

Mineral Physics I  
Chapter 4. Equation of State  
Section 7. Mie-Grüneisen-Debye equation of state

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# Concept of Mie-Grüneisen-Debye EOS

## □ Mie-Grüneisen-Debye equation of state

➤ The most frequently used thermal equation of state

➤ Along the CH path

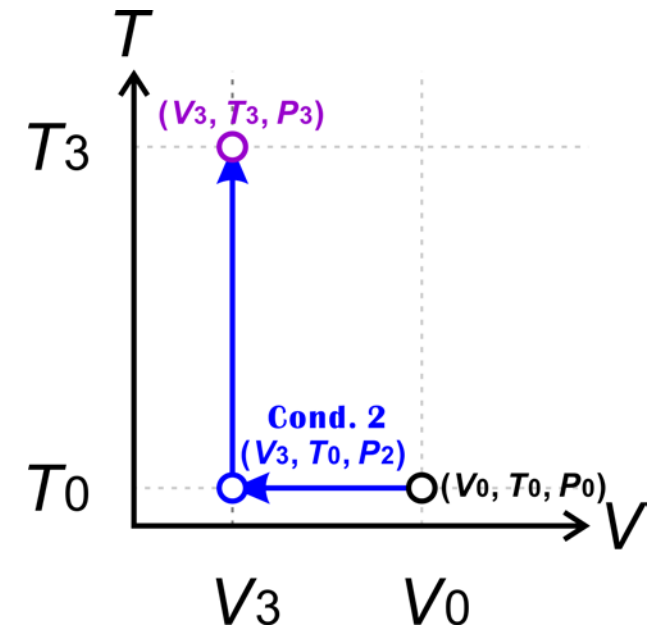
✓ First decreasing  $V$  at a constant  $T$ , then increasing  $T$  at constant  $V$

➤ Mie-Grüneisen EOS

$$\checkmark \Delta P_{\text{th}} = \gamma_{\text{th}}(\Delta E_{\text{th}}/V) \quad (4.6.8)$$

➤ Debye approximation

$$\checkmark C_V = 9Nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx \quad (3.7.18')$$



# Form of Mie-Grüneisen-Debye EOS

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□ Mie-Grüneisen-Debye equation of state

$$\triangleright P = -\frac{dE_0}{dV} + \gamma_D \frac{E_D}{V} \quad (4.7.1)$$

✓  $E_0$ : the internal energy at zero temperature

✓  $E_D$ : the thermal energy at high temperature in the Debye approximation

✓  $\gamma_D$ : the Debye-Grüneisen parameter

$$\blacksquare \gamma_D \equiv -\frac{d \ln \theta_D}{d \ln V} \quad (4.7.2)$$



# Derivation of Mie-Grüneisen-Debye EOS -1

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□  $P$ : defined by  $V$  derivative of the Helmholtz free energy,  $F$ , at constant  $T$ :

$$\triangleright P = - \left( \frac{\partial F}{\partial V} \right)_T \quad (1.1.23), (4.1.1)$$

□ The Helmholtz free energy,  $F$ , is divided into zero-temperature part,  $F_0$ , and the lattice vibration part approximated by the Debye model,  $F_D$ .

$$\triangleright F \cong F_0 + F_D \quad (4.7.3)$$

□ From the definition of the Helmholtz free energy (1.1.10)  $F \equiv E - TS$

$$\triangleright F_0 = E_0 - 0 \cdot S = E_0 \text{ at zero-temperature}$$

$$\triangleright \therefore F = E_0 + F_D \quad (4.7.3')$$



# Derivation of Mie-Grüneisen-Debye EOS -2

□ (4.7.3)  $F = E_0 + F_D$  is substituted into (4.1.1)  $P = -\left(\frac{\partial F}{\partial V}\right)_T$

➤  $\rightarrow P = -\left(\frac{\partial(E_0+F_D)}{\partial V}\right)_T = -\frac{dE_0}{dV} - \left(\frac{\partial F_D}{\partial V}\right)_T$  (4.7.4)

✓  $-\frac{dE_0}{dV}$ : zero-temperature pressure

▪ Can be obtained by isothermal compression at low  $T$

✓  $-\left(\frac{\partial F_D}{\partial V}\right)_T$ : thermal pressure at high  $T$

□ We need to obtain  $-\left(\frac{\partial F_D}{\partial V}\right)_T$ .

