

# Thermal expansion of solids

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## **references :**

- "Thermal expansion", B. Yates, Plenum, 1972
- "Solid State Physics", N.W. Ashcroft, N.D. Mermin, Saunders, 1976
- "Introduction to solid state physics", C. Kittel, Wiley & sons, 1968
- "Magnetostriction", E. du Tremolet de Lacheisserie, CRC Press, 1993
- ...

# Introduction

Changes in size, volume while cooling/heating

$$\text{volume thermal expansion : } \beta = \frac{1}{V} \frac{\partial V}{\partial T} \Bigg)_P$$

$$\text{linear thermal expansion : } \alpha = \frac{1}{L} \frac{\partial L}{\partial T} \Bigg)_P = \frac{1}{3} \beta$$

Orders of magnitude for  $\alpha$   
(room temperature and pressure)

Gases             $10^{-3} - 10^{-2}$             ideal gaz :  $\alpha = \frac{1}{3T}$

Liquids             $10^{-4} - 10^{-3}$

                        insulators      metals      polymers

Solids             $10^{-6} < 10^{-5} < 10^{-4}$

# Thermal expansion thermometry

contrast between gas and solid

Santorio Santorii (circa 1610) : liquid pushed by expansion of air in a glass tube.

contrast between liquid and solid

Galileo Galileis (1596) : water density change thermoscope.

Ferdinand II, Grand Duke of Tuscany (1641): bulb alcohol thermometer.

Gabriel Fahrenheit (circa 1710) : scaled mercury thermometer.

Anders Celsius (circa 1710) : centigrade water thermometric scale.

contrast between two solids

John Harrison (~1750): first bimetallic strip for temperature compensation  
latter used as thermometer and thermostat

# Technological issues

Since early human industry: buildings, ceramics, metallurgy  
in case of thermal/material inhomogeneity

➡ Thermal compatibility (reinforced concrete...)

Problem more acute with metals :

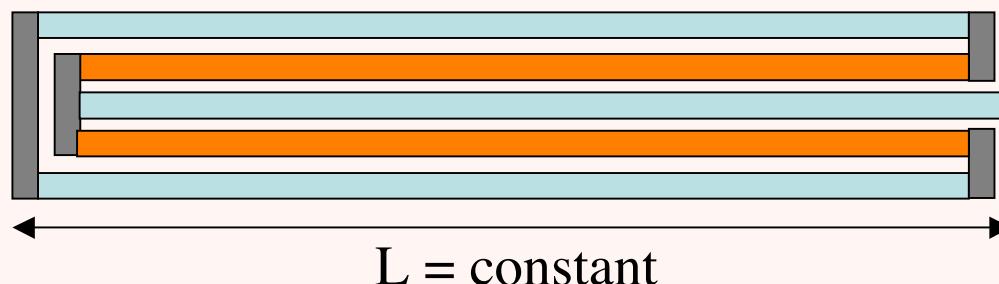
in railways, heat engines, bridges, large buildings,  
transonic planes... and cryogenic equipments

➡ expansion joints or other...

First systematic approaches : high precision mechanisms

measurement of time

John Harrison : gridiron pendulum (1726)



## Exercice : pendulum

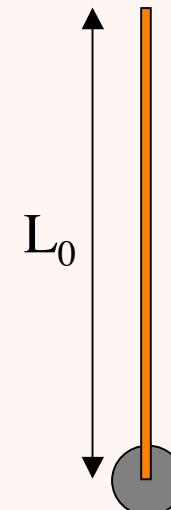
### 1) Pendulum Clock: arm made of brass

Length at  $T = 20 \text{ } ^\circ\text{C}$ ,  $L_0 = 50 \text{ cm}$

$$\alpha_{brass} = 1.9 \times 10^{-5} \text{ } K^{-1}$$

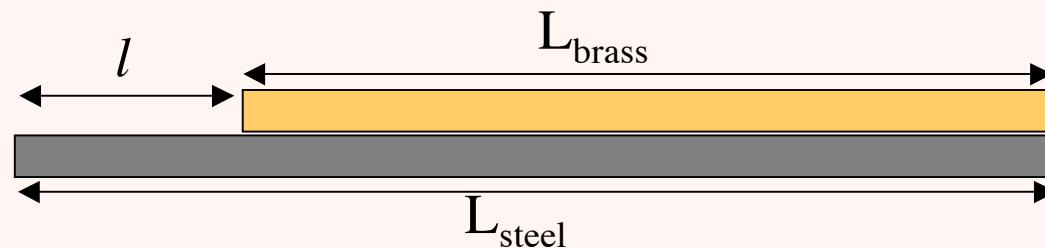
$$\tau_0 = 2\pi \sqrt{\frac{L_0}{g}} = 2 \text{ s}$$

- compute  $\tau$  at  $T = 15 \text{ } ^\circ\text{C}$
- by how much is the clock shifted one day latter ?



### 2) Brass+Steel compensation: "gridiron"

$$\alpha_{steel} = 1.3 \times 10^{-5} \text{ } K^{-1}$$



- compute the  $T = 20^\circ\text{C}$  ratio between  $L_{\text{brass}}$  and  $L_{\text{steel}}$  so that  $l$  is constant .

# Thermal expansion measurement

Probing a small change in length  $\Delta l$  : sensitivities better than  $10^{-4}$

- macroscopic

optical { optical lever : basic opto-mechanical amplifier  $10^{-6}$   
interferometric : Fizeau, fringes displacement  $10^{-9}$   
+ radio-frequency resonance  $10^{-11}$

electrical { capacitive :  $C(l)$   $10^{-9}$   
inductive : mutual inductance  $m(l)$   $10^{-7}$   
resistive : strain gauge  $R(l)$   $10^{-6}$

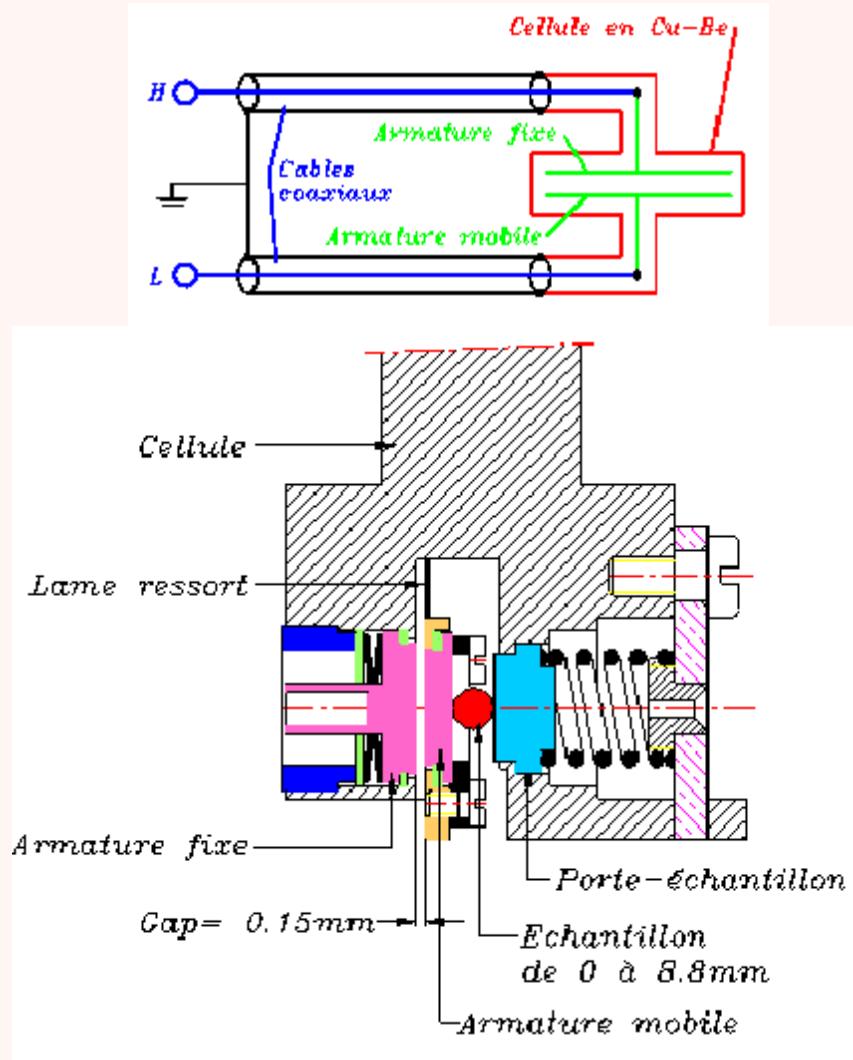
- microscopic : diffraction of monochromatic photons, neutrons

