

Crystal structure prediction using cluster expansion

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Abstract

Finding the most stable crystal structures of compounds is one of the classical problems in inorganic solid state physics and metallurgy, because knowing the structure of perfect crystalline solids holds the key to material properties. This in itself presents a complex problem as even for a binary solid described by a unit cell with N sites there can be 2^N possible structures. A direct quantum mechanical calculation of all these configurations in search of the ground state structure is not computationally feasible. A solution to this problem is the parameterization of the configurational energy so that the dependence of the energy on the configuration can be reproduced with high accuracy. One way to do this is to use the cluster expansion of the configurational energy in terms of effective atom-atom interactions. Cluster expansion is comparable to a generalized multibody Ising model. It can also be viewed as a basis-set expansion in n -body clusters associated with n Bravais lattice points and effective cluster interactions (ECI) that specify configurational energies. Using a truncated series expansion, the coefficients can be obtained by fitting the above equation to a small set of energies calculated directly from first principles. Once the coefficients are obtained the above approximation can be used to predict the energy of any configuration and can in turn be used to predict the ground state configuration. The objective of this work is to understand the idea of cluster expansion and apply it to some simple binary structures (e.g. Al-Ti, etc..) and predict the ground state configuration given its composition.

Introduction

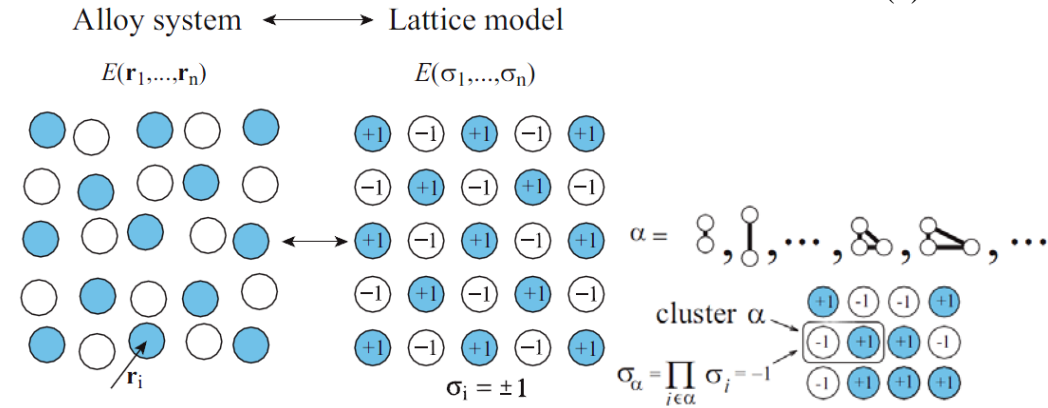
A classic dilemma in solid-state physics, structural inorganic chemistry and metallurgy is how to predict the stable crystal structure of a compound given only its composition. The cluster expansion (CE) is increasingly used as a valuable tool for predicting and interpreting thermodynamic effects in a wide class of materials and problems, including precipitation, solubility limits, ionic diffusion, surface alloying etc. As a means for multiscale modeling based on density-functional theory (DFT) electronic-structure energetics, the CE is a basis-set expansion in n -body clusters (associated with n Bravais lattice points) and effective cluster interactions (ECI) that specify configurational energies. With such a simple energy model in hand, it becomes feasible to explore quickly the large number of candidate crystal structures needed for structure prediction. Cluster expansion amounts to decomposing the energy of an alloy as a function of energies from several smaller clusters of atoms. In principle the energetic contribution of each type of cluster can be simply determined by a least-squares fit to the energies of a small number of atomic arrangements calculated with accurate quantum mechanical methods. Except for implicit DFT errors in the energy database, the CE is exact for an infinite

basis, but impractical if not vastly truncated. Once a cluster expansion has been constructed, it becomes possible to efficiently explore a large number of candidate structures by direct calculation of energies from the expansion.

