Site-specific Valence-electronic Structure of $SrTiO_3$ Probed by Photoemission and X-ray Standing Waves

S. Thiess[1], T.-L. Lee[2], F. Bottin[3], B.C.C. Cowie[4], and J. Zegenhagen[5]

[1]HASYLAB, Hamburg, Germany [2]Diamond Light Source, Didcot, U.K. [3]CEA, Bruyères-le-Châtel, France
[4]Australian Synchrotron, Clayton, Australia [5]ESRF, Grenoble, France

ESRF

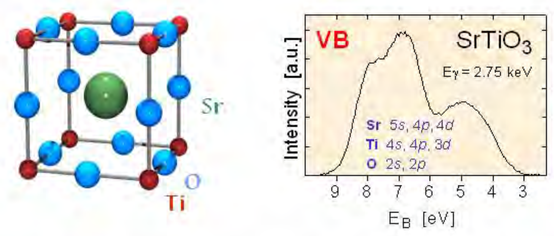
ID32

1. Motivation

Recently developed: Site-specific X-ray photoelectron spectroscopy (combination of XPS and the X-ray Standing Wave method)

- Goal: Identify the $SrTiO_3$ valence electronic contributions from the Sr, Ti, and O sites:

unit cell: XPS:



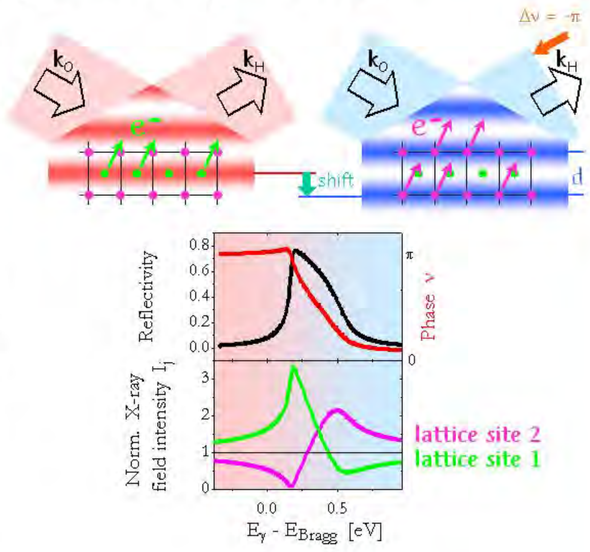
⇒ Verify theo. calculations of the partial DOS

⇒ Determine *a priori* unknown photoabsorption cross sections for valence electrons

2. X-ray Standing Waves

- Establish Bragg condition: Standing wave field generated by interference of incident (k_O) and Bragg-reflected (k_H) X-ray beam
- Traversing the Bragg reflection by increasing the photon energy E_γ, the phase shift $\Delta\nu = -\pi$ between the 2 beams causes the standing wave field to shift by d/2

⇒ Possibility to position the wave field arbitrarily with respect to the crystal lattice



3. Idea of the Measurement

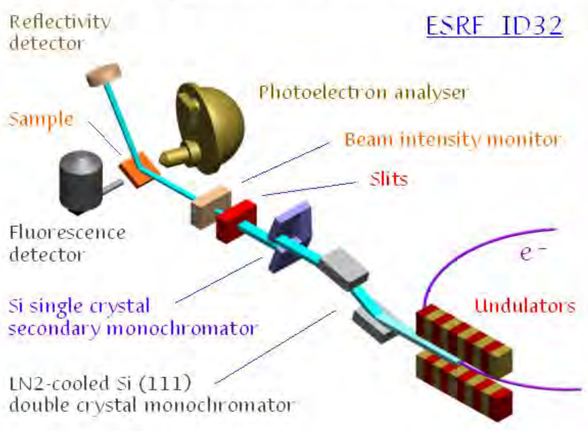
- Select photon energy E_γ to position the wave field in the unit cell such that photoelectrons are preferentially excited from atoms at lattice site j
  ⇒ valence yield contribution from site j increases
- Record VB spectra for n different wave field positions
  ⇒ each VB spectrum Y is a different linear combination of partial yields Y_j:

$$Y(E_B,E_\gamma) = \sum_j I_j(E_\gamma)\cdot Y_j(E_B)$$

total VB yield; X-ray field intensity at site j; partial VB yield excited from site j by X-ray beam of unity intensity

- Solve system of n linear equations
  ⇒ Result: valence yield contributions $Y_j(E_B)$ from lattice sites j = Sr, Ti, O

4. Experimental Setup



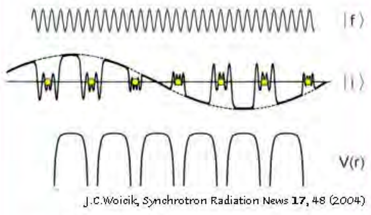
- 0.45 eV total energy resolution at E_γ = 3 keV

