Anisotropy in Anomalous Scattering in rutile TiO_2 and the influence of diluted point defects.

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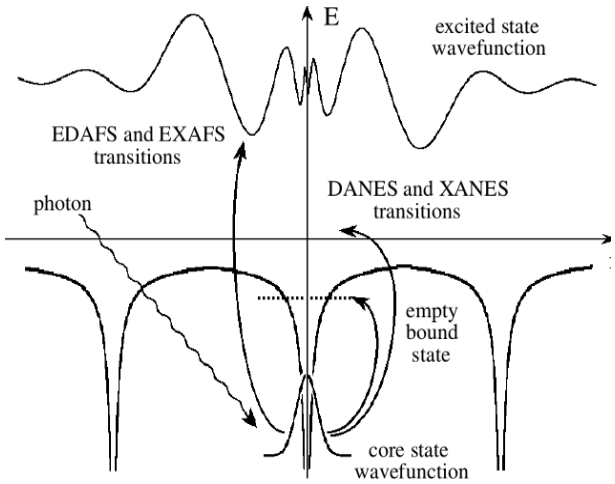
DESY

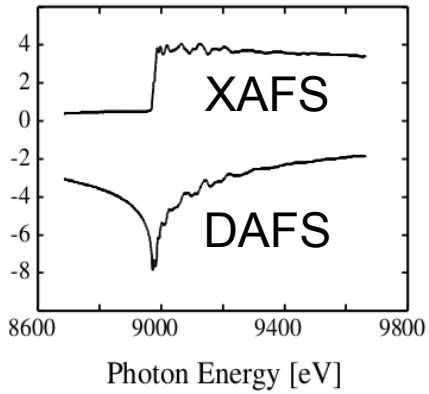
Outline.

- Basics
  - Anomalous Scattering / Anisotropy in scattering factors
  - tensor notation / symmetry restrictions
- Application: rutile structure
  - symmetry restrictions
  - forbidden reflection 001
  - partially forbidden reflection 111
- Influence of point defects
  - theoretical considerations
  - first experiments on 001 and 111 reflections
- Conclusion & Outlook

Anomalous Scattering / Anisotropy in scattering factors.

- Atomic scattering factor for elastic scattering near absorption edge





from: L. B. Sorensen et al., Resonant Anomalous X-Ray: Scattering: Theory & Applications, pages 389–420, Elsevier Science

» excitation of electrons into unoccupied states

single electron approach:

$$(f'+if'')(\omega)=(\hbar\omega)^2\sum_{i,c}\frac{\langle i|\boldsymbol{\varepsilon}_{sc}\boldsymbol{r}\,e^{i\boldsymbol{k}_{sc}\boldsymbol{r}}|c\rangle\langle c|\boldsymbol{\varepsilon}_{in}\boldsymbol{r}\,e^{i\boldsymbol{k}_{in}\boldsymbol{r}}|i\rangle}{\hbar\omega-(E_c-E_i)-i\Gamma/2}$$

- depends **linearly** on Polarization and **non-linearly** on wave vectors $\boldsymbol{k}_{in}$, $\boldsymbol{k}_{sc}$
  → anisotropic anomalous scattering (AAS)
- probing local density of unoccupied states
  → XAFS / DAFS

Tensor notation / Symmetry restrictions.

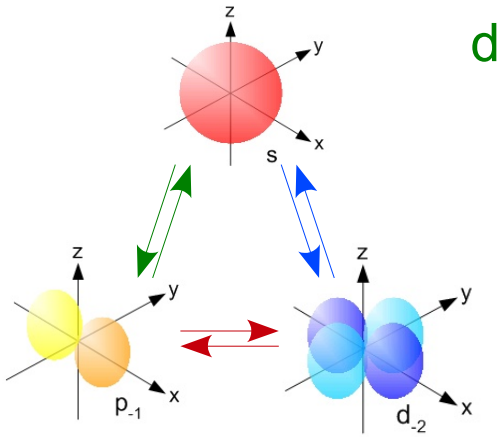
- linear **polarization dependence** can be described by **2nd rank tensors**
- tensor series expansion for wave vector dependency:

$$f'+if''=\varepsilon^{T}_{in,j}\,\varepsilon_{in,k}\left[D_{jk}-\frac{i}{2}\left(k_m I_{jkm}+k'_m I_{kjm}\right)+\frac{1}{4}k'_m k_n Q_{jkmn}+O\left(k^3\right)\right]$$

dipole-dipole

quadrupole-quadrupole

dipole-quadrupole

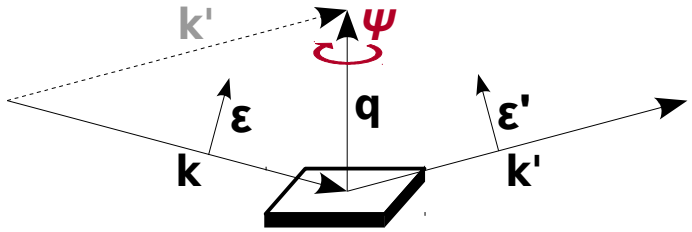


- must remain constant under site symmetry operations!
- **Structure Tensor:** (neglecting qq-terms)

