

## Thesis Changes Log

**Name of Candidate:** Vadim Sotskov

**PhD Program:** Materials Science and Engineering

**Title of Thesis:** Data-driven design of multicomponent alloys

**Supervisor:** Prof. Alexander Shapeev

*The thesis document includes the following changes in answer to the external review process.*

**Reviewer: Vladislav Blatov**

**Q1:** First of all, the on-lattice approach seems to be applicable only to the structures where the general arrangement of atoms in the space is already known. Is this restriction correct, and is there any way to expand this approach to the systems with a priori unknown positions of atoms? For example, not all high-entropy alloys belong to the three main structure types; can we predict the alloys beyond this triad?

**Re:** The following has been added to section 4.4:

Though on-lattice CSP can't operate in cases of an undefined geometry (which is a significant drawback in comparison with USPEX), the main takeaway of this work consists in possibility of applying a conceptually new generative approach in the CSP field. The extension of on-lattice CSP to materials with the undefined lattice geometry can be done by combining the algorithm with geometry-sensitive potentials like MTP. Once an atom is added to the structure, the growing configuration can be relaxed with the MTP. Thus, the geometry is defined in real time. Such direction is of high scientific importance and is expected to be performed in the future.

**Q2:** Have the author analyzed the experimental data on the Nb-Mo-Ta-W systems? For example, the Nb-W system contains a continuous series of solid solutions over the entire concentration range, without any intermetallic phases. Doesn't this mean that all the "new" phases found by the author are just approximations of solid solutions of the appropriate concentration? Have the author checked the stability of the revealed ordered phases compared with a (random) solid solution of the corresponding composition?

**Re:** The following has been added to the section 4:

Note that in this work all the predicted phases are benchmarked with AFLOW database, that contains only 0 K DFT calculations. Thus, phase stability of the predicted phases at finite temperature is not investigated. However, it is assumed that all the discovered phases remain ordered within a moderate range of temperatures (0 - 300 K), i.e. they are not approximations of a high-temperature disordered phases. The order-disorder phase transition in Nb-Mo-Ta-W alloys is out of the scope of this work.

**Q3:** The introduction of the “alchemical” atom concept is not entirely clear. In fact, it seems equivalent to considering the formation of an equiatomic alloy at the boundary of a system. Does this always correspond to the composition of the system?

**Re:** The description in section 3.1 was rephrased:

To minimize this effect a strategy which I called the “alchemical” potential was applied. It consists in representing the energy of an incomplete neighborhood as an average of energies of all the alternative neighborhoods that can be created instead of the incomplete one.

...

The idea of averaging instead of choosing a lowest energy neighborhood comes from the fact that initially the trajectory of a structure generation algorithm is unknown. The averaging allows one to minimize the possibility of missing the lowest energy structure without causing an abrupt change in growth trajectory, since during this process only one “real” atom is added. Choosing a lowest energy neighborhood instead might cause an opposite effect.

**Q4:** Page 33: “...in a BCC lattice the neighborhood consists of 9 atoms, while in a FCC lattice 13 atoms” – perhaps, the clusters including the central atoms are meant here since the neighborhood includes 8 and 12 atoms, respectively. But the question arises: Is the consideration of 8 most close atoms in BCC structure sufficient for correct description of the bonding? Usually, 8+6 atoms are considered in this case

**Re:** Added in section 2.3:

Thus, in a bcc lattice the neighborhood consists of 9 atoms, while in a fcc lattice 13 atoms form the neighborhood (including the central atom in bcc and fcc). However, in case of bcc it is common to include second nearest neighbors (i.e., 15 atoms in total).

**Q5:** why was the phase stability determined by Helmholtz energy values, not by Gibbs energy?

**Re:** The following added to section 5.1:

The stability of the competitive phases was analyzed by calculating Helmholtz free energy at finite temperature (the pressure was neglected since the experiment was conducted under atmospheric pressure)

All the listed minor issues were resolved in the thesis.

**Reviewer: Max Hodapp**

**Q1:** I did not realize until the middle of Section 2.4.1 that the on-lattice CSP is actually your own development since the section is somewhat “hidden” in the literature review section. Therefore, I propose to create a separate section for the Sections 2.4.1, and 2.4.2., or combine them into Section 3.

**Re:** Moved these sections into Chapter 3.

**Q2:** More to the content of Section 3: Section 3 discusses some very specific implementation aspects that seem to be of limited use for a reader who simply wants to understand the proposed methodology. Moreover, I couldn’t find any information on whether the code is actually published

somewhere. If this is the case, I recommend to mention the link to the GitHub page (or alike), and move Section 3.1 to the appendix. If not, then I recommend to remove Section 3.1.

**Re:** Moved technical details to Appendix. Added GitLab link.

**Q3:** I would also appreciate if you could give some more details on how the “growth part” in the on-lattice CSP works. I guess this growth should follow some symmetry operation? I would suggest to explain this in more detail by means of one of the structures that are shown in Figure 4-1.