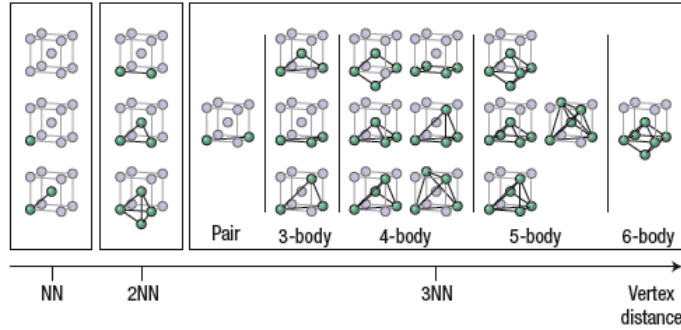
Theory: Cluster Expansion

Even for a binary A_nB_m solid described by a unit cell with N sites, there can be $\sim 2^N$ possible structures (denoted as σ in the following). A direct quantum-mechanical evaluation of the total energy, $E_{QM}(\sigma) = \langle \Psi | H(\sigma) | \Psi \rangle$ (where Ψ is the wavefunction and $H(\sigma)$ is the electronic Hamiltonian), of all 2^N configurations σ in search of one that minimizes the energy is practically impossible. Yet finding the stable structure among an astronomical number of possibilities is important because structure often decides many properties of the system and because our notions of bonding are based on our understanding of the stable structures. To access configurational energetics on a larger scale, one can renormalize away the explicit electronic coordinates of $E_{QM}(\sigma)$ and formulate instead a model Hamiltonian with fewer and more transparent parameters, reproducing the dependence of $E_{QM}(\sigma)$ on σ with high accuracy. An example is a cluster expansion of the configurational energy $E(\sigma)$ in terms of effective atom–atom interactions J ,

$$E_{CE}(\sigma) = J_0 + \sum_{\text{sites}} J_i \hat{S}_i + \sum_{\text{pairs}} J_{ij} \hat{S}_i \hat{S}_j + \sum_{\text{triples}} J_{ijk} \hat{S}_i \hat{S}_j \hat{S}_k + \dots \quad (1)$$



Here, \hat{S}_i denotes the fictitious spin variable which indicates if lattice site i is occupied by an A atom (in which case $\hat{S}_i = -1$) or a B atom ($\hat{S}_i = +1$). The variable $\{\sigma\}$ denotes collectively the set of all 2^N configurations. The interaction energies $\{J\}$ represent the contribution of each group of atoms to $E(\sigma)$. The following figure shows the smallest such ‘many-body interaction types’ (MBITs) for a body centered cubic (bcc) lattice, up to a maximum site separation of third nearest neighbors.



We could determine the numerical values of the corresponding coefficients $\{J\}$ by fitting equation (1) to a set of $\sim N$ directly calculated $E_{\text{QM}}(\sigma)$. Once we know the coefficients, we can then effortlessly compute $E_{\text{CE}}(\sigma)$ of many other configurations, thereby identifying the stablest ‘ground state structures’ out of 2^N possibilities, or performing desired thermodynamic averages over many configurations. Furthermore, once the coefficients are known, one can subject equation (1) to finite temperature modeling (such as Monte Carlo), finding the phase diagram, thermodynamic properties, short-range order and so on.

Enthalpy of formation and ground states

Stability of the phases of an alloy is completely described by the knowledge of their free energies. The enthalpy of formation (dH) is the cohesive energy of a compound relative to the composition-weighted average cohesive energies of its pure elements. Compound formation is favored when dH is negative. To determine the ground states of a system one needs to find, as a function of composition, the ordered structures that have a enthalpy of formation lower than any other structure (or) any linear combination of structures that gives the proper composition. A convex-hull can be obtained by connecting the lowest energy ordered phases. The convex-hull represents the free energy of the alloy structures at $T = 0\text{K}$. The minimization of free energy (and structure computation) requires the construction and minimization of a convex hull curve. Once the hull of ground state energies of various structures is constructed, the configurations with energy above the limiting boundary of the convex hull are deemed unstable. This result is important for ab-initio calculation of the phase diagram since these methods (monte-carlo based) require the knowledge of ground state energies.

