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Report on the PhD thesis "U-based thin films: electronic structure and physical properties" by Oleksandra Koloskova

The doctoral dissertation submitted for evaluation was prepared and written by Ms. Oleksandra Koloskova under the supervision of Prof. Ladislav Havela at the Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University in Prague. The work presents the findings of her experiments on the synthesis of thin films based on uranium, including alloys with transition metals and their hydrides, as well as their spectroscopic, structural, and physical properties. In particular, Ms. Koloskova investigated uranium hydrides UH_2 and UH_3, as well as alloys U-Mo and U-Zr in both their pure and hydrogenated forms.

In this study, reactive DC sputter deposition was employed as a fabrication method, with the use of a residual gas analyzer to allow for the monitoring of the deposition process. The electronic structure of the thin films was investigated using contemporary photoelectron spectroscopic techniques, including X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and bremsstrahlung isochromat spectroscopy. These techniques were complemented by band structure simulations conducted using density functional theory methods. The structural properties of the samples were investigated through the utilization of a range of X-ray diffraction techniques, including asymmetrical reflection measurements, pole figures, reciprocal space mapping, and X-ray reflectivity. Additionally, transmission electron microscopy was employed to gain further insights into the samples' microstructure. The characterization of the bulk physical properties included the measurement of the magnetization and electrical resistivity at low temperatures and high magnetic fields.

Such a wide range of highly sophisticated, technically difficult, safety regulated, and therefore time-consuming experiments used by Ms. Koloskova was a significant hurdle to the progress of her dissertation. The scientific objective of her research project, which sought to investigate the ground state of the uranium systems she had selected and to examine the evolution of this state as a function of various parameters, particularly hydrogenation, was similarly demanding. The primary sources of these challenges were uranium and its unstable 5f shell, hydrogen and the properties of hydrides, and the preparation and characterization of thin films themselves. In consideration of the aforementioned factors, **I regard the thesis as a noteworthy and ambitious contribution to the field.**

The introductory section of the thesis provides an excellent and comprehensive account of the physical phenomena and experimental techniques referenced in the text, outlining their respective strengths and weaknesses, the known obstacles in interpreting the experimental data, and the challenges associated with studying uranium alloys and hydrides. The text is noteworthy for its comprehensive information and effective writing style, with numerous

references from the existing literature. It was a pleasure to read, offering insights that were both intriguing and enjoyable. **It is evident that Ms. Koloskova possesses a high level of expertise**, which is not unexpected given the reputation of the Prague group of scientists for excellence in their field.

One of the primary accomplishments of the doctoral candidate was **the successful fabrication of a set of thin films with the desired composition, including a novel hydride UH_2,** utilizing a range of substrates (including conducting and insulating materials, amorphous and single-crystalline substrates with diverse crystal structures), as well as various coating and deposition conditions. This outcome is unique and was undoubtedly the result of dedicated efforts, commitment, and patience of the doctoral student and of her support.

Spectroscopic studies and a scrupulous examination of spectroscopic data have elucidated **the key role of uranium-hydrogen bonding in the formation of the magnetic ground state in uranium hydrides (UH_3 and UH_2)**, as postulated by previous band structure calculations. This is evidenced by the appearance of additional bands at about 4-8 eV below the Fermi level, which can be attributed to the strong hybridization of U-6d and H-1s electron states, and the reduction of the intensity of the 5f peak. Nevertheless, the 5f states of uranium were observed to exhibit only quantitative influence from the degree of hydrogenation, thus **maintaining the 5f electrons in an itinerant state in UH_3 and UH_2**, while also exhibiting some localized fraction. Furthermore, the photoemission experiments proved a very effective method for verifying the degree of hydrogenation of uranium and the stabilization of specific hydrides through the addition of Zr and Mo.

Ms. Koloskova's contribution also included **an investigation of the relevance of substitution thresholds in U-Mo and U-Zr thin films for the stabilization of the γ-U phase**, and subsequently also in their hydrides, which was effectively demonstrated by structural studies. Another aspect of the author's thin film studies is that it opens up a new opportunity for further investigation of known uranium compounds (e.g. unconventional superconductors) that have only been extensively studied in bulk form. As Ms. Koloskova has observed, **the deposition of uranium compounds on various substrates generates significant stresses within the sputtered layers**. Therefore, thin film growth could potentially replace the technically challenging application of very high pressures.

