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dr hab. Karol Szałowski *[Ph.D., postdoctoral degree holder]*, **professor at the University of Łódź**
Department of Solid State Physics
Faculty of Physics and Applied Informatics
University of Łódź

Review of the doctoral dissertation of Mr. Ghulam Hussain, M.Sc.

entitled: *Investigating the electro-optical properties of 3D superlattices and 2D materials: A DFT study*

The doctoral dissertation presented by the Author was written at the International Centre for Interfacing Magnetism and Superconductivity with Topological Matter – MagTop at the Institute of Physics of the Polish Academy of Sciences in Warsaw. The supervisor is dr hab. Carmine Autieri *[Ph.D., postdoctoral degree holder]*, professor of IF PAN (the Institute of Physics of the Polish Academy of Sciences in Warsaw), and the role of assistant supervisor is performed by dr Giuseppe Cuono *[Ph.D]* (the Institute of Physics of the Polish Academy of Sciences in Warsaw). The doctoral dissertation takes the form of a collection of published and thematically related scientific articles, which meets the requirements set out in Art. 187 sec. 3 and 4 of the Act of 20 July 2018 The Law on Higher Education and Science.[1]

The dissertation consists of 4 co-authored papers (5-7 authors in total), published in 2022 in journals from the Journal Citation Reports list (also included in the list referred to in Art. 186(1) of the Act - cf. Communication of the Minister of Education and Science of 1 December 2021 on the list of scientific journals and reviewed materials from international conferences). One of the articles was published in the prestigious journal *Applied Surface Science* (with an Impact Factor of 7.932 for 2021), the others in *Journal of Physics D: Applied Physics* (IF of 3.409), *Physica E: Low-dimensional Systems and Nanostructures* (IF of 3.369) and the *Journal of Magnetism and Magnetic Materials* (IF of 3.097). These are journals with an established reputation in the field of condensed matter physics – physics of nanostructures, low-dimensional systems, and surface physics. Therefore, the selection of journals should be assessed as accurate.

[1] i.e. Journal of Laws of 2022, item 574 as amended

In each of the works included in the submitted dissertation, the Ph.D. candidate is the first author. In addition, based on the attached statements of the Ph.D. candidate and each of the co-authors (including the supervisor and assistant supervisor), it can be stated that the Ph.D. candidate has a leading role in the presented works.

The Author of the doctoral dissertation is interested in three separate groups of modern materials: three-dimensional InAs/$InAs_{0.625}Sb_{0.375}$ superlattices, two-dimensional $MoSi_2N_4/WSi_2N_4$ and $MoSi_2N_4/TiSi_2N_4$ heterostructures, as well as Janus $MoGeSiP_2As_2$ and $WGeSiP_2As_2$ monolayers. The main purpose of the calculations carried out is to predict optical properties from the point of view of specific applications in infrared detectors, and thus, a detailed analysis of primarily the electronic structure (focused on the band gap) and properties related to the complex, alternating field electric susceptibility. For the third group of studied structures, the study is supplemented by the analysis of properties relevant to spintronics. The calculations themselves were made by the Author using the recognized tool, which is the Vienna Ab initio Simulation Package (VASP), which has been developed for over 30 years. This choice should be assessed as well justified.

The above-mentioned 4 publications were supplemented by the Author quite skilfully by creating the structure of the dissertation, preceded by a general introduction chapter explaining the motivation of interest in the studied systems and a chapter devoted to research methodology and research methods, and ending with common conclusions. The content written in English, preceding the Ph.D. candidate's publications (which were separated as specific subchapters in chapter 3 of the dissertation which is constructed in this way), has a total of 24 numbered pages; there is also a separate list of literature referred to in the introduction and a list of graphics contained therein. In accordance with the requirements of the Act, the dissertation is provided with an abstract in Polish and English.

The introduction opens with a brief explanation of the aim of the dissertation and the content of the publications it comprises. In the further part of the introduction, the Author explains the division of the infrared spectrum in relation to the aim of the research. Then, he presents a very extensive and interestingly detailed historical background, embedding his research on superlattices in the very broad context of work on the detection of infrared radiation. He does this by focusing on the evolution of the detectors themselves and specific technical solutions in conjunction with the development of knowledge about semiconductor materials suitable for such applications and highlighting the application aspects and functional characteristics of individual material solutions. As one of the alternatives to HgCdTe, which is somewhat a milestone in the field of infrared detection [cf. e.g. A. Rogalski, Rep. Prog. Phys. **68** (2005) 2267], he indicates the InAs/GaInSb superlattice.

The next stage of the introduction presents the application potential of various classes of two-dimensional materials, such as transition metal dichalcogenides, and further discusses more

complicated systems – hybrid two-dimensional materials and Janus-type monolayer materials, mentioning the recent achievements in their synthesis. Here, there is a description and discussion of Fig. 1.4, which could be supplemented with the statement that type 2H monolayers are shown [there is also no reference in the text mentioning panel (a) of this figure]. The introductory chapter ends with a walk-through of the content of the next parts of the work.

The Author dedicates the second chapter to a discussion of the theoretical formalism and the methodology of the performed calculations. Its beginning is the presentation of a general problem in solid state physics – the problem of a multi-electron system described by the Hamiltonian taking into account electrons and nuclei of atoms, and an explanation of the Born-Oppenheimer approximation, which is natural in this context. Further considerations lead to the formulation of the Hartree-Fock approach and, in general, serve to discuss the reduction of the multi-molecule description to the single-molecule description in the effective potential. When discussing Equation 2.7, for the sake of clarity, the full form of the Slater determinant could be given; in the context of the sentence following the formula, it is not fully clear how to go from one-electron orbitals to the ground state wave function. The Author also does not explain the meaning of the coefficients *C* in Equation 2.9 or η symbols in Equation 2.10; references to ϕ_i and $\phi_{i...N}$ are not always clear (cf. Equation 2.10 in the context of the preceding sentence). This section is an introduction to the discussion of the proper method of density functionals based on the fundamental results obtained by Kohn, Hohenberg, and Sham. The Author outlines the Kohn-Sham equations and then discusses the approaches to determining the correlation-exchange functional occurring in these equations. These are: the local density approximation and the generalized gradient approximation (where implementations in the Perdew-Burke-Ernzerhof or Perdew-Wang approximations were mentioned) and other (hybrid) formulations of the correlation-exchange potential. In this context, it seems to me that it would be fully justified to provide here the form of the Becke-Johnson potential used by the Author in the published calculations (paper 1). Similarly, the chapter could be extended to include the form of the used HSE06 (Heyd-Scuserii-Ernzerhof) hybrid functional and the explanation of the HSE abbreviation (paper 2, 3). The next part of the methodological chapter describes the approximation of plane waves and the necessary cut-off parameters, and then the motivation for introducing the pseudopotential and its construction within the *projector augmented wave* (PAW) concept. The discussed part of the chapter explains, usually with a reasonable level of detail, the theoretical formalism constituting the universal basis of the performed calculations, along with a discussion of the necessary simplifying assumptions, which makes the Author a conscious user of the selected calculation tool. In light of the content of the publications constituting the dissertation, which sometimes also include the determination of the phonon dispersion relation and some further thermodynamic calculations based on it, it would be valuable to supplement this methodological material with an explanation of issues related to the calculations for phonons made on the basis of DFT (based on the PHONOPY package).

The third chapter groups the Author's 4 publications, formally distinguished as subchapters and preceded by a joint short discussion of key results; each of the works is also provided with a separate concise introduction. My assessment of such a structure is positive as it serves consistency and facilitates the reading of the whole of the doctoral dissertation.

