THESIS REVIEWER'S REPORT

I. IDENTIFICATION DATA

Thesis title:	**Structural Tuning of Band Gap in Nanostructured Diamonds**
Author's name:	**Matúš Kaintz**
Type of thesis :	master
Faculty/Institute:	Faculty of Electrical Engineering (FEE)
Department:	Department of Control Engineering
Thesis reviewer:	Jan Zemen
Reviewer's department:	Department of Electrotechnology

II. EVALUATION OF INDIVIDUAL CRITERIA

Assignment **challenging**

How demanding was the assigned project?

The project involved quantum mechanical simulations of electronic structure of bulk crystalline material with a range of chemical compositions. The student had to gain insight into Density Functional Theory and develop practical skills required to run the ABINIT code and analyze large amounts of numerical data. The formulation of the problem to be addressed was quite ambitious in my opinion. Finding a link between the carbon-dopant bonding and the band gap width across a broad range of dopants is a significant challenge.

Fulfilment of assignment **fulfilled with minor objections**

How well does the thesis fulfil the assigned task? Have the primary goals been achieved? Which assigned tasks have been incompletely covered, and which parts of the thesis are overextended? Justify your answer.

The student carried out DFT simulations of band structure of diamond doped with 4 different concentrations of Al, B, Si, N, P, Sc, Ti, V, and Cr. He analyzed the band gap width as a function of different descriptors (atomic radius of dopant, Hirshfeld charge, bond length, bond covalency, orbital polarization). He was able to draw conclusions based on this analysis which are scientifically and technologically relevant. I believe that the extent of the study is broader than expected for a master thesis. However, a strict comparison with the assignment [zadání] shows that nanostructures and vacancies were not modelled (only bulk simulations with atomic dopants were carried out). Those are now planned as future work (suitable for doctoral thesis in my opinion).

Methodology **outstanding**

Comment on the correctness of the approach and/or the solution methods.

Density functional theory is used throughout the thesis. This is a state-of-the-art method in electronic structure simulations. The student checked carefully the convergence of the relevant quantities with respect to numerical input parameters such as the energy cutoff or the density of reciprocal space grid (k-mesh) dependent on the size of the supercell. Only one exchange correlation potential is used (GGA WC). Others are explored initially but the results are not reported in the thesis. The band gap width is underestimated by GGA WC as expected for a DFT simulation. I would expect that the choice of the exchange correlation potential may have a non-negligible impact on the reported results but repeating all the simulations for GGA alternatives or for GGA+U would be well beyond the scope if the master thesis.

Technical level **A - excellent.**

Is the thesis technically sound? How well did the student employ expertise in the field of his/her field of study? Does the student explain clearly what he/she has done?

The student has demonstrated broad expertise in the field DFT simulations of electronic band structure. The methods employed and the analysis of the results are explained very clearly.

Formal and language level, scope of thesis **B - very good.**

Are formalisms and notations used properly? Is the thesis organized in a logical way? Is the thesis sufficiently extensive? Is the thesis well-presented? Is the language clear and understandable? Is the English satisfactory?

The thesis is very well structured and written. There are minor typos but the language is on a level suitable for a scientific journal publication. I am confused by the labeling in Fig. 3.14 – the caption does not match the panel labels.

Selection of sources, citation correctness **A - excellent.**

Does the thesis make adequate reference to earlier work on the topic? Was the selection of sources adequate? Is the student's original work clearly distinguished from earlier work in the field? Do the bibliographic citations meet the standards?

The student has demonstrated broad awareness of the research field. The sources are selected adequately. The work is original and I expect it to be published in a peer-reviewed journal soon. The bibliography meets the scientific journal standards.

Additional commentary and evaluation (optional)

Comment on the overall quality of the thesis, its novelty and its impact on the field, its strengths and weaknesses, the utility of the solution that is presented, the theoretical/formal level, the student's skillfulness, etc.

Please insert your comments here.

III. OVERALL EVALUATION, QUESTIONS FOR THE PRESENTATION AND DEFENSE OF THE THESIS, SUGGESTED GRADE

Summarize your opinion on the thesis and explain your final grading. Pose questions that should be answered during the presentation and defense of the student's work.

The thesis presents a range of electronic structure simulations based on Density Functional Theory which is a computational method widely used in solid state physics and physical chemistry. The main aim of the study was to identify a link between the bad gap width of a doped diamond crystal and some descriptor of the bonding between the dopant and the diamond host. This link could then be used as guidance when engineering a novel diamond-based semiconductor, e.g., for photovoltaic applications. The student found that the "bond covalency" between the dopant and the surrounding carbon atoms seems to be a suitable parameter to control the width of the band gap. The effect of strain on the band gap is investigated too. I believe that the thesis is of very high quality as detailed above and I expect that publication of the results will contribute to this field of research.

Question 1: Is it possible to estimate the "bond covalency" with sufficient accuracy based on the atomic radius or electronegativity of the dopant without running DFT simulations? (If this could not be done for a wide range of dopants then it seems that running DFT for each dopant to get the band gap width directly is less complicated than evaluating it indirectly via the bond covalency from the same electronic structure obtained by DFT.)

Question 2: A 15% axial strain along all three crystallographic axes is mentioned in the thesis. Is the lattice relaxed in the remaining directions? Has the Poisson's ration been evaluated?

Question 3: Please comment on the exchange correlation potentials explored before GGA WC parametrization was selected. Can we be reasonably sure that the conclusions of the thesis would not change significantly if, e.g. GGA PBE was used instead?

The grade that I award for the thesis is **A - excellent.**

Date: **31.5.2022** Signature: