

data indicated that both the FM and the AFM domains have constant vertical size being equal to the layer thickness obtained from the X-ray reflectivity. At room temperature, the FM volume (although very small) is spread from the very bottom to the top of the thin layer, probably in the form of thin columns laterally distributed in the layer. Just these columns could be the seeds for the emerging FM phase during the heating.

1. Zakharov, A. (1964). *Soviet Physics JETP*, 46(6), 2003–2010.

- Lu, W., Huang, P., Chen, Z., He, C., Wang, Y., & Yan, B. (2012). *Journal of Physics D: Applied Physics*, **45**, 435001.
- Baldasseroni, C., Pálsson, G. K., Bordel, C., Valencia, S., Unal, a. a., Kronast, F., ... Hellman, F. (2014). *Journal of Applied Physics*, **115**, 043919

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Session X

Wednesday, September 7 - afternoon

I10

HIGH RESOLUTION X-RAY SPECTROSCOPY OF ELECTRONIC AND ATOMIC STRUCTURE OF TiO₂ NANOSTRUCTURES AND CHARGE TRANSFER PROCESSES

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Refined X-ray spectroscopy can play a key role in understanding the fundamental mechanisms responsible for the physical and chemical properties of advanced functional materials and devices. In this contribution, we will focus on TiO₂ – based nanostructures, which are actively studied for many applications, including photocatalysis. Despite many potential advantages, one limitation of TiO₂ is the wide

band gap, which limits solar light absorption. By using high resolution X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) we have recently studied the atomic and electronic structure of two materials systems designed to overcome this limitation: nanostructures formed by close assembly of Au and TiO₂ nanoparticles [1] and V-doped TiO₂ [2].

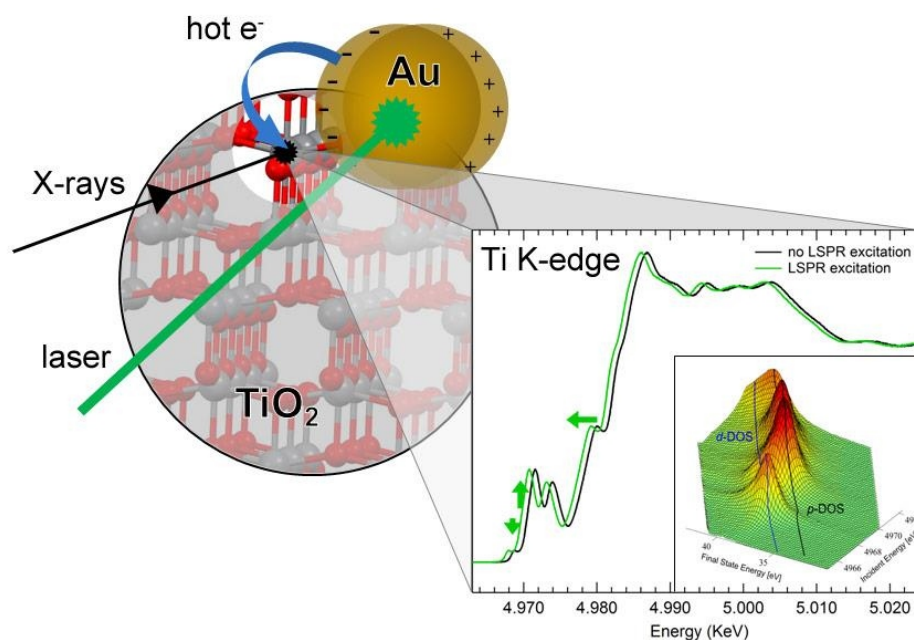


Figure 1: Graphical description of the experiment on Au:TiO₂ and of hot electron charge transfer. The inset reports the effect of laser illumination on high resolution XAS spectra and a typical RIXS plane.



Exploiting plasmonic Au nanoparticles to sensitize TiO₂ to visible light is a widely employed route to produce efficient photocatalysts. However, a description of the atomic and electronic structure of the semiconductor sites in which charges are injected is still not available. Such a description is of great importance in understanding the underlying physical mechanisms and to improve the design of catalysts with enhanced photoactivity. We investigated changes in the local electronic structure of Ti in pure and N-doped nanostructured TiO₂ loaded with Au nanoparticles during continuous selective excitation of the Au localized surface plasmon resonance with XAS and RIXS. Spectral variations strongly support the presence of long-lived charges localized on Ti states at the semiconductor surface, giving rise to new laser-induced low coordinated Ti sites.

