

4. Equation of state

7. Mie-Grüneisen-Debye equation of state

7.1 Concept of Mie-Grüneisen-Debye equation of state

Mie-Grüneisen-Debye equation of state (EOS) is one of thermal equations of state, which describe the relations of the **pressure** (P), **volume** (V), and **temperature** (T). This EOS is the most frequently used thermal EOS, and takes the imaginary “CH path” (cf. section 4.6) where P , V , and T at a high pressure and temperature condition are expressed as the result of the following **thermodynamic process**: first **compression** then heating from a reference condition P_0 , V_0 , and T_0 (Fig. 1). In **Mie-Grüneisen EOS**, the **thermal pressure** ΔP_{th} , which is the pressure increase while heating in the “CH path” and correspond to $P_3 - P_2$ in Fig. 1, is expressed as:

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

where γ_{th} is the thermodynamic **Grüneisen parameter** and ΔE_{th} is the energy increase. In Mie-Grüneisen-Debye EOS, **isochoric heat capacity** C_V is approximated adopting the **Debye heat capacity**:

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

where N is the number of atoms, k_B is the **Boltzmann constant**, and θ_D is the Debye temperature.

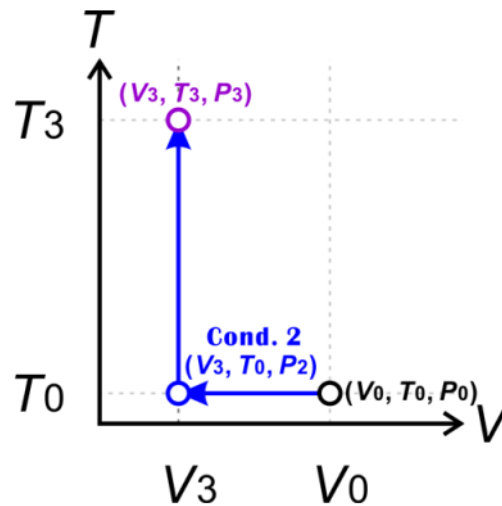


Fig. 1. Conceptual diagram of the thermodynamic path in Mie-Grüneisen-Debye equation of state. The volume V_3 temperature T_3 , and pressure P_3 at a high pressure and temperature condition are expressed as the result of imaginary compression from a reference condition (V_0, T_0, P_0) to (V_3, T_0, P_2) , and imaginary heating from (V_3, T_0, P_2) to (V_3, T_0, P_3) .

7.2 Form of Mie-Grüneisen-Debye EOS

Mie-Grüneisen-Debye EOS is expressed as:

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

where E_0 is the **internal energy** at zero temperature, E_D is the **thermal energy** at high temperature in the Debye approximation, and γ_D is the Debye-Grüneisen parameter which is defined as:

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

7.3 Derivation of Mie-Grüneisen-Debye EOS

In this section, Mie-Grüneisen-Debye EOS is derived from the definition of pressure. Pressure P is defined as the derivative of the [Helmholtz free energy](#) F with respect to V at constant T :

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

Then F is approximated to the sum of zero-temperature part F_0 and [lattice-vibration](#) part F_D which is from Debye model as shown below:

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

The definition of the Helmholtz free energy ($F \equiv E - TS$; Eq. 1.1.10) shows $F_0 = E_0 - 0 \cdot S = E_0$ at zero-temperature. Therefore, we obtain

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

Eq. (4.7.3') is substituted into Eq. (4.1.1) and we have

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

In Eq. (4.7.4), $-\frac{dE_0}{dV}$ is the zero-temperature pressure and can be obtained by [isothermal](#) compression at low temperature, and $-\left(\frac{\partial F_D}{\partial V}\right)_T$ is the thermal pressure at high temperature. The latter term $-\left(\frac{\partial F_D}{\partial V}\right)_T$ is difficult to measure with experiments, hence is transformed as follows in order to be expressed by other thermodynamic parameters.

$$\begin{aligned} - \left(\frac{\partial F_D}{\partial V} \right)_T &= - \frac{dF_D}{d\theta_D} \frac{d\theta_D}{dV} = \frac{dF_D}{d\theta_D} \frac{\theta_D}{V} \left(- \frac{d\theta_D}{dV} \frac{V}{\theta_D} \right) \\ &= \frac{dF_D}{d\theta_D} \frac{\theta_D}{V} \left(- \frac{d \ln \theta_D}{d \ln V} \right) = \frac{\gamma_D \theta_D}{V} \frac{dF_D}{d\theta_D} \end{aligned} \quad (4.7.5)$$

