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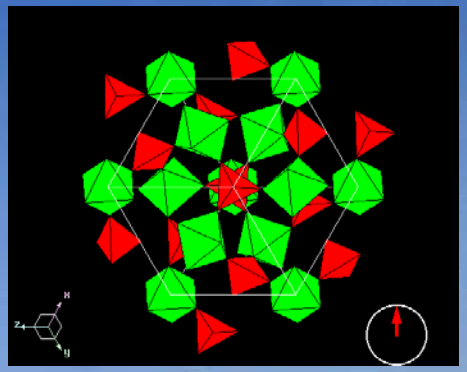
قسم الفيزياء

Negative Thermal Expansion (NTE)

التمدد الحرارى السالب



Dr. Naglaa AbdelAll

Assistant lecture,
Imam University,
1437/2016

Outline …

✓ Negative thermal expansion:

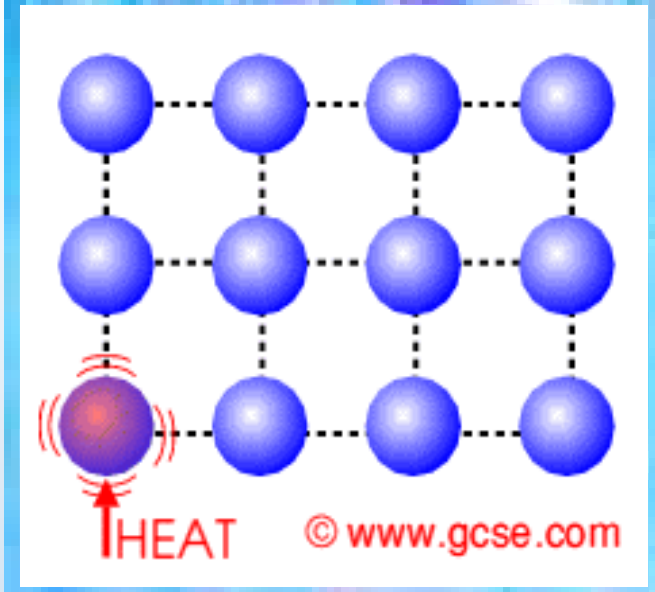
- Introduction → Thermal expansion
- Crystal Vibration → PTE and NTE
- Why EXAFS technique → Studying NTE
- EXAFS Vs. Diffraction → Complementarity
- Materials with Negative Thermal Expansion

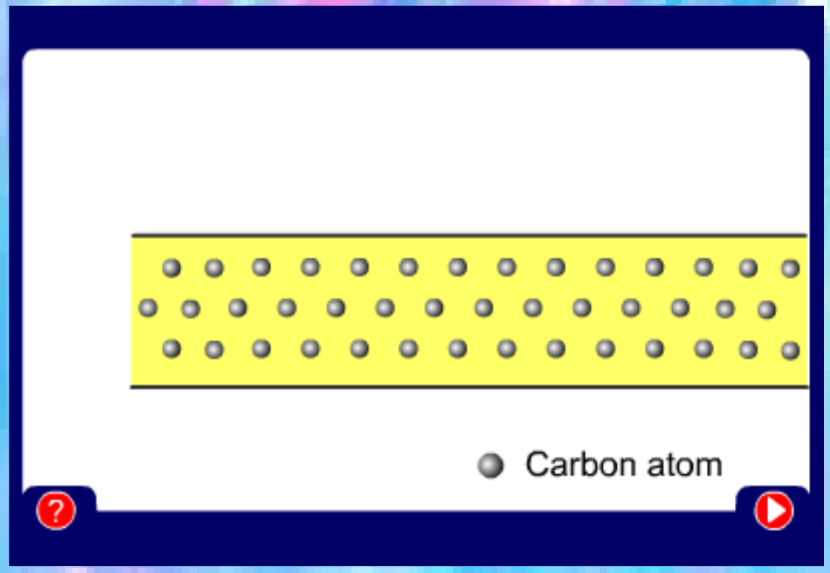
EXPANSION

Thermal expansion

Change in the dimension(s) of a substance due to change in temperature

- 1D ⟹ L : Linear Expansion
- 2D ⟹ A: Areal Expansion
- 3D ⟹ V : Volumetric Expansion



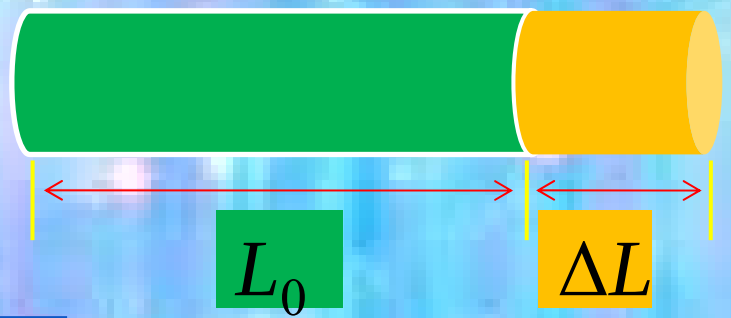


- **There is an addition of energy to the material**
- **The internal energy of the atoms of the material increase, causing atoms to vibrate**
- **The vibrating atoms now occupy more space when hot compared to when cold.**

❖ **Average distance between atoms increases**

- **Coefficient of thermal expansion is the ratio of the fractional change in size of a material to its change in temperature.**

✓ Materials of higher Expansion Coefficient have larger Expansion.



$$\Delta L = \alpha \cdot L_0 \cdot \Delta T$$

Change in dimension

Coefficient of expansion

Original length

Change in temperature

α (alpha) - solids
β (beta) – liquids

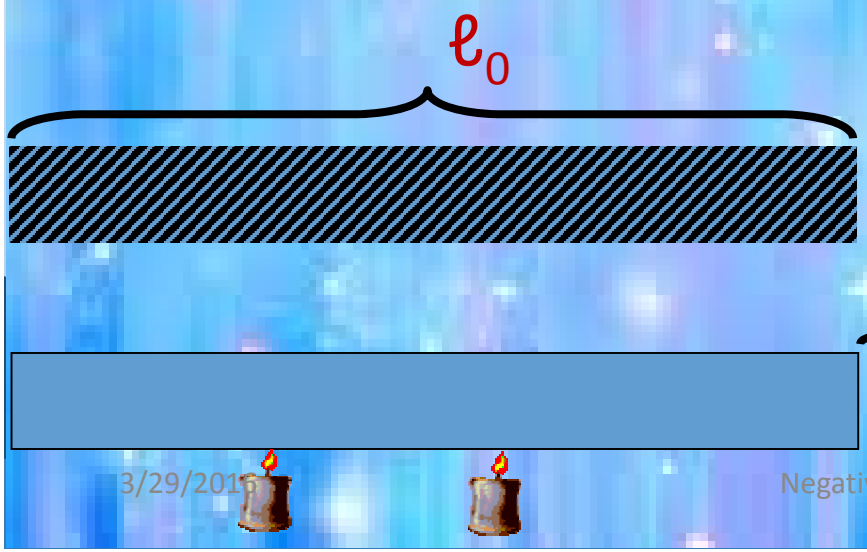
Types of Ex

➢ Solids

- **Linear expansion**

- Expansion is directly
- proportional

to temperature change.

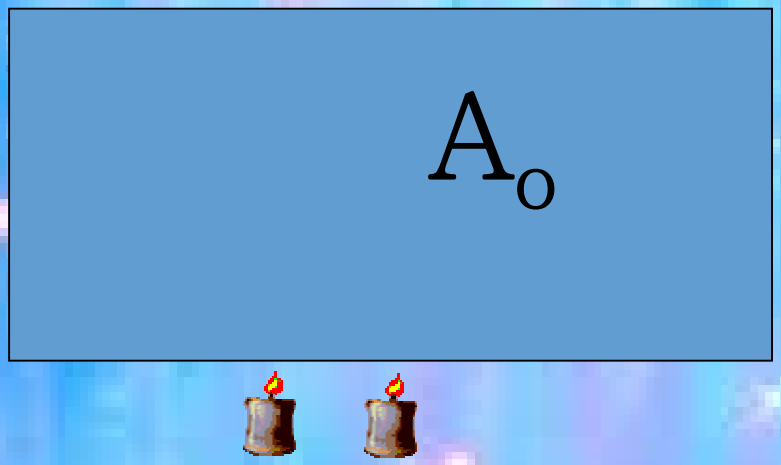


MATERIAL	*a* per °C
1. Aluminum	23 x 10^{-6}
2. Brass	19x 10^{-6}
3. Copper	17x 10^{-6}
4. Germanium	6.0x 10^{-6}
5. Glass, ordinary	9x 10^{-6}
6. Glass, Pyrex	3.3x 10^{-6}
7. Invar (nickel-steel alloy)	0.9x 10^{-6}
8. Iron	12x 10^{-6}
9. Platinum	9.0x 10^{-6}
10. Fused quartz	0.5x 10^{-6}
11. Silicon	2.4x 10^{-6}
12. Steel	11x 10^{-6}
13. Tungsten	4.4x 10^{-6}
14. Uranium	15x 10^{-6}
15. Wood, along grain	(3 to 6) x 10^{-6}
16. Wood, across grain	(35-60) x 10^{-6}

• Areal Expansion

Areas expand twice as much as lengths do.

$$\Delta A = 2\alpha A_0 \Delta T$$

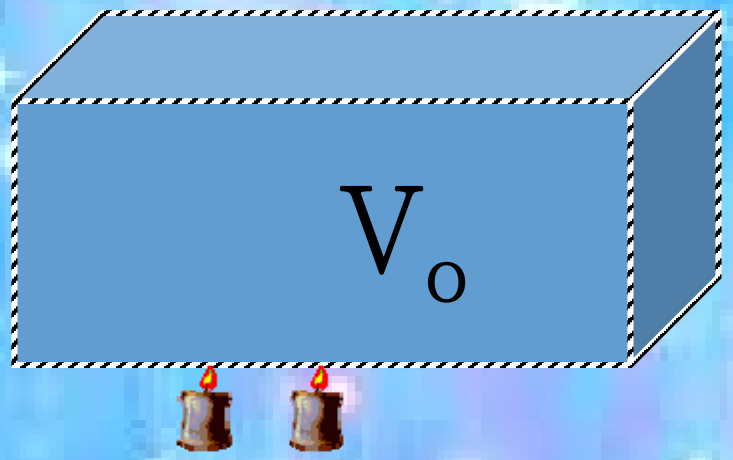


α : the Coefficient of Area expansion
A_0: Initial area of the object
ΔA: Area change of the object
ΔT: Temperature change of the object

• Volumetric Expansion (Cubical Expansion)

Volumes expand three times as much as lengths do.

$$\Delta V = 3\alpha V_0 \Delta T$$



ΔV

α : the Coefficient of volume expansion
V_0: Initial volume of the object
ΔV: Volume change of the object
ΔT: Temperature change of the object

➢ Liquids Expansion

- volumetric (or cubical) expansion

Liquids can only expand in volume.

$$\Delta V = \beta V_0 \Delta T$$

LIQUID	β, per °C
Alcohol, ethyl	$1.0\text{x}\mathbf{10^{-3}}$
Mercury	$1.8\text{x}\mathbf{10^{-4}}$
Water (15-100°)	$3.7\text{x}\mathbf{10^{-4}}$

Gases

Behavior of gases is more complicated, gases will expand as much as pressure will allow.

$$PV = nRT$$

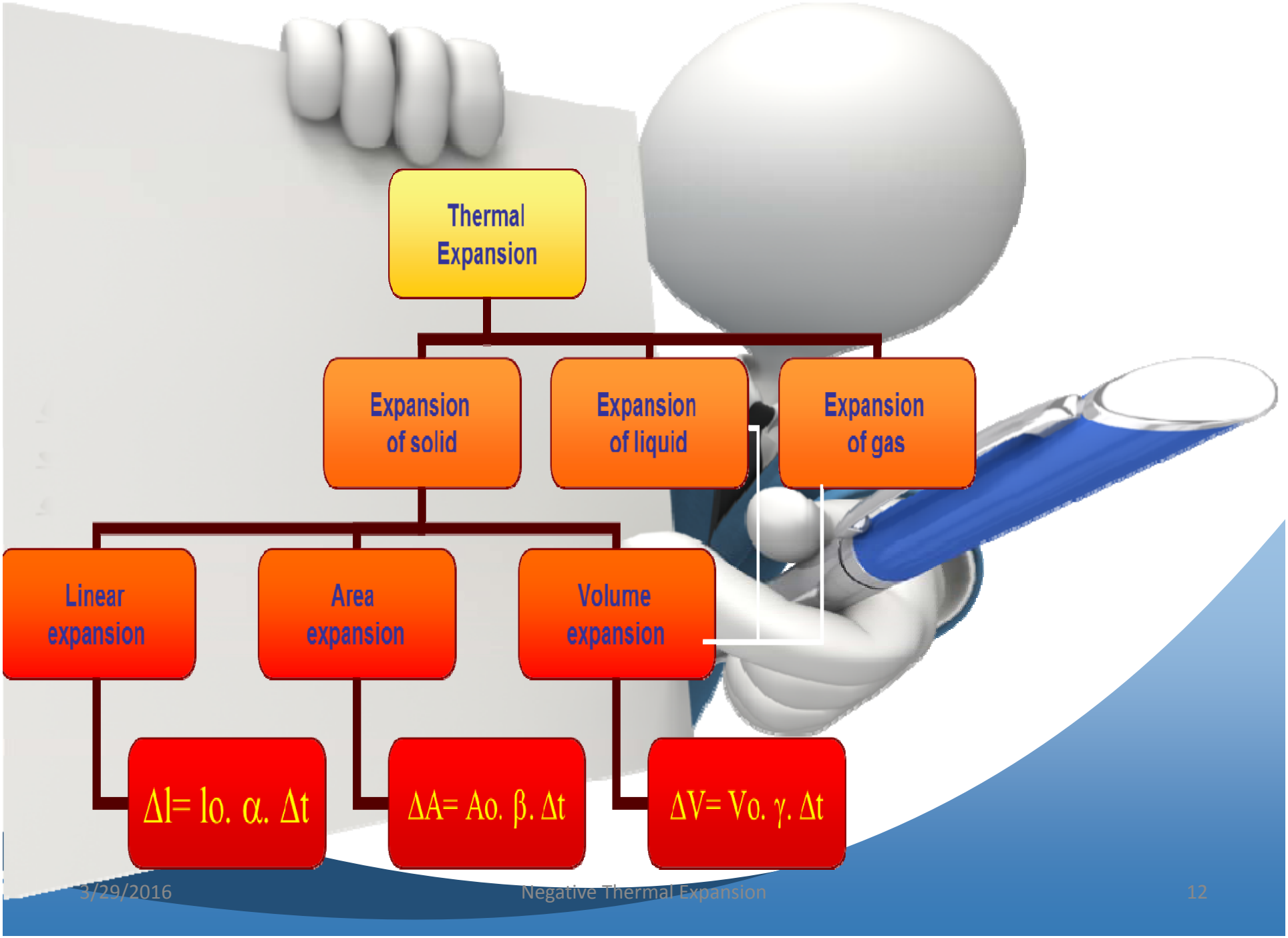
P	**absolute pressure**
T	**absolute temperature**
V	**volume**
n	**number of moles**
R	**gas constant = 8.315 J/mol K**

$$PV = NkT$$

P	**absolute pressure**
T	**absolute temperature**
V	**volume**

N = number of particles

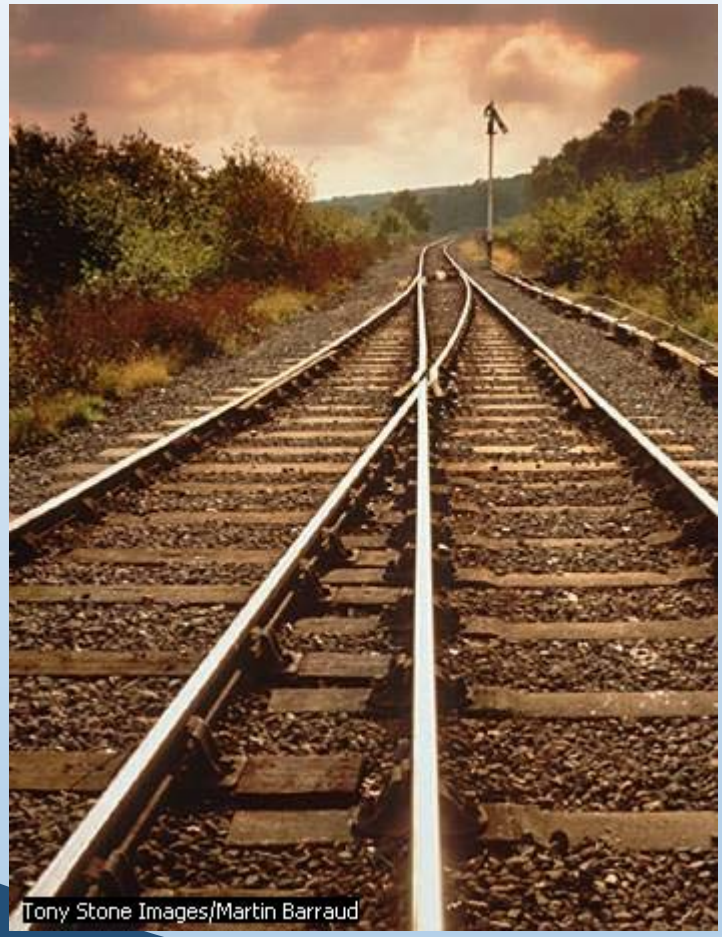
k = Boltzmann's constant = 1.382×10^{-23} J/K


Thermal Expansion
Expansion of solid
Expansion of liquid
Expansion of gas
Linear expansion
Area expansion
Volume expansion
Δl= lo. α. Δt
ΔA= Ao. β. Δt
ΔV= Vo. γ. Δt

SAMPLE PROBLEMS


I CAN'T GET THIS METAL LID OFF THE JAR··· SHOULD I HEAT THE LID OR COOL IT? WHY?

Apperception

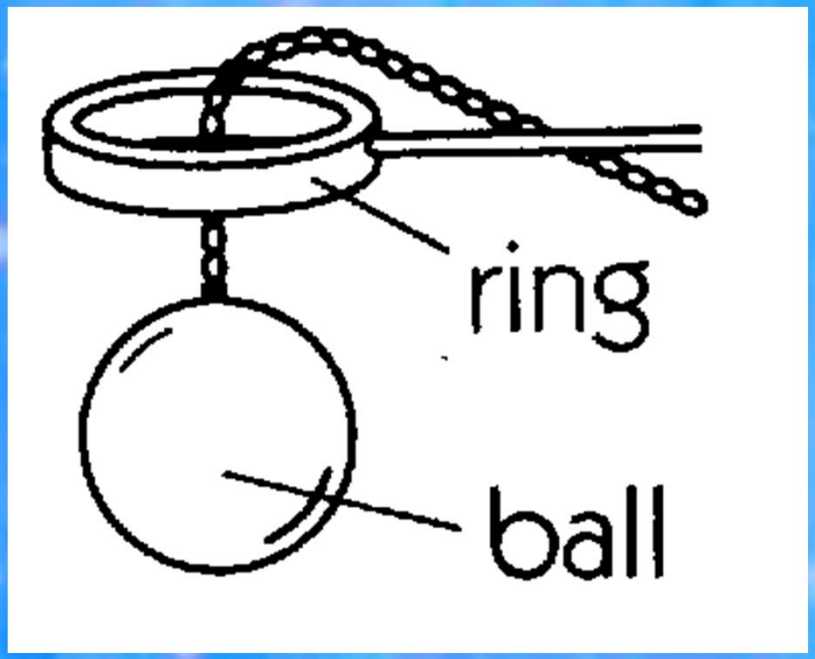


Why is *a space left* between the railway line where one piece joins the next?

