

Mineral Physics I  
Chapter 3. Lattice vibration  
Section 8. Thermal expansion

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# Atomic potential, harmonicity and anharmonicity

## ∅ Harmonic potential

ü The restoring force is proportional to the deviation from the equilibrium point,  $r_e$

ü The potential shape: parabolic

u Symmetric

## ∅ Interatomic potential

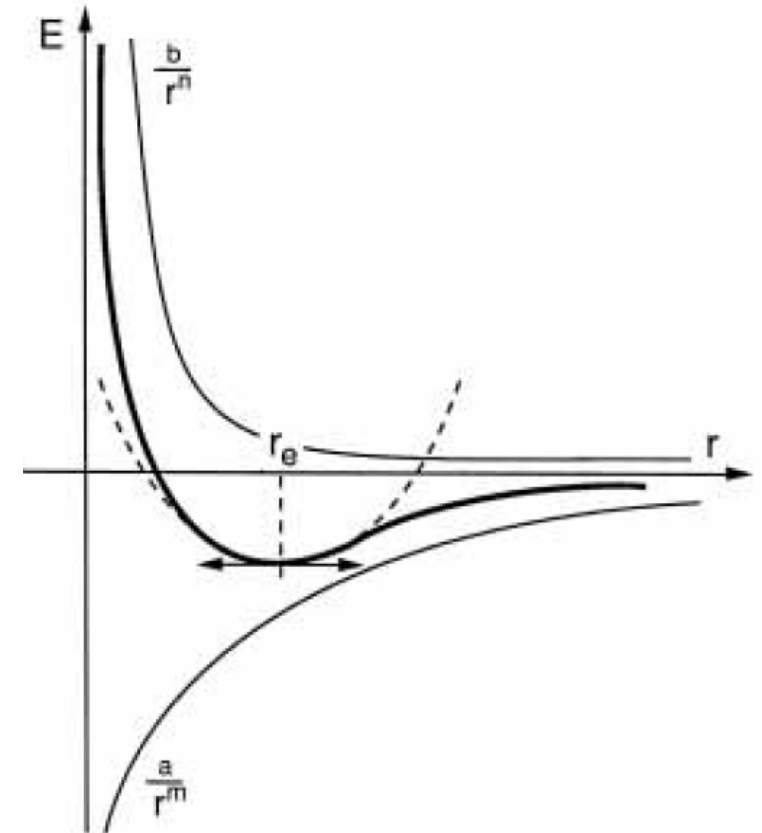
ü Approximately parabolic at small displacements,  $|r - r_e| \cong 0$

ü Asymmetric when at large displacements

o Strong restoring force when  $r - r_e \ll 0$

o Weak restoring force when  $r - r_e \gg 0$

u Anharmonic potential



# Origin of thermal expansion

∅ High temperature  $\rightarrow$  high energy

ü From the equipartition law

$$\epsilon(T) = \frac{1}{2} k_B T$$

ü The atom is “raised up” with respect to the atomic potential

∅ Average atomic position:

