodic boundary conditions:  $k_i = 2\pi n/L$  ( $i=x,y,z$ ), ( $n = 0, \pm 1, \pm 2, \dots$ )  $\rightarrow$  there is one allowed value of  $k$  for each cell of  $(2\pi/L)^3 = 8\pi^3/V \rightarrow$  number of allowed wave vectors per unit  $V$  of  $\vec{k}$  space is  $V/8\pi^3$

The lowest energy state is obtained by placing pairs of electrons in states with smallest  $\vec{k}$ , occupying all states within sphere of radius  $k_F$ :

$$\left(\frac{4\pi k_F^3}{3}\right) \frac{V}{8\pi^3} \cdot 2 = N \Rightarrow k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \Rightarrow \varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Fermi energy and radius of Fermi sphere depend only on electron density  $N/V$

Number of states  $N$  with  $\varepsilon < \varepsilon_F$  is:  $N = \frac{V}{3\pi^2} \left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}$ , density of states:  $n(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}$

Density of states at  $\varepsilon_F$ :  $n(\varepsilon_F) = \frac{m}{\pi\hbar^2} \left(\frac{3zN_A V_m^2}{\pi}\right)^{1/3}$  Where  $z=N/N_A$  is the conduction electron/atom ratio and  $V_m$  is the molar volume

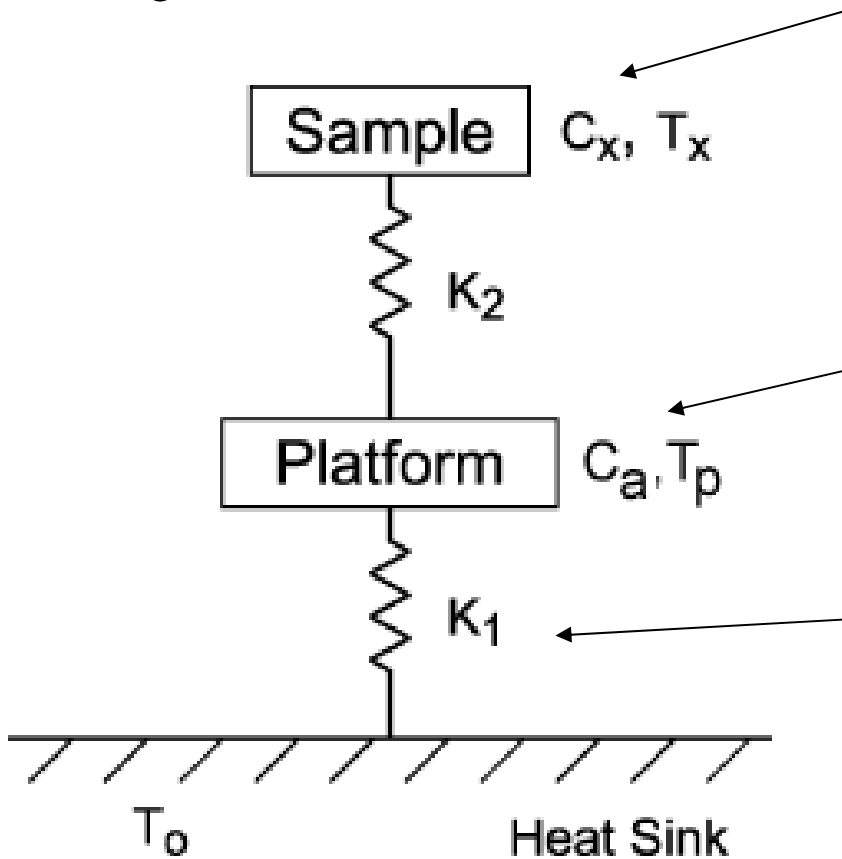
$$C_e = \frac{\pi^2}{3} n(\varepsilon_F) k_B^2 T = \gamma_0 T \Rightarrow \gamma_0 = \frac{m}{\hbar^2} (zN_A)^{1/3} \left(\frac{\pi V_m}{3}\right)^{2/3} k_B^2$$

**$C_e/T$  in free electron model**

# Thermal Relaxation Calorimetry 1

Based on a measurement of thermal response of a sample calorimeter assembly to a change in heating conditions.

Sample of unknown heat capacity  $C_x$  is attached to a sample platform with a thermal grease (e.g., apiezone N grease).



The platform consists of a thin sapphire or silicon disc, which has high thermal conductivity. A thin-film heater is evaporated onto the bottom of the platform, and the platform temperature  $T_p$  is determined from a bare temperature sensor attached to it.

Wires thermally link the platform to a copper heat sink held at a constant temperature  $T_0$ . They create a thermal link between the bath and platform with a thermal conductance  $K_1$ . They also provide electrical connections to the temperature sensor and heater.

Power  $P$  is applied to the platform via the thin-film heater, and a system of differential equations is solved

Heat flow diagram for a standard relaxation calorimeter

Cryogenics 43, 369 (2003)

# Thermal Relaxation Calorimetry: Single $\tau$

Combined addenda HC  
(platform, T sensor, heater,  
and grease)

$$P = C_a \frac{dT_p}{dt} + K_2(T_p - T_x) + K_1(T_p - T_0)$$

$$0 = C_x \frac{dT_x}{dt} + K_2(T_x - T_p)$$

Thermal conductance of  
sample – platform thermal link

Power  $P$  is applied to the heater, the platform sample assembly warms to a temperature  $T_0 + \Delta T = T_0 + P/K_1$ . If the thermal connection sample - platform is very strong ( $K_2 \gg K_1$ ,  $T_x \approx T_p$ ), we get:

$$P = (C_a + C_x) \frac{dT_p}{dt} + K_1(T_p - T_0)$$

Power  $P$  is discontinued and the platform/sample assembly will cool to the bath temperature  $T_0$ :

$$T_p(t) = T_0 + \Delta T e^{-t/\tau}; \tau = (C_a + C_x) / K_1$$

For small  $\Delta T$  ( $\Delta T/T \ll 1$ ), we can ignore  $T$  dependence of  $C_a$ ,  $C_x$  and  $K_1$  and get  $C_x$  via  $\tau$

In this method (**using single  $\tau$** ) a steady state at constant  $P$  and  $T_p > T_0$  followed by relaxation to  $T_0$  **can be used to determine both  $K_1$  and  $C_x$** .  $K_1$  is determined by measuring the temperature change  $\Delta T$  that results when power  $P$  is applied. , Addenda heat capacity  $C_a$  can be determined from a decay measurement with no sample attached to the platform.

# Thermal Relaxation Calorimetry: Double $\tau$

This method is applied when  ~~$K_2 \gg K_1$~~  due to poor sample - platform thermal link. Therefore  $T_x \neq T_p$ . Thermal decay of  $T_p$  is described using two exponentials:

$$T_p(t) = T_0 + Ae^{-t/\tau_1} + Be^{-t/\tau_2}$$

Time constant  $\tau_2$  is usually much shorter than the other. Thus, there are two relaxation times:

1. Shorter relaxation process ( $\tau_2$ ) between the sample and platform
2. Longer gradual process ( $\tau_1$ ) due to thermal relaxation between the platform/sample and the heat-sink temperature bath.

By measuring decay curves it is possible to determine  $\tau_1$ ,  $\tau_2$ ,  $K_2$ , and  $C_x$  given known values for  $C_a$  and  $K_1$ . Series of decays cycles (10–100) can be averaged at each temperature to obtain data scatter of less than 1%.

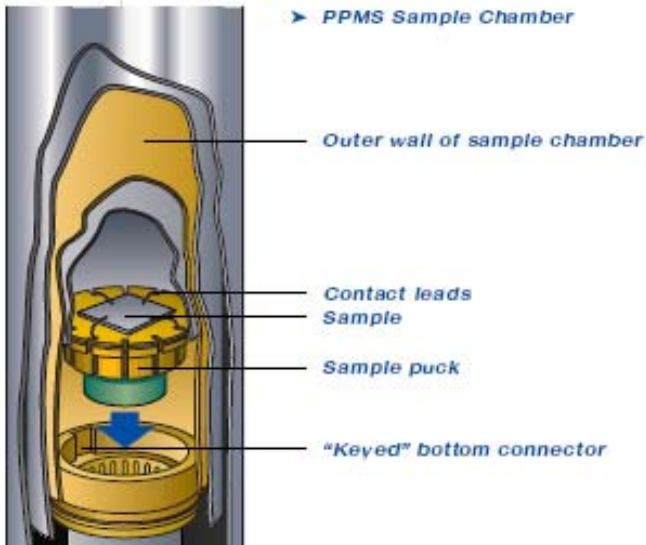
Drawbacks of the method:

1. Measurements can be time consuming and are becoming impractical for  $\tau_1 \sim 100s$
2. It is assumed that sample  $C_x$  does not vary much during  $T_0 + \Delta T$ , which may not be satisfied near the phase transition. Better results are obtained using single  $\tau$  method near the phase transition since near the phase transition  $C_x \gg C_a$  and we get:

$$C_x(T) = -K_1 \frac{T - T_0}{dT/dt}$$



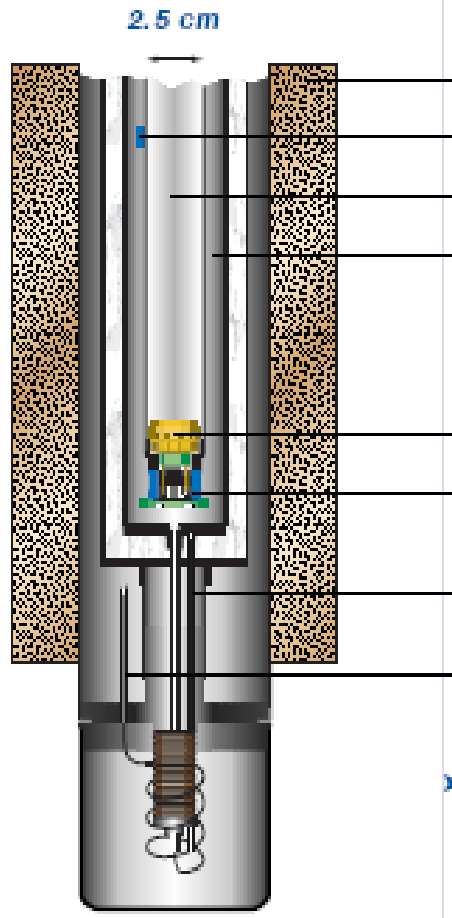
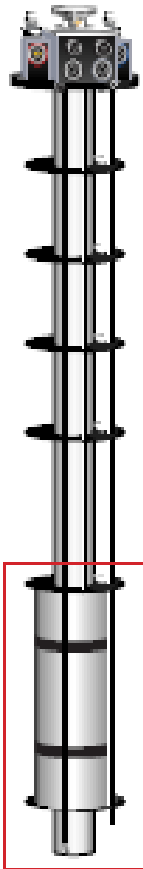
# Quantum Design PPMS



► **Specialized pucks, 2.4 cm in diameter, are used for different measurement applications.**

# PPMS Heat Capacity Option Hardware

PPMS Probe

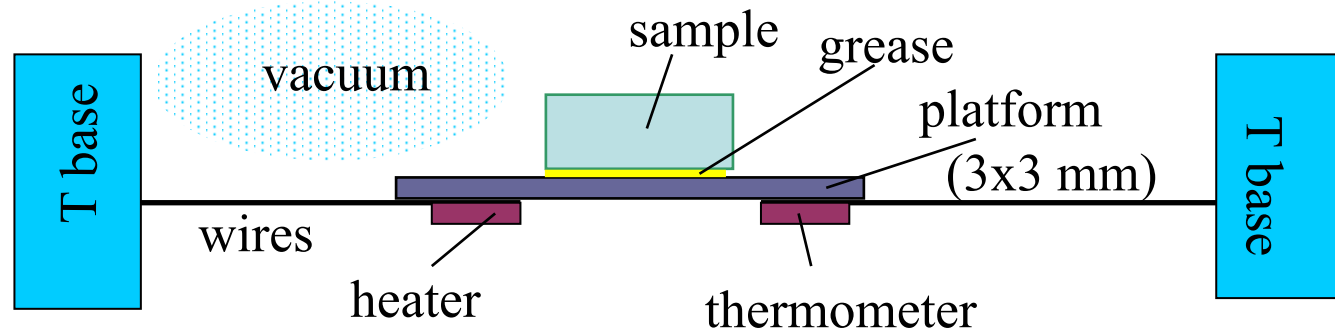
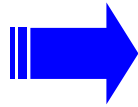


- Magnet
- Thermometer
- Sealed sample space
- Cooling annulus
- Puck
- Heaters and thermometers (2)
- Dual impedance system

► Multiple thermometers accurately monitor while heaters quickly control the system temperature.



