Evaluation of structure models of Ho_2PdSi_3 using DAFS, *inter alia* at a satellite reflection

M Nentwich[1], M Zschornak[1], C Richter[1,2] and D C Meyer[1]

[1] Institute of Experimental Physics, TU Bergakademie Freiberg, Leipziger Straße 23, 09599 Freiberg, Germany
[2] DESY Photon Science, Notkestraße 85, 22607 Hamburg, Germany

E-mail: Melanie.Nentwich@physik.tu-freiberg.de

Abstract. The compounds R_2PdSi_3, with R = rare earth, exhibit a very interesting magnetic behavior with two phase transitions. Substituting one in four Si atoms by Pd in $HoSi_2$ results in a modulation of the aristotype. There are several different variants discussed in literature about the nature of the modulation of this rare-earth compound. Two of the latest models were compared: a $2 \times 2 \times 1$ layer and a $2 \times 2 \times 8$ stack. The chosen method is *Diffraction Anomalous Fine Structure* (DAFS) and was applied both experimentally and by simulation at different absorption edges and reflections, *i. a.* a satellite reflection, aiming on finding the correct crystal structure.

1. Introduction

Diffraction Anomalous Fine Structure (DAFS) is a site selective X-ray diffraction method for studying the local structure of atoms. Relying on energy scans applied at an absorption edge, the DAFS method is closely related to *X-ray Absorption Fine Structure* (XAFS) and thus offers a similar kind of spectroscopic information. As an advantage over XAFS, DAFS is sensitive to the crystallographic structure factor $|F|^2$ and, hence, it is possible to differentiate between atoms that are of the same species, but located on different Wyckoff positions, see e. g. [1].

This work focuses on the rare earth compound Ho_2PdSi_3 which is of high interest due to its complex magnetic behavior [2–6]. The structure is based on the aristotype $HoSi_2$ with the hexagonal AlB_2 structure type (space group $P\,6/m\,m\,m$) and the lattice parameters $a = b = 3.8148(6)$ Å and $c = 4.1073(5)$ Å [7]. The occupied Wyckoff positions are $1a$ for Ho and $2d$ for Si. The lattice parameters of the structure change slightly with the substitution of $^1/_4$ Si by Pd ($a = 4.076$ Å, $c = 4.021$ Å), but the AlB_2-type remains [8].

Ternary R_2TX_3 compounds with $R = $ Sr, Y, rare earth, U, Th, $T = $ transition metal, Al, Ga, Ge and $X = $ Si, In, Ge, Ga, Sn have been studied by several groups in the last decades [9]. The research on this group started in 1966 [10] with the finding of the AlB_2-type structure in U_2FeSi_3 adopted from USi_2 [11]. The first work on rare earth-transition metal-silicides investigated by Raman followed in 1967 [12]. The earliest observations of a superstructure of R-T-silicides – indicated by almost doubled lattice parameters compared to their aristotypes – were reported by Chevalier *et al.* [13]. In respect to the structure of interest, in 1990, Kotsanidis *et al.* were the first to investigate Ho_2PdSi_3, finding a hexagonal cell with doubled lattice parameters a and c [2]. All following articles concerning Ho_2PdSi_3 reported structures based on the hexagonal AlB_2

type. In contradiction to Kotsanidis *et al.* [2], Szytuła *et al.* did not find any superstructure in Ho_2PdSi_3 [3]. Several years later X-ray diffraction measurements pointed out a $2 \times 2 \times 8$ superstructure [6, 14]. Still, there remain several open questions and contradicting experimental results which are addressed in the present investigations. Tang *et al.* [14] proposed a special stacking order as shown in Fig. 1, leading to a higher symmetry than the model based on partially statistically distributed Pd atoms as proposed by Szytuła *et al.* [3]. This stacking and a $2 \times 2 \times 1$ layer (see Figure 2) originally found in Tb_2PdSi_3 [15] are considered as unit cell models within this work and compared against resonant X-ray scattering measurements.
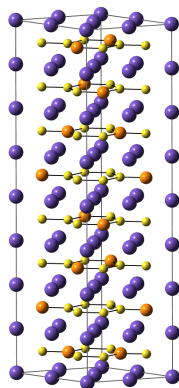

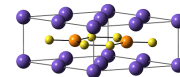**Figure 1.** $2 \times 2 \times 8$ supercell D_1.

Figure 2. $2 \times 2 \times 1$ layer A.

