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:

I confirm the absence of any conflict of interest **Vadim Brazhkin**	**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
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

Review of the Doctoral Thesis of Dmitrii Semenok

"COMPUTATIONAL DESIGN OF NEW SUPERCONDUCTING MATERIALS AND THEIR TARGETED EXPERIMENTAL SYNTHESIS"

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

The dissertation of Dmitrii Semenok consists of an introduction (Chapter 1), five chapters, a conclusion, a list of references, and an appendix. The relevance of the thesis research, its goal and main objectives, the author's approach to accomplishing the tasks, and the degree of novelty of the obtained results are all described and explained in the introduction, along with a summary of the contents of the thesis.

In Chapter 2, the author discusses the synthesis of thorium polyhydrides and their transport properties. The thorium hydrides ThH_{10} and ThH_9 were predicted theoretically in 2018, before their experimental discovery, which is a proof of the predictive power of the density functional theory and the Bardeen–Cooper–Schrieffer theory of superconductivity.

Chapter 3 presents a study of the yttrium–hydrogen system at pressures up to 213 GPa, including the experimental synthesis of YH_4, YH_6, and YH_9, and the investigation of their superconducting properties, magnetic phase diagram, and critical currents. The yttrium polyhydrides YH_6 and YH_9 and their high-temperature superconductivity were theoretically predicted many years before their experimental discovery.

In Chapter 4, Dmitrii Semenok discusses hydrides of lanthanides, particularly europium, which does not exhibit superconducting properties because of the presence of anisotropic scattering centers — Eu atoms — which change the electron spins, leading to the decay of the Cooper pairs. As a result, the magnetic order in lanthanide superhydrides dominates the superconducting properties, the lack of which in praseodymium and neodymium polyhydrides is also thus explained.

Chapter 5 is dedicated to an investigation of the ternary lanthanum–yttrium–hydrogen system in which La and Y form a solid solution metal sublattice; this study is the first of the kind for superhydrides. The theoretical analysis of this system is quite difficult because of the increased dimensionality. Nevertheless, the author does a detailed research of the superconducting properties of the $(La,Y)H_x$ series of compounds and proposes a classification of the ternary hydride systems.

In Chapter 6, the author considers general questions of the distribution of the superconducting properties in binary and ternary polyhydrides and in a series of similar compounds (XH_6, XH_9, XH_{10}) or polyhydrides of one element with different content of hydrogen. Specific rules are established that make it possible to predict the maximum critical temperature in binary and ternary systems on the basis of only the knowledge of the hydride-forming elements.

As a whole, Dmitrii Semenok's dissertation is a complete study representing a solution to urgent problems of hydride superconductivity. The work uses a common experimental–theoretical approach that provides an opportunity to overcome the complexities of synthesis and investigation of these new compounds at ultrahigh pressures.

Relevance of the topic of the dissertation work to its actual content

The dissertation of Dmitrii Semenok, "Computational design of new superconducting materials and their targeted experimental synthesis", is devoted to theoretical and experimental studies of polyhydrides at high pressures. The goal of the research is a computational search for hydride superconductors followed by experimental synthesis of the most promising compounds at high static pressure on diamond anvils.

At present, the attention of many experts in the field of superconductivity is focused on high-pressure stabilized polyhydrides because these compounds demonstrate outstanding superconducting properties. For instance, the sulfur trihydride H_3S, discovered in 2015, has a critical temperature of superconductivity T_C of about 200 K, and an unexpectedly low isotopic coefficient $\alpha = 0.22$. Another example of superhydride is the lanthanum decahydride LaH_{10}, discovered in 2018, which turns superconductive at 250 K (–23 ºC). No other class of superconducting materials can compare with hydrides in terms of critical temperature.

In many cases, the critical current density in hydrides (~50–100 kA/mm^2) and their upper critical field exceed similar parameters of all known superconductors. The main fundamental disadvantage of hydrides is the need to use high pressures (100–150 GPa) to stabilize them, which limits the volume and mass of the obtained compounds. Development of new hydride superconductors is of great interest; its relevance is in discovering compounds that do not require extremely high pressures and have the critical temperature of superconductivity close to room temperature.

