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 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
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