$$\text{Bragg law : } d = \frac{\lambda}{2 \sin \theta} \Rightarrow \Delta \theta = -\tan \theta \cdot \frac{\Delta l}{l} \quad \rightarrow \text{reflections at large } \theta$$

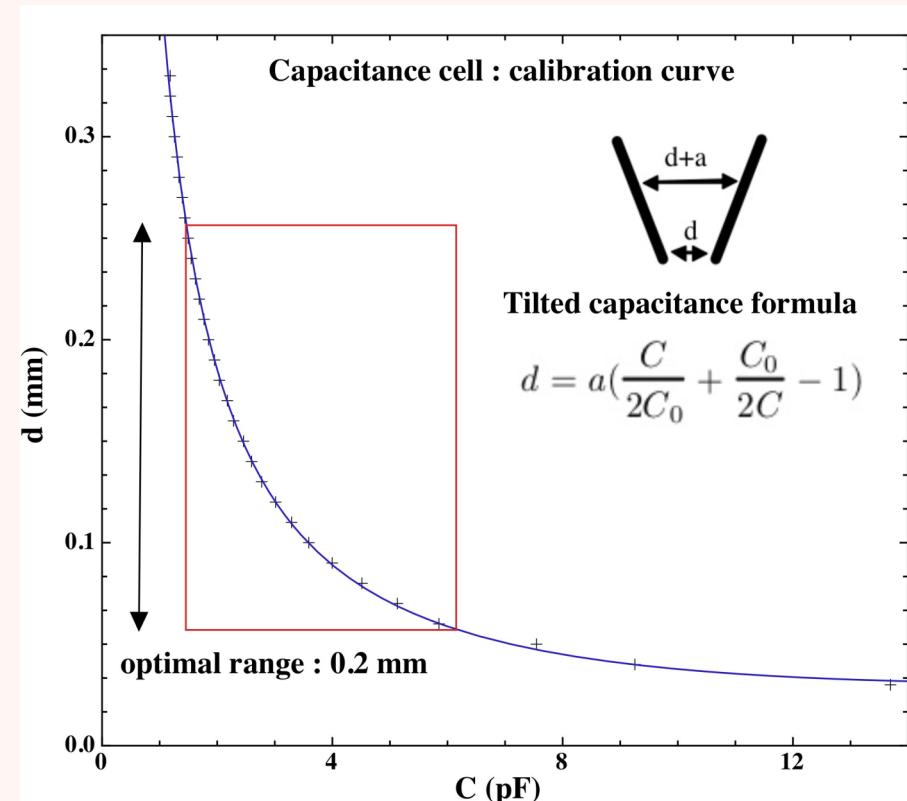
powder	single crystal
$10^{-5}$	$10^{-6}$

# A capacitance dilatometer

Three-terminal capacitance method



Courtesy of Didier Dufeu  
Institut Néel



resolution up to 1 Angström  
sensitivity  $10^{-6}$ - $10^{-8}$   
Temperature range 2-300 K  
Magnetic Field range 0- 6.5 T  
Angular range 360 °

# Some "reference" $\alpha$ curves

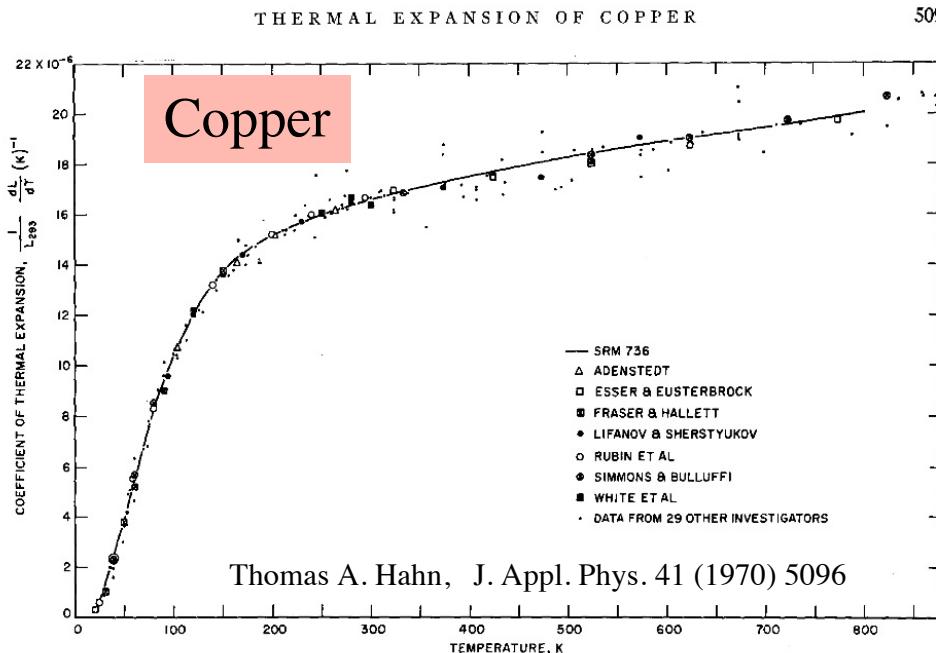


FIG. 5. Expansivity of copper. SRM 736 compared to values from prior investigators.

