



Applicability of special quasi-random structure models in thermodynamic calculations using semi-empirical Debye–Grüneisen theory



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ABSTRACT

In theoretical calculations, expressing the random distribution of atoms in a certain crystal structure is still challenging. The special quasi-random structure (SQS) model is effective for depicting such random distributions. The SQS model has not been applied to semi-empirical thermodynamic calculations; however, Debye–Grüneisen theory (DGT), a semi-empirical method, was used here for that purpose. The model reliability was obtained by comparing supercell models of various sizes. The results for chemical bonds, pair correlation, and elastic properties demonstrated the reliability of the SQS models. Thermodynamic calculations using density functional perturbation theory (DFPT) and DGT assessed the applicability of the SQS models. DGT and DFPT led to similar variations of the mixing and formation energies. This study provides guidelines for theoretical assessments to obtain the reliable SQS models and to calculate the thermodynamic properties of numerous materials with a random atomic distribution.

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1. Introduction

Theoretical approaches to investigating random solid solutions show many advantages, and are becoming increasingly attractive as computers become more powerful and the theories themselves are improved. However, most theoretical calculations use periodic boundary conditions to express an infinite array of atoms in 3D space; therefore, expressing a random distribution of constituent atoms remains challenging. The simplest method for expressing a random distribution is the supercell method, which uses models containing randomly distributed atoms as a repeating unit. Satisfactory calculation results require the models to be as large as possible. However, as the model size increases, the calculations become more time consuming and the error in convergence increases.

The special quasi-random structure (SQS) method [1] is the most efficient method for mimicking random solids solutions and alloys [2–4]. It uses pairs and multisite correlation functions to produce a number of random models representing random

structures with periodically repeated structures. These models will generate numerous correlations. Accordingly, structure generation is time consuming because it is unpredictable and almost limitless. However, given that the most important and decisive correlations are those between the first few nearest neighbors, it needs to consider only a few nearest-neighbor correlations. The correlation function of the random structure, $[\overline{\prod}_{k,m}]_{Random}$, is expressed by

$$[\overline{\prod}_{k,m}]_{Random} = (2x - 1)^k,$$

where x is the composition in substitutional binary system, such as $A_{1-x}B_x$ or $(A_{1-x}B_x)C$, k is the grouping of atoms (e.g., $k = 1, 2$, and 3 are a point, pairs, and triplets), and m is the m^{th} -neighbor distance [1].

The SQS assessment has been used to investigate various properties of random alloys and solid solutions. Jiang et al. used mono and triclinic SQS models to mimic bcc random alloys [5,6]. They reproduced the equilibrium structures and enthalpy of formation of the random alloys. Shin et al. calculated thermodynamic properties of several binary hcp random alloys using low-symmetry SQS models [7]. In the author's previous work, SQS was employed to obtain the thermodynamic properties of random solid solutions with a B1 structure by using first principles phonon

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calculations [8,9]. However, despite the importance and utility of SQS models, they have not been used to calculate thermodynamic properties with semi-empirical Debye–Grüneisen theory (DGT).

Herein, the thermodynamic properties of $\text{Zr}(\text{C}_{1-x}\text{N}_x)$ solid solutions are calculated by using SQS models with DGT. Transition metal carbonitrides are representative of materials with a random atomic distribution because of their excellent properties and wide applicability [10–13]. When transition metal carbides form solid solutions with nitrides, non-metal atoms such as carbon and nitrogen can only occupy non-metal sites, and they become disordered. Therefore, $\text{Zr}(\text{C}_{1-x}\text{N}_x)$ solid solutions were chosen to examine the suitability of DGT for SQS models. To determine the reliability for the SQS model calculations, the SQS models and supercell (SC) models of various sizes were compared. In addition, density functional perturbation theory (DFPT) calculations were performed to obtain the reliability. The semi-empirical calculations with the SQS models yielded suitable results for substitutional random solid solutions.

2. Calculation methods & theories

2.1. Structure optimization and total electronic energy and elastic properties calculations

The Vienna ab initio simulation package (VASP) was used to calculate the thermodynamic properties of the $\text{Zr}(\text{C}_{1-x}\text{N}_x)$ solid solutions [14,15]. Exchange–correlation effects were treated in the framework of the generalized gradient approximation (GGA) with Perdew–Burke–Erzerhof (PBE) parameterization [16]. Integration in the Brillouin zone was performed using $13 \times 13 \times 13$ Monkhorst–Pack k-points to model the pure ZrC and ZrN with B1 structures. A high energy cutoff of 500 eV with an energy convergence of 0.01 eV/Å and the tetrahedron method with Blöchl corrections for the energy calculations were employed to improve the accuracy of the results.