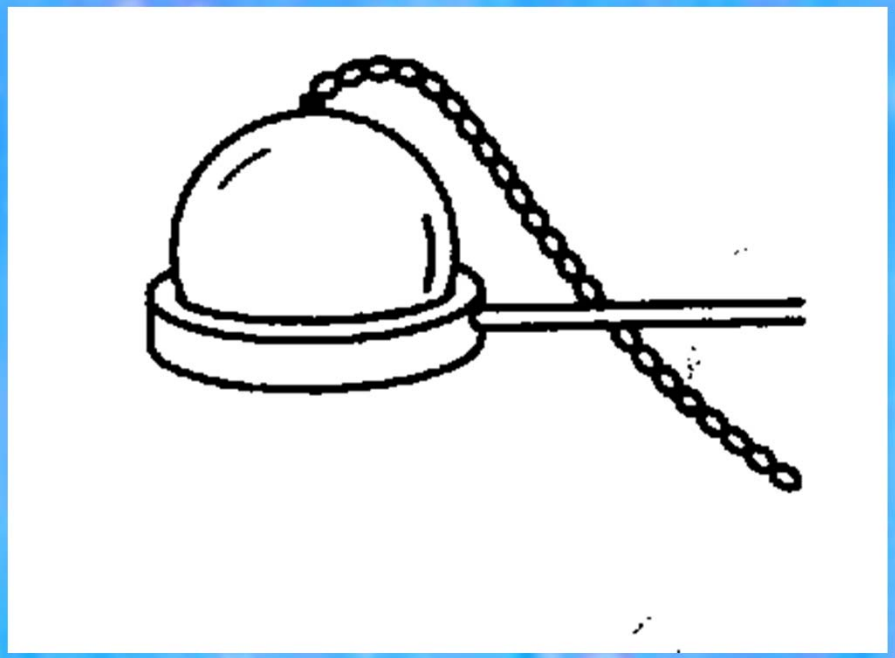
Solids EXPANSION

Ball and Ring

A solid expands when heated, contracts when its temperature decreases.

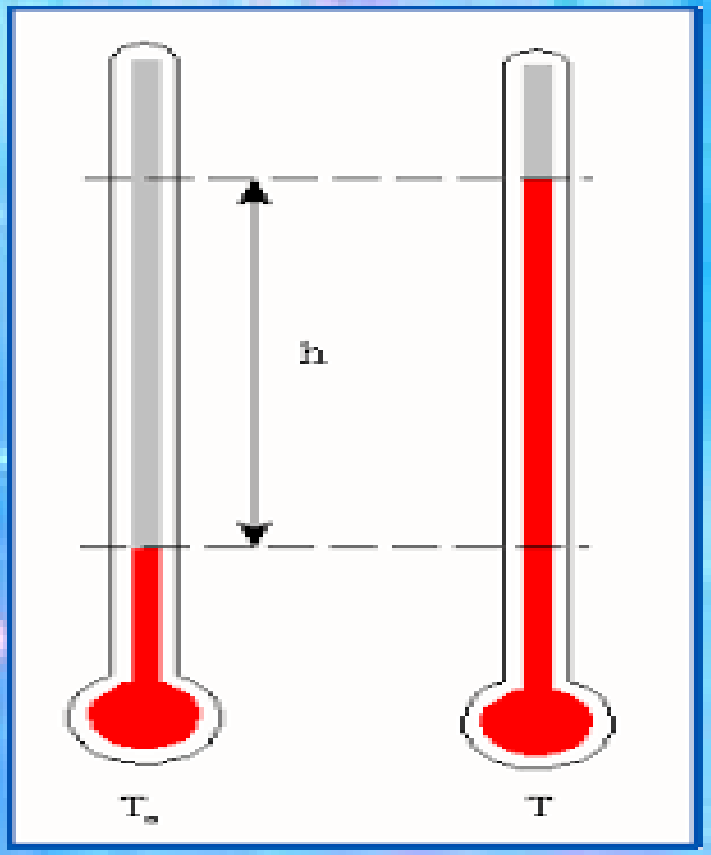


Before heating the ball

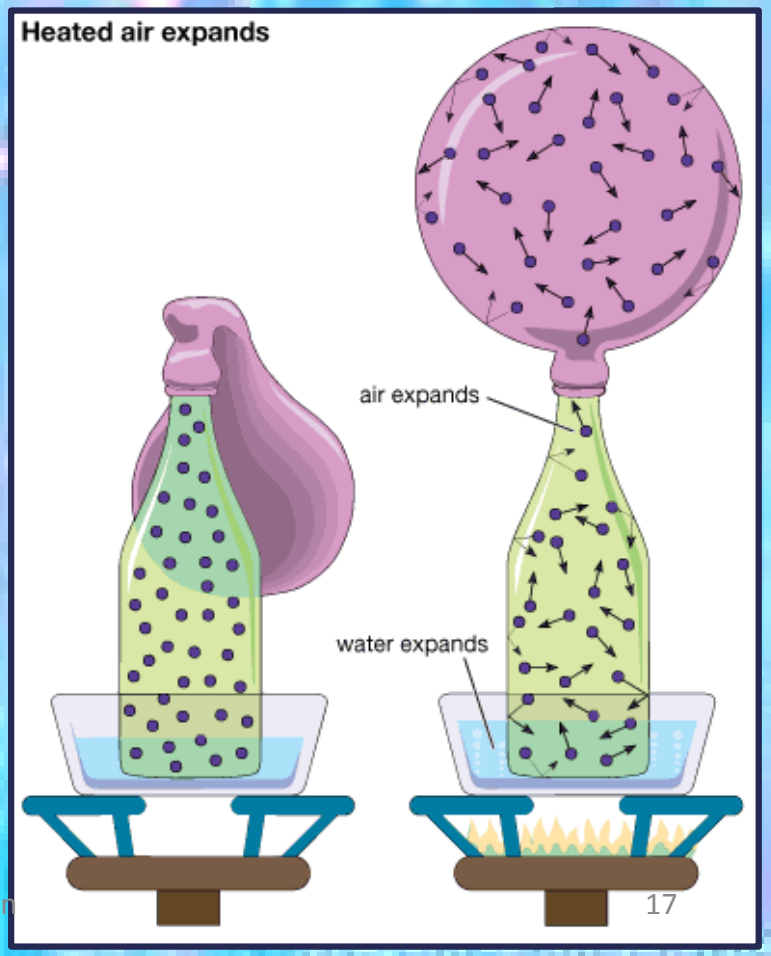


After heating the ball

Liquid Expansion



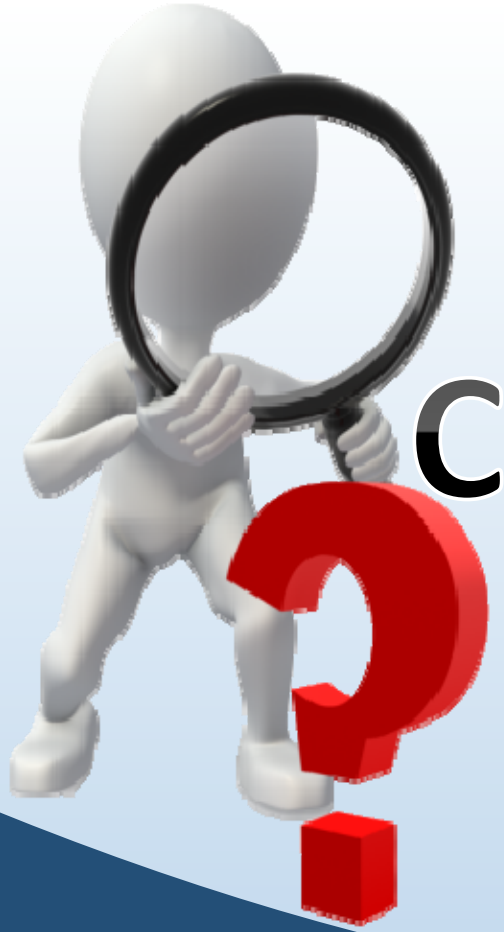
Gas



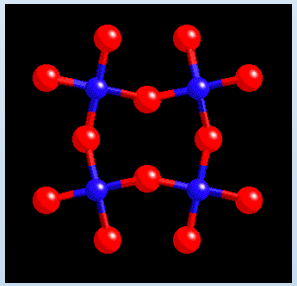
REAL LIFE APPLICATIONS OF THERMAL EXPANSION

Gases expand a lot when heated!

Bridges are built with ‘joints’ so they don’t crack when the temperature changes.



Crystal vibration



➢ Solids generally expand when heated (PTE), a courious example…

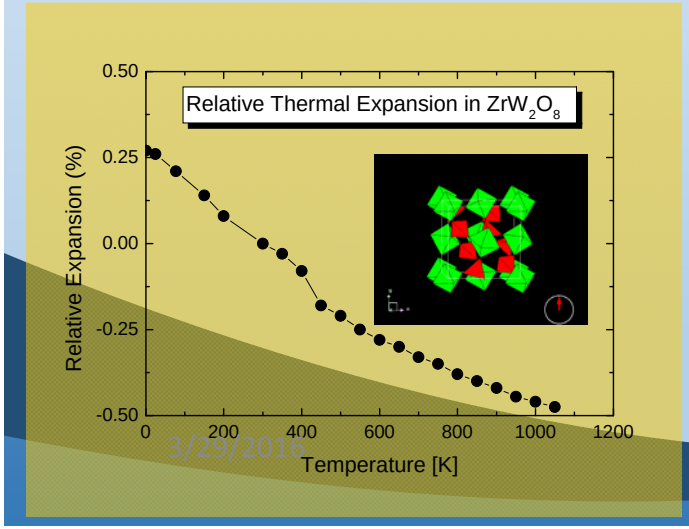
Standing at 442 m
and 110 stories high.