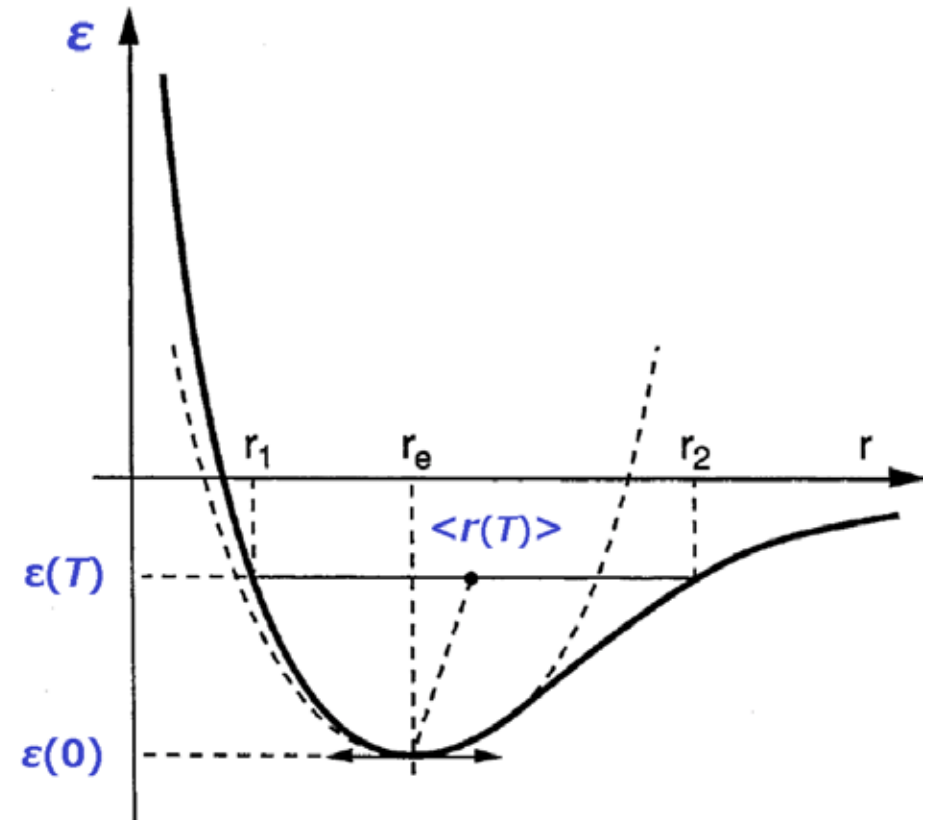
ü  $\langle r \rangle = r_e$

ü if harmonic oscillation

ü  $\langle r \rangle > r_e$

ü if the potential is asymmetric as the right figure

○ Thermal expansion



# Atomic vibration in the anharmonic potential -1

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∅ First consider the harmonic oscillation

ü The potential is

$$| U_2(r) = \frac{1}{2} a_1 (r - r_e)^2 \quad (3.8.1)$$

$$| U_2'(x) = \frac{1}{2} a_1 x^2 \quad x = r - r_e \quad (3.8.1')$$

ü The equation of motion for this atom is

$$| m \frac{d^2x}{dt^2} = F_2 = -\frac{dU_2'(x)}{dx} = -a_1 x \quad m: \text{mass of the atom} \quad (3.8.2)$$

ü The solution is:

$$| x(t) = A \cos(\omega t) \quad \omega = \sqrt{a_1/m} \quad (3.8.3)$$

$$| r(t) = A \cos(\omega t) + r_e \quad (3.8.3')$$



## Atomic vibration in the anharmonic potential -2

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Ø An anharmonic potential to the 5<sup>th</sup>-order term with skipping the 4<sup>th</sup>-term for convenience (the 4<sup>th</sup>-term is symmetric)

$$\ddot{U} U_4(r) = \frac{1}{2} a_1 (r - r_e)^2 + \frac{1}{3} a_2 (r - r_e)^3 + \frac{1}{5} a_4 (r - r_e)^5 \quad (3.8.4)$$

|  $a_2, a_4 < 0$  from the shape of the atomic potential

$$\ddot{U} U_4'(x) = \frac{1}{2} a_1 x^2 + \frac{1}{3} a_2 x^3 + \frac{1}{5} a_4 x^5 \quad (3.8.4')$$

Ø The equation of motion

$$\ddot{U} m \frac{d^2 x}{dt^2} = F_4 = -\frac{dU_4'(x)}{dx} = -a_1 x - a_2 x^2 - a_4 x^4 \quad (3.8.5)$$

$$\ddot{U} \frac{d^2 x}{dt^2} = -\omega^2 x + b_2 x^2 + b_4 x^4 \quad \omega = \sqrt{a_1/m} \quad (3.8.6)$$

$$\text{| } b_2 = -\frac{a_2}{m} > 0 \quad (3.8.7), \quad b_4 = -\frac{a_4}{m} > 0 \quad (3.8.8)$$



## Atomic vibration in the anharmonic potential -3

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∅ We assume much smaller contributions of the higher-order terms

$$\ddot{u} \quad |b_2 x^2|, |b_4 x^4| \ll |\omega^2 x| \quad (3.8.9)$$

∣ “perturbation”

∅ Under the assumption (3.8.9), an approximate solution of (3.8.6) has a formula with a slightly different angular frequency  $\omega'$

$$\ddot{u} \quad x(t) = A \cos(\omega' t) \quad (3.8.10)$$

$$\mid \quad |\omega^2 - \omega'^2| \cong 0 \quad (3.8.11)$$

∅ Eq. (3.8.6)  $\frac{d^2 x}{dt^2} = -\omega^2 x + b_2 x^2 + b_4 x^4$  can be written as

$$\ddot{u} \quad \frac{d^2 x}{dt^2} + \omega'^2 x = -(\omega^2 - \omega'^2)x + b_2 x^2 + b_4 x^4 \quad (3.8.12)$$