$$F_{jk}=F_0\delta_{jk}+F^{dd}_{jk}+k_m F^{dq}_{jkm}+k'_m F^{dq}_{kjm}+\ldots$$

Access via **azimuthal** Intensity **dependency**

$$I=I(\psi)$$



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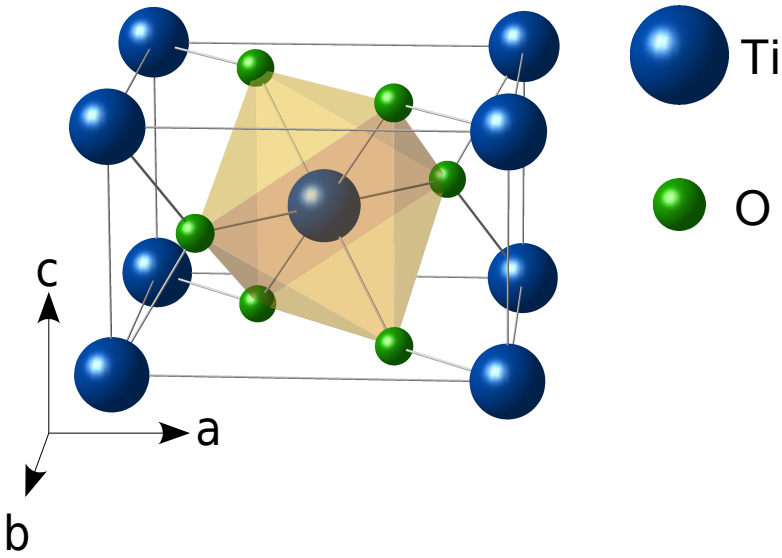
Application: Rutile Structure (TiO_2).



Space Group $P4_2/mnm$ (136), Tetragonal

Atom	Wyckoff site	Site symmetry	Coordinates		
Ti	2a	m.mm	0	0	0
O	4f	m.2m	x	x	0

Site symmetry reduces number of independent Tensor components:

→ 3 components left in dipole-dipole scattering

→ dipole-quadrupole scattering forbidden by symmetry

dipole-dipole contribution:

$$f_{dd}^{Ti}(\boldsymbol{q},E)=\begin{pmatrix} f_{11}^{Ti} & f_{12}^{Ti} & 0 \\ f_{12}^{Ti} & f_{11}^{Ti} & 0 \\ 0 & 0 & f_{33}^{Ti} \end{pmatrix}$$

Titanium scattering amplitude at resonance

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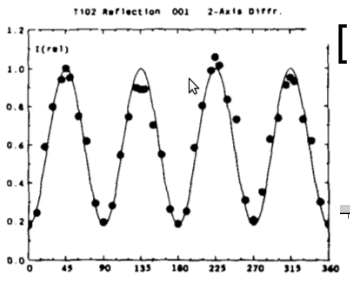
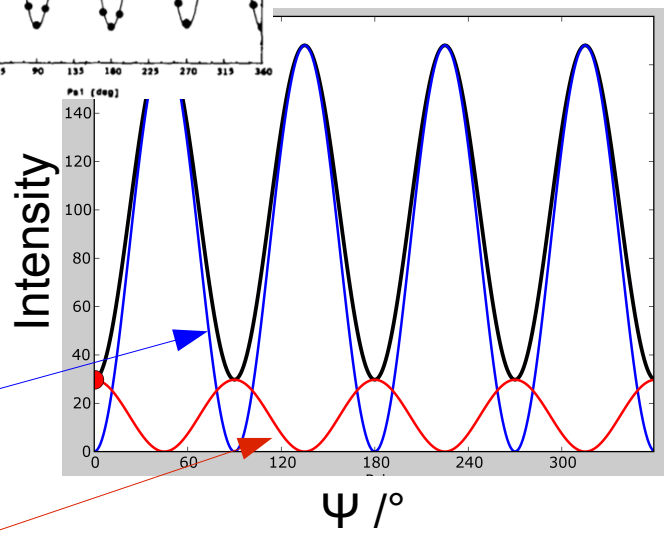
Forbidden Reflection 001.

- Thomson scattering forbidden due to 4-fold screw axis → $F_0 = 0$
  - Already investigated by Kirfel et al.[1]
  - only off-diagonal component f^{Ti}_{12} contributes:

$$\mathbf{F}_{001} = 2f^{Ti}_{12} \cdot \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



[1]



  - e.g. σ-polarized radiation

$$I_{\sigma\sigma'} \propto \left| f^{Ti}_{12} \sin(2\Psi) \right|^2$$

$$I_{\sigma\pi'} \propto \left| f^{Ti}_{12} \cos(2\Psi) \sin(\theta) \right|^2$$

→ only depends on absolute value
→ phase lost
→ absorption correction nessecary

[1] A. Kirfel et al., Acta Cryst. A47 (1991), 183-195

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Partially Forbidden Reflection 111.