➤  $-\left(\frac{\partial F_D}{\partial V}\right)_T = -\frac{dF_D}{d\theta_D} \frac{d\theta_D}{dV} = \frac{dF_D}{d\theta_D} \frac{\theta_D}{V} \left(-\frac{\frac{d\theta_D}{\theta_D}}{\frac{dV}{V}}\right) = \frac{dF_D}{d\theta_D} \frac{\theta_D}{V} \left(-\frac{d \ln \theta_D}{d \ln V}\right) = \frac{\gamma_D \theta_D}{V} \frac{dF_D}{d\theta_D}$  (4.7.5)

➤ We need to obtain  $\frac{dF_D}{d\theta_D}$ ,  $F_D$  should be expressed as a function of  $\theta_D$



# Derivation of Mie-Grüneisen-Debye EOS -3

□ The Helmholtz' free energy by the lattice vibration is divided into the internal energy and entropy parts

$$\text{➤ } F_D = E_D - TS_D = E_D + T \left( \frac{\partial F_D}{\partial T} \right)_V \quad (4.7.6)$$

□ Mathematically

$$\text{➤ } E_D = F_D - T \left( \frac{\partial F_D}{\partial T} \right)_V = \left( \frac{\partial \left( \frac{F_D}{T} \right)}{\partial \left( \frac{1}{T} \right)} \right)_V \quad (4.7.7)$$

$$\begin{aligned} \checkmark \therefore \left( \frac{\partial \left( \frac{F_D}{T} \right)}{\partial \left( \frac{1}{T} \right)} \right)_V &= \left( \frac{\partial \left( \frac{F_D}{T} \right)}{\partial T} \right)_V \left( \frac{\partial T}{\partial \left( \frac{1}{T} \right)} \right)_V = \frac{\left[ \left( \frac{\partial F_D}{\partial T} \right)_V \frac{1}{T} + F_D \left( -\frac{1}{T^2} \right) \right]}{\left( \frac{\partial \left( \frac{1}{T} \right)}{\partial T} \right)_V} = \frac{\left[ \left( \frac{\partial F_D}{\partial T} \right)_V \frac{1}{T} + F_D \left( -\frac{1}{T^2} \right) \right]}{\left( -\frac{1}{T^2} \right)} \\ &= F_D - T \left( \frac{\partial F_D}{\partial T} \right)_V \end{aligned}$$



# Derivation of Mie-Grüneisen-Debye EOS -4

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□ The internal energy of the lattice vibration is approximated by the Debye model (3.7.14)

$$\triangleright E_D = \int_0^T C_V^{\text{Debye}} dT$$

$$\triangleright S_D = \int_0^T \frac{C_V^{\text{Debye}}}{T} dT$$

$$\checkmark C_V^{\text{Debye}} = 9Nk_B \left(\frac{\theta_D}{T}\right)^{-3} \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx \quad (3.7.18')$$

□ The Helmholtz free energy by the lattice vibration is assumed to have a form:

$$\triangleright F_D = E_D - TS_D = T\eta\left(\frac{\theta_D}{T}\right) \quad (4.7.8)$$

$$\checkmark C_V: \text{ a function of } \frac{\theta_D}{T}, f\left(\frac{\theta_D}{T}\right)$$

$$\checkmark \text{Very roughly speaking, } E_D \sim C_V \cdot T \sim Tg\left(\frac{\theta_D}{T}\right), TS \sim T \frac{C_V}{T} \cdot T = Th\left(\frac{\theta_D}{T}\right)$$



# Derivation of Mie-Grüneisen-Debye EOS -5

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□ By substituting (4.7.5)  $F_D = T\eta\left(\frac{\theta_D}{T}\right)$  into (4.7.5)  $E_D = \left(\frac{\partial\left(\frac{F_D}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_V$ ,

$$\triangleright E_D = \left(\frac{\partial\left(\frac{F_D}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_V = \frac{d\left(\frac{T\eta\left(\frac{\theta_D}{T}\right)}{T}\right)}{d\left(\frac{1}{T}\right)} = \theta_D \frac{d\eta\left(\frac{\theta_D}{T}\right)}{d\left(\frac{\theta_D}{T}\right)} \quad (4.7.9)$$

