Referee report on PhD thesis:

Title: Superconductivity and electronic properties of γ-U alloys and their hydrides.

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The submitted PhD thesis is devoted to superconductivity and magnetism in rapidly solidified U-Mo and U-Zr alloys and their hydrides. Character of the work is mostly experimental and includes sample preparation by arc melting, splat cooling and hydrogenation of splats, characterization of sample by X-ray diffraction, scanning and transmission electron microscopy methods, study of physical properties by magnetization, heat capacity and resistivity measurements. The main goals of the thesis are clearly defined in the Introduction. Combination of Mo or Zr doping of uranium and the splat cooling technique was used for stabilization of *γ*-U phase at room temperature. Large attention was paid to study of superconductivity in *γ*-U phase alloys. Hydrogenation of splats was used as powerful tool which expands the lattice changing inter-uranium distances and affects ferromagnetic ground state. Study of magnetic properties of hydrogenated splats is second goal of the thesis.

From the formal point of view the thesis does not contain usual items like lists of used abbreviations, tables and figures. Division of the thesis to main Chapters does not follow the usual scheme e.g., the goals of thesis are not defined in a separate part and the thesis does not contain main Chapter "Stay of Art" but instead first four Chapters – related to description of Stay of Art – are written not as Subchapters but Chapters. SI units are used in majority cases, there is probably only one exception – lattice parameters are expressed in Å, and many times the unit of magnetic induction T is used as unit of magnetic field in the text. Formal processing of the thesis including text, figures, tables and use of references meets all usual standards. From the content point of view the thesis fulfils all requirements. Introduction contains goals of thesis and brief description of main Chapters. A brief introduction of electronic and magnetic properties as well superconductivity with particular emphasis to uranium – based compounds is provided by first two Chapters. More detailed description of *γ*-uranium phase and uranium hydrides is presented in Chapter 3 and Chapter 4. Stay of Art is presented on very good level, containing basic principles which are generally accepted as well the recent results. Experimental methods, results and conclusion are presented in remaining Chapters very well. Overall processing of thesis from both formal and content point of view is on very high level.

Experimental character of research presented in the thesis implies knowledge and use of experimental methods which are related to sample preparation and characterisation as well study of magnetic, thermal and transport properties. All chosen experimental methods are standard methods representing up-to-date trends of research in this field of solid state physics. Arc melting on water cooled crucible minimises contamination of prepared samples, splat cooling is power full method for rapid solidification; X-ray, SEM and TEM techniques are

standard technique for characterisation of samples; AC susceptibility, magnetization, heat capacity and resistivity measurements are very often used for study of superconductivity and magnetic properties, especially for study of transitions to superconducting or magnetically ordered stay. Outputs of research are usually obtained in the form of photographs or sets of data which are plot in the form of figures. Evaluation of data meets again all usual standards. In several cases basic statistic or fitting of data is used to demonstrate distribution of data or validity of physical laws. The obtained results are discussed in details and very carefully compared with already published up-to-day results as it is expected for any serious scientific work. All experimental methods related to preparation of sample, sample characterisation, acquisition and evaluation of data fulfil usual standards and were used by proper way.

Main results of the thesis, which are summarised in "*Conclusions and future Outlook",* represent original contribution to the field of γ-U phase stabilization at room temperature and basic research oriented to electronic properties and superconductivity of uranium phases and uranium hydrides. All these results have been already published in 11 papers mostly in reputable scientific journals with high impact factor, which underline their quality. Probably the most important result with application potential is synthesis of single phase γ-U samples with concentration of Mo $\geq$ 11 at.% or Zr = 30 at.% which can be used highly enriched uranium fuel for nuclear reactors. Splat cooling techniques provides γ-U phase with lower content of dopant. Study of low temperature properties of uranium splats and hydrides has character of basic research and enrich our knowledge in this field of science. Low-temperature study of electronic properties, magnetic properties and superconductivity in U-Mo and U-Zr splats revealed enhancement of the density of electronic states at the Fermi level due to enlarged U-U spacing or different superconductivity for U-Mo splats in γ-U phase with high upper critical field H_{c2} and α-U with low H_{c2}. The ground stay of uranium hydrides is ferromagnetic with pretty high Curie temperature and large coercive force is characteristic feature of these systems. The high magnetic anisotropy is related to large orbital moments in bonding 5*f* states. In conclusion the thesis of Ilya Tkach: Superconductivity and electronic properties of γ-U alloys and their hydrides meets all usual standards, used methods are up-to-date and results are original significantly contributing to research field that is why I recommend his thesis for defending procedure and after successful defence I suppose the award of PhD scientific degree.

Comments and remarks on the thesis:

1 Presented results have been obtained in collaboration with members of large scientific team. Will you specify your particular contribution to the results?

2 Presented X-ray powder diffraction patterns of splats do not contain any sign of Rietveld treating of data. No calculated profile is presented in figures, figures contain only experimental data. Will you explain what method was used for indexing of peaks? If patterns are not taken from the powders they will be affected by texture, which makes Rietveld refinement very difficult.

3 In the case of splats several different phases usually coexist in an intermediate region. Do you have any information what is solubility/content of Mo or Zr in γ-U, γ'-U or α-U phase for

the same nominal content of Mo or Zr? In the intermediate region e.g. 10 at.% Mo and 15 at.% Mo the lattice parameter $a = b$ decreases and c increases - what is the change of the elementary unit cell in this region? Is this change related to average U – U distance? It seems that the tetragonal phase γ'-U appears in the narrow intermediate region for Mo splats but was not observed for Zr splats. Is it possible that the broadening of peaks for 20 at.% Zr is related to γ'-U phase, and the intermediate region with γ'-U phase could be observed between 20 at.% Zr and 30 at.% Zr. Probably there is a misprint claiming "*γ-phase is the dominant for all splat samples with Zr concentrations ≥ 11 at.%*" on page 88.

4 Magnetization curves (Figure 6.41. and Figure 6.54.) show large hysteretic behaviour between ZFC and FC regimes, bifurcation temperature just below magnetic phase transition as well signature of magnetic pole inversion. No attention is paid to these observations in the thesis. What is an explanation for such behaviour?

5 Horizontal and vertical shift of hysteresis loop presented in Figure 6.57., which is attributed to the exchange bias effect, can be attributed to minority loops measurement due to the fact that the used magnetic field is not enough high in order to reach the saturated stay. What was the cooling field H_{cf} in this case?

In Košice, 3rd June, 2015 RNDr. Marián Mihalik, CSc.