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Review of the doctoral dissertation

entitled "Exploring electronic properties of topological semimetals $TaAs_2$ and NbP: crystal growth, electron transport, and ARPES studies"

by Ashutosh S. Wadge, M.Sc.

The doctoral dissertation of Ashutosh Wadge, M.Sc., was conducted at the International Centre for Interfacing Magnetism and Superconductivity with Topological Matter – MagTop, operating at the Institute of Physics of the Polish Academy of Sciences in Warsaw. The supervisor of the dissertation is Prof. dr hab. Andrzej Wiśniewski *[professor, Ph.D., postdoctoral degree holder]*.

Topological insulators with conductive surface or edge states protected by appropriate symmetry, topological semimetals (in the sense of "semimetals"), and an ever-growing range of other topological materials are of increasing interest due to a range of potential applications in contemporary electronics, spintronics and, notably, in the emerging field often referred to as "topotronics". The research carried out by the Ph.D. candidate aligns seamlessly with this trend, making it is undeniably important and pertinent. The doctoral dissertation focuses on two distinct topological semimetals, $TaAs_2$ and NbP.

The dissertation was prepared in English and, in my opinion, correct both in terms of grammar and style. In particular, the theoretical introduction reads well, while the chapters on own research are slightly less thorough – only those few errors that may be of substantive importance will be indicated later in this review. In total, the doctoral thesis is 117 pages long and consists of the legally required summary, as well as a list of figures, tables, six main chapters, supplements, and a bibliography.

The dissertation is based on three publications: in *J. Phys.: Condens. Matter* regarding the $TaAs_2$ compound, in *Phys. Rev. B* on the NbP system – in both cases the Ph.D. candidate is the first author – and in *J. Phys. Chem. Solids* on $TaAs_2$, where Ashutosh Wadge, M.Sc., is the fourth of seven authors.

The obtained results were also disseminated by the Ph.D. candidate in the form of a lecture at the JEMS 2022 conference and five posters at other conferences. Such advanced experimental research naturally involves a team effort, but it is intriguing to discern the specific aspects of the research in which the Ph.D. candidate has developed particular profound expertise.

Even before starting the main part of the dissertation, Ashutosh Wadge, M.Sc., comprehensively and clearly presented the motives that prompted him to research the topic of the dissertation. For $TaAs_2$, the Ph.D. candidate's intention was to use the angle-resolved photoelectron spectroscopy (ARPES) method supported by DFT calculations to more fully identify electron and hole pockets in the angular momentum space and to analyze the carrier mobility spectrum based on transport measurements. In contrast, for NbP crystals, the Ph.D. candidate planned to extend the previous studies known from the literature using the ARPES method for a crystal ending with a surface filled with P or Nb atoms to include the case when an additional layer of heavy atoms, in this case Pb and Nb, is placed on such a surface. Due to the spin-orbit coupling (SO), such additional layers can be expected to have a significant impact on the topological properties of the Weyl semimetal, which was confirmed in further research by the Ph.D. candidate.

As I mentioned above, the main part of the dissertation consists of six chapters. **Chapter 1** is an introduction in which Ashutosh Wadge, M.Sc., presents a concise but representative overview of topological materials and defines basic concepts and quantities later relevant to his own research. It is a well-selected range of topics, supported by clear and helpful graphics. There is a slight lack of introduction of more elementary concepts, such as Berry phases, Berry flux, types of topological indices, topological phase transitions, etc. Such a compendium would undoubtedly be helpful for readers outside this field.

The correctness or incorrectness of several symbols and formulas in **Chapter 1** requires an explanation by the Ph.D. candidate:

- Is the vector defining the location of the Weyl points on page 7 correctly marked as k_x?
- Mirror planes for TaAs are given on page 11, probably the correct designations are M_x and M_y.
- Do the Weyl point band calculations mentioned on page 12 take SO coupling into account?
- Shouldn't there be a minus sign in the numerator for the component of the conductivity tensor in Formula 1.5?
- The reference to Fig. 1.7 on page 17 actually refers to Fig. 1.9.