From now $\frac{dF_D}{d\theta_D}$ is transformed in order to be expressed as a function of θ_D . F_D , the lattice-vibration part of the Helmholtz free energy (cf. Eq. 4.7.3), is divided into the internal energy part and [entropy](#) part:

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

This equation can be transformed into the form:

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

because it follows the equation below:

$$\left(\frac{\partial \left(\frac{F_D}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_V = \left(\frac{\partial \left(\frac{F_D}{T} \right)}{\partial T} \right)_V \left(\frac{\partial T}{\partial \left(\frac{1}{T} \right)} \right)_V = \frac{\left[\left(\frac{\partial F_D}{\partial T} \right)_V \frac{1}{T} + F_D \left(- \frac{1}{T^2} \right) \right]}{\left(\frac{\partial \left(\frac{1}{T} \right)}{\partial T} \right)_V}$$

$$= \frac{\left[\left(\frac{\partial F_D}{\partial T} \right)_V \frac{1}{T} + F_D \left(-\frac{1}{T^2} \right) \right]}{\left(-\frac{1}{T^2} \right)} = F_D - T \left(\frac{\partial F_D}{\partial T} \right)_V$$

The internal energy E_D is expressed as an integral of isochoric heat capacity C_V (cf. Eq. 1.2.1):

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

Also, entropy S_D is expressed as (cf. Eq.1.2.2):

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

The isochoric heat capacity in the framework of Debye model is shown in Eq. (3.7.18'), and is a function of Θ_D/T . Therefore, the two parameters E_D and S_D are also functions of Θ_D/T , which implies that the Helmholtz free energy F_D (cf. Eq. 4.7.6) has a form:

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

Roughly speaking, E_D and S_D can be approximated as:

$$E_D \sim C_V \cdot T \sim Tg \left(\frac{\Theta_D}{T} \right)$$

and

$$TS_D \sim T \frac{C_V}{T} \cdot T = Th \left(\frac{\Theta_D}{T} \right)$$

where g and h are functions of Θ_D/T . Then Eq. (4.7.8) is substituted into Eq. (4.7.7), we have:

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

Finally, $\frac{dF_D}{d\Theta_D}$ in Eq. (4.7.5) is transformed using Eq. (4.7.8) and Eq. (4.7.9), and we obtain:

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

Lastly, we get Mie-Grüneisen-Debye EOS. Eq. (4.7.5) and (4.7.10) are substituted into Eq. (4.7.4), then we have the first equation (4.7.1):

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

The first term $-\frac{dE_0}{dV}$ is usually expressed using conventional P - V EOS such as 3rd-order [Birch-Murnaghan EOS](#) and Vinet EOS.

7.4 Equivalency of thermodynamic and Debye Grüneisen parameters

In this section, the Debye-Grüneisen parameter γ_D (Eq. 4.7.2) is shown to be identical to the thermodynamic Grüneisen parameter γ_{th} (Eq. 1.2.21). The thermal pressure based on the Mie-Grüneisen-Debye EOS is approximated as follows, assuming that V and γ_D are independent from T .

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

In the section 1.4, the thermal pressure is derived to be:

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

Then Eq. (4.7.11) is transformed using Eq. (1.4.1) and we have:

$$\gamma_D = \frac{V}{C_V} \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha V K_T}{C_V} = \gamma_{th} \quad (4.7.12)$$

which means that the Debye-Grüneisen parameter γ_D is identical to the thermodynamic Grüneisen parameter γ_{th} .

7.5 Volume dependence of Grüneisen parameter

The pressure dependence of the Grüneisen parameter is discussed in the section. The pressure effect on the Grüneisen parameter should be considered because thermal pressure $\Delta P_{th} = \frac{\gamma}{V} \Delta E_{th}$ decreases with compression (Fig. 2). The pressure dependence of Grüneisen parameter is usually expressed as:

$$\gamma(V) = \gamma_0 \left(\frac{V}{V_0}\right)^q \quad (4.7.13)$$

where γ_0 is the Grüneisen parameter at zero pressure. The equation is mathematically equivalent to:

$$q = \frac{d \ln \gamma}{d \ln V} \quad (4.7.14)$$

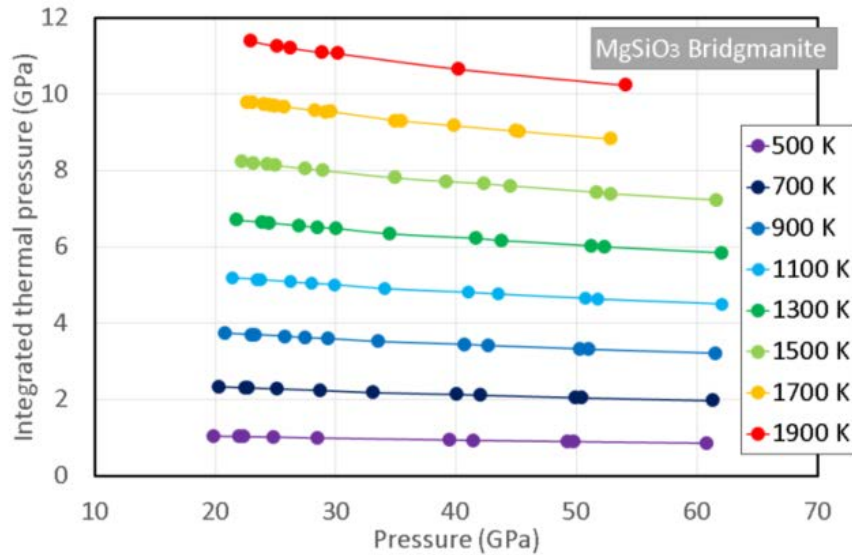


Fig. 2. Thermal pressure ΔP_{th} of $MgSiO_3$ bridgmanite. Integrated thermal pressure at a constant temperature decreases with pressure.

7.6 Relation of Θ_D , γ , and q

In this section, the relation between the Debye temperature Θ_D , Grüneisen parameter γ , and q (cf. Eq. 4.7.14) is derived. Eq. (4.7.2) and (4.7.14) are combined and we have:

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

then we obtain the relation:

$$\frac{d \ln \Theta_D}{d\gamma} = -\frac{1}{q} \quad (4.7.15)$$

The definite integral of Eq. (4.7.15) from “before (without) compression” to “under compression (at high pressure)” becomes:

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

where $\Theta_D(V)$ is Θ_D under compression, Θ_{D0} is Θ_D without compression, $\gamma(V)$ is γ under compression, and γ_0 is γ without compression. Therefore, we obtain:

$$\Theta_D(V) = \Theta_{D0} \exp \left[\frac{\gamma_0 - \gamma(V)}{q} \right] \quad (4.7.16)$$

7.7 Mie-Grüneisen-Debye EOS of bridgmanite

Mie-Grüneisen-Debye EOS of MgSiO_3 bridgmanite reported by Katsura et al. (2009) and Tange et al. (2012) is explained as an example of the EOS. Fig. 3. shows the relation between pressure and normalized volume at various temperature. The difference of volume among various temperature become smaller at higher pressure, which is because the thermal pressure decreases with compression.

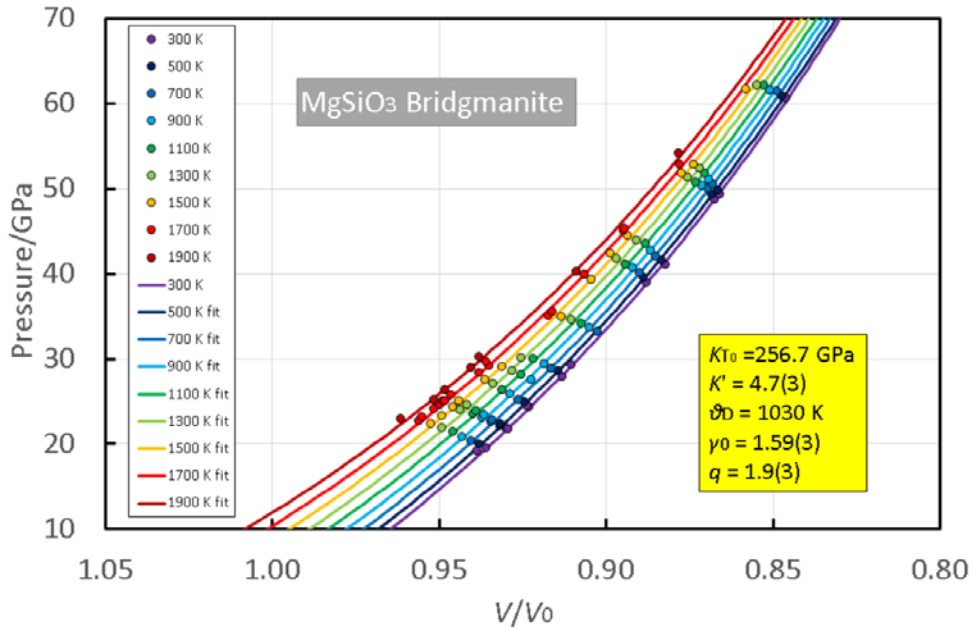


Fig. 3. Isothermal compression curves of MgSiO_3 bridgmanite at various temperature. At higher pressure, volume difference among different temperature is smaller.

