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Thermodynamics of mixing in an isostructural solid solution: Simulation methodologies and application to the rutile-cassiterite system

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Abstract

The accuracies of two different approaches to model thermodynamic mixing properties of solid solutions are explored using the rutile-cassiterite solid solution as an example. Both methods employ an expansion of the configurational enthalpy in terms of pairwise interactions energies. In the first method the partition function is directly computed from the excess energies of all Ti/Sn configurations within a $2 \times 2 \times 4$ supercell. In the second method the free energy of mixing is calculated by a thermodynamic integration of the thermally averaged enthalpies computed with the Monte Carlo method using an $8 \times 12 \times 16$ supercell. The phase relations derived from Monte Carlo simulations agree well with the available experimental data, under the condition that the free energy is corrected for the effect of the excess vibrational entropy. The direct calculation of the partition function provides reasonable phase relations only when the configurational entropy is corrected to be consistent with the ideal mixing in the high-temperature limit. Advantages and drawbacks of the both approaches are discussed. The findings are generally applicable to models of isostructural solid solutions.

Keywords: Rutile-cassiterite, solid solution, first-principles based calculations, pairwise interactions, Monte Carlo simulations, configurational statistics