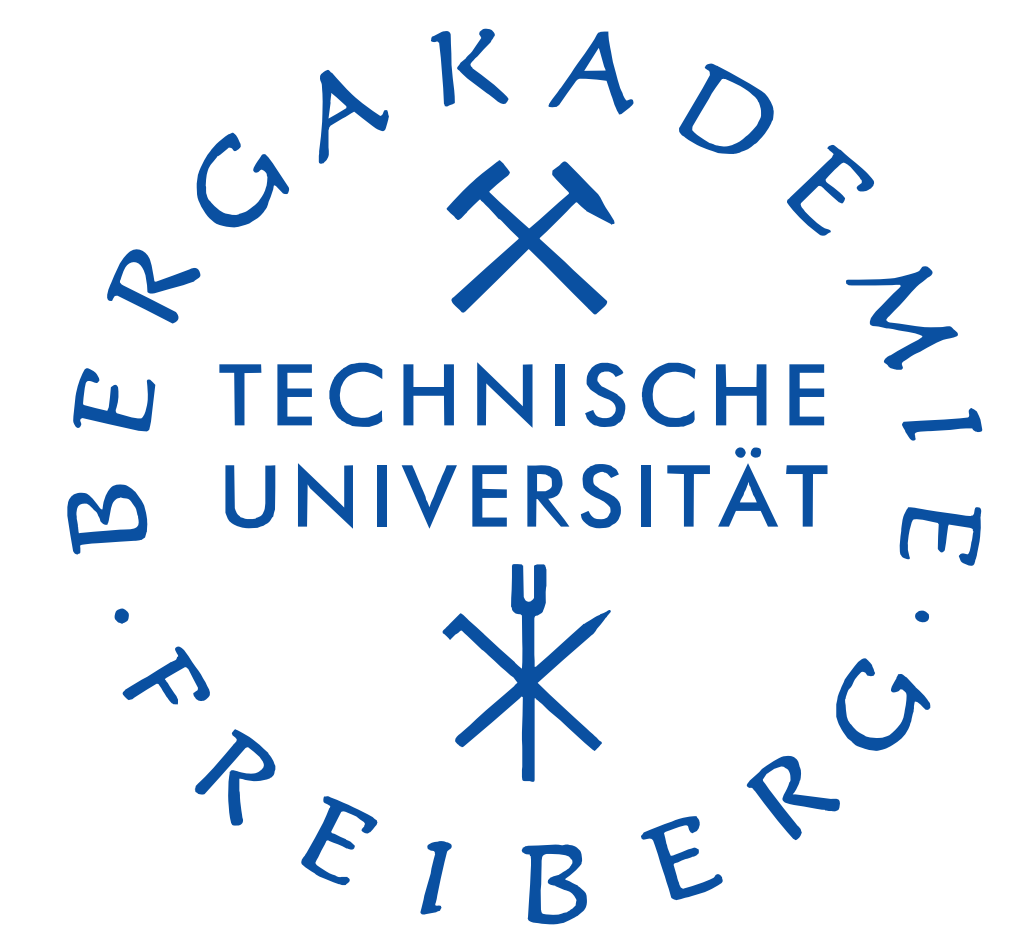


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Structure Determination of Selected Rare Earth Compounds using DAFS

