Specific Heat

A point of view from an experimentalist !

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- Introduction : - demystification of C_p
  - What you can or CANNOT tell ?
- Temperature : - definition, scales, characteristics of thermometers
  - how to reach low T ?
- Specific heat : - how to extract informations from Cp ?
  - Metals/Superconductors, Electron/Phonon
  - phase transitions (1st and 2nd order)
- Experimental : - (dis)advantages of different methods, (quasi-) adiabatic, Relaxation, modulation, dual slopes,...
  - recent developments in very high magnetic fields (35T DC), under pressure (15 GPa), and pulsed magnetic field (65T)

DEFINITION

heat

specific heat : $$C = \frac{\Delta Q}{\Delta T}$$

temperature increase

DEFINITIONS

- Δ or D difference
- δ small difference
- d total differential
- ∂ partial derivative

Thermodynamic measurement

- $T\,dS = \delta Q$ for an infinitesimal reversible process
- $C = \delta Q \,/\, dT$
- input power, energy
- output temperature T and time t

1^{st} law of thermodynamics

- energy U and entropy S are state functions and don't depend on path or history : U(T,p,H,...) and S(T,p,H,...)
- $dU = T\,dS - p\,dV + (H\,dM + \ldots)$
  is a total differential, U is a thermodynamic function of state
- Heat bath T, Coil H, Pressure p
  $d\Omega = d(U-TS+pV-HM) = -SdT-Vdp-MdH$

Definition of T

- $1/T = (\partial S/\partial U)_{X \text{ extensive variables}}$
- by definition at thermodynamic equilibrium !
- no time (frequency) dependence
- ≠ steady-state, fluctuations, Onsager relations, transport and thermoelectricity

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Here, we will limit ourself to applications in condensed matter and will suppose local equilibrium, and Fourier equation, and T > 0K

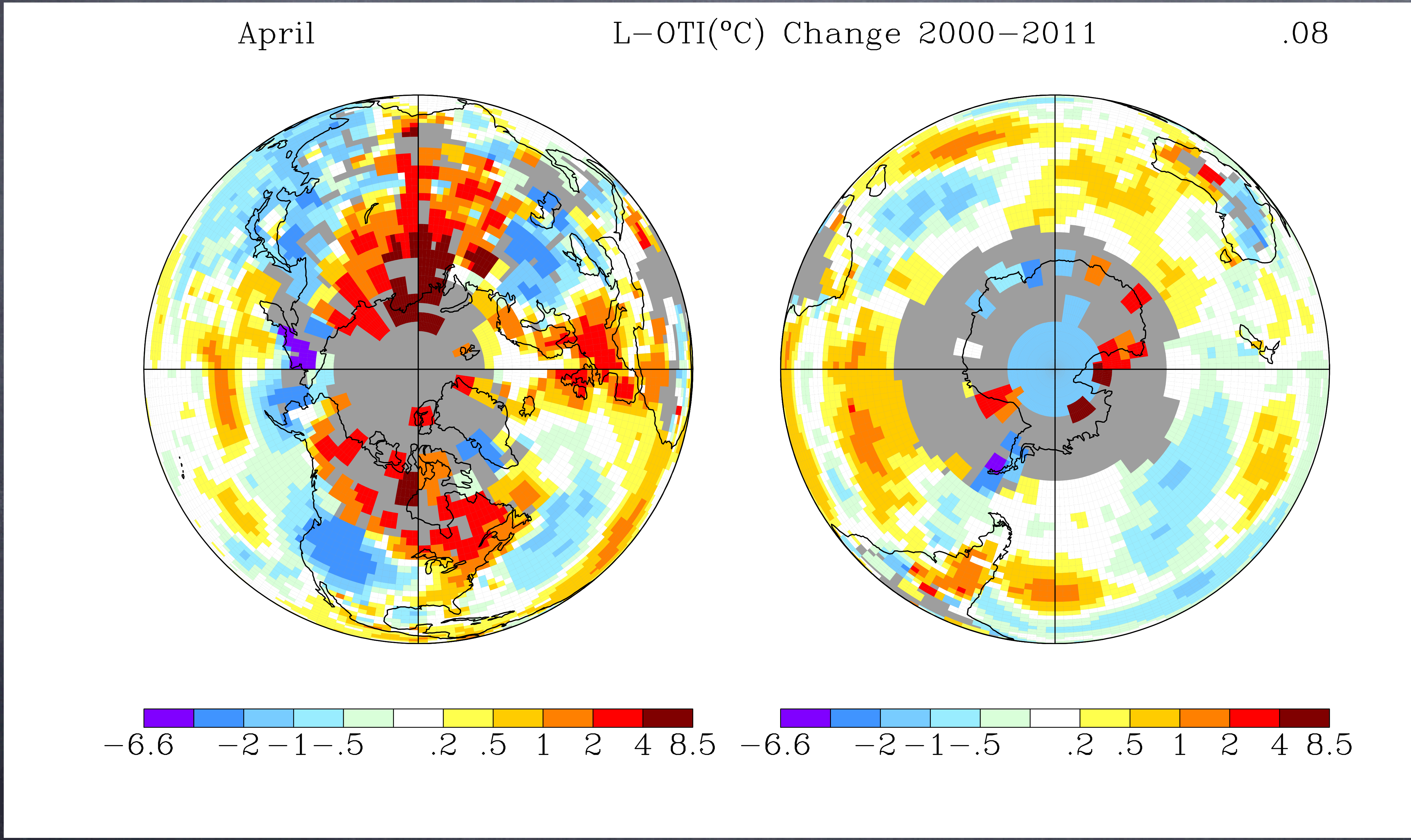
(out of scope star atmospheres, all universe, black holes, inversion of population, ...)