- Only Oxygen contributes to Thomson scattering
  → e.g. $\sigma\sigma'$ channel:

$$F_{jk} = F_0 \delta_{jk} + F^{dd}_{jk}$$

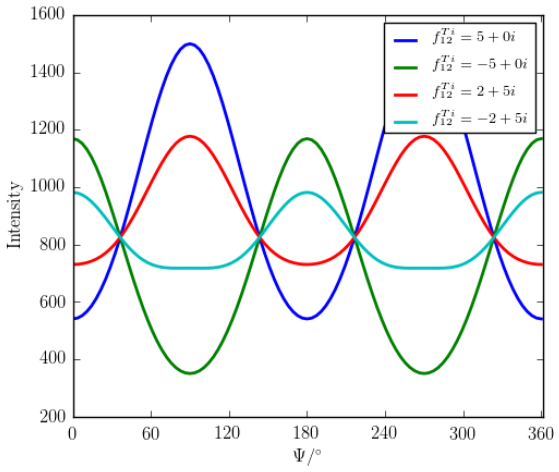
At Ti-resonance: mixture of non-resonant oxygen and resonant titanium scattering amplitudes: more complex patterns

Oxygen Titanium Interference term

$$I_{\sigma\sigma'} \propto c^2 |f^O|^2 + \xi(\Psi)^2 |f^{Ti}_{12}|^2 + 2c\xi(\Psi)\left(\Re(f^O)\Re(f^{Ti}_{12}) + \Im(f^O)\Im(f^{Ti}_{12})\right)$$

ξ: general Ψ-dependence

c: constant



Phase information for f_{12}

but weak influence of imaginary part

no absorption correction necessary

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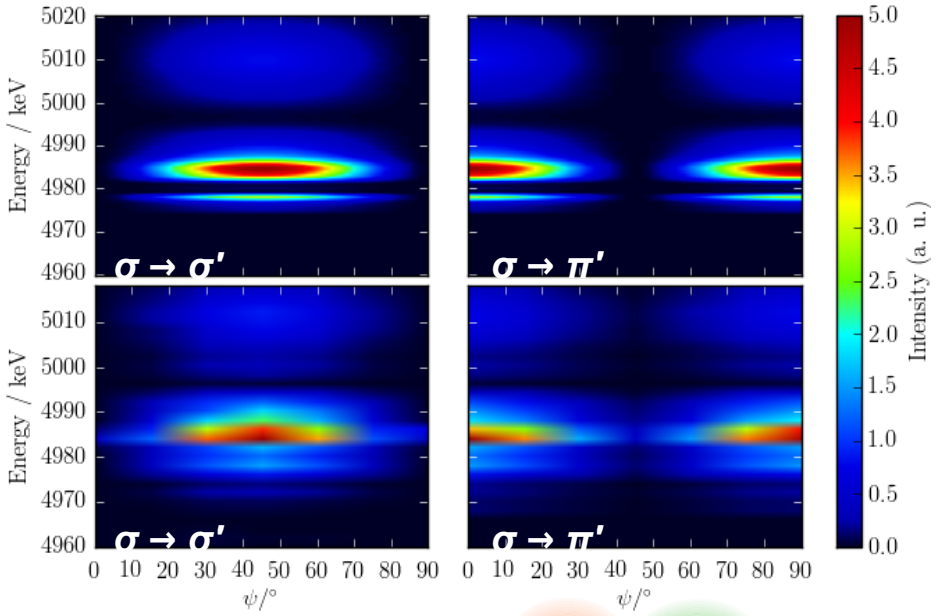
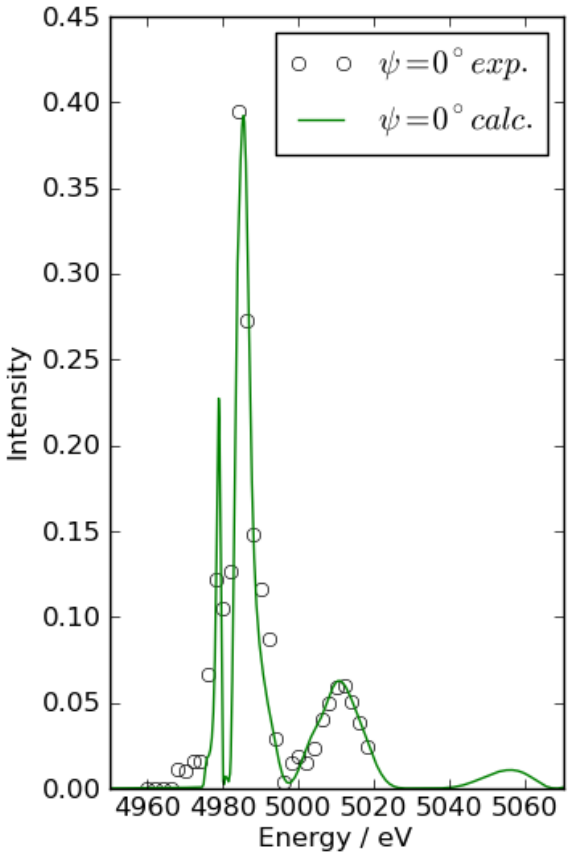
Measurement of forbidden reflection 001.