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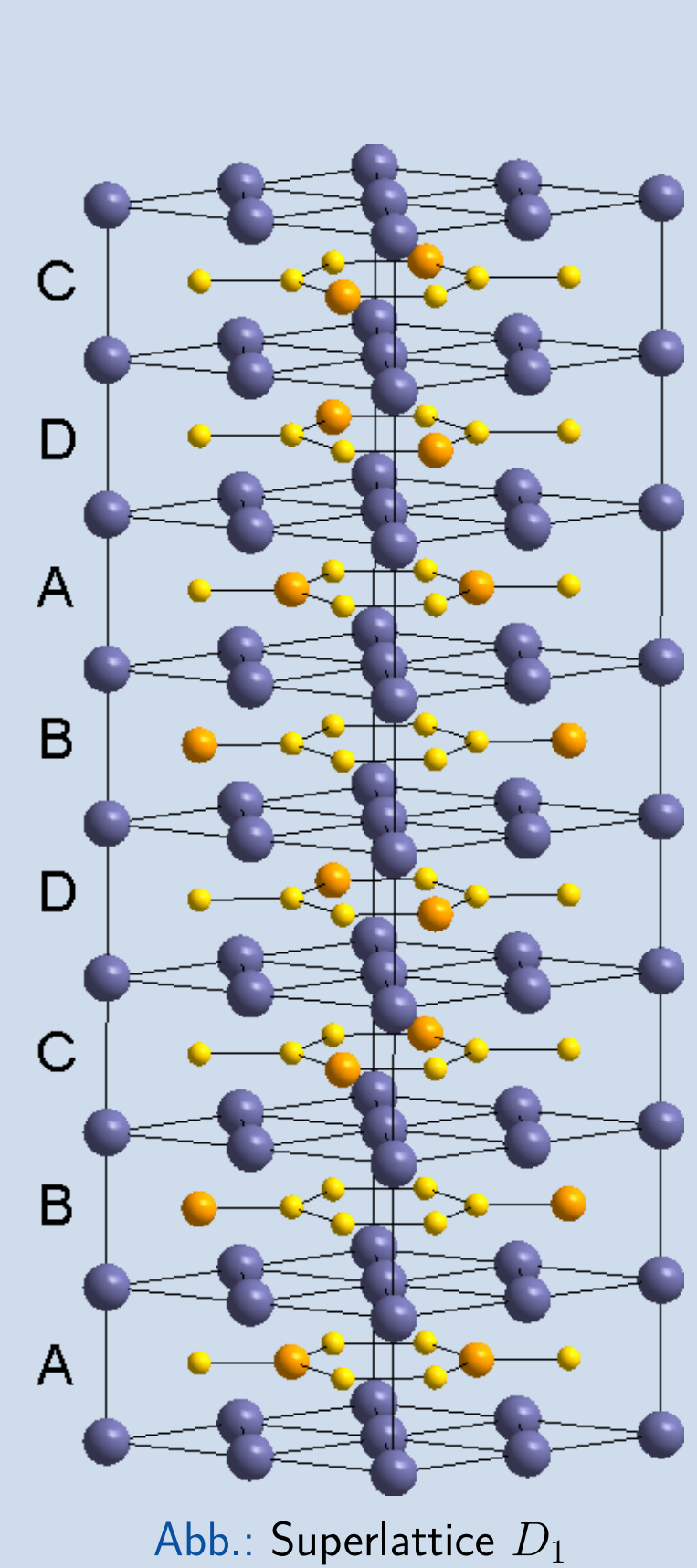
Motivation

Diffraction Anomalous Fine Structure (DAFS) is a method for studying the local electronic structure. Compared to the established method of *X-Ray Absorption Fine Structure* (XAFS) DAFS offers a similar kind of information but the advantage of distinction between atoms of the same element but different Wyckoff positions. DAFS is influenced by the crystallographic structure factor $|F|^2$. If the resonant atoms are located at symmetric inequivalent positions, it is possible to differentiate between the different local structure information due to the long range order. This property allows e. g. the analysis of mixed valence systems.

The Simulation has been performed using *Finite Difference Method for Near Edge Structure* FDMNES [1].

Structures of the Rare Earth Compounds

Superlattice of Holmium–Palladium–Silicide

Abb.: Superlattice D_1

The crystal Ho_2PdSi_3 (short: HPS) results from HoSi_2 by inserting Pd.

Space Group & Lattice Constants of HoSi_2

 $P6/mmm$ (191) $a_1 = 4.05 \text{ \AA}, a_3 = 4.00 \text{ \AA}$

Wyckoff Positions of HoSi_2

Atom	Wyckoff Site	Symmetry	Coordinates
Ho	1a	$6/mmm$	0 0 0
Si	2d	$\bar{6}m2$	$\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$

Applying Laue experiments to HPS revealed satellite reflections causing the assumption of a $(2 \times 2 \times 8)$ superlattice. A proposal was introduced by [2] and is based on four equivalent $(2 \times 2 \times 1)$ layers A, \dots, D . Considerations about stacking energy lead to one of the six isomorphous eightfold layers D_1, \dots, D_6 ($D_1 = ABCDBADC$, see figure on the left, Ho in purple, Si in yellow and Pd in orange).

Aim is to examine the correctness of model D_1 .

Mixed Valence System Yttrium–Mangan–Iron–Oxid

The crystal $\text{YMn}_{2-\xi}\text{Fe}_\xi\text{O}_5$, $\xi = 1$ (short: YMFO) results from YMn_2O_5 (short: YMO) by inserting Fe.

