Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Dmitrii Semenok

PhD Program: Materials Science and Engineering

Title of Thesis: Computational design of new superconducting materials and their targeted experimental synthesis

Supervisor: Professor Artem Oganov

Co-supervisor: Assistant Professor Alexander Kvashnin

Name of the Reviewer: Sergey V. Levchenko

I confirm the absence of any conflict of interest	**Date: 20.07.2022**

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

Brief evaluation of the thesis quality and overall structure of the dissertation.

Overall, the quality of Dmitrii Semenok's thesis on the topic "Computational Design of New Superconducting Materials and Their Targeted Experimental Synthesis" is outstanding. The amount of work put into the thesis is staggering. This is a rare example of both theoretical and experimental studies performed by the same person. It is clear from the thesis that the author is pushing forward the development of the whole field of science. The thesis is very well written in almost perfect English, and the structure is clear, with some minor issues mentioned below.

The relevance of the topic of dissertation work to its actual content.

The topic of the thesis is directly related to its actual content.

The relevance of the methods used in the dissertation.

Both experimental and theoretical methods were used in the thesis. The theoretical methods included ab initio (DFT) calculations and machine learning (neural networks). The relevance of the used theoretical methodology is convincingly demonstrated by comparison with experimental results. The choice of neural networks as a data analysis tool for such a small amount of data is questionable, but this is leveraged to some extent by the choice of good descriptors based on the literature analysis and the author's own experience.

The scientific significance of the results obtained and their compliance with the international level and current state of the art.

It is very clear that the author is the leading expert in the field. His work defines the directions in which the field (superconducting metal hydrides) will/should develop, and is now the new state of the art.

The relevance of the obtained results to applications (if applicable).

The author discusses some possible applications of the superconducting hydrides that are not prevented by the need for high pressures. The latter is the limiting factor. However, more importantly, the author clearly shows limitations and possible ways to overcome them for the given class of superconductors. This will for sure influence the direction of the search for high-temperature superconductors, which is of course very relevant for practical applications.

The quality of publications.

The author has five publications on the topic of the thesis, four of which are first-author. All publications are in influential, very high-impact journals. The publications are of outstanding scientific quality.

Below are listed the detailed comments. The idea of the comments is that the thesis text is modified directly in such a way that the issues are resolved and the questions do not arise anymore.

Major comments:

1) It remains unclear how sensitive T_c is to defects (in particular hydrogen content). This should be discussed (at least briefly) in the thesis.

2) I did not find in the thesis a clear description of computational methodology, such as which exchange-correlation functionals were used and why, which pseudopotentials were used and why they are accurate for high-pressure studies, etc.. Also, there should be a general discussion of challenges in computational modelling of superconductor properties.

3) "This allows us to hope for a correlation between the behavior of superconductivity in pure metals and superhydrides under pressure. " - Since the candidate has so much data on several different metal hydrides, why not check this and other correlations directly? Also, one of the interesting properties (descriptor) of hydrides is the partial ionicity of hydrogen-metal bonds. This could be analyzed with different tools, e.g. Bader charges. Was such an analysis performed? It would be interesting to see a correlation between T_c and bond character. There is some analysis based on electronegativity, but the connection between electronegativity and ionicity can be non-trivial, especially at high pressures.

Minor comments:

" Higher hydrides LaH10" - clarify what you mean by "higher hydrides"

"In this thesis, I try to outline future research in this area." - sounds a bit strange, as if no research is done, just some future research is discussed; this needs a clarification/reformulation

"The simultaneous realization of superconductivity in the hydrogen sublattice of hexagonal (e.g., NdH9) or layered (such as FeH5) hydrides and antiferromagnetic ordering in the metal sublattice can in principle lead to some exotic physical effects typical of cuprates and iron pnictides." - give examples of the exotic physical effects

