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Evaluation of structure models of Ho$_2$PdSi$_3$ using DAFS, inter alia at a satellite reflection

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Abstract. The compounds R$_2$PdSi$_3$, 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$_2$PdSi$_3$ 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 $P6/mmm$) 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$_2$FeSi$_3$ 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$_2$PdSi$_3$, finding a hexagonal cell with doubled lattice parameters $a$ and $c$ [2]. All following articles concerning Ho$_2$PdSi$_3$ reported structures based on the hexagonal AlB$_2$
type. In contradiction to Kotsanidis et al. [2], Szytula et al. did not find any superstructure in $\text{Ho}_2\text{PdSi}_3$ [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 Szytula et al. [3]. This stacking and a $2 \times 2 \times 1$ layer (see Figure 2) originally found in $\text{Tb}_2\text{PdSi}_3$ [15] are considered as unit cell models within this work and compared against resonant X-ray scattering measurements.

![Image](image1.png)

**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 001, 301, 110 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 24347 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 8116 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 $\text{Ho}_2\text{Pd}_{1.01(1)}\text{Si}_{2.99(1)}$ 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 $\text{radius}$ and $\text{Rself}$ 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 measurements.

For the simulations shown below relativistic corrections as well as quadrupolar transitions have been taken into account using the refining non-standard keywords \texttt{relativism} and \texttt{quadrupole} along with the keyword \texttt{memory\_save} for computational feasibility. The influence of the strongly changing absorption of the diffracted beam was taken into account using the additional option \texttt{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 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.](image)

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 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,
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 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.

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 statistical distribution of Pd and Si are in progress and will be presented in future reports.

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