# PPMS Heat Capacity Puck



After applying heat pulse  $P(t)$ , thermal response of a system is:

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

Base temperature

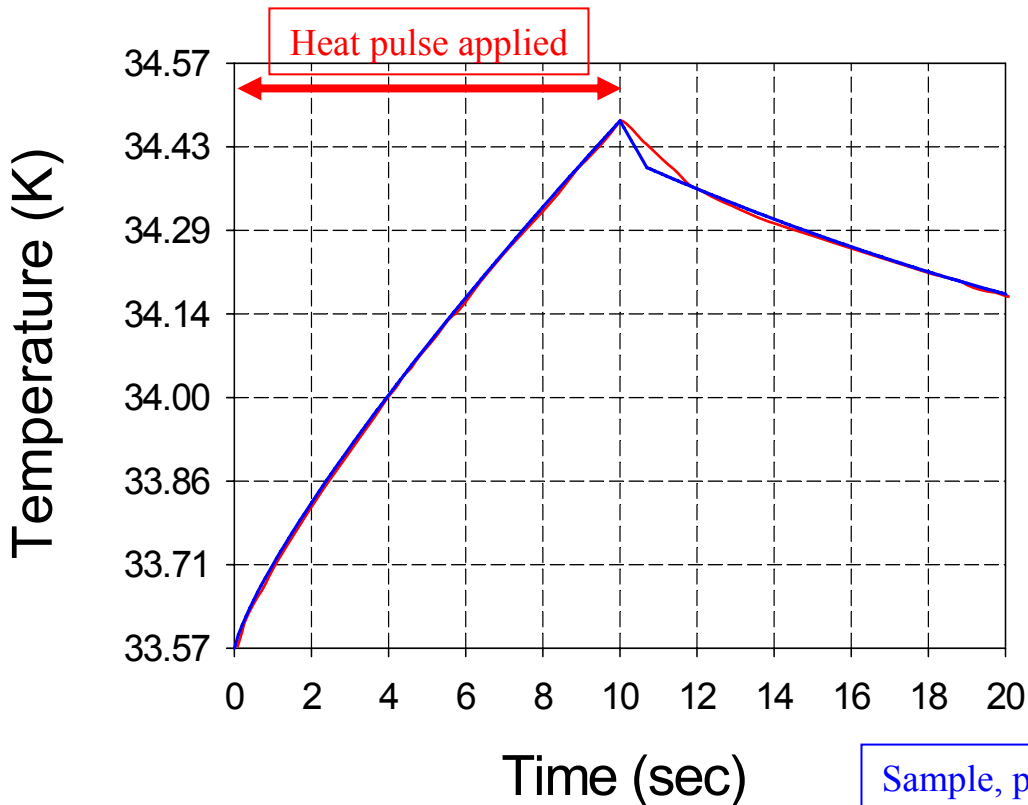
Heat coupling through wires, thermal conductance

$C_{\text{total}} = (\text{sample} + \text{platform} + \text{grease})$ . Heater power  $P(t)$  is varied, and  $T$  vs time  $t$  is measured, minimizing the difference between measured temperatures and the model. Here,  $T_b$  is the base temperature,  $K_w$  is the heat coupling through the wires.

We choose heat pulse as:

$$P(t) = \begin{cases} P_0 & (0 \leq t \leq t_0) \\ 0 & (t > t_0) \end{cases}$$

# Quantum Design Two $\tau$ Method



Sample is not 100% thermally attached to the platform, so we have to solve two coupled differential equations. The  $T(t)$  then usually looks like the blue curve.

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

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

Thermal coupling sample – platform through grease

# Data Fitting Procedure

Let's consider first ideal case of 100% coupling:  $C_{\text{total}} \frac{dT(t)}{dt} = P(t) - K_w(T(t) - T_b)$

For applied heat pulse:  $P(t) = \begin{cases} P_0 & (0 \leq t \leq t_0) \\ 0 & (t > t_0) \end{cases}$  and boundary conditions:  $T_{\text{on}}(0) = T_b$   
 $T_{\text{on}}(t_0) = T_{\text{off}}(t_0)$ ,

We obtain  $T(t)$ :  $T(t) = \begin{cases} T_{\text{on}}(t) = P_0 \tau (1 - e^{-t/\tau}) / C_{\text{total}} + T_b & (0 \leq t \leq t_0) \\ T_{\text{off}}(t) = P_0 \tau (1 - e^{-t_0/\tau}) e^{-(t-t_0)/\tau} / C_{\text{total}} + T_b & (t > t_0) \end{cases}$  Where:  $\tau = C_{\text{total}} / K_w$

$P_0, t_0$  are known.

All unknowns are obtained by minimizing the difference between measured temperatures  $T_i$  and those obtained from the model at the same time  $t_i$ .

$$\sum_i (T(t_i) - T_i)^2$$

↓ model      ↓ measured

In the real case of non-ideal coupling, more unknowns are fitted at the same time. The process is more extensive numerically. We fit only to the expression for  $T_p$  since the thermometer in the system is on the platform, no thermometer is attached to the sample and we assume  $T(\text{sample}) = T(\text{platform}) = T(\text{wires})$ .

# Schottky Anomaly 1

Consider system with discrete energy levels. When temperature is comparable to level separation  $\Delta$ , specific heat has a broad peak (Schottky anomaly).

Consider a general case of a system with multiple non-degenerate levels  $\varepsilon_1, \dots, \varepsilon_n$ .

Average thermal energy is:

$$U = N_A \frac{\sum_{i=0}^n \Delta_i e^{-(\Delta_i/k_B T)}}{\sum_{i=0}^n e^{-(\Delta_i/k_B T)}} \Rightarrow C_{schottky} = \frac{dU}{dT} = \frac{R}{T^2} \left\{ \frac{\sum_{i=0}^n \Delta_i^2 \exp\left(\frac{-\Delta_i}{k_B T}\right)}{\sum_{i=0}^n \exp\left(\frac{-\Delta_i}{k_B T}\right)} - \frac{\left( \sum_{i=0}^n \Delta_i \exp\left(\frac{-\Delta_i}{k_B T}\right) \right)^2}{\left( \sum_{i=0}^n \exp\left(\frac{-\Delta_i}{k_B T}\right) \right)^2} \right\}$$

Now reduce this to a two level system with energies  $\varepsilon_0=0$  and  $\varepsilon_1=\Delta$  with degeneracies  $g_0$  and  $g_1$ :

$$U = \frac{N_A g_1 \Delta e^{-(\Delta/k_B T)}}{g_0 + g_1 e^{-(\Delta/k_B T)}} \Rightarrow C_{schottky} = \frac{dU}{dT} = R \frac{g_0}{g_1} \left( \frac{\Delta}{k_B T} \right)^2 \frac{e^{(\Delta/k_B T)}}{\left[ 1 + (g_0/g_1) e^{(\Delta/k_B T)} \right]^2}$$

$T_\Delta = \Delta/k_B$   
Level separation in K



Low temperature limit ( $T \ll T_\Delta$ ):

High temperature limit ( $T \gg T_\Delta$ ):

Entropy:

$$C_{schottky} = R \frac{g_0}{g_1} \left( \frac{T_\Delta}{T} \right)^2 e^{-(T_\Delta/T)}$$

$$C_{schottky} = R \frac{g_0 g_1}{(g_0 + g_1)^2} \left( \frac{T_\Delta}{T} \right)^2$$

$$S_{schottky} = \int_0^\infty \frac{C_{schottky}}{T} dT$$

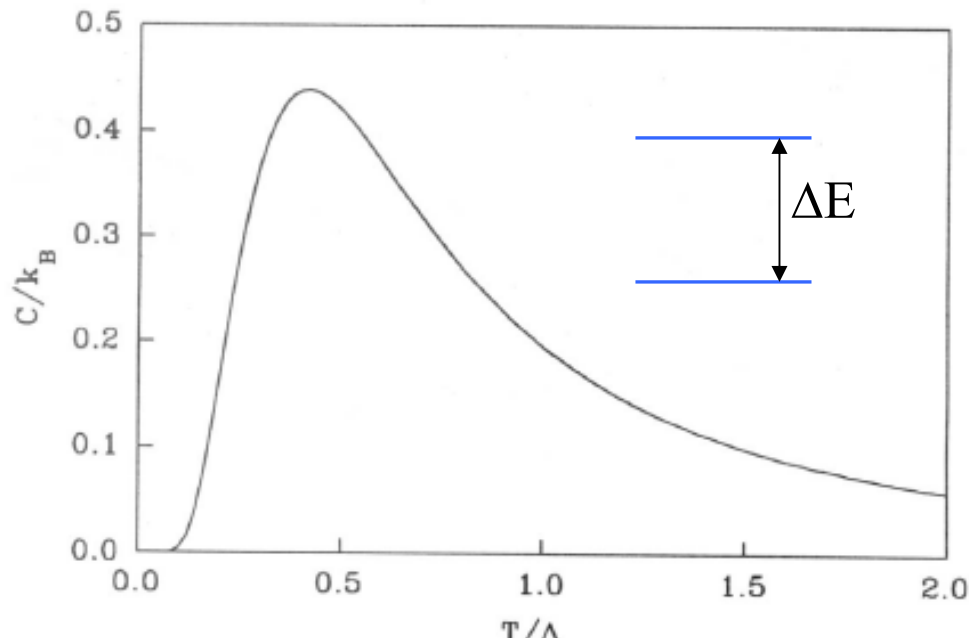
$$S_{schottky} = R \ln(1 + (g_1/g_0))$$

# Schottky Anomaly 2

Peak magnitude depends on ratio of  $g$ 's. It increases with degeneracy difference. Usually large when compared with other contributions, and dominant if occurs at low temperatures:

$$C_{\text{schottky}} \sim R, \text{ other contributions} \sim 10^{-2}R$$

In everyday life presents a problem since separation of other contributions is non - trivial



In the simplest case of two-level system,  $C_{\text{schottky}}$  shows as an anomaly with maximum at  $\sim 0.4 \cdot \Delta E$ . For a more complex level system, the Schottky specific heat is smooth function without any clear anomalies, but it can be fit with exponential and  $\sim T^{-2}$  terms

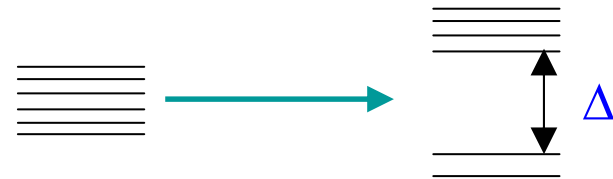
Nuclear Schottky anomaly – when interaction removes degeneracies of nuclear levels – could be produced by external magnetic field, by hyperfine magnetic field from conduction electrons or by CEF gradients.



# Schottky Anomaly Example

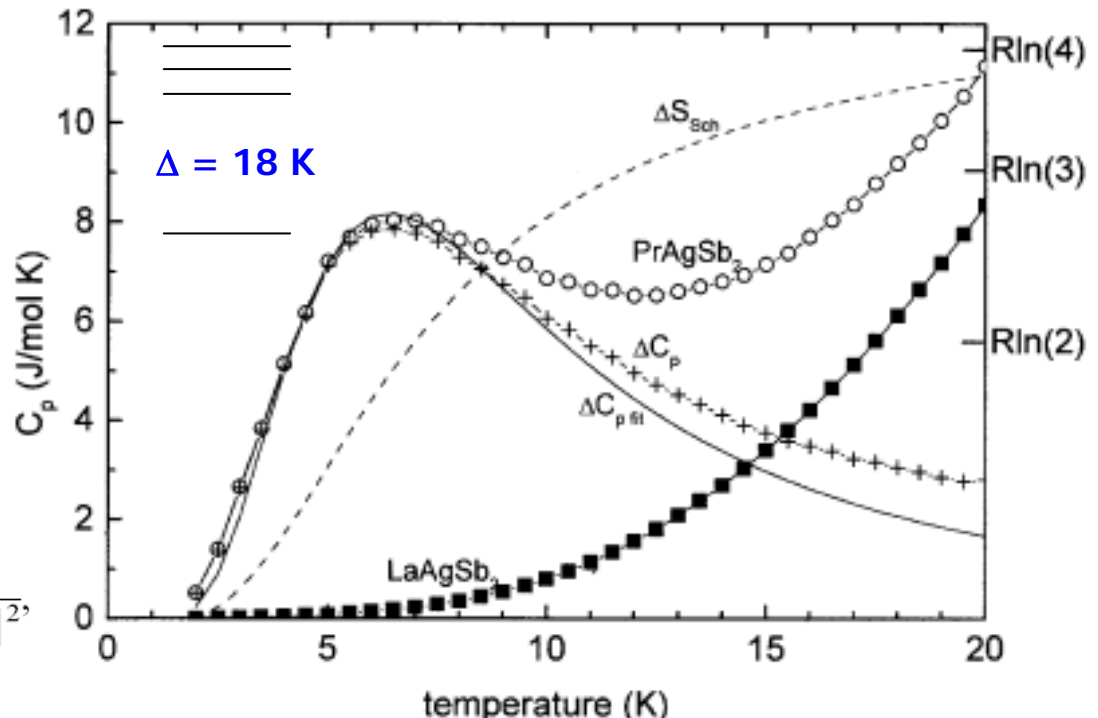
Given the Hund's rule, groundstate multiplet  $J$  we would expect  $R \ln(2J + 1)$  entropy associated with the magnetic state. This is what we find for Gd: ( $S = 7/2$ ,  $L = 0$  and  $J = 7/2$ ) therefore  $S \sim R \ln(8)$ . For other rare earths the spin-orbit coupling gives rise to crystalline electric field (CEF) splitting.

e.g.: Ce ( $J = 5/2$ ) in cubic point symmetry



This can be seen in the  $C_p$  as a Schottky anomaly. This is clearly shown at the right in  $\text{PrAgSb}_2$ .  $C_p$  is modeled as a two level system.