Local T

Local thermodynamic equilibrium of matter means that conceptually, for study and analysis, the system can be spatially and temporally divided into cells of small (infinitesimal) size, in which classical thermodynamical equilibrium conditions for matter are fulfilled to good approximation

Wikipédia

Earth temperature simulated in Goddard Institute for Space Studies



THERMODYNAMIC

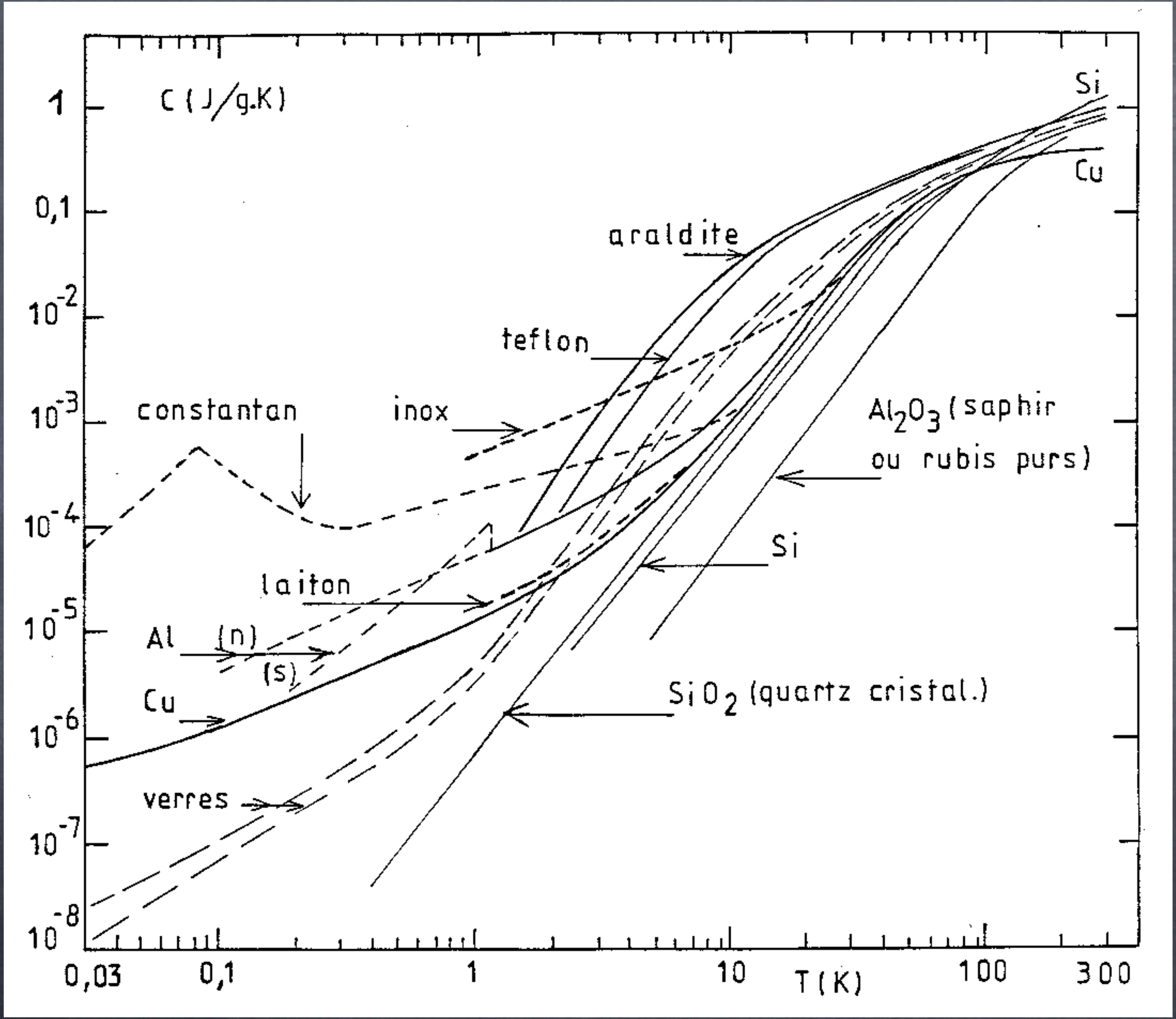
$$C_i = (\partial E/\partial T)_i = T(\partial S/\partial T)_i \quad i= V,p,...$$

- important thermodynamic quantity related to the energy and the entropy

in any system: metal/isolant

solide/liquide

organique/inorganique


C (J/g.K)
1
0,1
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
0,03
0,1
1
10
100
300
T (K)
Si
Cu
araldite
teflon
constantan
inox
Al_2O_3 (saphir ou rubis purs)
Si
laiton
Al (n)
(s)
Cu
SiO_2 (quartz cristal.)
verres

Knowing C_p for materials choice for low temperature technics:

- Large specific heat means large $\Delta H = \int_{T_i}^{T_f} C_p dT$

so it requires cooling power (for examples to cool a big superconducting magnet or 1 ton of lead for wimps detection, ...) and time

- Be careful about magnetic materials (spin entropy) :

  - choice of thermometers (speer/Matsushita, RuO_2, ...)

  - beware of hyperfine contributions (Ag/Cu) for measurements in field

- or use those magnetic materials :

  - to stabilize the temperature (large Cp at phase transitions, max of Schottky anomaly, ...)

  - adiabatic demagnetization (paramagnetic salt, nuclear spins of copper...)

THERMODYNAMIC

$$C_i = (\partial E/\partial T)_i = T(\partial S/\partial T)_i \quad i = V, p, \ldots$$

anomalies at phase transitions:

liquide/gaz

supraconducteur/métal

magnétique/non magnétique

order/disorder

...

