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Phys. Rev. Lett. **116**, 105501 — Published 8 March 2016

DOI: [10.1103/PhysRevLett.116.105501](https://doi.org/10.1103/PhysRevLett.116.105501)

Efficient *ab initio* modeling of random multi-component alloys

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We present in this Letter a novel small set of ordered structures (SSOS) method that allows extremely efficient *ab initio* modeling of random multi-component alloys. Using inverse II-III spinel oxides and equiatomic quinary bcc (so-called high entropy) alloys as examples, we demonstrate that a SSOS can achieve the same accuracy as a large supercell or a well-converged cluster expansion, but with significantly reduced computational cost. In particular, because of this efficiency, a large number of quinary alloy compositions can be quickly screened, leading to the identification of several new possible high entropy alloy chemistries. The SSOS method developed here can be broadly useful for the rapid computational design of multi-component materials, especially those with a large number of alloying elements, a challenging problem for other approaches.

PACS numbers: 61.66.Dk

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Ab initio modeling based on density functional theory (DFT) is a powerful tool that has greatly accelerated the design and discovery of materials [1-5]. The recently developed *ab initio* evolutionary methodology [6] further enables crystal structure prediction without any experimental input, making truly predictive materials design feasible. Despite its great success, extending *ab initio* calculations to multi-component alloys exhibiting configurational disorder remains a difficult problem. To date, the three most widely used techniques for modeling disordered alloys are the single-site coherent potential approximation (CPA) [7], the special quasirandom structure (SQS) approach [8], and the “coarse-graining” cluster expansion (CE) method [9]. While CPA can elegantly treat both chemical and magnetic disorder (e.g. paramagnetic state) in random alloys at arbitrary composition, its mean-field nature limits its application to systems where local environmentally-dependent effects such as local displacements of atoms away from their ideal lattice positions are insignificant. A SQS represents the best possible periodic supercell that mimics the local pair and multisite correlation functions of a random alloy under the constraint of a given unit cell size N . Due to the $O(N^3)$ scaling of traditional DFT methods, small-unit-cell SQSs are preferred for computational efficiency. To date, SQSs with $N \leq 36$ have been successfully generated for random binary and ternary alloys [8,10-14]. However, with increasing number of alloying elements, it becomes increasingly difficult to find a small-sized SQS that can still adequately mimic the statistics of a random alloy due to the large number of correlation functions that need to be reproduced (see Fig. 1). Finally, while a CE is decidedly powerful and is capable of capturing short-range order effects at finite temperatures when used as the basis for canonical Monte Carlo simulations, the parameterization of a multi-component CE can be

computationally very expensive. To the best of our knowledge, no application of the CE technique to quaternary, quinary and higher-order alloy systems has yet been reported in the literature.

In this Letter, motivated by the well-known Gaussian quadrature rule for numerical integration that approximates a definite integral as a weighted sum of function values at specific points, we propose to calculate a physical property f of a random alloy from a weighted average of the properties of a small set of ordered structures (SSOS) as:

$$\langle f \rangle_R \approx \sum_{i=1}^n w_i f(\sigma_i^{SSOS}) \quad (1)$$

where n is the number of structures in the set. w_i and $f(\sigma_i^{SSOS})$ denote the weight and property of the i -th structure in the SSOS, respectively. The weights should be positive and satisfy the normalization condition $\sum_{i=1}^n w_i = 1$.

To find the optimal SSOS and the corresponding weights for a given random alloy, we resort to the multi-component CE technique [9]. For a M -component alloy containing N lattice sites, we assign a pseudo-spin variable S_i to each site, which can take the value between 0 and $M-1$ depending on which element occupies site i . The atomic arrangements on an underlying parent lattice can thus be completely characterized by the vector $\sigma = \{S_1, S_2, \dots, S_N\}$. We further define a cluster α as a group of k lattice sites, where $k=1, 2, 3, 4, \dots$ indicates single site, pair, triplet, and quadruplet cluster, etc. Formally, the dependence of a scalar property f on lattice configuration σ can be expanded as:

$$f(\sigma) = J_0 + \sum_{\alpha} \sum_s D_{\alpha}^s J_{\alpha}^s \bar{\Phi}_{\alpha}^s(\sigma) \quad (2)$$

