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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Artem Samtsevich

PhD Program: Materials Science and Engineering

Title of Thesis: Simulation of the mechanisms of solid-solid phase transition

Supervisor: Professor Artem Oganov

Name of the Reviewer: Sergey Levchenko

I confirm the absence of any conflict of interest  Sergey V. Levchenko	**Date: 19-07-2021**

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

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

The scientific quality of the thesis is excellent. The author has made significant contributions to the area of solid-solid phase transitions. This is a challenging unsolved problem of current scientific interest, which attracts attention of many researchers worldwide. However, the presentation of the work is not very good. The English text quality is low, with some sentences being difficult to understand because of this. Also, a large portion of the thesis is devoted to discussions of known methodology, while the relation of this discussion to the scientific developments by the author is difficult to discern. Despite these problems, the thesis contains all information necessary to understand the scientific significance of the results. The overall logic of the structure can still be recognized.

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

The topic of the thesis accurately summarizes its scientific content. However, as mentioned above, the relevant content is diluted with too many details with no direct relation to the topic.

The relevance of the methods used in the dissertation

The applied methods are directly relevant to the problem under consideration. One of the methods (TNMST) is very new. The author has not only used existing methods, but also developed his own computer code to combine the existing methods into a seamless automated workflow. This significantly improves accessibility of the methods to other researchers, and allowed the thesis author to apply the methods to complex realistic systems.

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.

The scientific significance of the results is demonstrated by their publication in high-level international journals: the journal of physical chemistry letters, Physical Review B, and JETP Letters. The work has a potential to influence the way how computational materials design and understanding is achieved, in particular for materials under high pressures. The implemented workflow and the use of state-of-the-art structure-mapping approaches can be of great appeal for scientists working in this area. The study of Cr-N and W-B systems is relevant for design and understanding of superhard materials. The study of CaCO3 reveals chemically complex phase transitions of this Earth-abundant material at lower mantle pressures, which is important for understanding properties of Earth's lower mantle. The study is also important, since it demonstrates the complexity of high-pressure phase transitions even in such "trivial" materials as CaCO3. Finally, the author has studied phase transitions in Al2SiO5, also important for Earth's sciences, as well as a construction and structural material. Notably, the author has collaborated with experimentalists and helped to interpret the experimental results.

The quality of publications

The publications by Artem Samtsevich are of high quality. There are three published papers related to the topic of the thesis in high-level international peer-reviewed journals: the journal of physical chemistry

letters, Physical Review B, and JETP Letters. There is one more publication submitted to Zapiski RMO (Proceedings of the Russian Mineralogical Society). Only in this latter publication Artem is the first author. However, the contribution of Artem to the other collaborative publications is clear and significant. In addition, there are two more publications with participation of Artem on topics unrelated to the thesis' topic. His personal contribution to these publications is difficult to evaluate.

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

Note: all comments are meant to be answered directly by changing the thesis text, to clarify or answer raised questions

Major comments:

1) "It uses the system lattice parameter as a variable in a new configurational space. As a result, the simulation bypassing

the direct treatment of many single degrees of freedom, so the system evolves to the new state with low efforts." - This is a confusing description of metadynamics. While using collective variables may reduce the effort to evolve system to another state, the main driving force is the modification of the potential that pushes the system out of the well.

2) "The vibrational prefactor nu, which describes the characteristic atomic vibrational frequencies at the minimum and the saddle point, can be calculated explicitly to capture entropic contributions to the transition rate. The prefactor nu is small if the passageway at the saddle point is narrow and large if it is wide." - The prefactor mainly reflects the number of escape attempts per time unit. This should be mentioned as well.

Similarly, in other places where entropic contribution is mentioned, I am not sure if you actually mean entropic contributions or the frequency of escape attempts through the saddle point, or perhaps both.

3) There are parts of the text that repeat in different words what was already said previously. For example, paragraphs starting with "The picture of rare transitions between two stable states can be described in the language of statistical mechanics as two free energy minima separated by a high activation barrier" and "Figure 2.2 illustrates a simple PES as a hilly landscape with peaks..." discuss what was already discussed previously. This can be organized much better.

4) "For the particular structure, several topologies can be defined depending on the bond length cutoff parameter." - Please explain the role of cutoff parameter. When there are two minima that differ by small displacements of atoms relative to each other, one would need to tune the cutoff parameter to distinguish the topology of the two minima. How is it done in practice?

5) It would be good to illustrate the section describing supernets and subnets by examples.

6) "The main result of this thesis is the development of the topology-based approach for the initial path generation and the adaptation of the geometrical mapping approach with its further application for MEP search." - This should be discussed much more across the thesis than it is now. The introduction is too long, with a lot of repetitions and details whose relation to the work done in the thesis is not clear. More details should be given specifically on the proposed unified workflow and its implementation. Similarly, when you write "My contribution to this work was investigating the phase transition mechanism from Pnma-CrN to newly predicted P-6m2-CrN.", the discussion should be focused more on this, rather than on the detailed results on convex hulls for Cr-N system.

7) "...with U-J=1 eV (see Figure 4.6). Details of the calculations can be found in related publication 193." - All important details of calculations should be described in the thesis. It was never mentioned that Hubbard U correction approach was used. Explain how a particular value of U_eff was chosen.

Minor comments:

"Furthermore, these transitions are infrequent in the sense that the average time between events is many (perhaps very, very many)" - give an order estimate

"between polymorphs of a given compound consideration" - "under consideration"?

"The unclear criterion in the two qualitative approaches always arises some discrepancy" - "always raises"

"In reality, there is not an instantaneous transfer " -> "In reality, there is no instantaneous transfer "

"It was studied how pressure gradient enhanced energy barrier crossing and promotes the collective motion of particles" - "promoted"

" as the Taylor series into terms of eta" - "...in terms of eta"

"Landau theory do not cover" - "does not cover"

"The resulting space groups are then used to generate a cell and both structures are brought to this cell." - please clarify this statement; what does it mean "are brought to this cell"?

"one capable to map structures onto each other" - "one is capable"

"The biggest problem of these methods, that they can be used for the system that has not so many atoms in the unit cell" -> "The biggest problem of these methods is that they can only be used for a system with a small number atoms in the unit cell"; give an estimate of the maximum reasonable number

"Due to a large number of degrees of freedom in the crystals and, usually, reaction coordinates are unknown from the beginning" - something is wrong, maybe "and" is redundant

Equation 1.4 and other places - put the dot on top of C, not on top of C(t)

"either recross the TS surface or recross before a reaction occurs" - clarify

"While this prefactor can play a role in some cases, it is usually the exponential dependence of Δ□ which is the dominating factor. However, the exponential term typically dominates reaction rates." - seems that the second sentence just repeats the message of the first one.

"Usually, there are higher energy vibrational modes that should be considered where standard TST is not working." - clarify why standard TST is not working for higher vibrational modes

"Second step consist on the determination" -> "Second step consists of the determination "

"Moreover, the pattern of symmetry breaking that exists in solids means that these transitions are not only technologically important, but that there are a lot of them. " - clarify what you mean by "a lot of them"; many different phase transitions? happenning often?

"Most of these techniques are based on employing either classical or ab initio-based atomistic force fields 85,86 such as molecular dynamics (MD)" - MD is not a force field

"Unfortunately, the straightforward application of MD impractical to the study of rare events" - "IS impractical"

"simulating even nanoseconds of dynamics is an effort" - "is a huge effort"

"Moreover, even many billions of simulation steps are not guaranteed even a single event occurrence." -> "Moreover, even many billions of simulation steps are not guaranteed to result in even a single event occurrence."

"The picture of rare transitions between two stable states can be described in the language of statistical mechanics as two free energy minima separated by a high activation barrier" - the paragraph starting with this sentence repeats what was already said before.

"Here illustrated the energy profile of a system at room temperature with two minima and the energy barrier of 0.5 eV and with typical pre-exponential factor occurs 1000 times per second" - at which temperature?

"Obviously, there must be used more advance techniques that help to overcome the rare event problem." - "more advanced"; but you already discussed this before; moreover, as you already mentioned there are MD methods that can treat rare events, such as metadynamics; therefore, this paragraph is a bit misleading

"transport in or on solids" - clarify transport of what

"The vibrational motion of the system about the reactant and product equilibrium geometries considering the zero-point energy and thermal corrections, which are required for free energy and enthalpy calculation" - not good English

"Figure 2.2 illustrates a simple PES as a hilly landscape with peaks..." - why is this described in such detail again? it is a repetition of what was said before

"Because the forces are zero at energy minima, TSs are termed stationary points." - sounds like energy minima and transition states are the same thing; please reformulate the sentence

"The current approach helps to pass the transition region of PES " - clarify which current approach you mean

"how the interested phases are connected" - "the phases of interest"

"As a result, numerous unique methods have been developed" -> "As a result, numerous methods have been developed"

"Overall, the general concern of all these methods is their efficiency in overcoming the high barrier and simulate phase transition." -> "Overall, the general concern regarding all these methods is their low efficiency in overcoming the high barrier and simulating phase transition."