THERMODYNAMIC

$$C_i = (\partial E/\partial T)_i = T(\partial S/\partial T)_i \quad i = V, p, \ldots$$

In one sample many contributions

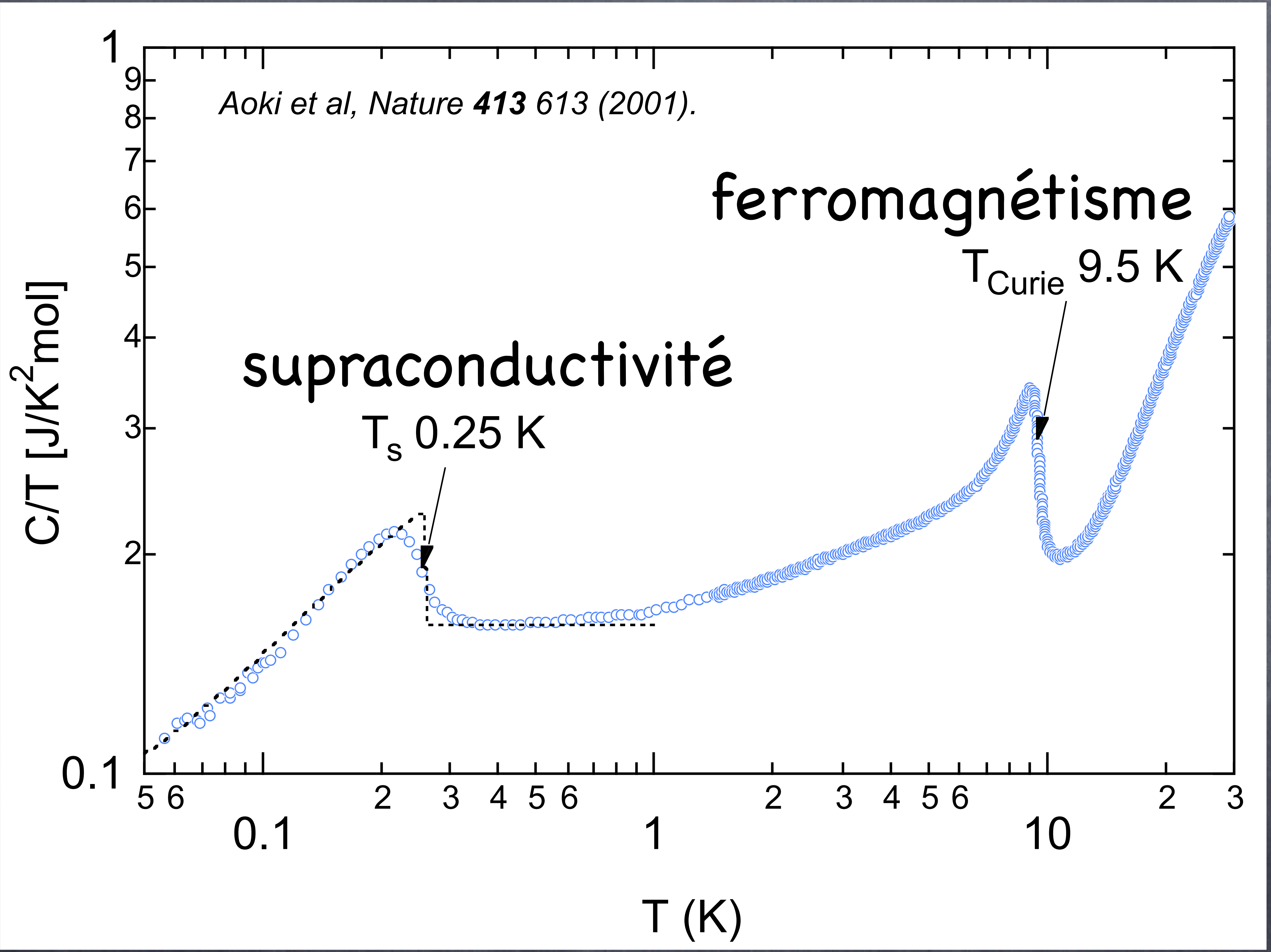
- phonons : E_{ph}
- electrons : E_e
- magnons, rotons, anything-ons, impurities,
- …

Specific heat is sensitive

to all T dependent contributions !!