Doping with transition metals is an effective method to enhance visible-light absorption in TiO₂ nanoparticles and to improve the efficiency of many photocatalytic processes

under solar radiation. We have performed an in-depth XAS study of V dopants in TiO₂ nanoparticles deposited by gas-phase condensation with a local structure similar to anatase, rutile, or intermediate. The combination of K- and L-edge spectra in the pre-edge, edge, and extended energy regions with full potential ab initio spectral simulations shows that V ions occupy substitutional cationic sites in the TiO₂ structure, irrespective of whether it is similar to rutile, anatase, or mixed. Very recently we have also performed.

RIXS measurements which highlight changes in the occupation of electronic states localized on Ti and V induced by visible light absorption.

1. L. Amidani, A. Naldoni, M. Malvestuto, M. Marelli, P. Glatzel, V. Dal Santo, and F. Boscherini, *Angew. Chem. Internat. Ed.* **54**, 5413–5416 (2015). DOI: 10.1002/anie.201412030.
2. G. Rossi, M. Calizzi, V. Di Cintio, S. Magkos, L. Amidani, L. Pasquini, and F. Boscherini, *Jour. Phys. Chem. C* **120**, 7457 (2015). DOI: 10.1021/acs.jpcc.5b12045.

C31

DYNAMIC X-RAY DIFFRACTION IN AMINO ACID CRYSTALS: A STEP TOWARDS IMPROVING STRUCTURAL RESOLUTION OF BIOLOGICAL MOLECULES VIA PHYSICAL PHASE MEASUREMENTS

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From inorganic crystals to protein crystals, structure determination with atomic resolution is mostly based on diffraction techniques (electrons, X-rays, and neutrons). However, since the coherent scattering cross-section for X-ray by atoms have intermediate values between those for electrons and neutrons, experimental measurements of structure factor phases have been successfully carried out

with X-rays [1]. Dynamical diffraction taking place within perfect domains is another requirement for physical phase measurements via multi-beam diffraction experiments. In crystals with small unit cells, dynamical diffraction regime is achieved in much smaller domains than in crystals with large cells such as protein crystals. Fact that has allowed phase measurements to reveal structural details-inaccessi-

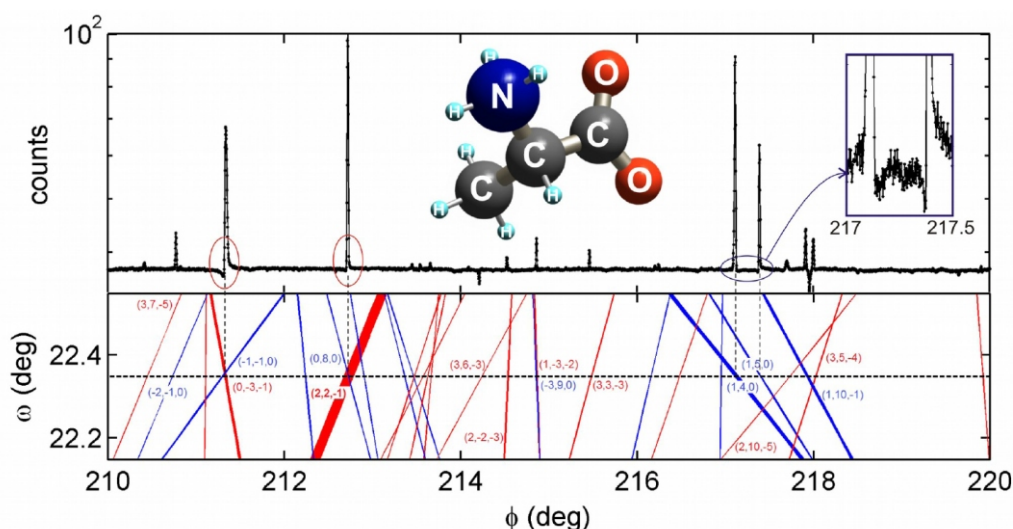


Figure 1. Dynamical diffraction in amino acid crystal giving rise to asymmetric peak profiles of multi-beam cases. Base line intensity (top panel) is from 261 reflection (dashed Bragg-cone line, bottom panel).

