Referee's report on the doctoral Thesis

Synthesis and study of new hydrides based on f-metals

by Mgr Khrystyna Miliyanchuk

The work contained in this Thesis was carried out under the supervision of doc. RNDr. L. Havela at the Department of Electronic Structures and some additional experimental data were collected at several other laboratories, e.g., at Instituto Tecnologico e Nuclear/CFMC-UL, Sacave, Portugal and Hahn-Meitner Institute, Berlin, Germany. The main object of the study is well described by the title of the Thesis; in particular the effect of hydrogenation and also deuterization of two types of uranium intermetallic compounds was studied - UTX and U_2T_2X, where T stands for a transition 3-d metal and X means a p-element.

The Thesis comprises 84 pages of text, 51 figures, list of 100 references and 6 appendices. The text is divided into 5 chapters of rather unequal length and brief Conclusions. The first three introductory chapters (together 25 pages) very briefly summarize the electronic and magnetic properties of uranides, the main characteristic changes caused by hydrogenation of these intermetallics and finally bring some more concrete data for the UTX and U_2T_2X systems. The 4th chapter describes the technological and experimental methods used. The gist of the Thesis is contained in the most extensive chapter 5: Results and discussion.

The thesis is clearly written, the introductory parts demonstrate that the candidate got firm theoretical background during her study. The chapter on experimental methods describes in turn the hydrogenation procedure, the used X-ray and neutron diffraction methods, the magnetic and specific heat measurements, and finally the basics of the Mössbauer spectroscopy.

The material of the Chapter 5, where the own results are presented, is structured according to the various materials that were studied. At this point it is necessary to stress that the amount of experimental material is unusually rich and covers a very broad spectrum of various problems. It was not easy to organize the presentation in a transparent way, but the candidate successfully fulfilled, according to my opinion, this uneasy task.

The brief Conclusions – Chapter 6 – summarize on a little more than 2 pages the most prominent results.

The text is clearly written and even the linguistic standard is at an acceptable level with some non-essential slips.

I would comment more thoroughly on the part concerned with the use of Mössbauer spectroscopy and also ask some question relevant to this part. First I would stress the fact that in contrast to the overwhelming majority of "Mössbauer works", the isotope used here is not the ^{57}Fe but ^{119}Sn. This choice was natural, as the studied materials did contain Ni and Co from 3d transition metals and not Fe, but in some of them Sn was present. The description of the idea of the Mössbauer effect, given on pp. 38-41, goes along the usual lines, but is not free of some errors. Though it is correctly stated in the first paragraph that the "Mössbauer spectroscopy is based on the recoil-free γ-ray resonance emission and absorption in solids, called the Mössbauer effect", in the following text the case of an isolated nucleus is actually treated ending with the relation (4.21). The "recoil-less factor f" connected to the atom, and thus the nucleus, embedded into a solid is not even mentioned. I would like to hear the explanation what does M from (4.21) mean in these two cases.

It would be probably more suitable to point out the fact that we were dealing here with the Mössbauer spectroscopy of the ^{119}Sn nucleus already at the beginning of part 4.6 when mentioning "Sn-containing compounds". As correctly given in the text, the γ-ray is emitted by the transition of the nucleus from an excited to the ground state – by which radioactive transition this excited state is arrived at in the case of ^{119}Sn "source"? It is clear, how the isomer shift was defined, but I would like to hear a closer explanation of the calibration of the velocity scale. And to finish with the general presentation of the Mössbauer spectroscopy, I would like to learn, what consequences the comparable magnitude of the quadrupole splitting and the Zeeman splitting may have beside the fact that "the exact Hamiltonian has to be solved".

In Chapter 5, Mössbauer spectroscopy is mentioned in connection with $UCoSnD_{0.6}$ and $URuSnD_{0.6}$, pp. 56-59 and also on pp. 79-80 for $U_2Ni_2SnD_{1.8}$. For the former case I would like to ask how many lines the Zeeman-split components shown in Fig. 5.15 have, in particular that one for $UCoSnD_{0.6}$? And what does the statement "Quadrupole splitting QS was calculated as $S=\frac{1}{2}e^2QV_{zz}$" in Table 5.6 mean? What sense has the comparison of e.g. the isomer shifts with the results of ref. [40], when they are given with respect to the source of Sn in another compound and at different temperature? Similar question applies to data in Table 5.7.

And finally, what are the conclusions made from the use of Mössbauer spectroscopy in this work in general, as this information is missing in "Conclusions" – Chapter 6?

In conclusion I am convinced that the presented work demonstrated the ability of the candidate to orient herself in a very complex and intricate field and to independently reach new and valuable results and I recommend to take the Thesis as a basis for awarding Mgr Khrystyna Miliyanchuk the title of PhD.

Praha, 18.9.2006