



Comparison of two calculation models for high entropy alloys: Virtual crystal approximation and special quasi-random structure



Shen Wang, Jun Xiong, Da Li ^{*}, Qiang Zeng, Min Xiong, Xiaosong Chai

Key Laboratory of Advanced Technologies of Materials, Ministry of Education, College of Material Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China

ARTICLE INFO

Article history:

Received 2 September 2020

Received in revised form 22 September 2020

Accepted 25 September 2020

Available online 15 October 2020

Keywords:

Metals and alloys

Crystal structure

ABSTRACT

We investigated the suitable range of virtual crystal approximation (VCA) and special quasi-random structure (SQS) for estimating lattice constants (LCs) of high entropy alloys (HEAs). For the HEAs composed of the atoms with similar atomic radius and electronic configuration, such as FeCoNiCr combined with Cu or V, the LCs obtained by SQS and VCA methods are close to each other. When combined with atoms with quite different atomic radius and electronic configuration, such as Nb, Ge or Ti, there is obvious lattice distortion in the SQS supercell, and the LCs of VCA models are quite different from that of SQS models. The SQS method can be replaced by VCA when estimating LCs of HEAs composed of atoms with similar properties, which is helpful to increase computation efficiency.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

High-entropy alloys (HEAs), as a kind of disordered solid solution (DSS), have attracted considerable attention in materials science and engineering. The first-principles calculation is an effective method to predict the properties of supercells, such as electronic properties[1,2] and magnetic properties[3–6]. Accurate estimation of lattice constants (LCs) is the premise for predicting the properties of supercells. One way to calculate DSS is to build a large supercell and then randomly arrange atoms on the lattice point. This method is limited to computing resources, so more concise theories to study DSS was developed. One of the commonly used methods is virtual crystal approximation (VCA), based on the mean-field theory. Generally, the potentials which represent atoms of two or more elements are averaged into a composite atomic potential. This is an overly simplified approach to substitutional solid solutions[7]. Because there is no need to build a supercell, the calculation time can be saved greatly. Mayahi[8] calculated the LCs of FeCoNiCr and FeCoNiCrMn HEAs using VCA method, and the results were in good agreement with the experimental value, with the error less than 4%. However, the lattice distortion of the VCA model cannot be reflected. To solve the problem, Zunger et al.[9] proposed the SQS model. The SQS combines the idea of cluster expansion with the use of supercells. It is guided by the principle of close reproduction of the perfectly random network for the first few shells around a given site, deferring period-

icity errors to more distant neighbors. Compared with the VCA method, the calculation of the supercell is inefficient. Hu[10] investigated the properties of NbMoTaW HEAs, which is composed of atoms with similar properties. The lattice constants of VCA and SQS models were compared, and the results of each method are close to the experimental value. However, there are few investigations about the applicability of SQS and VCA methods for the HEAs consisting of atoms with quite different properties. Can the SQS method be replaced by the VCA method for estimating the LCs of HEAs with various components? Answering this question will be meaningful for the theoretical calculation of HEAs.

In this paper, we calculated several representative HEAs by SQS and VCA methods. Besides, the LCs and lattice distortion of HEAs composed of atoms with similar and quite different properties were compared. Finally, we determined the suitable range of each method for estimating the LCs of HEAs.

2. Calculated details

In the present study, we employed Cambridge Sequential Total Energy Package[11] based on the density functional theory within the generalized gradient approximation, treated by Perdew-Burke-Ernzerhof exchange–correlation potentials. The ultrasoft pseudopotentials were used to represent the interactions between the ionic cores and the valence electrons. The plane wave cutoff energy were 500 eV for SQS model and 1000 eV for VCA model. The Brillouin zone sampling was performed using special k-points generated by the Monkhorst-Pack scheme with density parameters 0.04 1/Å. A high convergence tolerance level (the max force is

^{*} Corresponding author.

E-mail address: hardfacing@home.swjtu.edu.cn (D. Li).

about 0.05 eV/Å, and the max stress is about 0.1 GPa) was also chosen. The “mcsqs” model[12] installed in Alloy Theoretical Automated Toolkit (ATAT) was used to generate SQS supercells. The VCA model was obtained from a single cell whose atoms were mixed by pseudopotentials of different elements of HEAs in proportion.