"Another strategy is based on the exploration of the PES by locating as many minima and saddle points. This approach lay on the basis of the kinetic Monte

Carlo (MC) technique" - Unclear wording. Kinetic Monte Carlo requires knowledge of reaction rates, it cannot be used to explore PES.

"Finally, a totally different approach consists of procedures that use artificially controlled enhancements of rare event probability." - this does not sound different from metadynamics; explain the differences better

"Another approach that increases the probability of the rare event on raising the temperature is calling temperature accelerated dynamics " - "is CALLED"

"where it is shown how many different pathways can exist and how hard the MEP is." -> "where it is shown how many different pathways can exist and how hard the MEP is to find."

"Finally, there are other ways to study the rare event problem are based on the minimization" - "THAT are based on"

"Unfortunately, the phase transition simulation methods are based on the mean field approximation, where all unit cells of the constructed lattice evaluate equally and simultaneously." - this is not mean field, this is periodic boundary conditions problem; the same methods can be used for a supecell.

"For any kind of aperiodic systems such as molecules or clusters, this task can be solved easily" - this depends on the size of the molecule/cluster, jsut like for periodic systems it depends on the size of the supercell.

"Here are presented several algorithms that search for the most compatible representations of pair of crystal structures and provide the structural correspondence to represent a diffusionless transformation." - explain what a difusionless transformation is

"Thus, it is highly effective for systems with a small number of atoms in the unit cell." -> "Thus, it is highly ineffective for systems with a large number of atoms in the unit cell."

"The algorithm search for such combination of two unit cells" - "searchES"

"At the second stage, atoms of the structure are placed back into two generated supercells. " - what does it mean "placed back"?

"Among the set of possible combinations, taken only those where an atomic representation gives the minimum of trajectory lengths; i.e., the trajectory mileage of atoms during the transition from the initial structure to the final structures must be as less as possible" - not good English

"Also, there is a search algorithm for the identification of identical (duplicate) periodic structures that help to map the unit cells was developed by Lonie and Zurek" - "Also, a search algorithm for..."

"configuration space" -> "configurational space"

"Any region around local minima (LM) on the configurational space is presented by unique topology and can be considered as a topologically stable region." - explain in what sense it is stable

"4. Energetically more favorable are those paths, which cross the least number of boundaries on the CS." - is this an assumption or a proven theorem?

"In general, the subnet of a net is formed by subsets of nodes and subsets of edges of the supernet and the subnet can be considered part of the supernet." - please clarify definitions of subnet and supernet. You did not mention before that the number of nodes can be also different.

"The transition pathway with the lowest activation energy of the transition state expects to represent" - "is expected to represent"

"Different geometrical embeddings can have symmetry, which is a subgroup of G either coincide with G" - did you mean "is a subgroup of G or coincide with G"

"Both networks have been decomposed by symmetry. " - clarify what this means

"It was found that the topological mapping algorithm generates transitions with several different schemes and some of them are shown in Figure 3.3a." - I guess you wanted to refere to the whole Figure 3.3

"However, such condition will not be satisfied and generated initial pathway will have atoms trajectories intersection as illustrated in Figure 3.3b-d." - "will not always be satisfied"?

"Hence, properly prepared initial pathways explain how particles are moving during the transition and already at this step it can intuitively understand whether this transition is realistic or not." - improve English

"represent the discrete version of the transition pathway in the VCNEB method, like As in the original NEB method" - I guess "As" is redundant

"The strain components of □ on the lattice are the derivatives of H with respect to" - I think you forgot to write with respect to what

"The VCNEB and G-SSNEB methods treat the problem in different metric spaces..." - This discussion appears suddenly, please add a short intro, like "There is another approach called G-SSNEB (explain the abbreviation) that is ..."