Here, the vector s is called a “decoration” that specifies the type of point function associated with each site in cluster α . $\bar{\Phi}_\alpha^s$, J_α^s and D_α^s denote the correlation function (see Ref. 12 for detailed definition), the effective cluster interaction (ECI), and the degeneracy factor for cluster α with decoration s , respectively. J_0 is the ECI for the empty cluster. For a truly random multi-component alloy, the ensemble average of its correlation function $\langle \bar{\Phi}_\alpha^s \rangle_R$ can be calculated analytically since there is no correlation in the occupation between various sites. We search for a SSOS and associated weights such that the weighted averages of their correlation functions match $\langle \bar{\Phi}_\alpha^s \rangle_R$ for as many clusters as possible. In the spirit of the SQS approach [8,10-14], we make a fundamental assumption that the relative importance of ECIs decreases with increasing cluster size and focus on the physically most relevant correlation functions between the first few nearest neighbors.

To generate a SSOS- $n \times N$ set that contains n ordered structures each containing N atoms per cell, we exhaustively enumerate all possible combinations of n symmetrically distinct N -atom/cell structures based on an underlying parent lattice using the ATAT code [15]. For large N , a linearly scaling numeration algorithm recently developed by Hart and Forcade [16] can be used to overcome the combinatorial explosion and the associated increase in computational time to enumerate the structures associated with larger cells. Each structure in the SSOS must have the same alloy composition as that of the alloy of interest. For computational efficiency, both n and N should be as small as possible. For each candidate set of structures, we determine their optimal weights using least-square regression such that the periodicity error, which measures the deviation from random

correlation, is minimized for a specified set of clusters under the normalization constraint:

$$\sum_{\alpha} \sum_s \left(\sum_{i=1}^n w_i \bar{\Phi}_{\alpha}^s(\sigma_i^{SSOS}) - \langle \bar{\Phi}_{\alpha}^s \rangle_R \right)^2 = \min \quad (3)$$

Among all enumerated candidate sets, the best SSOS is the one with the lowest periodicity error. The generation of a SSOS is thus an intrinsically two-step optimization process: the inner one is with respect to weights and the outer one is with respect to structure selection among a pool of small ordered structures. **We note that such an optimization process may be valuable for identifying reference structures used in machine learning approaches as well.**

To test the validity of the SSOS approach, we first apply it to predict the relative stability of normal vs. inverse structures of MgAl_2O_4 and ZnAl_2O_4 spinel oxides [17]. In a normal II-III AB_2O_4 spinel, A^{2+} cations occupy one-eighth of the tetrahedral interstitial sites of the fcc oxygen sublattice, and B^{3+} cations occupy half of the octahedral interstices. When all the A cations exchange positions with the B cations, the spinel is referred to as ‘inverse’. To model the inverse spinel structure in which A and B cations are randomly distributed within the octahedral (B) sublattice, we have developed a SSOS-2 \times 28 [18] and various SQS- N structures (with $N=28, 56, 84$ and 168 atoms per unit cell). Furthermore, we have constructed high fidelity CEs using 17 pair, 16 triplet, and 2 quadruplet interactions by fitting to DFT calculated total energies of 146 input structures. For MgAl_2O_4 and ZnAl_2O_4 , the leave-one-out cross-validation (LOOCV) score is only 3.4 and 4.7 meV per AB_2O_4 formula unit (f.u.), respectively. The CE results are herein considered as ‘benchmarks’ against which the accuracy of SSOS can be

judged. For DFT calculations, we employ the all-electron projector augmented wave method [19] within the LDA, as implemented in VASP [20]. To fully consider the effects of local lattice relaxations, all structures are fully relaxed with respect to both cell-internal and cell-external degrees of freedom according to quantum mechanical forces and stress tensors. More computational details can be found in the Supplementary Material [18].