Another noteworthy finding of the thesis is **the observation of superconductivity in the $U_{0.92}Mo_{0.08}$ thin film at temperatures below approximately 0.55 K**, which was in close proximity to the lower temperature limit of the performed experiments. The transition temperature was found to be considerably lower than the 2.11 K previously observed in the bulk $U_{0.85}Mo_{0.15}$ alloy. Additionally, the upper critical field of 1.0 T is markedly reduced from the 5 T observed in splat-cooled samples. It is regrettable that the analysis of the superconducting state presented in the thesis is constrained by the unavailability of data on specific heat, which is technically nearly impossible to measure for thin films.

The thin film form of the samples presented a challenge for the magnetization measurements, which were primarily utilized for **the determination of the magnetic ordering temperatures of the alloys and hydrides under investigation**. Furthermore, an attempt was made **to**

estimate the magnetic moments of uranium in the studied thin films. Despite the limitations, the quality of the experimental data is noteworthy, and the results obtained are consistent with those obtained for bulk samples, supporting Ms. Koloskova's findings that the magnetism of her samples is reliable and valuable. Similarly good results were obtained from electrical resistivity measurements, which confirmed the presence of (mostly) long-range magnetic order in the alloys studied and **the dominant negative slope in the resistivity versus temperature curves**.

The dissertation references a substantial number of sources, up to 162, offering a comprehensive and representative overview of existing knowledge on the subject matter. This selection of literature evidences **the doctoral student's commendable preparation in meeting the standards for a meritorious dissertation**.

As I perused the thesis, only a few thoughts and queries came to mind.

1. While Ms. Koloskova outlined in detail potential challenges associated with the use of reactive sputter deposition and the interpretation of spectroscopic and diffraction data obtained from the resulting films, a relatively limited overview of magnetization and resistivity measurements can be found in Sections 2.5 and 2.6, respectively. In order to provide an even more comprehensive overview, it would be helpful to present some quantitative analysis of the possible magnetic response of the sample holders at various temperatures and fields, as well as a more detailed account of the potential sources of inaccuracy associated with the Van der Pauw method. Additionally, it would be beneficial to include a discussion of the distribution of electric currents in layered structures (capped thin films), particularly in light of any potential challenges that may arise in such configurations.
2. The author made use of a focused ion beam to perform a cut on a sample for subsequent measurement via transmission electron microscopy. It would be advantageous to also prepare microdevices using this method to measure electrical resistance using the four-contact method, which is more accurate. Have there been any attempts to do so?
3. In addition, a more comprehensive analysis of the temperature dependence of electrical resistivity and magnetoresistivity would be beneficial. I realize that this could be a challenging endeavor to account for all possible scattering processes, but I am curious if the author has attempted to analyze these curves quantitatively.
4.

Minor points:

5. Page 81, bottom: The caption for Fig. 3.32 has been accidentally included in the main body of the text.
6. The author employs a variety of sample designations. At times, the chemical composition of the system under study is referenced (e.g., $(UH_3)_{0.82}Zr_{0.18}$), at other times, the symbol associated with a substrate is used (e.g., SO3), and on occasion, the phase designation is employed (e.g., α-UH_3 and β-UH_3). While a comprehensive table of all the designations is provided at the end of the dissertation, during the reading

process, it would have been beneficial to have a more consistent approach to naming the samples, particularly in the figures.

Summarizing, I consider Ms. Koloskova's work to be a significant and largely pioneering contribution to the field of uranium hydrides and actinides thin films. This is further evidenced by her contributions to the publication of 10 papers in peer-reviewed journals (including two as a first author) and 15 conference presentations. She has a high level of expertise in the subject matter, including a profound understanding of many sophisticated measurement methods and their application in her experiments. The thesis is well written, with an impressive introduction, a comprehensive discussion of the obtained results, and well-supported conclusions based on a review of the literature–it is of high quality in terms of both the results obtained and the manner in which they are presented and discussed. **This clearly demonstrates Oleksandra Koloskova's ability for creative scientific work and independent research.** Therefore, **I recommend accepting this doctoral thesis as the basis for awarding the PhD degree**.

Wrocław, August 1, 2024