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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Vadim Sotskov

PhD Program: Materials Science and Engineering

Title of Thesis: Data-driven design of multicomponent alloys

Supervisor: Professor Alexander Shapeev

Name of the Reviewer: Vladislav Blatov

I confirm the absence of any conflict of interest	**Date: 02-10-2023**

Reviewer's Report
The dissertation by Vadim Sotskov is devoted to development of a special group of methods for mathematical modeling of crystalline substances. The main purpose of the work is to extend these methods to multicomponent chemical systems and to overcome the problem of combinatorial explosion when sampling the corresponding configurational space. The text of the dissertation is written in good and clear English and is organized in a traditional way. A brief introduction proves the importance of the main goal and states that the computational modeling becomes an essential part of the creation of new materials. However, a crucial bottleneck is the complexity of the chemical system under consideration: even four different components can make the exploration of the configurational space too time-consuming. At the same time, the development of multifunctional materials or tuning the properties of existing materials often requires doping with many components. Moreover, new classes of intermetallic substances such as compositionally complex alloys or high-entropy alloys are inherently multicomponent and consist of five or more different metals. Thus new approaches are needed to deal with such complicated systems. The next part of the dissertation contains a more detailed overview of the multicomponent

intermetallic systems with a special stress on the high-entropy alloys, which exploration had an explosive growth in the past 10-15 years. The author mentions an important feature of the high-entropy alloys to belong to one the three structure types, face-centered cubic, body-centered cubic or hexagonal close packing. This feature is crucial for the method that the author proposes further. Next, the author describes the main existing methods for the computational modeling of materials and their properties and pays special attention to the approaches where empirical potentials are parametrized using the results of DFT modeling. Such approaches essentially accelerate the modeling but again they face the problem of combinatorial explosion. Thus we come to the main part of the dissertation, which includes the theoretical description of the proposed approach and its technical implementation. The theoretical base of the approach is given along with the description of the background and problems of the known computational methods. In general, Vadim Sotskov proposes to generate possible atomic configurations using a regular lattice as a template. This idea is not novel, but the author develops an original algorithm where the positions of the lattice are subsequently occupied that mimics crystal growth. The potentials of the atoms are calculated in accordance with the schemes developed by the scientific advisor of the author, Alexander Shapeev, and as a result, the energy of the trial configurations is computed very fast. Then this algorithm is extended to the canonical Monte Carlo scheme to make it applicable for modeling chemical systems at non-zero temperatures.

The next part contains a comprehensive description of technical details of the computer implementation of the proposed approach. The author uses a combination of C++ and Python to gain an optimal efficiency and to provide a user-friendly interface as well as multi-platforming.

Finally, three last parts present applications of the proposed approach to multicomponent intermetallic Nb-Mo-Ta-W system, high-entropy carbide $HfTaTiNbZrC_5$ and three-component CrCoNi system. The examples are perfectly chosen to demonstrate the main advantages of the approach in finding stable phases, exploring systems at different temperatures, and studying local ordering in alloys.

In general, reading the dissertation leaves quite good impression. Vadim Sotskov proves his deep knowledge of the subject; he has good skills in the application of all main methods of computational modeling of crystalline materials at the micro-level. He is also aware of theoretical and experimental state-of-the-art achievements in the field of intermetallic compounds including multicomponent systems and high-entropy alloys. His critical analysis of

these achievements is sufficiently complete and correct. Thus the goal of the work is well substantiated and topical. The literature is cited appropriately and the list of the references provides a nice overview of the topic. This is especially valuable since thousands of papers have been published in this field in the last few years.

The proposed approach is certainly viable and useful. The theoretical base of the developed algorithm of the on-lattice generation of crystal structures is quite robust; the algorithm is original and easy to implement. The examples of complicated intermetallic systems convince that the approach is rather universal to be applied to other multicomponent crystalline phases. The use of various computational tools, the description of the results and the conclusions made in this principal part of the dissertation are professional and persuasive. This impression is confirmed by two publications of the author in high-level international journals npj Computational Materials and Physical Review Materials.

Nonetheless, some issues and questions remain after reading.

1. 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?

2. 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?

3. 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?

4. 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 a BCC structure sufficient for correct description of the bonding? Usually, 8+6 atoms are considered in this case.

5. Page 60: why was the phase stability determined by Helmholtz energy values, not by Gibbs energy? On the contrary, Gibbs energies are mentioned in the caption to Fig. 5-4.

Minor issues:

- How can formulae 2.2 and 2.3 be derived from 2.1?
- Are functions in 2.15 invariant under reflections? If not, why only rotations are taken into account?
- Page 32: "chemical degrees of freedom" – what does it mean?
- Page 52: you talk first about B2(Nb;W), then about B32(Nb;W). Is it a typo?
- Fig. 5-5: why does the figure not show the distribution of each metal atom individually? For example, it is unclear from the figure that NbC perfectly mixes with all other carbides.

I hope, these issues will be resolved in the thesis defense. In any case, my strong opinion is that the dissertation is very well prepared and Vadim Sotskov certainly deserves a PhD degree.

Provisional Recommendation

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*