Anna Maria Adamska:

Variations of actinide magnetism in uranium-based hydrides and other selected systems

Vyjádření školitele

- Opinion of the supervisor

The thesis presented deals with actinides and their magnetism in three types of materials. The research of hydrides of UTGe compounds was intended as a parallel to the UTSi hydrides studied previously (by K. Miliyanchuk). The UTGe hydrides turned actually much more rich in phases, and as they include the famous ferromagnetic superconductor UCoGe, new challenges appeared in the course of the study. Therefore this part represents a major pportion of the thesis. New, modern, fields of reseach are represented by the nanostructured U-Fe materials in the form of sputter-deposited films, which is a continuation of the project of ultrafast-cooled U-Fe alloys. Finally, transuranium systems in the form of U-Pu compounds are included in the short third part.

The thesis covers thus the major research activities, pursused by A. Adamska at the Charles University and the supervising partner universities in Poland, namely the AGH University and pegdagogical University in Cracow, for the last 4 years. In addition, numerous experiments have been performed by A. Adamska at research partners, as ITN Sacavem, Portugal, TU Darmstadt, and ITU Karlsruhe. She had therefore to get involved actively in various techniques, as Mössbauer spectroscopy, Rutherforrd Backscattering, or high-pressure XRD studies using a diamond anvil and image plate. The work with glove boxes in the transuranium institute ITU was a particular personal challenge.

During her study at the Charles University, Ms. Adamska was dealing independently with sample synthesis (arc melting), hydrogenation, X-ray diffraction and FullProf analysis, and magnetic and specific-heat measurements using the automated PPMS and MPMS systems. In the same time, when learning those techniques, she gained an insight into the condensed matter physics, quite remarkable considering her background (having a master degree in „physics and computer science“ from the Pedagogical University).

As mentioned above, large part of the thesis deals with metal hydrides based on U ternary intermetallic compounds. Unlike research of standard intermetallics, which are well defined single- or polycrystals, hydrides are mostly in the form of fine powders with inherent defects due to grain boundaries and not well defined occupancies of hydrogen positions. Moreover, every synthesis can give slightly different occupancies of hydrogen sites, depending on hydrogen pressure and heat treatment during the synthesis. 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, by fine tuning of magnetic properties to some extent analogous to a negative pressure, etc..

Although the primary target is modification of the U magnetism by H absorption, the hydride studies have to be based on technology and crystallography, and the work of the candidate was to a large part concentrated in this part. It soon turned out that the most interesting case of UCoGe has in fact the most complicated technology, with a striking (and dozen times reproduced) paradox of increasing H pressure apparently decreasing the amount of H absorbed. The suggestion that a higher hydride forms at still higher pressure but is unstable and decoposes into the form with lower H concentration sounds logical, but has to be tested by an in-situ XRD experiment.

The case of UCoGe and its hydrides became actually a textbook example of the fact that the hydrogenation and the concomitant volume expansion are not fully equivalent of negative pressure. The finding that a slight volume expansion in the alpha hydride does not support the ferromagnetism but unexpectedly suppresses it similarly to hydrostatic pressure brought the candidate to the investigation of anisotropic compressibility of UCoGe. The observed anisotropy, which correlates with the expected participation of the 5f states in the bonding, is so dramatic that in some directions the lattice reacts similarly to the hydrogen absorption. This finding has far reaching implications for very popular pressure tuning of physical properties, at which one should first establish the reaction of the lattice to hydrostatic pressure. The directionality of the 5f bonding is later also used to explain the anisotropy of themal expansion.

The research was systematic enough to map all possible hydrides on the basis of UTGe compounds, although besides UCoGe also some other cases (as UNiGe) were rather complicated. A special case is UFeGe undergoing a monoclinic distortion, which is removed by the hydrogenation, bringing it almost to the verge of magnetic ordering. For additional information the ^{57}Fe Moessbauer spectroscopy was successfully deployed, with a nice anlysis of the spectra taking into account the irregular occupancies of H positions. In general, the data follow the known general line, that the H uptake and volume expansion support the 5f magnetism.

The section on metal hydrides is followed by a two brief sections. The first, on U-Fe films, represents a „high-risk“ research, an attempt with an uncertain outcome. The goal was to have U atoms incorporated in a system with magnetic-ordering temperature higher than the room temperature. Previous attempts with ultrafast cooling of Fe-rich laves phase UFe_2 showed that if a still higher Fe concentration could be achieved without the α-Fe segregation, the Curie temperature may get to or over the room temperature. After few attempts with different substrates and a struggle against oxidation this was really achieved. As the products were actually amorphous, additional diagnostics should be applied for the characterization. RBS turned out particularly useful, as it gives also an idea about the the burried interfaces etc. The price was mainly in the tedious modelling of the RBS spectra, by far not easy, which the candidate managed very well.

The other short part deals with two alloys of U and Pu, forming the so-called ζ-phase, the physical properties of which remained unknown. The general aim was to demonstrate that the volume and inter-actinide spacing does not play the same role for U and Pu. This finding, illustrating the inadequcy of the band theory for Pu, has a far-reaching consequences for theoretical description of Pu system.

In general the thesis is reasonably structured, well written, with appropriate graphics. In few cases the figures look, though, over-complicated (as Fig.3.19.). The Fig. 3.14. is well illustrating how the desorption experiment develops in time, but it may give more direct insight if pressure would be plotted as a function of temperature, not time. That would, thou, request a careul approximation of the temperature-versus-time curve, wiggled because of the PID control. In the section on thin films one has a problem with orientation, as the table listing all samples with their stoichiometries is 70 pages before, in the section of experimental techniques. It may have been useful to give more details of sputter deposition, as the ion currents or Ar gas pressure. One could also have also included photoelectron spectra and other details of the films characterization, with the related discussions the thesis volume would grow over a resonable limit.

So looking for a weak point, one realizes that the text would deserve a clearly manisfested „future outlook“ section, summarising unclear points and suggesting a future development. Its absence is particularly painful in the case of the U-Fe films, for which the candidate covered in her PhD work a first pilot study, and a more systematic research, revealing the relation of depostion conditions, structure and magnetism should follow.

I am nevertheless convinced that the thesis and its content (considering both volume and quality of the results and discussions included) deserve to be accepted as a basis for the PhD degree. It proves that A. Adamska has knowledge and insight necessary for independent research work in condensed matter physics.

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