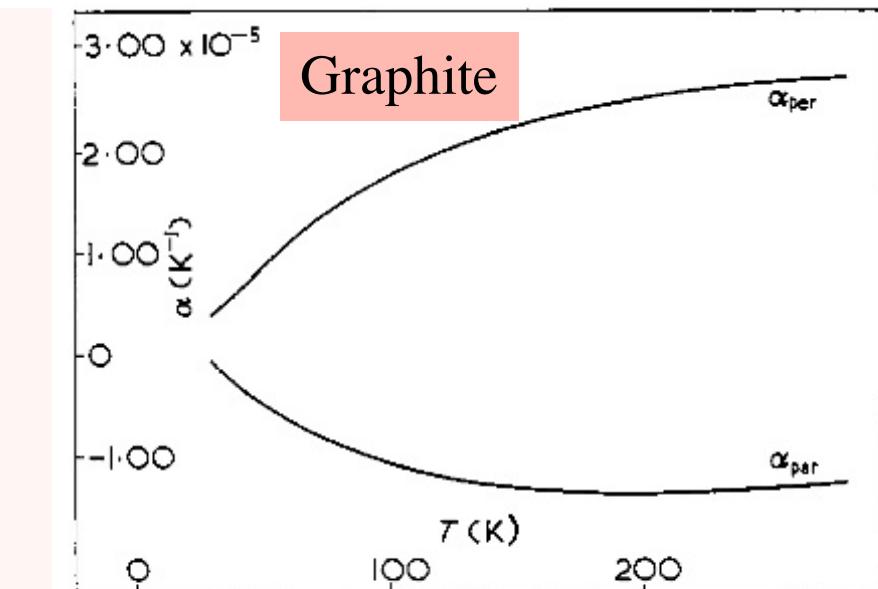


Figure 2 The thermal expansion of pyrolytic graphite (Bailey and Yates 1969)

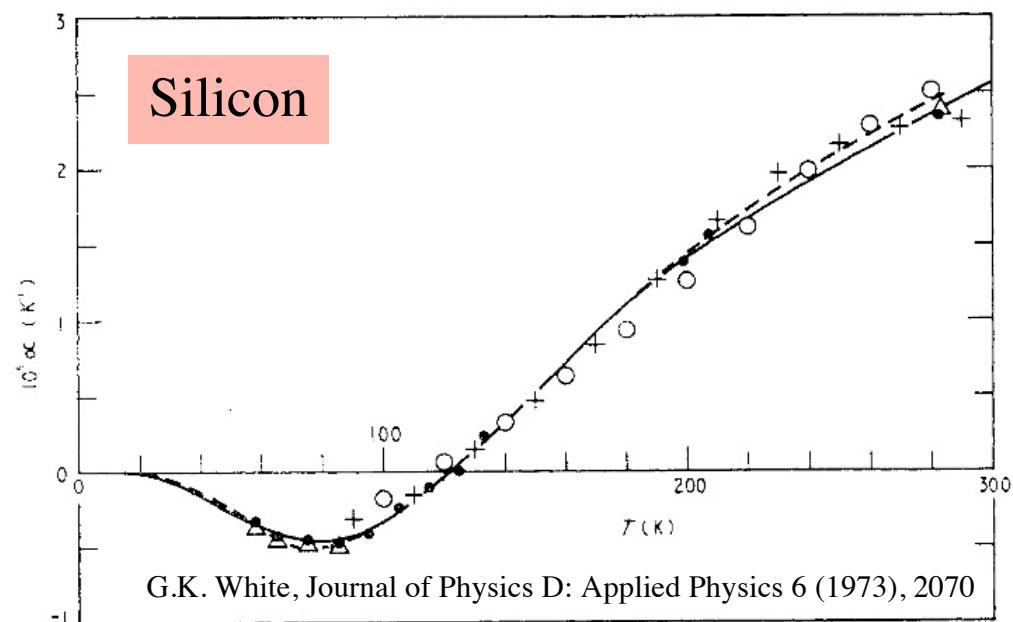


Figure 3.  $\alpha$  for silicon:  $\triangle$  Si1 1970 and  $\bullet$  Si1 1973 using 'smoothed'  $\alpha$ (Cu);  $+$  Gibbons 1958;  $\circ$  Batchelder and Simmons 1964; — Ibach 1969; - - Carr et al 1965.

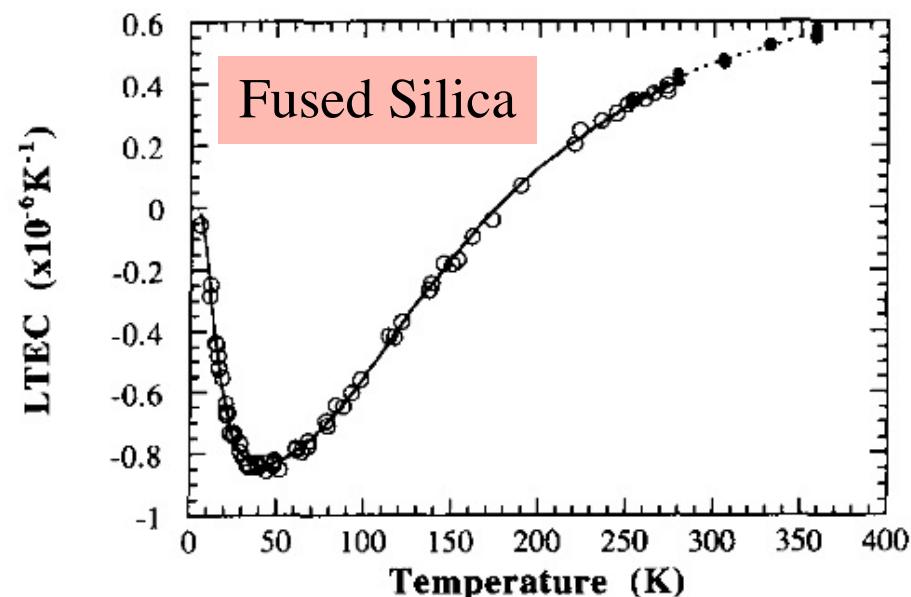


Figure 5 Measurement results of fused silica SRM 739:  $\circ$ , present data;  $\bullet$ , references 5 and 6

# Expansion : microscopic interpretation

Atomic :

inflation ?  $\psi(\vec{r}) = R_{nl}(r)Y_l^m(\theta, \varphi)$  thousands of K to change  
radial electronic configuration !

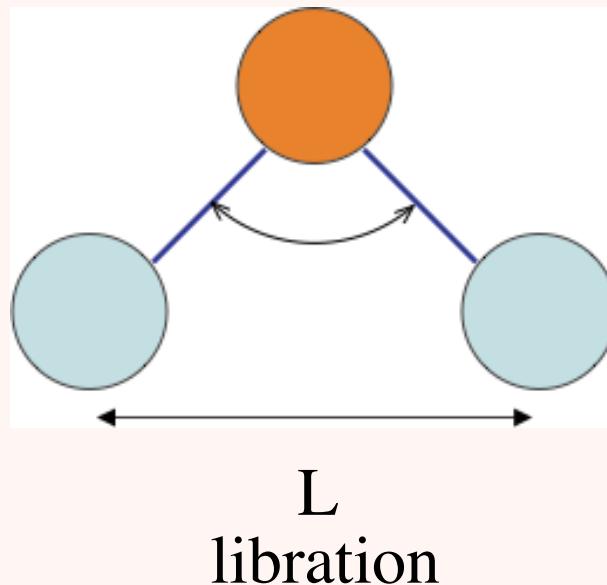
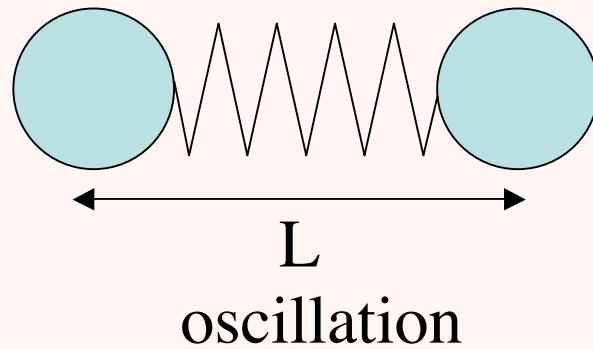
"free" movement/kinetic energy ? gaz, liquids but not solids

vibrations ? solids, liquids  $\Rightarrow$  change in volume ?

