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Review of the doctoral dissertation of Ashutosh S. Wadge, M.Sc., entitled *"Exploring electronic properties of topological semimetals $TaAs_2$ and NbP: crystal growth, electron transport, and ARPES studies".*

The doctoral dissertation submitted for review by Ashutosh Wadge, M.Sc., was made at the *International Centre for Interfacing Magnetism and Superconductivity with Topological Matter – MagTop* under the supervision of Prof. dr hab. Andrzej Wiśniewski *[professor, Ph.D., postdoctoral degree holder]*. The results of the study were published in 2022 in three scientific journals, *J. Phys.: Condens. Matter, Phys. Rev. B* and *J. Phys. Chem. Solids.* The paper concerns the preparation of $TaAs_2$ and NbP crystals, followed by studies of electrical transport and surface band structure using the ARPES (angle-resolved photoemission spectroscopy) technique. $TaAs_2$ is characterized by an interesting and not fully explored electronic band structure. Without the presence of a magnetic field, it is a crystalline topological insulator protected by rotational symmetry, but after applying a magnetic field and breaking the symmetry with respect to time reversal, it shows the presence of type-II Weyl points. The second tested material, NbP, is a type-I Weyl semimetal. The undertaken topic is highly relevant and connects to recent findings in the topological classification of phases of matter (band structures), which are fundamental for condensed matter physics. **The main achievement of this work is a systematic analysis of the magnetotransport properties of $TaAs_2$ correlated with band structure imaging.** Even though the analysis concerned the bulk properties of the material, it should be considered a valuable contribution to the literature on the subject in the context of a comprehensive approach to the issue. **The second achievement is the observation of a topological Lifshitz transition (a change in the topology of the Fermi surface without breaking any symmetry) by covering the NbP surface (terminated with P) with an ultrathin Pb layer.** This is a very interesting result, requiring careful design of the experiment, production of NbP crystals, and selection of the material for the ultrathin surface modifying layer.

The dissertation was written in English. It consists of 6 chapters, divided into shorter subchapters, and an introduction entitled *"Motivation",* where the research concept is discussed. The paper also contains an extensive bibliography, which proves the Ph.D. candidate's knowledge of the relevant scientific achievements. Additionally, it includes acknowledgments, especially recognizing the contributions of team members.

Chapter 1 presents an introduction to the subject of topological materials, in particular Weyl semimetals. The properties of electrical transport in topological materials are also discussed, with particular emphasis on large unsaturated magnetoresistance, Shubnikov-de Haas (SdH) oscillations, and the chiral anomaly. A noteworthy observations is the paper's somewhat cursory treatment of certain topics, notably magnetotransport, without any attempt to explain the essence of the discussed phenomena. This applies, for example, to Chapter 1.4.1 *"Large unsaturated magnetoresistance"*. The Ph.D. candidate limits himself to providing entries and references to the literature, while he studies the phenomena of magnetoresistance later in the work, so the issue is important.

Chapter 2 is entitled *"Crystal growth and characterization"* and is divided into several subchapters. It contains an interesting historical introduction and a description of several techniques for obtaining crystals. It raises a question about the rationale behind detailing so many techniques when the doctoral dissertation uses only the chemical vapor transport (CVT) method. However, this part can be successfully treated as a reflection of the Ph.D. candidate's interests. In the rest of Chapter 2, the Ph.D. candidate describes the details of the preparation and characterization results by transmission electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy (EDX) of $TaAs_2$, NbP crystals and preliminary results regarding $ZrAs_2$. The results presented concern single, arbitrarily selected samples. There is no description (list) of the samples produced throughout the study. There is no description of the efforts undertaken to optimize the characteristics of the obtained crystals – tuning the growth parameters to obtain crystals with the desired characteristics. There is no specificity as to what characteristics of the samples are desirable. Nevertheless, the receipt of $TaAs_2$ and NbP crystals by the Ph.D. candidate for his own research should be considered a greater success of this doctoral dissertation. It is a pity that the Ph.D. candidate does not emphasize his contribution to the development of crystal growth techniques at the IF PAN *[Institute of Physics, Polish Academy of Sciences]* (he often uses the English pronoun "we" throughout the paper, which I interpret as a nod to teamwork). The Ph.D. candidate points out, for example, that receiving NbP is something of a challenge due to the high melting point of Nb (2477 °C) and the low sublimation temperature of chemically active phosphorus. This required the design of a safe and fully controlled system for the growth of NbP to avoid excessive pressure and, as a result, explosion. However, it is not clear how the Ph.D. candidate contributed to this project? If he had participated in the construction and/or design of the system, it would undoubtedly be a great achievement. Unfortunately, I cannot assess this by reading the doctoral dissertation.

Chapter 3 is devoted to the description of the main experimental techniques and measurement systems. This is a system for magnetotransport measurements at the Polish Institute of Physics of the Polish Academy of Sciences and the URANOS line (formerly UARPES) at the SOLARIS National Synchrotron Radiation Centre in Krakow, where ARPES measurements were performed.

Chapters 1-3 present the Ph.D. candidate's general knowledge and demonstrate his familiarity with methodology and scientific achievements in the field. The main results of the doctoral dissertation are contained in Chapters 4 and 5. Chapter 4 contains the results of magnetotransport and ARPES measurements of $TaAs_2$ crystals. These data were supplemented by an examination of the band structure obtained from DFT calculations. Magnetotransport measurements showed strong compensation of electric charge carriers, which was associated with the occurrence of strong unsaturated magnetoresistance (although it is worth noting that the simplified two-band model used does not explain the magnetoresistance values in high magnetic fields). The basic parameters of electric current carriers in $TaAs_2$, concentration, mobility, and effective mass, were estimated. Numerous Fermi pockets of both *n*- and *p*-type electric charge carriers, characterized by elliptical Fermi surfaces, have been identified. The magnetotransport results are in good agreement with the results of studies of the surface band structure using the ARPES technique, which also revealed numerous electron and hole pockets. Their location in the *k* vector space was identified. ARPES studies showed the volume-related states (projected onto the surface) much better than the surface states. The latter were not described in the dissertation. Within this chapter, it is important to recognize the comprehensive approach to studying the electronic properties of $TaAs_2$, the use of complementary experimental methods and data analysis, and contrasting the results with those obtained from with DFT calculations. This allowed us to obtain a coherent picture of the electronic band structure and the resulting electrical transport properties. These results undoubtedly constitute a valuable contribution to the development of the subject and will appear in the literature because they describe the basic features of the material.

Chapter 5 describes the results of studies on the electronic structure of NbP with a pure or decorated Pb or Nb surface. The influence of these elements on the surface bands visible in the ARPES technique was examined. The concept of the experiment is interesting, and consistent with current research trends seeking to understand the complex nature of topologically trivial and non-trivial surface states and actual topological protection. The work shows that a different band structure is visible on the (0 0 1) surface terminated with P and a different one on the terminated Nb. Both non-trivial (spoon-shaped - surface Fermi arcs characteristic of Weyl metals) and trivial (bow-tie-shaped – resulting from the presence of broken bonds) surface states were identified on the P-terminated surface, while on the Nb-terminated surface, these characteristic shapes were absent. The Nb-terminated surface was characterized by the presence of circular electron and hole pockets and surface Fermi arcs associated with Weyl points. The most interesting results were observed after applying one monolayer of Pb on a P-terminated surface. The topologically trivial bow-tie-shaped states disappeared due to the saturation of broken bonds. In contrast, the surface Fermi arcs moved from one pair of Weyl points to the neighboring pair, on the border of the Brillouin zone, creating an eight-shaped figure. This phenomenon has been associated with the topological Lifshitz transition. The dissertation clearly lacks a deeper explanation of the nature of this transition. Covering the Nb-terminated surface with Pb had a minimal impact on the surface states; the surface Fermi arcs remained unchanged, but there were new hole pockets observed, which were attributed to the less significant bands of the Pb monolayer. These changes have been referred to as a simple Lifshitz transition. Then, 0.8 monolayers of Nb were evaporated onto the P-terminated surface, and 1.3 monolayers of Nb onto the Nb-terminated surface. The effect of Nb on the P-terminated surface is similar to that observed for Pb, but much weaker, which is defined as the critical point of the topological Lifshitz transition. Conversely, the evaporation of Nb onto the Nb-terminated surface led to blurring of the ARPES spectra, and this was attributed to lattice distortion, potential defects, or the formation of Nb clusters. The results described in this chapter address the most intriguing phenomena that topological materials provide: the existence of topologically protected surface states and the possibility of controlling and modifying them. The results presented in this chapter are very up-to-date, consistent with the latest research trends aimed at determining the control potential and, consequently, the use of these unusual features of topological materials.

As previously noted, the results of this study are interesting and important for the topic discussed. What stands out in the presented dissertation, in my view, is the absence of information regarding the diversity of the acquired samples and the extent to which their properties could be controlled by growth parameters. It would also be useful to have a deeper description of the key phenomena observed in the conducted

research and more synthetic summaries of individual parts of the work. I also need to comment and ask for clarification on a few issues, which are summarized below:

1. In Chapter 1.4.3 *"Chiral anomaly"*, the Ph.D. candidate warns about the phenomenon of "current jetting", which, as a result of non-uniform injection of an electric current into materials with high conductivity anisotropy and high mobility, may lead to the formation of negative magnetoresistance. Has the Ph.D. candidate encountered this phenomenon while working on his doctoral dissertation and examining his own samples? This is not described anywhere further in the text of the dissertation.
2. In Chapter 1.4.2 *"Shubnikov-de Haas oscillations"* the Ph.D. candidate writes that the amplitude of the SdH oscillation is affected by temperature, the effective mass of the electric current carriers, and the dissipation time τ, and then gives Formula 1.9 describing the amplitude of the oscillation, in which the dissipation time τ does not occur. Why was the dissipation time τ neglected when describing the oscillation amplitude? How would the effective mass values determined in Section 4.1 *"Low-temperatures electron transport"* on page 60 change if τ were taken into account? Another question for this chapter is why the estimation of carrier concentration from the frequency of SdH oscillations was abandoned, and did the Ph.D. candidate try to determine the Berry phase from SdH oscillations?
3. In several places in the dissertation (on pages 51 and 52), the Ph.D. candidate emphasizes the possibility of the existence of a temperature dependence of the electronic band structure of $TaAs_2$. Did the Ph.D. candidate perform band structure measurements using the ARPES technique at various temperatures? Did he notice any differences in the spectra?
4. On page 51 in Chapter 4 *"Tantalum di-arsenide: $TaAs_2$"*, the Ph.D. candidate discusses the RRR (residual resistivity ratio) parameter, emphasizing that the higher the RRR parameter, the better the quality of the sample, the fewer impurities and defects. In contrast, on page 28, the Ph.D. candidate indicates two methods of obtaining TaAs2 – a one-stage and a two-stage process. Has the Ph.D. candidate tested the RRR parameter of samples from both processes? Which approach results in a higher RRR? Is it possible to increase the RRR parameter by changing the growth parameters? To what extent?
5. On page 52 in Chapter 4 *"Tantalum di-arsenide: $TaAs_2$"*, the Ph.D. candidate describes Figure 4.2 of the dependence of the longitudinal resistance on temperature with a clearly marked plateau below approximately 28 K. The doctoral student writes: "*This behavior is thought to be a result of the balance between the density of states and the mobility of the carriers in the material. The interplay between the material's topological properties, such as the Berry curvature, and the magnetic field is believed to play a role in this balance."* Could the Ph.D. candidate expand on this idea? What is this plateau really caused by? The above statement seems to be generally true for any temperature dependence of resistance.
6. Figure 4.4 on page 54 shows the longitudinal and transverse magnetoresistance measured over the range 0 to 10 T, while modeling of the two-band model, the results of which are shown in Figure 4.5, was performed up to 4 T. Could the doctoral student comment on why the higher range of magnetic fields was omitted from this modeling?
7. In Chapter 4.1 "*Low-temperatures electron transport"*, the Ph.D. candidate used three approaches (Hall effect described by the two-band model, mobility spectrum analysis, and SdH oscillation analysis) to determine the parameters of electric current carriers in $TaAs_2$, concentration, mobility, and effective mass. In this chapter, there is no summary of the obtained results, no comparison of the obtained parameters, no discussion of similarities and differences, as well as no discussion on the limitations of the methods used (including question no. 2).
8. Why were Nb and Pb chosen to modify the NbP surface? Why does Pb have a greater effect on the surface than Nb?

As for the technical side of the work, it has a pleasant graphic design, but unfortunately, the style in which it was written is incoherent and chaotic. As an example: in Chapter 4.1, the Ph.D. candidate describes the resistance of a $TaAs_2$ sample measured as a function of temperature without an applied magnetic field. In the caption under Figure 4.1 we read that at low temperatures this relationship is described by a quadratic power law, which indicates electron-electron interactions, and at high temperatures it shows a linear relationship due to electron-phonon interactions. Such a linear dependence of resistance on temperature is indeed characteristic of metals. However, when we move to the main text, in the paragraph describing Fig. 4.1., the Ph.D. candidate only describes the low-temperature regime, and writes only one sentence about the high-temperature regime: *"At higher temperatures it shows linear behavior with slight bending as shown in Figure 4.1 which may occur due to temperature-dependent bands in the electronic structure".* It is not clear why the discussion of the high-temperature regime and the electron-electron interaction was omitted, since a few sentences were previously devoted to describing the low-temperature regime and the electron-electron interaction, and this is how the caption under the figure was constructed. There is no coherent statement here. It is not clear what the author wanted to convey in this paragraph.

Another example is on page 28 in Chapter 2.3.1, where the Ph.D. candidate describes how to obtain $TaAs_2$ crystals for Ph.D. research. It refers to the two crystal growth methods previously described, the one-step method and the two-step method. He writes that a one-step method was used at the beginning and describes the parameters and details of the growth extensively. He concludes the paragraph by saying that both $TaAs_2$ and TaAs were obtained in this way. Then, directly below this paragraph, Point 1 appears: "*Synthesis of polycrystalline $TaAs_2$*" and point 2: '*Single crystal growth of $TaAs_2$*". The reader can, of course, guess that since a one-stage method was used at the beginning, a two-stage method may have been used later, and Points 1 and 2 may refer to two stages of growth. However, there was a lack of clarification here as to what subsections 1 and 2 refer to. Many more examples of this type could be given. The work also contains errors in the construction of single sentences, e.g. on page 22 we read: "*The rate of cooling depends on [...] the rate of cooling*". On page 27 we read: "*During the reaction of iodine with solid precursor form gaseous iodides with four types of reactions which determines the transport of volatile derivatives and given as follows:*". Again, these are not isolated examples. Typos, grammatical errors, and stylistic errors in the structure of entire statements (often followed by unrelated or very weakly logically connected sentences) make the work very difficult to read. As a reviewer, I also include obvious editorial errors that I noticed.

- ✓ Figure 1.4 on page 9 is from ref. [45] and not as reported in ref. [43].
- ✓ Figures: 1.8 on page 16, 2.12 on page 32 are not described in the text (no reference in the text).
- ✓ Figure 1.7 on page 16 is not described in the main text, while the reference to Figure 1.7 on page 17 actually refers to Figure 1.9.
- ✓ The reference on page 59 to Figure 4.8 (b) actually refers to Figure 4.7 (b).
- ✓ There is no number for some equations. Though it is true that sometimes the convention is used that only those formulas that are referred to later in the text are numbered. However, the Ph.D. candidate does not follow this convention either.
- ✓ The font in many Figures (especially those with ARPES results) is too small, making it difficult to read.
- ✓ No references to Patterns 4.2 and 4.3. Maybe the Ph.D. candidate brought them out himself?
- ✓ No explanation of the symbol S(p) used in Formulas 4.4 and 4.5. There is no description of the MSA (mobility spectrum analysis) method in the introduction.
- ✓ On page 56, the symbols n_e and n_h are confused.
- ✓ Undefined symbols appear on page 26: *X(s), T(g), XT(g), X(g), M(s), 1(g).*
- ✓ Sometimes the units are written in italics instead of normal font.

In spite of some critical comments, primarily related to the manner in which the results are presented, I hold a favorable assessment of the Ph.D. candidate's work. The Ph.D. candidate undertook a very interesting and ambitious research issue. After discovering the "surprises in the band structure" provided by topological materials, it became clear that they required in-depth examination and confrontation with theoretical predictions. The Ph.D. candidate undertook this task, starting with the production of his own samples, which is a distinctive feature of this dissertation. I am very positive about this approach because based on random samples supplied from outside, it is often impossible to achieve the intended results. The balance between the effort put into obtaining crystals and performing magnetotransport and ARPES tests should be appreciated. The Ph.D. candidate skillfully used the equipment available in both the home unit and the SOLARIS National Synchrotron Radiation Centre. He effectively analyzed and imaged experimental data and published the results in scientific journals. It should be emphasized that this experimental approach constitutes an important contribution of the dissertation to the research on the band structure of Weyl semimetals. The entire field of topological materials seems to be dominated by theoretical considerations, which lead to spectacular conclusions. Researchers specializing in experimental methods are obligated to show phenomena that actually occur in nature, which is quite a challenge. Therefore, the approach chosen by the Ph.D. candidate, and which allowed him to obtain original and valuable results, should be recognized.

To conclude, I state that the doctoral dissertation of Ashutosh Wadge, M.Sc., entitled "*Exploring electronic properties of topological semimetals* $TaAs_2$ *and NbP: crystal growth, electron transport, and ARPES studies*" meets the requirements of the Act of July 20, 2018 – Law on Higher Education and Science, for doctoral dissertations, and I am requesting permission to publicly defend it.

[illegible signature]
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