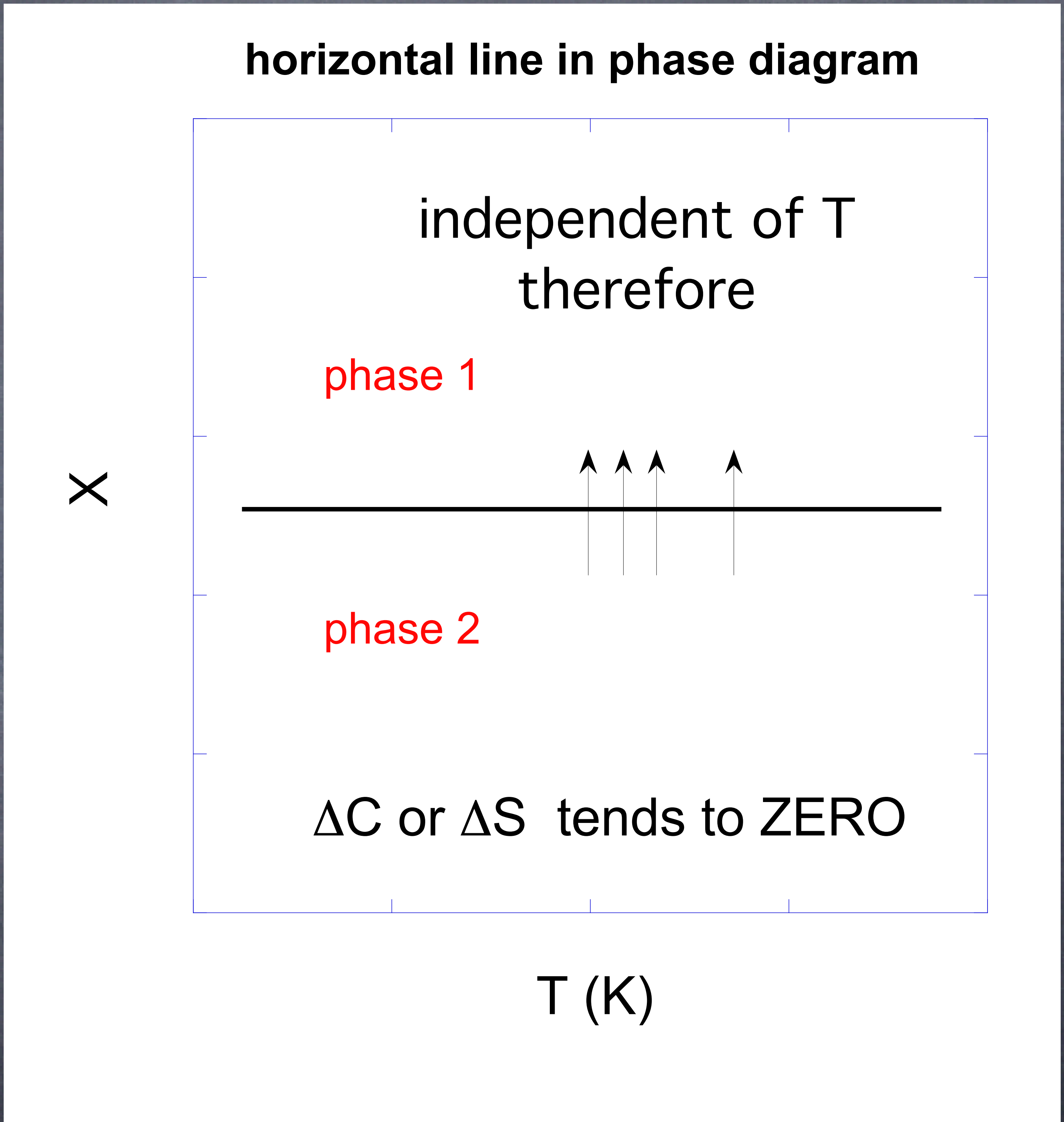
How to extract the information ??

EXAMPLE : URhGe

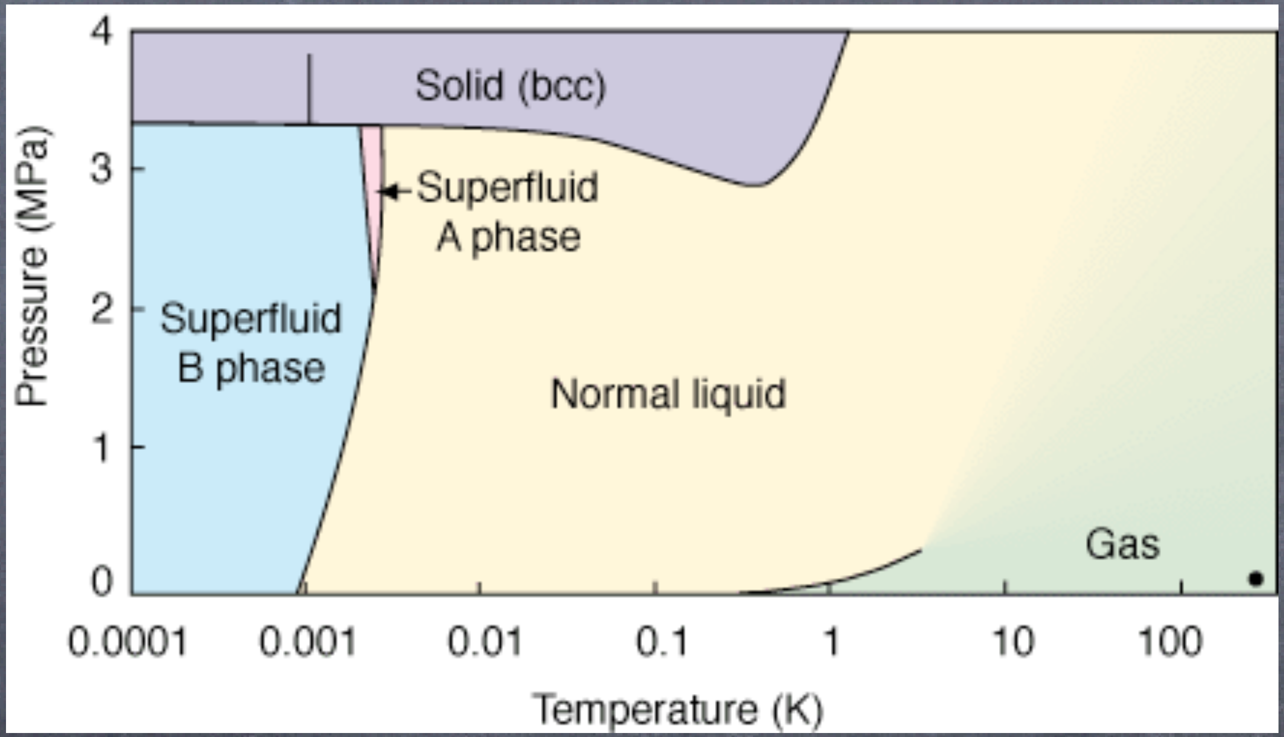


- only sensitive to temperature dependent phenomena only sensitive to temperature dependent phenomena