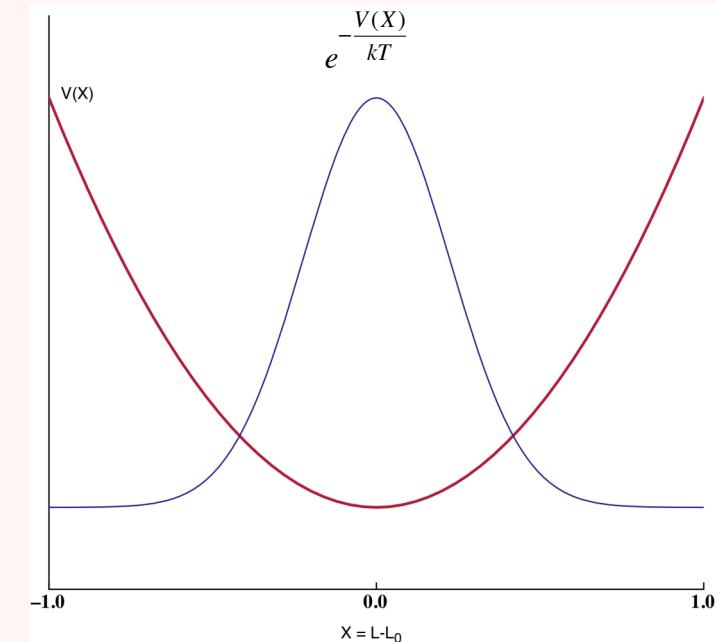
Electronic: Bonding electrons ? few levels well separated

Free electrons in metals... but fermions

# Small amplitude: harmonic approximation



Crystals  
Glasses  
Liquids  
Polymers



Liquids  
polymers

$$\langle L - L_0 \rangle = \frac{\int_{-\infty}^{+\infty} X e^{-\frac{AX^2}{kT}} dX}{\int_{-\infty}^{+\infty} e^{-\frac{AX^2}{kT}} dX} = 0$$

No thermal expansion !

# Failure of the harmonic approximation

Zero thermal expansion

No volume/Thermal dependence of elastic constants

"high" temp. specific heat doesn't depart from Dulong and Petit  
infinite thermal conductivity ...

## Anharmonicity

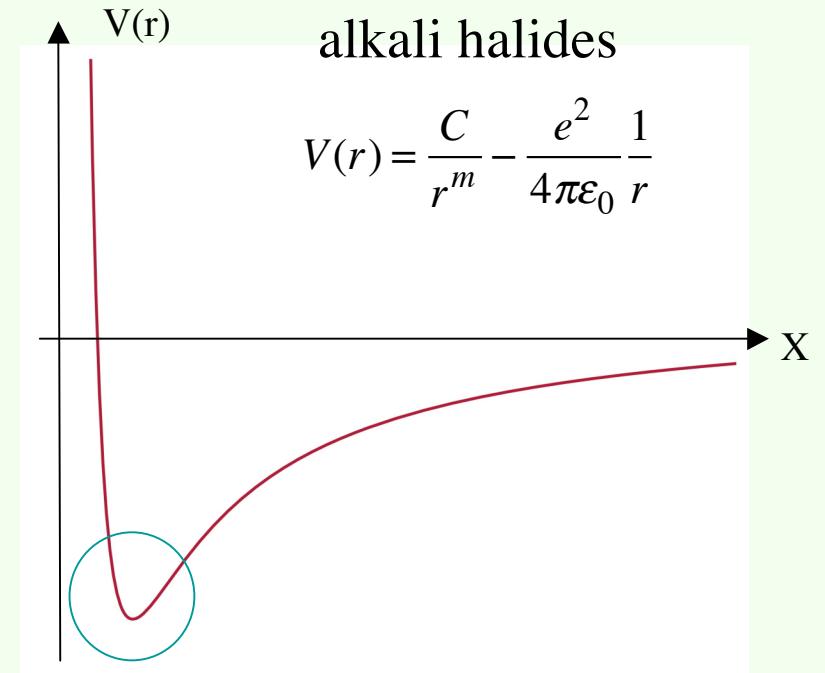
More realistic form of the interaction potential

strongly repulsive for  $L < L_0$

slowly varying attractive for  $L > L_0$

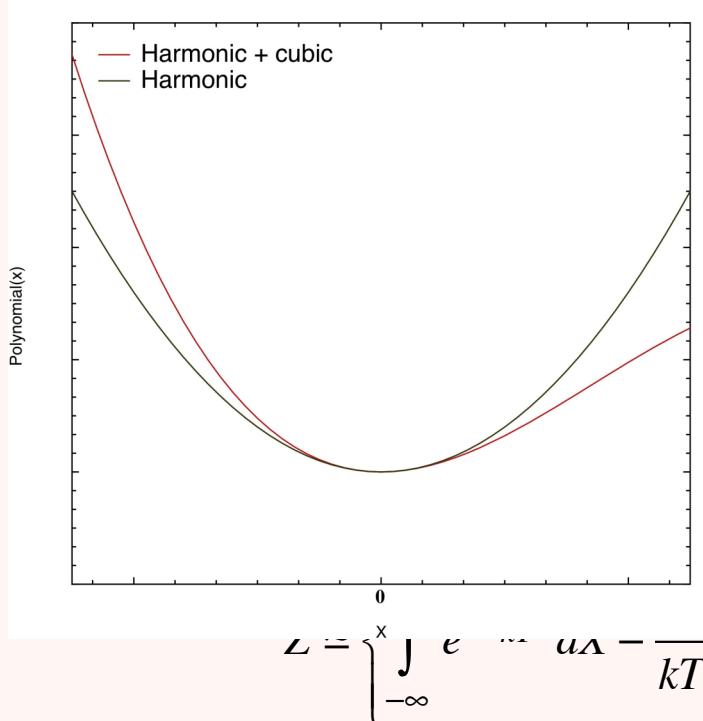


odd powers in the expansion of  $V(X)$



# Classical anharmonic "description"

Expansion :  $V(X) = \cancel{V_0} + aX^2 + bX^3 + cX^4 \implies$  low temperature approximation



$$Z = \left\{ \int_{-\infty}^{+\infty} e^{-\frac{aX^2}{kT}} dX \right\} = -\frac{1}{Z} \frac{b}{kT} \int_{-\infty}^{+\infty} X^4 e^{-\frac{aX^2}{kT}} dX = -\frac{1}{Z} \frac{b}{kT} \frac{3\sqrt{\pi}}{4} \left( \frac{kT}{a} \right)^{5/2}$$

$$\left. \int_{-\infty}^{+\infty} X^3 e^{-\frac{aX^2}{kT}} dX \right\} = \int_{-\infty}^{+\infty} e^{-\frac{aX^2}{kT}} dX = \sqrt{\pi} \sqrt{\frac{kT}{a}}$$

$$\langle L - L_0 \rangle \approx -\frac{3}{4} \frac{b}{a^2} kT \quad \alpha = \frac{d}{dT} \langle L - L_0 \rangle \approx -\frac{3}{4} \frac{b}{a^2} k$$