Fig. 2 shows the disordering energies (defined as the total energy difference between the inverse and normal configurations) of MgAl_2O_4 and ZnAl_2O_4 calculated using the SSOS, SQS and CE methods. The ECIs of the CEs are also shown. Remarkably, by performing DFT calculations on only two 28-atom structures, our SSOS calculations give results in excellent agreement with those from the CE and the large 168-atom SQS, but with significantly lower computational cost. In contrast to metallic systems such as Nb-Mo and Ta-W [11], the slow convergence of the SQS results with respect to N observed for spinel oxides is a consequence of the long-ranged pair interactions typical of Coulomb interactions in these materials (see Figs. 2a-b). It is worth noting that, compared with SQS-28, calculations using SSOS-2 \times 28 lead to a greater than ten-fold reduction in computational error for disordering energy, but with only an approximately two-fold increase in computational effort. Here, by collaboratively employing several supercells of small size instead of a single large one to model the random state, the convergence with respect to cell size has been greatly accelerated, which can effectively overcome the limitation imposed by the $O(N^3)$ scaling of DFT.

As our second example, we apply the SSOS method to model the random quinary body-centered cubic (bcc) alloy at the equiatomic composition, the so-called high-

entropy alloys (HEAs) that have rapidly emerged as a new class of engineering materials due to their excellent physical and mechanical properties [21, 22]. Remarkably, a SSOS-3×5 containing only three 5-atom/cell structures (Figs. 3a-3c) can already perfectly match the 20 pair correlation functions of the random alloy for the first- and second-nearest neighbors [18]. To archive the same level of accuracy in terms of the range of perfectly matched correlations in a single supercell, we find it necessary to use a much larger 125-atom SQS (Fig. 3d), which has been developed in this study using the Monte-Carlo simulated annealing technique [12].

Using both the SSOS and SQS methods, we have performed DFT calculations on 12 random quinary bcc alloys using VASP [20] with PAW-PBE pseudopotentials [23]. A plane-wave cutoff energy of 341.5 eV and dense Monkhorst-Pack k -point meshes are employed to guarantee high numerical accuracy. As shown in Figs. 3e and 3f, even a SSOS-3×5 can already provide results in excellent agreement with those obtained using a much larger 125-atom bcc SQS. The SSOS approach agrees quantitatively with SQS despite the significantly less computational cost of the former: the root-mean-square deviation (RMSD) of the formation energy and equilibrium volume of the 12 alloys is only 4.8 meV/atom and 0.028 Å³/atom, respectively. Here we define formation energy as the total energy difference between an alloy and the composition-weighted average of its constituent pure elements in their respective ground-state structures at $T=0$ K.

For the comparison shown in Fig. 3, we only allow the unit cell volume to relax, with all atoms occupying their ideal bcc lattice positions. In a multicomponent solid solution, significant lattice distortion can occur due to the large size mismatch between its many constituent elements. Consequently, there can exist a large dispersion of nearest-

neighbor bond lengths, the average of which corresponds to the average lattice. To further consider the effects of local lattice relaxations, we fully relax all atoms in a random bcc alloy from their ideal lattice sites into their equilibrium positions. We find that the results predicted by SSOS and SQS calculations remain in excellent agreement with each other even after full atomic relaxations (see Fig. S2). For obtaining the atomically relaxed formation energy, we estimate that the SSOS calculations are more than 40-fold faster than SQS calculations, although the RMSD between the two calculations is only 9.5 meV/atom. This good agreement confirms the suitability of using the SSOS approach for modeling local lattice relaxations in size-mismatched multicomponent alloys and predicting properties of these high-order alloys.

The combined accuracy and high computational efficiency of the SSOS method make it possible to perform high-throughput screening of the phase stability of a large number of potential bcc HEA compositions with only limited computing resources. As a demonstration of the approach, we consider all possible equiatomic quinary alloys that can be formed from the 13 elements Al, Cr, Cu, Ir, Mo, Nb, Ni, Pd, Pt, Ta, Ti, V and W. Furthermore, all possible five-combinations of the eight refractory metals Hf, Mo, Nb, Ta, Ti, V, W and Zr are also considered. Here we use “instability energy” [24] to measure the phase stability of a bcc HEA defined as the total energy difference between an alloy and the ground state convex hull, which can be estimated using the Open Quantum Materials Database (OQMD) [25]. A large instability energy would indicate a high tendency towards ordering and thus low chance of obtaining a single phase solid solution. Furthermore, the bcc lattice should be energetically more favorable than other competing crystal structures such as face-centered cubic (fcc). For this screening, we consider the