ex: at the minimum of $p_m(T)$ in ^4He



discussion about the slopes in the phase diagram



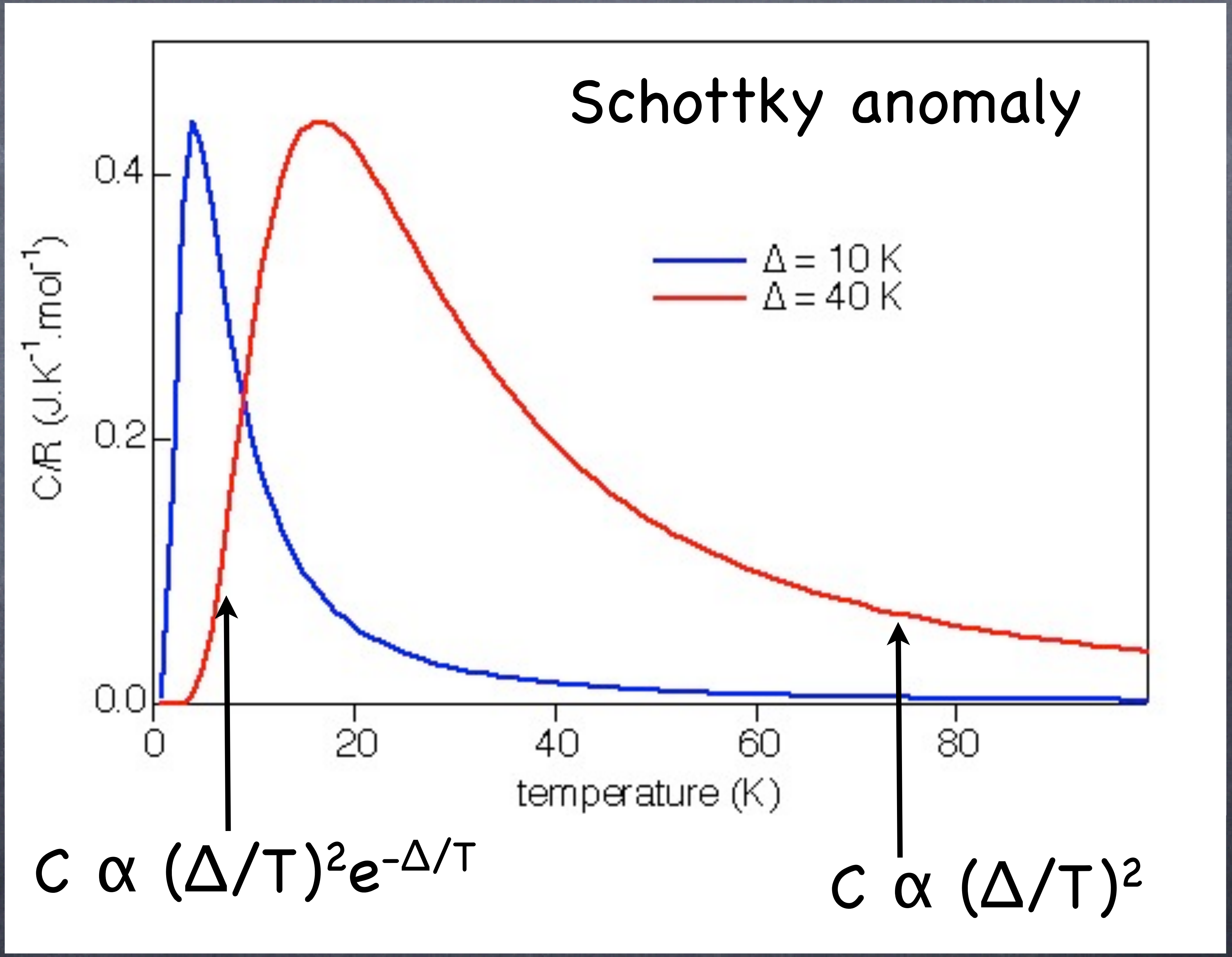
two-level model

- T<< Δ, the energy is independent of T, hence C tends to zero
- T>> Δ, the energy is also independent of T due to equipartition, hence C tends to zero
- T $\sim$ Δ, a lot of excitations,