## Atomic vibration in the anharmonic potential -4

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Ø By substituting the approximate solution Eq. (3.8.10)  $x(t) = A \cos(\omega't)$  to the right side of Eq. (3.8.12)  $\frac{d^2x}{dt^2} + \omega'^2 x = -(\omega^2 - \omega'^2)x + b_2 x^2 + b_4 x^4$

$$\begin{aligned} \ddot{u} \frac{d^2x}{dt^2} + \omega'^2 x &= -(\omega^2 - \omega'^2)A \cos(\omega't) + b_2 [A \cos(\omega't)]^2 + b_4 [A \cos(\omega't)]^4 \\ &= -(\omega^2 - \omega'^2)A \cos(\omega't) + \frac{b_2 A^2 + b_4 A^4}{2} \cos(2\omega't) + \frac{b_2 A^2}{2} \\ &\quad + \frac{b_4 A^4}{8} \cos(4\omega't) + \frac{3}{8} b_4 A^4 \end{aligned} \quad (3.8.13)$$



## Atomic vibration in the anharmonic potential -5

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Ø From the form of (3.8.13), the solution of (3.8.12)  $\frac{d^2x}{dt^2} + \omega'^2 x = -(\omega^2 - \omega'^2)x + b_2 x^2 + b_4 x^4$  has the form of

$$\ddot{x}(t) = C_1 \cos(\omega' t) + C_2 \cos(2\omega' t) + C_4 \cos(4\omega' t) + C_0 \quad (3.8.14)$$

Ø This solution should satisfy Eq. (3.8.13)

Ø The left side of (3.8.12)  $\frac{d^2x}{dt^2} + \omega'^2 x$  by substituting (3.8.14):

$$\begin{aligned} \frac{d^2x}{dt^2} + \omega'^2 x &= \left[ -\omega'^2 C_1 \cos(\omega' t) - 4\omega'^2 C_2 \cos(2\omega' t) - 16\omega'^2 C_4 \cos(4\omega' t) \right] + \\ &\left[ \omega'^2 C_1 \cos(\omega' t) + \omega'^2 C_2 \cos(2\omega' t) + \omega'^2 C_4 \cos(4\omega' t) + \omega'^2 C_0 \right] \\ &= (-\omega'^2 + \omega'^2) \cdot C_1 \cos(\omega' t) - 3\omega'^2 C_2 \cos(2\omega' t) - 15\omega'^2 C_4 \cos(4\omega' t) + \omega'^2 C_0 \\ &= 0 \cdot C_1 \cos(\omega' t) - 3\omega'^2 C_2 \cos(2\omega' t) - 15\omega'^2 C_4 \cos(4\omega' t) + \omega'^2 C_0 \quad (3.8.15) \end{aligned}$$





## Atomic vibration in the anharmonic potential -6

ü By comparing each term of (3.8.13)  $-(\omega^2 - \omega'^2)A \cos(\omega't) + \frac{b_2A^2 + b_4A^4}{2} \cos(2\omega't) + \frac{b_4A^4}{8} \cos(4\omega't) + \frac{b_2A^2}{2} + \frac{3}{8}b_4A^4$  and  $0 \cdot C_1 \cos(\omega't) - 3\omega'^2 C_2 \cos(2\omega't) - 15\omega'^2 C_4 \cos(4\omega't) + \omega'^2 C_0$  (3.8.15),

$$\text{ü } \cos(\omega't): 0 \cdot C_1 = -(\omega^2 - \omega'^2)A \Rightarrow \text{Let it } C_1 = A \quad (3.8.16)$$

$$| \omega^2 - \omega'^2 | \cong 0$$

$$\text{ü } \cos(2\omega't): -3\omega'^2 C_2 = \frac{b_2A^2 + b_4A^4}{2} \Rightarrow C_2 = -\frac{b_2A^2 + b_4A^4}{6\omega'^2} \quad (3.8.17)$$

$$\text{ü } \cos(4\omega't): -15\omega'^2 C_4 = \frac{b_4A^4}{8} \Rightarrow C_4 = -\frac{b_4A^4}{120\omega'^2} \quad (3.8.18)$$

$$\text{ü } \omega'^2 C_0 = \frac{b_2A^2}{2} + \frac{3}{8}b_4A^4 \Rightarrow C_0 = \frac{4b_2A^2 + 3b_4A^4}{8\omega'^2} \quad (3.8.19)$$