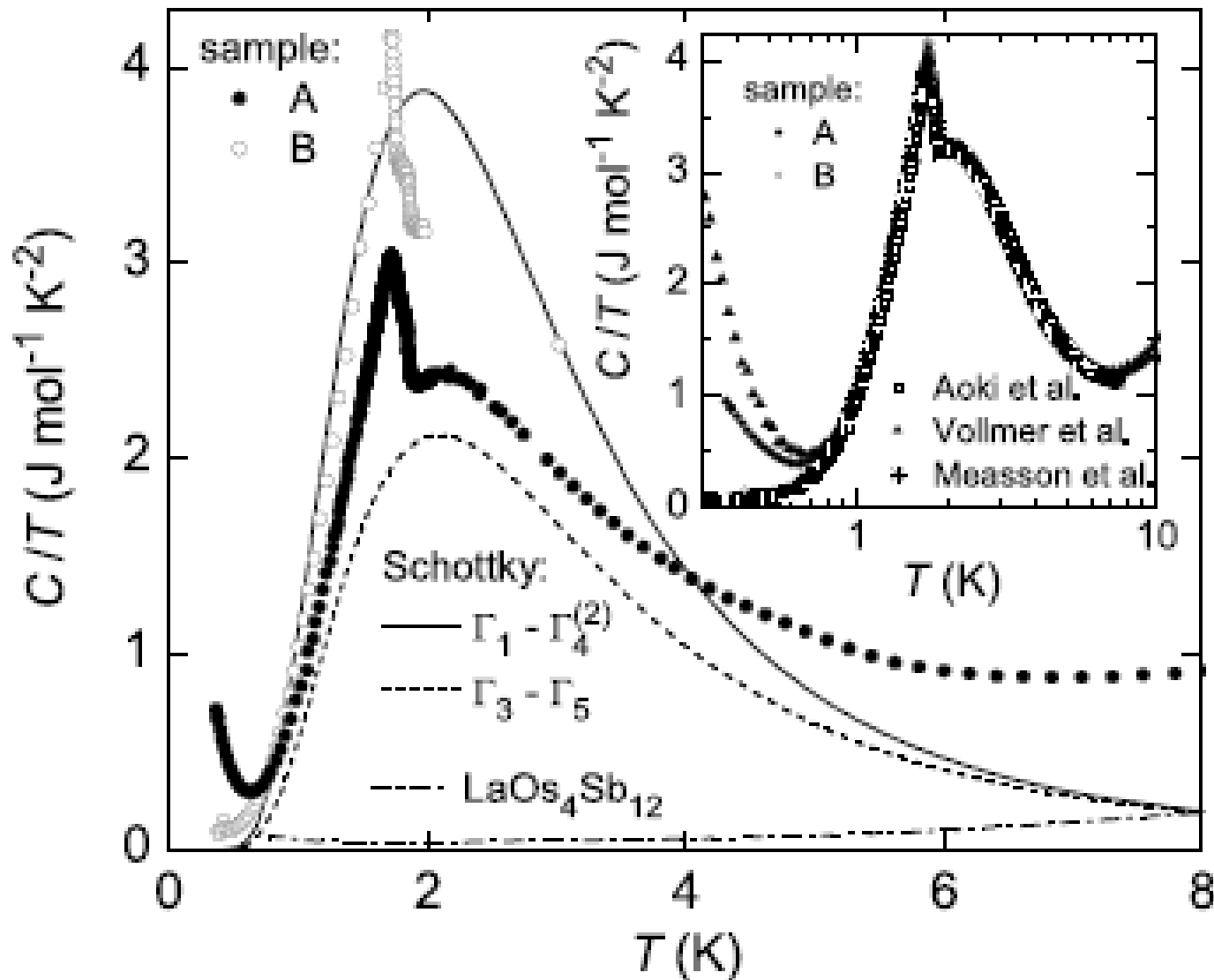
$$C_{\text{Sch}} = R \left( \frac{\Delta}{T} \right)^2 \frac{g_0}{g_1} \frac{\exp(\Delta/T)}{[1 + (g_0/g_1) \exp(\Delta/T)]^2}$$



K.D. Myers et al. / Journal of Magnetism and Magnetic Materials 205 (1999) 27–52



# Heavy fermion superconductor $\text{PrOs}_4\text{Sb}_{12}$



Phys. Rev. B 73, 104503 (2006)

# Specific Heat in Disordered Solids

Think of Schottky for two single level system with energy configurations  $\pm\varepsilon$ :

$$C_{schottky} = k_B \left( \frac{T_\Delta}{T} \right)^2 \text{sech}^2 \left( \frac{T_\Delta}{T} \right)$$

Disordered solids  $\sim$  collection of two level systems characterized by  $\pm\varepsilon$ :

$$C_V = 2k_B \int P(\varepsilon) \left( \frac{\varepsilon}{k_B T} \right)^2 \text{sech}^2 \left( \frac{\varepsilon}{k_B T} \right) d\varepsilon = 2k_B^2 P_0 T \int_0^\infty x^2 \text{sech}^2 x dx$$

Low T upper limit  $\infty$

$\pi^2/12$

Assume  $P(\varepsilon) = \text{const} = P_0$  and  $x = \varepsilon/k_B T$

Specific heat of disordered two level system has **linear** T contribution to heat capacity:

$$C_V = \frac{\pi^2}{6} P_0 k_B^2 T$$

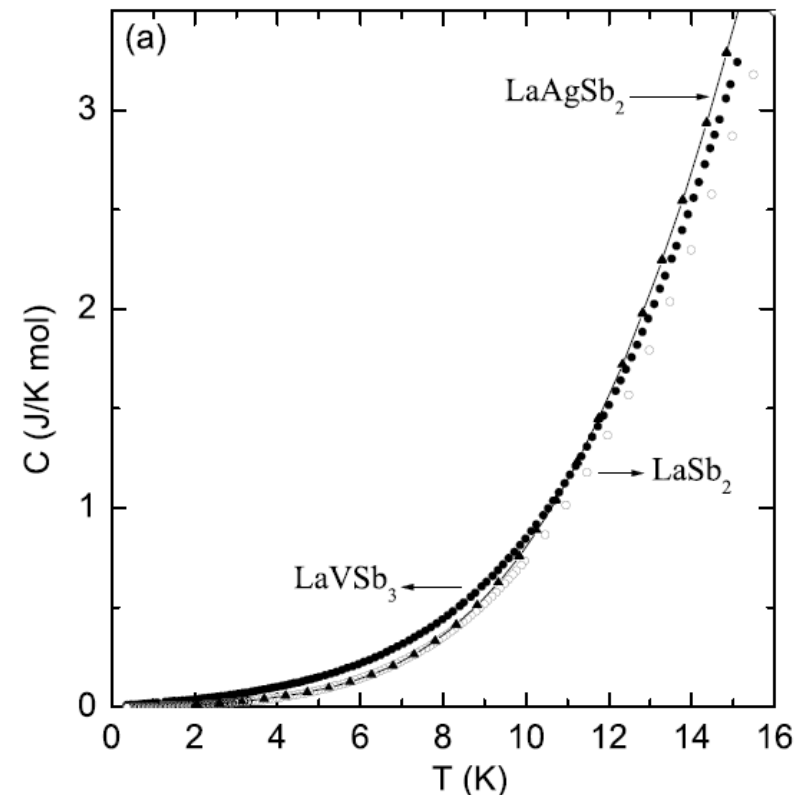
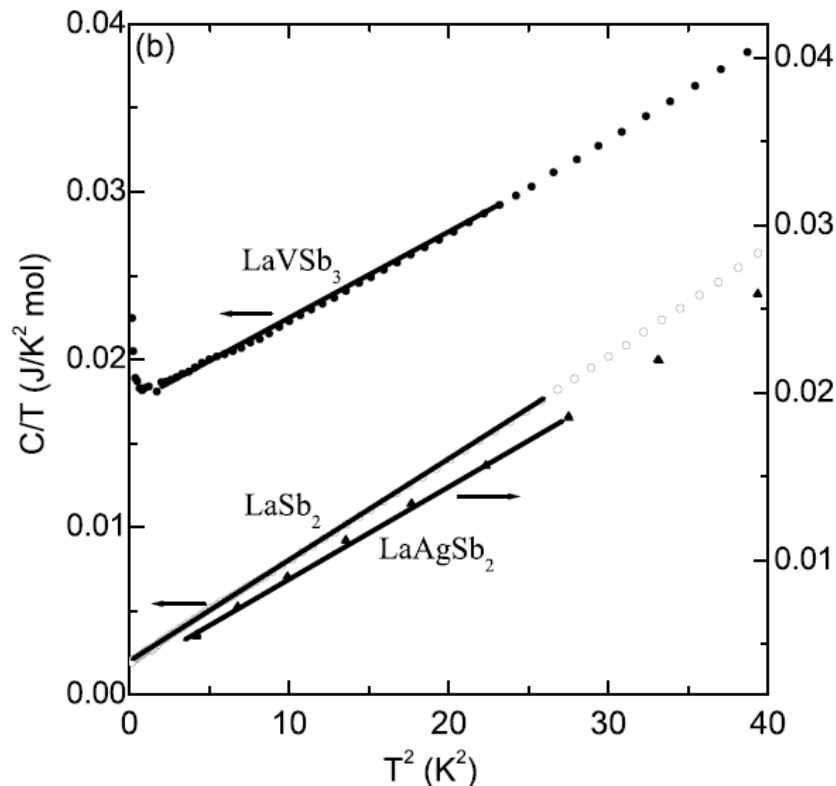
# Paramagnetic Metals at Low Temperatures

At low temperatures both electronic and vibrational excitations contribute:

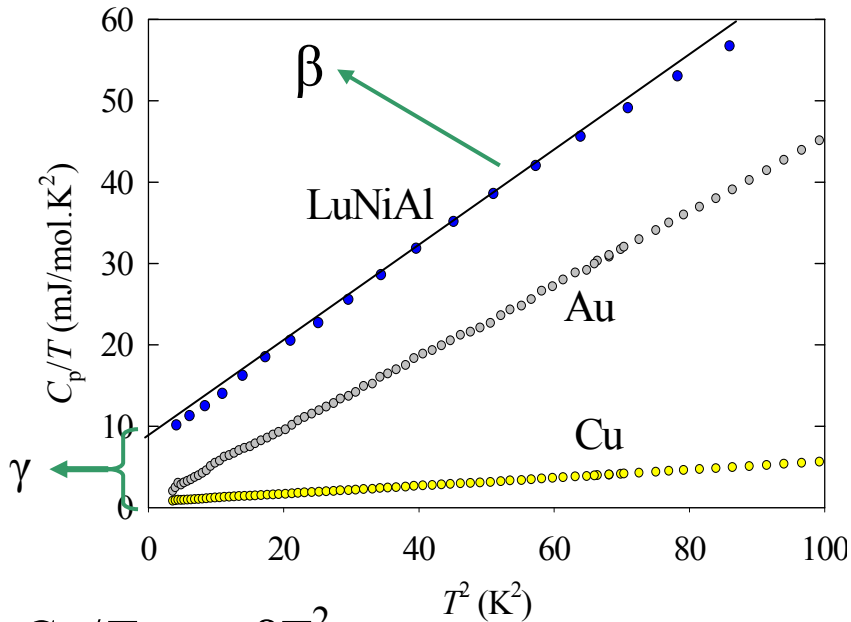
$$C_p = aT + bT^3$$

Clean separation of  $a$  and  $b$  is usually done by plotting  $C/T$  versus  $T^2$ .