- Polarization resolved measurements at beam line W1 at DESY
- Calculations done with FDMNES[2]

  → good agreement with measured data



separate dependencies: $I \propto I_1(E) \cdot I_2(\Psi)$ DAFS x AAS

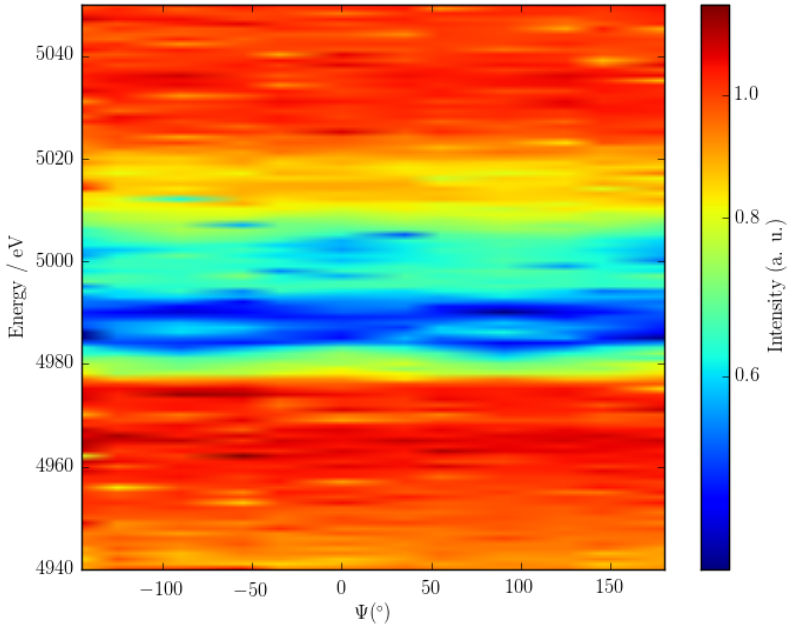


Ψ-integrated DAFS spectra

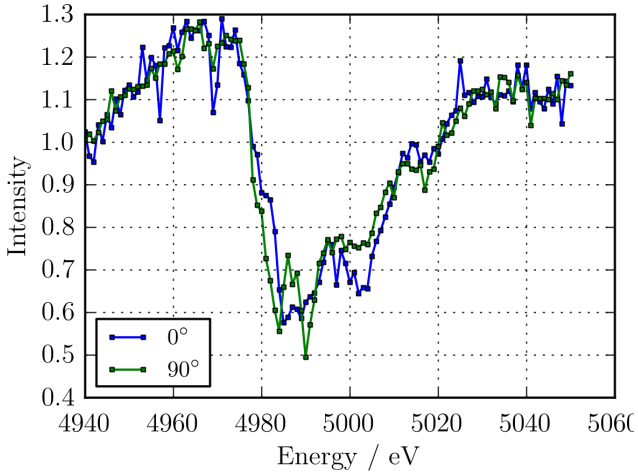
[2] Yves Joly, Phys. Rev. B **63**, 125120 (2001)

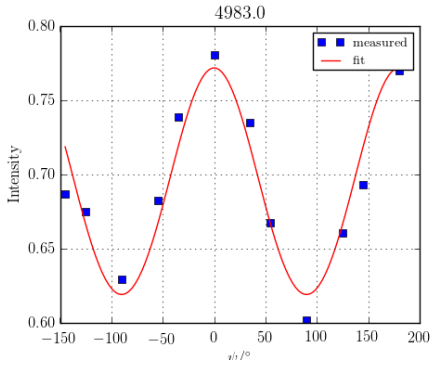
Measurement of Allowed reflection 111.

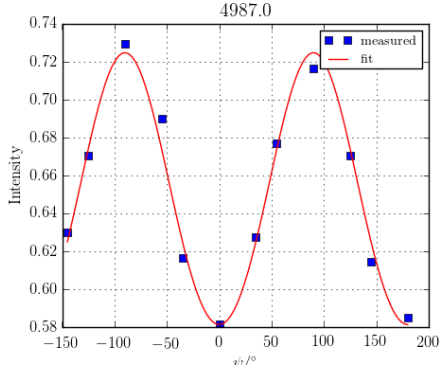
- Ti-K resonance – polarization resolved measurements at PETRA III beamline P09
  - pure untreated rutile:



combined AAS / DAFS map



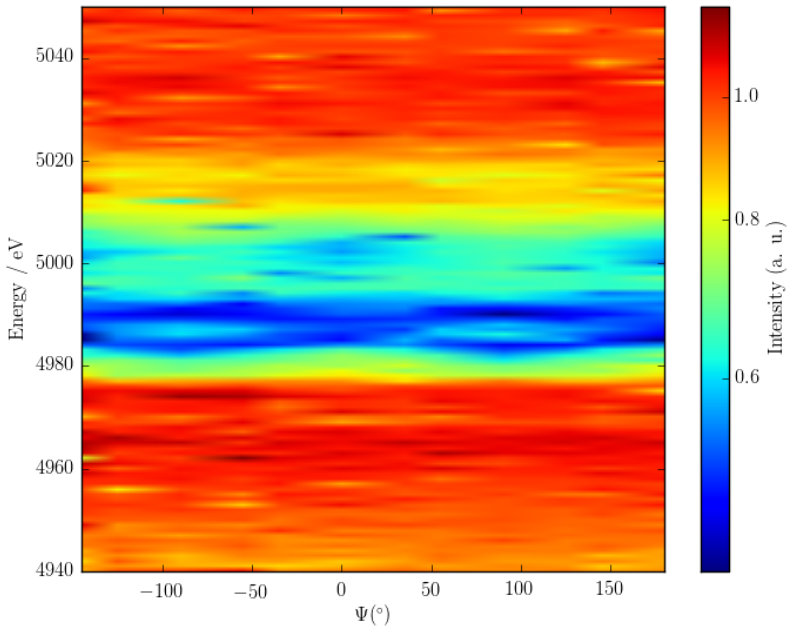




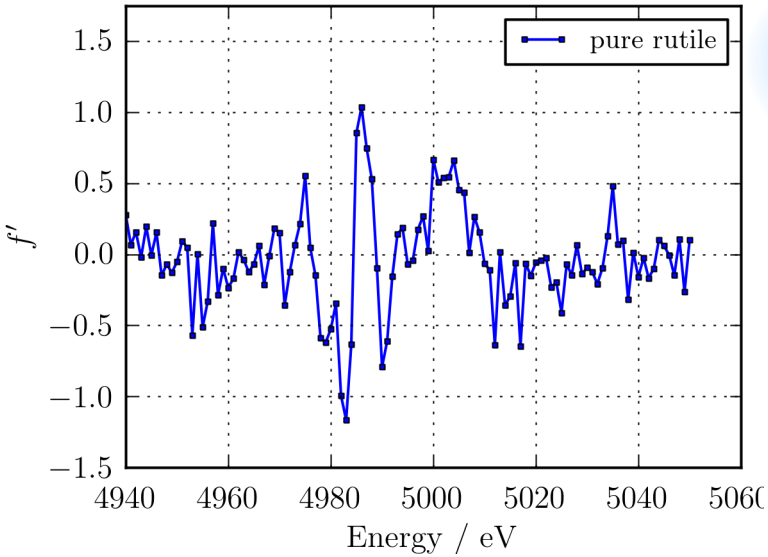
  - shows expected azimuthal behavior
  - energy dependency varies with different Ψ

Measurement of Allowed reflection 111.

- determination of f_{12}' from AAS profiles – untreated rutile



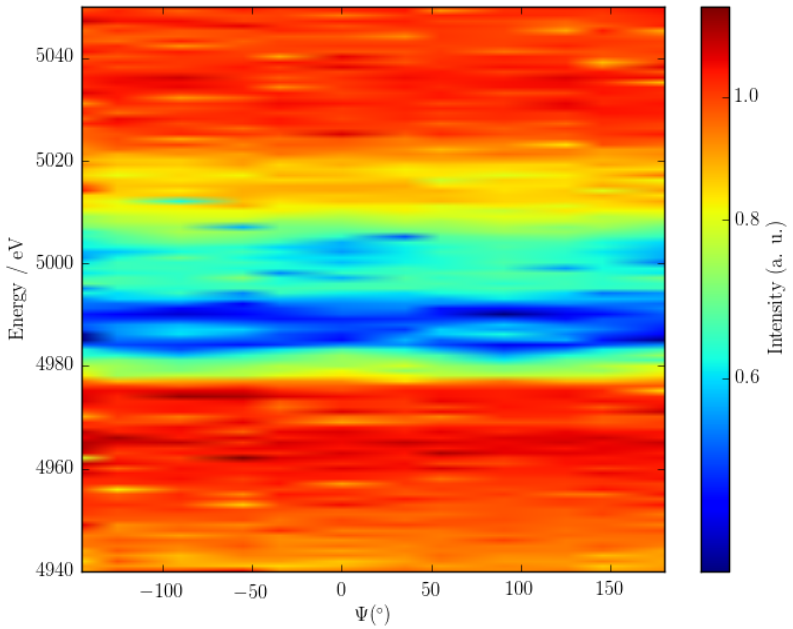
combined AAS / DAFS map



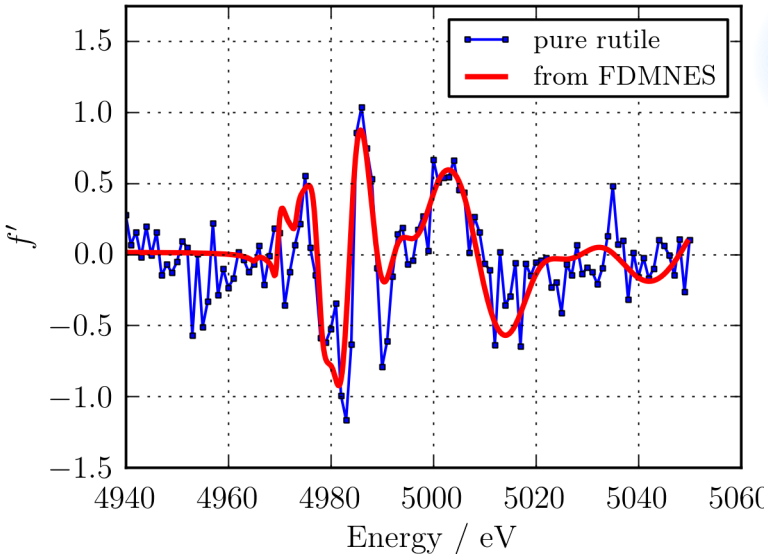
interference with constant oxygen background yields sign for f'_{12}

Measurement of Allowed reflection 111.