The Sears tower in Chicago, USA grows by 15 cm in the summer!

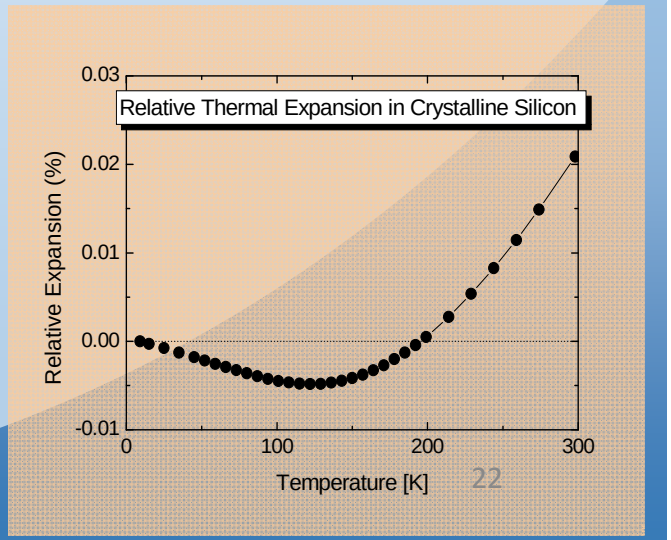
There are however exceptions:
solids that contract when heated (NTE)!

Examples…

- ZrW_2O_8 beetwen 0.3÷1050 K!



- Crystalline Silicon at low temperature



Thermal Expansion

Positive Expansion

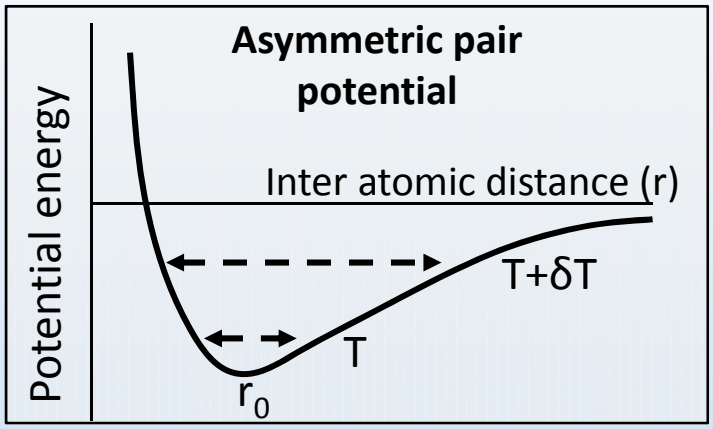
(PTE)

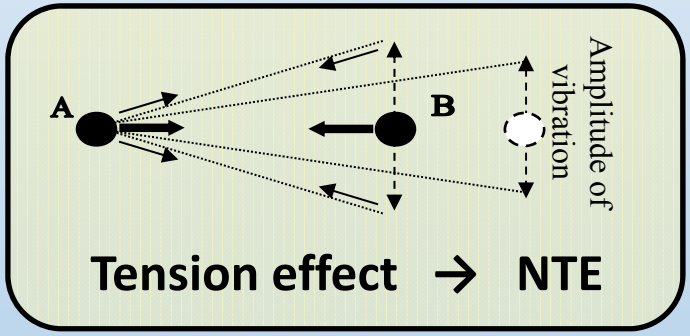
Negative Expansion

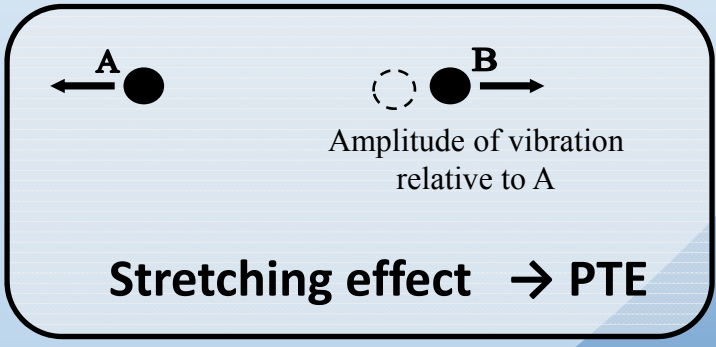
(NTE)

Vibrational mechanisms of NTE

- **vibrations play the major part.**
  - ✓ Bond stretching effect.
  - ✓ Tension effect .



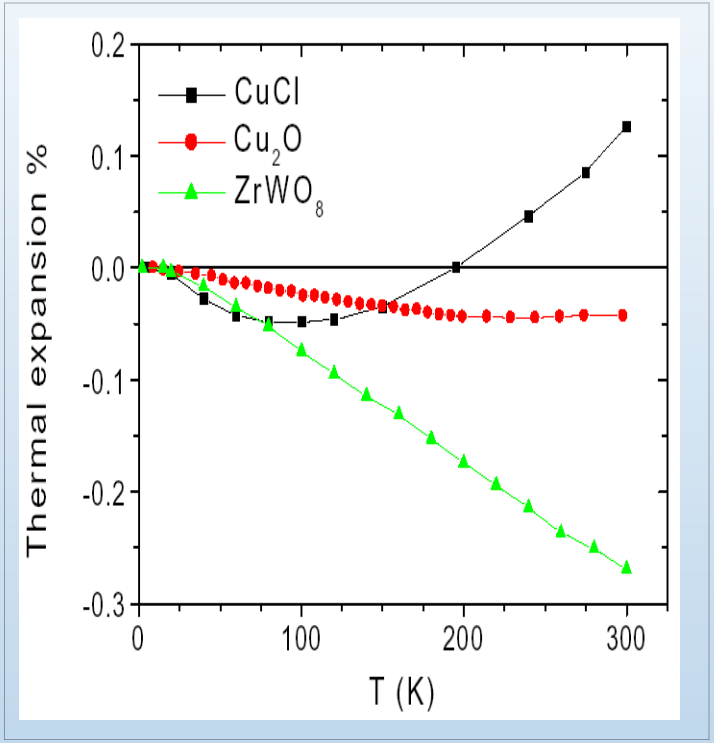




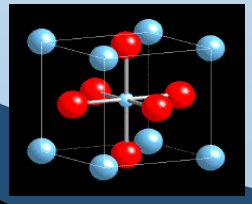
Which is larger? ⟹ **Anisotropy of the vibrations** ⟹ **Open structures**

T. H. K. Barron et al. Adv. Phys. **29**,609 (1980), G. D. Barrera et al. J. Phys.: Condens. Matter 17, R217 (2005)

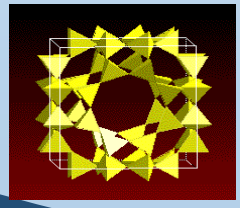
Negative Thermal Expansion (NTE)



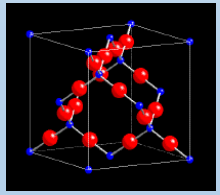
Perovskites

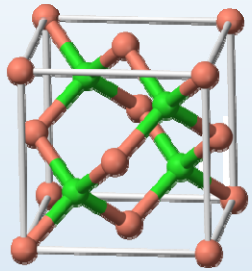


Zeolites



SiO_2



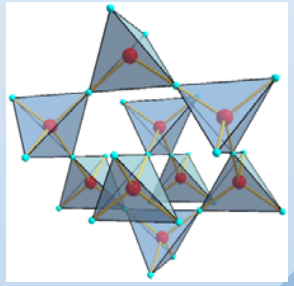


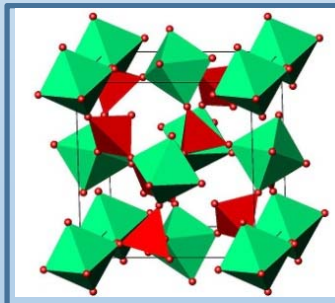
✓ Tetrahedral:

- CuCl has zincblende (N =4)
- isotropic NTE.
- ⊥ vibrations of Cu.

✓ Cuprite:

- cubic framework (M_4O)
- Cu_2O (*N*=2)
- RUMs or M-O ⊥ vibrations.





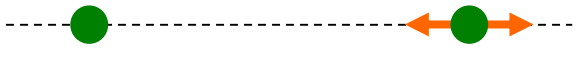
✓ Framework:

- rigid MO_4 / MO_6.
- ZrW_2O_8 (NTE: large T-rang)
- NTE by RUMs.

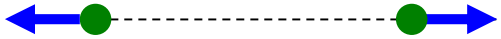
An experimental challenge

Lattice thermal expansion =

Bond-stretching effect



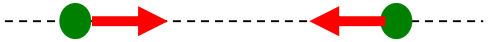
POSITIVE contribution



+

Tension effect

NEGATIVE contribution

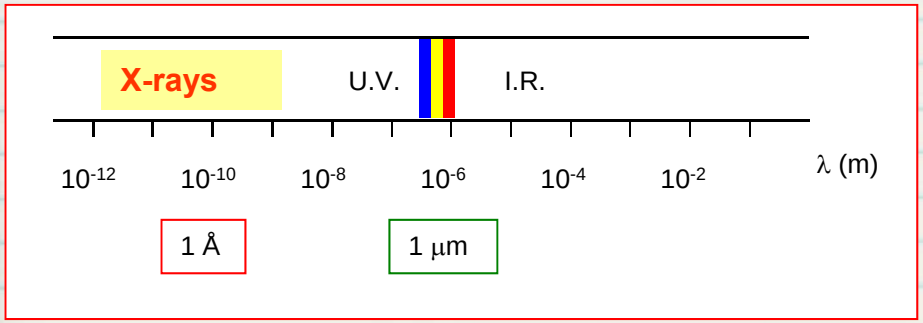


Measured by

- *Dilatometry*
- *Bragg diffraction*

Can we experimentally disentangle the two effects ?

