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Skolkovo Institute of Science and Technology

Thesis Changes Log

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

Supervisors: Professor Artem R. Oganov, Assistant Professor Alexander G. Kvashnin

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

Dear Jury Members,

Thank you very much for helpful comments and suggestions on how to improve my thesis. Please find below both the description of changes I made in the thesis, and answers to the questions.

Based on the Jury member Report from **Professor Evgeny Antipov**, there have been made corrections according to the following recommendations:

Q1. *Why different chemical formulas (Th4H15 and Th16H60) are used for the same compound as well as Th4O8 instead of ThO2?*

Answer: This remark is absolutely correct. I fixed this issue (see Table 5) and used the chemical formula Th_4H_{15} almost everywhere. The formula $Th_{16}H_{60}$ refers to the unit cell of this compound. The same applies to Th_4O_8.

Q2. *How the author can explain the coexistence of ThO2 and Th4H15 in the samples after synthesis?*

Answer: Thorium oxide is the product of the slow oxidation of Th in air. This oxide film was not completely removed by HNO_3 before loading the microsample into the high-pressure diamond anvil cell. Thorium oxide cannot be reduced by hydrogen. This information was added to the thesis.

Q3. *What does it mean: "The superconducting properties of cerium hydrides are weaker than those of thorium hydrides (p. 57)?*

Answer: The maximum critical temperature of superconductivity and the electron–phonon interaction parameter λ in thorium polyhydrides are higher than those in cerium polyhydrides. This explanation was added to the thesis.

Q4. *What are the La/Y ratios in the (La,Y)H10 and (La,Y)H6 compounds (p.109)? Did the author try to prepare these compounds with another La/Y ratios?*

Answer: Yes, we studied polyhydride samples obtained from La-Y alloys with different yttrium content — from 20 to 75 atom % (see the original paper, *Materials Today* 2021). This explanation was added to the dissertation.

Based on the Jury member Report from **Professor Haiyang Niu**, there have been made corrections according to the following recommendations:

Q1. *The author is suggested to add how exactly Tc is calculated based on the BCS Migdal-Eliashberg theory in Chapter 1.*

Answer: This material is available in Appendix of this dissertation. For readers' convenience, I added additional references in the first paragraph.

Q2. *A few subtitles are suggested to be added to make the thesis more readable, especially in Chapter 1.*

Answer: Four additional subtitles were added in Chapter 1 (1.5.1–1.5.4)

Q3. *All the computational and experimental setups to reproduce the findings should be given.*

Answer: I added two additional paragraphs devoted to the details of the DFT calculations and experimental synthesis to Appendix.

Q4. *The correspondence between column 2 and 3 is not clear in Table 4.*

Answer: In Table 4, column 2 lists the maximum critical temperature of superconductivity observed by scientific groups presented in column 3 for the compounds shown in column 1. I made some changes in column 3, making it more detailed.

Q5. *The "75 atom%" on page 60 should be "75 at%".*

Answer: Corrected.

Q6. *Please check the font type of letter "K" on pages 81-82.*

Answer: I checked it out, "K" is used everywhere to denote the temperature in kelvins.

Q7. *For those structures discovered both in theoretical predictions and experiments, the comparisons of structural details between experiments and calculations are suggested to be added.*

Answer: Structural information that can be obtained in experiment concerns the parameters of the unit cell of polyhydrides. At this moment, we cannot see the most important hydrogen sublattice of polyhydrides in experiment because of the low ability of hydrogen atoms to scatter X-rays. Therefore, the experimental estimation of the distance d(H–H) can only be indirect. In general, by studying the deviation of the experimental unit cell volume from the theoretical one, the distances d(H–H), which are the most important for superconductivity, can be determined with an accuracy of about 1% (e.g., in LaH_{10}). This information was added to the thesis (pp 17, 18).

Based on the Jury member Report from **Academician Vadim Brazhkin**, there have been made corrections according to the following recommendations:

Q1. *In the future, I would like to see a systematics of the types of hydrides and the fractions of electrons at the Fermi level from hydrogen and atoms of the framework. For example, in H3S, a comparable proportion of electrons at the Fermi level is from hydrogen and from sulfur. And in lanthanum or thorium hydrides, apparently, the main contribution to the density of electronic states comes from hydrogen.*

Answer: Additional Figure A5 with total and partial densities of electron states at the Fermi level was added to Appendix. In all high-temperature superconducting hydrides, the hydrogen contribution to N_F is significant and can sometimes exceed the contribution from metal. In pure metals and lower hydrides, the hydrogen contribution $N_F(H)$ is very small, therefore we can call the criterion $N_F(H) \sim N_F(\text{metal})$ necessary for realization of high-temperature superconductivity in polyhydrides. However, this criterion is not sufficient: as the example of BaH_{12} shows (Figure A5f), where the hydrogen contribution far exceeds that of the metal, $N_F(H)$ itself does not lead to high-temperature superconductivity.