□ The “Debye-temperature derivative” of the Helmholtz’ free energy at constant temperature in the Debye model, with (4.6.19)

$$\triangleright \frac{dF_D}{d\theta_D} = \frac{dF_D}{d\left(\frac{\theta_D}{T}\right)} \frac{d\left(\frac{\theta_D}{T}\right)}{d\theta_D} = \frac{dF_D}{d\left(\frac{\theta_D}{T}\right)} \frac{1}{T} = \frac{d\left(T\eta\left(\frac{\theta_D}{T}\right)\right)}{d\left(\frac{\theta_D}{T}\right)} \frac{1}{T} = \frac{d\eta\left(\frac{\theta_D}{T}\right)}{d\left(\frac{\theta_D}{T}\right)} = \frac{E_D}{\theta_D} \quad (4.7.10)$$





# Derivation of Mie-Grüneisen-Debye EOS -6

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□ Eq. (4.7.5)  $-\left(\frac{\partial F_D}{\partial V}\right)_T = \frac{\gamma_D \theta_D}{V} \frac{dF_D}{d\theta_D}$  and (4.6.10)  $\frac{dF_D}{d\theta_D} = \frac{E_D}{\theta_D}$  are substituted into

$$(4.7.4) \quad P = -\frac{dE_0}{dV} - \left(\frac{\partial F_D}{\partial V}\right)_T$$

$$\triangleright P = -\frac{dE_0}{dV} + \frac{\gamma_D \theta_D}{V} \frac{dF_D}{d\theta_D} = -\frac{dE_0}{dV} + \frac{\gamma_D \theta_D}{V} \frac{E_D}{\theta_D} = -\frac{dE_0}{dV} + \gamma_D \frac{E_D}{V} \quad (4.7.1)$$

✓ Mie-Grüneisen-Debye equation of state

➤ The term  $-\frac{dE_0}{dV}$  is usually expressed using the 3<sup>rd</sup>-order Birch-Murnaghan or Vinet equation of state



# Equivalency of thermodynamic and Debye Grüneisen parameters

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□ The thermal pressure based on the Mie-Grüneisen-Debye equation of state:

$$\blacktriangleright \left(\frac{\partial P}{\partial T}\right)_V \cong \left(\frac{\partial\left(-\frac{dE_0}{dV} + \gamma_D \frac{E_D}{V}\right)}{\partial T}\right)_V \cong \frac{\gamma_D}{V} \left(\frac{\partial E_D}{\partial T}\right)_V = \frac{\gamma_D}{V} C_V \quad (4.7.11)$$

✓ approximation: independence of  $V$  and  $\gamma_D$  from  $T$

□ The thermal pressure was expressed as

$$\blacktriangleright \left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T \quad (1.4.1)$$

□ Combination of (4.7.11) and (1.4.1) leads to (1.1.20)

$$\blacktriangleright \gamma_D = \frac{V}{C_V} \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha V K_T}{C_V} = \gamma_{th} \quad (4.6.12)$$

✓ The Debye Grüneisen parameter is identical to the thermodynamic Grüneisen parameter



# Volume dependence of Grüneisen parameter

□ Thermal pressure  $\Delta P_{\text{th}} = \frac{\gamma}{V} \Delta E_{\text{th}}$

decrease with  $P$

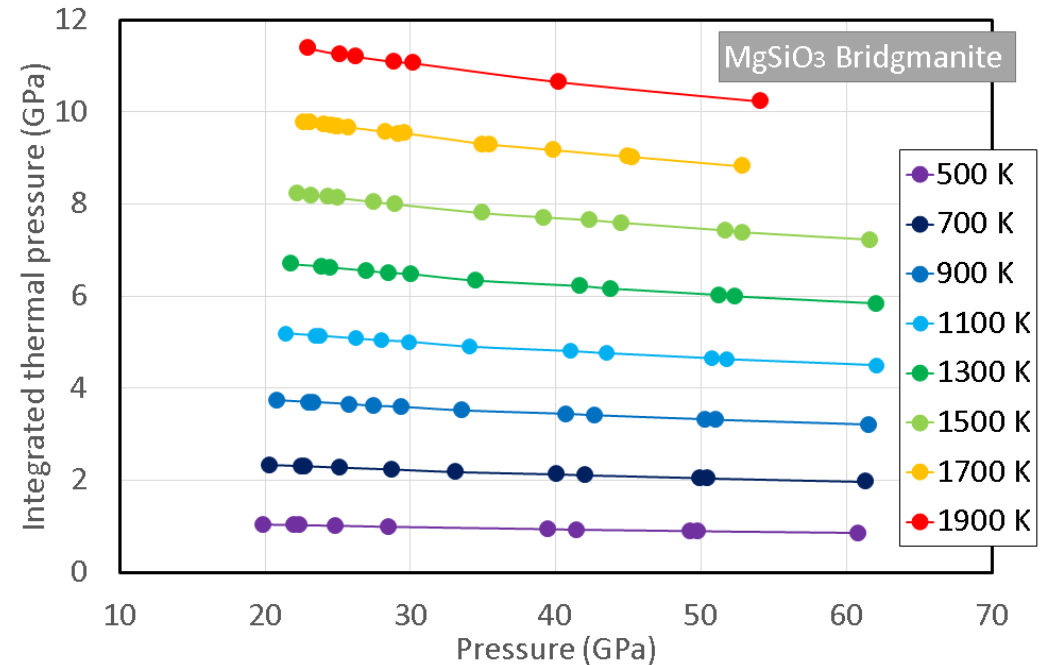
✓ Necessity of HP correction of  $\gamma$

□ The  $P$  dependence of the  $\gamma$ : usually expressed using the  $V$  exponent:

$$\text{➤ } \gamma(V) = \gamma_0 \left( \frac{V}{V_0} \right)^q \quad (4.7.11)$$

▪  $\gamma_0$ : the Grüneisen parameter at zero pressure

✓ Or equivalently,  $q \equiv \frac{d \ln \gamma}{d \ln V}$  (4.7.12)



$\Delta P_{\text{th}}$  of MgSiO<sub>3</sub> bridgmanite from 300 K  
(Katsura et al., 2009; Tange et al., 2012)



## Relation of $\Theta_D$ , $\gamma$ , and $q$

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□ Combining (4.7.2):  $\gamma_D = -\frac{d \ln \Theta_D}{d \ln V}$  and (4.7.12):  $q = \frac{d \ln \gamma}{d \ln V}$

$$\text{➤ } \frac{\gamma}{q} = \frac{-\frac{d \ln \Theta_D}{d \ln V}}{\frac{d \ln \gamma}{d \ln V}} = -\frac{d \ln \Theta_D}{d \ln \gamma} = -\frac{d \ln \Theta_D}{\frac{d\gamma}{\gamma}} = -\gamma \frac{d \ln \Theta_D}{d\gamma}$$

$$\text{➤ } \frac{d \ln \Theta_D}{d\gamma} = -\frac{1}{q} \quad (4.7.13)$$

□ By integrating (4.7.13)

$$\text{➤ } \ln \Theta_D(V) - \ln \Theta_{D0} = -\frac{\gamma(V) - \gamma_0}{q} = \frac{\gamma_0 - \gamma(V)}{q}$$

✓  $\Theta_D(V)$ :  $\Theta_D$  under compression,  $\Theta_{D0}$ :  $\Theta_D$  without compression

✓  $\gamma(V)$ :  $\gamma$  under compression,  $\gamma_0$ :  $\gamma$  without compression

$$\text{➤ } \Theta_D(V) = \Theta_{D0} \exp \left[ \frac{\gamma_0 - \gamma(V)}{q} \right] \quad (4.7.14)$$



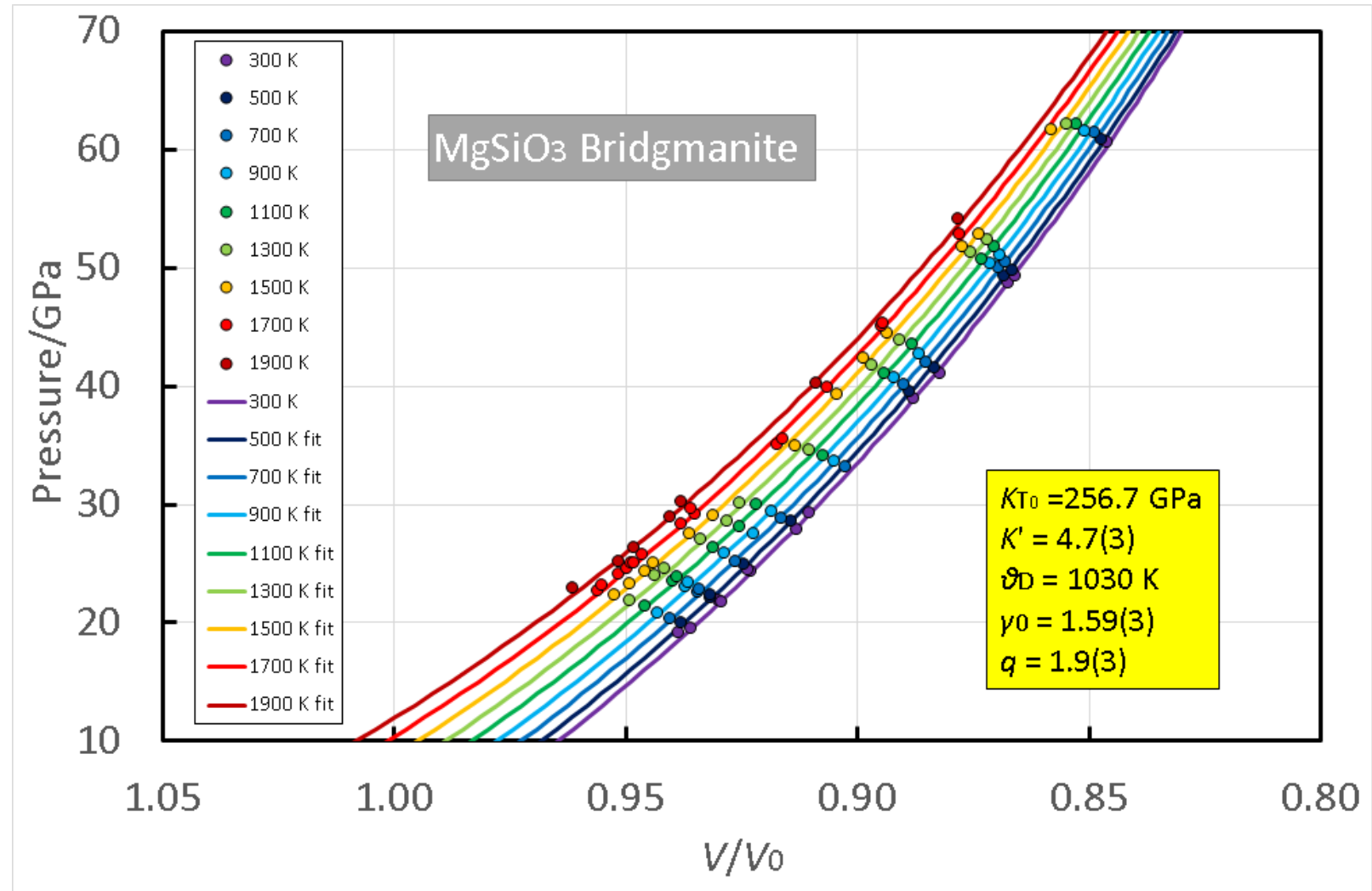
# MGD-EOS Bridgmanite

MgSiO<sub>3</sub> bridgmanite

Katsura et al. (2009)

Tange et al. (2012)

