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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 reviewed dissertation was prepared at the Institute of Physics of the Polish Academy of Sciences in Warsaw, as part of research conducted at the "MagTop" Centre (full name: International Centre for Interfacing Magnetism and Superconductivity with Topological Matter), and the dissertation supervisor is prof. dr hab. Andrzej Wiśniewski *[professor, Ph.D., postdoctoral degree holder]*.

The review was prepared following the latest recommendations of the Council for Research Excellence and therefore differs slightly from the usual documents of this type. In accordance with the Council's recommendations, the review of a doctoral dissertation should include the following elements:
1) an assessment and justification of whether the doctoral dissertation presents the general theoretical knowledge of the person applying for a doctoral degree in a specific discipline;
2) an assessment and justification of whether the doctoral dissertation demonstrates the ability of the person applying for the doctoral degree to independently conduct scientific work;
3) an assessment and justification of whether the doctoral dissertation is an original solution to a scientific problem.

I. In my review, I will first address the issue of whether the doctoral dissertation of Ashutosh S. Wadge, M.Sc., is an original solution to a scientific problem.

The subject of the dissertation is the examination of selected electronic properties of $TaAs_2$ and NbP semimetals exhibiting topological features. The research included measurements of transport properties such as electrical resistance, Hall effect, and Shubnikov-de Haas oscillations, based on which the shape of the Fermi surface was determined, and the determination of the electronic structure by angle-resolved photoelectron spectroscopy (ARPES) supplemented with theoretical calculations. The topological properties of the tested compounds include the presence of Dirac and Weyl points in the band structure, and understanding the consequences of the presence of these points in relation to the observed unusual (anomalous) electronic properties, including the Lifshitz-type phase transition, was one of the most important goals of the reviewed work.

Since the topological properties of bulk insulators and semimetals are strongly influenced by the surface state of the samples, the research incorporated the use of single-crystal materials. The surface of one of the compounds, NbP, was modified by applying a layer of Pb or Nb with a thickness on the scale of a single monolayer (from 0.8 to 1.9) to the crystal surface terminated with Nb or P atoms. As a result of these procedures, which

demanded proficiency in challenging and even sophisticated experimental techniques, a certain variety of electronic states were achieved, topologically protected or not, subject to topological or ordinary Lifshitz phase transitions, which were analyzed and related to selected properties tested crystals.

Let me now list the most important achievements of this study, which could have motivated the Ph.D. candidate to undertake the research, and which, in my opinion, are also examples of solving original scientific problems. I would like to include:

- demonstrating the topological properties of the $TaAs_2$ compound by examining selected transport characteristics and determining the shape of the Fermi surface,

- mastering the method of obtaining single crystals of the NbP compound with a defined type of atoms constituting the surface, which can be further modified in situ by depositing Pb or Nb atoms in monolayer sizes,

- showing the possibility of generating and modifying the Lifshitz phase transition by applying a monolayer of heavy metal (Pb, Nb) to the sample surface, depending on the type of atom constituting the final/outer layer of this surface (Nb, P),

- showing that a relatively simple model, assuming a spherical Fermi surface and using the Lifshitz-Kosevich formula to analyze Shubnikov-de Haas oscillations, allows to obtain quite reliable/real (meaning: experimentally confirmed) values of several parameters characterizing a material with a complex Fermi surface, which additionally shows topological properties (here $TaAs_2$),

- in relation to the study of the Fermi surface using the ARPES method, obtaining results that agree well with the results of calculations: own calculations, in the case of the $TaAs_2$ compound, and those taken from the literature, in relation to the NbP compound.