5. XPS on the VB

$$\frac{d\sigma}{d\Omega} \propto |M_{fi}|^2 \propto |\langle f\,|\,\hat{\varepsilon}\cdot\nabla V(r)\,|\,i\rangle|^2$$

classical force; in dipole approximation

- Photoexcitation only in regions where the overlap integral of the 3 functions |f(r)>, ∇V(r), and |i(r)> does not vanish:



⇒ No photoeffect for quasi-free electrons inbetween atomic cores

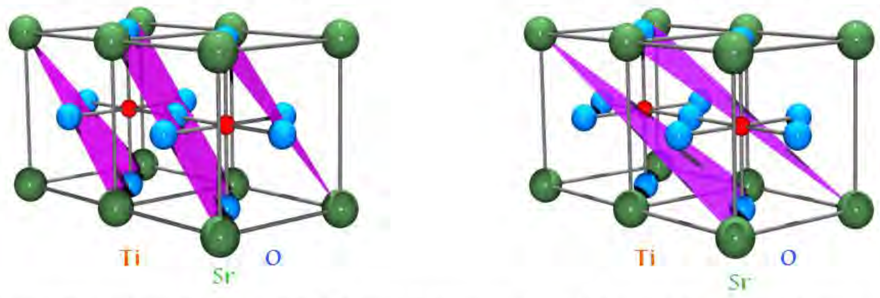
⇒ XPS spectra not representative of all valence charge

⇒ Inherent site-specificity of XPS

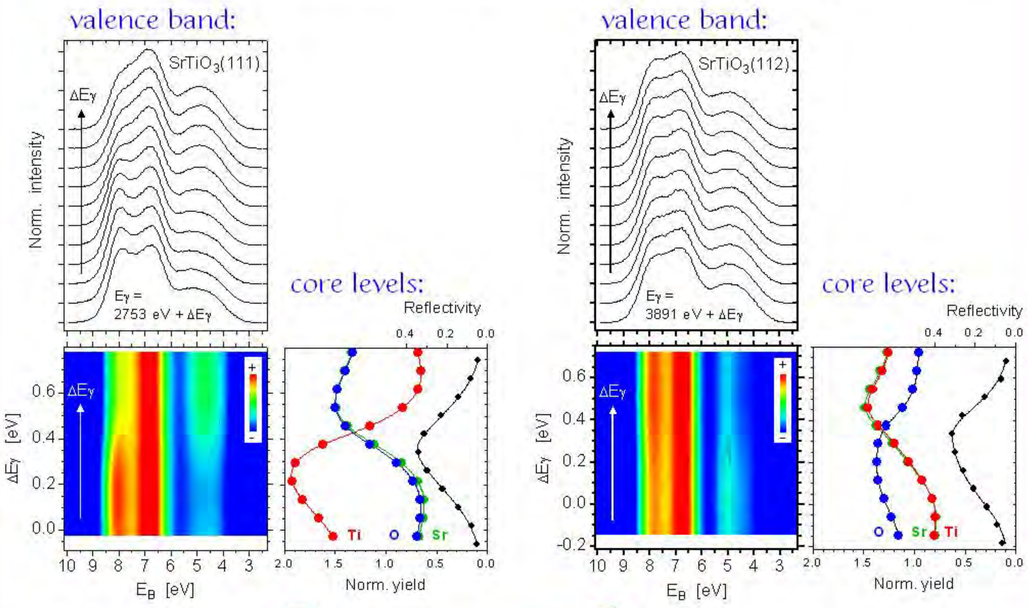
6. Site-specific VB Decomposition

- $SrTiO_3$(001) surface prepared by annealing at 930°C at p < 1×10⁻⁸ mbar for 3h
- Surface condition checked by XPS and LEED

STO(111) separates Y_{Ti} and Y_{SrO_3} STO(112) separates Y_{SrTi} and Y_{O_3}

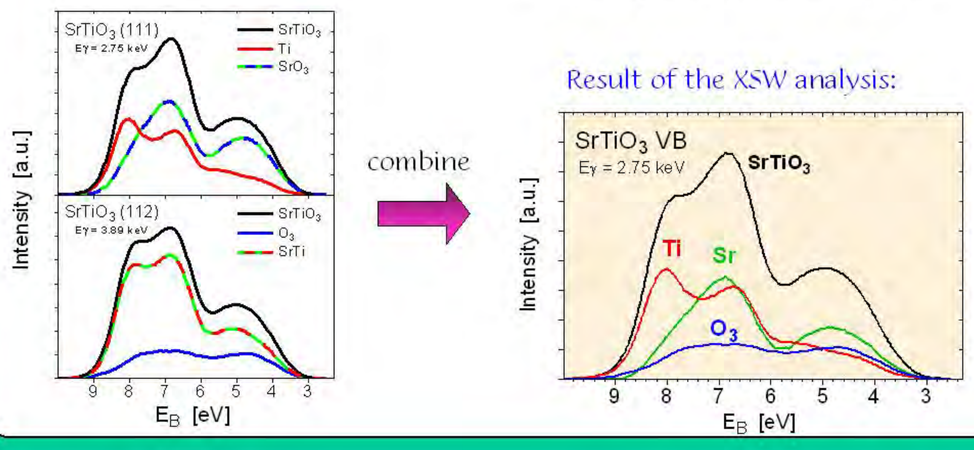


- XPS spectra recorded for 11 different X-ray standing wave field positions:



- VB decomposition:

- For each reflection: overdetermined system of 11 equations in 2 unknowns
- All XSW-specific information exploited



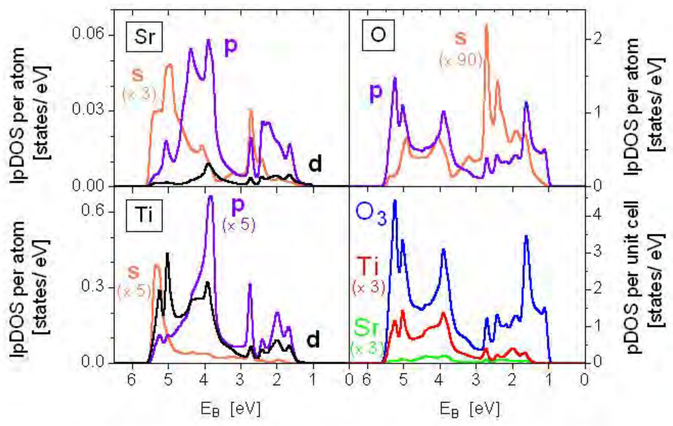
7. Angular-momentum Dependent VB Analysis

State-of-the-art DFT calculations:

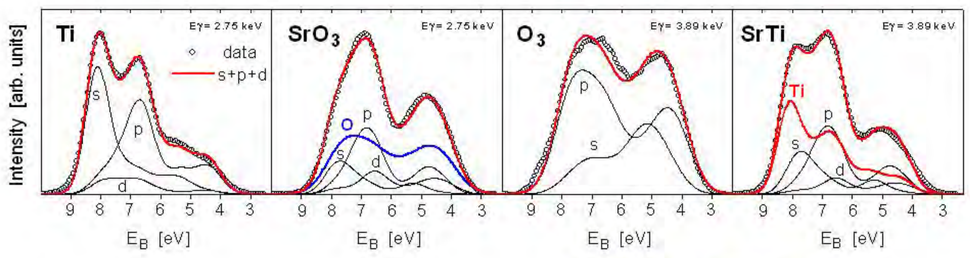
- Troullier-Martins pseudopotentials
- Local density approximation
- Plane-wave cutoff energy 140 Ry
- 6×6×6 Monkhorst-Pack *k*-point sampling scheme
- Projection over angular momentum within spheres of 1.2 atomic units radius for all elements

Comparison of calculations and data:

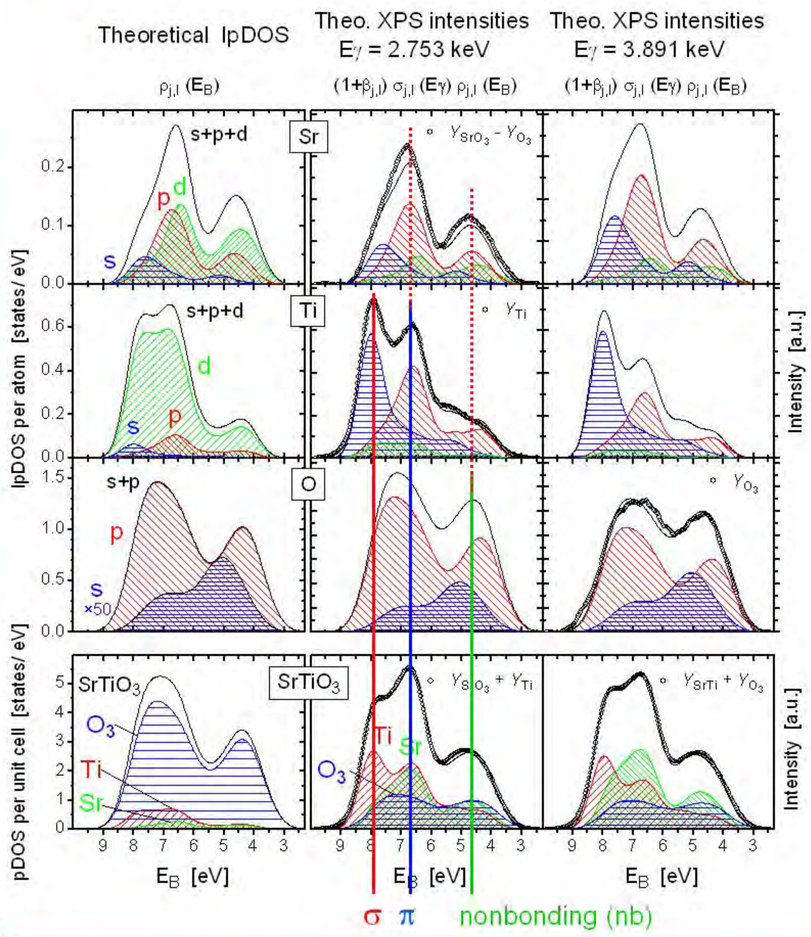
- 0.75 (Sr, Ti) and 1.3 eV (O) convolution (instrumental resolution, band bending, *final-state and/or correlation effects*); linear rescaling of energy axes
- Fit angular-momentum dependent partial density of states $\rho_{j,l}$ to the partial yield $Y_j(E_B) = \sum \sigma_{j,l}\cdot\rho_{j,l}(E_B)$ from site j = Sr, Ti, O by adjusting photoabsorption cross section $\sigma_{j,l}$