As we have seen  $a$  is proportional to  $N(E_F)$  and  $b$  is proportional to the Debye temperature.



# Effective mass



$$C_p / T = \gamma + \beta T^2$$

$\gamma$  (mJmol<sup>-1</sup>K<sup>-2</sup>):

	Li	Na	K	Fe	Mn	Cu	Zn	Ag	Au	Al	Ga
Free e	0.8	1.1	1.7	0.6	0.6	0.5	0.8	0.6	0.6	0.9	1.0
exp.	1.6	1.4	2.1	4.6	15.2	0.7	0.6	0.6	0.7	1.3	0.6

Electronic specific heat coefficient  $\gamma$  can be estimated from the low-temperature specific-heat data, where the lattice part reduces to  $\sim T^3$  dependence.

In real metals, the  $\gamma$  value is often different from that obtained by free electron model.

We can introduce an effective mass  $m^*$  to account for this difference, since  $n(E_F)$  is proportional to the carrier mass  $m_e$ .

$$\frac{m^*}{m_e} = \frac{\gamma_{\text{exp}}}{\gamma_{\text{f.e.}}}$$

# Heavy Fermions

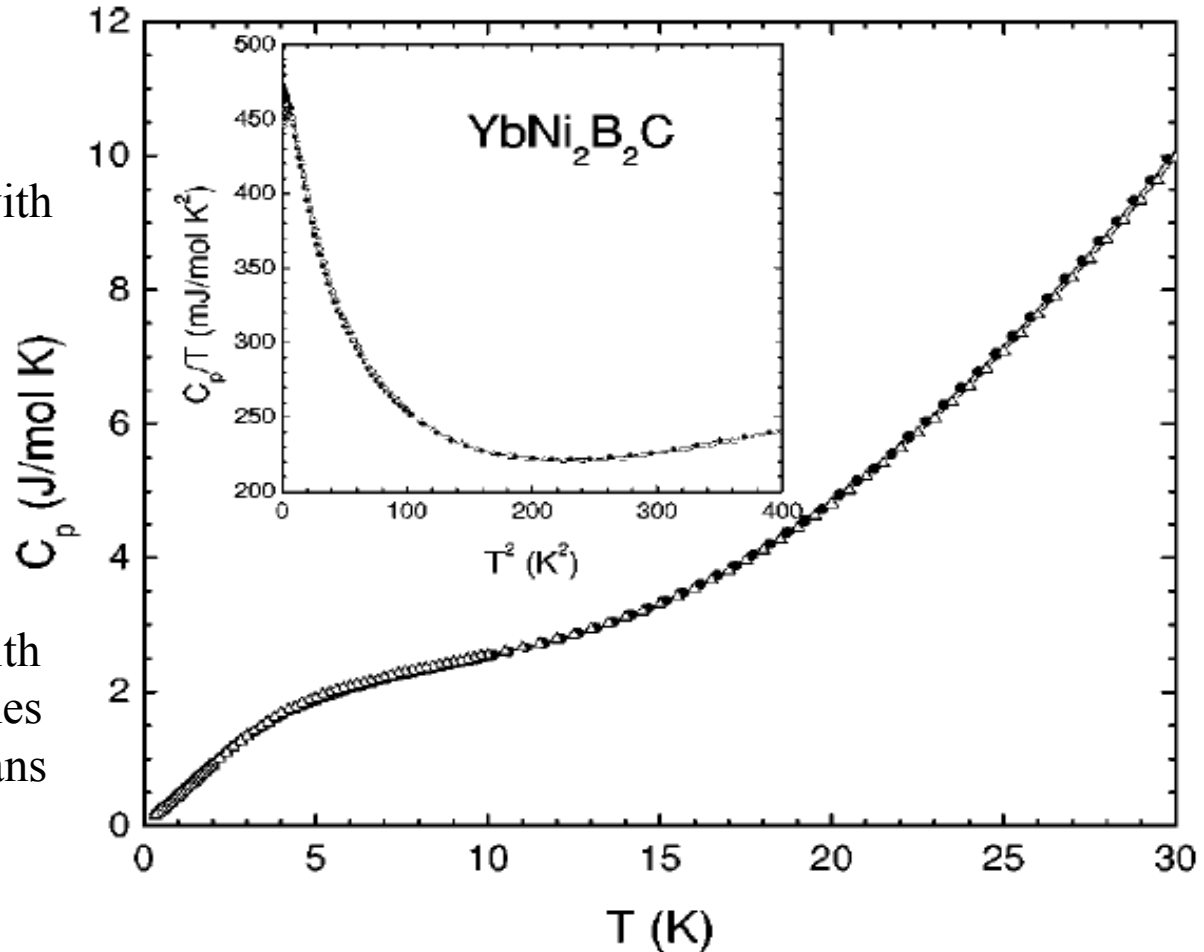
The electronic specific heat can be used as a measure of the electron effective mass, based on the free electron result of:

$$\gamma = k_B^2 T \cdot (mk_F/3\hbar^2)$$

Heavy Fermions are compounds with exceptionally high values of  $\gamma$  for

$T < T_K$ , the Kondo temperature.

They are defined as compounds with  $\gamma > 100 \text{ mJ/mol-K}^2$ , about 100 times the value of  $\gamma$  for Cu. Large  $\gamma$  means large electron mass, ergo, heavy fermion.

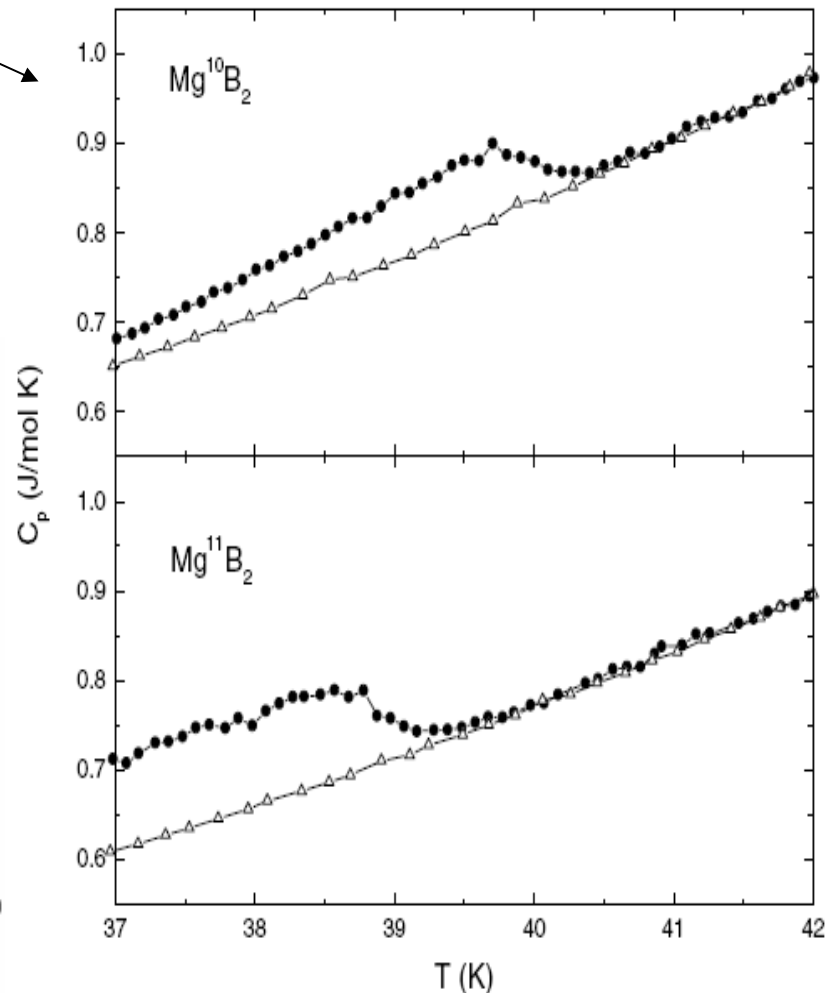
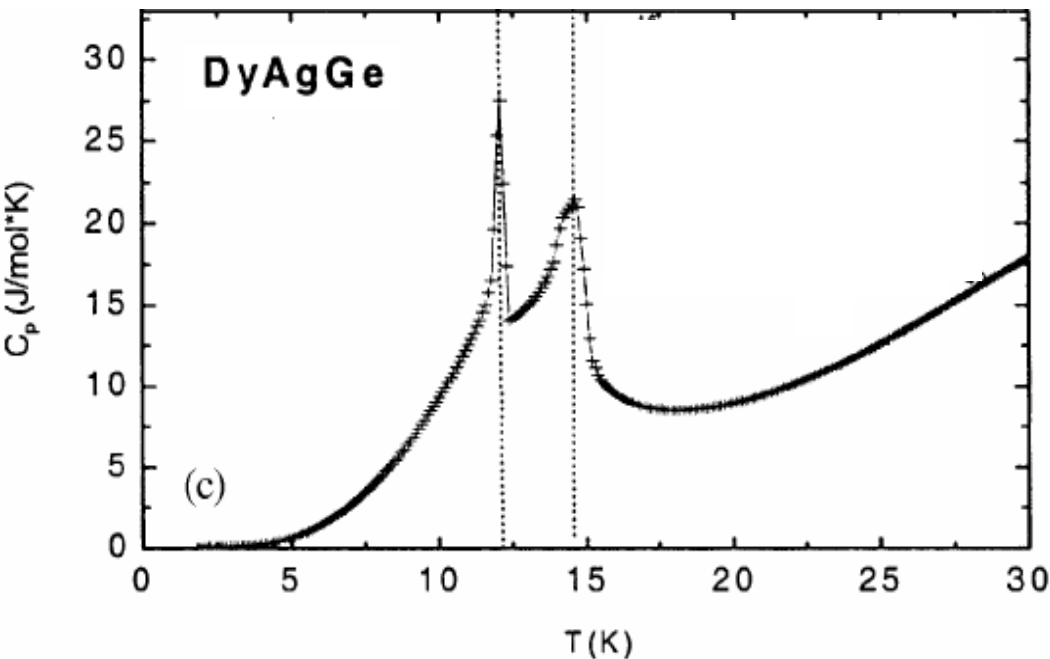


M. A. Avila,\* S. L. Bud'ko, and P. C. Canfield PHYSICAL REVIEW B 66, 132504 (2002)

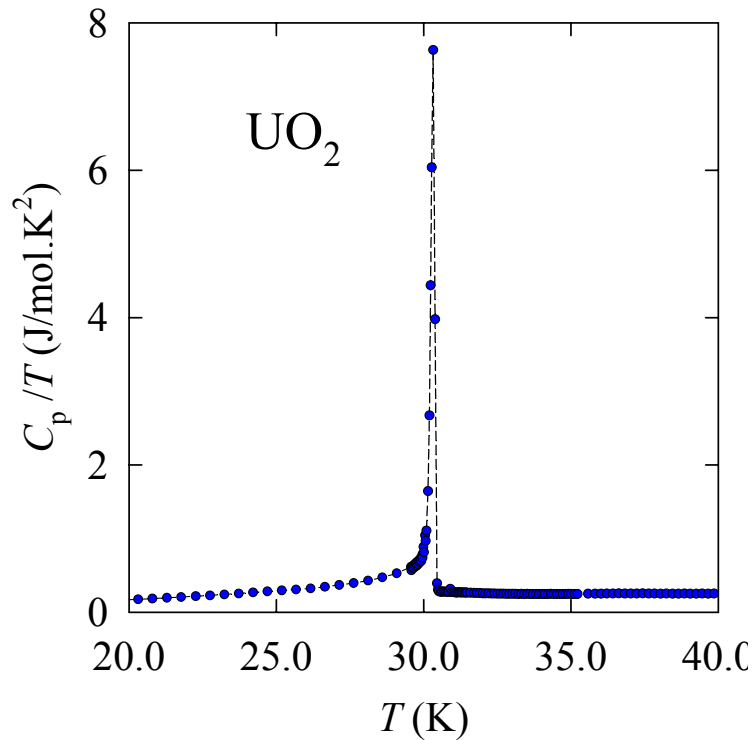
# Phase Transitions

Specific heat can also be used to locate and characterize phase transitions. We can suppress superconducting  $T_c$  with an applied magnetic field, so the  $C_p$  feature can be more clearly seen via comparison to the non-superconducting (in high applied magnetic field) compound.

Local moment ordering can be seen even more clearly (larger entropy). Shown here are a series of transitions in antiferromagnetic DyAgGe.