Q2. *I would like to see up to what pressures (when the pressure is reduced) superconducting structures will still be dynamically stable - i.e. to determine the regions of metastable existence of these lattices. Such a systematic was also extremely useful, although for this, apparently, one should go beyond the limits of the quasi-harmonic approximation.*

Answer: In the harmonic approximation, the region of dynamic stability of polyhydrides, as well as the region of their thermodynamic stability, correlates poorly with the experimental results. Some improvement is achieved by taking into account the anharmonicity of the hydrogen sublattice. In Table A6 (Appendix), I added the calculated minimum stabilization pressure for different hydrides. Most superhydrides decompose when the pressure decreases below 100 GPa.

I would like to express my deep gratitude to Prof. Giovanni Hearne for his kind words and the great work he has done to improve the dissertation.

Based on the Jury member Report from **Professor Giovanni Hearne**, there have been made corrections according to the following recommendations:

Q1. *Editorial improvements. I have annotated or marked in red where minor issues throughout the thesis need to be addressed. For the majority of cases these are cosmetic changes including, minor improvements to grammar in some of the statements, incomplete phrases, stylistic issues where subscripts should be used in some of the references (formatting issues), etc. These do not detract from the excellent overall presentation style and organization of the thesis.*

Answer: Most of the comments were considered, with appropriate corrections made to the text of the dissertation.

Q2. *Bibliography list. There seem to be numerous cases of minor formatting issues, e.g., subscripts required for chemical formulae. I have marked many of these. Some journal titles are abbreviated and most others are full titles. So some consistency is required here. The candidate should scan through the full reference list and rectify these minor issues. It's a tedious job, but implementing these corrections would make the thesis an almost unblemished body of work.*

Answer: Most of the comments were considered, with appropriate corrections made to the text of the dissertation.

Q3. *I also have some annotations or markings in blue, which are for highlighting certain points for my benefit as the reviewer. These may be ignored by the candidate.*

Answer: I tried to understand the problems and make corrections where possible.

Q4. *Scientific content. Chapter-2 thorium polyhydrides. For example Fig. 17(a) depicts the resistance in the superconducting state where the resistance plateaus at ~13.5 μΩ. Can this really be considered as zero resistance ? A similar reservation holds for Fig. 16(b). Chapter-5 La-Y tenary polyhydrides. Fig. 51 (a) and (b), resistances in the "superconducting" state are ~1 mΩ and ~0.2 mΩ. Where are these residual resistances emanating from ? Can this really be considered as zero resistance ? The candidate will need to comment on these "superconducting states" having finite resistances, in the respective chapters.*

Answer: According to the definition, a superconductor is a compound with zero electrical resistance at a temperature below T_C. The electric current can pass through a superconductor without losses. Indeed, recent frozen magnetic flux experiments show that current vortices in superhydrides do not fade for many days, confirming the superconducting nature of the compounds.

However, when it comes to measuring the electrical resistance using normal metals (wires, contacts), we encounter interface phenomena like N–S–N contacts, van der Pauw circuit asymmetry, pickups from other parts of the electrical circuit, external electromagnetic radiation, noise from electronic equipment, and other interference. As a result, the average resistance below the T_C sometimes remains finite. In some cases, the average resistance value is significantly smaller than the noise of the electronic equipment. In such cases, the moment when the resistance formally becomes negative is chosen to be a moment of $R = 0$.

I would like to express my deep thanks to Prof. Sergey Levchenko for his kind words about my work and great efforts to improve this thesis.

Based on the Jury member Report from **Assistant Professor Sergey Levchenko**, there have been made corrections according to the major comments:

Q1. *It remains unclear how sensitive T_c is to defects (in particular hydrogen content). This should be discussed (at least briefly) in the thesis.*

Answer: The corresponding discussion was added to the thesis. According to Anderson's theorem, the presence of defects and nonstoichiometric composition of polyhydrides do not affect the critical temperature (onset T_C).

Q2. *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.*

Answer: The required section was added to Appendix. More detailed information on the computational methods is given in the Methods sections in the published articles on the topic of the dissertation. Some problems of the computational approach in the field of hydride superconductivity are covered in the end of Section 1.3 (page 22) and Section 1.5. The main problem is the low efficiency of the crystal structural search algorithms focused on building the convex hulls.