Pearson index for the representation of the crystal structures

The ground states in this work are represented in terms of its Pearson index as it provides a compact notation summarizing all the information regarding any crystal structure. The Pearson symbol indicates the crystal symmetry and the number of atoms in the unit cell. The notation is in the form $pTnn$ where p labels the point symmetry and takes values a, m, o, t, h, c for asymmetric, monoclinic, orthorhombic, tetragonal, hexagonal and cubic. T describes translational symmetry and can be P, A, B, C, I, F, R for Primitive, (A, B, C) centered, Body centered, Face centered and Rhombohedral. The final segment, nn , gives the number of atomic sites per unit cell. For example, NaCl has a face-centered (F) cubic (c) structure with 8 atoms in the cube, so it is designated **cF8**.

Implementation

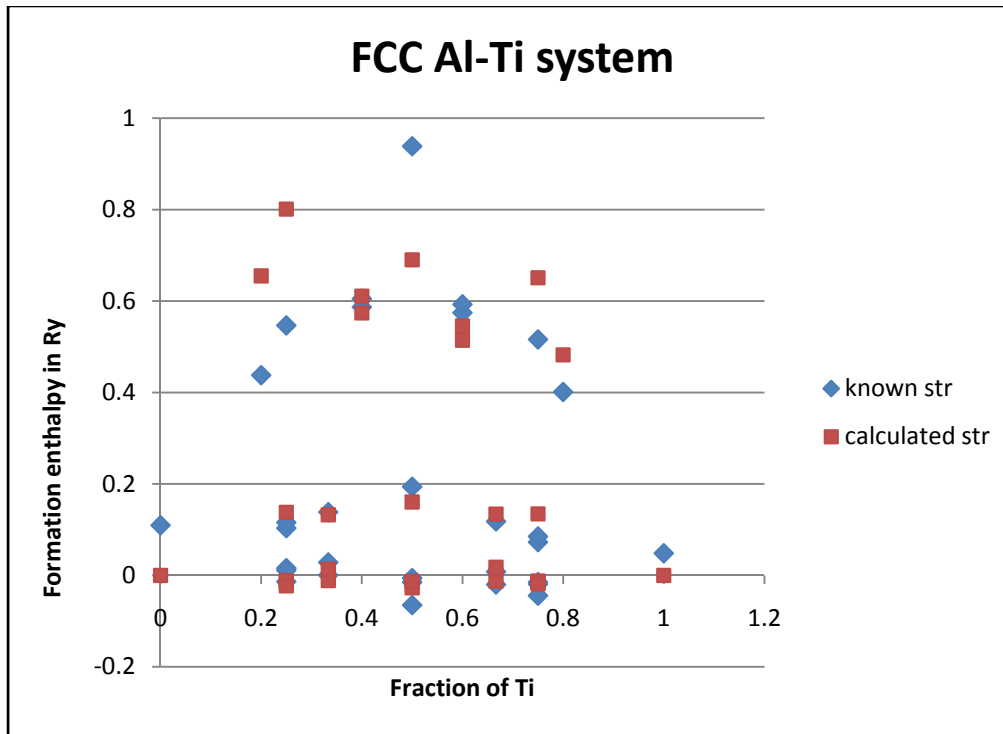
The software MAPS included in the package Alloy theoretic tool kit (ATAT) was used to construct the cluster expansion. Given a parent lattice and the type and the number of atoms, MAPS proposes several structures with fixed basis. Two shell scripts (runstruct_pwscf and copy_run) were written to combine the functioning of both PWSCF (gives the energy of the structure from first principle calculation) and MAPS. The shell script runstruct_pwscf reads in the structure generated to convert it to appropriate input file readable by the PWSCF executable (pw.x) and retrieves the final energy from the output file of the PWSCF and prints it to a new file named 'energy' so that MAPS can perform the cluster expansion. Once sufficient number of structures are generated the second shell script 'copy_run' goes through each of these structures and invokes the shell script 'runstruct_pwscf' and moves on to the next structure once the energy of the structure is made available by the former shell script.