  max of C

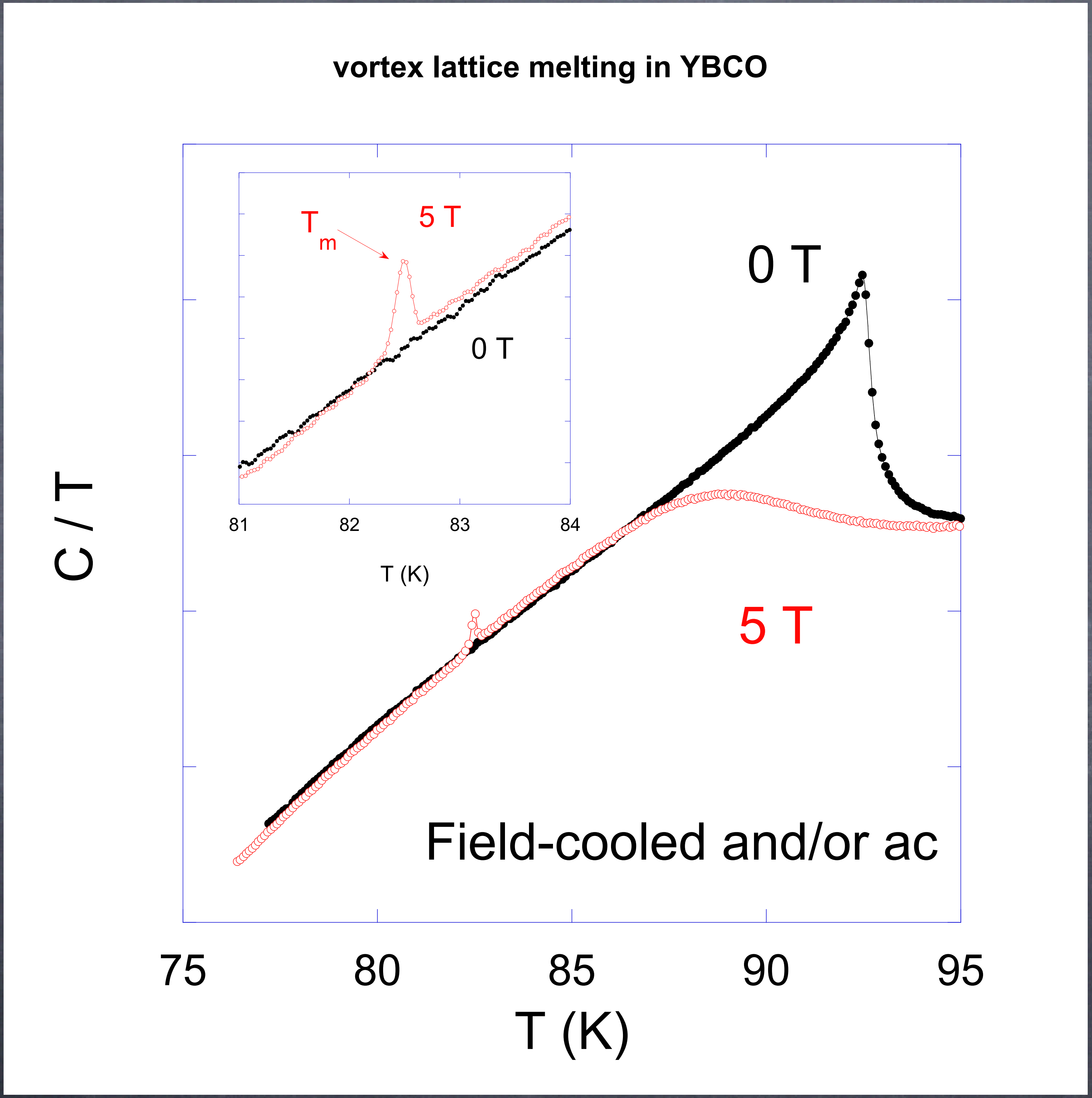
Schottky contribution

discrete energy levels

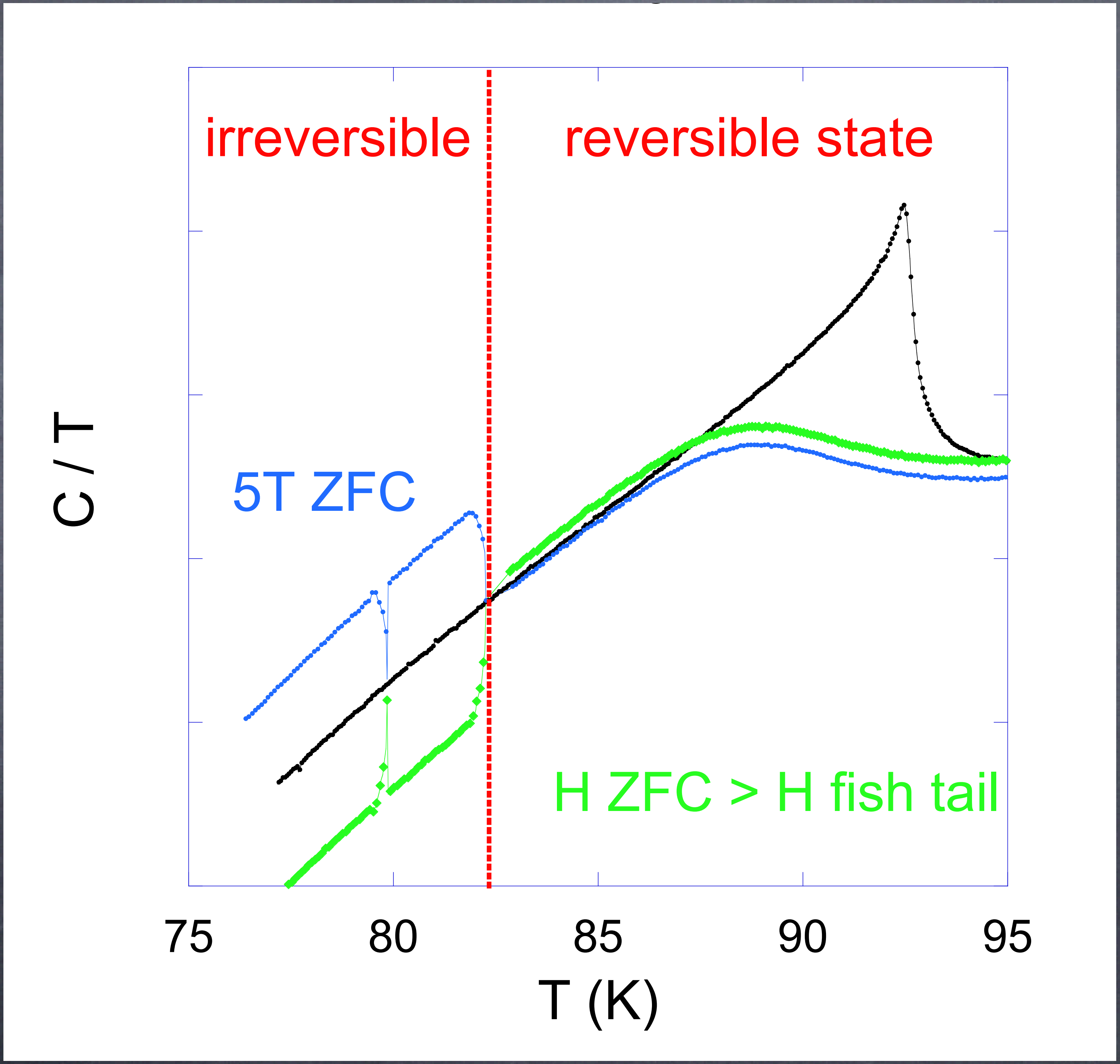


- only sensitive to temperature dependent phenomena
- CARE : equilibrium   Supra ZFC, glass, 1storder,...

Transition in vortex state ?



irreversibility line !!!

