

Crystal structure prediction using cluster expansion

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 (σ) in search of the ground state structure is not computationally feasible. A solution to this problem is the parameterization of the configurational energy ($E_{CE}(\sigma)$) 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 J:

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

Where \hat{S}_i denotes the pseudo spin variable which indicates whether the lattice site is occupied by atom A ($\hat{S}_i = +1$) or an atom B ($\hat{S}_i = -1$). The interaction energies J represent the contribution of each group of atoms to the energy. Cluster expansion is comparable to a generalized many-body 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. Au-Cu, Ni_3V etc..) and predict the ground state configuration given only its composition.

References:

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