Phenomena in topological semimetals showing the presence of Dirac and Weyl points are still relatively poorly explored, primarily due to the complexity of the processes controlling these phenomena and the need to use sophisticated measurement methods and high-quality materials, often in the form of single crystals. From this point of view, the Ph.D. candidate undertook an ambitious task, although it was carried out in a scientific community employing outstanding specialists in topological issues, and therefore he could count on the help of specialists. And he received such help, as can be seen from two-page acknowledgments to 30 people. Based on the results contained in the dissertation, I am convinced that they provide solutions to several original scientific problems, including those mentioned in the previous paragraph. This is confirmed by three publications with the participation of the Ph.D. candidate in very good scientific journals, Physical Review B, Journal of Physics: Condensed Matter, or Journal of Physics and Chemistry of Solids, where in two publications the Ph.D. candidate is the lead author. The Ph.D. candidate also presented the research results at conferences and international schools in Poland (5 presentations) and abroad (2 presentations), in oral (2 presentations) and poster (5 presentations) form. Both this fact and the description contained in the dissertation show that the Ph.D. candidate played a leading role in carrying out the discussed research.

II. Does the doctoral dissertation present the general theoretical knowledge of the person applying for a doctoral degree?

I can confidently answer this question affirmative as well. The author of the dissertation presented the issues related to the research concisely and clearly, quoting extensively from the literature on the subject. He demonstrated general knowledge of topological materials, with particular emphasis on Dirac and Weyl semimetals, their non-trivial electronic structure, and Fermi surfaces with characteristic arcs. He presented methods for measuring and analyzing electrical resistance and magnetoresistance, including Scubnikov-de Haas oscillations, and discussed the impact on these results of non-uniform distribution of measurement current resulting from incorrect contact geometry and the so-called chiral anomaly associated with Weyl points. In the chapter devoted to the synthesis of single crystals, the Ph.D. candidate characterized the most important techniques, including the methods used in his study. He discussed the basics of the ARPES technique and presented in detail advanced methods of sample preparation for planned measurements. It should be stated that the knowledge presented by the Ph.D. candidate proves good knowledge of topics related to the research being conducted and is sufficient to understand the presented results. Nevertheless, I will ask him to complete some of the issues to verify his full competence in the field.

Notes related to this aspect of the review:

- during the defense, I would like to ask the Ph.D. candidate to explain the difference between an ordinary and a topological Lifshitz transition, which terms he uses in his work and even illustrates, but without appropriate commentary (see Fig. 6.1),

- electron-hole compensation is considered a probable cause of the extremely high and saturation-free transverse magnetoresistance observed in Weyl semimetals; please explain this phenomenon,

- I would also like to ask him to explain what the anomaly in electron transport related to the chirality of Weyl points would be; the sparse description of the phenomenon presented in the paper does not convince me that the Ph.D. candidate understands this issue well, which may be crucial for the proper interpretation of some results.

III. Assessment and justification of whether the doctoral dissertation demonstrates the ability of a person applying for a doctoral degree to independently conduct scientific work.

This question also receives an affirmative answer from me. The Ph.D. candidate correctly designed and conducted experiments that led to significant new results and contributed to a significant expansion of knowledge in the field of topological semimetal research. He mastered the chemical gas transport method of growing single crystals and obtained crystals of $TaAs_2$, $ZrAs_2$, and NbP compounds with sizes sufficient for the planned research. He made current-voltage contacts on these crystals and mastered the technique of transport measurements, including: longitudinal resistance and Hall resistance, using a non-

commercial rotator measurement system. He mastered the technique of preparing samples for testing using ARPES spectroscopy, including a method that allows in situ to obtain a surface terminated with Nb or P atoms and a method of applying a monolayer of other atoms (here Nb and Pb) on it. He also seems to have well understood and analyzed the results of magnetoresistance measurements, including Shubnikov-de Haas oscillations, and learned the detailed interpretation of the results obtained using ARPES spectroscopy. I do not know what the Ph.D. candidate's role was in calculating the band structure of the $TaAs_2$ compound, but knowing his direct involvement in the remaining stages of the doctoral dissertation, I can assume that he also showed a certain inquisitiveness that allowed him to understand the method and the obtained results. An additional argument proving the Ph.D. candidate's scientific maturity is his first position on the list of co-authors in two out of three published works and a concise and clear presentation of the most important achievements in the abstract and summary of the discussed dissertation.