most common case (highly repulsive):  $b < 0 \Rightarrow \alpha > 0$

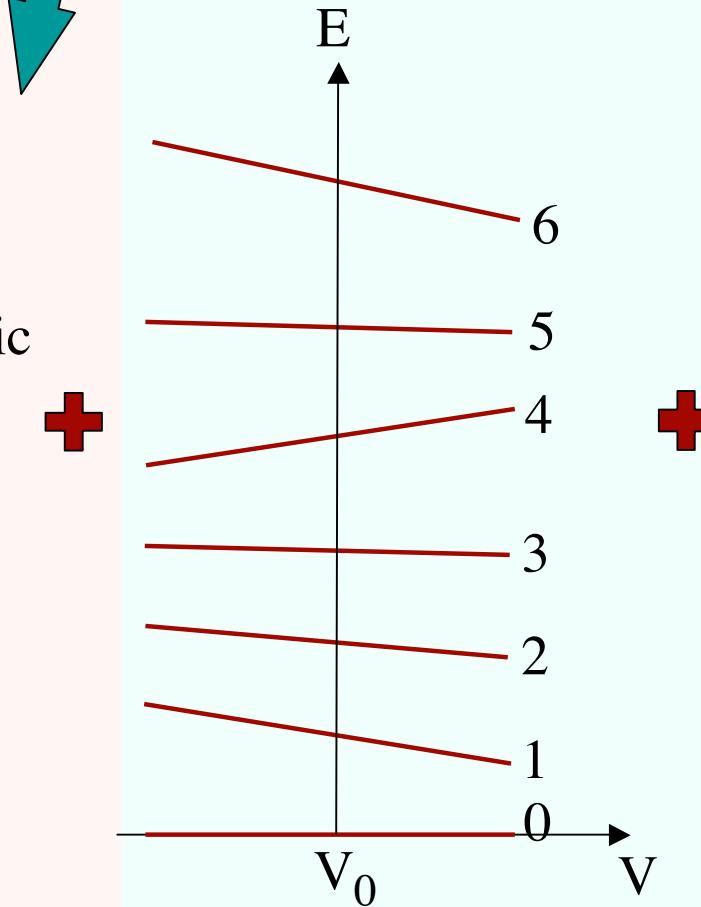
but constant thermal expansion !!!

# Quantum description

Interactions

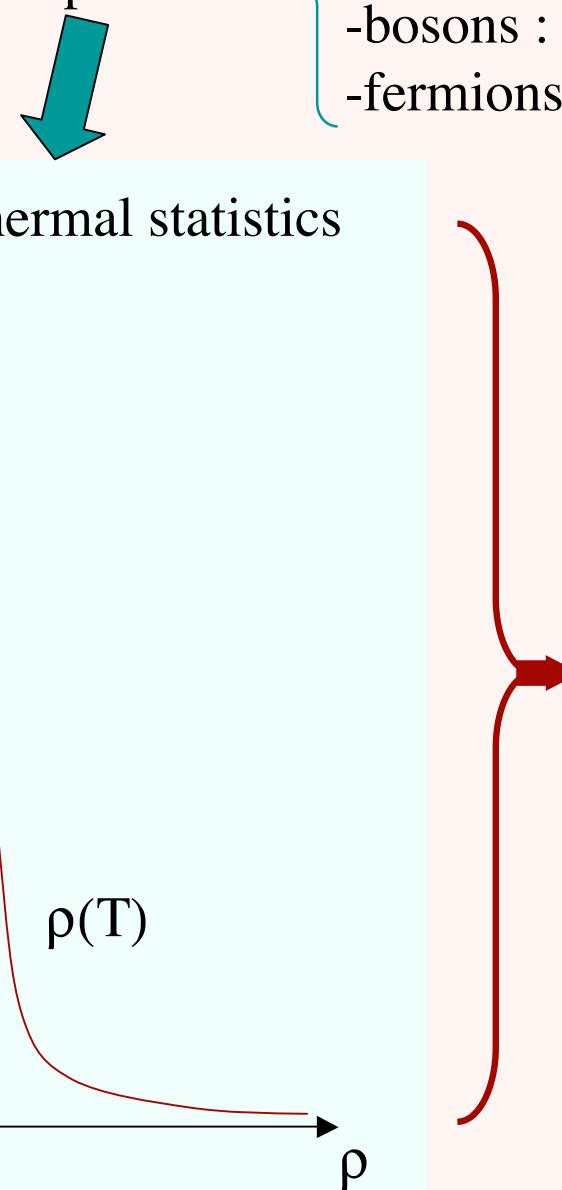
Anharmonic spectra

0 K  
harmonic  
lattice

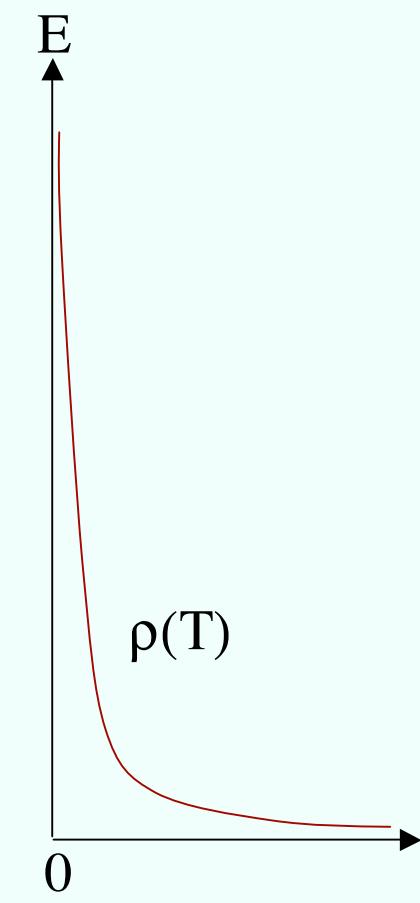


Set of particles

single particle  
indistinguishable particles:  
-bosons : phonons...  
-fermions : electrons...



Thermal statistics



Equilibrium  
volume  
 $V(T)$

# Phonons

Solid = collection of quantum "harmonic" oscillators : Einstein, Debye etc.

Normal mode  $p$ , "phonon" :  $\mathbf{k}_p$ ,  $\omega_p$ , energy  $\hbar\omega_p(V)$ , population  $n_p(T) = \frac{1}{e^{\frac{\hbar\omega_p}{kT}} - 1}$

Internal energy :  $U = U_0 + \sum_p \frac{1}{2} \hbar\omega_p + \sum_p n_p \hbar\omega_p$

Free energy:  $F = U - TS = U - T \int_0^T \frac{\partial U}{\partial T'} \Big)_V \frac{dT'}{T'} = U - T \sum_p \hbar\omega_p \int_0^T \frac{1}{T'} \frac{\partial n_p}{\partial T'} \Big)_V dT'$

Phonons' pressure :  $P = -\left. \frac{\partial F}{\partial V} \right)_T = -\frac{\partial(U_0 + \sum_p \frac{1}{2} \hbar\omega_p)}{\partial V} - \sum_p n_p \frac{\partial(\hbar\omega_p)}{\partial V}$

$$dV = \left. \frac{\partial V}{\partial P} \right)_T dP + \left. \frac{\partial V}{\partial T} \right)_P dT = 0$$

$$\Rightarrow \left. \frac{\partial V}{\partial T} \right)_P = - \left. \frac{\partial V}{\partial P} \right)_T \left. \frac{\partial P}{\partial T} \right)_V = 3\alpha V$$

$$\alpha = \frac{1}{3} \left( -1 \left. \frac{\partial V}{\partial P} \right)_T \cdot \left. \frac{\partial P}{\partial T} \right)_V \right)$$