∅ The final solution is:

$$\text{ü } x(t) = A \cos(\omega't) - \frac{b_2A^2 + b_4A^4}{6\omega'^2} \cos(2\omega't) - \frac{b_4A^4}{120\omega'^2} \cos(4\omega't) + \frac{4b_2A^2 + 3b_4A^4}{8\omega'^2} \quad (3.8.20)$$



## Thermal expansivity from the anharmonic potential

Ø From (3.8.23)  $x(t) = A \cos(\omega' t) - \frac{b_2 A^2 + b_4 A^4}{6\omega'^2} \cos(2\omega' t) - \frac{b_4 A^4}{120\omega'^2} \cos(4\omega' t) + \frac{4b_2 A^2 + 3b_4 A^4}{8\omega'^2}$

, the average position is

$$\ddot{u} \langle x \rangle = \frac{4b_2 A^2 + 3b_4 A^4}{8\omega'^2}, \quad \langle r \rangle = \frac{4b_2 A^2 + 3b_4 A^4}{8\omega'^2} + r_e \quad (3.8.21)$$

Ø The energy of the oscillator:  $\varepsilon = \frac{1}{2} a_1 A^2$

Ø From the equipartition law (3.3.4) and (3.3.5):  $\varepsilon = \frac{1}{2} k_B T$  (3.8.22)

Ø Eq. (3.8.21) is expressed using the temperature  $T$ :

$$\ddot{u} \langle r \rangle = \frac{4b_2 \left(\frac{a_1}{k_B}\right) T + 3b_4 \left(\frac{a_1}{k_B}\right)^2 T^2}{8\omega'^2} + r_e$$

Ø The linear thermal expansivity:

$$\ddot{u} \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \cong \frac{3}{l_0} \left(\frac{\partial l}{\partial T}\right)_p \propto \frac{3}{r_e} \left(\frac{\partial \langle r \rangle}{\partial T}\right)_p = \frac{3}{4r_e \omega'^2} \left\{ 2b_2 \left(\frac{a_1}{k_B}\right) + 3b_4 \left(\frac{a_1}{k_B}\right)^2 T \right\} \quad (3.8.23)$$



## Physical meaning of the solution

Ø Eq. (3.8.22):

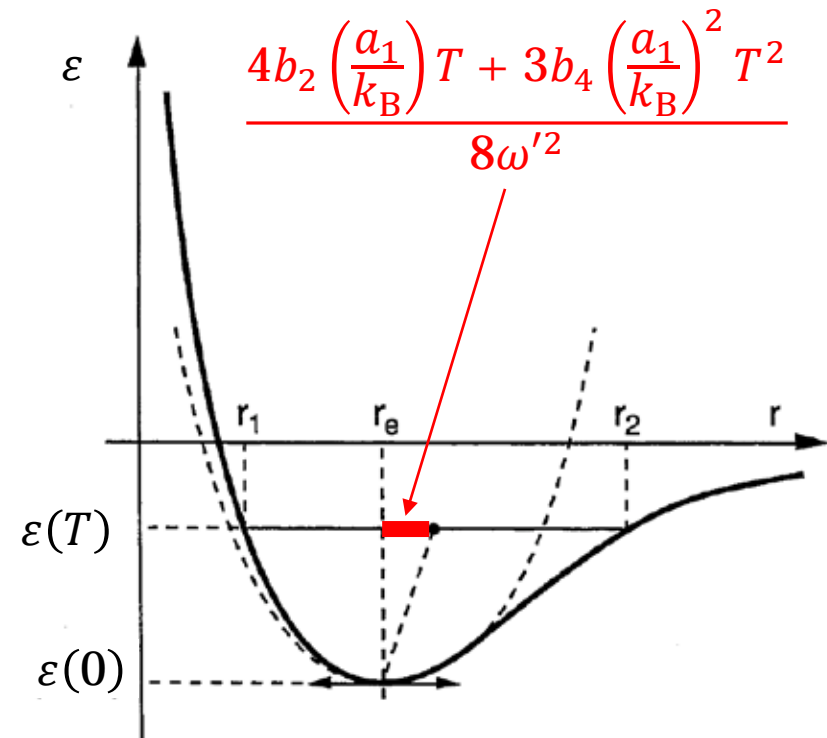
$$\ddot{U} \langle r \rangle = \frac{4b_2 \left(\frac{a_1}{k_B}\right) T + 3b_4 \left(\frac{a_1}{k_B}\right)^2 T^2}{8\omega'^2} + r_e$$