Comments on the experiment: during the defense, I would also like to ask the Ph.D. candidate to discuss the following issues:

- how was the degree of uniformity of current flow in the sample determined and hence the reliability of the results of transport measurements related to the chirality of the tested materials?

- how the signal related to the asymmetry of voltage contacts was compensated in Hall effect measurements (see Fig. 3.3); at what specific frequencies of the measurement current were the tests carried out, because the phrase "acoustic frequency" is probably insufficient due to the possible skin effect disturbing the measurement results; what was the contact resistance, which may be important in transport tests due to the non-point nature of these contacts?

- in Fig. 4.1 and on page 51, for the $TaAs_2$ sample, the resistance ratio psoo/pi.e = 3.65 is given, and as shown in Fig. 4.1, this ratio is psoo/pi.e = 3.1; where does this inaccuracy come from?

- on page 53 we have the sentence "The MR does not show much deviation up to 20 K and significantly reduces to 48 % at 300 K (see Figure 4.4 (b))", but, as shown in Fig. 4.4(b), MR reduces to 25%; where does this inaccuracy come from?

There are of course typos and other errors in the work, but overall it is well-written and edited. Perhaps in some parts it is too condensed, but then the Ph.D. candidate's publications become a perfect complement and this dissertation should be read as such. As a reviewer, I will list the errors that seem to have been made as a result of writing in a hurry, which has been happening quite often recently, due to new regulations:

- minor errors: the text of the paper lacks an explicit reference to Figures 1.7 and 1.8; on page 17 there is an error in the numbering of figures: instead of a reference to Fig. 1.7 there should be a reference to Fig. 1.9; on page 26, p (ii), instead of "sold" it should be "solid"; on page 33, instead of a reference to Fig. 14, there should be a reference to Fig. 2.14; on page

35, when listing the contents of the ampoule, As was forgotten; further, on the same page, in the sentence starting “The investigate...” a fragment of the text is missing; on page 70, in chapter 5.2, instead of a reference to Fig. 5.5 there should be a reference to Fig. 5.4,

- other errors: in the caption under Fig. 1.4, instead of a reference to the bibliography [43], there should be a reference to [45]; on page 59, the sentence “We have plotted the data from 1.6 K to 20 K as frequency vs FFT amplitude (see Figure 4.8 (b))” should read “We have plotted the data from 1.6 K to 20 K as FFT amplitude vs frequency (see Figure 4.7 (b)).”; in the caption under Fig. A.3, instead of “P-terminated NbP” it should be “Nb-terminated NbP”.

And a general comment regarding the way of presenting the results: some drawings are poorly legible (e.g. Figures 4.13, 5.5, 5.7, 5.9, Al, A2, A3) or unreadable at all (Fig. 2.11, Fig. 2.14(c), Fig. 3.5). This is difficult to accept because for most of these drawings, enlarging the format would not require changing their arrangement. The Ph.D. candidate should remember that the main purpose of drawings is to convey information and facilitate understanding of the content, which may be significantly difficult due to problems with reading.

Fortunately, shortcomings and inconveniences such as those mentioned do not occur very often in the work and of course do not detract from its substantive level, which I rate very highly.

In summary, I state that following the requirements of the provisions of the Act of July 20, 2018, Law on Higher Education and Science, and the recommendations of the Council for Research Excellence, I positively evaluate all aspects of the doctoral dissertation of Ashutosh Wadge, M.Sc., and I am requesting that he be admitted to the next stages of the doctoral program.

Moreover, taking into account the obtained and published results, the multi-aspect nature of the scientific goal pursued, the high level of extensive research, and the Ph.D. candidate’s involvement in conducting it, **I am requesting that** the dissertation **be distinguished**.

[illegible signature]
Krzysztof Rogacki