3. Results and discussion

With the increase of atoms number, the properties of SQS will be closer to DSS. So it is necessary to select the appropriate size of the SQS supercell. Fig. 1 illustrates the relationship between the total energy of each atom (E_{tot}) and the number of supercell atoms (N). E_{tot} decreases with the increase of N , indicating the structure tends to be stable. E_{tot} is the highest when N is the minimum, such as FeCoNiCr SQS supercell with $N = 4$ or FeCoNiCrMn SQS supercell with $N = 5$, owing to the significant periodicity. For all SQS supercells, E_{tot} converges at N less than 60, such as FeCoNiCrMn, the difference of E_{tot} between $N = 40$ and $N = 100$ is less than 0.005 eV, indicating it is sufficient to construct FeCoNiCrMn SQS supercell consisting of 40 atoms.

Fig. 2 shows six representative SQS and VCA models. The SQS model is inclined because the correlation function of this structure is closest to DSS. Fig. 3 shows the LCs calculated by SQS and VCA methods and obtained by experiment. For FeCoNiCr, FeCoNiCrMn, FeCoNiCrMnCu and FeCoNiCrMnV, the LCs of SQS and VCA are close to each other. For FeCuNi₂CrAl, FeCoNiCrMnNb, FeCoNiCrMnGe and FeCoNiGeMnTi, the LCs of SQS and VCA are quite different, and the LCs of VCA are quite different from the experimental value. The atomic radii of Fe, Co, Ni, Cr, Mn, Cu, V are 1.27 Å, 1.26 Å, 1.24 Å, 1.27 Å, 1.32 Å, 1.28 Å and 1.35 Å, and these atoms belong to the transition elements in the fourth period, indicating the properties of these atoms are similar. The atomic radii of Ge, Al, Nb and Ti are 1.40 Å, 1.43 Å, 1.48 Å and 1.45 Å. According to the formula of atomic radius difference: $\delta = \sqrt{\sum_{i=1}^n c_i (1 - \frac{r_i}{\bar{r}})^2}$, where c_i is the content of element i ; r_i is the atomic radius of element i ; \bar{r} is the expectation of atomic radius, the δ of FeCoNi₂CrAl, FeCoNiCrMnNb, FeCoNiCrMnGe and FeCoNiGeMnTi are larger than 4.1%. In contrast, the δ of FeCoNiCr, FeCoNiCrMn, FeCoNiCrMnCu and FeCoNiCrMnV are smaller than 3.0%. Ge and Al belong to the main group element, and Nb belongs to transition element in the fifth period, indicating the properties of these atoms are quite dif-

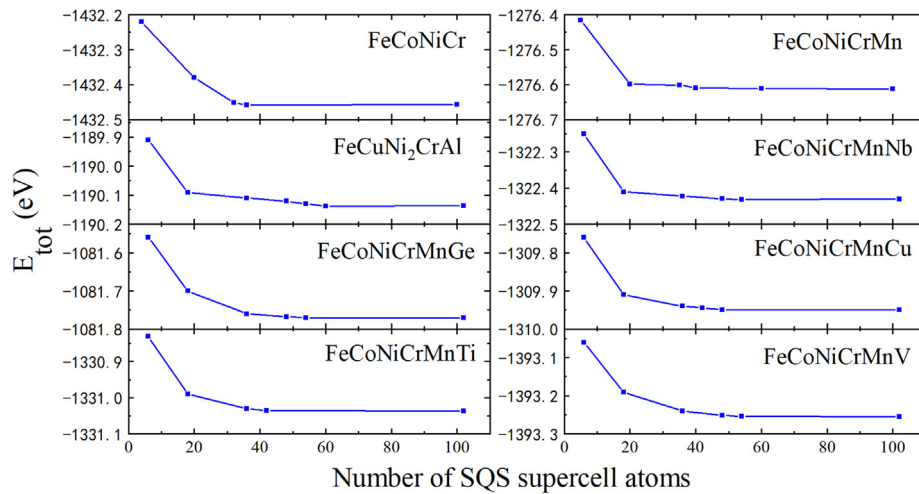


Fig. 1. The total energy of each atom varying with the total number of face-centered cubic (fcc) SQS supercell atoms.

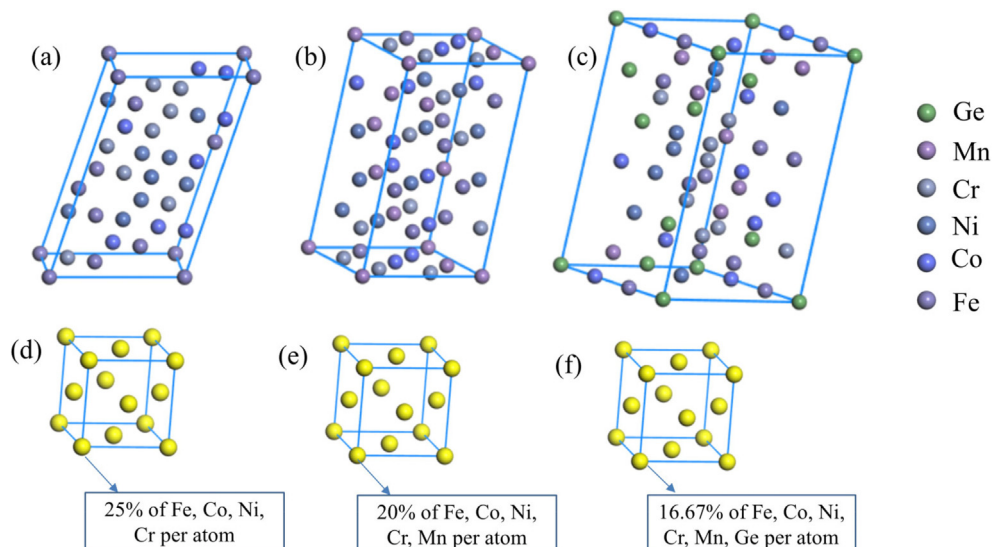


Fig. 2. Unoptimized fcc model: (a, d) FeCoNiCr SQS and VCA model; (b, e) FeCoNiCrMn SQS and VCA model; (c, f) FeCoNiCrMnGe SQS and VCA model.

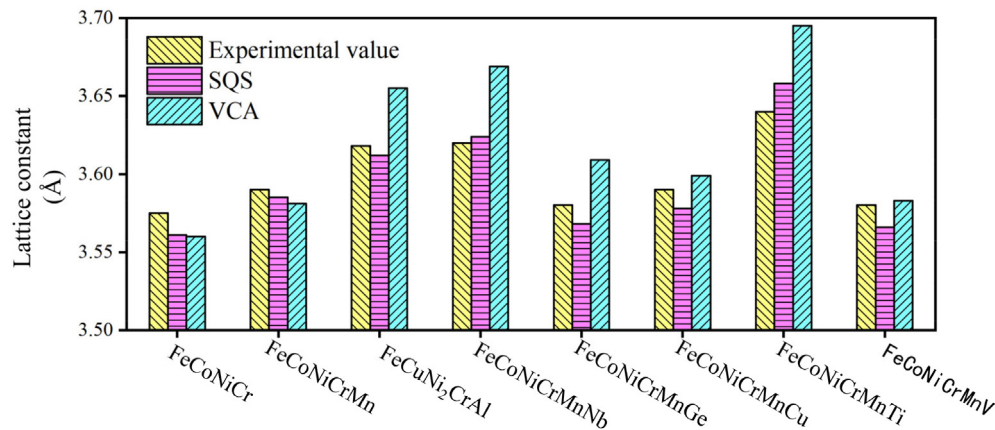


Fig. 3. The LCs calculated by SQS and VCA and obtained by experiment. The experimental fcc LCs of FeCoNiCr and FeCuNi₂CrAl are from Ref. [13] and Ref. [14], respectively; The experimental LCs of fcc FeCoNiCrMn, FeCoNiCrMnNb, FeCoNiCrMnGe, FeCoNiCrMnCu, FeCoNiCrMnTi and FeCoNiCrMnV are from Ref. [15].