- The average atomic distance increases with increasing temperature

Ø EQ. (3.8.23):

$$\ddot{U} \alpha = \frac{3}{4r_e \omega'^2} \left\{ 2b_2 \left(\frac{a_1}{k_B}\right) + 3b_4 \left(\frac{a_1}{k_B}\right)^2 T \right\}$$

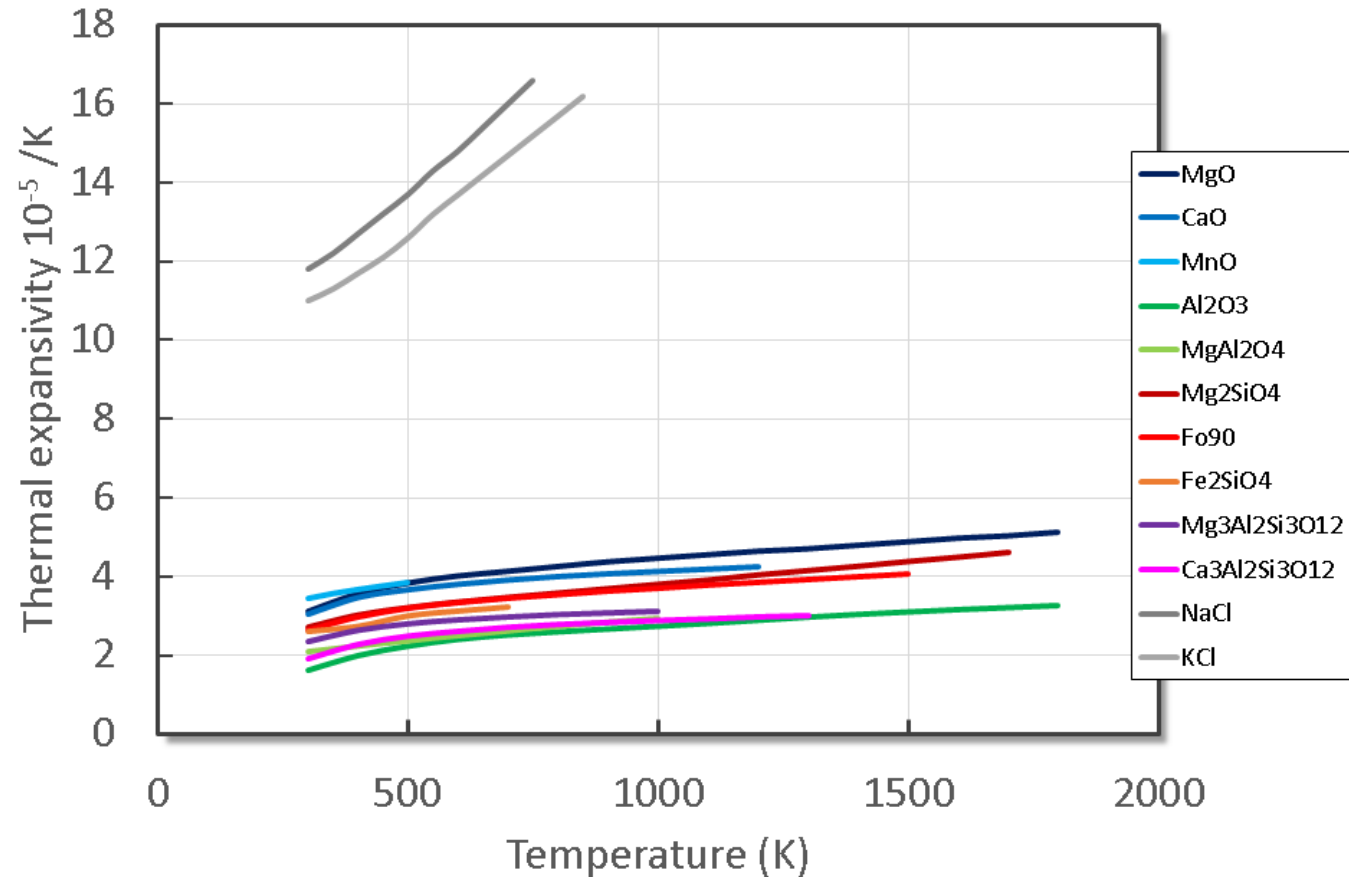
- Thermal expansivity increases with increasing temperature
- Although experimental results indicate that the  $\alpha$  goes to zero with decreasing  $T$  to zero, the solution (3.8.23) does not.