Space Group & Lattice Constants of YMO

 $Pbam$ (55) $a_1 = 7.27 \text{ \AA}, a_2 = 8.48 \text{ \AA}, a_3 = 5.67 \text{ \AA}$

Wyckoff Positions of Fe/Mn in YMO

Atom	Wyckoff Site	Symmetry	Coordinates
Mn/Fe	4f	$\dots 2$	0 $\frac{1}{2}$ z_{4f}
Mn/Fe	4h	$\dots m$	x_{4h} y_{4h} $\frac{1}{2}$

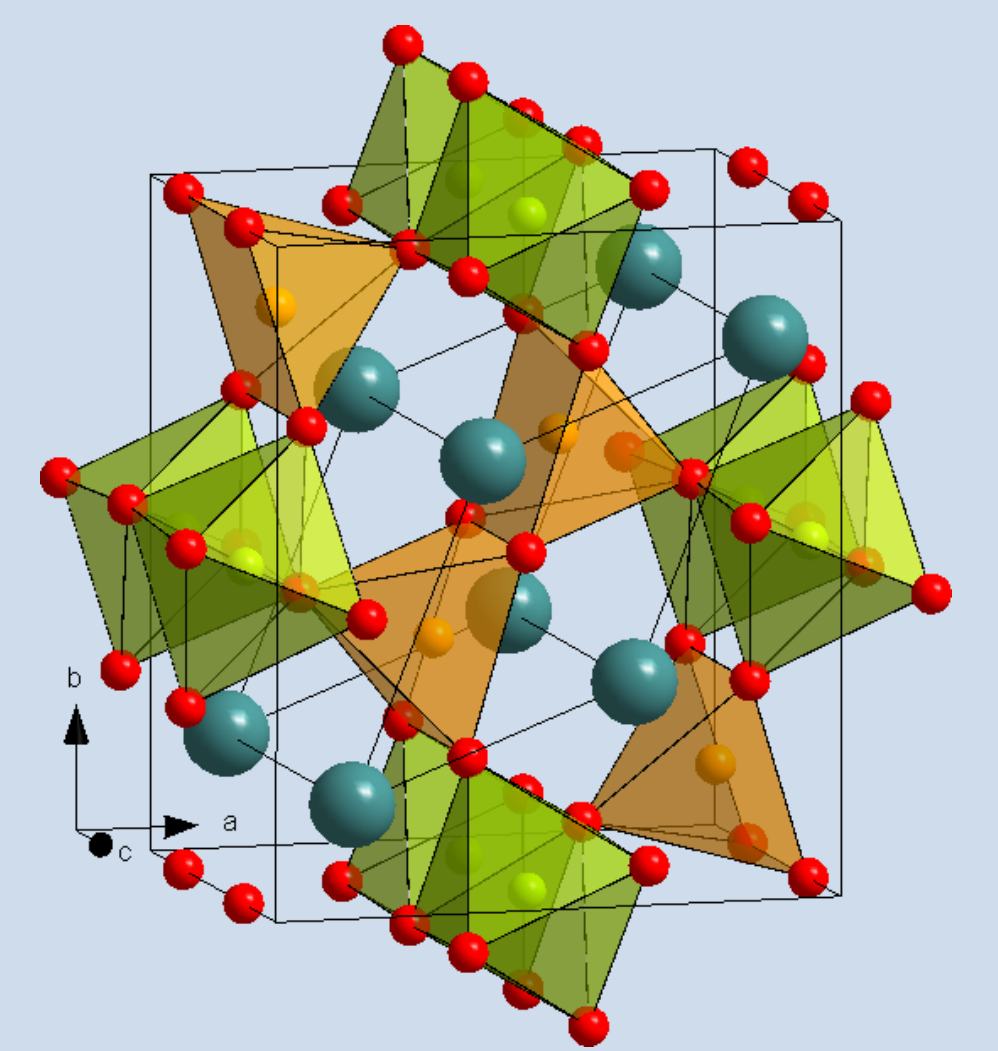


Abb.: Mixed valence system YMO

YMO is a mixed valence system: $4h$ requires the $3+$ valence state and $4h$ needs $4+$. Possible distributions of Fe are [3]:

- (A) homogeneous distribution of Fe on $4f$ and $4h$
- (B) complete localisation of Fe on $4f$
- (C) complete localisation of Fe on $4h$
- (D) inhomogeneous distribution of Fe on $4f$ and $4h$

Aim is to determine the distribution of Fe on $4f$ and $4h$.