The first of the Author's publications (in *Journal of Physics D: Applied Physics*) is devoted to the presentation and discussion of the results of calculations of the properties of three-dimensional superlattices InAs/$InAs_{0.625}Sb_{0.375}$ with the orientation (001), consisting in the direction of growth of 26 InAs elementary cells and 8 In(As,Sb) elementary cells. After the introduction, the choice of detailed calculation methods is discussed, e.g. the issue of considering the spin-orbit interaction, as well as the issue of the choice of correlation-exchange potential. When discussing the results for three-dimensional superlattices, one could mention the procedure of relaxation of atomic position for the large system under study – I think it is worth discussing it during the doctoral defense. As a reference point, the Author first performed calculations for the InAs and InSb massive material, discussing the energy gap value and band structure, as well as optical properties, which are the contents of the first two subunits of the divided published work. In particular, the effective masses of electron and hole carriers for individual bands along different directions in the wave vector space were determined, and compared with literature results of a theoretical and experimental nature. In the context of the discussed publication, it would be worthwhile for the Ph.D. candidate to explain the features of the Type III superlattice mentioned there during the defense (in analogy to the explanation of the features of the Type II superlattice in chapter 1.1).

The next part of the first publication begins with a discussion of the proper results for a superlattice, where structures with three lattice constants were taken into account: pure InAs, pure InSb and pure GaSb at 300 K, which leads to stresses in the superlattice obtained. It should be noted that the considered system contained many atoms, posing a considerable computational challenge. The band structure, including the anisotropic effective masses of the carriers, was determined again, and the key influence of the lattice constant in the plane on the values of these masses and the energy gap was found. The formation of two heavy-hole bands was also predicted, in contrast to the situation in the solid material, and other differences in relation to the solid material were found (resulting primarily from the clearly marked anisotropy of the system), including different degrees of the location of holes and electrons. The following part is used to describe in detail the results regarding optical properties – resulting from the complex permittivity, which also shows a clear anisotropy in the tested system (part of the graphs in the supplement). One of the features of the superlattice, in relation to the homogeneous solid material, is the increased absorption coefficient. The conclusion contains an interesting discussion of factors that, if taken into account, could improve the quality of the obtained predictions (e.g. the possibility of using the Berthe-Salpeter equation) and the physicality of certain assumptions, such as stress uniformity, which proves well the Author's critical attitude towards the results. There is also a discussion of further computational challenges. The published supplementary materials

contain valuable methodological explanations (in the context of the Author's calculations of optical properties based on complex permittivity, the method of calculating this quantity based on the DFT results, and further definitions of the relevant optical parameters discussed). In addition, the supplement also presents the procedure for selecting the c^{MBJ} factor in the Becke-Johnson potential. The found influence of stresses on superlattice properties opens the door to property engineering from the point of view of far infrared detection.

The subject of another Ph.D. candidate's publication (in *Applied Surface Science*) concerns the study of the properties of two-dimensional systems, built of monolayers of materials with the general formula MA_2Z_4, where M is a transition metal, A is a group IV element, and Z is a group V element. In this paper, also lateral and vertical MoSi2N4/WSi2N4 and MoSi2N4/TiSi2N4 heterostructures were studied. The initial step was to determine the stability of the $MoSi_2N_4$, WSi_2N_4, and $TiSi_2N_4$ monolayers by their structural relaxation, and then to calculate the cohesion energy and determine the phonon structure. In each case, the stability of the analyzed structures was confirmed. The same stability was confirmed for the $MoSi_2N_4/WSi_2N_4$ and $MoSi_2N_4/TiSi_2N_4$ heterostructures. The analysis of the electronic structure includes a discussion on the density of states along with contributions from individual elements and the band structure itself. The energy gap of the $MoSi_2N_4/WSi_2N_4$ heterostructures corresponds to the energy of infrared photons, while for $MoSi_2N_4/TiSi_2N_4$ it is in the visible light range; corresponding gaps for monolayers also correspond to visible light. For heterostructures, the results obtained using the PBE potential and the hybrid HSE potential (Heyd-Scuseria-Ernzerhof) were compared. Typical, previously discussed optical properties were also calculated, primarily for this structure, which shows the potential for applications in infrared detection. The presented results are complemented by calculations of Helmholtz free energy, entropy, and specific heat capacity at constant volume. In the context of the content of this publication, it would be useful to supplement Chapter 2 with a discussion of phonon calculations based on the DFT formalism and approximations used in the modeling of Helmholtz free energy, entropy, and specific heat capacity.