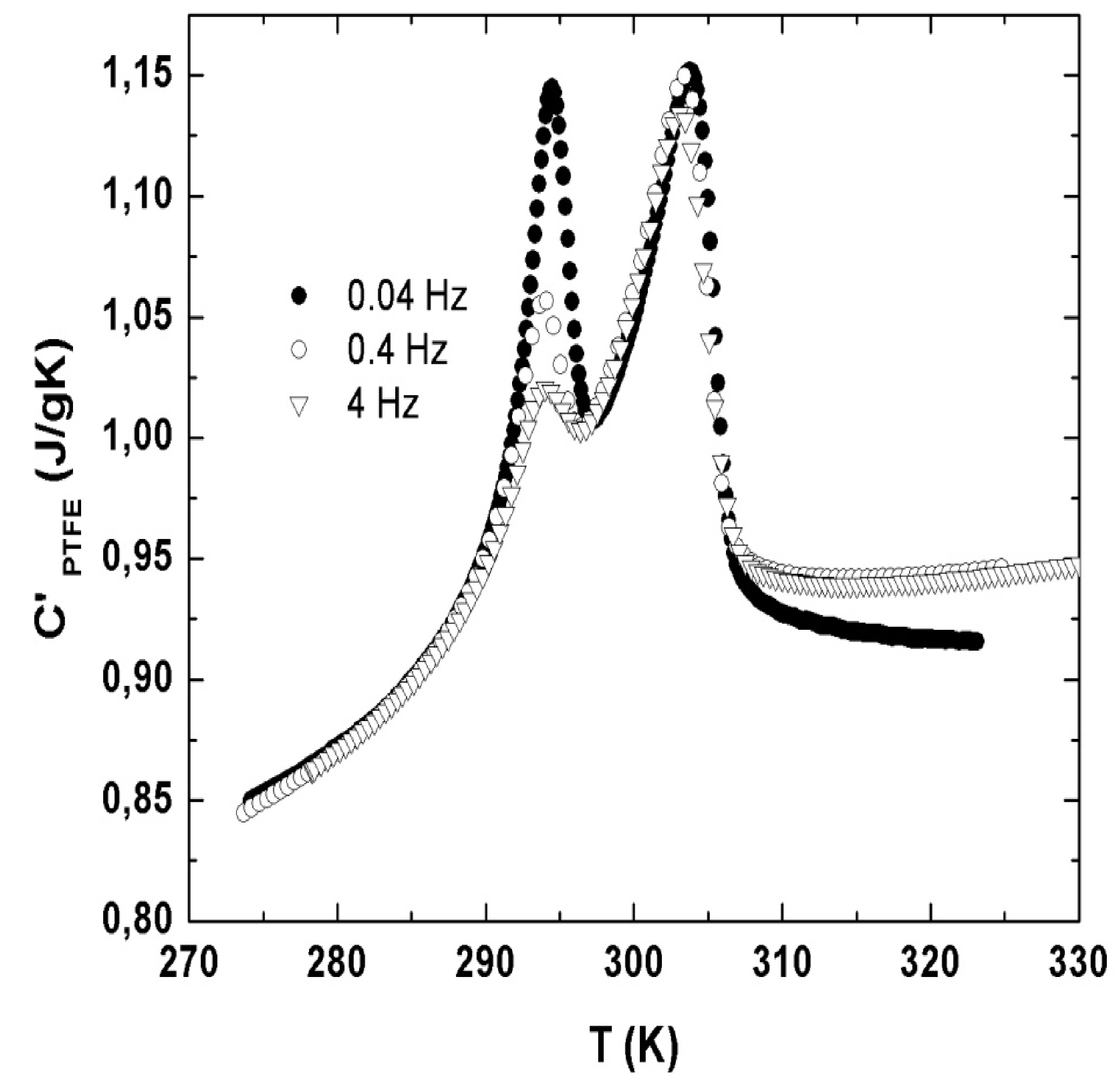


frequency dependence !

Polytetrafluoroethylene PTFE = polymer

out-of equilibrium
hysteresis
1st order
...
signal only if
t degree of freedom < 1/f