$\alpha = -\frac{1}{3} K_T \sum_p \frac{\partial n_p}{\partial T} \frac{\partial(\hbar\omega_p)}{\partial V}$

$K_T$  isothermal compressibility  
= 1/(bulk modulus)

# Grüneisen Parameter

$$\alpha = -\frac{1}{3} K_T \sum_p \frac{\partial n_p}{\partial T} \frac{\partial(\hbar\omega_p)}{\partial V} = \sum_p \alpha_p$$

$$C_{V_p} = \frac{1}{V} \hbar \omega_p \frac{\partial n_p}{\partial T} \quad p \text{ specific heat}$$

$$\alpha_p = -\frac{1}{3} K_T \frac{\partial n_p}{\partial T} \frac{\partial(\hbar\omega_p)}{\partial V} = \frac{1}{3} K_T \left( \frac{\partial n_p}{\partial T} \frac{\hbar\omega_p}{V} \right) \left( -\frac{V}{\omega_p} \frac{\partial \omega_p}{\partial V} \right) = \frac{1}{3} K_T \cdot C_{V_p} \cdot \gamma_p$$

$$\gamma_p = -\frac{V}{\omega_p} \frac{\partial \omega_p}{\partial V} = -\frac{\partial(\ln \omega_p)}{\partial(\ln V)} \quad p \text{ Grüneisen factor}$$

$$\alpha = \frac{1}{3} K_T \sum_p C_{V_p} \gamma_p$$

$$\alpha = \frac{1}{3} K_T \frac{\sum_p C_{V_p} \gamma_p}{\sum_p C_{V_p}} \cdot \sum_p C_{V_p} = \frac{1}{3} K_T \cdot \gamma \cdot C_V$$

**Grüneisen Parameter**

$$\gamma = \frac{3}{K_T \cdot C_V} \cdot \alpha$$

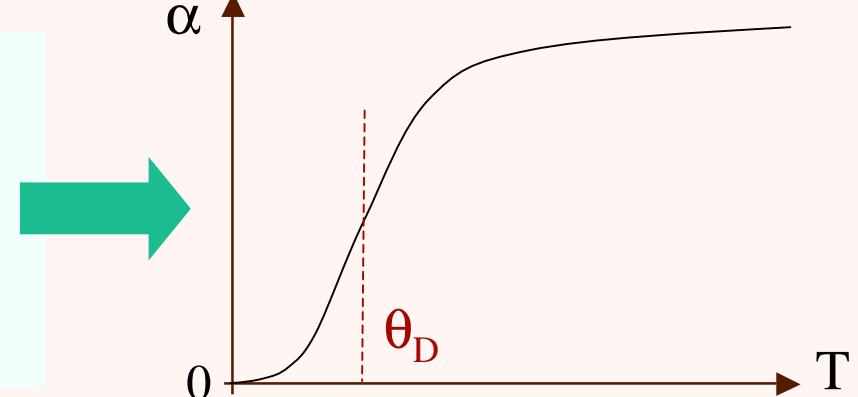
$$\text{Debye simplification} \quad \omega_p = a \cdot \omega_D = \frac{a k}{\hbar} \cdot \theta_D \quad \gamma_p = \gamma = -\frac{V}{\theta_D} \frac{\partial \theta_D}{\partial V} = -\frac{\partial(\ln \theta_D)}{\partial(\ln V)}$$

$$\alpha = \frac{1}{3} K_T \cdot \gamma \cdot C_V$$

"constants"

$$T \ll \theta_D \quad \alpha \sim T^3$$

$$T \gg \theta_D \quad \alpha \rightarrow \text{const.}$$



## Example: Alkali-Halides

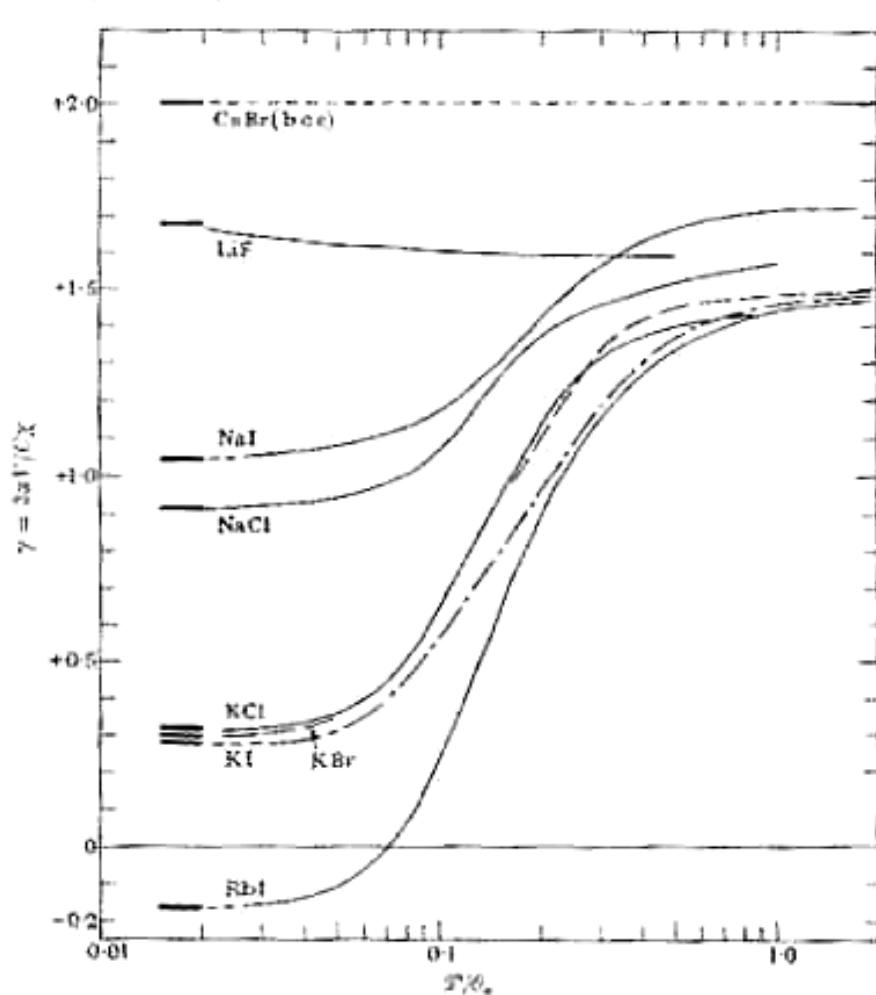


FIGURE 2. Grüneisen function,  $\gamma(T) = 3\alpha V K_d / C_p$ . Heavy bars near  $T = \theta_0/50$  represent values of  $\gamma_0$  obtained from  $T^3$  terms.