O – red, Y – green, $4f$ – green octahedron, $4h$ – orange pyramid

Simulation and Experiment

Holmium–Palladium–Silicide

- absorption edges:
Ho– L_1 (ca. 9 399 eV) and Pd– K (ca. 24 347 eV)
- measurements from beamline E2 at DESY/HASYLAB

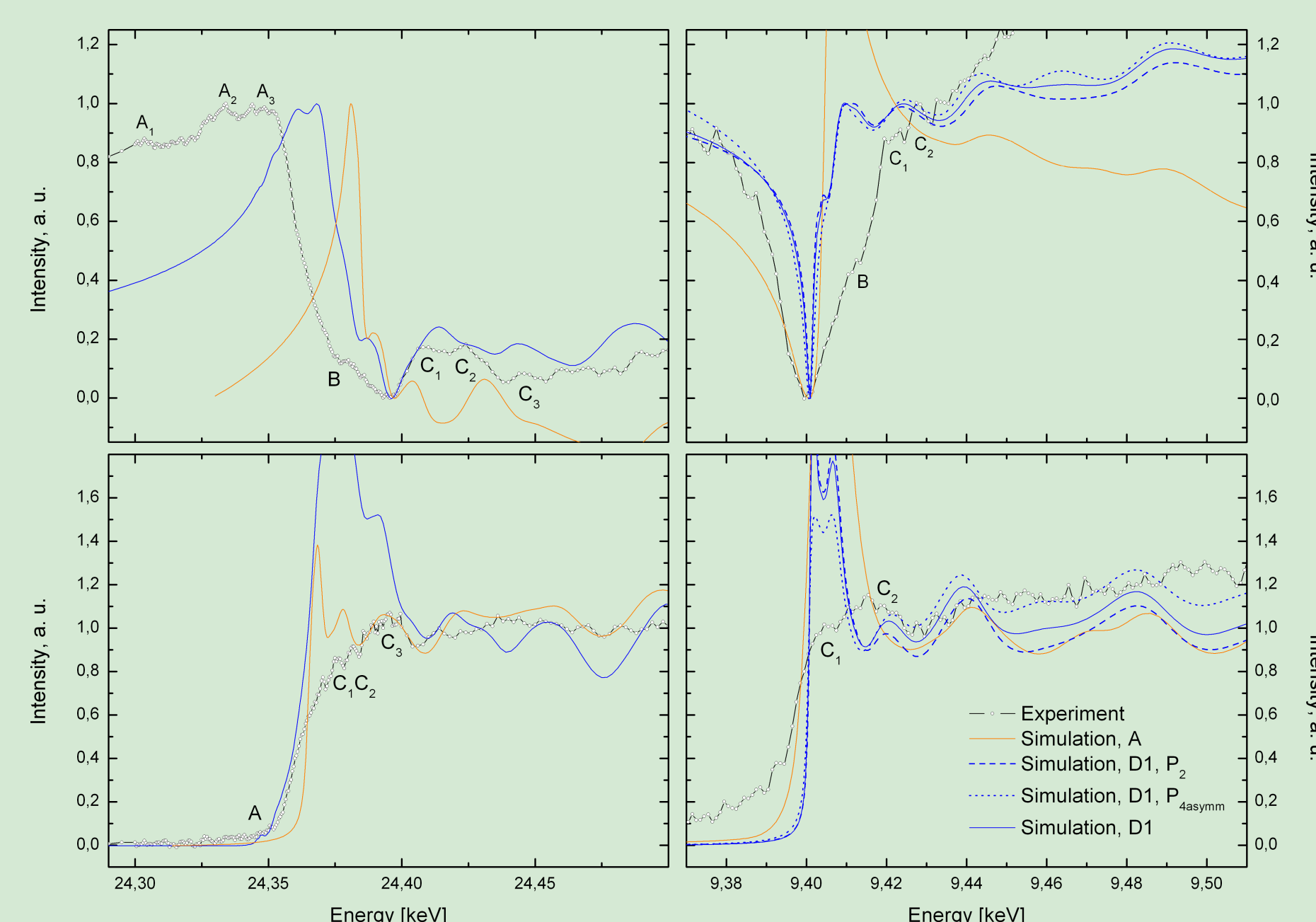
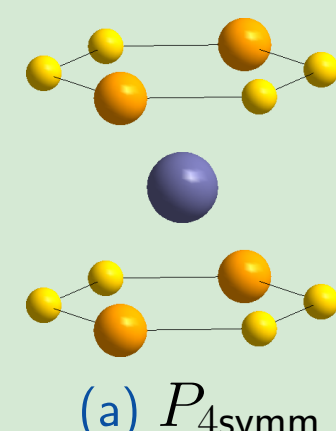