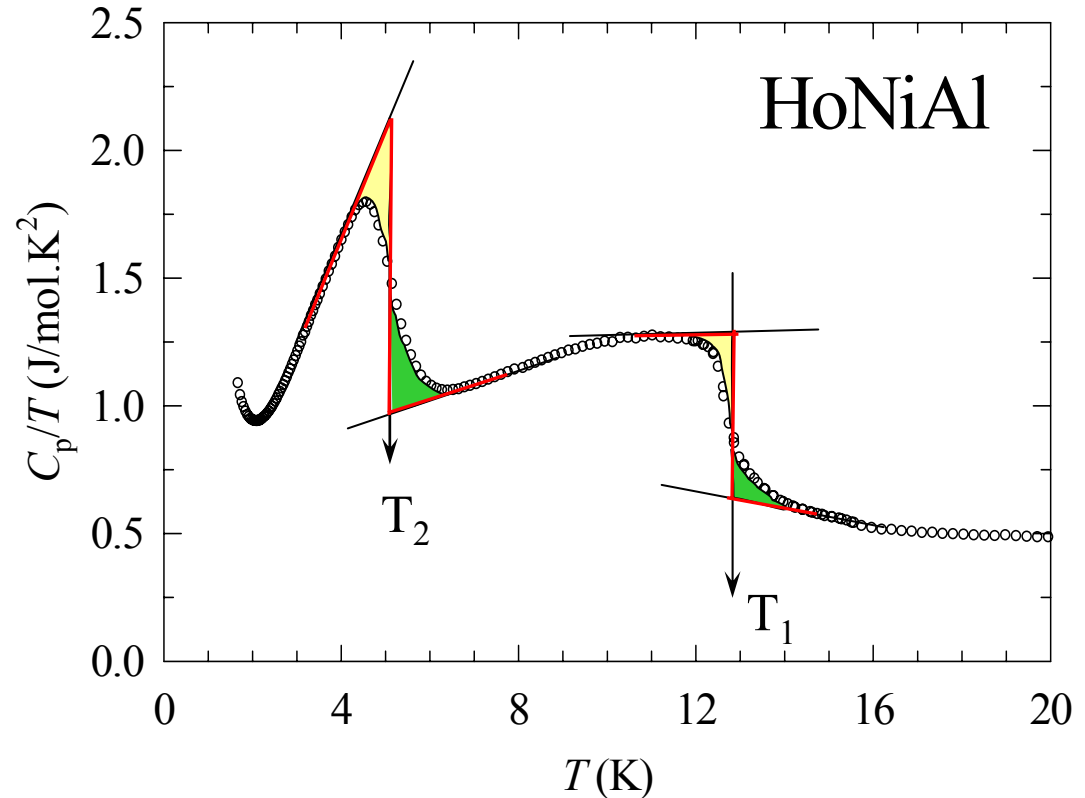
# First and Second Order Phase Transitions



Not ideal  $\delta$  function but sharp anomaly.  
Clear identification of  $T_C$ .

Think that 
$$C_P = T \left( \frac{\partial S}{\partial T} \right)_P$$

So if S has discontinuity,  $C_p$  will have sharper  
(like  $\partial\rho/\partial T$  at magnetic transition)



$T_C$  can be determined e.g. by idealization of the specific heat jump under the constraint of entropy conservation. Circles are real experimental points, red line is the idealization drawn in the way that the yellow and green areas are equal to satisfy the entropy conservation.

# Specific Heat and Critical Region

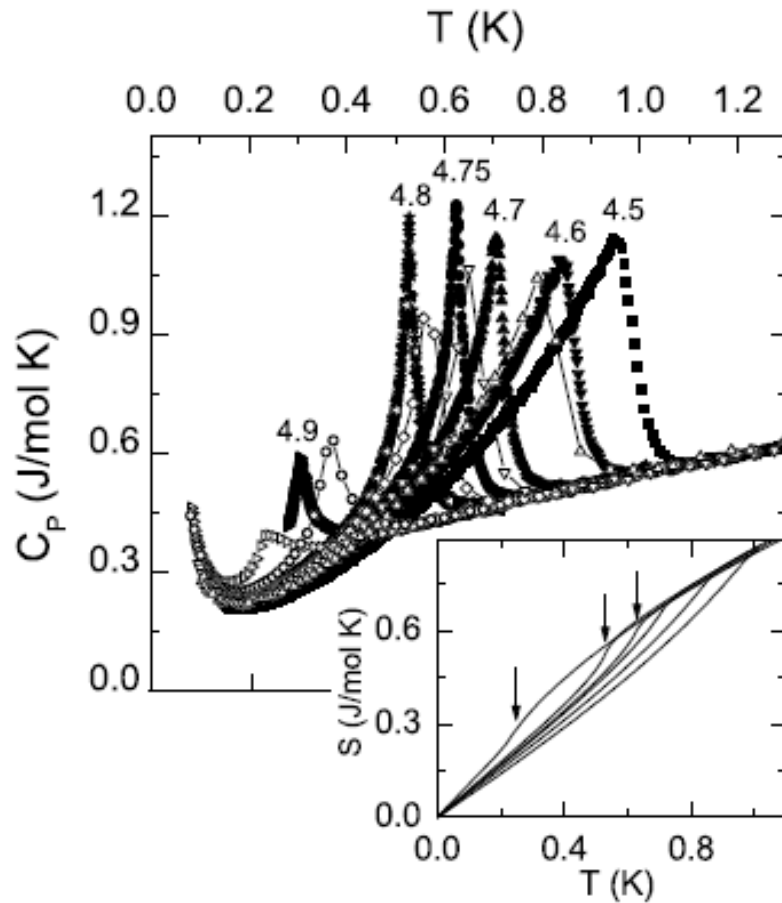


FIG. 1. Specific heat vs temperature of  $\text{CeCoIn}_5$ . Closed symbols—decay method, for indicated fields in Tesla; open symbols—heat pulse method: ( $\Delta$ ) 4.62 T, ( $\nabla$ ) 4.72 T, ( $\diamond$ ) 4.77 T, ( $\blacktriangleleft$ ) 4.8 T, ( $\circ$ ) 4.87 T, ( $\blacktriangleright$ ) 4.925 T. Inset: calculated entropy  $S$ ; left to right: 4.925, 4.8, 4.75, 4.7, 4.6, and 4.5 T. Arrows indicate steplike features in  $S$  at  $T_c$  for  $H > 4.7$  T.

Basic scaling in the critical region (near critical temperature that corresponds to order – disorder transition):

$$C_{p,V} \approx |t|^{-\alpha} \text{ for } T > T_c \text{ and } C_{p,V} \approx |t|^{-\alpha'} \text{ for } T < T_c$$

$\alpha$  is the critical exponent and  $t = \frac{T - T_c}{T_c}$

Magnetic specific heat in Heisenberg magnetic systems scales with  $\alpha = \alpha' \approx 0.01$  (Fe, Ni,  $\text{EuO}$ ...)

Sometimes nature of transition may change in magnetic field: Magnetic field induced first order transition in heavy fermion superconductor  $\text{CeCoIn}_5$  detected by specific heat measurement



# Specific Heat of Spin Waves 1

For  $T > 0$  thermal excitations create spin waves in magnetically ordered materials that propagate due to exchange coupling between neighboring spins. Heisenberg hamiltonian:

$$\hat{H} = -2J \sum_{i,j} \vec{S}_i \vec{S}_j$$

Sum over all spins  $i$  and all  $j$  of their NN's  
Each spin has associated magnetic moment

$$\vec{\mu}_i = \gamma \hbar \vec{S}_i$$

Gyromagnetic ratio

Consider spin oscillations along linear ferromagnet. Ground state: all spins are aligned along  $z$  with excitation:

$$-2J \vec{S}_l (\vec{S}_{l-1} + \vec{S}_{l+1}) = -\frac{2J}{\gamma \hbar} \vec{\mu}_l (\vec{S}_{l-1} + \vec{S}_{l+1}) = -\vec{\mu}_l \vec{B}_e$$

Effective magnetic (exchange) field

Exchange field  $B_e$  will induce a torque on spin  $\vec{S}_l$ :  $\frac{d(\hbar \vec{S}_l)}{dt} = \gamma \hbar \vec{S}_l \times \vec{B}_e \Rightarrow \frac{d\vec{S}_l}{dt} = \frac{2J}{\hbar} \vec{S}_l \times (\vec{S}_{l-1} + \vec{S}_{l+1})$

With approximation of small spin deviation (good at low  $T$ ):  $S_l^z \approx S, S_l^x, S_l^y \ll S$

$$\frac{d(S_l^x)}{dt} = \frac{2JS}{\hbar} (2S_l^y - S_{l-1}^y - S_{l+1}^y), \frac{d(S_l^y)}{dt} = -\frac{2JS}{\hbar} (2S_l^x - S_{l-1}^x - S_{l+1}^x), \frac{dS_l^z}{dt} = 0$$

We look for wave solutions ( $a$  = lattice parameter):  $S_l^x = \xi_x e^{i(\omega t + lqa)}, S_l^y = \xi_y e^{i(\omega t + lqa)}$

And get new sets of equations:  $-i\omega \xi_x + \frac{4JS}{\hbar} (1 - \cos qa) \xi_y = 0, \frac{4JS}{\hbar} (1 - \cos qa) \xi_x + i\omega \xi_y = 0$

# Specific Heat of Spin Waves 2

Nontrivial solutions if determinant is zero, we get spin wave dispersion relation:

$$\omega = \frac{4JS}{\hbar} (1 - \cos qa) \approx \frac{4JS}{\hbar} \frac{(qa)^2}{2} = \frac{2JSa^2 q^2}{\hbar}$$

At low T where low frequencies (long wavelength) dominate so  $(1 - \cos qa) = (1/2)(qa)^2$

Now in 3D in the small q limit this becomes:

$$\omega = \alpha_f \cdot \frac{2JSa^2 q^2}{\hbar}$$

$\alpha_f$  - constant that depends on crystal structure  
Works well in long wavelength limit for metallic ferromagnets too.

Antiferromagnets:

$$\omega = \alpha_a \cdot \frac{2J'Sa^2 q}{\hbar}$$

Solutions doubly degenerate, Two spin wave modes with  $\omega$  for each q (see Rev. Mod. Phys. 30, 1 (1950))

We can write:  $U = \sum_q \frac{\hbar\omega_q}{e^{(\hbar\omega_q/k_B T)} - 1} = \frac{V}{2\pi^2} \int_0^\infty \frac{\hbar\omega_q q^2 dq}{e^{(\hbar\omega_q/k_B T)} - 1} = \frac{V}{2\pi^2} b^{-3/2} (k_B T)^{5/2} \int_0^\infty \frac{x^4 dx}{e^{x^2} - 1}$

(long wavelength, small frequencies)  
 $(x^2 = q^2 b/k_B T$  and  $b = 2\alpha_f J S a^2)$

Sum over allowed values of q (1<sup>st</sup> BZ) Number of modes with q, q+dq is  $n(q)dq = (dN/dq)dq = (V/2\pi^2)q^2 dq$   
(Recall Debye model)

Specific heat is then:  $C_M = \left( \frac{dU}{dT} \right)_V = c_f N_A k_B \left( \frac{k_B T}{2JS} \right)^{3/2}$

For antiferromagnets:

$$C_M = \left( \frac{dU}{dT} \right)_V = c_a N_A k_B \left( \frac{k_B T}{2J'S} \right)^3$$

In insulators:

In metals:

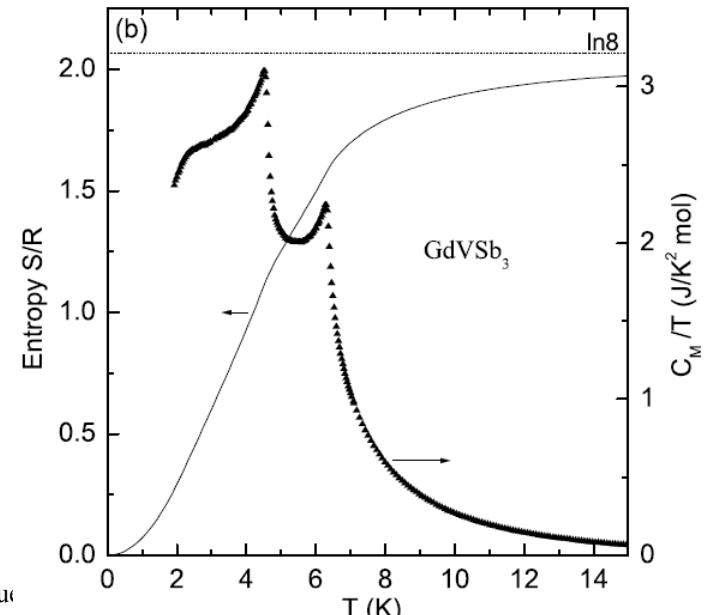
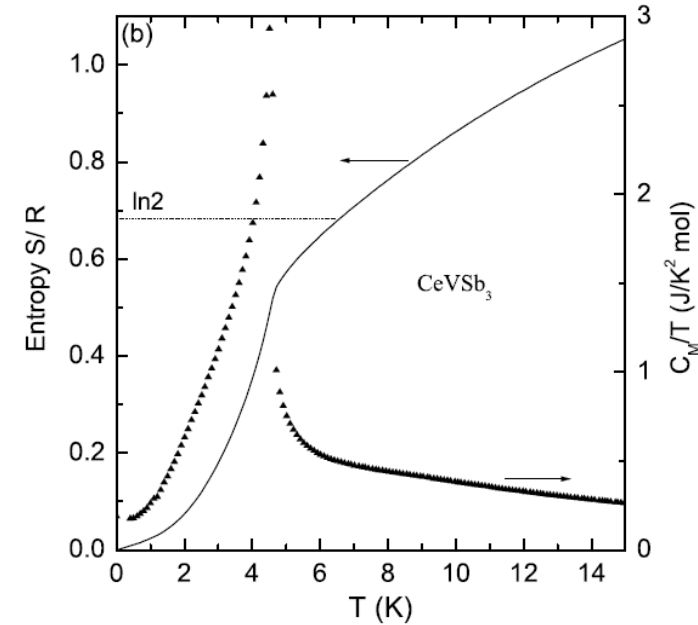
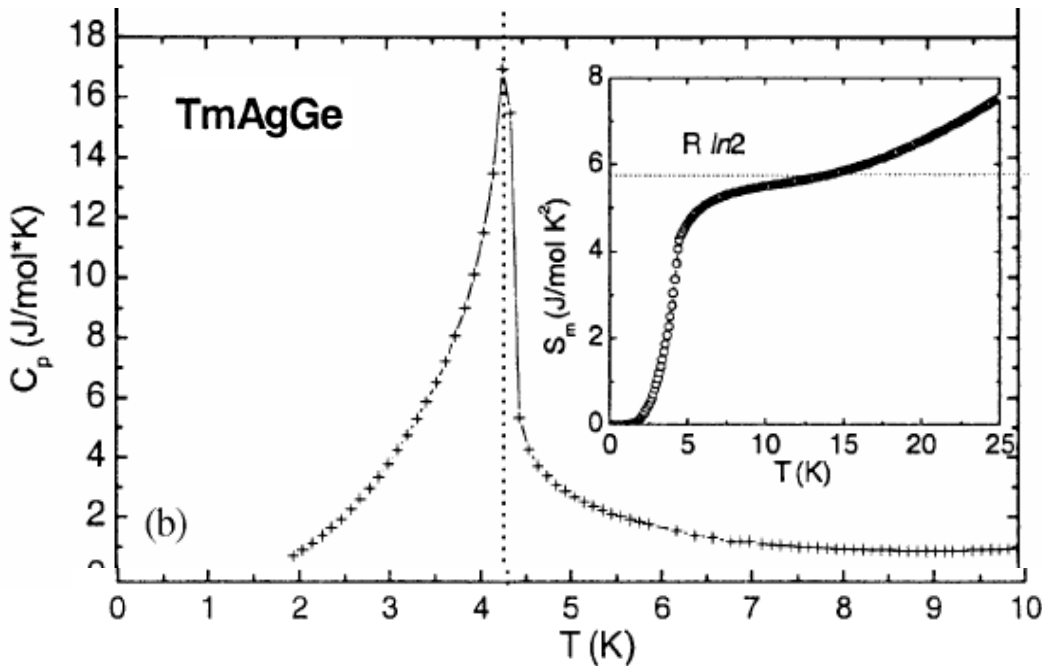
$$C_p = \beta T^3 + \delta T^{3/2} \quad C_p = \gamma T + \beta T^3 + \delta T^{3/2}$$

# Entropy Associated with Magnetic Order

$$S = \int (C_p/T) dT$$

For these local moment systems  $S \sim R \ln D$

We can determine how much entropy (change) is associated with a given state. For magnetic systems we need to use the magnetic  $C_p$ . In practice, this is done by subtracting off the  $C_p(T)$  data from a non-magnetic analogue (e.g. LuAgGe from TmAgGe).



# Specific Heat of BCS Superconductors

Attraction of electron pairs by virtual phonon exchange, leading to  $T$  – dependent gap  $2\Delta$  at the Fermi level. At  $T = 0$ :  $2\Delta(0) = 3.52k_B T_C$

Number of broken pairs as the temperature is increased is proportional to  $\exp[-2\Delta(0)/k_B T]$ , so contribution to electronic specific heat in superconducting state is:

$$\frac{C_{el}^s}{\gamma T_C} = a e^{(-bT_C/T)}$$

$a = 8.5, b = 1.44$  for  $2.5 < T_C/T < 6$   
 $a = 26, b = 1.62$  for  $7 < T_C/T < 12$

Schrieffer, J. R. *Theory of Superconductivity*, Benjamin, New York 1965

Near  $T_C$  there is abrupt discontinuity since gap vanishes at  $T_C$ . No latent heat is released (second order phase transition):

$$\frac{C_{el}^s(T_C) - \gamma T_C}{\gamma T_C} = 1.43$$

Other complications may involve : strong coupling, gap anisotropy, presence of two distinct energy scales (two gaps).

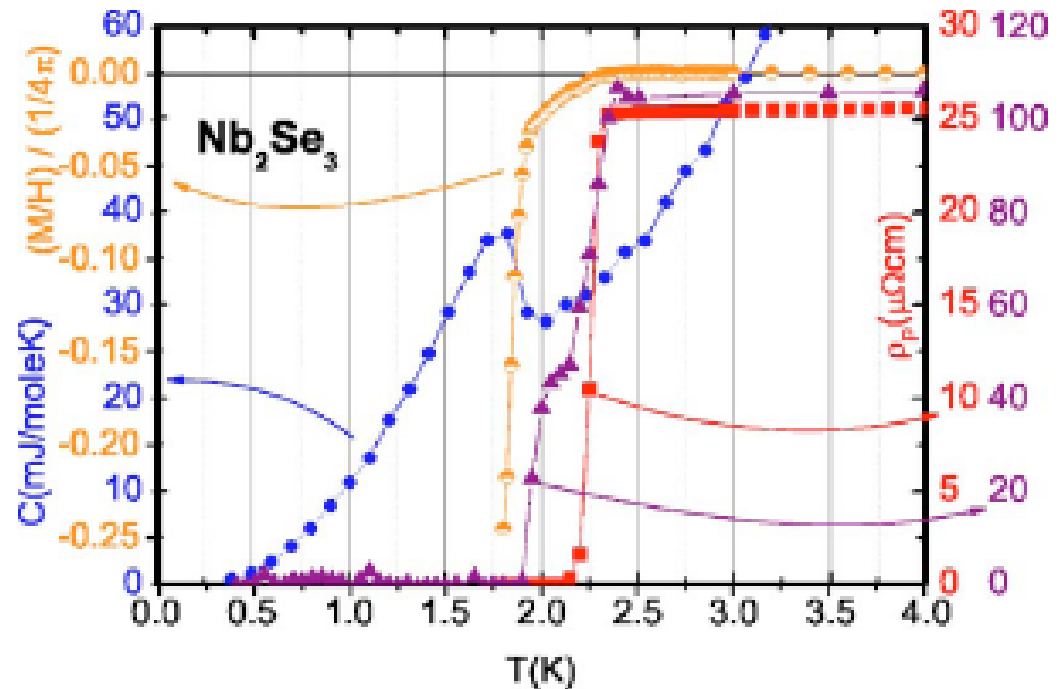
# Some Other Contributions to Specific Heat

Spin fluctuations (critically – damped spin waves) in nearly ferromagnetic systems when exchange interaction is not strong enough to produce ordered state, for  $T \ll T_{sf}$ :

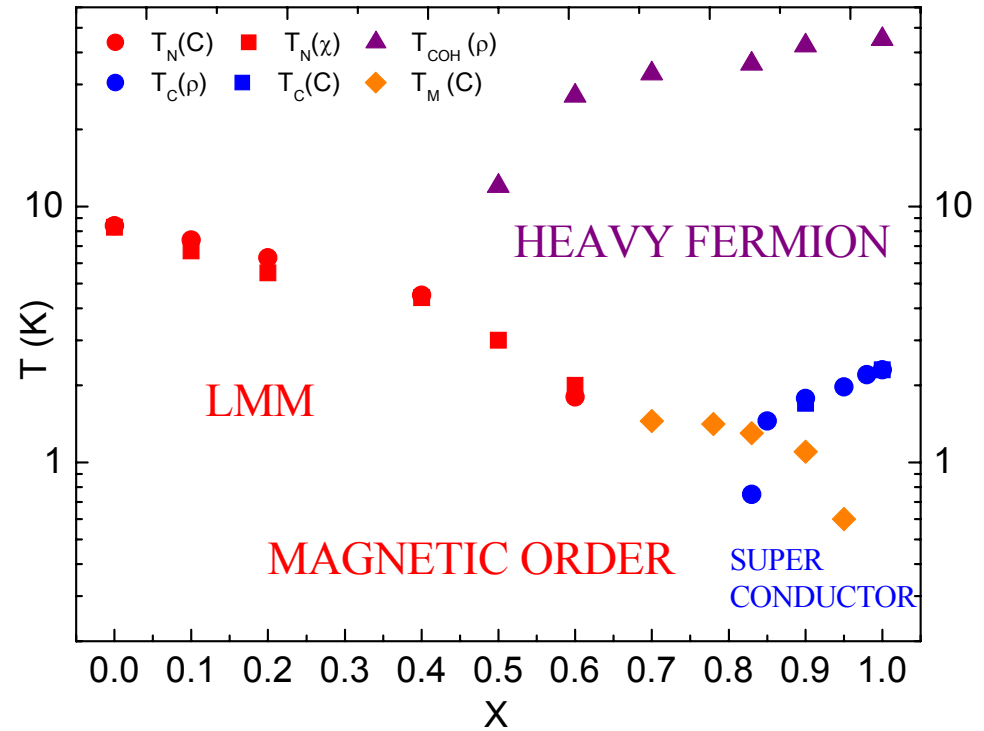
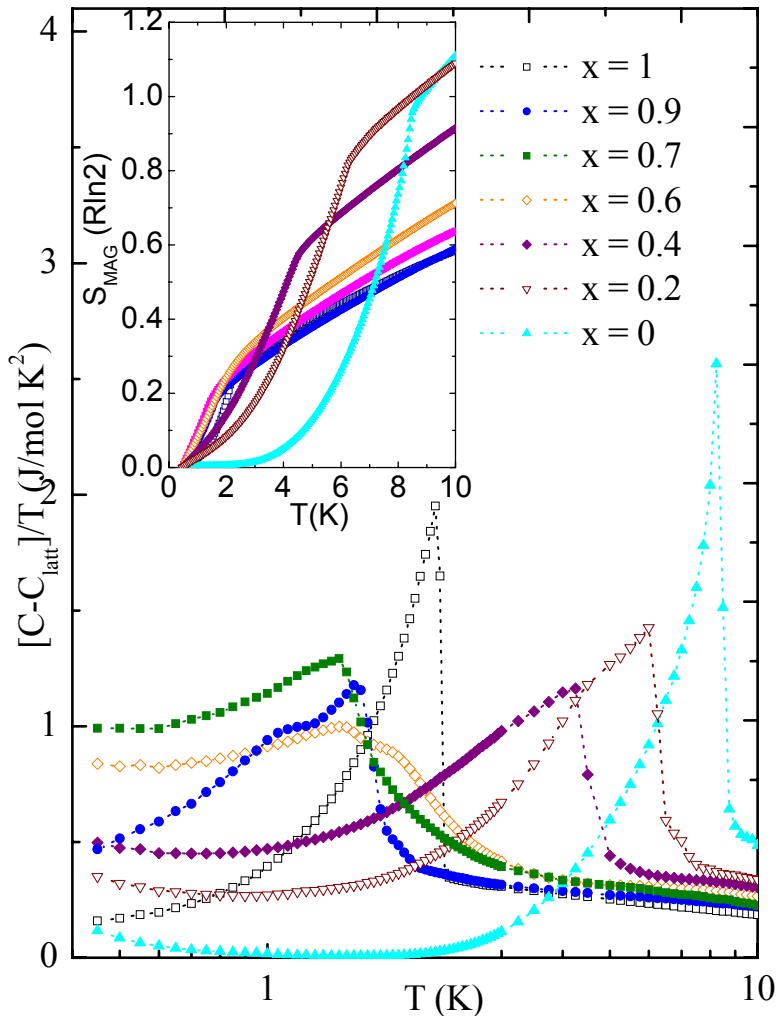
$$C_e = \gamma T + \alpha \left( \frac{T}{T_{sf}} \right)^3 \ln \left( \frac{T}{T_{sf}} \right) \quad (\text{Phys. Rev. Lett 17, 750 (1966)})$$