The volume dependence of the Grüneisen parameter (Eq. 4.7.13) and the Debye temperature (Eq. 4.7.16) is shown in Fig. 4. And lastly, Fig. 5. shows the pressure dependence of the thermal pressure.

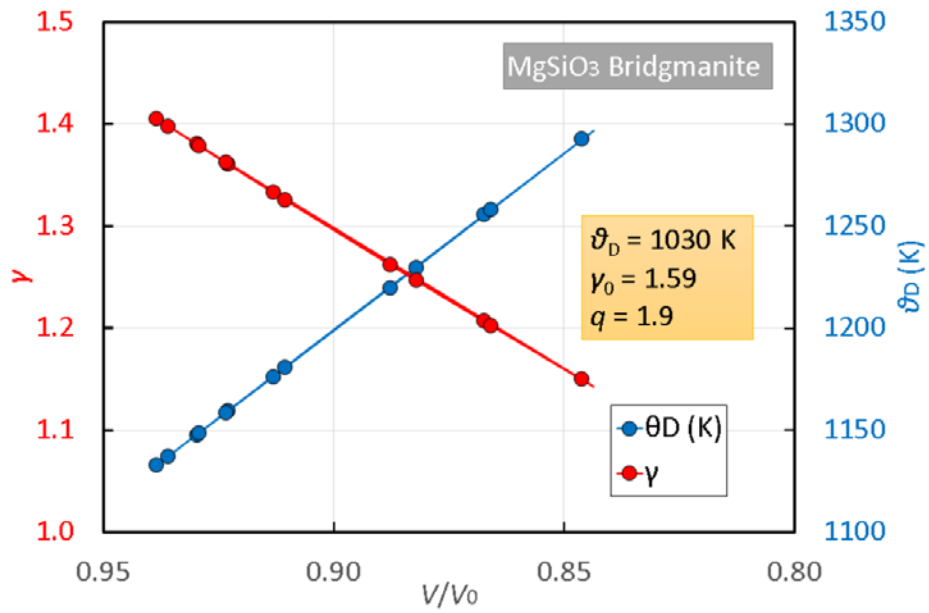


Fig. 4. The Grüneisen parameter and Debye temperature of MgSiO₃ bridgmanite against normalized pressure. The Grüneisen parameter is negative correlation and the Debye temperature is positive correlation with pressure.

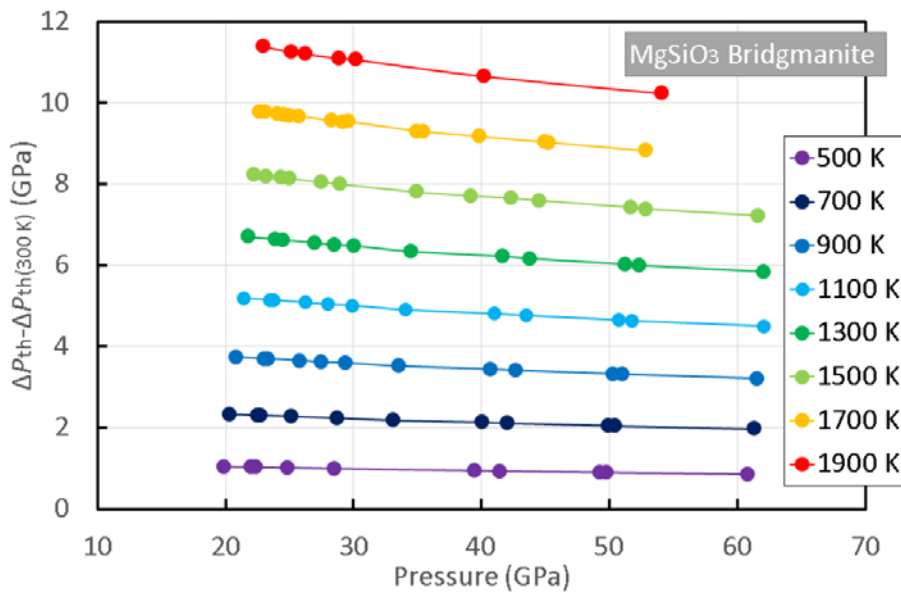


Fig. 5. The thermal pressure of MgSiO₃ bridgmanite normalized against the thermal pressure at 300K against pressure. The thermal pressure at a constant temperature decreases with pressure.