$P$  vs.  $V/V_0$  at various  $T$



# MGD-EOS Bridgmanite

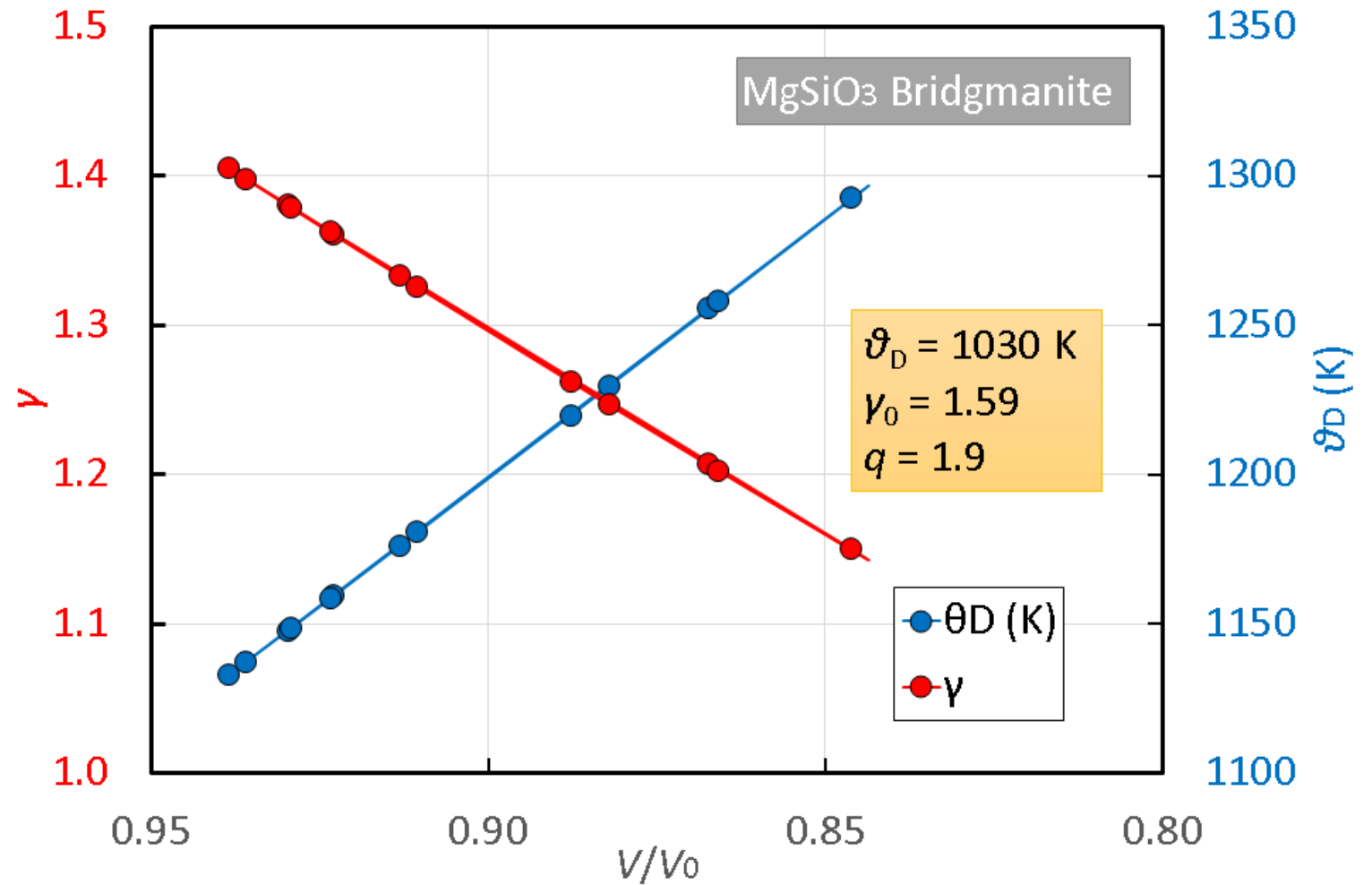
MgSiO<sub>3</sub> bridgmanite

Katsura et al. (2009)