Grüneisen Parameter :

$$\gamma = \frac{3}{K_T \cdot C_V} \cdot \alpha$$

of order of a few units

not constant/  $T \rightarrow \gamma(T)$

stable at low T or high T

at low T,  $K_T \cdot \gamma = cst \rightarrow \alpha \sim C_V$

# Conduction electrons in metals

$$\text{Drude model : } P_e = \frac{N_e}{V} kT = \frac{2}{3} \frac{U_e}{V} \quad \alpha_e = \frac{1}{3} K_T \cdot \frac{\partial P_e}{\partial T} \Big|_V = \frac{1}{3} K_T \frac{N}{V} k = \frac{1}{3} K_T \frac{2}{3} C_{Ve}$$

Electrons pressure

$$\text{Free electron gaz with Fermi statistics : } P_e = \frac{2}{3} \frac{U_e}{V} \quad \alpha_e = \frac{1}{3} K_T \frac{2}{3} C_{Ve}$$

$$\alpha = \frac{1}{3} K_T (\underbrace{\gamma_e C_{Ve}}_{\text{electrons}} + \underbrace{\gamma_l C_{Vl}}_{\text{phonons}}) \quad \gamma_e (= 2/3) \text{ electronic Grüneisen Parameter}$$

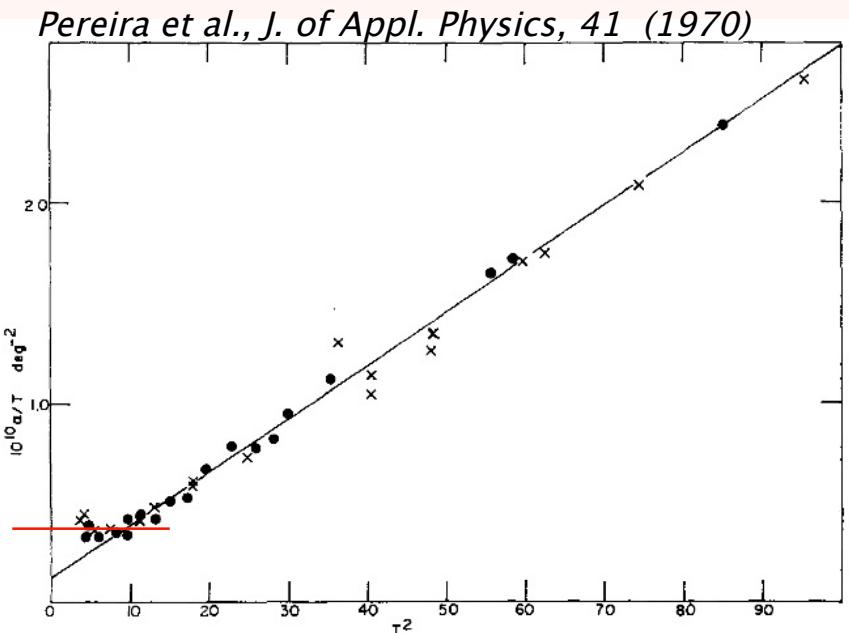
$$C_{Ve} = \frac{\pi^2}{2} k^2 g(E_F) T$$

at low temperature :  $\alpha \approx aT + bT^3 + \dots$

Copper at low. temp.

$$\alpha \approx 1.3 \times 10^{-10} T + 2.7 \times 10^{-11} T^3 + \dots$$

$\gamma_e = 0.57$



# Atomic configurations

change in shape/size as function of T

Orbital effects:  $L \neq 0$  ions

Crystal Field Splitting

Jahn Teller : symmetry lowering

B. Lüthi, H.R. Ott, Solid State Comm., 33 (1980) 717

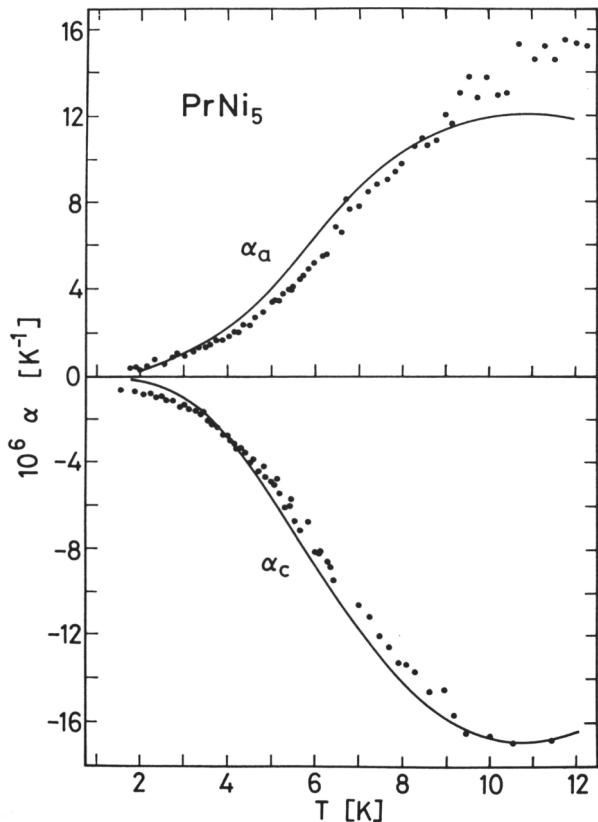
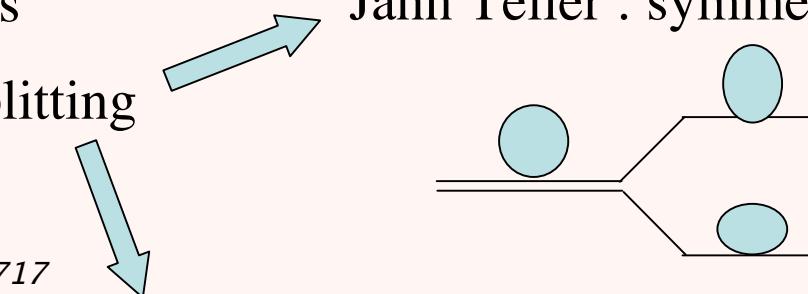
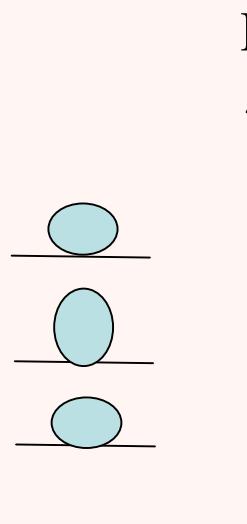


Fig. 1 Thermal expansion of  $\text{PrNi}_5$ . Experimental points from reference 2. Solid lines are based on calculations as described



"Schottky type" thermal expansion



Change in valence  
B. Kindler et al., Phys. Rev. B, 50 (1994) 704

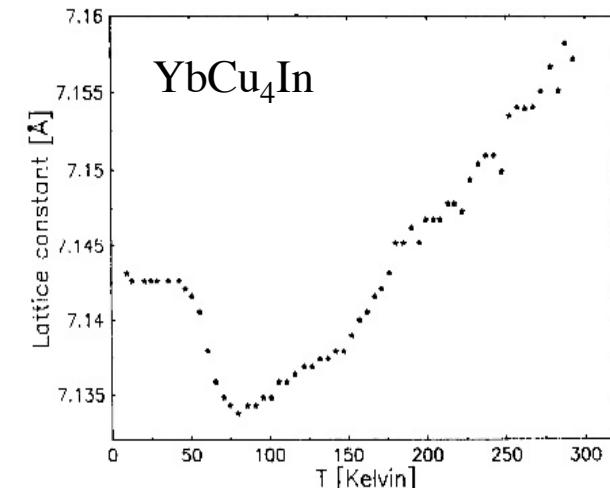


FIG. 1. Lattice constant  $a$  as a function of temperature.

