

Appendix

Let us briefly recall the quasi-harmonic approximation approach used to obtain P - T - V thermodynamic and thermoelastic properties of mineral phases. The main quantity involved in these calculations is the Helmholtz free energy (F) of the system, which is given by:

$$F(V, T) = U_0(V) + F^{QHA}(V, T) \quad (3)$$

where $U_0(V)$ is the static energy of the crystal at $T = 0$ K. F^{QHA} is calculated as:

$$F^{QHA}(V, T) = U_0^{ZP}(V) + \beta^{-1} \sum_{\mathbf{q}p} \left[\ln \left(1 - e^{-\beta \hbar \omega_{\mathbf{q}p}(V)} \right) \right] \quad (4)$$

with $U_0^{ZP}(V) = \sum_{\mathbf{q}p} \hbar \omega_{\mathbf{q}p}(V) / 2$ and $\beta = 1/k_B T$, \mathbf{q} indicates the sampled k -points in reciprocal space and ω_p is the p -th harmonic frequency.

By definition, the pressure state of the system is the first derivative of Eq.(3):

$$P(V, T) = - \frac{\partial U_0(V)}{\partial V} - \frac{\partial F^{QHA}(V, T)}{\partial V} \quad (5)$$

Eq.(4) and Eq.(5) gives us the possibility to obtain the volume of the system at any desired pressure and temperature condition by minimizing the Helmholtz free energy of the crystal. This task can be accomplished by using different approaches, such as numerical first derivative of Eq.(5) (Erba, 2014). Here we employed the phenomenological approach of Belmonte (2017), using the volume-integrated 3rd-order Birch-Murnaghan EoS formulation reported in Eq.(1) to fit the $F(V, T)$ curves from Eq.(3). Besides providing a description of the evolution of the crystal in pressure and temperature closer to the experimental approaches, this method has the advantages of being both more robust and able to provide at the same time the mechanical properties of the system (K_T and K').

Then, other properties, such as the volumetric thermal expansion, the isothermal bulk modulus, the isobaric heat capacity and the adiabatic bulk modulus can be straightforwardly calculated as. respectively:

$$\alpha_v(T) = - \frac{1}{V(T)} \left(\frac{\partial V(T)}{\partial T} \right)_P \quad (6)$$

$$C_p(T) = C_v(T) + \alpha_v^2(T) K_T(T) V(T) T \quad (7)$$

$$K_s(T) = K_T(T) + \frac{\alpha_v^2(T) V(T) K_T^2(T) T}{C_v(T)}. \quad (8)$$

In the present work, the properties related to Eqs.(7) and (8) were calculated using the molar volume ($\text{\AA}^3 \text{mol}^{-1}$) and isochoric heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$).