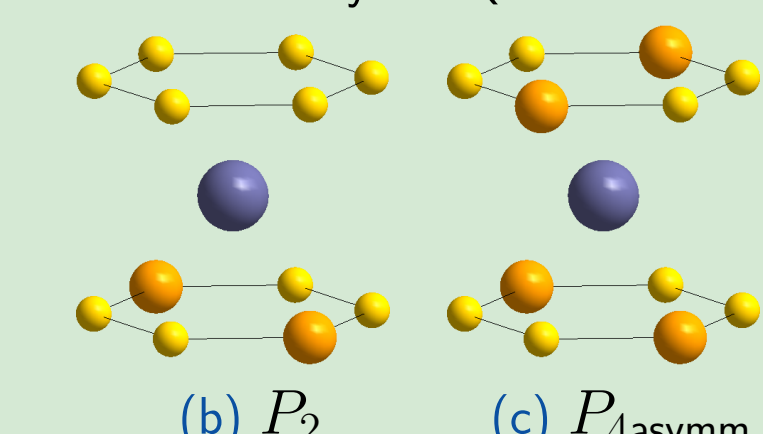
Abb.: Normalized DAFS and XAFS curves. Top DAFS, bottom XAFS. Left Pd– K , right Ho– L_1 absorption edge

- models: superlattice D_1 and layer A

- three different Ho sites:
 $P_{4\text{symm}}$ (model A),

(a) $P_{4\text{symm}}$

- P_2 and $P_{4\text{symm}}$ (model D_1)



- reflections: 001, 301 and 110

Yttrium–Mangan–Iron–Oxid

- absorption edges:
Mn– K (ca. 6 538 eV) and Fe– K (ca. 7 111 eV)
- measurements planned at DESY/HASYLAB