BCS superconductors with anisotropic gap have reduced value of specific heat anomaly at superconducting transition (see Ann. Phys. 40, 268 (1966)):

$$\frac{\Delta C}{\gamma T_C} = 1.426 \left( 1 - 4 \langle a^2 \rangle \right)$$



# Superconducting and Magnetic Entropy



Heat capacity and magnetic entropy of electronic system that evolves from local moment magnetism to heavy fermion superconductivity via disordered heavy fermion magnetic states

# Thermal Expansion in Thermodynamics

At  $T = 0$   $C_p = C_v$  (entropy  $S = 0$ ): 
$$C_p = \left( \frac{dQ}{dT} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p$$

At  $T \neq 0$   $C_p$  is always greater than  $C_v$  (heating with  $P = \text{const}$  for  $dT$  cost energy to do work expanding against external pressure; if  $V = \text{const}$ , there is no work done):

General relation between  $C_p$  and  $C_v$  at  $T \neq 0$  is

$$C_p - C_v = \frac{\beta^2 V_m T}{B}$$

$$\beta = \frac{1}{L^3} \left( \frac{\partial L^3}{\partial T} \right)_p = \frac{3}{L} \left( \frac{\partial L}{\partial T} \right)_p = 3\alpha$$

$\beta$  (volumetric expansion)

$\alpha$  (linear expansion)

$V_m$  (molar volume)

$B$  (isothermal compressibility)

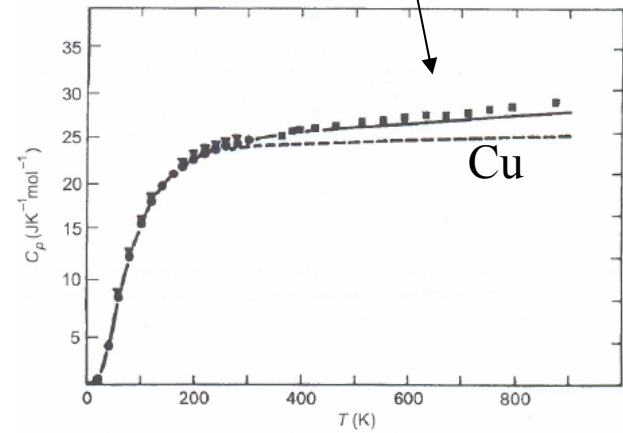
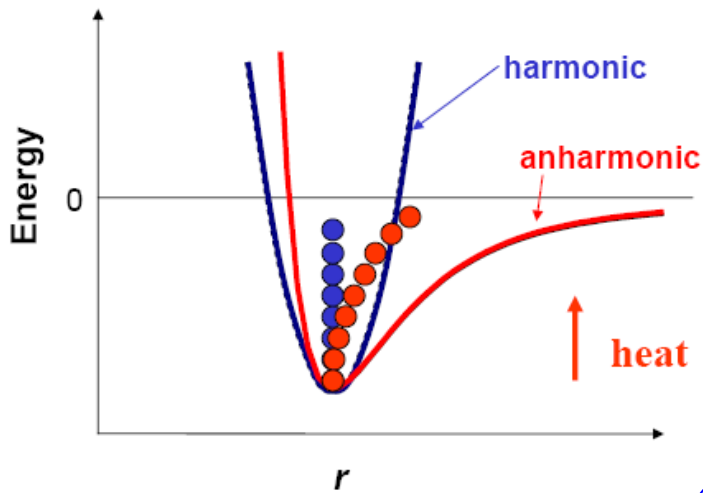
$$B = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

In practice,  $C_p - C_v \sim 1\%$  of  $C_p$  at  $\theta_D/3$  and  $0.1\%$  of  $C_p$  at  $\theta_D/6$  and is maximum ( $\sim 10\%$ ) at  $T_m$  (melting temperature).

# Thermal Expansion of Anharmonic Crystals

Harmonic crystals do not expand when heated and do not shrink when cooled since average interatomic spacing does not increase with T.

Real materials have non-parabolic U(r) so there is thermal expansion and  $C_V$  increases above Dulong – Petit at  $T > \theta_D$



$$\beta_T = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

**Grüneisen approximation:  $\Delta\omega/\omega \sim \gamma\Delta V/V$**   
**Grüneisen parameter is a measure of anharmonicity**

$$\beta_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V = \frac{1}{B} \left( \frac{\partial P}{\partial T} \right)_V \quad T \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V \quad P = -\left( \frac{\partial F}{\partial V} \right)_T \quad U = \left( \langle n \rangle + \frac{1}{2} \right) \hbar\omega + U_{eq} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{1 - e^{-\beta\hbar\omega}}$$

$$P = -\frac{\partial}{\partial V} \left[ U_{eq} + \sum_{q,s} \frac{1}{2} \hbar\omega_s(q) \right] + \sum_{q,s} \left[ -\frac{\partial}{\partial V} \frac{(\hbar\omega_s(q))}{(e^{\beta\hbar\omega_s(q)} - 1)} \right] \Rightarrow \beta_T = \frac{1}{B} \sum_{q,s} \left[ -\frac{\partial}{\partial V} \hbar\omega_s(q) \right] \frac{\sigma}{\partial T} n_s(\vec{q})$$

Harmonic = 0      this      We get       $\gamma_{s,q} \sim 2$        $\gamma_{s,q} = \frac{\partial(\ln \omega_s(q))}{\partial(\ln V)}$

$$C_V = \sum_{s,q} \hbar\omega_s(q) \frac{\partial}{\partial T} n_s(\vec{q})$$

**Grüneisen**

$$\beta_T = \frac{\gamma C_V}{BV}$$



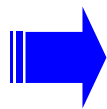
# Thermal Expansion by Capacitive Dilatometry 1

Rev. Sci. Instr. 77, 123907 (2006)

In a capacitive dilatometer the dilation  $L$  of a sample of length  $L$  manifests as a change in the gap  $D$  between a pair of capacitor plates. For an ideal parallel-plate capacitive dilatometer in vacuum the relationship between the measured capacitance  $C$  and  $D$  is

$$C = \frac{\epsilon_0 A}{D}$$

$\epsilon_0 = 8.854 \cdot 10^{-12}$  pF/m  
 $A$  = area of capacitor plates



Thermal expansivity  
 Thermal expansion

$$\epsilon = \frac{[L(T) - L(0)]}{L(0)}$$

$$\alpha = \frac{1}{L} \frac{dL}{dT} = \frac{d(\ln L)}{dT}$$

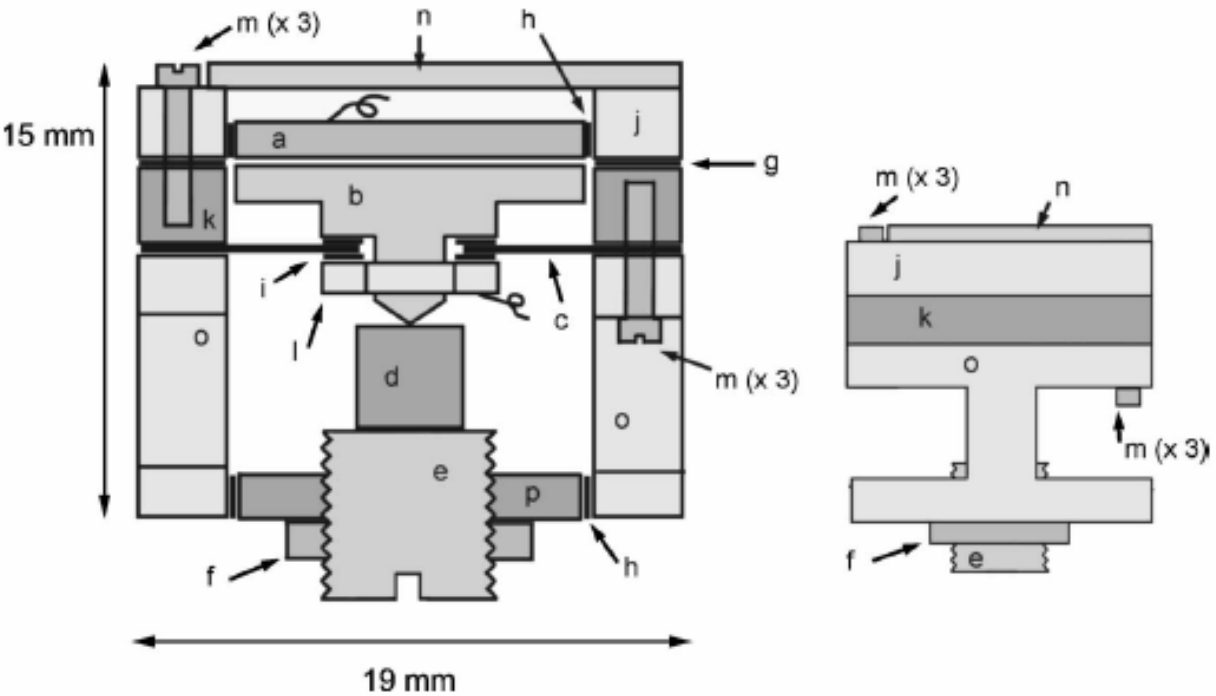


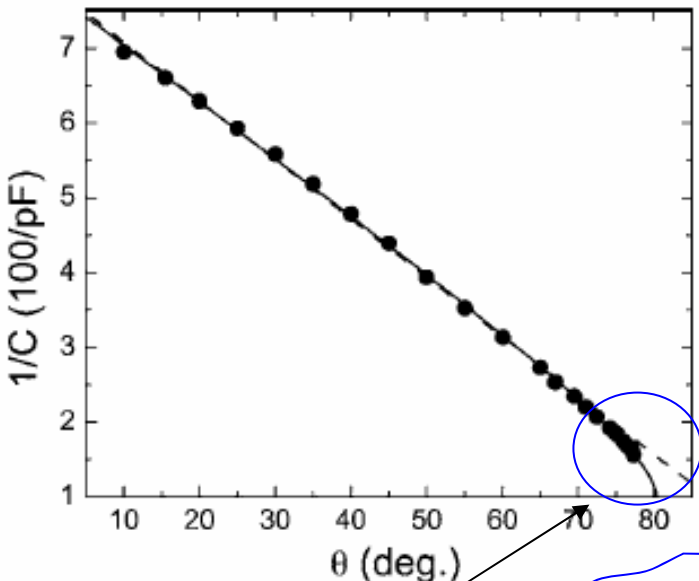
FIG. 1. A schematic of the capacitive dilatometer. The left panel shows a front "cut-away" view identifying parts: (a) upper (fixed) capacitor plate, (b) lower (movable) capacitor plate, (c) BeCu spring, (d) sample, (e) sample platform, (f) lock ring, (g) copper shims, (h) electrical isolation (Sty-cast 2850 FT and Kapton), (i) electrical isolation (Kapton washers), (j) upper guard ring, (k) lower guard ring, (l) nut, (m) 0-80 copper screws (six in total), (n) mounting plate, (o) main flange, and (p) lower flange. The right panel represents a side view of the dilatometer.

# Thermal Expansion by Capacitive Dilatometry 2

Rev. Sci. Instr. 77, 123907 (2006)

Commercial capacitance bridges have  $\sim 10^{-7}$  pF resolution at 1kHz  $\rightarrow 3 \cdot 10^{-3}$  Å for dilatometer operation at 18 pF.

Part of calibration process is to find an appropriate functional relationship between the capacitor gap  $D$  and the measured capacitance  $C$ . This is done using a sample platform  $e$  long enough to adjust the capacitor gap from its largest zero-force to its smallest shorted value.