Results

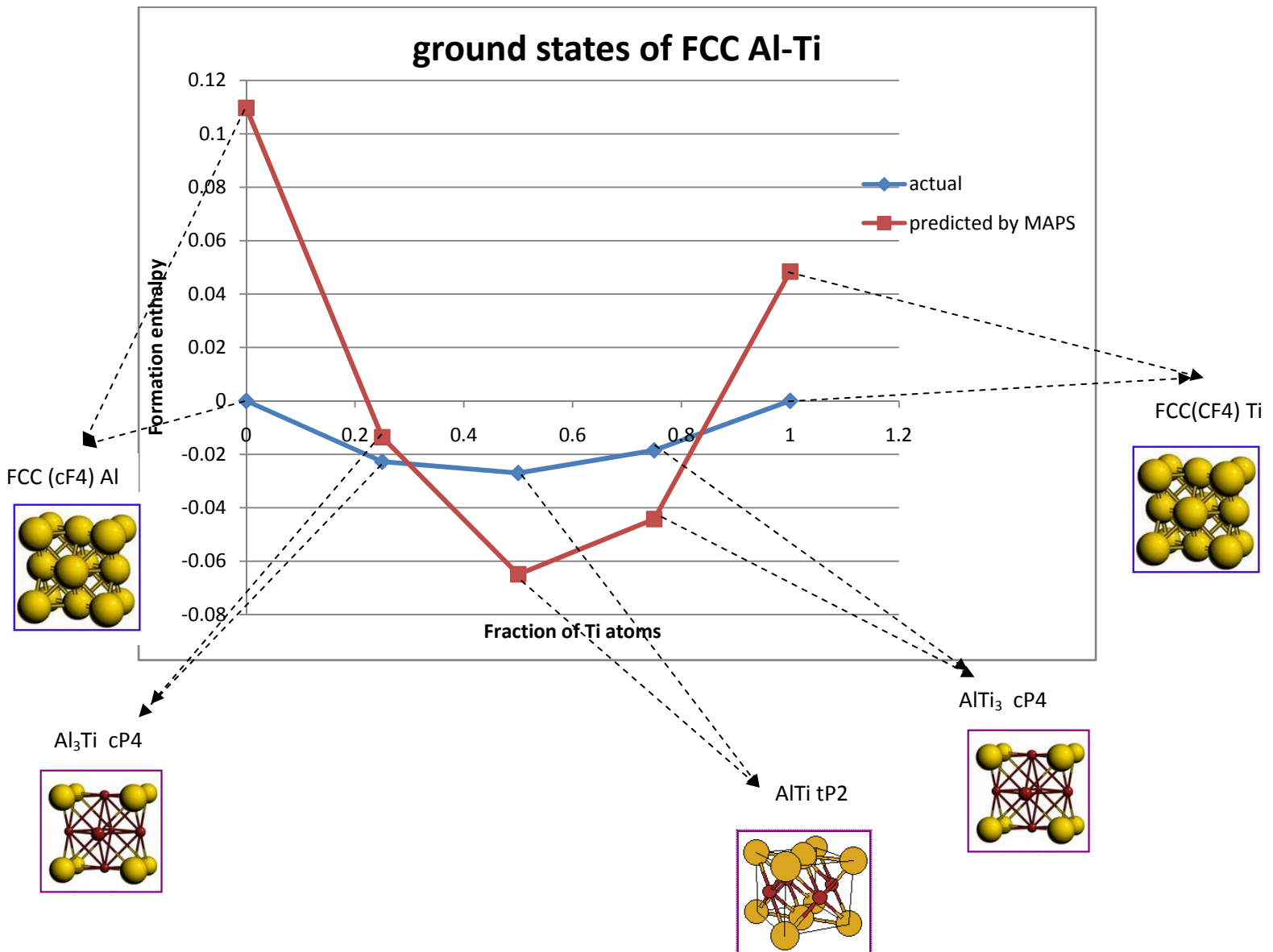
Two Al-Ti systems (FCC and HCP) are considered here. Using the MAPS software around 40 structures of both the system were generated and cluster expansion performed. It took around 2-3 days for a Pentium 3GB 2.8 GHz machine to compute the energies of 40 structures and corresponding cluster expansion. Convergence of k points and the cutoff were checked for both Al and Ti and the highest value of both the cases used (10x10x10 and 80Ryd).

FCC Al-Ti system

The following figure shows the formation enthalpy obtained through first principle calculations and predicted by MAPS. Both the energies are pretty close to each other indicating the cluster expansion is capable of predicting the formation energies of any arbitrary configuration of FCC Al-Ti system.