The Author devoted a separate publication (in *Physica E: Low-dimensional Systems and Nanostructures*) to the $MoSi_2N_4/WSi_2N_4$ heterostructure (and, to a slightly lesser extent, $MoSi_2N_4/TiSi_2N_4$) of a lateral nature; the research concerns the impact of biaxial stresses on the band structure and optical properties, indicating the way of modifying the above-mentioned material properties by selecting stresses (e.g. selection of the substrate for culture). In particular, the tensile stress reduces the value of the energy gap, while the compressive stress first increases the value of this gap, and then primarily changes its character from oblique to straight. This is related to the change in the contribution of individual orbitals to the state at the top of the valence band. A similar analysis was carried out by the Author for $MoSi_2N_4/TiSi_2N_4$ (here only the HSE reproduces the oblique energy gap; it is interesting that for calculations made using the hybrid potential the energy gap may close for a sufficiently

strong compressive stress). The optical properties of the tested structures are also modifiable by biaxial stress. The performed calculations indicate the importance of taking into account the spin-orbit interaction for reliable prediction of the electronic structure. In the context of the calculations performed, the issue of non-equivalence of K1/K2 and M1/M2 points for the superlattice is discussed – here it would be interesting to discuss the diagram explaining the form of this zone in the wave vector space.

Monolayer Janus materials are a highly promising class of low-dimensional materials and the subject of intense research interest, as confirmed by, among others, the abundance of reviews published in recent years on this subject, focused primarily on MXY structures [W.-J. Yin et. al., Mater. Adv. **2** (2021) 7543; L. Zhang et. al., J. Appl. Phys. **131** (2022) 230902; X. Tang. L. Kou, Phys. Stat. Sol. B **259** (2022) 2100562; R. Li, Y. Cheng, W. Huang, Small **14** (2018) 1802091]. Continuing his interest in two-dimensional materials, the Ph.D. candidate performed calculations for Janus structures of the $MGeSiP_2As_2$ type, where M means Mo or W, the results of which he presented in the fourth publication (in the *Journal of Magnetism and Magnetic Materials*). Here, the phonon structure and thermodynamic stability also became of interest, as well as the work function and its difference between the two planes terminating the layer (as the electric dipole moment perpendicular to the plane appears in the studied structures). The most interesting, however, are the calculations of the electronic structure. Due to the breaking of the inversion symmetry (the symmetry group for the studied Janus structures is C_{3v}), the appearance of the Rashba-type spin-orbit interaction is possible in the studied structures. The publication discusses the contribution of specific atomic orbitals of individual elements to the band structure and extracts the parameters of valence and conduction band splitting, as well as the Rashba-type spin-orbit interactions at the K point (present only in Janus structures). Furthermore, the orientation of the spin in the k_x-k_y plane was plotted across the first Brillouin zone, finding interesting chiral structures, and the constant energy contours of the valence bands near the Γ point were analyzed, discussing the results in terms of symmetry. The obtained results show the potential for spintronics and valleytronics applications. An interesting extension of the work carried out could be the study of the effect of the electric field applied perpendicularly to the plane, as well as the modeling of band structures with effective tight-binding Hamiltonians. In supplementary studies, a dynamic instability of the $MoSnSiP_2As_2$ and $MoPbSiP_2As_2$ monolayers was found. As in previous works, also in this work, the Author determined the optical properties of the tested materials.

The dissertation ends with concise conclusions, collecting and recapitulating the basic results obtained in the 4 discussed papers.