**Re:** Added the following to the section 3.1:

Note that at this stage the “growing” configuration is not periodic (does not have a supercell) and it can be considered as the collection of individual atoms. Therefore, during this stage the growth do not follow any symmetry operations. The growth is guided only by an interatomic interaction model.

**Q4:** As mentioned previously, the advantages (and possibly disadvantages) of your CSP algorithm with respect to others methods, like the one used in USPEX, should be discussed in more detail. For example, some estimate of the computational complexity would be helpful for the reader who simply wants to know which method to use for, say, an n-component alloy.

**Re:** The following was added to the section 4.4:

In general, the advantage of on-lattice CSP in comparison with the state-of-art CSP methods like USPEX can be observed when discovering materials with a pre-defined lattice. For example, USPEX was used to search the structures in quaternary C-H-N-O chemical space, where configurations have an undefined geometry Naumova *et al.* [2021]. USPEX runs were performed with 8-36 atoms per unitcells. Eventually nearly 1800000 DFT structural relaxations were performed, which require significant computational resources. In case of Nb-Mo-Ta-W alloys, that are presented in this work, only a few hundreds of DFT calculations were required. Such reduction, first of all, is possible due to application of LRP and CE for energy evaluation. Secondly, the presence of a fixed geometry significantly reduces the size of the configurational space of candidate materials. Moreover, the presented algorithm can discover multicomponent structures among supercells with larger number of atoms. Thus, several structures, discovered in Nb-Mo-Ta-W, had more than 140 atoms in the supercell. Though on-lattice CSP can't operate in cases of an undefined geometry (which is a significant drawback in comparison with USPEX), the main takeaway of this work consists in possibility of applying a conceptually new generative approach in the CSP field.

**Q5:** Moreover, the use of the alchemical potential is not fully clear to me. LRPs should be efficient enough to loop over all possible neighborhoods, and then take the one with the lowest energy, or maybe not?

**Re:** The following was added to the section 3.1:

The idea of averaging instead of choosing a lowest energy neighborhood comes from the fact that initially the trajectory of a structure generation algorithm is unknown. The averaging allows one to minimize the possibility of missing the lowest energy structure without causing an abrupt change in growth trajectory, since during this process only one “real” atom is added. Choosing a lowest energy instead might cause an opposite effect.

**Q5:** It is also not obvious to me why you are using a combination of CE and LRPs. If LRPs are more efficient, as mentioned in Section 2.3.5, then why not use them all the time?

**Re:** The following was added to the section 4.1:

For binary as well as ternary systems on-lattice CSP was used in combination with CE, since in this case it has accuracies comparable to that of LRP. In case of Nb-Mo-Ta-W the LRP was applied in order to limit the number of DFT calculations.

**Q6:** As mentioned under point 3, details on the magnetic LRP should be discussed, if applicable.

**Re:** Actually, it is not a “magnetic” LRP. It is ordinary LRP fitted to the energies, obtained with spin-polarized DFT calculations.

The following explanation was added to the section 6.2:

here and further LRP fitted to non-spin polarized DFT is called “non-magnetic”; to spin-polarized DFT - “magnetic”

**Reviewer: Sergey Levchenko**

**Q1:** “In this work I propose a methodology for designing multicomponent alloys using on-lattice modeling.

This approach assumes that the simulated system has an ideal lattice with fixed atomic positions.”

– Was

some relaxation still accounted for by fitting cluster expansion model to relaxed energies?

**Re:** The following was added to the abstract:

In each simulation method LRP and CE are fitted to energies of the structures relaxed with DFT.

**Reviewer: Artem Oganov**

Minor comment has been addressed.

**Reviewer: Gus Hart**

**Q1:** This is exactly the same as the CE. In the CE, we may limit the clusters to short range interactions, just like you are selecting a neighborhood here. I would like to see more discussion about CE vs. LRP. Given this short description, I think they are actually the same. I think the tensor contraction gives a way to limit the number of interactions, but this can be done (efficiently) in CE too.

**Re:** Indeed LRP can be considered as a special case of CE where many-body interactions are represented using a tensor-train format. The following was added to the section 2.3.5:

The number of ECIs can be truncated, but this requires additional techniques such as compressed sensing Nelson et al. [2013], that, on practice, do not sufficiently reduce the amount of required *ab initio* data in case of multicomponent systems. Hence, this model requires an additional improvement.

The solution, proposed recently by A. Shapeev, consists in representing a fixed-lattice interaction model in a tensor-train format Shapeev [2017]. The proposed model was named the low-rank potential (LRP). Similarly to CE, an atomic structure in the LRP model is represented by an ideal crystalline lattice, where each site corresponds to an atom of a certain chemical type. The sequence of chemical types of atoms, surrounding any atom of the crystalline lattice is called the neighborhood of this atom. This sequence is given by a collection of neighbors of a chosen site on a defined crystalline lattice.

All the personally given comments were addressed.