relative lattice stability between fcc and bcc structures, each modeled using a SSOS-3×5 [18]. As shown in Fig. 4, our SSOS calculations correctly predict the bcc structure to be more stable for the six experimentally synthesized bcc HEAs: Mo₁Nb₁Ta₁V₁W₁ [26], Hf₁Nb₁Ta₁Ti₁Zr₁ [27], Al₁Nb₁Ta₁Ti₁V₁ [28], Mo₁Nb₁Ti₁V₁Zr₁ [29], Al₁Mo₁Nb₁Ti₁V₁ [30] and Hf₁Nb₁Ti₁V₁Zr₁ [31]. Among the 1337 HEA candidates screened, the top 2% most promising (having the lowest instability energies) bcc HEA compositions are reported in Table I. Four of them (Mo₁Nb₁Ta₁V₁W₁ [26], Hf₁Nb₁Ta₁Ti₁Zr₁ [27], Mo₁Nb₁Ti₁V₁Zr₁ [29] and Hf₁Nb₁Ti₁V₁Zr₁ [31]) have already been experimentally verified. The remaining 23 alloy compositions are thus new predictions that await experimental confirmation.

In summary, here we propose a new method to predict the properties of random multi-component alloys using *ab initio* calculations. Instead of relying on a single large supercell to mimic the random state, we model a random alloy using a set of small ordered structures, whose weight-averaged properties approximate those of the truly random alloy. Due to the $O(N^3)$ scaling of DFT, the SSOS method has significant advantage in terms of computational efficiency, particularly for high-order alloy systems. Using inverse AB₂O₄ spinels and random quinary bcc alloys as examples, we demonstrate that the SSOS method can predict the energetics and structural properties of random alloys in excellent agreement with those obtained using much larger supercells, even when the effects of local lattice relaxations are accounted for. Since the SSOS method relies on small cells, it allows for the possibility of high-throughput DFT calculations of high-order multi-component systems such as high-entropy alloys and is ideally suited for use with more accurate but costly electronic structure approaches, such

as hybrid functionals [32] and GW [33]. Finally, the SSOS approach can be used to calculate any property that can be modeled by a short-range cluster expansion, such as bandgap, vibrational entropy and bulk modulus, and such should become a valuable tool for materials discovery of multi-component systems.

Acknowledgments

B.P.U. acknowledges support by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the (U.S.) Department of Energy under contract DE-AC52-06NA25396.

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Table I. Top 2% most stable single-phase bcc HEA compositions identified from the present high-throughput screening. Phase stability of HEAs is ranked according to their fully relaxed instability energies. The four experimentally verified bcc HEA compositions are shown in bold.

bcc HEAs	Instability energy (eV/atom)
Mo ₁ Nb ₁ Ta ₁ Ti ₁ W ₁	0.046
Mo ₁ Nb ₁ Ti ₁ V ₁ W ₁	0.048
Mo₁Nb₁Ta₁V₁W₁ [26]	0.068
Hf ₁ Mo ₁ Nb ₁ Ti ₁ Zr ₁	0.081
Mo ₁ Ta ₁ Ti ₁ V ₁ W ₁	0.081
Mo ₁ Nb ₁ Ta ₁ Ti ₁ V ₁	0.084
Hf ₁ Mo ₁ Nb ₁ Ta ₁ Ti ₁	0.086
Nb ₁ Ta ₁ Ti ₁ V ₁ W ₁	0.087
Hf₁Nb₁Ta₁Ti₁Zr₁ [27]	0.089
Hf ₁ Mo ₁ Nb ₁ Ti ₁ V ₁	0.092
Hf ₁ Nb ₁ Ta ₁ Ti ₁ W ₁	0.096
Mo ₁ Nb ₁ Ta ₁ Ti ₁ Zr ₁	0.101
Cr ₁ Mo ₁ Ti ₁ V ₁ W ₁	0.102
Mo₁Nb₁Ti₁V₁Zr₁ [29]	0.102
Cr ₁ Mo ₁ Nb ₁ V ₁ W ₁	0.104
Nb ₁ Ta ₁ Ti ₁ W ₁ Zr ₁	0.104
Hf ₁ Mo ₁ Nb ₁ Ti ₁ W ₁	0.113
Al ₁ Mo ₁ Ta ₁ V ₁ W ₁	0.114
Hf ₁ Mo ₁ Ta ₁ Ti ₁ Zr ₁	0.115
Cr ₁ Mo ₁ Nb ₁ Ti ₁ V ₁	0.115
Hf₁Nb₁Ti₁V₁Zr₁ [31]	0.116
Cr ₁ Mo ₁ Ta ₁ V ₁ W ₁	0.117
Hf ₁ Mo ₁ Nb ₁ Ta ₁ Zr ₁	0.118
Cr ₁ Nb ₁ Ti ₁ V ₁ W ₁	0.118
Mo ₁ Nb ₁ Ti ₁ W ₁ Zr ₁	0.121
Cr ₁ Mo ₁ Nb ₁ Ti ₁ W ₁	0.123
Al ₁ Cr ₁ Mo ₁ V ₁ W ₁	0.123

