

Virtual Solid Solution Laboratory: A Tool for Thermodynamic Modelling of the Effects of Mixing and Ordering in Minerals

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The invention of the method of cluster expansion by Connolly and Williams (1983) revolutionized the study of solid solutions. It has become possible to parameterize the enthalpy of mixing in an $A_xB_{1-x}R$ solid solution by calculating formation energies of a set of supercell structures with randomly varied distributions of the exchangeable atoms. In mineralogical studies, such a parameterization is often achieved via the so-called pair interaction constants, the J_s , which describe of the enthalpies of the exchange reactions of “AA + BB = 2AB” type at different distances within the supercell (e.g. Bosenick et al., 2001). Recently, it has been shown that a complete set of the J_s can be determined by sampling the structures with single (A and B) and double (AA and BB) defects inserted at all possible distances in the supercells of the pure end-members BR and AR, respectively (Vinograd et al., 2008). The limited number of such structures makes it possible to calculate the excess enthalpies using first principles methods. Our Virtual Solid Solution Laboratory (VSSL) permits the automatic generation of the structures with single and double defects and simplifies their processing with first principles and force-field packages. The pair interaction constants which are extracted from the first principles or force-field calculations are combined to get effective Hamiltonians, which are further used within Monte Carlo algorithms to calculate temperature dependent enthalpies of mixing. The Gibbs free energies of mixing are evaluated from the Monte Carlo results by thermodynamic integration. The VSSL methodology will be illustrated by predicting the effects of mixing and ordering in rhombohedral (Ca,Mg)-carbonates, Si-rich rutiles and (Ca,Mg)-garnets.

References

Connolly JWD and Williams AR (1983) Density-functional theory applied to phase transformations in transition-metal alloys. *Phys. Rev. B* 27, 5169 – 5172

Bosenick A, Dove MT, Myers ER, Palin EJ, Sainz-Diaz CI, Guiton BS, Warren MC, Craig MS (2001) Computational methods for the study of energies of cation distributions: applications to cation-ordering phase transitions and solid solutions. *Mineralogical Magazine* 65, 193–219

Vinograd VL, Sluiter MHF, Winkler B. (2008) Prediction of the effective pairwise interactions in binary solid solutions from the enthalpies of single- and double-defect structures: I. Calculations based on empirical force-fields. *Geochim et Cosmochim Acta* (submitted)

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