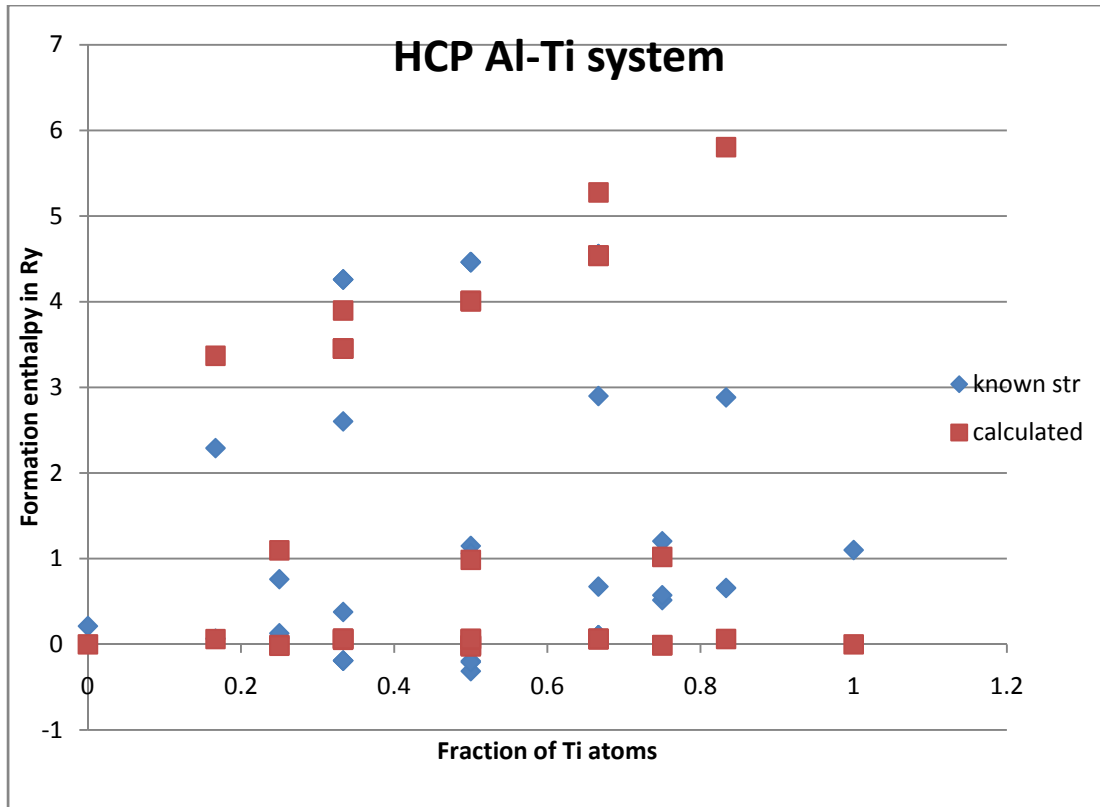


The ground states predicted by MAPS are compared with the ones calculated through first principle calculations in the following plot. Even though both (MAPS and first principle calculation) agree on the structure of the ground state configuration at the given composition (the most stable one is the primitive tetragonal Bravais lattice), the ground state energies computed by MAPS are a bit off from the actual ground state energies. This indicates energies of more structures (MAPS user guide recommends around 30-50 structures for a reasonable cluster expansion) are needed for an accurate cluster expansion. But it comes at a high cost in terms of the computational time required.