# Thermal expansivity of halides

Halides: much higher  $\alpha$   
Thermal expansion seems controlled by the anions ( $O^{2-}$  and  $Cl^-$ ) rather than cations ( $Si^{4+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ )

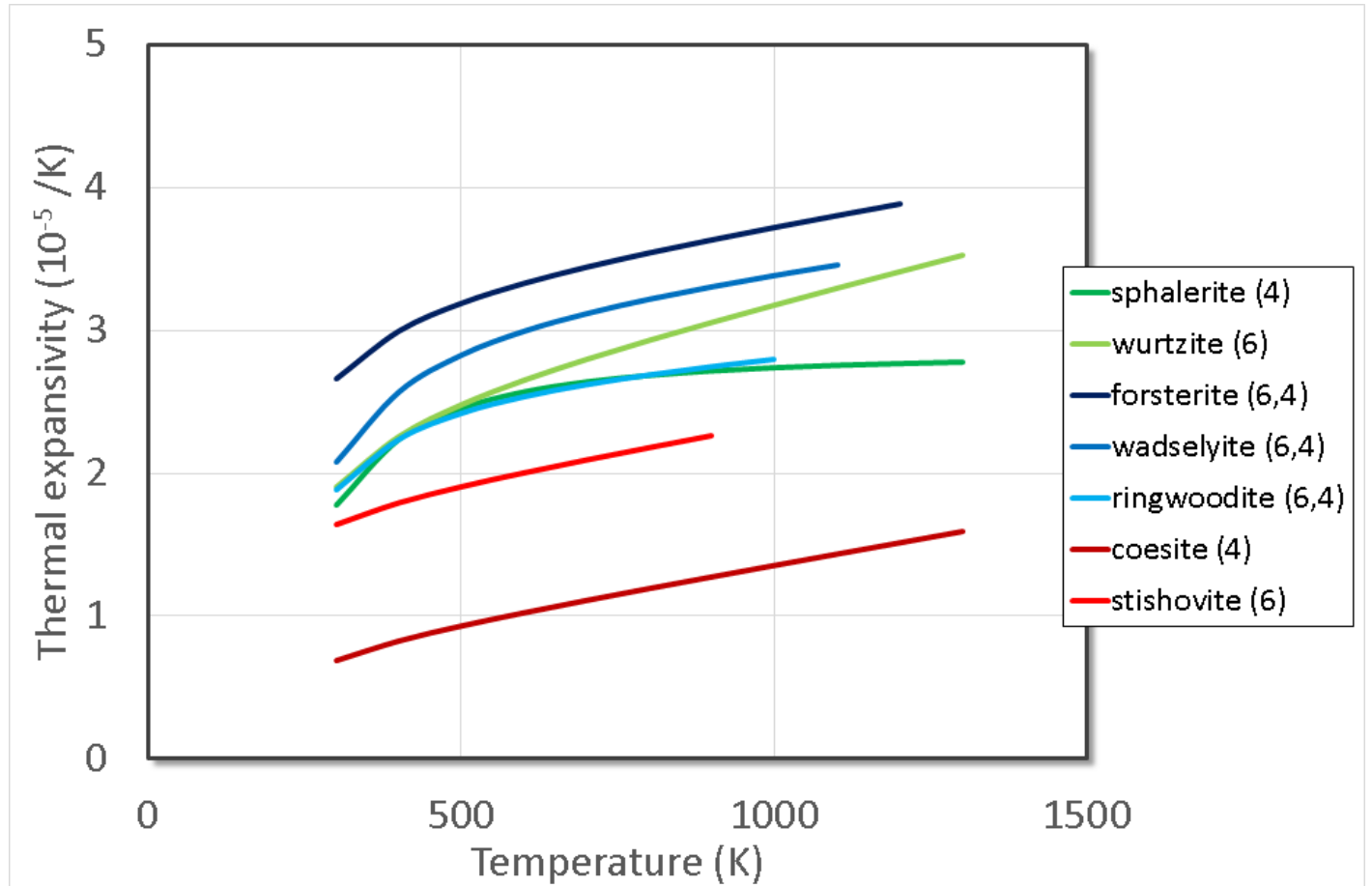


## Thermal expansivity change with phase transition

Forsterite → wadsleyite, ringwoodite in  $\text{Mg}_2\text{SiO}_4$ : decrease

Sphalerite to wurzite in ZnO: increase

Coesite → stishovite in  $\text{SiO}_2$ : increase



## Thermal expansivity change with phase transition

Ø Forsterite à wadsleyite, ringwoodite

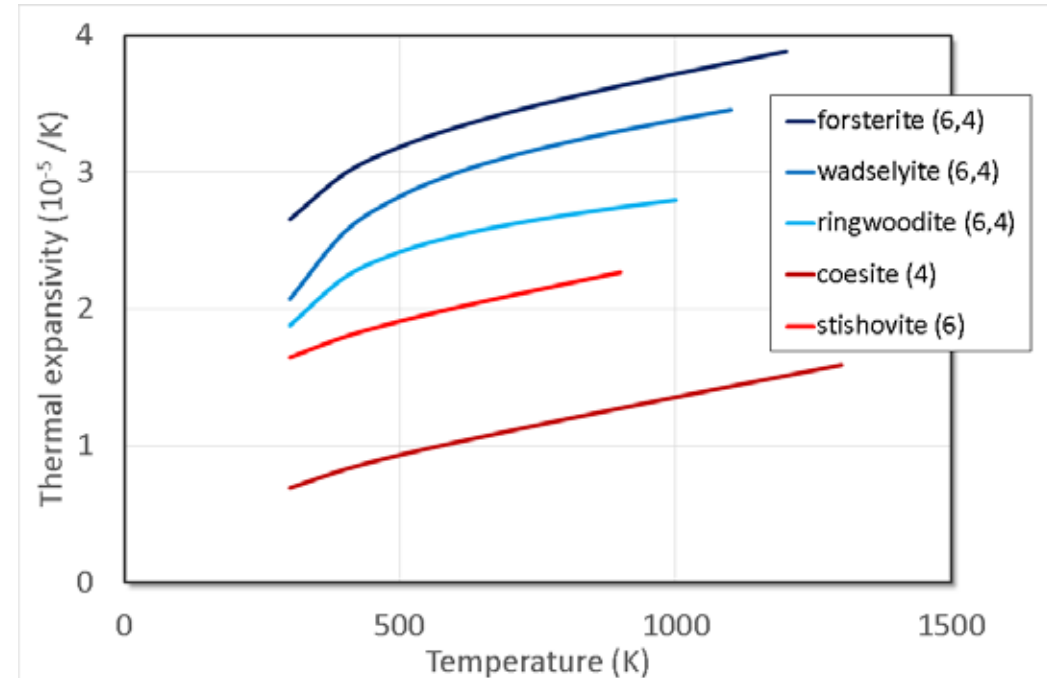
in  $\text{Mg}_2\text{SiO}_4$ : decrease

