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Jury Member Report – Doctor of Philosophy thesis.

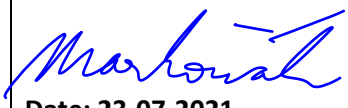
Name of Candidate: Artem Samtsevich

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: Prof. Roman Martoňák

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	 **Date: 23-07-2021**

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

The thesis has a high quality and provides a number of interesting and original results. The author presents a detailed introduction into the field of structural phase transitions in crystals and discusses their theoretical description, including kinetics. Afterwards he explains the pertinent state-of-the-art computational methods with a special focus on the geometrical and topological approaches for mapping two crystal structures and the workflow based on their combination with the variable cell nudged elastic band (VCNEB) method. This workflow is then applied to the determination of the transition mechanism in several interesting cases, namely CrN, $CaCO_3$, tungsten monoborides and Al_2SiO_5 phases. Each of the cases is discussed in detail and the atomistic mechanism is illustrated together with the energy profile. The final chapter summarizes the results.

The problems addressed in the thesis are of topical interest in high-pressure physics/chemistry and the results are relevant for solid state physics and materials science. The search for new approaches to the problem of determining the mechanisms of structural phase transitions in crystals is currently in rapid development and it is highly important to develop new methods and test their applicability on various problems. The results presented in the thesis were published in 3 papers in high-quality journals and one manuscript is submitted.

I suggest to include the following corrections/improvements:

- p.5 "*It does not take into account consideration of the interatomic interactions and structures of the substances.*" The problem with the Ehrenfest classification is different - it ignores the singularity of the free energy in case of continuous (2^{nd} order) transitions.
- "*Homogeneous nucleation is described by classical nucleation theory (CNT)[29]*" there is also non-classical nucleation theory, see B. Moran, Y. Chu, and G. Olson, International Journal of Solids and Structures 33, 1903 (1996)
- p.10 "*metadynamics method[64]*" should read "*metadynamics-based method[64]*"
- p.13 Eq. (1.3) C(t) should be defined
- p.25 "*Laio-Parrinello method*" - it should be called metadynamics as is common in the literature
- p.39 in Eq.(3.5) the sum of $(1+\sigma^T)$ is not correct because of different physical dimension of the two terms
- p.46 "*The results of Pareto optimization shown in Figure 4.1b*" it should be explained what is the meaning of the Pareto optimization
- p.64 it would be useful to include a graph of enthalpy vs pressure for the 3 phases as part of Fig. 4.13

Overall, the thesis reads well but would benefit from a careful proofreading and correcting some sentences (e.g. missing words).

I would like to ask the author two questions to be addressed during the thesis defense:

1 p. 57 In Fig 4.9 a P-T phase diagram is shown where the transition pressure decreases from 12 GPa at T=0 to zero at T=200 K. Such large Clapeyron slope appears surprising. Is there a particular reason for such behaviour, e.g. a soft phonon mode in the high-temperature phase resulting in large entropic contribution?

2 p.64 What is the reason to analyze the pathway from a more stable structure A to a less stable structure B (e.g. kyanite → sillimanite at both 0 and 10 GPa)? Such transition is unphysical.

I assign the thesis the "A" grade. I suggest to award to the author the PhD degree after successful defense of the thesis.

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*