The list of literature referred to in the introduction includes 148 items. As a reviewer, I noticed errors regarding the use of subscripts in the spelling of the titles of cited papers and the use of capital letters in journal titles, as well as incomplete (historical) data of item 9 or item 44.

I believe that the entire introduction and additions contained before individual publications competently present the background and motivation of the undertaken research, justify their importance for the physics of materials and application potential, and finally inform about specific systems for which calculations predicting their properties were carried out.

In the context of reading the dissertation, certain questions and remarks arise (basically already signaled earlier in the content of the review), which I present and expand on below.

During the defense, I would like the Ph.D. candidate to present the form of the original potential proposed by Becke and Johnson (BJ) [A. D. Becke, E. R. Johnson, J. Chem. Phys. **124** (2006) 221101] and the essence of its modification (MBJ) made in the work of F. Tran. P. Blaha. Phys. Rev. Lett. **102** (2009) 226401. This would also explain the essence of the c^{MBJ} parameter used in the dissertation.

Referring to the effectiveness of the MBJ potential in modeling the energy gap in semiconductors, the Ph.D. candidate could also refer to the work of D. Koller, F. Tran, P. Blaha, Phys. Rev. B **83** (2011) 195134 devoted to the analysis of the applicability of the mentioned potential to various classes of solids and the physical background of the identified advantages and disadvantages of the method, as well as the work of J. Camargo-Martinez, R. Baquerro, Phys. Rev. B **86** (2012) 195106. A more recent work on a similar topic is H. Abu-Farsakh, A. Qteish, Comput. Mater. Sci. **208** (2022) 111324. I would like the Ph.D. candidate to briefly discuss the aforementioned issues of applicability during the defense of the dissertation. The issue of the applicability of MBJ to inhomogeneous systems is raised by T. Rauch, M. A. L. Marques, S. Botti, J. Chem. Theory Comput. **16** (2020) 2654.

I would suggest that the Ph.D. candidate explain the features of the type III superlattice mentioned there (in analogy to the explanation of the type II superlattice in chapter 1.1). I would also like the Ph.D. candidate to present a schematic drawing of the first Brillouin zone for the $MoSi_2N_4/WSi_2N_4$ superlattice, where the relevant diagram would be of particular importance, explaining the issue of inequivalence of K1/K2 and M1/M2 points.

Referring to the results of the second publication, I would suggest that the Ph.D. candidate explain what the quasiharmonic approximation used in the PHONOPY package is all about, which allows you to calculate such thermodynamic quantities as specific heat capacity or entropy for solids.

In the context of interesting calculations concerning the spin-orbit coupling in Janus structures, a question arises whether in the studied structures one could expect

the Rashba coefficient anisotropy – a different value for the Γ–K and Γ–M directions (as predicted for PtSSe, PtSTe, and PtSeTe in the paper of P. A. L. Sino et. al., Nanoscale Adv. **3** (2021) 6608)?

The Author, while creating the dissertation, did not avoid mistakes of a purely editorial nature, which I will mention as the duty of the reviewer. There are also sometimes incomplete or awkwardly worded sentences. For example, formula 2.12 is missing the bra vector. Sometimes there are semicolons instead of colons (see page 22). On page 8, the sentence "the d electrons varies from zero to six" sounds awkward ("the number of electrons" would be better); on page 16 "wave of functions" sounds awkward. On page 12, the statement about MA_2Z_4 would be clearer if “IV/V group element” were used. There are also linguistic errors related to the inconsistency of the use of singular and plural in a sentence (e.g. on page 24). I consider the language used in the dissertation to be generally readable and used to communicate the content efficiently.

The presented critical remarks do not diminish my positive substantive evaluation of the reviewed doctoral dissertation.

The Author of the dissertation demonstrated the ability to competently use a properly selected computational tool to predict the electronic structure and the resulting optical properties in the visible and infrared range for several 3D superlattices and interesting 2D materials. The obtained results are original and valuable, contributing to the knowledge of the physics of modern semiconductor materials, especially those showing the potential for applications both in the field of optoelectronics and spintronics and its related areas. The extensive computational material discussed in the dissertation proves the Author's ability to conduct scientific work in the field of condensed phase theory. The Author convincingly justified the selection of the research topic, embedding it in the context of the current state of knowledge, and selected the appropriate tools and research methods to achieve the goals set in the dissertation.

The works constituting the doctoral dissertation have so far obtained 25 citations (according to the Scopus database), which is a good result, taking into account their publication in 2022.

The publications of the Ph.D. candidate, in addition to the 4 items included in the doctoral dissertation, also include other works. One of the latest publications of the Ph.D. candidate, prepared as part of the work in the current team and concerning topological materials, "Fast electrically switchable large gap quantum spin Hall states in MGe_2Z_4", is available as a preprint (https://doi.org/10.48550/arXiv.2211.06443). Another paper on this topic, "Correlation-Driven Topological Transition in Janus Two-Dimensional Vanadates", appeared this year in the journal *Materials*, and the Ph.D. candidate is its first author. Another paper, "Topological Phase Diagram of $Pb_{1-x}Sn_xSe_{1-y}Te_y$ Quaternary Compound", appeared in *Acta Physica Polonica A*.

In addition, the Ph.D. candidate is a co-author of the work "Anisotropic phonon dispersion and optoelectronic properties of a few-layer HfS_2", which was published this year in the prestigious *Journal of Materials Chemistry C* with an impact factor exceeding 8. In addition, the Candidate's scientific achievements demonstrated in Google Scholar (https: //scholar.google.com.pl/citations?hl=pl&user=nVD6_7YAAAAJ) includes other papers from the earlier period of scientific activity, on the issues of spintronics or research on transition metal chalcogenides, in journals such as the *Journal of Magnetism and Magnetic Materials*, *RSC Advances*, *Journal of Material Chemistry C*, *Solid State Communications*, *Microelectronic Engineering*, *Superlattices and Microstructures* and *Microelectronic Engineering*, in which the Ph.D. candidate is listed in lower places on the list of authors; including e.g. review papers "Recent advancements in 2D-materials interface based magnetic junctions for spintronics" in *Journal of Magnetism and Magnetic Materials* (25 citations), "A review of Raman finger prints of doping and strain effect in TMDCs" in *Microelectronic Engineering* (43 citations) and "Chemical doping of transition metal dichalcogenides (TMDCs) based field effect transistors: A review" in *Superlattices and Microstructures* (26 citations).

The general scientific achievements of the Ph.D. candidate can therefore be assessed very well.

The results obtained by the Ph.D. candidate, both in terms of the subject of the dissertation and other research areas (related to nanowires and topological materials) were the subject of conference presentations – posters at the International School and Conference of Semiconductor Physics "Jaszowiec 2021" and "Jaszowiec 2022" and a poster during the APS March Meeting 2023, as well as an oral paper at the Nano-Pak 2021 conference "International E-conference on Emerging Trends and Innovations in Nanotechnology" (on-line) in Pakistan.

In conclusion, I unequivocally state that the doctoral dissertation presented by Mr. Ghulam Hussain, M.Sc. entitled *Investigating the electro-optical properties of 3D superlattices and 2D materials: A DFT study* is an original solution to a scientific problem. This dissertation presents the candidate's general theoretical knowledge in the discipline of physical sciences and proves his ability to independently conduct scientific work in this field. Therefore, he meets all the requirements of the Act of 18 July 2018 The Law on Higher Education and Science (specified by Article 187 of the Act). I therefore request the Doctoral Commission appointed by the Scientific Council of the Institute of Physics of the Polish Academy of Sciences to admit Mr. Ghulam Hussain, M.Sc. to further stages of the procedure for conferring a doctoral degree, including the defense of the doctoral dissertation.

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Department of Solid State Physics
Faculty of Physics and Applied Informatics
University of Łódź
ul. Pomorska 149/153, 90-236 Łódź

→ www.uni.lodz.pl