

Excess properties of solid solutions: Modelling phase relations and seismic velocities in the mantle

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Abstract

Keywords: high pressure, excess properties

1. Introduction

2. Motivation

2.1. Bulk moduli

The regular solution model implicitly defines many of the thermoelastic prop-
5 erties of solid solutions. For example, it defines the bulk modulus as the Reuss
average of the endmembers:

$$K_T = -V \left(\frac{\partial P}{\partial V} \right) \quad (1)$$

$$= \left(\sum_i n_i V_i + V_{\text{excess}} \right) \left(\frac{1}{\sum_i \left(n_i \frac{V_i}{K_{Ti}} \right)} + \frac{\partial P}{\partial V_{\text{excess}}} \right) \quad (2)$$

V_{excess} is often approximated as zero, or as a scalar term with no pressure
dependence. There are potential problems with this approximation:

- Excess enthalpy terms may change sign and/or become very large as
10 pressure increases. For example, pyrope-grossular in Green et al., 2012

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has an enthalpy interaction of 31 kJ/mol, and an excess volume of 0.164 kJ/kbar/mol, leading to a doubling of enthalpy over its stability field.

- The model predicts an excess bulk modulus with the same sign as the excess volume, conflicting with the Anderson-Anderson (1970) rule of thumb that $V K_T = c$

- Higher order excess volume terms to fit excess bulk moduli cause large deviations from a given equation of state at high pressure, as polynomial expansions of equations of state converge very slowly.

In many circumstances, these shortcomings are unimportant. However, there is a fundamental need to adjust the solid solution model where

- the stability range of the solid solution extends over pressure regimes large enough to contribute significantly to changes in excess enthalpy inconsistent with data, or
- mineral phases exhibit significant excess bulk moduli. The latter is especially important for those studies where velocities are obtained from the models.

2.2. Shear moduli

Thermodynamic variables do not include any input/constraints on shear moduli, which appear to deviate significantly from Voigt and Reuss averages.

3. Strategies

Taylor expansion of EoS converges extremely slowly, and leads to rapid divergence at pressures greater than the last crossing. This is part of the reason that Stixrude and Lithgow-Bertelloni (2011) set excess volumes as zero. Thus, simply adding a bulk modulus term is inappropriate.

Best fit elastic properties for an ideal intermediate can be found, from which deviations can be applied.

4. Excess properties

Most existing solid solution models define an excess enthalpy, entropy and volume, which leads to the following expressions for thermodynamic potentials:

$$\mathcal{H}_{\text{ss}} = \sum_i n_i \mathcal{H}_i + \mathcal{H}_{\text{excess}} + P V_{\text{excess}} \quad (3)$$

$$\mathcal{S}_{\text{ss}} = \sum_i n_i \mathcal{S}_i + \mathcal{S}_{\text{conf}} + \mathcal{S}_{\text{excess}} \quad (4)$$

$$\mathcal{G}_{\text{ss}} = \mathcal{H}_{\text{ss}} - T \mathcal{S}_{\text{ss}} \quad (5)$$

$$V_{\text{ss}} = \sum_i n_i V_i + V_{\text{excess}} \quad (6)$$

40 The derivatives of volume with respect to pressure and temperature can then be calculated

$$\alpha_{P,\text{ss}} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{1}{V_{\text{ss}}} \right) \left(\sum_i (n_i \alpha_i V_i) \right) \quad (7)$$

$$K_{T,\text{ss}} = -V \left(\frac{\partial P}{\partial V} \right)_T = V_{\text{ss}} \left(\left(\sum_i \frac{n_i V_i}{K_{Ti}} \right)^{-1} - \frac{\partial P}{\partial V_{\text{excess}}} \right) \quad (8)$$

$$K'_{T,\text{ss}} = -\frac{\partial}{\partial P} \left(V \left(\frac{\partial P}{\partial V} \right)_T \right) \sim V_{\text{ss}} \left(\sum_i \frac{n_i V_i}{K'_{Ti}+1} \right)^{-1} \quad (9)$$

Making the approximation that the excess entropy has no temperature dependence

$$C_{P,\text{ss}} = \sum_i n_i C_{Pi} \quad (10)$$

$$C_{V,\text{ss}} = C_{P,\text{ss}} - V_{\text{ss}} T \alpha_{\text{ss}}^2 K_{T,\text{ss}} \quad (11)$$

$$K_{S,\text{ss}} = K_{T,\text{ss}} \frac{C_{P,\text{ss}}}{C_{V,\text{ss}}} \quad (12)$$

$$\gamma_{\text{ss}} = \frac{\alpha_{\text{ss}} K_{T,\text{ss}} V_{\text{ss}}}{C_{V,\text{ss}}} \quad (13)$$

5. Conclusions

⁴⁵ **References**

Stixrude, L., Lithgow-Bertelloni, C., 2011. Thermodynamics of mantle minerals
- II. Phase equilibria. *Geophysical Journal International* 184, 1180–1213.