Skoltech

Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Zahed Allahyari

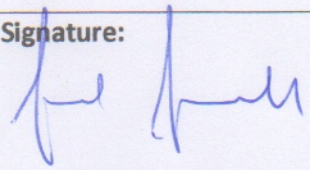
PhD Program: Materials Science and Engineering

Title of Thesis: Coevolutionary Search for Materials with Optimal Properties in the Space of Binary Systems

Supervisor: Prof. Artem Oganov

Date of Thesis Defense: 6 April 2020

Name of the Reviewer: Prof. Sandro Scandolo

I confirm the absence of any conflict of interest.	**Signature:**  17/03/2020 **Date: DD-MM-YYYY**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

It's been a pleasure for me to read the thesis submitted by Mr Zahed Allahyari as a requirement for the PhD degree in Materials Science and Engineering at Skoltech.

The thesis summarizes an impressive amount of work, both methodological and computational, aimed at discovering new materials with enhanced hardness or magnetic properties.

The thesis is structured in six chapters, three of which lay the theoretical bases of the methods, the forth one introduces a simple, yet crucial strategy to speed up the search, and the remaining two chapters describe the application of the methods to specific classes of chemical compounds.

Chapter 1 describes the basic elements of structural optimization within a given crystal structure and the level of theory used to determine its cohesive energy, an essential indicator to determine the stability of a compound. The choice of the GGA-PBE level of theory is a good compromise between chemical accuracy and need to consider a very large number of candidate structures.

Chapter 2 reviews the general ideas at the basis of the evolutionary algorithm employed throughout the thesis. The presentation is complete and clear, but occasionally a bit too succinct. For example, I suggest the candidate adds a short explanation of the rationale behind the choice of a quadratic dependence on the fitness rank in the roulette wheel method (p. 10).

Chapter 3 introduces one of the original contributions of the candidate to the problem, namely the development of a method for the search and structural optimization of compounds that optimize several properties simultaneously. The candidate focuses on methods based on Pareto optimization theory and provides a complete overview of the different approaches and of their complexity. Finally, the candidate describes the application of the method to a set of binary systems (Mo-N, Fe-B, Mo-B), obtaining impressive predictive results both in terms of "predicting" known compounds (here prediction is equivalent to validation of the method) and in terms of identifying new compounds with potentially interesting properties. A few minor remarks regarding this Chapter: (a) the author says, on p. 14, that "generally there is no utopian solution for MO problems". I guess he means "MO problems do not necessarily have an utopian solution" (unless there are reasons to think that utopian solutions are almost never present in MO); (b) at p. 21 the author says that Chen's model for hardness is "more sensitive to numbers"- which numbers? And if so, do we have any reason to believe than the LO approach is better, even considering the problems with Chen's model?

Chapter 4 describes a clever rearrangement of the order of chemical elements with respect to Mendeleev's, aimed at grouping elements based on specific target properties of the compounds they form, rather than on their electronic states. The reordering is a crucial ingredient to speed up the search for new compounds. The idea is certainly interesting and appears to work, at least qualitatively. I believe though that the argument could be made more solid if a quantitative approach was used to determine its superiority. For example, on p. 34 the candidate says "it seems that USE has provided a slightly better map"; this is a very generic statement and to be honest it's hard see it on the figure. A quantitative assessment would be useful.

Chapter 5 describes how the different ingredients introduced in the previous chapters are combined into a single, powerful method for the computational search of new compounds with desired properties. The work of the candidate focuses in particular on the search for materials with enhanced magnetic or hardness properties. The results are indeed remarkable, as described in more detail in Chapter 6. Again the description is occasionally a bit too concise. For example, the superiority of the new Mendeleev number is not discussed in quantitative terms. Also, the question obviously arises as to whether the definition of the Mendeleev number can itself be optimised based on the target properties, instead of being based on an educated chemical guess. It is clear that the answer to these questions, especially the last one, goes beyond the scope of this work, however I would appreciate it if the candidate at least raises these questions in the thesis, as an outlook.

Finally, Chapter 6 describes an impressively large amount of calculations on a variety of different systems, where, once again, the candidates "predicts" both known and new compounds. I believe it will take a while before the materials science community will be able to "digest" the entire list of predicted compounds. There's certainly plenty of work ahead, not only for the candidate, but more broadly for the computational materials science community (to characterize these compounds in more detail), and for the materials synthesis community (to try and synthesise them). I have a few minor remarks on this chapter: (a) it would be nice to add a short description also of the Lyakhov–Oganov model of hardness; (b) at p. 48 I read that among the Mo-B compounds only MoB2 was studied before, but this in contradiction with what is reported three lines below; (c) I wonder whether B6P is composed of B12 icosahedra and therefore belongs to the well known class of hard B12 borides (it seems so, from the picture); (d) I'm not sure I understand the distinction between "suns" and circles/triangles in Fig. 30. I would understand a distinction between stable and unstable compounds, or between new and known compounds, separately though; (e) it would have been nice to understand the microscopic origins of the high hardness in some of the new compounds, though I agree that this goes beyond the scope of the present work.

A few additional typos are listed below:
1) p. 4: remove delta^2 in V(r) (below eq (1.4))
2) Most Figure numbers are incorrectly referenced in the text (especially from Fig. 20 onward). Please check also letters (e.g. on page 53, Fig. 29(1) is referenced as Fig 30a in the text.

In summary, the thesis presents an impressive amount of work and of results. Further analysis of the outcomes of this thesis will keep the community busy for several years. The results have been made possible thanks to important methodological developments resulting from the successful merging of USPEX, an established powerful algorithm for structural search and optimization, with multi-objective optimization methods. The result is a robust universal method to search for compounds with desired properties, within a much broader range of chemical parameters than normally done so far. The thesis is well written and even though the description appears occasionally a bit too succinct, reference is made to literature when appropriate. If possible, I would however recommend that the final version of the thesis contains a short section where the main conclusions of the entire work (and not only of the single chapters) are summarized. Except for this minor comment, I'm convinced that the thesis meets in full the criteria for the PhD degree, and I have no hesitation in recommending that the candidate be awarded the 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*