ü No coordination change

Ø Coesite à stishovite in  $\text{SiO}_2$ : increase

ü 4 coordinate à 6 coordinate

ü Si-O distance: 160~161 pm à 161 pm



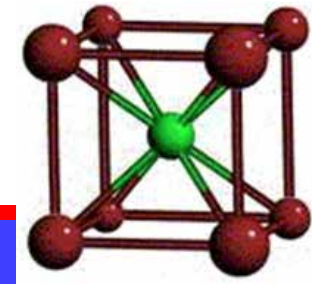
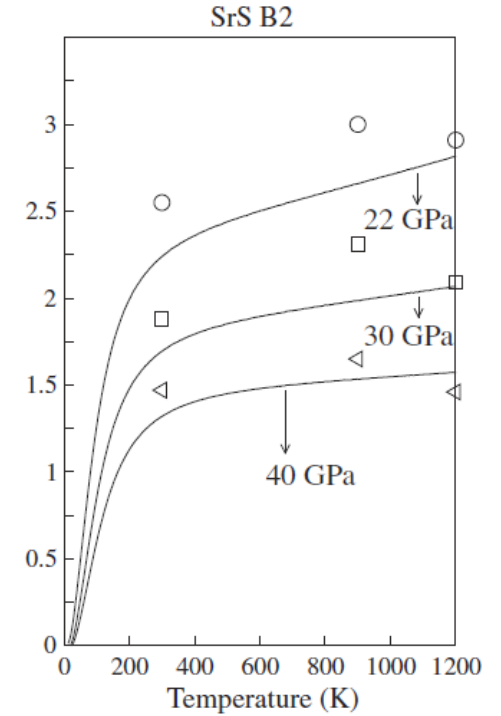
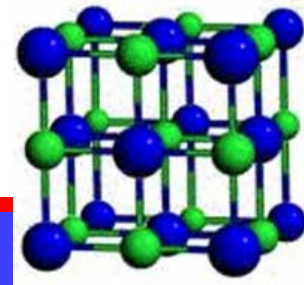
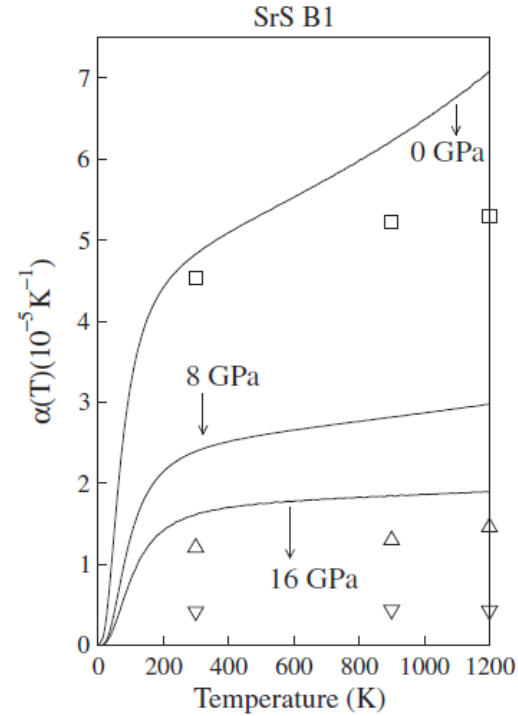
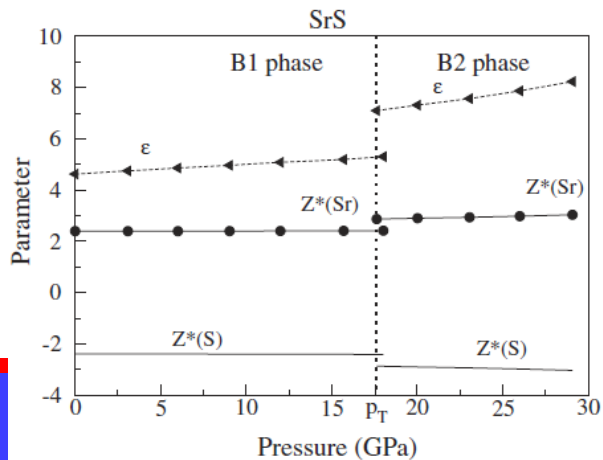
# Thermal expansion change with B1-B2 transition

Ø SrS by ab initio calculation (Souadkia et al., *Comp. Mater. Sci.* 50, 1701-1710)

ü B1:  $a = 605 \text{ pm}$  à Sr-S:  $303 \text{ pm}$

ü B2:  $a = 365 \text{ pm}$  à Sr-S:  $315 \text{ pm}$

ü B1 à B2:  $\alpha \uparrow \Leftrightarrow \text{Sr-S} \uparrow$





## Typical values of thermal expansion coefficient

| Mineral   | $P$ (GPa) | $T$ (K)  | $\alpha$ ( $10^{-5}/\text{K}$ ) | Reference                          |
|---|-----------|----------|---------------------------------|------------------------------------|
| MgO   | 0         | 298      | 3.1                             | (Suzuki, 1975)                     |
| $\alpha$ -Mg <sub>2</sub> SiO <sub>4</sub> (forsterite) | 0         | 1700     | 2.5                             | (Isaak <i>et al.</i> , 1989)       |
| $\gamma$ -Mg <sub>2</sub> SiO <sub>4</sub>              | 0         | 23       | 2.7                             | (Suzuki <i>et al.</i> , 1979)      |
| MgSiO <sub>3</sub> (perovskite)                         | 0         | 298–381  | 2.2                             | (Ross & Hazen, 1989)               |
| MgSiO <sub>3</sub> (perovskite)                         | 10.7      | 677–1024 | 1.9                             | (Wang <i>et al.</i> , 1994)        |
| MgSiO <sub>3</sub> (perovskite)                         | 0–20      | 298–773  | 1.8–2.5                         | (Utsumi <i>et al.</i> , 1995)      |
| MgSiO <sub>3</sub> (perovskite)                         | 25        | 298–1473 | 2.0                             | (Kato <i>et al.</i> , 1995)        |
| MgSiO <sub>3</sub> (perovskite)                         | 30        | 2000     | 2.1                             | (Funamori <i>et al.</i> ,<br>1996) |
| MgSiO <sub>3</sub> (perovskite)                         | 0         | 300–1600 | 2.6                             | (Jackson & Rigden,<br>1996)        |
| Fe  | 243       | 4500     | 1.3                             | (Stacey, 1993)                     |



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End