- f_{12}' compared with FDMNES calculations



combined AAS / DAFS map

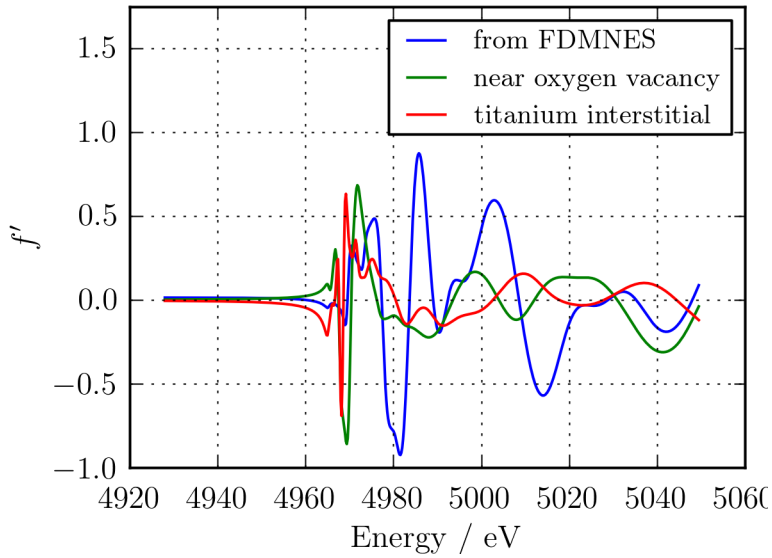


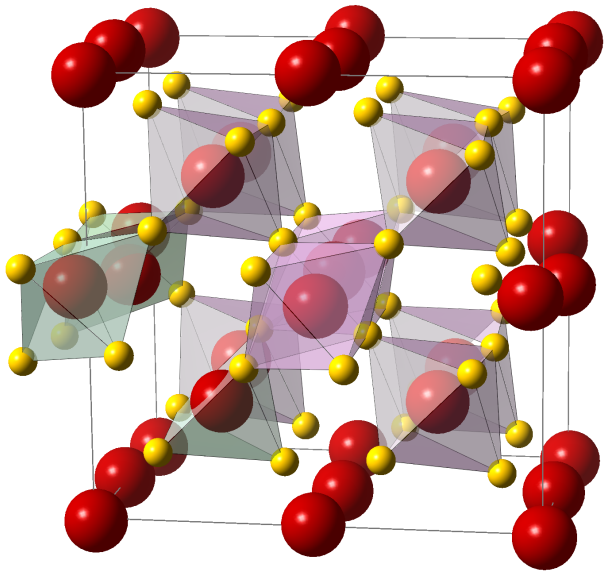
- excellent agreement with simulations

Influence of point defects.

- point defects, e.g. oxygen vacancies, strongly influence the resonant scatterers short range order and also the unoccupied electron states
  - local site symmetry can be broken[3]
  - Energy dependancy changes

  → first attempts to simulate different cases using FDMNES:





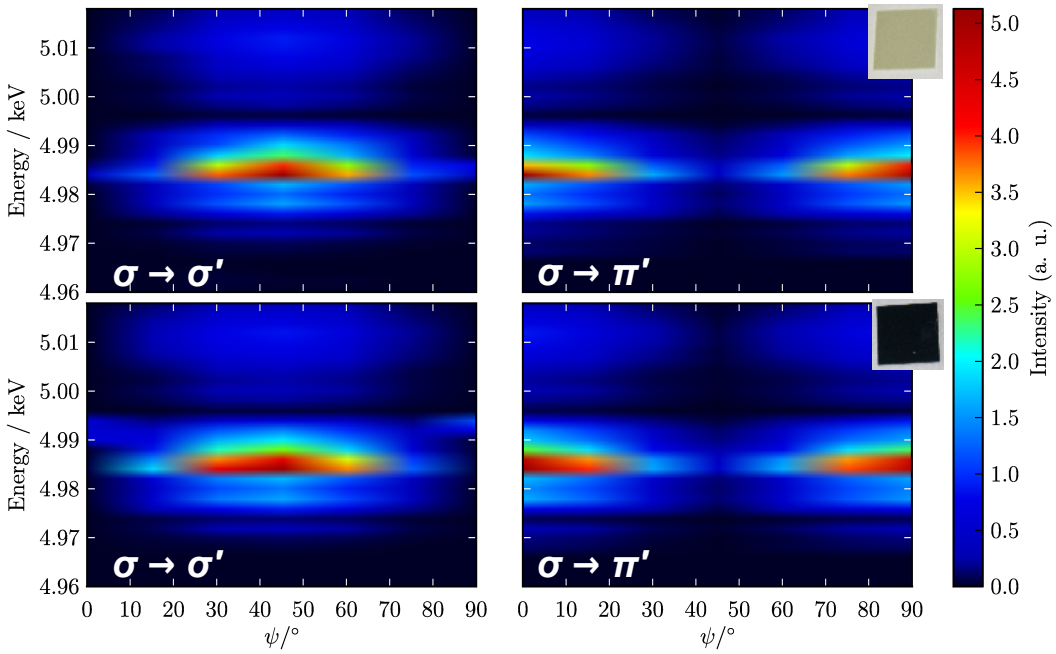
2x2x2 supercell with oxygen vacancy

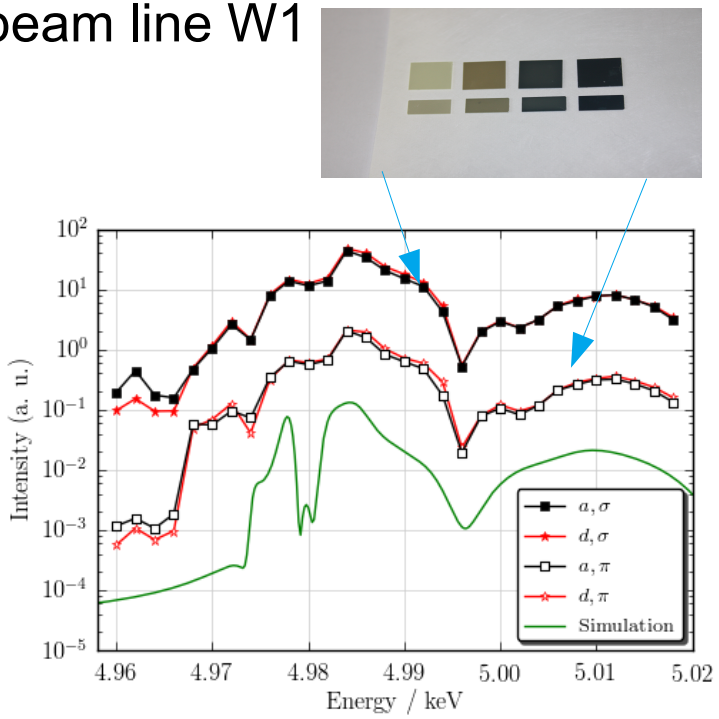
site symmetry strongly reduced near vacancy

[3] V.E. Dmitrienko, E.N. Ovchinnikova, *Acta Cryst.* **A56** (2000), 340-347

Forbidden reflection 001 for defect structure.

- Point defects introduced by heat treatment under high vacuum
- Polarization Resolved Measurements at beam line W1
- Comparison with untreated rutile



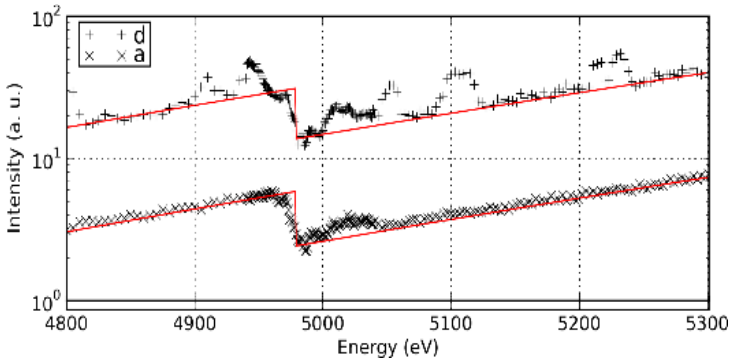


integrated DAFS spectra

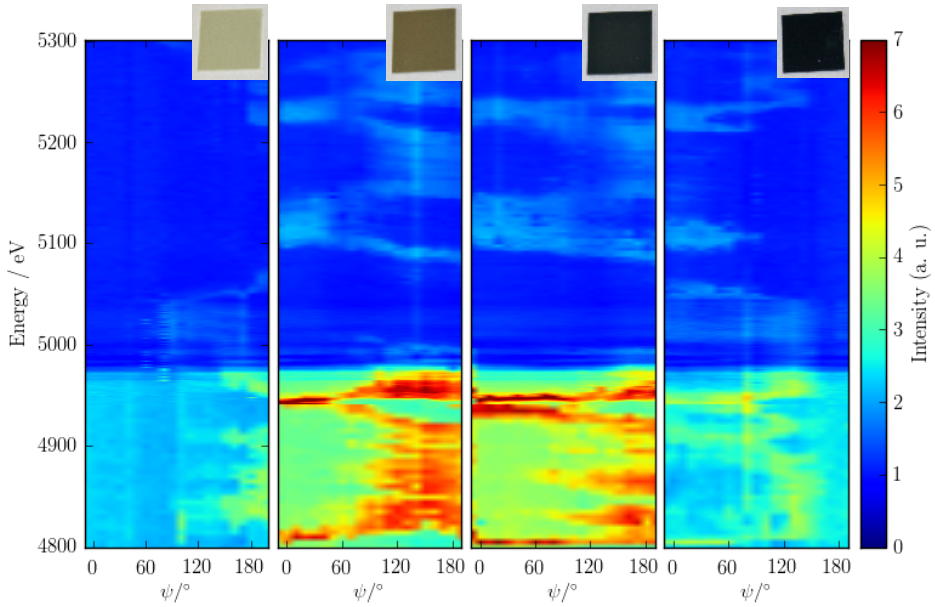
defects have no measurable effect on near edge anisotropy $|f_{12}|$