Chapter 2 of the doctoral dissertation was devoted to methods related to the synthesis of single crystals. In the following subsections, the Ph.D. candidate clearly and comprehensively presented the basic methods of growing single crystals and then described the details of the synthesis and structural characterization of the compounds that are the subject of his research, i.e. TaAs2 and NbP. The transition on page 29 from discussing the one-step to two-step synthesis method is not signaled in the introductory sentence, which may pose some difficulties for the reader. Apart from that, I consider the Ph.D. candidate's description of technological issues to be an excellent training material for people who want to grow similar single crystals.

The description of X-ray diffraction measurements for $TaAs_2$ seems rather superficial. In Fig. 2.11, only some of the reflections have been described, so the question arises whether a full analysis of the powder XRD spectrum was carried out and whether reflections from foreign phases were visible. The same figure shows EDX spectra, which reveal significant carbon content. Is it built into the structure and influences the results?

In point 2.3.3 Ashutosh Wadge, M.Sc. discusses the synthesis and structural studies for the ZrAsz compound. Technological activities related to Zr were provided, but the Ph.D. candidate omitted the fact that As is also needed in the synthesis. Above all, however, the purposefulness of the presence of a $ZrAs_2$ crystal in the dissertation is questionable. This system is not the main subject of research in this doctoral dissertation and the results for it are not presented in detail. On page 33, instead of “Figure 14”, it should read “Figure 2.14”.

The experimental techniques used in the research are described by the Ph.D. candidate in **Chapter 3.** In point 3.1.2, Fig. 3.3 shows a photo illustrating the attachment of electrodes for electrical transport measurements. Since the results of resistivity are presented later in the dissertation, I have doubts as to whether it was possible to determine the cross-section for the visible shape of the sample. When discussing the ARPES method on page 41, it is unfortunate to use the same symbol for work function and angle a few lines later. Moreover, the definitions of angles in the text are not consistent with Figure 3.4. These minor comments do not change the fact that this chapter was very well prepared, the drawings and photos are clear and helpful, and the descriptions are concise and factual.

Chapter 4 of the dissertation begins with the presentation of the measurement results obtained by the Ph.D. candidate along with his analysis and interpretation and concerns $TaAs_2$ single crystals. First, the temperature dependence of resistivity was discussed. To adjust the $\rho(T)$ dependencies, the Ph.D. candidate used the Bloch-Grüneisen model, or rather its limiting approximations. Therefore, a linear relationship at high temperatures and a T^5-type relationship at low temperatures should be expected. However, there is a visible deviation from the linear relationship, which the Ph.D. candidate attributes to band effects, while below 150 K he obtained a T^2 relationship, which he attributes to the electron-electron interaction. However, such interactions usually play a role at very low temperatures, when the phonon contribution becomes less important. So how can we explain the dominance of exponent 2 over such a wide temperature range? It should be noted that the quality of the fit is not very good; the sum of several contributions must probably be taken into account. Some explanation may be the fact that in the tested crystal there are not only electron carriers, but also hole carriers, and the electron-hole interaction may maintain the T^2 dependence up to higher temperatures [Maldague *et al.,* prb 19, 6172 (1979)]. It would also be helpful to refer to the Debye temperature, which the Ph.D. candidate could estimate using the full Bloch-Grüneisen formula in the analysis of the results.

Later in the dissertation, Ashutosh Wadge, M.Sc., describes the results of magnetoresistance measurements. At times, it may not be explicitly clear whether the reference is to magnetoresistance in the presence of a magnetic field perpendicular to the sample or to longitudinal magnetoresistance (LMR), i.e. a geometry in which both the magnetic field and the electric current are directed along the *b* axis direction. For example, the caption of Fig. 4.4 mentions LMR, but the discussion on page 52 describes the situation when the field is parallel to the direction [201]. Due to these doubts, it also needs to be confirmed whether Figure 4.7a really applies to LMR. The discussion of the sign change of the Hall effect in Figure 4.4 is also unclear.

In the context of transport measurements, the results analysis based on the two-band model, especially the analysis of the mobility spectrum analysis (MSA) of carriers, is very interesting. This allowed the Ph.D. candidate to conclude the presence of two different electron channels and two hole channels at low temperatures, which, combined with ARPES experiments, is of great importance for the interpretation of the properties of the $TaAs_2$ single crystal. The Ph.D. candidate states that the computational code was prepared in FORTRAN, but does not state whether he is the author of the code or the reference explaining it.