Relevance of the methods used in the dissertation

To ensure validity and reliability, the results obtained by Dmitrii Semenok using theoretical methods (DFT calculations of the hydride formation enthalpy, an evolutionary search for crystal structures under pressure, and calculations of the band structure and electron–phonon interaction) were verified experimentally via first-principles methods. This "double-check" approach makes it possible to draw more reliable conclusions on the structure of the hydrogen sublattice in hydrides and to better predict the properties of compounds not yet obtained in experiment. The results of the thesis have been presented and discussed at several international conferences and scientific seminars. The author has published five high-quality papers on the subject of the thesis and 16 articles on the study of polyhydrides.

Scientific significance of the obtained results and their compliance with the international level and current state of the art

The results presented in the thesis have a significant scientific novelty and great practical importance:

1. The author is the first to study the formation of new thorium–hydrogen compounds under pressures of up to 180 GPa — ThH_4, ThH_6, ThH_9, and ThH_{10}, — the last of which is a high-temperature superconductor with T_C = 161 K at a pressure of about 170 GPa.

2. The transport properties of the yttrium hydrides YH_6 and YH_9, which exhibit high-temperature superconductivity with $T_C(YH_6)$ = 224–227 K and $T_C(YH_9)$ = 237–243 K at pressures of 160–215 GPa, were also investigated. Moreover, the extrapolated upper critical field of YH_6 reaches about 200 T for a number of samples, and the extrapolated critical current density at 0 K is about 50 kA/mm^2.

3. The reactions of lanthanides with hydrogen at high pressures, especially for europium, praseodymium, and neodymium, were also studied in detail. It was shown that none of the hydrides of

these metals is a high-temperature superconductor, and many of them probably exhibit magnetic properties.

4. Dmitrii Semenok also studied the formation of hydrides in the ternary lanthanum–yttrium–hydrogen and lanthanum–neodymium–hydrogen systems at pressures of 160–190 GPa. In both cases, the formation of a solid solution in metal sublattices with a random distribution of La–Y and La–Nd atoms was observed, whereas the hydrogen sublattice retained high symmetry and superconducting properties. The critical temperature T_C in the La–Y–H system reaches 253 K.

5. The author investigated the general question of the distribution of superconducting properties in ternary and binary metal polyhydrides. Using both experimental data and theoretical calculations, he showed that metal polyhydrides with one or two d electrons, as well as hydrides of alkaline-earth elements, are the most promising regarding the superconducting properties.

On the basis of the obtained results, the author created algorithms for analyzing the superconducting properties of polyhydrides, highlighting the main directions of future search for the most promising hydride superconductors and the pressure and composition ranges in which the synthesis should be performed. The table of the most promising combinations of elements for designing ternary superconducting hydrides deserves a special attention.

Relevance of the obtained results to applications

The results of the research can be used as a basis for obtaining new high-temperature superconducting hydrides at high pressures, especially in ternary systems. The studied binary hydrides may find practical applications in electronic superconducting devices and sensors. The structural motifs found in this work can help in the interpretation of X-ray diffraction data for other polyhydrides, whereas the empirical rules found in the analysis of the distribution of the superconducting properties of polyhydrides can be used to accelerate the search for the most promising ternary hydrides.

Quality of publications

The main results of the thesis have been published in five scientific papers in high-quality peer-reviewed journals. The results of the dissertation have been presented at several international conferences and seminars; the author has received a patent for the invention of hydride superconductors. The published papers sufficiently reflect the main content of the thesis. The level of the problems solved in the dissertation corresponds to the requirements for a PhD thesis in the field of materials science.

The dissertation of Dmitrii Semenok, "Computational design of new superconducting materials and their targeted experimental synthesis", is a complete research which meets the requirements for awarding a PhD degree according to the criteria of relevance, scientific novelty, and validity and reliability of the conclusions. The PhD student Dmitrii Semenok deserves to be awarded a PhD degree.

Summary of the issues to be addressed before the thesis defense

The following remarks can be made on the content of the thesis:

1) 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.

2) 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.

These remarks do not reduce the significance of the obtained results and do not affect the overall positive evaluation of Dmitrii Semenok's dissertation.

Vadim Brazhkin

Academician RAS

Director of the Institute for High Pressure Physics RAS

Provisional Recommendation

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