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Krakow 10.06.2023

Dr hab. Jacek Gregorowicz, professor of the institute
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Review of the doctoral dissertation of **Ilia Smirnov, MSc**
Dissertation title:
" Morphology evolution in mono- and bimetallic FCC nanoparticles ".
Dissertation supervisor: Prof. dr hab. **Zbigniew Kaszkur**,

The dissertation was prepared within International Doctoral Studies of the Institute of Physical Chemistry Polish Academy of Sciences in Warsaw. The dissertation was written in English.

First, I would like to declare that I am qualified to conduct the review. I have been a professor of chemistry since 2007. In my scientific work I perform diffraction research using laboratory and synchrotron X-ray sources. I am involved in structural studies of polycrystalline materials and single crystal samples.

General remarks

In his doctoral thesis, **Ilya Smirnov** raised an important scientific issue - how to study the structures of bi-metallic nano clusters based on fcc-type initial structures. Single nano domains can be examined, then we obtain results typical for a given nano object. We have methods for studying assemblages of nano objects (e.g. XRD methods); then we obtain averaged statistical data. Each nano domain can be slightly different from one another. Near the surface, the nano domain atoms may shift their positions slightly, to achieve optimal energy. Additionally, we have two different elements Au and Pt in the system. However, we have laboratory and synchrotron diffraction patterns, electron diffraction studies. We can also calculate diffraction patterns for postulated arrangements of atoms. We also have an experienced team of researchers of prof. Kaszkur, who

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has been calculating diffraction effects for various metallic clusters for years. The research described above promises to be really interesting. And as expected for a dissertation carried out in such a good and experienced research group, they ended with a series of important and interesting results!

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The layout of the doctoral thesis and general data

The doctoral thesis has a classic layout. It consists of three main parts: 'Introduction', 'Experimental and methodology section' and 'Results and discussion'. These key passages are supplemented by the chapters 'Conclusion', 'List of Abbreviations' and 'References'. For the sake of order and completeness, I mention that the number of cited literature includes 142 items, the oldest of which appeared in 1857 (and it is the work of M. Faraday himself), the latest is the work of the author of the dissertation - published in Nanoscale 2023. The entire doctoral thesis has 109 pages. Thesis is written in very good English.

The drawings are of very good quality. Each of the drawings is usually multi-part, thoroughly and extensively described. The individual terms are logically connected to each other and are usually a description of a larger, complex 'research episode' that one reads and discovers its full meaning with pleasure and interest. The theoretical introduction is concise, but sufficient to introduce the theoretical concepts and research methods used.

Research methodology

Various research methods were used in the work, including X-ray diffraction methods with particular emphasis on powder diffraction methods with the use of laboratory and synchrotron radiation sources. Electron diffraction methods, especially the TEM method, and methods of detection and mapping of the distribution of elements using EDX probes were important for the study of nanomaterials. Complex and laborious chemical syntheses were supported by XRF methods. The SAXS method was of great importance for the study of the shape of nano-objects. Computational simulations carried out using the Cluster program, created under the supervision of the thesis supervisor, were of fundamental importance for the research conducted in the doctoral thesis.

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Questions and comments to the author.

Minor inaccuracies noted are rare, and do not detract from the high rating of the doctoral thesis, however, due to the reviewer's duty, I will mention a few.

- fig. 14, page 32; point b) at the very bottom of the page should be point e)
- pages 59 and 60 the melting point of Au is given as 850K and 800K, Mp in figure 47 is close to the published in literature value 1064^{0}C, please comment?
- fig. 39; picture c) being the difference *2-*1 is more similar to picture a) than to pictures: b,d,e), please check and comment?
- page 57, 'This parameter is size independent and universal. The exact origin and physical meaning of this value (13.1%) are unclear'

Finally, a question to satisfy the reviewer's curiosity. Au and Pt are neighbors in the periodic table of elements, they crystallize in the regular system (sg. Fm3m, fcc) with similar values of period a, they have similar 'metallic' atomic radii - so why do they not show full miscibility in the entire composition range? I mean, among the others, a more detailed description of the phase diagram (including the 'Onion' area) in Fig. 6b)?

Description of the obtained results

Nanoparticles are important research objects for chemistry, catalysis physics, medicine and many other fields. However, nanomaterials are very demanding objects. They change during storage without stabilizing agents, they change during thermal treatment as well as irradiation with X-rays during research. For their study, it is necessary to use the basic formulas of diffraction physics (without simplifications resulting from lim→±∞), or modified - that is, adapted to the limitations resulting from the specificity of nanoobjects - crystallography methods.

In the first part of the thesis, the author studied Au and Au-Pt nanoobjects using MDXRD methods, in correlation with SAXS and TEM methods. The ability to monitor the evolution of morphology, including the ordering of NPs in Au@SiO2 materials, monitoring the number of domains in Au@PVP nano-objects, and the study of twinning in AuPt@C materials, was demonstrated.

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In the second part of the doctoral thesis, the participation of vacancies in the twinning process in nano-objects was investigated. An increase in the 'concentration' of vacancies (above 13.1%) triggers the formation of 'stacking faults', leading to an increase in the 'degree of twinning'. In the next part of this fragment, the stability of nano-objects irradiated with laboratory and synchrotron X-rays was investigated. Prolonged irradiation may cause the vacancy content to increase above the threshold value, resulting in twinning.

The third part of the experimental research concerned the study of the formation of bimetallic AuPt objects in a wide spectrum of conditions. The ranges of occurrence of nanoparticles with the structure of: alloys, core-shell or Janus type particles were examined. The type of structure obtained depends on many factors; including size of NPs, temperature, etc.

Conclusion

To sum up, the subject of the research is up-to-date and very important, the research methodology is innovative. The research results are interesting and well documented.

In conclusion, In my opinion dissertation of MSc. **Ilia Smirnov** meets the requirements of a doctoral dissertation (Art. 187 ustawy z dnia 20.07.2018. Prawo o szkolnictwie wyzszym i nauce (dz.U. z 2022 r, poz 574 ze zmianami) and I hereby recommend to admit the author of the dissertation to further stages of PhD procedure.

Wiesław Łasocha

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