

Khrystyna Miliyanchuk:

Synthesis and study of new hydrides based on f-metals

Vyjádření školitele

- Opinion of the supervisor

The thesis presented deals with synthesis and experimental studies of several groups of hydrides of intermetallic compounds of uranium. It represents a major part of the research activities of K. Miliyanchuk at the Charles University for the last 4 years. When assessing the quality (and quantity) of results, one has first to mention the specifics of hydrides problematics. Unlike research of standard intermetallics, which are well defined single- or polycrystals, hydrides mostly in the form of fine powders with inherent defects due to grain boundaries and not well defined occupancies of hydrogen positions represent more a situation from research of artificial structures – every synthesis can give slightly different occupancies of hydrogen sites, depending on hydrogen pressure and heat treatment during the synthesis. Moreover, they can be much less stable in time. It is therefore more difficult to extract features belonging to a pure phase. This is compensated by the fascinating capability to absorb and release reproducibly huge amount of hydrogen, allowing for example volumetric determination of hydrogen content on samples much below one gram.

The hydride studies have to be therefore firmly anchored in the technology and crystallography, and the work of the candidate was to a large part concentrated in this part. Her meticulous analyses of X-ray diffraction patterns using full profile refinement provided a solid basis for further studies of physical properties. She was able to benefit partly from previous research of hydrides UTX ternaries with the ZrNiAl structure, concentrating on compounds with Sn. She identified hydrides based on UCoSn and URuSn. Similarly, she discovered that in the UTSi group (TiNiSi structure type), besides UPdSi and UNiSi also UCoSi forms a hydride. One has to recognize that these discoveries were accompanied by more numerous attempts with isostructural compounds, which do not absorb hydrogen in pressures up to about 130 bar. A large part of her work was though oriented to hydrides of U_2T_2Sn type of compounds, which she first indicated on the case of U_2Co_2Sn . Intriguing variations of magnetic properties of hydrides of this compound led to orienting a lot of research effort on this group of hydrides. One has to recall that this group of U intermetallics, discovered in 1994 was a highlight of late 1990's, well illustrating, due to a specific crystal structure, basic tendencies of variations of U magnetism, and exhibiting emergent phenomena at the verge of magnetic ordering. The possibility to add an additional variable to tune on the fine scale the system across the onset of magnetism gives further impetus to the studies of the so called 221 family. K. Miliyanchuk thus successfully synthesized hydrides of U_2Co_2Sn , U_2Ni_2Sn , U_2Ni_2In , U_2Co_2In , and U_2Fe_2Sn . It was found that besides those hydrides prepared by a high pressure synthesis, and which contain more than 1.5 H atom/f.u. and exhibit a volume expansion 5-10%, there exist solid solutions on a small amount of hydrogen and much smaller expansion. The synthesis of this α -hydride without the β -hydride admixture is very difficult, and a systematic effort was exerted only for U_2Co_2Sn .

From the point of view of physics, more interesting than the structure and thermodynamic studies as thermally induced desorption are studies of magnetic

properties. For U intermetallics, the hydrogenation leads typically to enhanced magnetic properties (higher ordering temperatures and magnetic moments), at least partly originating from the volume expansion and reduced $5f$ - $5f$ overlap. This tendency was observed for ferromagnet UCoSn with $T_C = 82$ K. UCoSnH_{1.4} has $T_C = 102$ K. The recognition that its sister compound URuSn does not follow this pattern led to studies of hydrides in the pseudoternary system UCoSn-URuSn. The suggestion that hydrogen occupies different lattice sites on opposite sides of the phase diagram was finally confirmed by neutron diffraction on respective deuterides.

The most interesting cases are those, at which controlled hydrogenation of a system, which is close to the verge of magnetism, sweeps it to a weakly magnetic state. That was a plan with UCoSi, for which besides the mother compound and the full hydride UCoSiH_{1.4} also two intermediate hydrides were synthesized. Unfortunately, the hydrogenation leads in this case only to gradually more emphasized spin fluctuation features; the borderline to magnetic order is not crossed.

Such situation was eventually found for U₂Co₂Sn, which is non-magnetic spin fluctuator. Its α -hydride is a weak ferromagnet, whereas β -hydride is antiferromagnet, resembling by its volume and T_N value other antiferromagnets from the uranium 221 family. As no other case of ferromagnetism has been so far documented in this group of compounds, the case of the α -hydride brings up an interesting possibility (explaining also a ferromagnetic character of spin fluctuations in U₂Co₂Sn) that a narrow island of ferromagnetism occurs due to fundamental reasons just at the verge of magnetic ordering. For other 221 compounds only β -hydrides were studied so far. From numerous results it is particularly worthwhile to mention the change of magnetic structure between U₂Ni₂Sn and its hydride, attributed to a small but substantial change of the U coordination due to the anisotropic expansion. It is very interesting to see that the known fundamental features of magnetic anisotropy in U systems work on a very fine scale. This part amounts into a discussion, revealing that the effect of hydrogenation as reducing the $5f$ -ligand hybridization is more pronounced in cases of a stronger hybridization in parent compounds, i.e. in those including transition metals in the more early part of respective transition metal series.

The magnetic data are complemented by data obtained using other experimental techniques, namely neutron diffraction on deuterides, ¹¹⁹Sn Mössbauer spectroscopy and specific heat. For the last one, extended experimenting with forming powder samples into pellets, which could be used in the PPMS microcalorimetry system, had to be undertaken. It was practically demonstrated that composite pellets formed by adding a fine powder of Cu or Ag could be in most of cases replaced by bond-free pellets obtained in a WC die using pressures of several kbar. These experiments open new possibility for further studies. Although the thesis does not contain any "future prospects" section, from the results it is evident that more systematic research (using specific heat or e.g. the isomer shift from the Mössbauer spectroscopy) mainly on the "221" hydrides, can put more light on systematic variations of the $5f$ -ligand hybridization and its modifications with increasing hydrogen content. The data obtained can be also a good basis for *ab-initio* electronic structure calculations. From this point of view, the thesis of K. Miliyanchuk represents an important reference source information on structure and basic magnetic data. It also raised, due to several successful presentations at international conferences, an attention of a broad research community dealing with actinides and of researchers in the field of metal hydrides.

Although the presented thesis does not involve all research achievements of K. Miliyanchuk (the aim was to maintain the monothematic character) I am convinced

that the thesis and its content (considering both volume and quality of the results and discussions included) deserves to be accepted as a basis for the PhD degree.

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