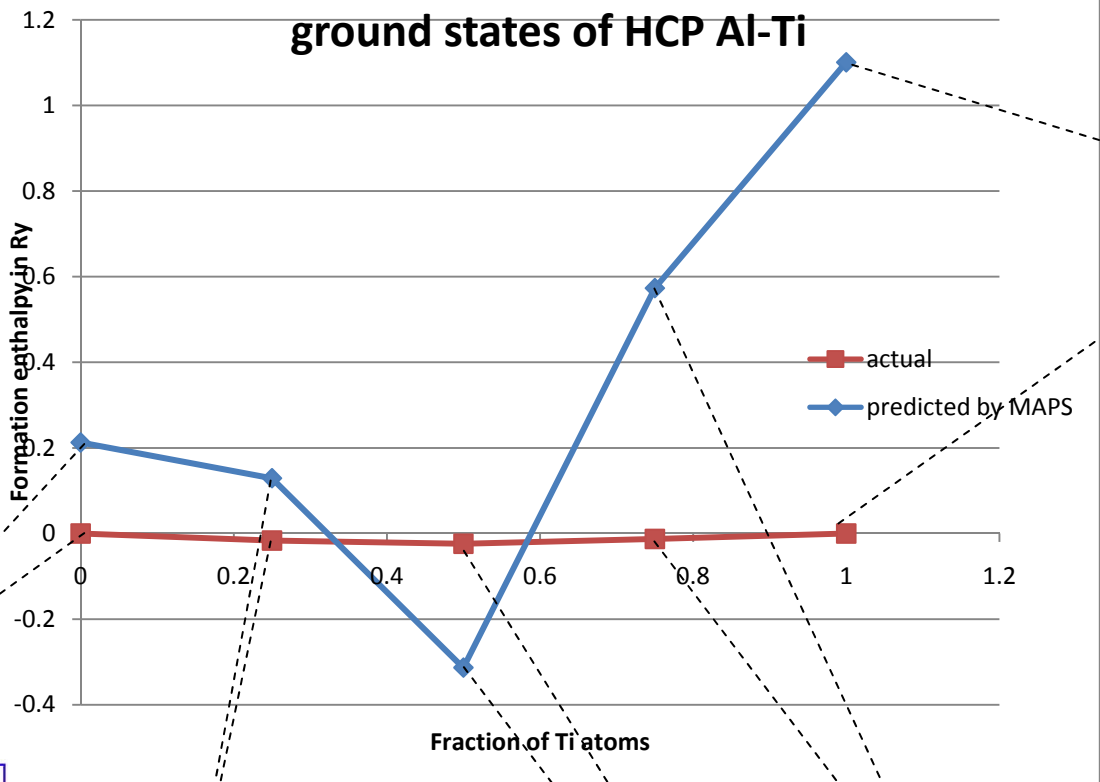
HCP Al-Ti system

Comparison between the predicted energies and the actual energies is given below. Compared to the FCC system the deviation of the predicted values are much larger in this case though the number of structures used is almost the same as before.

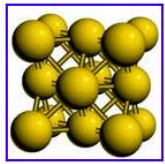


The ground states (both predicted by MAPS and the actual ones) are given in the plot below. As before, both (MAPS and first principle calculation) agree on the structure of the ground state configuration at the given composition, but the ground state energies computed by MAPS are far off from the actual ground state energies whereas the deviation wasn't this large in the case of FCC Al-Ti system. This might point to the fact that the requirement of the number of input structures for an accurate cluster expansion can vary from one crystal structure to another. In the reference [6] the cluster expansion for AuCu has been obtained by considering only 21 input structures.

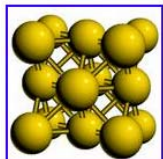
ground states of HCP Al-Ti



FCC (cF4) Al



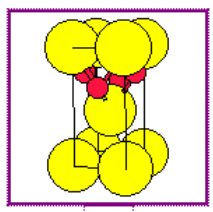
FCC (cF4) Ti



Al₃Ti oP4

AlTi₃ oP4

Al₂Ti₂ oP4



Conclusion

The accuracy of the cluster expansion in predicting the ground state structures is crucial because the ab-initio calculation of the phase diagram (monte-carlo based methods) require the knowledge of ground state energies. The cluster expansions of two systems (FCC and HCP Al-Ti) were studied. The cluster expansion for the FCC structure was found to be reasonable and can be used further for the computation of the phase diagrams. On the other hand, the error was found to be very high for the HCP structure. This means a refinement of the cluster expansion by including more input structures is needed. It also points to the fact that the number of input structures required for the learning of the proper cluster expansion varies from system to system. Though cluster expansion is a powerful tool its application is limited by the fact that it can be applied only to a fixed parent lattice structure, but several other phases are known to exist.

References:

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