# Phase transitions

$$F(T, \eta, V) = F(T, \eta, V_0) - A\eta^m \frac{\Delta V}{V_0} V_0 + \frac{1}{2} \frac{1}{K_T} \left( \frac{\Delta V}{V_0} \right)^2 V_0$$

Coupling between V and order parameter  $\eta$

Elastic energy

$$\begin{aligned} \varepsilon_V = \frac{\Delta V}{V_0} &\quad \longleftrightarrow \quad \eta \\ \varepsilon_V = A \cdot K_T \cdot \eta^m &\quad \rightarrow \quad \alpha_\eta = \frac{1}{3} \frac{\partial \varepsilon_V}{\partial T} \Big)_P = \frac{1}{3} A \cdot K_T \cdot \frac{\partial \eta^m}{\partial T} \Big)_P \\ \eta = (T_C - T)^\beta &\quad \rightarrow \quad \alpha_\eta = -\frac{1}{3} A \cdot K_T \cdot (\beta + m) \cdot (T_C - T)^{\beta+m-1} \end{aligned}$$

Microscopic origin of A

ordering = collective phenomena

pair interactions

example : localised magnetism  $\mathcal{H}_{ij} = -2J_{ij} \vec{S}_i \cdot \vec{S}_j$

$J_{ij}$  depends on distance  $A \sim \sum_j \frac{\partial J_{ij}}{\partial V}$

most commonly  $\frac{\partial J_{ij}}{\partial r_{ij}} < 0 \Rightarrow \frac{\partial J_{ij}}{\partial V} < 0 \Rightarrow A < 0 \Rightarrow \alpha_\eta > 0$

superconductivity in  $\text{CeCu}_2\text{Si}_2$   
G. Bruls et al., Phys. Rev. Lett. 72, (1994) 1754

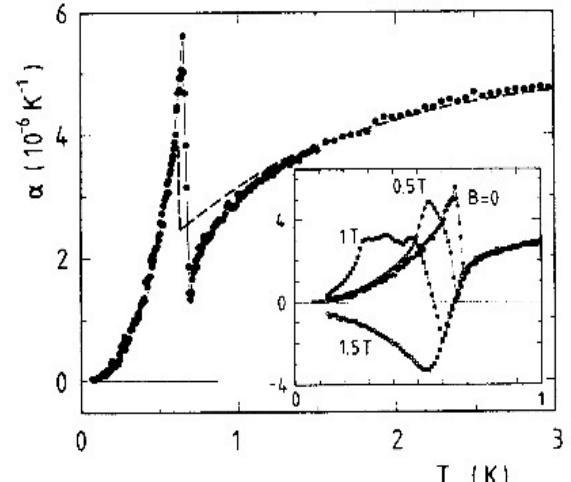


FIG. 4. Coefficient of thermal expansion along the  $a$  axis of an NR-type  $\text{CeCu}_2\text{Si}_2$  sample (●) and of an R-type sample (---) [7] in zero magnetic field. Inset:  $a$  axis thermal-expansion coefficient of the NR-type sample in different magnetic fields with  $B \parallel a$ .

## Example: Spontaneous magnetostriiction and Invar effect

### Thermal expansion of Iron

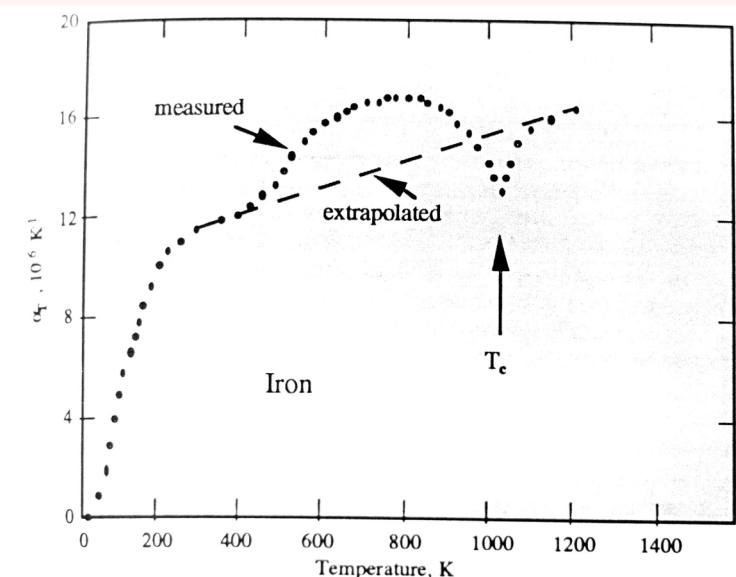
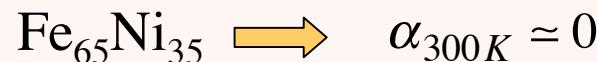


FIGURE 24. Temperature dependence of the linear thermal expansion coefficient of iron, after Gersdorff.<sup>71</sup>

### Instability of iron magnetic moment

$$\frac{\partial m}{\partial V} < 0 \Rightarrow \frac{\partial V}{\partial T} < 0 \quad \text{below } T_C$$

In Invar the anomaly is shifted below room temp.



### Thermal expansion of Nickel

F. C. Nix and D. MacNair, Phys. Rev. (1941)

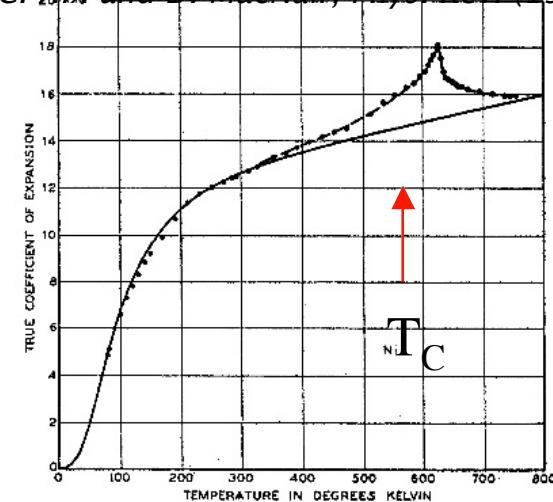


FIG. 4. True coefficient of thermal expansion vs. temperature for Ni. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with  $\theta = 410$ ,  $\frac{1}{6}(m+n+3) = 4.0$ ,  $Q_0 = 151.5 \times 10^6 \text{ cal}$ .

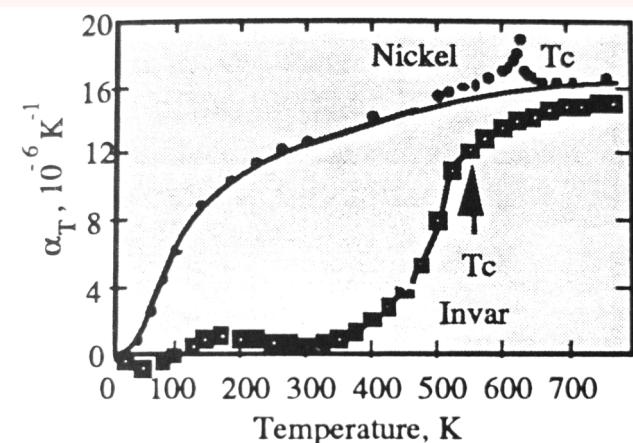


FIGURE 7. Anomalies in the thermal expansion coefficient of ferromagnets: Nickel after Kollie,<sup>17</sup> and Fe-Ni Invar alloy, after Metalimphy Products.<sup>18</sup>



