Mineral Physics I
Chapter 1. Thermodynamic properties
Section 3. Bulk modulus

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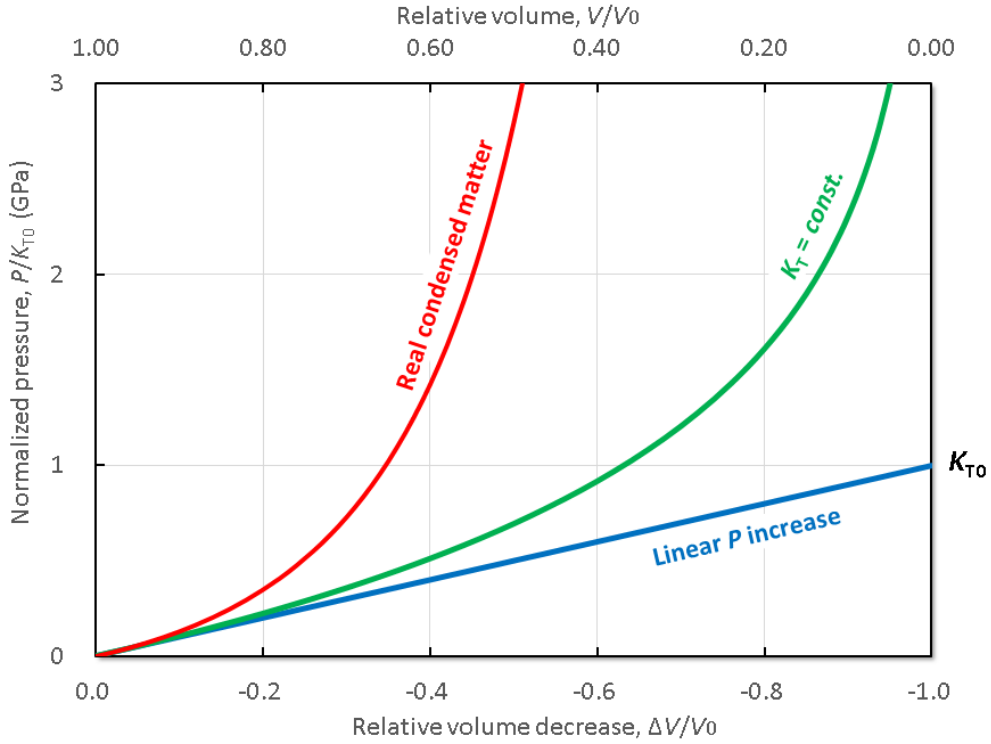
Bulk modulus

- P in a body increases by compression
  - ✓ The P increase, δP: proportional to the relative V decrease, $-\delta V/V$, in cases of infinite compression
  - ✓ $\delta P \propto -\delta V/V$
- Bulk modulus, K
  - ✓ $K \equiv -\frac{\mathrm{d}P}{\mathrm{d}V/V} = -\frac{\mathrm{d}P}{\mathrm{d}\ln V}$ (1.3.1)
    - ◆ The rate of P increase to the relative V decrease
    - ◆ Index of how difficult the matter is to compress by P
    - ◆ P necessary to make V zero if linear



Two kinds of bulk moduli
Isothermal bulk modulus, K_T

- Compression: V decrease by $P \Rightarrow W$ to the matter
  - ✓ E of the matter primarily increases by W
- In the case that the increase in E is released from the matter by thermal conduction to keep T constant
  - ✓ Isothermal bulk modulus, $K_T = -\left(\frac{\partial P}{\partial \ln V}\right)_T = -V\left(\frac{\partial P}{\partial V}\right)_T$ (1.3.2)
    - Slow process
    - Static compression

Two kinds of bulk moduli
Adiabatic bulk modulus, K_S

- In the case that the work W is completely stored as H in the matter
  - The process is too fast to release heat by thermal conduction
    - Elastic wave
  - No heat: adiabatic
    - $\mathrm{d}Q = T\mathrm{d}S = 0 \rightarrow \mathrm{d}S = 0$

✓ Adiabatic bulk modulus, $K_S \equiv -\left(\frac{\partial P}{\partial \ln V}\right)_S = -V\left(\frac{\partial P}{\partial V}\right)_S$ (1.3.3)

- T increase by compression and decrease by decompression

- In general, $K_S > K_T$
  - Compression is hampered by thermal expansion due to the T increase by the work W
  - How much are K_T and K_S different?

Relations between K_T and K_S -1

- Relation between K_T and K_S ⇒ Relation between $\left(\frac{\partial P}{\partial V}\right)_T$ and $\left(\frac{\partial P}{\partial V}\right)_S$
- Consider that P is a function of V and S
  - ✓ $\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_S \mathrm{d}V + \left(\frac{\partial P}{\partial S}\right)_V \mathrm{d}S$ (1.3.4)
- The partial derivative of P with respect to V at constatnt T
  - ✓ $\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_S + \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T$ (1.3.5)
- Eq. (1.3.5) is expressed by the two bulk moduli.
  - ✓ $-V\left(\frac{\partial P}{\partial V}\right)_T = -V\left(\frac{\partial P}{\partial V}\right)_S - V\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T$
  - ✓ $K_T = K_S - V\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T$ (1.3.6)

Relations between K_T and K_S -2

- By substituting one of the Maxwell's relations (1.1.24) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ into (1.3.6) $K_T = K_S - V\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T$, we have
  - $K_T = K_S - V\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial P}{\partial T}\right)_V$ (1.3.7)

✓ To express $\left(\frac{\partial P}{\partial T}\right)_V$ of Eq. (1.3.7) by well known quantities, the chain rule (1.1.31) $\left(\frac{\partial y}{\partial x}\right)_z = -\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y$ is applied to (1.3.6)

