Oponentský posudek

na dizertační práci Sikandera Azama
„First principle studies of optical, thermoelectric and electronic characteristics of complex materials“

Reviewer's report

on the doctoral dissertation of Sikander Azam
„First principle studies of optical, thermoelectric and electronic characteristics of complex materials“

The progress in developing new materials for electronic and optoelectronic devices is not a straightforward path. Most of the effort is naturally concentrated on synthesis and experimental characterization. Getting new results or even making a breakthrough naturally requires more than just a trial and error approach. Understanding the principles and mechanisms behind the desired property is necessary. Ab-initio calculations are slowly becoming an integral part of this effort. One of the challenges here is to extract useful information from the sometimes vast number of theoretical results.

The author investigates properties of complex chalcogenides which is a good choice. It is a sufficiently focused and narrow group of materials so that specific conclusions can be obtained. At the same time, the class is broad enough to supply necessary degrees of freedom. Author presents theoretical results on electronic, optical and transport properties, therefore can offer quite a comprehensive view on the topic. This is certainly valuable.

The author uses predominantly quantum-mechanical ab-initio calculations, sometimes he combines them with semiclassical Boltzman transport theory. This combination is potentially very useful – it goes in the direction of multiscale modeling, which is one of the pursued directions in theoretical materials science. All ab-initio calculations were achieved by relying on the full-potential linearized augmented plane waves method (FLAPW). This is somewhat a limitation because certain aspects of the electronic structure are better described by other methods. On the other hand, the FLAPW method is generally considered as the most accurate method so this drawback is not serious. The core of the dissertation is a collection of six papers containing the original research of the author (and of other collaborators). This is perhaps too large a number to be assessed as a whole. However, the author presents a concise summary of all the papers and draws conclusions common to all of them. So he avoided the trap of having the dissertation too manifold. His Conclusions section contains practical hints for further technological research, fulfilling thus aims of the work.

The results of the authors seem to be technically correct. Perhaps the most valuable of them is a collection of computed band gaps for a number of compounds, compared to experiment. Interesting and potentially useful is also his assessment of thermoelectric properties of the systems under consideration. Another worthy aspect is that the author employs various exchange-correlation functionals and us thus able to give a recommendation in this regard as well.

I have got few comments and questions related to specific issues. As I mentioned above already, the author used solely the FLAPW method. I think it would be desirable to compare the FLAPW method to other frequently used calculation techniques (such as pseudopotential method, LMTO

method, KKR Green function method). What are the strengths and weaknesses of the FLAPW method in comparison with these techniques? A similar question would concern the BoltzTrap code the author uses. How reliable are its results in comparison with more advanced methods, say based on the Kubo formula? Another point I would raise concerns the description of how the thermoelectric properties are studied in Sec.3.9.1. I wonder whether the author could present a more intuitive meaning of the figure of merit ZT. Why is this quantity so important for assessing the potential usefulness of materials?

Another issue I am curious about is the effect of structural relaxations. The author does not discuss it in the dissertation explicitly but he pays attention to it in some of the papers. Is the structural relaxation essential for his conclusions? Would the results differ substantially if it had not been performed?

From the technical side, I would appreciate if the dissertation was prepared with more care in some places. The presentation style could be improved, there are few unnecessary English mistypes as well. As a whole, the dissertation style is nevertheless acceptable. More technical care should have been given to the Bibliography section – some references are all in upper case, which does not harm legibility but still disturbs. Reference [71] seems to be incomplete.

The publication record of the author is surely satisfactory, he is author or co-author of few dozens of research papers and in many of them he is the main author.

To conclude, I recommend the dissertation to be defended.

Praha, 4. April 2016

RNDr. Ondřej Šipr, CSc.

Oponentský posudek na dizertační práci

Sikander Azam

„First principle studies of optical, thermoelectric and electronic characteristics of complex materials“

Reviewer's report on the PhD thesis

by Sikander Azam

„First principle studies of optical, thermoelectric and electronic characteristics of complex materials“

The thesis investigates properties of quaternary chalcogenides, i.e. compounds containing the chalcogen elements (S, Se, or Te), which are widely investigated for a large variety of technological application – for example, thermoelectric, optoelectronic, photoelectric, and solid-state electrolytes for lithium secondary batteries. The aim is to understand the electronic structure of this class of materials, which can contribute to the progress in optical telecommunications and optical computing devices. The choice of the class of materials seems to be felicitous for the study within the thesis – sufficiently specific and, at the same time, broad enough to make some more general conclusions possible.

The author performs quantum-mechanical ab-initio calculations within DFT by means of the FLAPW method as implemented in WIEN2k package by Blaha, Schwarz and Luitz. In some cases, these calculations are combined with semiclassical Boltzman transport theory, indicating thus the direction to multiscale approach, which is a moderm trend in computational materials science.

The merit of the thesis lies in six attached research papers containing the original results of the author and other collaborators. That doesn't seem to be an ideal way of presenting results in the thesis, but, on the other hand, a concise summary and conclusions common to all the papers are appended in the thesis, which seems to be satisfactory. The results of calculations presented in the papers seem to be technically correct. For a series of compounds, an electronic structure calculations, compared to experiment, is presented together with an assessment of optical, transport and thermoelectric properties, offering thus a quite valuable, comprehensive view. Another interesting results is a comparison among various exchange-correlation functionals (note: a more complex analysis concerning differences among xc-functionals would be meritable – even if beyond the scope of the thesis). The “Conclusions” section contains practical findings and recommendations for next work.

By that, the aims of the work can be considered fulfilled.

Comments and questions:

I would appreciate explaining
- the motivation for using FLAPW and particularly WIEN2k package,
- general comparison with other methods (pseudopotentials with plane-waves, LMTO, KKR) and possibly comparison with other FLAPW codes (e.g. FLEUR)
- more detailed discussion on “technical parameters” (section 3.5) and their particular values used

during calculations
- the last sentence in Section 3.5 (do the special k-points really produce a uniform grid? under which conditions?)
- structural relaxations: in which cases and which way they were performed and what was their effect on the results
- the exact meaning of the term "greater optical coefficients" used only once in the thesis (at the beginning of abstract)

The thesis might have been written more carefully. The presentation style could be improved, few English mistypes could be avoided. As a whole, the style is nevertheless acceptable.

The publication record of the author is more than satisfactory (author or co-author of a series of research papers, the first author in many cases).

To conclude, I recommend the dissertation to be defended.

Praha, 9. April 2016

RNDr. Jiří Vackář, CSc.