Structural techniques

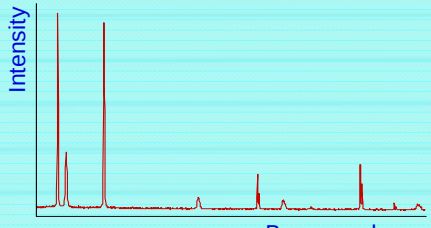


X-rays

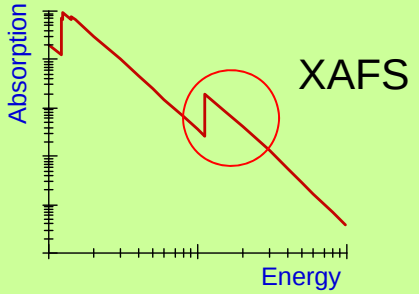
$$E[\mathrm{keV}] = \frac{12.4}{\lambda[\text{Å}]}$$

Scattering

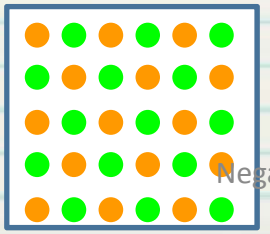
$$\lambda = 2d\sin\theta$$



Spectroscopy



Long-range order (Crystals)

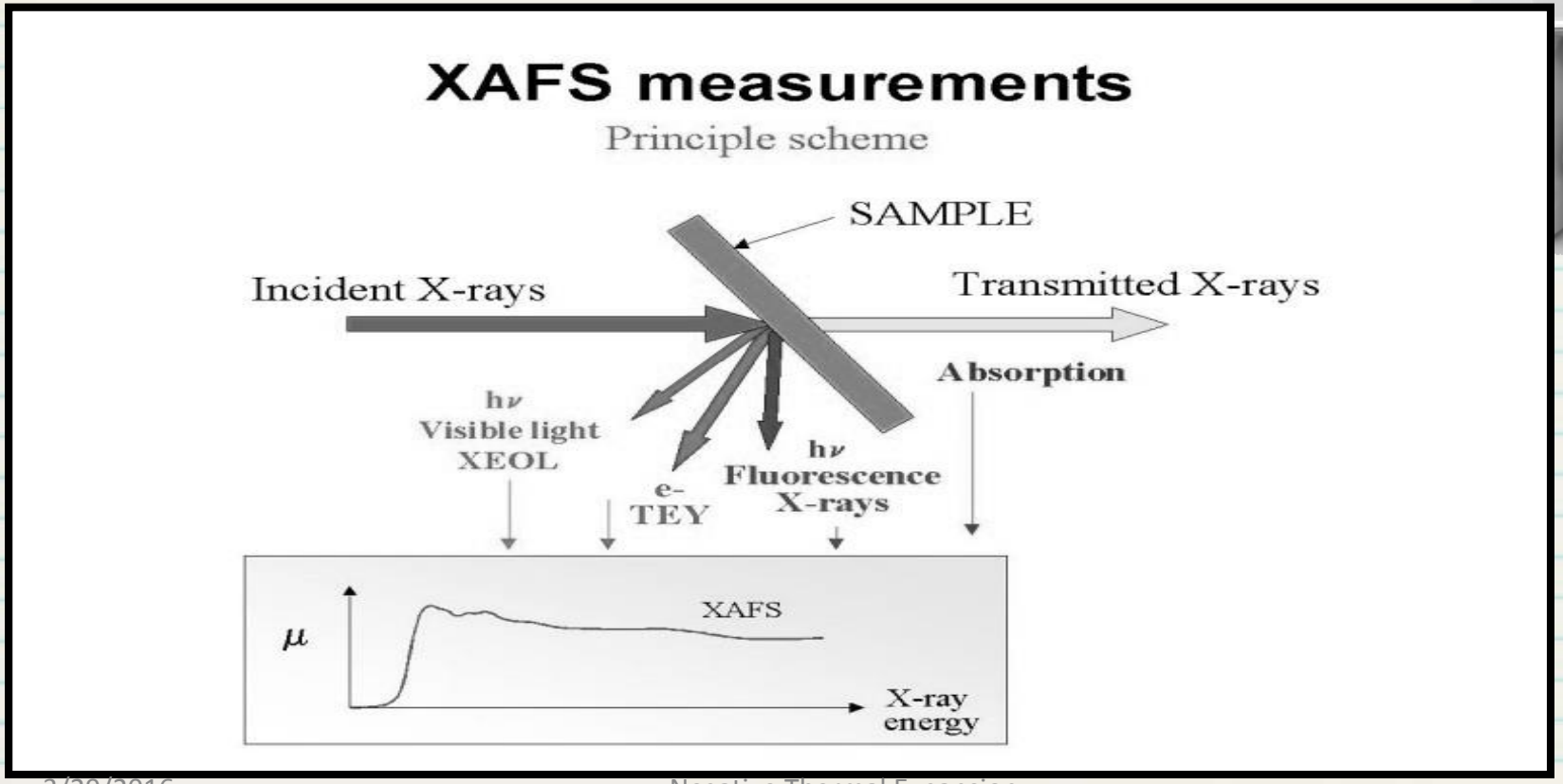


Short-range order

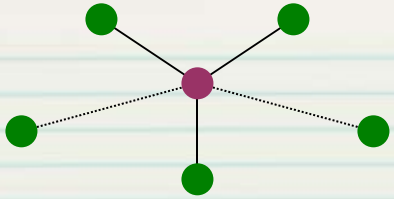
- **EXAFS :**

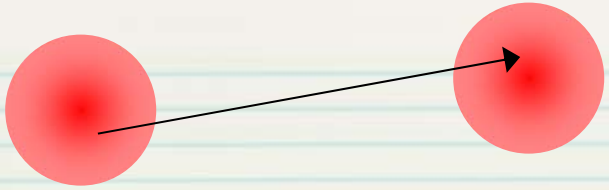
(Extended X-ray Absorption Fine Structure)

✓ is based on studying the absorption of X-ray photons by the material



EXAFS is …





… a local structural probe

- selectivity of atomic species
- short-range order sensitivity

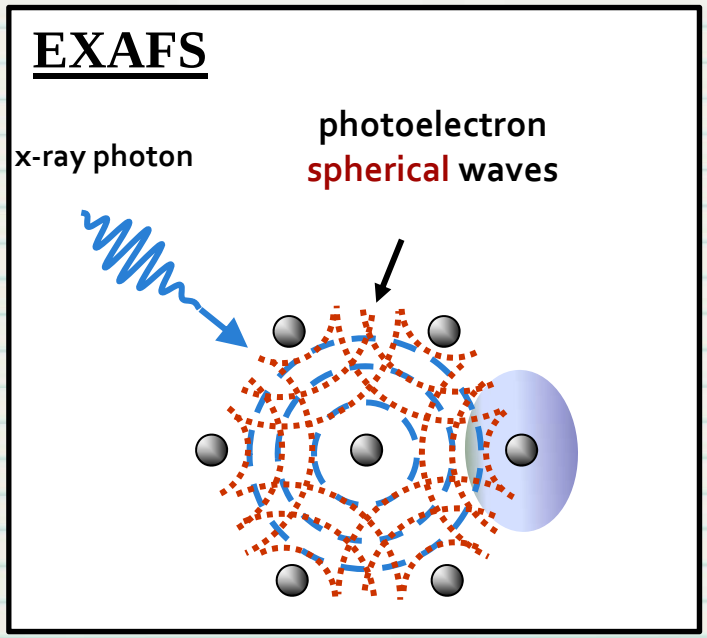
- inter-atomic distances
- coordination numbers

… a local dynamical probe

- sensitivity to correlation
- sensitivity to anharmonicity

- Debye-Waller factors
- local thermal expansion

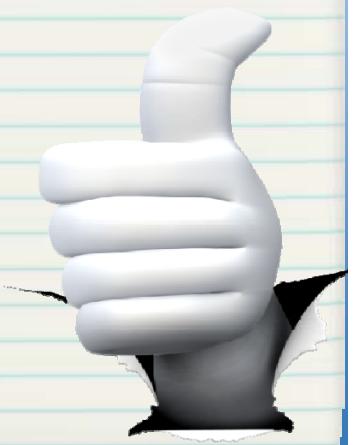
EXAFS peculiarities:



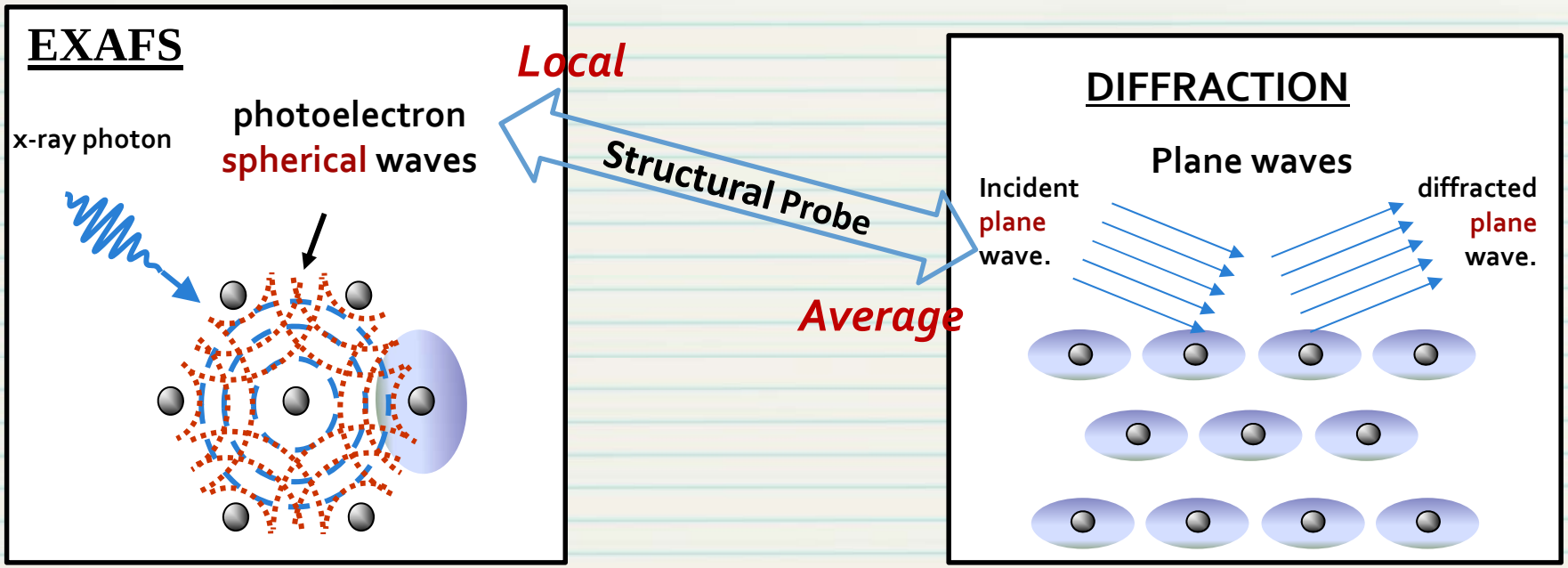
→ atomic selectivity
→ sensitivity only to short-range
⇒gives information on the surroundings of the absorber atom

✓ We can get original information about:

local structural and vibrational dynamics.



EXAFS VS. DIFFRACTION



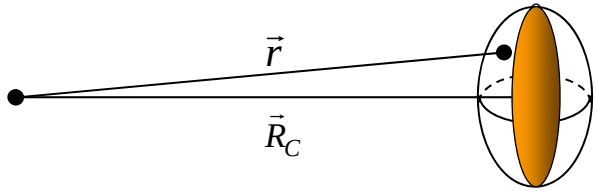
- short-range sensitivity
- inter-atomic distances
- relative displacements

Structural probe

- long-range sensitivity
- atomic positions
- atomic thermal factors

EXAFS Vs. Diffraction: Local Dynamics: Bond distances (I)

EXAFS

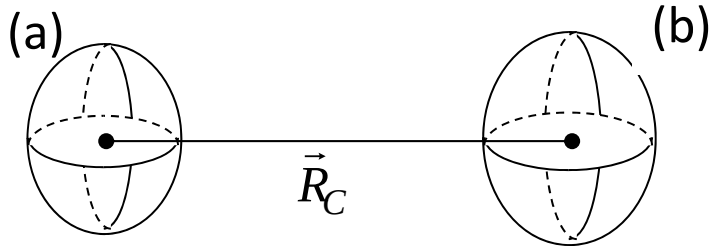


average inter- atomic distance

$$\langle r \rangle = \langle |\vec{r}_2 - \vec{r}_1| \rangle$$

"True" bond expansion

Bragg diffraction



distance between average positions

$$R_C = |\langle \vec{r}_2 \rangle - \langle \vec{r}_1 \rangle|$$

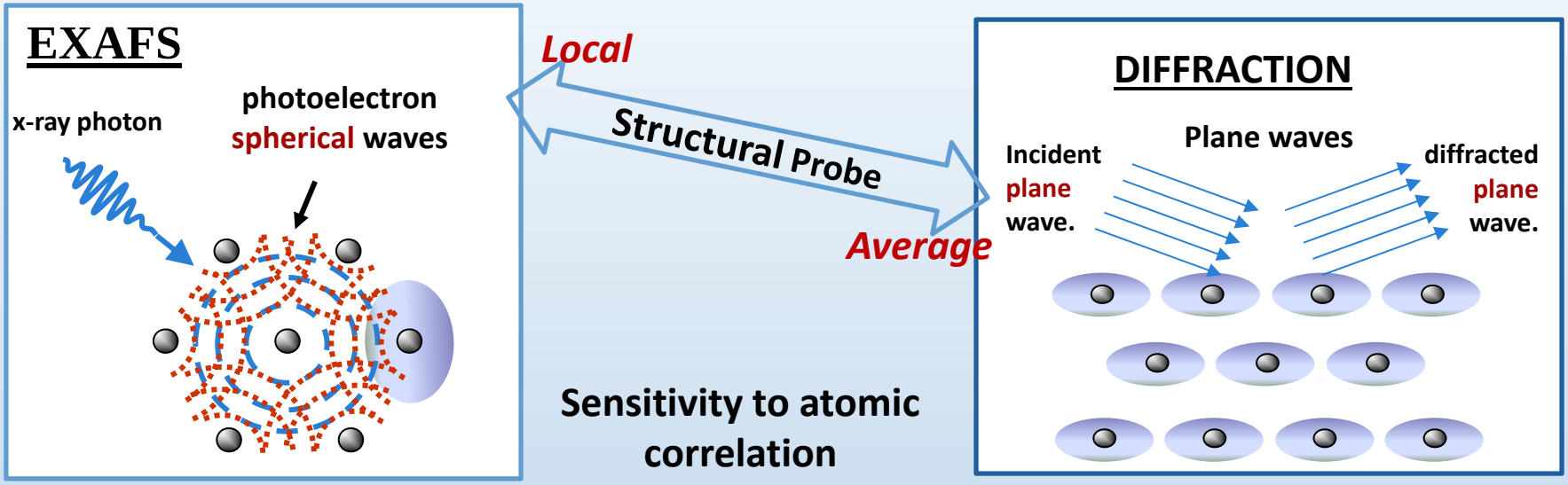
"Apparent" bond expansion

Perpendicular MSRD

$$\langle r \rangle = R_c + \frac{\langle \Delta u_\perp^2 \rangle}{2 R_c}$$

Why EXAFS for studying NTE?

✓ can get original information about **local structural and vibrational dynamics**



→ sensitive to selected bond lengths → **measure the true bond length**

→ parallel relative motion

➢ **Through a comparison with Bragg diffraction:**

➢ **perpendicular relative motion**

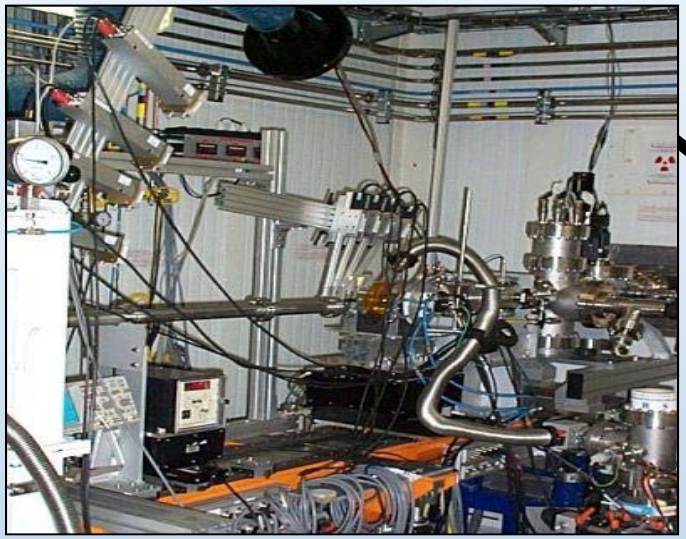
⇒ || and ⊥ correlation → **Anisotropy of relative vibration**

[Tension effect]

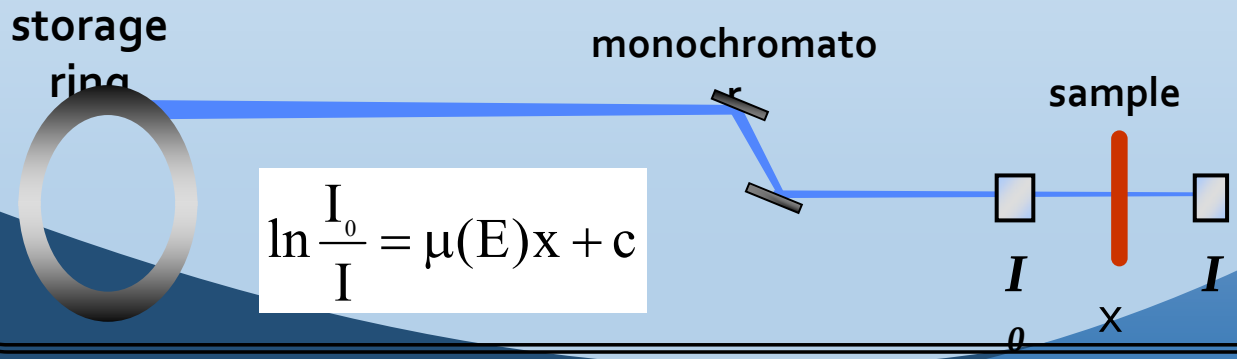
Negative Thermal Expansion Materials

EXAFS Experiment at E.S.R.F

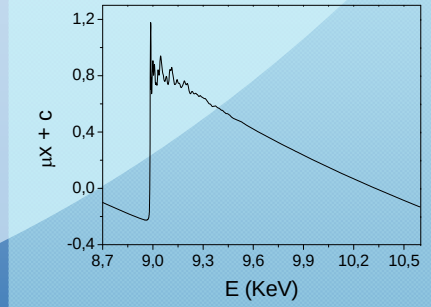
- ✓ X-ray energies for most of XAFS applications are between about 1 to 30 keV.
- ✓ **Transmission mode**



BM29 (ESRF)