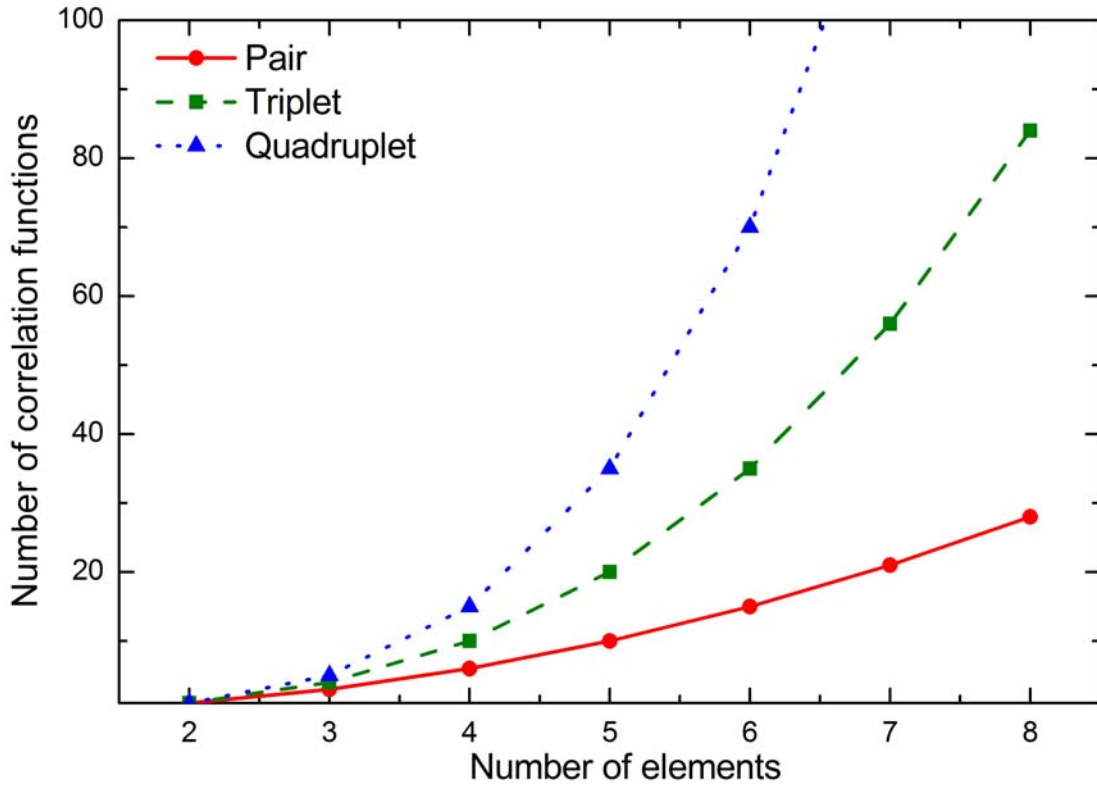


FIG. 1 Total number of correlation functions for a single cluster in high order multi-component alloys. Results for the nearest-neighbor pair, triplet, and quadruplet cluster in a fcc lattice are shown as a function of the number of alloying elements. Unlike in a binary alloy where the point function is unique, many distinct decorations for a cluster exist in a multicomponent alloy. For example, for a M -component alloy, there are $M(M-1)/2$ different types of decorations for each pair cluster.