phase, harmonics

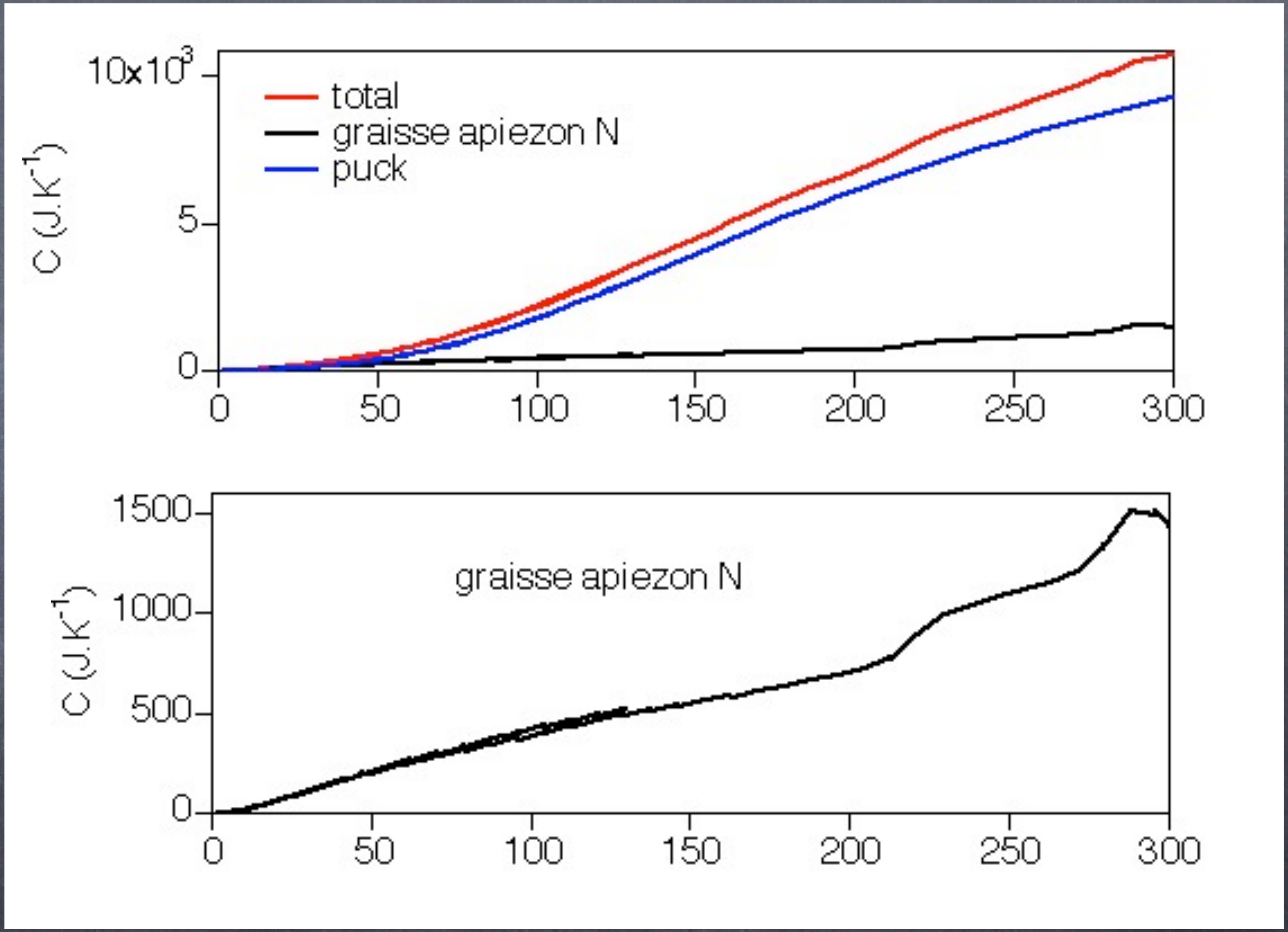


J.-L. Garden et al, Thermochimica Acta 461, 122 (2007)

Glass transition

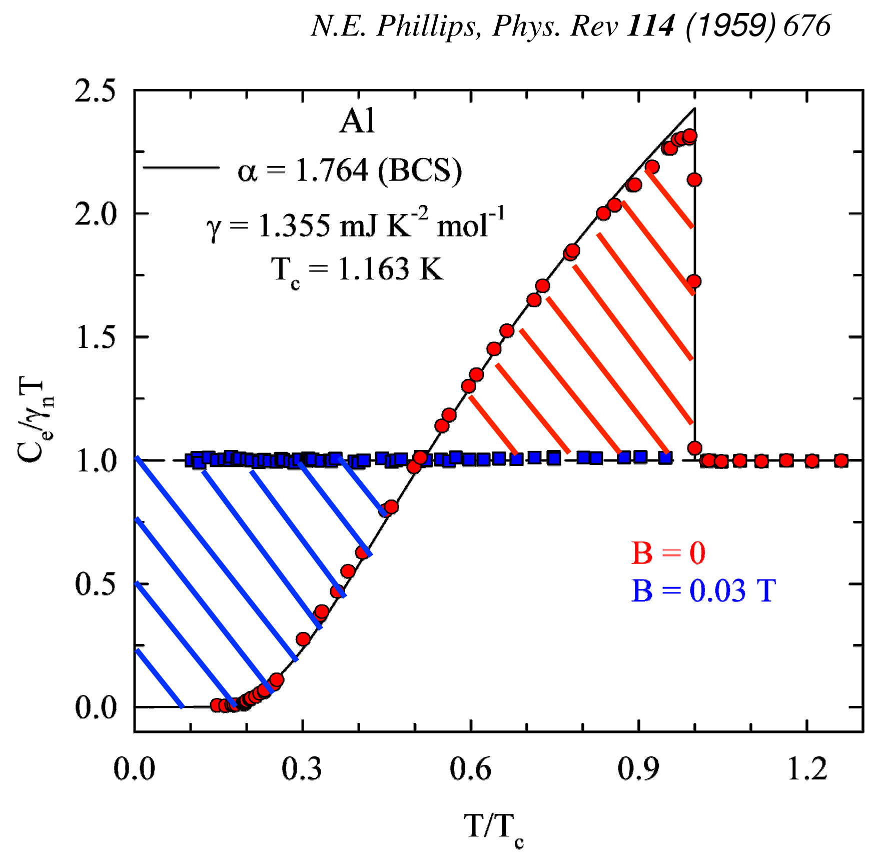
will depend on the cooling rate and history

% of crystallization close to Tg



- equilibrium Supra ZFC, glass, 1^{st}order,...
- C tends to 0 at 0K (3^{nd} law)
- conservation of entropy !

Aluminium : an example of superconducting transition



- equilibrium ??? Supra ZFC, glass, 1st order,...
- C tends to 0 at 0K (3nd law)
- conservation of entropy !
- C > 0 stability ($\partial V/\partial p > 0$) max of S, min of Ω, second derivatives of Ω: $\partial^2\Omega/\partial X\,\partial Y < 0$
- Maxwell's relations via: $\partial^2\Omega/\partial X_i\partial X_j = \partial^2\Omega/\partial X_j\partial X_i$

Maxwell's relations

$$\partial^2\Omega/\partial X_i \partial X_j = \partial^2\Omega/\partial X_j \partial X_i$$

- $\partial T/\partial V)_S = - \partial p/\partial S)_V = \partial^2 U/\partial S \partial V$
- $\partial S/\partial p)_T = - \partial V/\partial T)_p = \partial^2 G/\partial T \partial p$
- $\partial S/\partial H)_T = \partial M/\partial T)_H$
  and $\partial(C/T)/\partial H)_T = \partial^2 M/\partial T^2)_H$