- $\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \left\{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right\}\left[-V\left(\frac{\partial P}{\partial V}\right)_T\right] = \alpha K_T$ (1.3.8)

Relations between K_T and K_S -3

- The factor $\left(\frac{\partial P}{\partial S}\right)_V$ in Eq. (1.3.6) $K_T = K_S - V\left(\frac{\partial P}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_T$ is modified by applying two of the Maxwell's relations (1.1.18) $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$ and (1.1.24) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, and the chain rule (1.1.31) $\left(\frac{\partial y}{\partial x}\right)_z = -\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y$ twice,

✓ $$\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial P}{\partial T}\right)_V$$

$$= \left(\frac{\partial T}{\partial S}\right)_V\left[-\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right] = -\left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \qquad (1.3.9)$$

$$\left(\frac{\partial y}{\partial x}\right)_z = -\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y$$

Relations between K_T and K_S -4

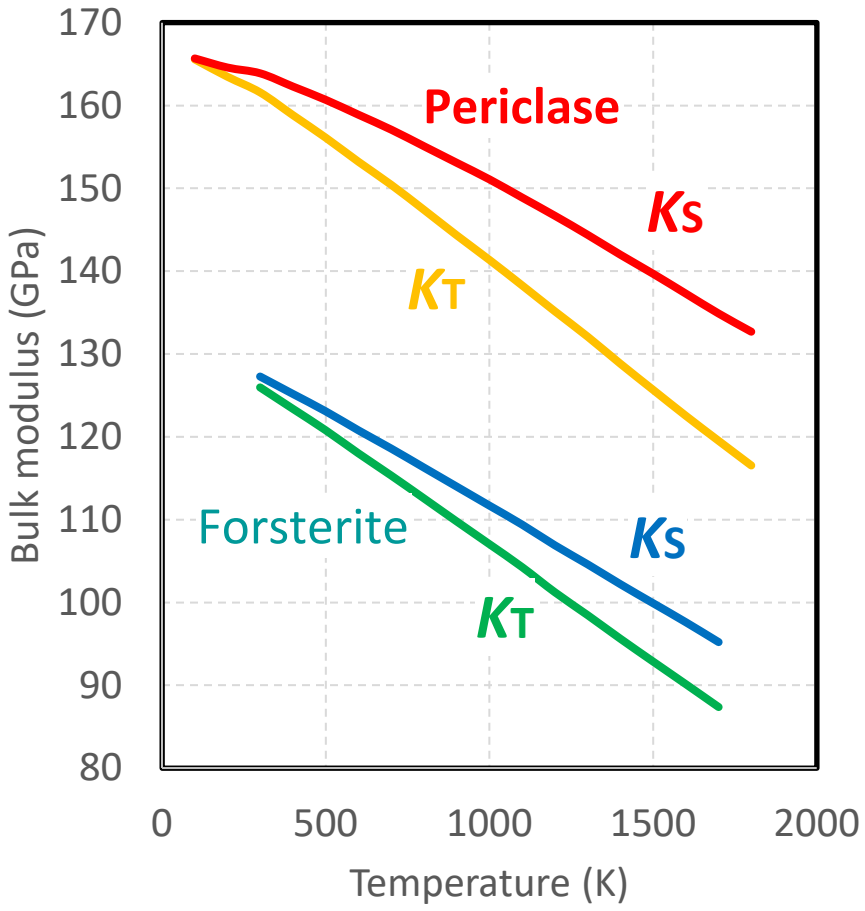
- Each factor of $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$ in (1.3.9) can be expressed using known physical properties
  - ✓ $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T\left(\frac{\partial S}{\partial T}\right)_V}\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]\left\{-V\left(\frac{\partial P}{\partial V}\right)_T\right\}T = \frac{\alpha K_T T}{C_V}$ (1.3.10)
- Eq. (1.3.8) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T$ and (1.3.10) are substituted into Eq. (1.3.6) $K_T = K_S - V\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T$, and we have
  - ✓ $K_T = K_S - V\left\{\frac{\alpha K_T T}{C_V}\right\}[\alpha K_T] = K_S - \alpha\left\{\frac{\alpha K_T T}{C_V}\right\}K_T V$ (1.3.11)

Relations between K_T and K_S -5

- Using the thermodynamic Grüneisen parameter $\gamma_{\mathrm{th}} \equiv \frac{\alpha K_T V}{C_V}$ (1.2.20), Eq. (1.3.11) $K_T = K_S - \alpha \frac{\alpha K_T V}{C_V} T K_T$ becomes
  - ✓ $K_T = K_S - \alpha \gamma_{\mathrm{th}} T K_T$ ➔ $K_S = (1 + \alpha \gamma_{\mathrm{th}} T) K_T$ (1.3.12)
- K_S is larger than K_T because of the pressure by thermal expansion
  - ✓ <u>K_T is a thermodynamically more essential quantity than K_S</u>
- Eq. (1.3.12) is similar to the relation for the heat capacities (1.2.22) $C_P = (1 + \alpha \gamma_{\mathrm{th}} T) C_V$
  - ✓ $\frac{K_S}{K_T} = \frac{C_P}{C_V} = 1 + \alpha \gamma_{\mathrm{th}} T$ (1.3.13)

Examples of bulk moduli

- Periclase and forsterite at elevated T and ambient P_0
  - ✓ Bulk moduli of mantle minerals: several tens to hundreds GPa
  - ✓ Bulk moduli are very different among different matters
  - ✓ Bulk moduli decrease with T
  - ✓ K_S's more slowly decreases with T than K_T's
    - because of the $1 + \alpha\gamma_{th}T$ factor
- K_S can be more precisely measured than K_T thanks to sound velocity measurement, although K_T is thermodynamically more essential.



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