Q3. *"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?*

Answer: The data on superconductivity in pressurized metals is very limited. This is especially true for the area of formally "negative" pressures, when the elementary cell of metals expands by including inert atoms in its composition (voids).

Q4. *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.*

Answer: Yes, this has been analyzed in a number of publications. For example, Belli, F., Novoa, T., Contreras-García, J. et al. Strong correlation between electronic bonding network and critical temperature in hydrogen-based superconductors. Nat Communication 12, 5381 (2021). https://doi.org/10.1038/s41467-021-25687-0.

In the structure of molecular polyhydrides, like recently studied SrH_{22} and SrH_6 [*Semenok, D. V. et al., Adv. Mater. 2022, 34, 2200924*], there are anions H^- and H_3^-, just as in LaH_{10} [*Liangliang Liu et al. Phys. Rev. B 99, 140501(R), 2019*], and in CeH_9 [*Inorg. Chem. 2021, 60, 17, 12934–12940*]. However, strontium polyhydrides are superionic semiconductors, whereas metal polyhydrides are high-temperature superconductors.

Q5. Minor comments:

" Higher hydrides LaH10" - clarify what you mean by "higher hydrides"
Answer: Corrected, should be "Higher lanthanum hydrides: LaH_{10}…."

"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
Answer: This sentence was removed.

"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.
Answer: An example was added [doi: 10.3367/UFNe.2021.05.039018].

"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)
Answer: Done.

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

"showed that ThH_{10} 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.
Answer: The issue was corrected.

Figure 14 (a) - is the arxiv reference [1] still not published?
Answer: Figure 14a was replaced with an improved one which does not need this reference.

"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.

Answer: A part of the electrical resistance is independent of the temperature because of the presence of defects. The corresponding explanation was added to the thesis.

" 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
Answer: Corrected. In this case we are talking about the Y–H system, where there is no contribution from the configurational entropy.

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

Figure 31 b) - unclear what the different values for each frequency mean
Answer: Clarification was added. Now it sounds as "(b) Energy dependence of the superconducting gap along the imaginary axis at 10 K. Only the Kohn–Sham states nk with an energy within 0.2 eV from the Fermi level are shown."

"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?
Answer: This sentence was reformulated to "…for the different spins are separated from each other by 7–8 eV, implying the emergence of a spontaneous magnetic order in the material at 0 K because only states with a certain spin will be filled."

“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.
Answer: Corrected.

"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
Answer: Added: “…at pressures of 160–180 GPa”.

"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.
Answer: This sentence was removed.

"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..."
Answer: Corrected.

"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
Answer: Corrected.

"For cubic and hexagonal crystals, the energy levels of phonons are degenerate in direction" - in which direction?
Answer: Replaced by “…are degenerate in the k-space”.

"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
Answer: Corrected.

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
Answer: The figure was improved and the necessary explanations were added. Unfortunately, it is difficult to add the pressure, because it is different in each case.

"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
Answer: This paragraph was reformulated.

Figure 64 - explain the color scale
Answer: Different colors in this figure refer to elements of different groups of the periodic table.

"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
Answer: The term “stable” is used here in the sense of thermodynamic and dynamic stability in the harmonic (mostly) approximation for the polyhydrides studied in the works given in Tables 1-2, A3, and others.

I would like to thank Prof. Alexei Buchachenko for his exceptional appreciation of my dissertation.

Based on the Jury member Report from **Professor Alexei Buchachenko**, there have been made corrections according to the major comments:

Q1. *With this high assessment, I have little to recommend for improvement. Perhaps adding a list of ``other author`s publications relevant to the thesis topic`` after page 4 is instructive to emphasize overall impact of the author in the field.*
Answer: Done, additional 14 publications were added.

Q2. *I would also add DOI in the for-thesis publication list, to comply with publisher`s permission for reusing materials in the dissertations.*
Answer: Done.

Q3. *Reference 46 looks funny – better to put it ``unpublished``. Formatting inaccuracies, mostly in the tables, are worthy of fixing.*
Answer: Corrected.

Q4. *Just for curiosity, in section 3.3, the anomalously low Tc for YH6, which cannot be explained by standard models, is emphasized. It would be interesting to discuss at the defense if any new ideas, hints or data have been emerged after thesis completion.*
Answer: Unfortunately, not much progress has been achieved on this issue. One version is that spin fluctuations in this material suppress superconductivity. The second version is the high value of the Coulomb pseudopotential (>0.15) caused by the high value of the average phonon energy. This latter version seems preferable.