A protractor (with an appropriately sized hole in its center) is attached to the main flange  $o$ . The dilatometer is inverted and the sample platform  $e$  is then rotated and tightened in small steps; after each step the angular position of the sample platform (read off the protractor) and the capacitance  $C$  are measured. The capacitor gap is:

$$D = c_1(\theta_m - \theta) \Rightarrow \frac{1}{C} = \frac{c_1}{\epsilon_0 A} (\theta_m - \theta)$$

Thread pitch, # threads/mm  $\rightarrow$  # $\mu$ m/mm

Angle of dilatometer shorting

Distance from straight to tilted plate

$C$  when they short

Deviation from linear behavior since plates are not perfectly parallel. Can be estimated as:

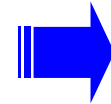
$$D = \frac{\epsilon_0 A}{c_1} \left( 1 + \left( \frac{C}{C_{max}} \right)^2 \right)$$

# Thermal Expansion by Capacitive Dilatometry 3

Rev. Sci. Instr. 77, 123907 (2006)

Data acquisition process in temperature or magnetic field consists of two steps:

1. Measurement of reference sample (Cu)
2. Measurement of unknown sample.



Since distance between plates is T,H dependent but is independent of length or nature of the sample in dilatometer

$$\alpha = \frac{1}{L} \frac{dL}{dT} = \frac{1}{L} \frac{d}{dT} [D_c - D_s] + \alpha_{Cu} \left[ 1 + \frac{D_s - D_c}{L} \right]$$

When the reference Cu or Sample are mounted

For long samples with thermal expansion close to Cu  $[D_s - D_c]/L \approx 0$ , therefore (since  $dL = -dD$ ):

$$\alpha = \frac{1}{L} \frac{dL}{dT} = \frac{1}{L} \left( \frac{dL}{dT} \right)_{cell+sample} - \frac{1}{L} \left( \frac{dL}{dT} \right)_{cell+Cu} + \alpha_{Cu}$$

Cell effect, measurement with Cu standard installed

**Resolution ~ 0.03 – 0.11 Å**  
**Depends on cryogenic system used and cell**

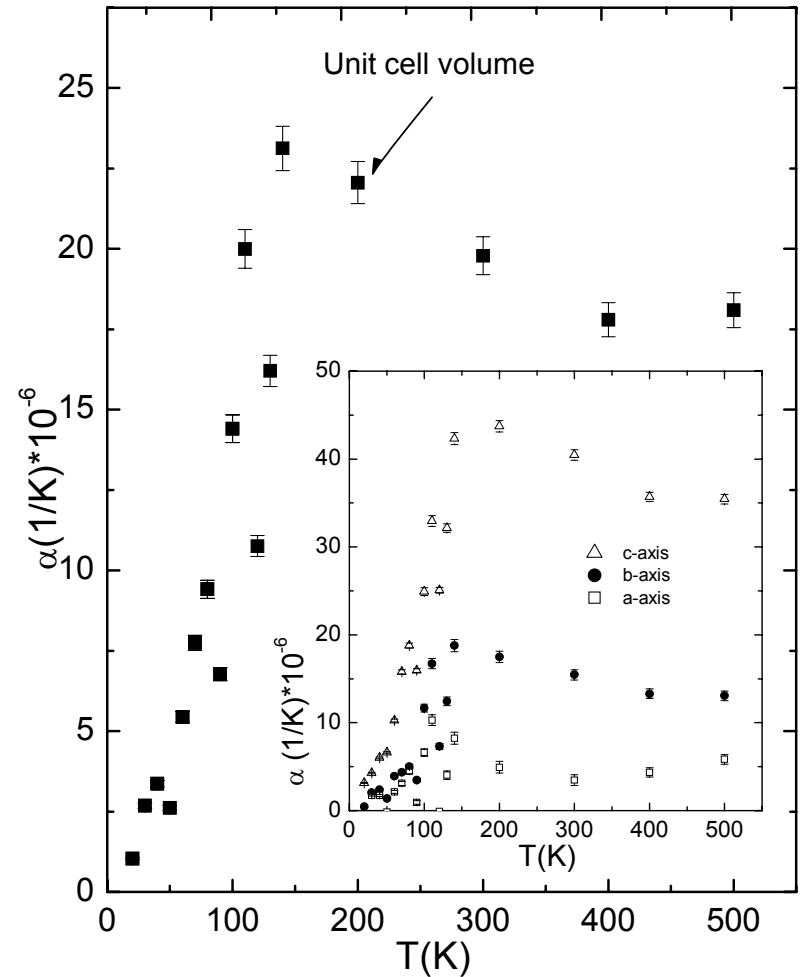
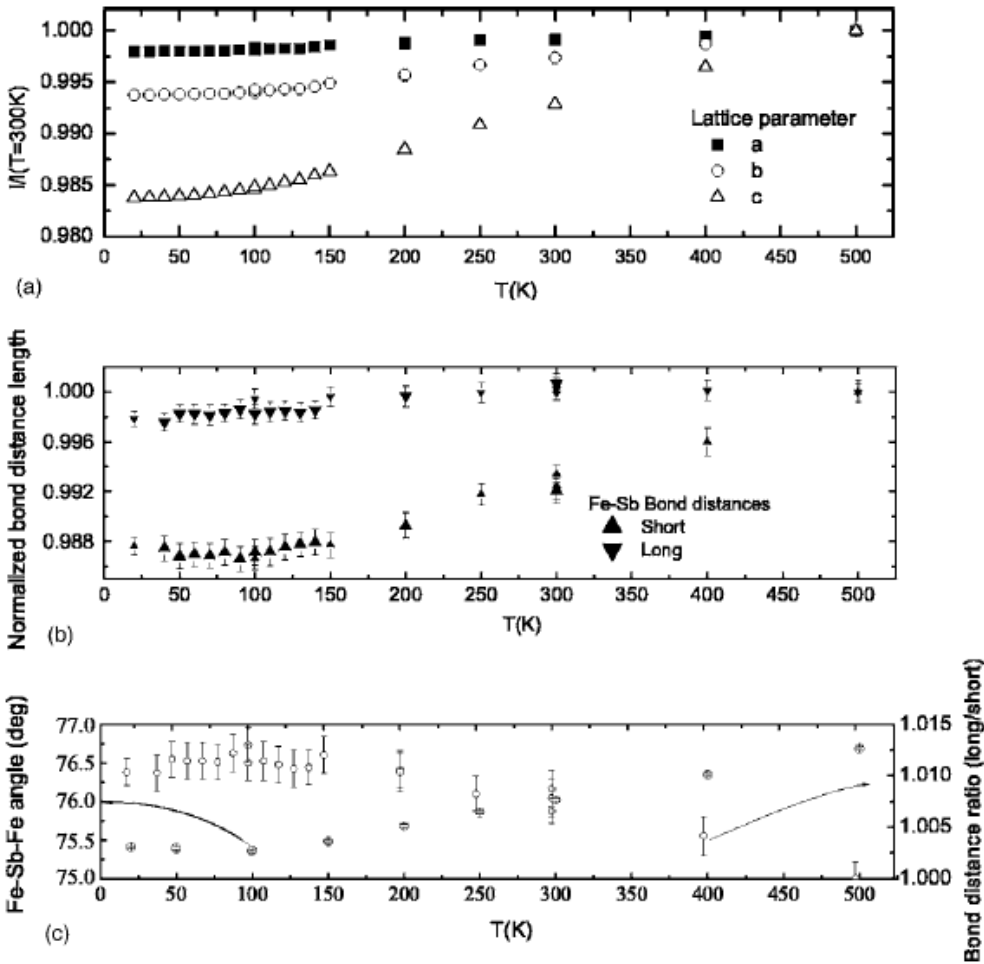
Derivatives are evaluated as:

$$\left( \frac{dD}{dT} \right)_i = \frac{1}{2} \left[ \frac{D_{i+1} - D_i}{T_{i+1} - T_i} + \frac{D_i - D_{i-1}}{T_i - T_{i-1}} \right]$$

Dilatometer is surrounded by Cu can to provide electrical and thermal insulation.

# Thermal Expansion by Diffraction

Based on the measurement of unit cell by X-ray, neutron methods (will be discussed later in the course).



**High resolution data are required. Resolution comparable or smaller than for capacitive dilatometry. Advantage: bond length, angles, atomic position information is available**

Phys. Rev. B 72, 045103 (2005)

# Thermal Expansion in CeCoIn<sub>5</sub>

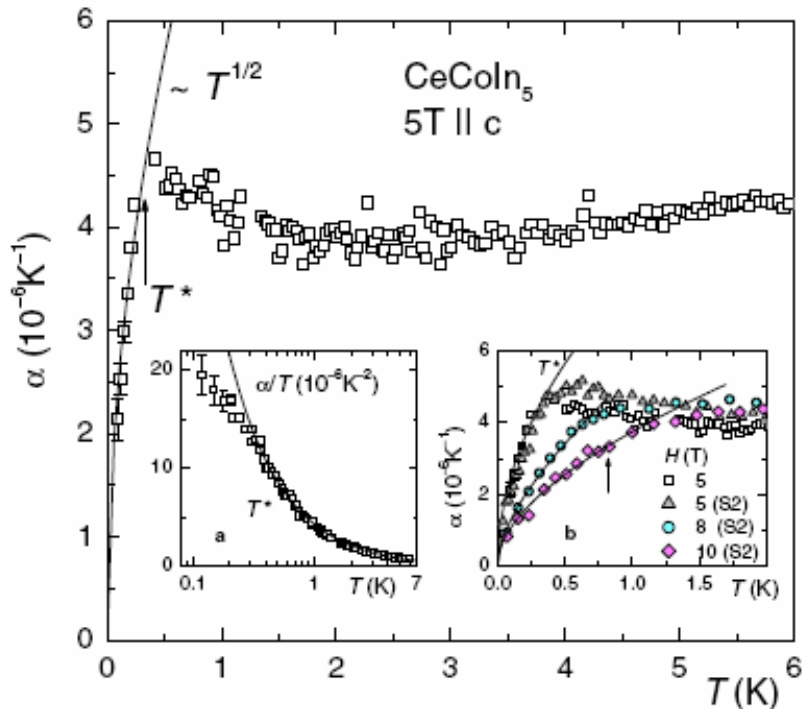


FIG. 2 (color online). Temperature dependence of the linear thermal expansion coefficient of CeCoIn<sub>5</sub> at  $H = 5$  T ( $\parallel c$ ). The line and arrow indicate  $\alpha \propto \sqrt{T}$  and crossover temperature  $T^*$ , defined as an upper limit for this  $T$  dependence, respectively. Inset (a) displays data from the main part as  $\alpha/T$  vs  $T$  (on a logarithmic scale). The line indicates  $T^{-1}$  dependence. Inset (b) compares data from the main part in the low-temperature regime with 5, 8, and 10 T data obtained from a second sample (S2). Lines display square-root behavior.

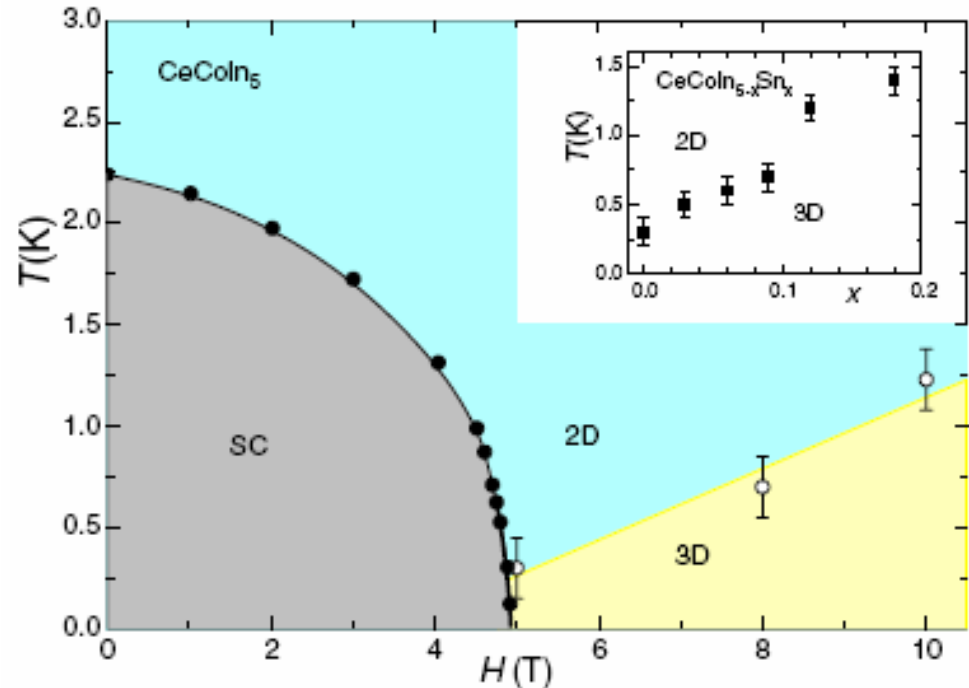


FIG. 1 (color online). Phase diagram of CeCoIn<sub>5</sub> for  $H \parallel c$  as determined from thermal expansion. Superconducting phase in gray with first-order boundary below 0.7 K indicated by thick black line. Regions where thermal expansion follows 2D and 3D quantum critical behavior are marked in blue (lighter gray) and yellow (lightest gray), respectively. The inset displays the evolution of the crossover with Sn-doping in CeCoIn<sub>5-x</sub>Sn<sub>x</sub> at the respective  $H_{c2}(x)$ .