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Referee's opinion on the PhD thesis of M.Sc. Haijing Meng

entitled:

„High Pressure X-ray and Raman Studies of the Selected Metal Hydrides"

The doctoral thesis of Mrs. Haijing Meng was done within the International PhD Studies at the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw. The thesis presents the research of high pressure behavior of dysprosium, lanthanum molybdenum and tantalum hydrides and deuterides. The investigations were made with the use of structural and optical techniques. The main goal of this work was to obtain new high pressure hydrides and describe their properties. The most valuable result concerns the high pressure hcp-fcc structural transformation of dysprosium trihydride obtained for the first time.

The work consists of four chapters, presenting theoretical background, description of experimental methods used in this work, the presentation of results and their interpretation. The first, introductory chapter consists of general description of hydrides, theoretical background of high pressure thermodynamics and description of techniques used to obtain high pressure and enabling measurements of physical parameters at high pressure conditions.

Chapter 2 concerns the rare earth trihydrides and deuterides of Dy and La. In the beginning a literature review is presented pointing out that for Dy there were no experimental reports on the high pressure phase transformation of its trihydride, what gave motivation for the research presented in the thesis. This review is followed by the presentation and analysis of high pressure X-ray diffraction and Raman spectra measurements for DyH_3 and DyD_3. It is worth noting here that the high pressure DyH_3 phase transformation from hcp to fcc phase obtained by the author was observed at pressure close to that theoretically predicted. The interesting changes of vibrational modes in the Raman spectra depending on pressure were observed. There is also presented an interesting analysis of the isotope effect due to substitution of hydrogen by deuterium. To understand the observed vibrational modes in the Raman spectra for dysprosium trihydrides/deuterides the investigations of the Raman spectra for LaH_3 and LaD_3 under ambient and high pressure were made and presented in the next sub-chapter. The observed pressure shift and vibrational modes in the Raman spectra for lanthanum trihydrides are interpreted as related to pressure induced ordering of D (H) atoms in the lattice.

The chapter 3 presents the similar logical structure as the previous one, but concerns the transition metal hydrides obtained at high pressure of hydrogen, in particular the molybdenium and tantalum hydrides investigated in situ and in addition ex-situ for tantalum. The literature review is presented at first followed by the presentation of experimental results and their analysis. Very interesting is the reported hydrogen pressure induced unit cell increase for molybdenium to reach $MoH_{1.4}$ hydride at ~15 GPa instead of expected dihydride. A different, stepwise unit cell increase for tantalum due to hydrogen pressure allowed to reach the ~TaH_2 hydride at ~6 GPa with expanded unit cell. In both cases further increase of hydrogen pressure causes unit cell volume decrease up to ~40 GPa as expected. It is interesting, that by the use of the thermodesorption technique the hydrogen content was estimated to be higher than expected theoretically (2.2 instead 2.0).

The experimental chapters are followed by a chapter 4 with a summary and conclusions pointing out to the main achievements of the work which, in my opinion, is too short. Anyhow the presentation of the results and their interpretations given in the experimental chapters proves the broad knowledge of the literature, good and deep understanding of high pressure behavior of metals and their hydrides by the author, which is very important for her future scientific development.

It is worth noting here, that besides of the complicated sample preparation and hydrogenation technique the author used difficult research techniques – the typical ADXRD, the EDXRD and Raman spectroscopy both detected in situ during pressurizing the samples in the diamond high pressure cell. The thermodesorption technique was also used to determine hydrogen content in the tantalum hydrides. The possibility to perform such measurements gave Mrs Haijing Meng a good opportunity to gain experience in high pressure measurement methods and to develop her experimental skills.

Mrs. Haijing Meng presents her experimental data very precisely. For each group of samples the presentation and discussion of obtained structural, optical and complementary results is very clear and consistent. The interpretation of results is well based on the theoretical background and literature.

With respect to the presented results and interpretations I have following questions and remarks:

What was the accuracy of unit cell parameters obtained from the XRD spectra analysis obtained at CHESSS for DyH_3 and the accuracy of the resultant molar volume (Fig. 2.4)?

It is not clear if the Raman scattering experiment for DyH_3 and DyD_3 was made during the same experimental run as the XRD measurements at the synchrotron facility at CHESS or separately?

Why does for DyD_3 between deuterium modes in Raman pressure dependencies (Fig. 2.8) appear horizontal mode for octahedron sties not observed for DyH_3?

Page 37. The statement "General overall pictures of the pressure dependence of Raman modes for the dysprosium hydride and deuterides are quite similar to those of yttrium hydride and deuteride." should have the literature reference.

In the discussion of the isotope effect (page 40) the anharmonic contribution to vibrational modes is suggested. What are the reasons of this effect?

In the subchapter 2.3 the Raman scattering spectra of LaH_3 and LaD_3 (the same cubic structure as DyH_3 and DyD_3) are presented and analyzed, but lacks discussion concerning the relation of these spectra with the spectra for DyH_3 and DyD_3.

In the analysis of high pressure loading of hydrogen in Mo and Ta the explanation of the observed structural effects is based on the Switendick's rule concerning H-H distance. It would be interesting to see how the H-H distance changes with pressure in the investigated hydrides. What is the author's opinion - can this Switendic's border distance 2.14 A be changed by pressure?

As concerns increased hydrogen content observed for the Ta dihydride I would like to ask for the accuracy of hydrogen content estimation. The big number of lattice imperfections and surface effects could also increase the hydrogen content.

The above expressed remarks and questions concern in fact some details and interesting aspects of the work and do not influence my high opinion of this work. It is worth to mention, that the results described in this PhD work have been already published in 4 scientific papers in the prestigious journals with Mrs. Haijing Meng as the coauthor, and 2 of them are with her as the first author. This clearly proves high scientific level presented in her PhD work.

To conclude, I would like to emphasize that the results presented in this PhD thesis are new, valuable and scientifically sound. They bring important contribution to our knowledge of structural properties of Dy, La Mo and Ta hydrides and deuterides under pressure. The information concerning properties of obtained hydrides and deuterides of Dy, La Mo and Ta broadens our knowledge on materials absorbing hydrogen. The thesis proves, that Mrs. Haijing Meng is a very good researcher, especially skillful in experiment and in future can create further valuable scientific works.

The PhD work of Mgr Haijing Meng represents high scientific level, fulfills all the formal requirements of the Polish regulations concerning the PhD theses and I recommend it for further proceeding of the doctoral procedure by the Scientific Council of the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw.

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Prof. Henryk Figiel