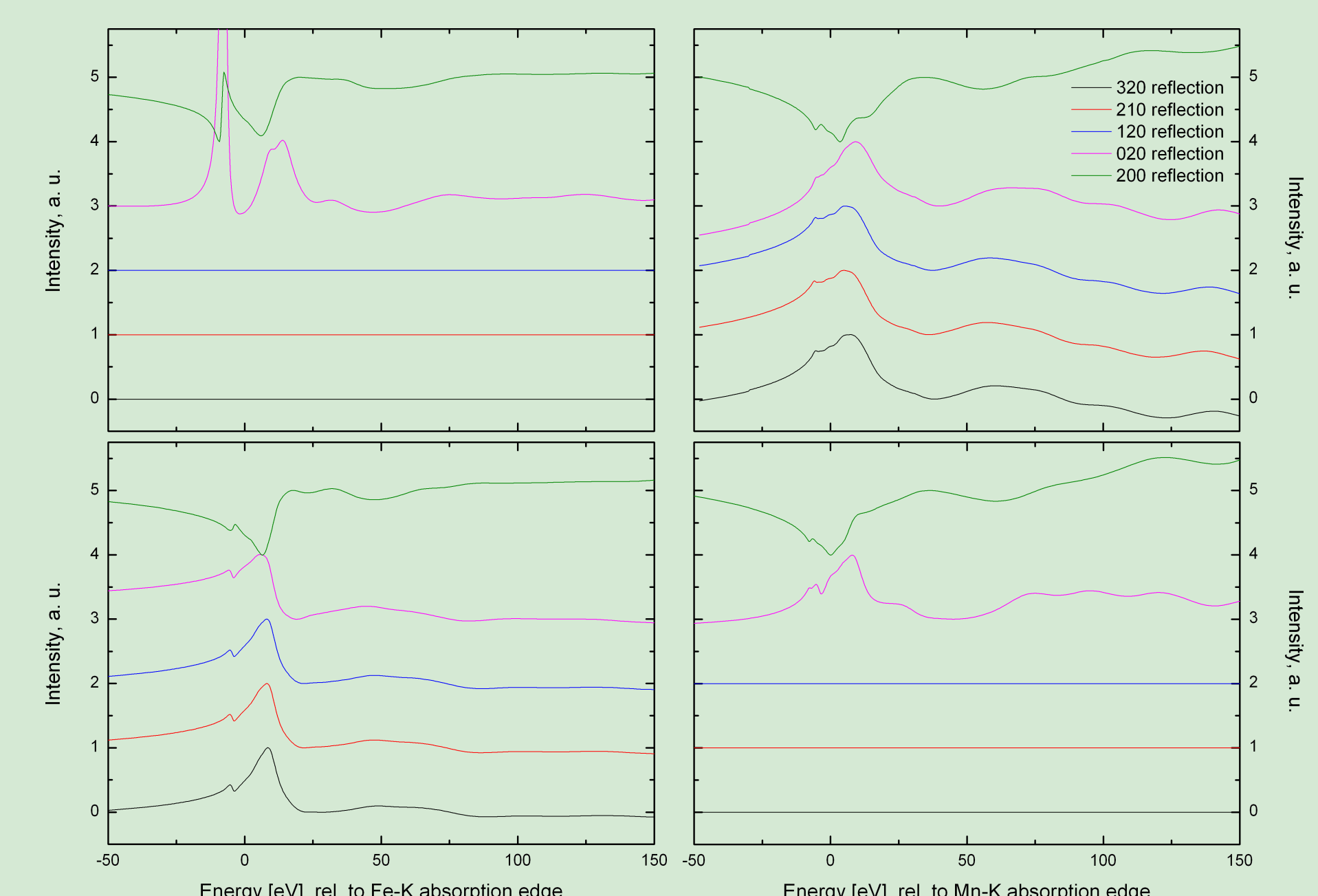


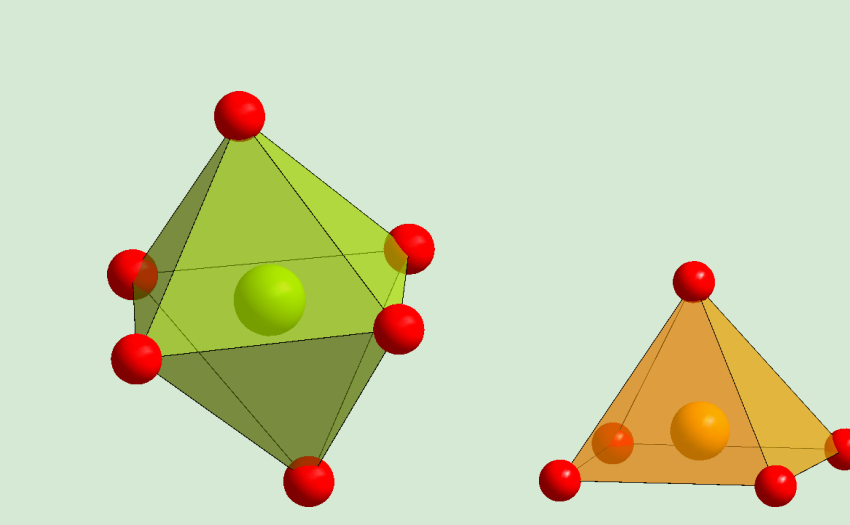
Abb.: Simulated DAFS curves. Top model B, bottom model C. Left Fe– K , right Mn– K absorption edge

- reflections 320, 210 and 120 chosen due to reflection condition of $4f$

$$h + k = 2n, n \in \mathbb{Z}$$

- reflections 020 and 200 chosen due to relation α_{4f}/α_{4h} of crystallographic weights

- analysed sites



- models B and C

Conclusion

Holmium–Palladium–Silicide

Comparing the experimental data with the two models A and D_1 none of them is showing throughout satisfying results. Model D_1 fits better especially in the pre-edge area of the Pd– K absorption edge and the whole Ho– L_1 absorption edge. But model A fits better in the post-edge area of Ho– L_1 .

The differences between the simulations are caused by variations in the local structures of the absorbing atoms.

Probably neither model for itself explains the structure completely and a combination of both will answer the question for the stacking.

Simulations of the Ho– L_2 and Ho– L_3 absorption edges are in progress. Even better results are expected due to a better signal-to-noise ratio of the already measured experimental data.

Yttrium–Mangan–Iron–Oxid

In case of localisation of the absorbing atom at the $4f$ site DAFS should be a constant signal. This means the Fe– K absorption edge for model B alternatively the Mn– K absorption edge for model C.

The experimental research of YMFO is planned for a future measurement period at DESY/HASYLAB. A constant signal detected at the Fe– K absorption edge would confirm model B. If the DAFS curves are constant at the Mn– K absorption edge, this would be a confirmation of model C.

In case of a non-constant signal at both edges a weighted convolution of both models would be necessary to determine the distribution of Fe on both sites.