The Ph.D. candidate's observation of the Shubnikov-de Haas (SdH) oscillation is impressive. The analysis of these results raises no objections except for a few technical issues. On page 59 there is mention of Fig. 4.8b, but the author did not include such a figure. A similar note applies to the reference to Figure 4.10c on page 61.

Another element that complements the picture of the properties of the $TaAs_2$ compound built by the Ph.D. candidate refers to the results of electronic structure calculations and ARPES measurements. An important observation was the need to shift the Fermi level to obtain good agreement between theory and experiment. It was also possible to assign the characteristic frequencies obtained from SdH oscillations to the corresponding Fermi surfaces.

In **Chapter 5**, Ashutosh Wadge, M.Sc., described the research results obtained for NbP, the second compound that was the basis of his doctoral dissertation. While the research on $TaAs_2$ was complementary and based on several complementary measurement methods and theoretical calculations, in the case of the NbP crystal, the Ph.D. candidate limits himself to the ARPES technique and compares the obtained results with similar experimental and theoretical studies known from the literature. The main goal was to observe the effect of a thin layer of Pb or Nb applied on the NbP crystal on the properties of the tested compound. As expected, the modification of surface conditions was significant. The case of Pb deposited on an NbP crystal terminated with a phosphorus surface turned out to be particularly interesting due to the appearance of a topological Lifshitz transition. The identification and discussion of various types of Fermi surfaces, Weyl points, surface Fermi arcs, etc., demonstrate the Ph.D. candidate's good understanding of the ARPES method and the information it provides.

For the Nb layer deposited similarly to the Pb layer, it was found that the system is only on the border of the topological Lifshitz transition. Is it possible to indicate a modification that will lead to a full Lifshitz transition? It is worth noting that the thicknesses of the Pb and Nb layers were different, what is the significance of the thickness of the deposited layer and what is the type of growth of these layers? On page 70, the references to Figs. 5.5e and 5.5f actually refer to Fig. 5.4.

The doctoral dissertation is finalized in **Chapter 6,** in which the Ph.D. candidate collected the main conclusions resulting from the research carried out on the semimetals $TaAs_2$ and NbP.

The comments, questions posed, and identified shortcomings presented in the review do not diminish my overall very positive assessment of the doctoral dissertation of Ashutosh Wadge, M.Sc. Its implementation required a thorough grasp of essential theoretical principles, considerting the conceptual complexity of topological materials. The Ph.D. candidate also faced a technological challenge – the need to synthesize high-quality single crystals, as well as the challenge related to the characterization of samples, in particular the detection of surface states. I believe that the Ph.D. candidate met these challenges very well. In my opinion, the most important achievements of the Ph.D. candidate are:

1. Synthesis of good quality $TaAs_2$ single crystals and coherent interpretation of their properties based on transport measurements, ARPES, and electronic structure calculations. In my subjective opinion, the analysis of the carrier mobility spectrum was particularly valuable. Of course, the unique observations available thanks to such an advanced technique as ARPES are extremely valuable, including the identification of trivial and non-trivial surface topological states.

2. Demonstrating, using the example of an NbP single crystal, that applying elements with high SO coupling values to the surface significantly modifies the electronic structure, observing the topological Lifshitz transition, and presenting the possibility of manipulating surface Fermi arcs.

The dissemination of the results obtained by the Ph.D. candidate does not raise any doubts, and activity in this area already includes the above-mentioned three publications and several conference presentations, including lectures.

The title of each chapter is enriched with a quote from maxims expressed by classic physicists, which may indicate the scope of the Ph.D. candidate's interests going beyond the strict subject of the doctoral dissertation. Among other things, **Chapter 4** begins with the quote "God made the bulk; the surface was invented by the devil". So my question to the Ph.D. candidate is who invented the edges?

To sum up my review, I say that the doctoral dissertation of Ashutosh Wadge, M.Sc., covers extremely important, current, and scientifically fascinating issues. The research carried out is at a high level both in terms of technology, characterization of the properties of single crystals, and theoretical analysis of the results obtained. These results, as well as the publication achievements and other scientific activity of the Ph.D. candidate, leave no doubt that the doctoral dissertation of Ashutosh Wadge, M.Sc., meets the conditions specified in Art. 187 of the Act of July 20, 2018 – Law on Higher Education and Science (Journal of Laws of 2020, item 85, as amended). In connection with the above, I request the admission of Ashutosh Wadge, M.Sc., for further stages of the doctoral process.

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