Tange et al. (2012)

$$\gamma(V) = \gamma_0 \left( \frac{V}{V_0} \right)^q$$

$$\theta_D(V) = \theta_{D0} \exp \left[ \frac{\gamma_0 - \gamma(V)}{q} \right]$$



# MGD-EOS Bridgmanite

MgSiO<sub>3</sub> bridgmanite

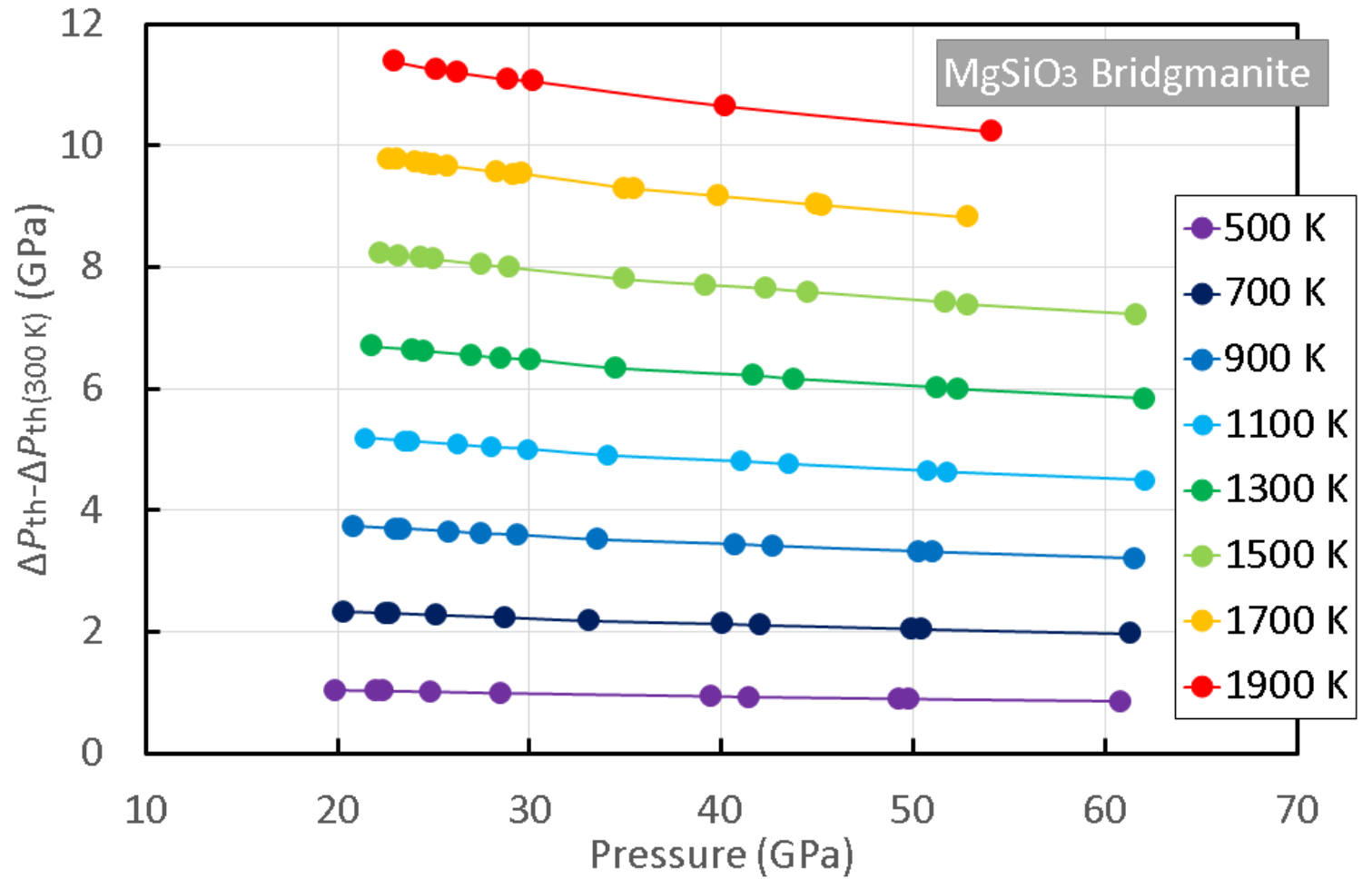
Katsura et al. (2009)

Tange et al. (2012)

$\Delta P_{th}(T) - \Delta P_{th}(300\text{ K})$

vs.  $P$

$$\Delta P_{th} = \int_{300\text{ K}}^T \frac{\gamma}{V} C_V^{\text{Debye}} dT$$



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End