Allowed reflection 111 for defect structure.

- First data collected at DORIS beamline E2:
  - **new maxima** occur at extended energy range and in pre-edge region → depend on **energy** and **azimuth**
  - reproducible in later beam time
  - still problems with interpretation



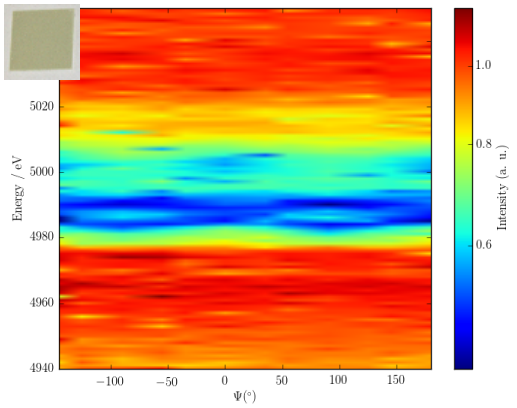
comparing DAFS curves



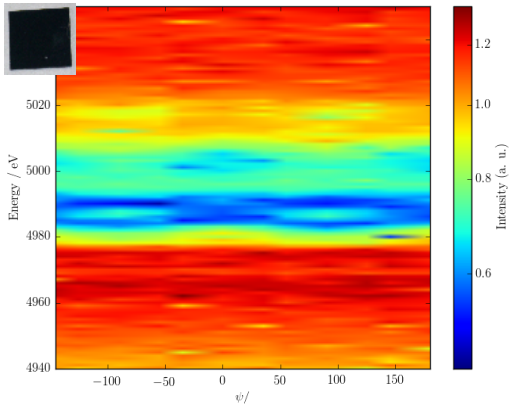
- probably no resonant scattering effects
- interpretations suggested by colleagues:
  parasitic signal from diffuse scattering

Allowed reflection 111 for defect structure.

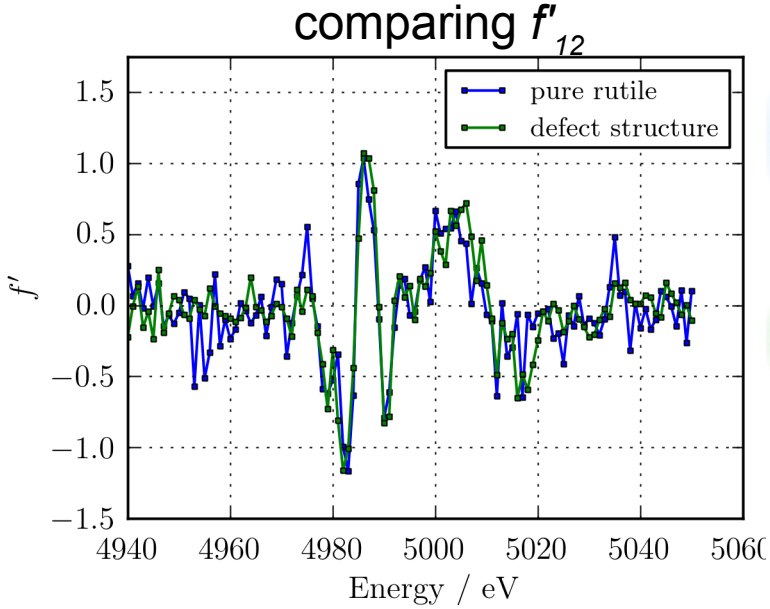
- Closer look by polarization resolved measurements at P09



pure rutile



defect structure



- no changes due to defects visible within the measurement accuracy

Conclusion / Outlook.

- pure rutile structure:
  - combined AAS and DAFS is a powerful method to obtain information about local site symmetry and short range order
  - partially forbidden reflections can be utilized to get full complex atomic scattering amplitudes

- defect structure:
  - Influence of point defects in present concentration not strong enough to be visible in the near edge spectra
  - however, an azimuthal and energy dependency has been observed in the 111 reflection of heat treated samples with high density of point defects
    → origin still has to be determined, maybe non resonant effects
  - **next step:** in-situ measurements with higher temperatures
    parallel monitoring of diffuse scattering
    (*as suggested by Prof. J.L. Hodeau and Prof. E.N. Ovchinnikova)*

Thank you for your attention.