2. Experiments

The DAFS experiments were carried out at beam lines E2 and BW1 of the former DORIS III synchrotron at DESY. For our measurements, the Bragg reflections $0\,0\,1$, $3\,0\,1$, $1\,1\,0$ and $^1\!/_2\,^1\!/_2\,^5\!/_8$ were chosen carefully with respect to maximum anomalous signal at the edge, in previous considerations on the system [16]. Energy spectra of these reflections were obtained at the Pd K and Ho L_1 to Ho L_3 absorption edges evaluating the integrated intensities of rocking scans at each energy. Simultaneously, fluorescence was recorded to gain absorption spectra (XAFS). These can be used to perform an absorption correction and to find initial simulation parameters, since they contain the average spectroscopic signal of all symmetrically inequivalent resonant atoms in the structure.

The measurements at the Pd K edge at $24\,347$ eV were realized by using the third harmonic radiation of the Si 111 monochromator, since this energy was out of range for the fundamental. Meanwhile, the fundamental at $8\,116$ eV was filtered out using an aluminum absorber.

The investigated single crystals were grown by Behr *et al.* [17] and have already been studied in related work [14, 18, 19]. The chemical composition was determined as $Ho_2Pd_{1.01(1)}Si_{2.99(1)}$ corresponding to an almost ideal ratio of $2 : 1 : 3$.

3. Simulation

The DAFS curves were modeled using the FDMNES code [20]. Due to the large models and hence large computing times, we started with the cluster radii `radius` and `Rself` of about 4.1 Å within the simulation. The corresponding Ho L calculations are only sensitive to the first coordination shell. However, our simulations showed that, in order to reproduce the white line in the XAFS spectrum, a radius of at least 5.4 Å must be used. Thus, each resonant Ho atom is additionally influenced by the next Ho neighbor in c-direction. This leads to the reduction of the different Pd environments to a single one and of the Ho environments to two different

ones for model A and five different environments for model D_1 (determined by FDMNES). The different environments have to be averaged using the proper crystallographic weights and symmetry operations to obtain final quantities for each model, which in turn, can be compared against the measurments.

For the simulations shown below relativistic corrections as well as quadrupolar transitions have been taken into account using the refining non-standard keywords `relativism` and `quadrupole` along with the keyword `memory_save` for computational feasibility. The influence of the strongly changing absorption of the diffracted beam was taken into account using the additional option `self_abs` that performs a division by the linear absorption coefficient and, thus, corresponds to the description of integral intensities from a thick crystal in kinematic approximation.

4. Results and Discussion

The experimental data were corrected for intensity jumps due to positron injection at the synchrotron. Additionally, energy shifts of different measurements were aligned and the XAFS spectra of several reflections were averaged. For comparison, the maxima of the data – experimental as well as simulated – have been normalized to 1.

In Figure 3 the experimental and simulated XAFS data are plotted for the Ho L_3 edge. It can be seen that, in terms of position and magnitude, the resonances of the experimental XAFS fit well to the simulated curves. The whiteline of the XAFS is reproduced by both models. Model A shows a worse agreement with the experiment at energies higher than approximately $50\,\text{eV}$ after the edge where the features are more pronounced than in the experiment. This can be related to a higher degree of order of the nearest Ho neighbors with respect to the diversity of Wyckoff sites in model D_1.
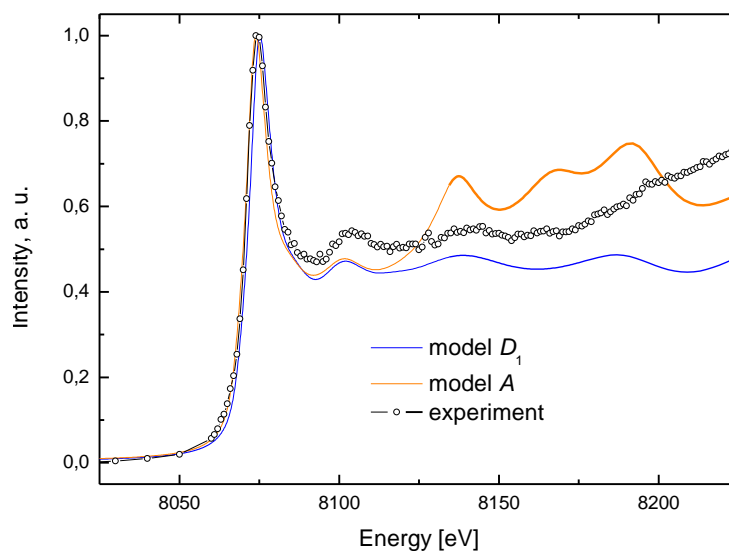

Figure 3. XAFS-Experiment (black circles) as well as simulations for model D_1 (thin blue line) and model A (thick orange line) at the Ho L_3 edge.

