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Review of W. Khan doctoral thesis

Title: Theoretical investigations of spectroscopic, electronic and magnetic properties of new low dimensional systems

This thesis deals with the theoretical and experimental study of materials appropriate mainly in the solar energy conversion using photo-catalytic reactions between Sun light and semiconductors in the water electrolyte. Spectroscopic, electronic and magnetic properties are especially in interest. The thesis contains eight chapters, summary and conclusions. Materials under the interest are: Niobium oxides, hematite and ilmenite. Theoretical study contains mainly Density functional theory and electronic structure methods. The experimental procedures used were especially transmission electron microscopy and electron energy-loss spectroscopy.

In the first (1-3) chapters some principles and the theoretical background of the procedures for structure evaluation are explained in detail. Chapter 4 deals with the materials selection and chapters 5-8 are devoted to the theoretical and experimental study of materials selected. All theoretical and experimental results and consequences obtained from the analysis are described in detail. Theoretical and experimental results are mostly in a good agreement as can be seen in many figures presented in the thesis. Materials selected for the analysis belong to the top materials for the object of interest (solar technology). Nevertheless, because there is a lot of information in the whole text, one can very quickly “lose ground”. On the other hand, the manuscript is well-organized and structured.

The results of the research presented in the thesis were already published in journals with the impact factor. Mgr. W. Khan presents in the end of the thesis altogether 21 papers published.

Because Mgr. W. Khan displayed in this work his high theoretical and experimental erudition, I recommend present the thesis to be defended.

My question is: I would like to know how can be exactly defined the following quantities:

- Thermoelectric conductivity and
- Optical conductivity

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Reviewer's report

on the doctoral thesis of Mgr. Wilayat Khan
"Theoretical investigations of spectroscopic, electronic and magnetic
properties of new low dimensional systems"

The development of the alternative energy suppliers provides a pathway into a secure, environmentally friendly and economically successful future. The basic power sources such as the nuclear plants and fossil fuels are gradually substituted by the renewable energy means. A significant role in this process is played by the solar energy conversion systems, e.g., the so-called solar cells, which convert the absorbed solar light into the electric voltage. Optimization of these devices in terms of their efficiency, manufacture costs, toxicity of the components, operational timescales and conditions constitutes an intensive technological process in which new materials and new functional principles are actively introduced and combined. In this context, the present theoretical study of Mgr. Khan aimed to understand the properties of the state-of-the-art solar cell materials on the fundamental level, i.e., based on their first-principles electronic structure, is undoubtedly important and timely.

The first chapter of his thesis justifies the importance of the topic followed by the description of the photo-catalytic reaction and comparative overview of the materials used in the photo-catalysis. The second chapter outlines the details of the first-principles methodology used by Mgr. Khan to describe the electronic structure of the studied materials. This includes the conventional density functional theory (DFT) and various approximations to the exchange-correlation functional, such as the local density approximation (LDA), general gradient approximation (GGA) and the specific approximations, which are vital for the adequate description of the wide band gap nonmagnetic (e.g., Trans-Blaha modified Becke-Johnson (TB-mBJ)) and magnetic (e.g., DFT+U) semiconductors. Third chapter outlines the formalism (based on the Augmented Plane Waves plus Local Orbitals) of the computational scheme which implements these approaches numerically. It also contains the description of applications of the method to the optical, X-ray absorption and energy loss spectroscopies, thermal and electronic conductivity coefficients. Chapter four describes the materials which are studied in this work: the oxides of Niobium and Iron. The core chapters 5 and 6 of the thesis present the study of these materials and their spectral properties. In particular Mgr. Khan studies the effects of their modifications by dopants: admixture of Ti in Nb-O and of Sn in Fe-O. These chapters clearly outline the results obtained by Mgr. Khan including their detailed analysis and comparison with experiments.

Comments and questions:

1. Though the manuscript is well-structured and clearly written, it still contains plenty of grammatical mistakes which are necessary to improve, as well as the inconsistencies in figure captions: for example, whenever there are sub-figures marked a,b,c, ... the corresponding explanation in the caption must refer them by following the same sequence.
2. By comparing his results, e.g., energy loss spectra with experiment (e.g., in Fig.5.6), the author did not mention the absence of the phonon-mediated transitions in his calculations as one of the reasons for the discrepancy. For example, from the band structure of Nb₃O₇(OH) (Fig.5.2(b)) it follows, that the material contains an indirect gap, i.e., the phonon-mediated transitions might occur at finite temperature. At the same time, the deviation of theory from experiment in this case is comparatively large. I would recommend that the author adds a short statement/remark about the influence of the indirect transitions.
3. The author performed a systematic study of the doping effects in Nb-O (with Ti) and Fe-O (with Sn) systems. I would suggest to add a clear conclusion (i) which doping rate would be optimal for the solar cell performance with the given material and (ii) how does the stability of the system changes at this doping rate.
4. The author has considered the effect of dopants by explicitly taken them into account within the super-cell. I think, that adding few sentences about alternative methodologies which take into account such effects without a need to use super-cells, such as Virtual Crystal Approximation (VCA) and the Coherent Potential Approximation (CPA), will make this aspect more complete. What would be their advantages and disadvantages with respect to the description of the present systems?

To summarize:

Theoretical results obtained by Mgr. Khan on Nb- and Fe-O materials and the influence of their doping on spectral properties are undoubtedly interesting both from the fundamental as well as from the application viewpoints. I believe that connection between the atomic structure, electronic structure, and their spectral properties, which he has established by ab-initio calculations provides useful information for the electrical engineers and indicates the possibilities of further optimization. The publication record of the author is definitely satisfactory.

Based on that, I suggest the dissertation of Mgr. Khan to be defended.

Sincerely,



Dr. Stanislav Chadov