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Review of the doctoral dissertation
of Ghulam Hussain, M.Sc.:
"Investigating the electro-optical properties of 3D superlattices and 2D materials: A DFT study"

The doctoral dissertation was prepared at the Institute of Physics of the Polish Academy of Sciences in Warsaw under the supervision of dr hab. Carmine Autieri *[Ph.D., postdoctoral degree holder]*, professor of IF PAN. The assistant supervisor was dr Giuseppe Cuomo *[Ph.D.]*.

The doctoral dissertation of G. Hussain is based on four publications:

***G. Hussain**, G. Cuono, R. Islam, A. Trajnerowicz, J. Jureńczyk, C. Autieri, T. Dietl, Electronic and optical properties of InAs/$InAs_{0.625}Sb_{0.375}$ superlattices and their application to far-infrared detectors, Journal of Physics D: Applied Physics 55, 49531 (2022)*

***G. Hussain**, M. Asghar, M. Waqas Iqbal, H. Ullah, C. Autieri, Exploring the structural stability, electronic and thermal attributes of synthetic 2D materials and their heterostructures, Applied Surface Science 590,153131 (2022).*

***G. Hussain**, M. Manzoor, Waqas Iqbal, I. Muhammad, A. Bafekry, H. Ullah, C. Autieri, Strain modulated electronic and optical properties of laterally stitched $MoSi_2N_4/XSi_2N_4$ (X=W, Ti) 2D heterostructures, Physica E 144, 115471 (2022).*

***G. Hussain**, A. Samad, M. Ur. Rehman, G. Cuono, C. Autieri, Emergence of Rashba splitting and spin-valley properties in Janus $MoGeSiP_2As_2$ and $WgeSiP_2As_2$ monolayers, Journal of Magnetism and Magnetic Materials 563, 169897 (2022).*

From the documentation provided with the doctoral dissertation, it appears that all calculations presented in the 4 publications were performed by Ghulam Hussain, M.Sc.

The topic of the doctoral dissertation covers theoretical results obtained in four papers of which Ghulam Hussain is the first author and corresponding co-author.

The doctoral dissertation consists of copies of 4 publications with the Author's commentary. In total, the dissertation has 79 pages plus a collection of co-authors' statements.

The first chapter presents extensive literature information about the researched materials and the main goals of the doctoral dissertation.

The second chapter contains textbook information about the DFT method. The third chapter presents four publications constituting a doctoral dissertation. In the final part, Ghulam Hussain presented a summary and conclusions.

The aim of the doctoral dissertation, as the author writes, was to study the electronic and optical properties of selected three-dimensional and two-dimensional superlattices and Janus structures whose absorption spectra are located in the infrared region.

The second chapter discusses the DFT method. Unfortunately, there is no information about the adopted models for the calculation of electronic and optical properties for $InAs/InAs_{0.625}Sb_{0.375}$, for two-dimensional superlattices MSi_2N_4 (M=Mo, W, Ti) and $MoSi_2N_4/WSi_2N_4$, $MoSi_2N_4/TiSi_2N_4$ and the model for Janus structures. Calculations of the electronic structure were performed for the MBJ and HSE exchange-correlation potentials. In my opinion, their form should be described in this chapter. Calculations from the first principles, as results from the publication, were made based on VASP and PHONOPY software. Unfortunately, there are no literature references to these methods in Chapter 2. The literature list also lacks papers on the VASP and PHONOPY software. Of course, the literature data for the software are provided in the attached publications. I believe that the details of the calculations should be presented in the doctoral dissertation.

Evaluation of the doctoral dissertation

As I mentioned in the introduction, the doctoral dissertation shows the results presented in four publications. According to the Law on Higher Education and Science, this form is acceptable. Nevertheless, I have found a few elements missing in the doctoral dissertation presented for review. In chapter 2, despite the title, there are no details of the calculations. This is an important element because, in the calculations in the first principles (using the available VASP and PHONOPY software), the adopted model and approximations are important. Of course, all the elements can be found in publications, but when evaluating a doctoral dissertation, one cannot limit oneself only to copies of already published works. Since the topics of the works are diverse, I have found that there is no information on which result the author considers to be the most important.

Research topics of Ghulam Hussain, M.Sc. include studies of electronic structure, optical properties of three-dimensional $InAs/InAs_{0.625}Sb_{0.375}$ superlattices, two-dimensional $MoSi_2N_4/WSi_2N_4$, $MoSi_2N_4/TiSi_2N_4$ superlattices, MSi_2N_4 compound, and Janus $Mo/WGeSiP_2As_2$ structure. The above research was aimed at searching for new infrared (IR) detectors. The electronic structure was determined by first-principles (ab-inito) methods. Calculations of electronic and optical properties for complex structures were made using the VASP software. Photon spectra were calculated based on the PHONOPY software, which uses the electronic structure determined by VASP. For the studied superlattices, these calculations are time-consuming and require knowledge of complex computational techniques.

Because the DFT LDA methods do not correctly describe the electron structure of semiconductors, modified forms of exchange-correlation potentials are used in the calculations. The publications used the Heyd-Scuseria-Ernzerhof (HSE06) and Becke-Johnson (MBJ) forms with the GGA (Generalized Gradient Approximation). In the calculation of the electronic structure, the spin-orbit (SO) interaction necessary for the considered systems was also taken into account.

Chapter 3 consists of copies of four publications preceded by a commentary of Ghulam Hussain, M.Sc.

In the first publication (J. Phys. D Appl. Phys. 55, 495301 (2022)) the electronic and optical properties of InAs and InSb and three-dimensional InAs/$InAs_{0.625}Sb_{0.375}$ superlattices were presented. The calculations were made in MBJ approximation, taking into account the S-O interaction. Figure 4 is interesting, showing the band structure at the Gamma point for different values of lattice parameters. For the InAs/$InAs_{0.625}Sb_{0.375}$ superlattice, the calculations were made for the value of the lattice parameter at T=300K. The electronic structure and optical properties changed strongly with lattice parameters. The far-infrared absorption spectra of InAs/$InAs_{0.625}Sb_{0.375}$ were strongly enhanced relative to InAs and InSb bulk compounds. Calculations indicated that InAs/$InAs_{0.625}Sb_{0.375}$ is a good candidate for a long-wave infrared detector.

The second publication (Applied Surface Science 590, 153131 (2022)) presents calculations of the electronic structure, optical properties, and photon spectra for the lateral heterostructure (LH) and vertical heterostructure (VH) of two-dimensional $MoSi_2N_4/WSi_2N_4$ and $MoSi_2N_4/TiSi_2N_4$. The new structures were optimized and photon spectra were calculated for them, which confirmed the stability of these systems. In the paper, electronic densities of states (DOS) and band structures approximation were calculated using PBE and HSE06. For $MoSi_2N_4/WSi_2N_4$, there is a gap density of states of 1.92 eV (PBE) and 2.32 eV (HSE06), while in the case of $MoSi_2N_4/TiSi_2N_4$ for LH the gap was 0.14 eV and 0.30 eV for PBE and HSE. Calculations showed that MoSi2N4/TiSi2N4-VH is metallic. The appearance of the band gap in the visible region enables the use of these systems in photovoltaics and optoelectric devices. $MoSi_2N_4/TiSi_2N_4$-LH superlattices can be used in IR detectors.

The next publication (Physica E 144, 115471 (2022)) is a continuation of the research started in the previous work. The band structure and optical properties of the $MoSi_2N_4/XSi_2N_4$ heterostructures for X=W, Ti were investigated using various PBE and HSE approximations. An interesting element of the doctoral dissertation was the study of the effect of biaxial strains on the optoelectronic properties of two-dimensional sublattices. A significant change in the band structure and optical spectra of the transition (from semiconductors to metal) was observed (Fig. 3 and 4). Calculations of optical properties pointed to the possible application of two-dimensional materials in nano- and optoelectronics.

The most important achievements of this work include a comprehensive analysis of electronic and optical properties as well as the study of the thermodynamic stability of the two-dimensional $MoSi_2N_4/WSi_2N_4$ and $MoSi_2N_4/TiSi_2N_4$ superlattices.

In the fourth publication (Journal of Magnetism and Magnetic Materials 563, 169897 (2022)) electronic, optical properties and photon spectra of $MoSi_2N_4$ compounds and Janus $MoGeSiP_2As_2$ and $WGeSiP_2As_2$ structures were presented. Theoretical calculations showed that such structures are stable and possible for experimental implementation. The band gap in $MoSi_2N_4$ was 0.61 eV, which makes it possible to use it in NIR detectors.

The calculation results presented in Chapter 3 are interesting and will certainly inspire further research on new systems. Nevertheless, it is difficult for me to determine which theoretical result is the most important in the doctoral dissertation of Ghulam Hussain. The Ph.D. candidate did a lot of first-principles calculations that are strongly related to the experiment. DFT methods, in particular VASP, are constantly being developed and the main problem is the exchange-correlation potential, the form of which significantly affects the electronic structure of semiconductors.

Editorial Notes:

1) *Lack of literature references in the doctoral dissertation to the VASP and PHONOPY software and MBJ and HSE correlation potentials*

   (PHONOPY, Atsushi Togo and Isao Tanaka, Scr. Mater., 108, 1-5 (2015)).

   (VASPs and pseudopotentials)

   G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993); ibid. 49, 14 251 (1994).

   G. Kresse and J. Furthmuller, Comput. Mat. Sci. 6, 15 (1996).

   G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11 169 (1996).

   G. Kresse and J. Hafner, J. Phys.: Condens. Matt. 6, 8245 (1994).

   G. Kresse and D. Jaubert, Phys. Rev. 59, 1758 (1999).06.

2) *Omission of detailed calculations in Chapter 2.*

3) *Electronic and optical properties of semiconductors depend on the form of correlation-exchange potentials. For some systems, agreement with the experiment gives METAGGA=SCAN.*

   The SCAN (strongly constrained and appropriately named) (Phys. Rev. Lett. 115, 036402 (2015))

Summary

The doctoral dissertation of Ghulam Hussain, submitted for review, contains many interesting results presented in the attached publications. One can only comment on the form of the dissertation itself. The descriptive part is very sparing. I have found that a description of the models, a discussion of the adopted approximations and an indication of the most important scientific achievement were missing. The Ph.D. candidate performed time-consuming calculations of the electronic structure and optical properties of two- and three-dimensional superlattices using the VASP software. An important element in these calculations was to construct a superlattice structure model. The photon spectra were calculated based on the PHONOPY software. The results presented in the dissertation provide valuable clues for experimental groups on new systems.

Having read the doctoral dissertation of Ghulam Hussain, I find that it meets the requirements set out in art. 187 of the Act of 20 July 2018 Law on Higher Education and Science, and I motion to admit Ghulam Hussain to further stages of the proceedings.

Considering the large amount of work involved in obtaining interesting theoretical results and the publication of the results in significant scientific journals, I believe that, despite reservations about the form of chapter 2, the doctoral dissertation of Ghulam Hussain, M.Sc. may deserve a mention.

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