"To date, more than 90–95% of the works on hydrides are still theoretical. It is important that in almost all cases, first-principles calculations resulted in an overestimation of the critical temperature of superconductivity (Table 1) due to the failure to take into account the anharmonic vibrations of the hydrogen sublattice as well as because of a possible increase in the effective Coulomb pseudopotential \mu^* to 0.2 (usually, \mu^* = 0.1–0.15 is assumed in calculations)." - clarify if quantum effects could play a role, and explain what Coulomb pseudopotential is (I see you explain this later, maybe you can refer to the later discussion using "see below", or better explain it earlier)

"Experimental studies have revealed the following properties of superhydrides" - clarify if these are your experimental studies or not; if not, add some references

"showed that ThH10 should exhibit very high critical temperature T_c = 200–240 K (Table 6), which increases with decreasing pressure." - "increases with decreasing pressure" sounds counterintuitive and is valid down to some minimal pressure, if I understand correctly; if this is not a mistake, it may be better to write "decreases with increasing pressure", or better clarify the pressure dependence.

Figure 14 (a) - is the arxiv reference [1] still not published?

"Considering the ratio R(300 K)/R(T_c), which is in the range of 1–1.5 for most hydrides, a conclusion can be made that the sample has many defects." - explain the physics of the relations between R(300 K)/R(T_c) and the number of defects; you mention this later, but it should be clear already here.

" taking into account the ZPE and the entropy (-TS) contribution to the Gibbs energy of formation" - I guess you mean vibrational contributions, clarify this; discuss configurational entropy

Figure 28 a) - the different colored lines a not labelled (I guess they correspond to different magnetic fields)

Figure 31 b) - unclear what the different values for each frequency mean

"For europium hydrides, the positions of the electron state density maxima for the different spins are at 7-8 eV, implying the emergence of a spontaneous magnetic order in the material." - The logic of this sentence is unclear. Why does the position of DOS peaks at 7-8 eV means there is magnetic order?

"This factor fundamentally limits the predictive ability of DFT calculations" - I suggest "This factor fundamentally limits the predictive ability of standard DFT approximations". DFT is in principle exact.

"Here we would like to make a small digression and comment on the recent work of A.D. Grockowiak et al. [208], where the authors claim to have found superconductivity at 550 K in doped LaH10" - clarify at which pressure

"Stable crystal structures were searched at a pressure of 200 GPa as it was predicted by our neural network." - neural network appears suddenly here; some details should be given about machine-learning methodology used in the thesis, maybe even in a separate section; I see the details appear later, but this is too late.

"This compound could be the first example of such true ternary polyhydride synthesized at a high pressure." - why "could be"? are you not sure? I suggest to write "To the best of our knowledge, this is the first example...", or even simply "This is the first example..."

"First, superconductivity with T_c = 39 K in P6/mmm-MgB2 [266], which remained unknown until 2001, and a recent discovery of hexagonal MoB2, superconducting below 32 K at a pressure of 100 GPa [267]." - there is no verb in the sentence, check the grammar

"For cubic and hexagonal crystals, the energy levels of phonons are degenerate in direction" - in which direction?

"For instance, the well known cubic superconductor Nb3Sn (T_c = 18 K) of type AX3 (or A15), on the basis of which many other superconductors have been obtained by atom substitution, such as V3Si and V3Ge." - there is no verb in the sentence, check the grammar

Figure 58 - some improvements are needed: explain what the grey bars show, panel c - according to legend, experiment is shown by a blue rhomb, but in the panel it is written that the red squares for LaH10 TaH3 show experiment, it should be explained what "ref data" and "refinement" mean, would be good to know pressure for the presented data

"As the density of states increases, spin splitting in the band structure appears, leading to scattering of the Cooper pairs with spin flipping, their destruction and, as a consequence, suppression of the superconducting state. This corresponds to B. Matthias's rule No. 2: "high density of electronic states is good"." - the two sentences seem to contradict each other, please clarify

Figure 64 - explain the color scale

"Analysis of the results obtained after applying our neural network to an array of parameters of the experimentally known or ab initio predicted binary and ternary hydrides stable in the pressure range of 0-300 GPa is shown in Figures 66A and B" - explain how the stability of the materials with different hydrogen content was evaluated

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*