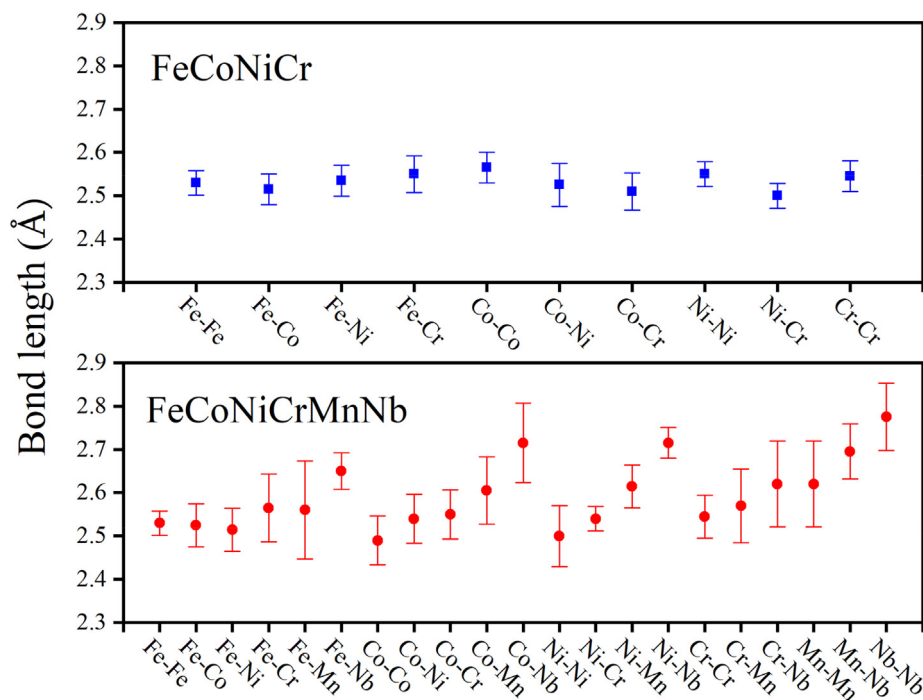


Fig. 4. Average distances of the nearest-neighbor bonds for FeCoNiCr and FeCoNiCrMnNb SQS supercell. The error line represents the standard deviation of the bonds connecting with the same atoms.

ferent from Fe, Co, Ni and Cr. Fig. 4 shows the average distances of the nearest-neighbor bonds for FeCoNiCr and FeCoNiCrMnNb SQS supercell. The error line represents the standard deviation of the bond lengths. The change ranges of bond lengths of FeCoNiCrMnNb supercell are larger than that of FeCoNiCr, indicating the lattice distortion is more obvious for HEAs composed of atoms with quite different properties. Therefore, the VCA method is only suitable for estimating the LCs of HEAs composed of atoms with similar properties. However, the SQS method is still suitable for estimating the LCs of HEAs consisting of atoms with quite different properties.

4. Conclusion

In conclusion, for the HEAs composed of atoms with similar atomic radius and electronic configuration, the LCs of SQS and VCA are close to each other. For the HEAs composed of atoms with

quite different atomic radius and electronic configuration, the LCs obtained by SQS and VCA methods are quite different. The SQS model can well consider the effect of lattice distortion, while the LCs of VCA model is quite different from the experimental value. Compared with SQS, the VCA method is only suitable for estimating the LCs of HEAs composed of atoms with similar properties, which is significant for the calculation of HEAs.

CRediT authorship contribution statement

Shen Wang: Conceptualization, Methodology, Software, Investigation, Writing - original draft. **Jun Xiong:** Validation, Formal analysis, Visualization, Software. **Da Li:** . **Qiang Zeng:** Validation, Formal analysis, Visualization. **Min Xiong:** Resources, Supervision, Data curation. **Xiaosong Chai:** Resources, Writing - review & editing, Supervision, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] S. Idrissi, H. Labrim, S. Ziti, et al., *Phys. Lett. A* 384 (2020) 12645324.
- [2] S. Idrissi, H. Labrim, S. Ziti, et al., *Appl. Phys. A-Mater.* 126 (2020) 1903.
- [3] S. Idrissi, H. Labrim, S. Ziti, et al., *J. Electron. Mater.* 48 (2019) 3579.
- [4] G. Kadim, R. Masrour, A. Jabar, J. Magn. Mater. 499 (2020) 166263.
- [5] R. Masrour, A. Jabar, H. Khelif, et al., *Solid State Commun.* 268 (2017) 64.
- [6] R. Masrour, A. Jabar, E.K. Hlil, *Intermetallics* 91 (2017) 120.
- [7] S. Huang, F. Tian, L. Vitos, *J. Mater. Res.* 33 (2018) 2938.
- [8] R. Mayahi, *J. Alloy. Compd.* 818 (2020) 152928.
- [9] A. Zunger, S.H. Wei, L.G. Ferreira, et al., *Phys. Rev. Lett.* 65 (1990) 353.
- [10] Y.L. Hu, L.H. Bai, Y.G. Tong, et al., *J. Alloy. Compd.* 827 (2020) 153963.
- [11] M.D. Segall, P. Lindan, M.J. Probert, et al., *J. Phys.-Condens. Mat.* 14 (2002) 2717.
- [12] A. van de Walle, P. Tiwary, M. de Jong, et al., *Calphad* 42 (2013) 13.
- [13] X. Li, D.L. Irving, L. Vitos, *Sci Rep-Uk* 8 (2018) 11196.
- [14] T. Borkar, B. Gwalani, D. Choudhuri, et al., *Acta Mater.* 116 (2016) 63.
- [15] B. Cantor, *Entropy-Switz* 16 (2014) 4749.