"Crystal structures of predicted phases and were generated using VESTA software" - "and" is redundant

"Chromium nitrides are mostly studied with experimental works devoted to CrN and reporting the existence of a cubic paramagnetic B1-phase (NaCl-type) with Fm-3m space group" - English needs to be improved

"was based on experimental data made by Eriksson 219, which reported about hexagonal close-packed structure " -> "was based on experimental data obtained by Eriksson 219, who reported hexagonal close-packed structure"

"However, the only work where the global optimization of Cr-N systems was done by Kvashnin et al." -> "However, the only work on the global optimization of Cr-N systems was done by Kvashnin et al."

"The phases located in the first Pareto fronts, shown by red circles, lie on the convex hull or close to it (see Figure 4.1b)." - clarify if the red points in panel b correspond to red points in panel a

"The limitations to the mapping were to cut and to create less interatomic contracts and with higher symmetry of the obtained subnet-supernet pair." - the sentence is difficult to understand, please clarify; also, I guess "contracts" -> "contacts"

"While Cr and N atoms are topologically equivalent, and thus, the topologies of both structures can be described by unimodal nets." - bad English

"All of mentioned common subnets, i.e. sqp, vma and wlj, are 5-coordinated" - would be nice to see figures with examples illustrating different topologies

"As one can see, the list of common symmetry subgroups is not full and represented by few of possible." -> Perhaps "As one can see, the list of common symmetry subgroups is not complete but represented by a few possible subgroups."

"Lobanov et al. 231 investigated the high-P behavior of CaCO3, one of the most abundant carbonates near the Earth's surface and a good proxy for carbonate chemical composition in the mantle 232,233." -> Add the following after this sentence for clarity: "It is an sp2 carbonate at normal pressure."

"Also, the stability field of sp3-bonded..." - clarify what the "stability field" is

Page number is missing in ref. 231

"Because of mapping algorithm is not commutative," -> "Because mapping algorithm is not commutative,"

"The time step for the pathway relaxation has been set to 0.1 " - clarify which method you use to relax the pathway; where the time step comes from?

"The barrier height is quite large, 0.14 eV/atom" - tell again for which transition

"However, our results show this not to be the case as the values of critical C-O bond lengths vary for different transitions." - explain which results show this

"An anharmonic contribution does not influent significantly the phase boundary " -> "The anharmonic contribution does not influence significantly the phase boundary "

"Thus, the newly predicted ... phase can be obtained only at very high pressure." - did you mean "at very high temperature"?

"and then 2 interatomic contacts will be broken in during the transition to" -> "and then 2 interatomic contacts will be broken during the transition to"

"This description allows the representation of the motion of tungsten atoms in terms of change in their coordination number, i.e., the creation and breaking of interatomic contacts" - almost the same as the previous sentence, please remove duplicate

"Coexistence at normal conditions is due to high barriers of transitions, leading to metastable persistence of phases." - after this sentence, before computational details, it would be good to tell which phase transformations of Al2SiO5 you study (maybe all).

"Supporting Materials present the full set of optimized barriers for each kind of transition (10 pathways for A → B and 10 pathways for B → A)." - There should be no separate supporting materials for thesis

"Indeed, the canonical approach, which usually involves only the movement of atoms in the crystal structure, is well-known and intuitive, but it is not the best description of such complex transitions." - the sentence seems misplaced; I do not see a logical connection with the previous statement implied by "indeed"

"We find that SiO4 tetrahedra are presented during all transitions" - "are present"

"For andalusite-sillimanite transition at 0 GPa, the changes of coordination are morevcomplex than at 10 GPa. In general, at high pressure, the drops of average coordination numbers are smaller." - how sensitive is this to bond cutoff value?

"These improvements help investigate free energy landscapes of solids and locate MEP phase transitions in a more complex way." -> "These improvements help investigate free energy landscapes of solids and locate MEP for more complex phase transitions."

"The former is based on the purely geometrical compliance of two structures, i.e. cell parameters and coordinates of atoms. The least is based on the relation of chemical bonds periodic graphs (topological nets) and the atom-toatom mapping comes from the nets compatibility." -> "The first one ... . The second one ... ."

"However, such an approach has several valuable restrictions. For instance, when the considered transition happens between structures with different low symmetries, topological analysis can fail." - I guess you meant "However, such an approach has several important limitations".

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*