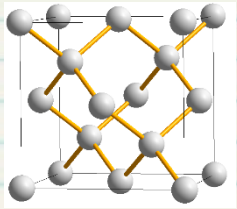


$$\ln\frac{I_0}{I} = \mu(E)x + c$$



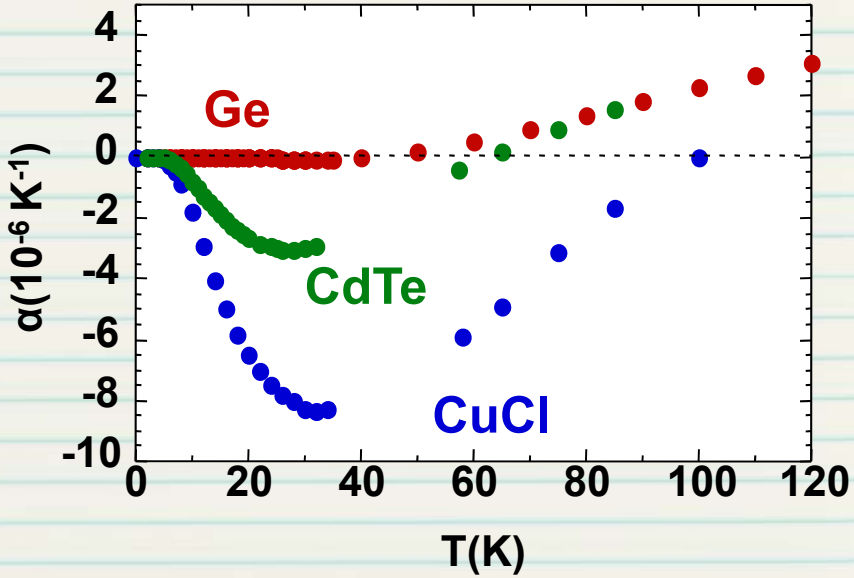
NTE MATERIALS :

- NTE is expected from open structures.
- Non-central or long range forces will hinder the NTE.
- Tetrahedrallly coordinated crystals (N = 4) are the first candidates.

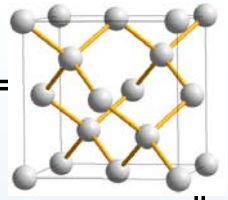


Ge has the diamond structure

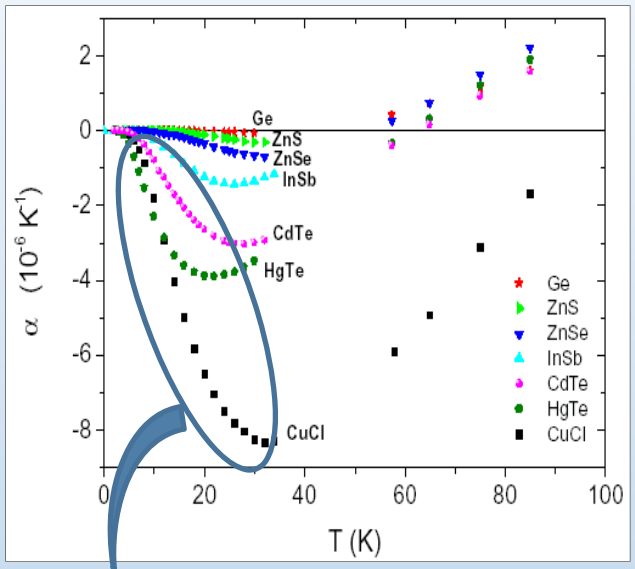
- Diamond structure → no charge separation → strong covalent bonding → ZTE.
- Zinc-blende → the stronger charge separation → the stronger NTE
- Even stronger charge separation → rock-salt structure → no NTE.



NTE in Tetrahedral Semiconductors

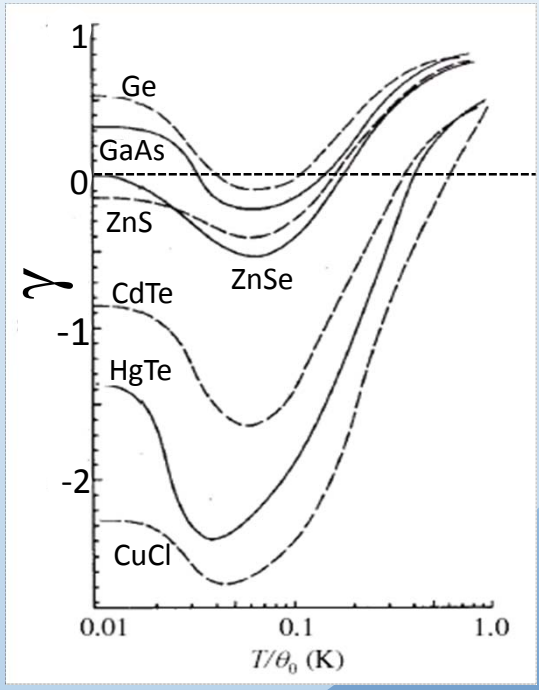


$\beta = 3\alpha$ (cubic symmetry)



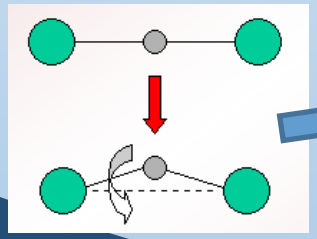
- Zinc-blende → stronger charge separation → the stronger NTE

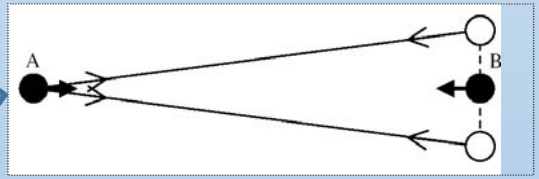
✓Grüneisen function



T. H. K. Barron et al. Adv. Phys. **29**, 609 (1980)

Transverse modes

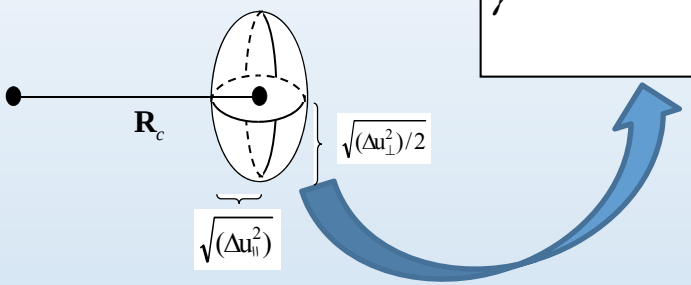


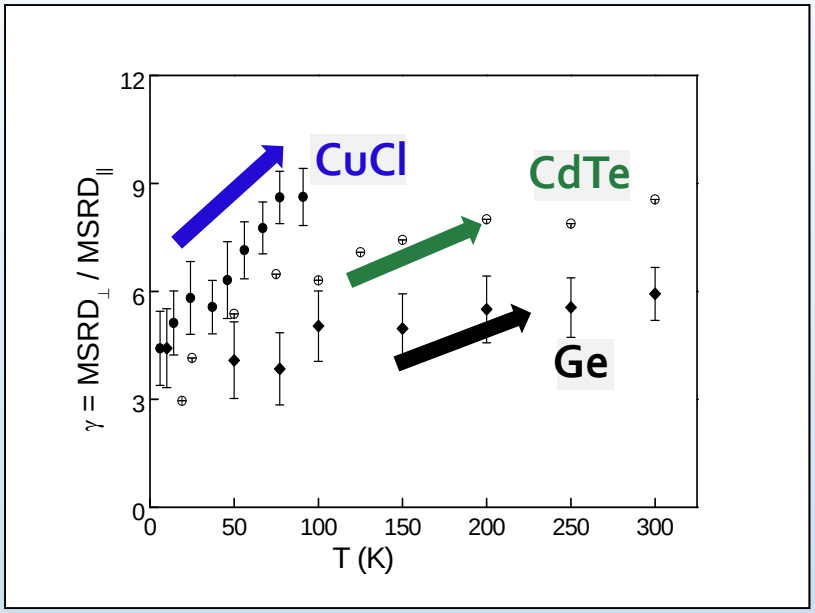


Tension effect → NTE

MSRDs : Anisotropy, γ

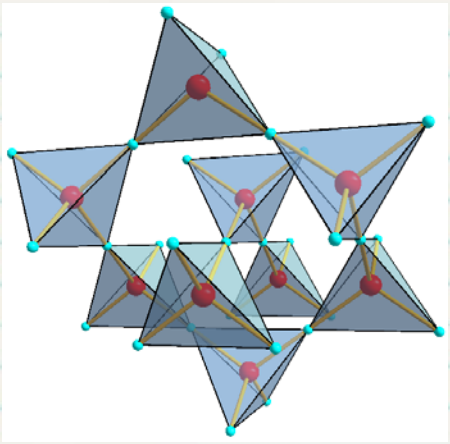
$$\gamma^{MSRD} = \frac{\langle \Delta u_{\perp}^{2} \rangle}{2\langle \Delta u_{\parallel}^{2} \rangle}$$



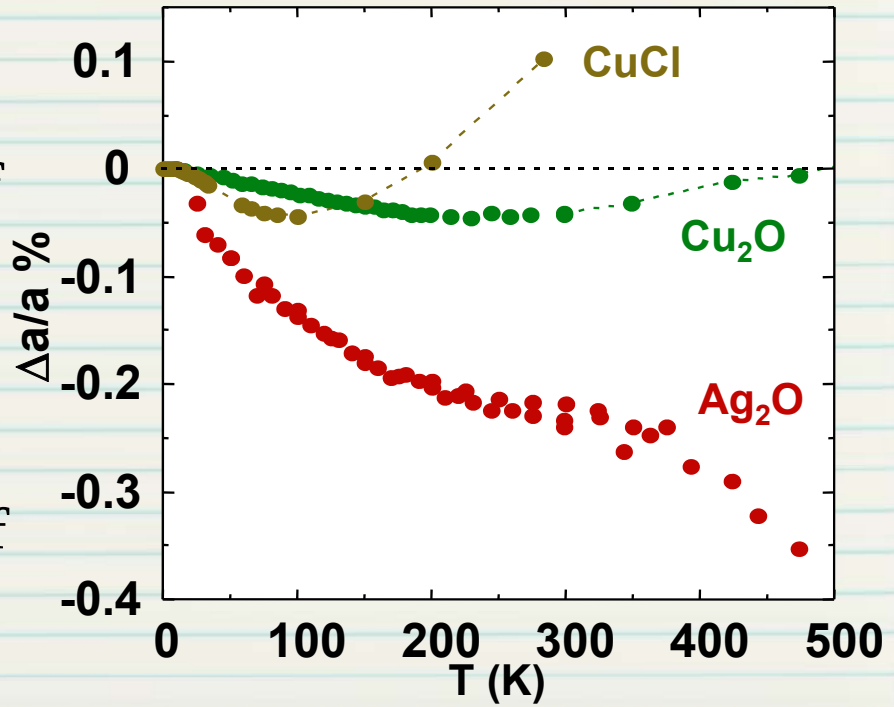


*".. strength of negative expansion is **correlated** to larger ⊥ / || anisotropy .."*

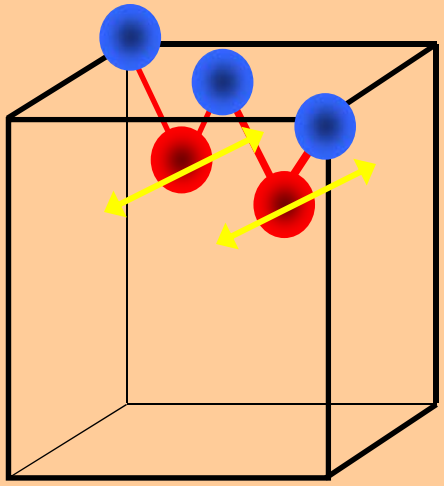
NTE MATERIALS



- In cuprites : M_2O (M = Ag, Cu).
- O → 4M, M → 2O.
- M_4O form 2 inter-penetrating networks.
- Strong MSRD⊥/ MSRD|| anisotropy of M vibrations → NTE for each network.
- The two networks → PTE.
- Deformation of M_4O → inadequacy of the RUM.

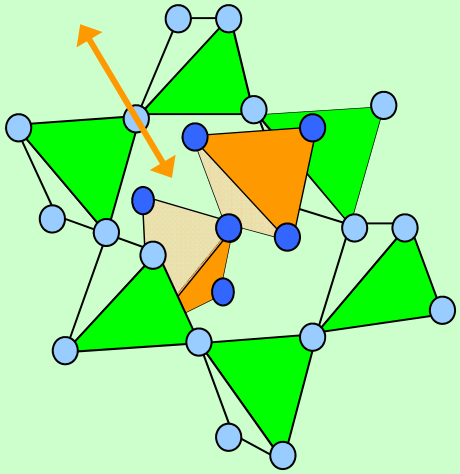


NTE structures studied by EXAFS



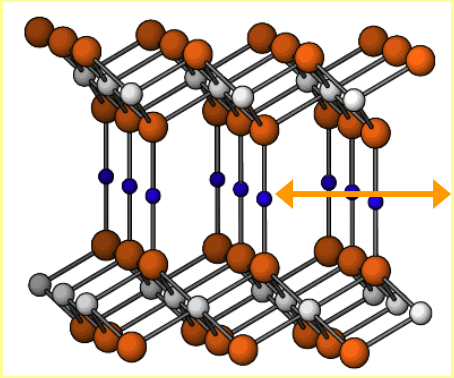
TA acoustic modes
at BZ boundary
with negative
Grueneisen parameters

Zincblende



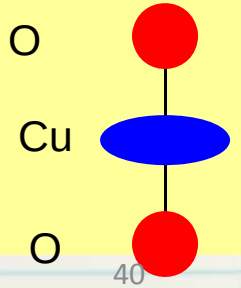
Framerwork structure:
2 networks of
M_4O tetrahedra

Cuprite

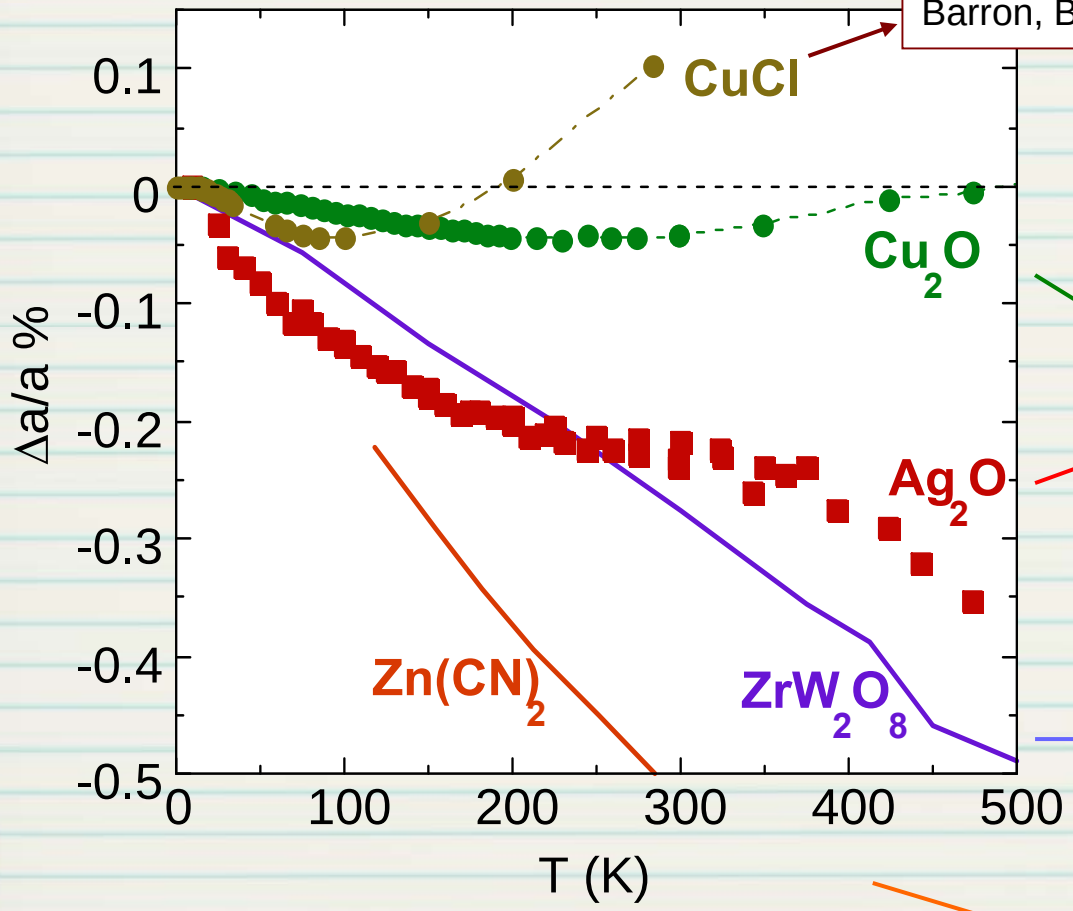


Neutron diffraction:
Cu-O NTE
Anisotropic Cu motion

Delafossite



NTE in framework structures



Barron, Birch, White - J. Phys. C 10, 1617 (1977

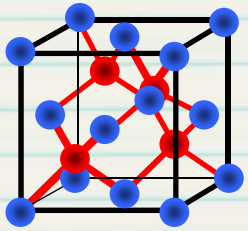
Cuprite structure

Tiano, Dapiaggi, Artioli,
J. Appl. Cryst. 36, 1461 (2003)

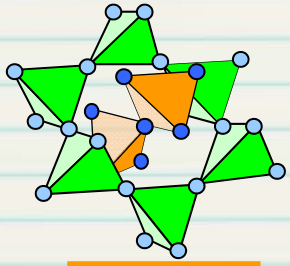
Mary, Evans, Vogt, Sleight
Science, 272 (1996)

Chapman, Chupas, Kepert
J. Am. Chem. Soc. 127, 15630 (2005)

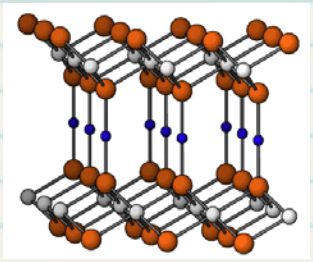
Local dynamical properties of NTE materials



zincblende



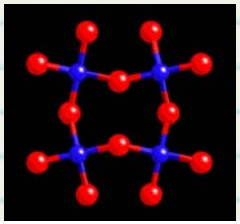
cuprite

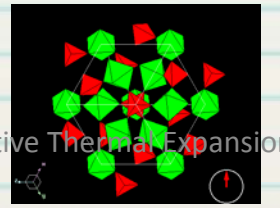


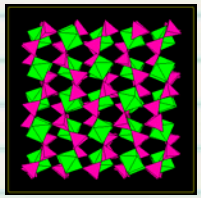
delafossite

	Cu	Ge	CdTe	CuCl	Cu_2O	Ag_2O	$CuLaO_2$	$CuScO_2$	
$k_\perp (eV/Å^2)$	2.72	2.9	0.9	0.3	2.9	0.5	2.5	1.0	Bending
$k_\parallel (eV/Å^2)$	3.2	8.5	3.8	1.4	11.6	5.9	15.5	24.2	Stretching
$\xi = \frac{k_\parallel}{k_\perp}$	1.17	2.9	4.2	5.4	4.0	11.8	6.0	24.2	Anisotropy

NTE strength







شكراً لحسن استماعكم