Report on the thesis Khrystyna Miliyanchuk "Synthesis and study of new hydrides based on f – metals"

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The presented thesis deals with the structural and magnetic properties of selected hydrides of uranium compounds. It is divided into six chapters. The first two chapters give the basic general overview of the magnetic properties of actinides, introduction to metal-hydrogen systems with formation criteria and expected effects on magnetism. The summary of previous results on the compounds of interest is given in chapter three. The fourth section describes the experimental methods used, with most details on the diffraction experiments that are essential in this work. The main part of the thesis represents then achieved results and their discussion and finally main conclusions are given in chapter six. The structure of the thesis is appropriate, the text is mostly clearly written, the results properly documented by figures and I did not find almost any misprints what is quite unusual.

The thesis represents large amount of experimental work that can be basically divided into two parts: i) synthesis of the hydrides (very difficult task by itself) and their structural characterization and ii) subsequent investigation of magnetic properties mainly by magnetization measurements and some specific-heat, neutron diffraction and Mössbauer spectroscopy measurements. The relation between the structure and magnetism is very well discussed.

Also the materials studied can be divided into two groups: i) hydrides of UTX compounds – U(Co,Ru)Sn, UCoSi and ii) hydrides of U_2T_2X compounds – U_2Co_2Sn , U_2Ni_2Sn , U_2Ni_2In , U_2Co_2In and U_2Fe_2Sn . The first group studied completes previous work on isostructural UTX materials. The second group represents completely new large group of uranium-based hydrides, presented for the first time here. All the experimental data obtained on hydrides are original and represent an important contribution to the understanding of the electronic properties of actinides. I assume that the data were published in several reviewed papers, although the list is not given in the thesis. I appreciate especially very precise structural studies that include determination of hydrogen position by neutron diffraction and also description of sample preparation that is crucial in this type of work. Concerning magnetic properties, I find also very important that the study is based on several complementary types of experimental techniques.

The magnetic studies nicely demonstrate how the hydrogen absorption can be used to tune magnetic properties of the uranium compounds. Generally, the ordering temperatures increase considerably except for URuSn hydride. The possible microscopic mechanisms responsible for the observed behavior, including the exceptional URuSn, are well discussed. I believe that the work presented in this thesis will continue as the subject is rather interesting and many questions remain still open. I have few minor remarks and questions:

1) The scattering amplitude, b_j , for the neutron case is introduced (page 34) as a constant value for each element. So it is the same e.g. for hydrogen and deuterium?

2) the magnetic properties of studied materials is characterized also by the values of the effective magnetic moment, μ_{eff} , paramagnetic Curie temperature, θ_p , and χ_0 parameter derived from the fit of magnetization data to a modified Curie-Weiss law. However, the formula is not given in the thesis. Concerning χ_0 derived from the fits, is it the same χ_0 as introduced on page 9?

To what extent one can believe these parameters; the error bars are not given (except for θ_p for one compound - UCoSi in Table 5.8, you mention rather poor precision in this case).

3) Could you comment on the tendencies for U_2Ni_2Sn and U_2Ni_2In (Table 5.10, page 73) – the Néel temperature increases whereas the absolute value of θ_p decreases upon hydrogenation. I would expect the same tendency for both characteristics.

4) I do not see any metamagnetic transition on the 10 K curve for $U_2Co_2InH_{1.9}$ (Fig. 5.38 on page 83). How did you determine the critical fields shown on the next figure (5.39) ?

5) I highly regard the technique established for specific-heat measurements on powder materials. The specific heat gives rather important information about the electronic properties. Why there are so few data measured? Why the magnetic entropy for UCoSn and URuSn deuterides cannot be estimated (at least roughly as for U_2Ni_2Sn) – because of lack of data on uranium or other analogue? Do you plan to measure more data in the future?

As conclusion, the presented work clearly demonstrates the ability of Khrystyna Miliyanchuk to perform individual research and I recommend acknowledging this work as successful thesis of Khrystyna Miliyanchuk.

Praha, 8.9.2006