Figure 4 shows the DAFS-curves of the $0\,0\,1$ reflection at the Ho L_3 edge. Both models agree well with the experiment in the edge region (edge $+35\,\text{eV}$), beyond this region only model D_1 fits to the experiment concerning oscillation width and height.

Measured and simulated DAFS-curves of the satellite reflection $1/2\,1/2\,5/8$ at the Ho L_3 edge are compared in Figure 5. For this special reflection, only model D_1 is shown due to the expected,
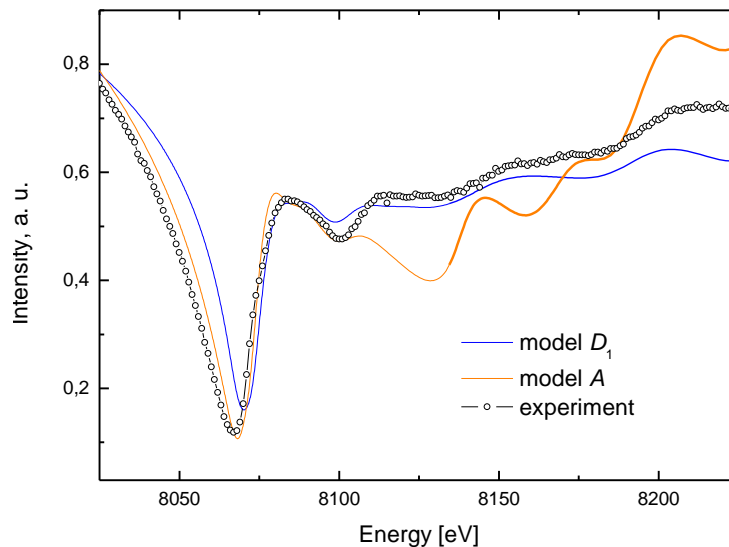
Figure 4. DAFS-Experiment (black circles) as well as simulations for model D_1 (thin blue line) and model A (thick orange line) of the $0\,0\,1$ reflection at the Ho L_3 edge.

negligible intensities for model A. In lieu of model A, we present here the double corrected intensities (I_d, bright blue) additionally to the corrected (I_c, dark blue). Figure 5 emphasizes the enormous effect of self absorption, that is underevaluated by the standard correction and overevaluated by the double correction. Both curves depict the oscillations of the experimental data. Currently a combination of integrated and maximum intensity is considered to explain the disproportionate influence of the absorption.
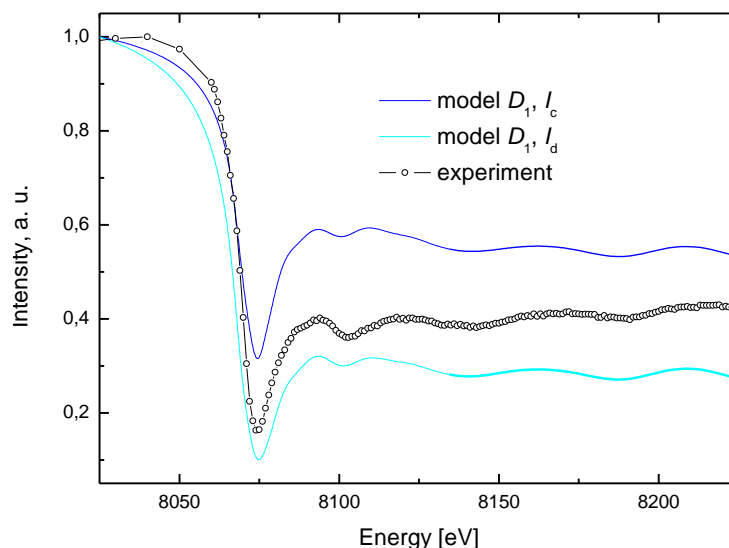

Figure 5. DAFS-Experiment (black circles) as well as simulations for corrected (I_c – thin, dark blue line) and double corrected (I_d – thick, bright blue line) model D_1 of the $1/2\,1/2\,5/8$ reflection at the Ho L_3 edge.

Comparing the simulated data of all reflections from both models with the according

experiments, model D_1 shows a significantly better fit. Another fact supporting model D_1 is the appearance of the superlattice reflection in general.

Currently, FDMNES calculations of a further stacking model as proposed by Dshemuchadse [18] and a partially statitical distribution of Pd and Si are in progress and will be presented in future reports.

Acknowledgments

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