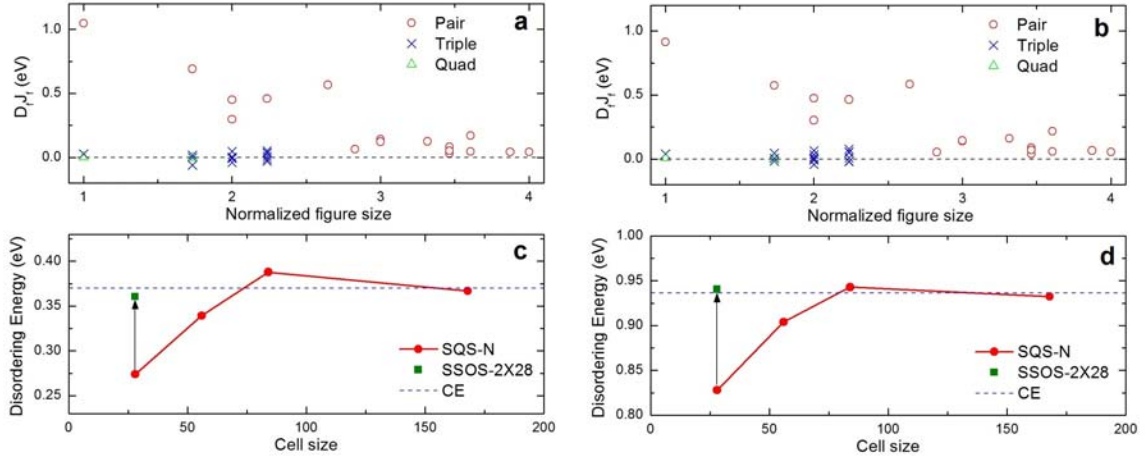


FIG. 2 Comparisons of disordering energies (eV per f.u.) of spinel oxides calculated using SSOS, SQS, and CE methods. Fitted ECIs for cation distribution in the octahedral sublattice in inverse MgAl_2O_4 and ZnAl_2O_4 are shown in (a) and (b), respectively. All figure sizes are normalized with respect to that of the nearest-neighbor pair. The slow-decaying pair interactions and the weak many-body (triplet and quadruplet) interactions are characteristic of Coulomb interactions. The calculated disordering energies for MgAl_2O_4 and ZnAl_2O_4 are shown in (c) and (d), respectively.

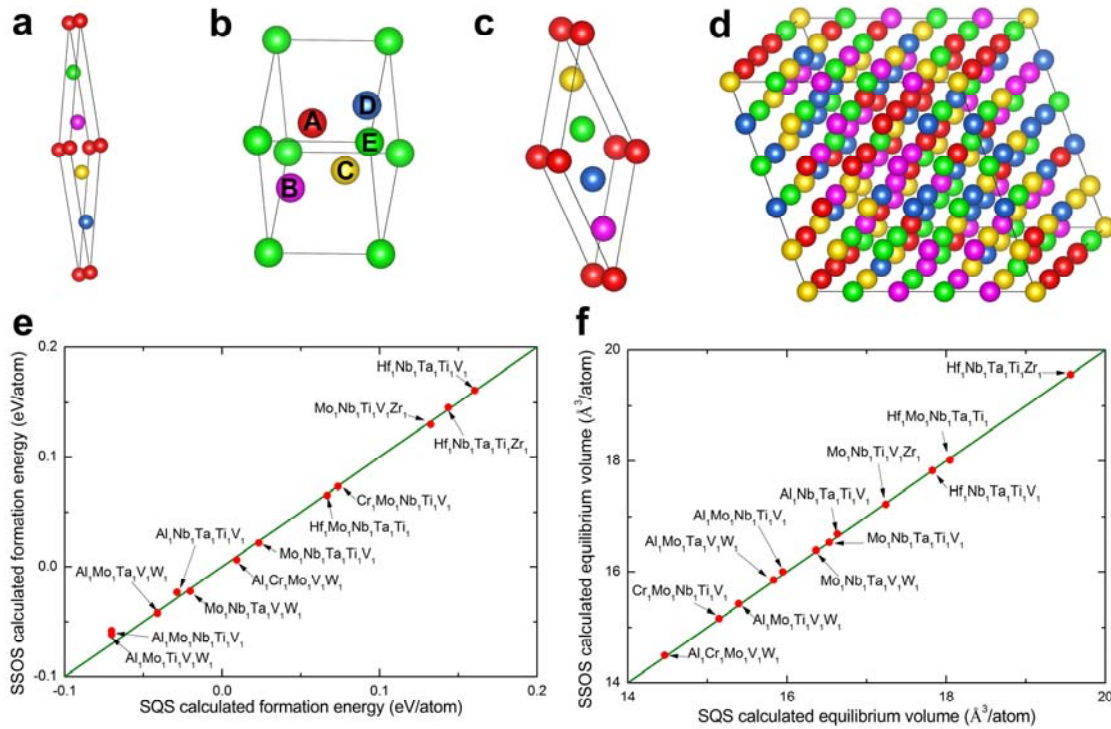


FIG. 3 Modeling the random bcc $A_1B_1C_1D_1E_1$ alloy using the SSOS and SQS approaches. The three 5-atom/cell structures σ_1^{SSOS} , σ_2^{SSOS} , and σ_3^{SSOS} in SSOS-3 \times 5 are shown in (a), (b) and (c), respectively. The 125-atom SQS structure is shown in (d). All structures are shown in their ideal, unrelaxed forms. Comparisons between SSOS calculated and SQS calculated formation energies and equilibrium volumes for 12 random bcc $A_1B_1C_1D_1E_1$ alloys are shown in (e) and (f). Only volume relaxations have been performed for this comparison. The green solid lines represent perfect agreement between the two methods.

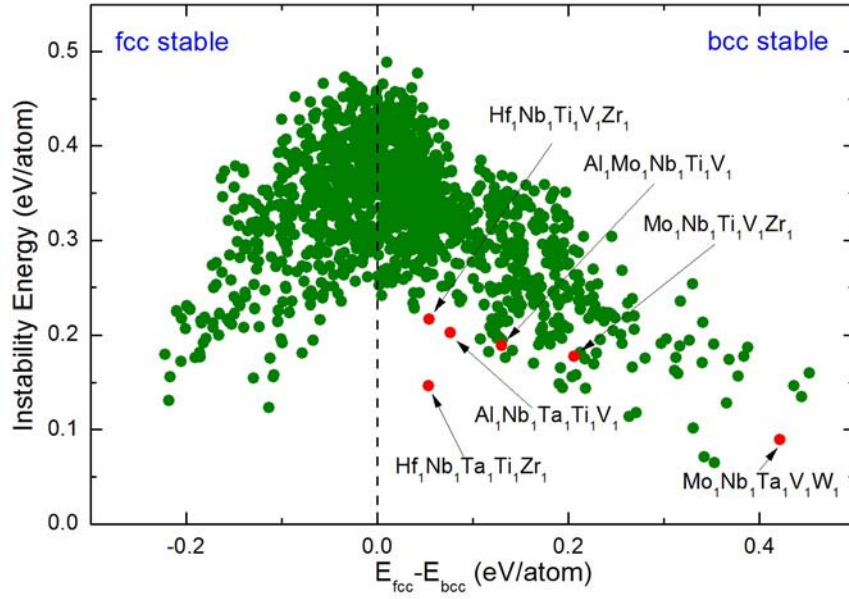


FIG. 4 High-throughput screening of potential single-phase bcc HEA compositions. Instability energy vs. lattice stability plot for 1337 HEA candidates is shown. The six experimentally confirmed bcc HEA compositions are marked in red. For reasons of efficiency, only volume relaxations have been performed for this initial screening. For HEA candidates with relatively low volume relaxed instability energies, we further allow all internal atomic positions to relax in our SSOS calculations, and such results are reported in Table I.