- Excellent agreement:

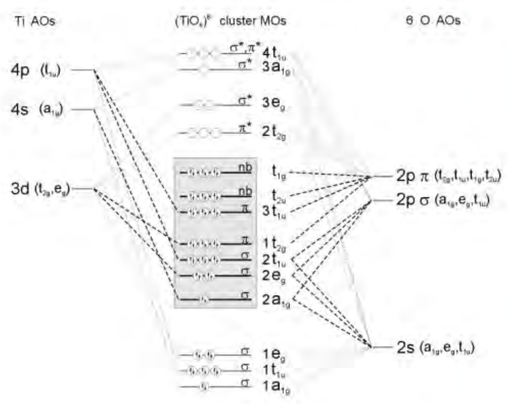


Summary:



Electronic structure:

- Sr: - Highly ionic
  - Competing Sr σ and Ti π interactions with O p_y and p_z (⊥ Ti-O-Ti bonds)
- Ti, O: σ and π bonding scheme within tight binding description:
  - Ti-O bonding partially covalent
  - Splitting (at $E_B \approx 5.5$ eV) into bonding and nonbonding sub-bands
  - Ti character: bonding sub-band only



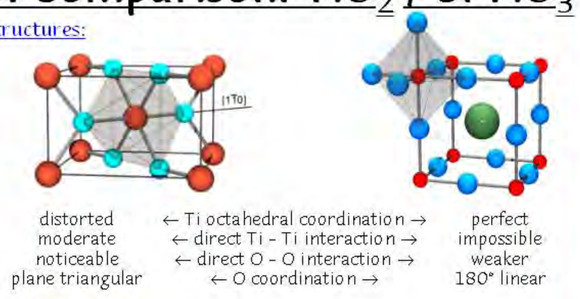
- DOS: Predominantly O p + Ti d states

⇔

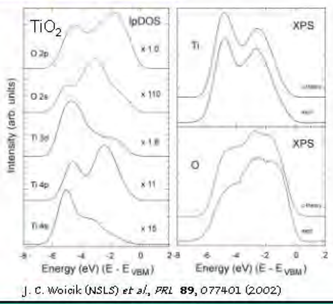
XPS: - O p + Ti d states underrepresented
- Sr component exists and is magnified by a large cross section

8. Comparison: TiO_2 / $SrTiO_3$

Structures:



Electronic structures:



J. C. Woicik (NSLS) et al., PRL 89, 077401 (2002)

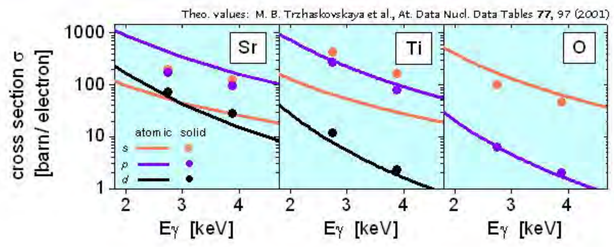
Compared to $SrTiO_3$,

- the distinction of bonding and nonbonding sub-bands is blurred for TiO_2
- the distinction of σ and π bonding oxygen bands is blurred for TiO_2 due to O sp^2 hybridization

9. Photoabsorption Cross Sections

- Theoretical photoabsorption cross sections exist mainly for the free atom
- Tabulated values widely lack experimental confirmation
- Tabulated values valid for atoms in the solid ?

Comparison: free atom ⇔ solid state:



- Cross section of metal *s* states are much larger in the solid than for the corresponding atomic state.