SC models (8, 64, 256, and 512 atoms) with random substitutions of C by N were employed to depict the intermediate compositions of $\text{ZrC}_{1-x}\text{N}_x$ ($x = 0.25, 0.50, \text{ and } 0.75$). The random substitutions module which is implemented in MedeA-VASP package was employed to generate the randomly substituted SC models [17–20]. The SQS models suggested by Zunger et al. [1] were adopted to express random solid solution models. Figs. 1 and S1 illustrate the SQS and the SC models, respectively, which were used in the present calculations. The largest SC models containing 512 atoms did not converge after hundreds of iterations regardless of their composition or atomic configuration (Fig. S1), and were excluded from further analyses. Integration was conducted using Monkhorst–Pack grids of $15 \times 15 \times 15, 5 \times 5 \times 5$, and

$3 \times 3 \times 3$ for the 8, 64, and 256 atom SC models and $7 \times 5 \times 3$ and $5 \times 11 \times 5$ for the 32 and 16 atom SQS models, respectively [21], to optimize the structures and to obtain force constants. Energy cut-offs of 300–520 eV with an energy convergence of 0.01 eV/Å were employed, and the tetrahedron method with Blöchl corrections [22] and the first-order Methfessel–Paxton technique [23] with a smearing parameter of 0.05 eV were used for the energy calculations of the 8 and 64 atom SC models and the SQS models, respectively. To assess the reliability of the monoclinic SQS models [24], the elastic properties of both the SQS models and the randomly substituted SC models with cubic structures calculated and then compared. The strain–stress relation [12,25,26] was employed to obtain the elastic constants of cubic and monoclinic structures. Volume conserving distortions ($\epsilon = \pm 0.02$) were applied to each model to obtain the elastic constants. Detailed calculation methods are provided elsewhere [12,27–29].

2.2. Free energy calculations with Debye–Grüneisen theory

Formation Gibbs free energies at 0 K were directly derived from the formation enthalpies as the entropy term was eliminated [30]. The temperature effects on the Gibbs free energies were calculated using semi-empirical DGT [26,31] and DFPT [9,32,33]. A system of configuration x at fixed temperature (T) and hydrostatic pressure (P) has its equilibrium state determined by the minimization of the non-equilibrium Gibbs free energy ($G^*(x,P,T)$) of the relevant crystal, which is expressed as [34],

$$G^*(x, P, T) = E_{\text{el}}(x) + A_{\text{tot}}(x, T) + PV(x) - TS_{\text{conf}}(x), \quad (1)$$

where E_{el} is the total energy at 0 K (which can be directly calculated from first principles), $PV(x)$ accounts for the constant hydrostatic pressure condition (and can be ignored in condensed matter), $-TS_{\text{conf}}(x)$ includes configurational effects, and $A_{\text{tot}}(x,T)$ is the total Helmholtz free energy.

The Helmholtz free energy of DGT can be expressed by

$$A_{\text{tot}}(x, T) = E_{\text{D}}(x, T) - TS_{\text{D}}(x, T) + E_{\text{el}}(x, T) - TS_{\text{el}}(x, T), \quad (2)$$

where E_{D} and S_{D} are the internal energy and entropy of the quasi-harmonic Debye vibrational lattice, and E_{el} and S_{el} are the internal energy (Eqs. (3) and (4)) and entropy of electronic excitation, respectively (Eqs. (5) and (6)).

$$E_{\text{D}}(x, T) = \frac{9}{8} Nk_B \theta_D + 3Nk_B T D\left(\frac{\theta_D}{T}\right), \quad (3)$$

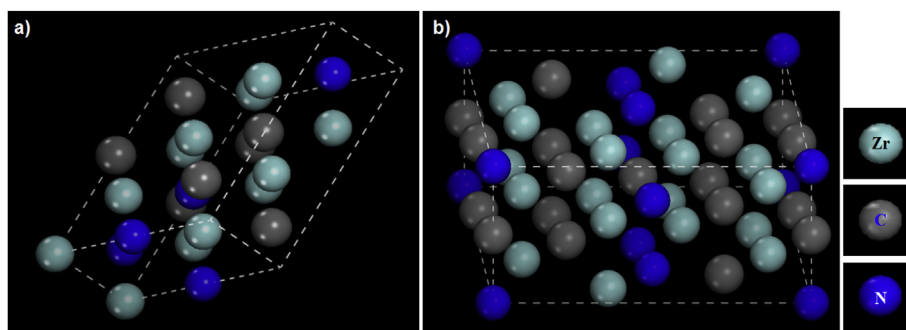


Fig. 1. SQS models for depicting random solid solutions of ZrC and ZrN. (a) 16 atom models of $\text{Zr}(\text{C}_{0.5}\text{N}_{0.5})$ and (b) 32 atom models of $\text{Zr}(\text{C}_{0.75}\text{N}_{0.25})$. $\text{Zr}(\text{C}_{0.25}\text{N}_{0.75})$ is described by swapping the C and N positions of $\text{Zr}(\text{C}_{0.75}\text{N}_{0.25})$.

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