ble by other techniques—of optical crystals with dopant ions [1,2], as well as to solve chirality in crystals with no resonant atoms [3]. Differently from any other method in X-ray crystallography based on structure refinement of intensity data, phase measurements pinpoint a specific feature of the structure and directly prove its existence beyond of any reliability parameter or goodness-of-fitting values. In this work, we first present a simple approach to the graphic indexing of appropriate cases for phase measurements, e.g. Fig. 1 (bottom panel), which is also very useful for other diffraction techniques in semiconductor devices and single crystals in general [4,5]. Then, we present diffraction data in single crystals of D-alanine carried out at two synchrotron facilities and with different instrumentation (flux, optics, and goniometry). Model structures taking into account ionic charges of hydrogen atoms are proposed and compared to experimental data, leading to an ideal model to describe X-ray diffraction by this simple amino acid molecule in terms of invariant phase triplets. Moreover, dynamical diffraction calculation of critical domain size (perfect crystal lattice) for phase measurements in large molecule crys-

tals, how to plan an experiment in non-perfect crystals, sensitivity to detect hydrogen atoms, and other applications are discussed.

1. Z. G. Amirkhanyan, C. M. R. Remédios, Y. P. Mascarenhas, S. L. Morelhão. *J. Appl. Cryst.* **47**, (2014), 160.
2. S. L. Morelhão, C. M. R. Remédios, R. O. Freitas, A. O. dos Santos. *J. Appl. Cryst.* **44**, (2011), 93.
3. S. L. Morelhão, Z. G. Amirkhanyan, C. M. R. Remédios. *Acta Cryst.* **A71**, (2015), 291.
4. J. Z. Domagała, S. L. Morelhão, M. Sarzyński, M. Maździarz, P. Dłużewski, M. Leszczyński. *J. Appl. Cryst.* **49**, (2016).
5. A. G. A. Nisbet, G. Beutier, F. Fabrizi, B. Moser, S. P. Collins. *Acta Cryst.* **A71**, (2015), 20.

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C32

REVERSIBLE DISCRETE MONOLAYERS OF C8-BTBT-C8 MOLECULES ON SILICON OXIDE SURFACES AS A RESULT OF THERMODYNAMIC EQUILIBRIUM

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During the last years, the molecule dioctyl-benzothienobenzothiophene (C8-BTBT-C8) has attracted large attention, since thin film transistors based on this organic semiconductor show outstanding device performance. The high quality of C8-BTBT-C8 films may be one of the key features for this successful application. The presence of a liquid crystalline smectic state at elevated temperatures to-

gether with a crystalline state at low temperatures allows for special film preparation methods resulting in high structural perfectness. Films in the monolayer (thin films) and in the multilayer regime (thick films) are accessed by spin coating, a method known to work far from thermodynamic equilibrium. Heat treatment of such films results in strong islanding (for thick films). The structure of these or-

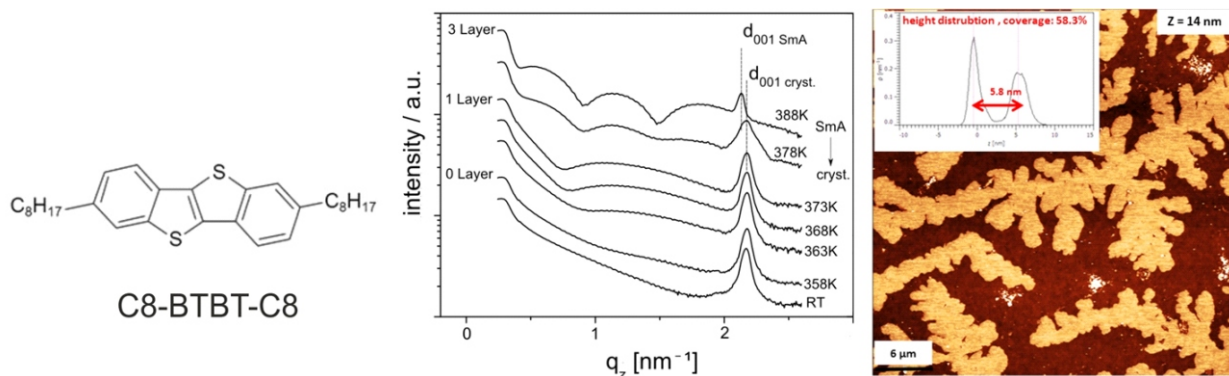


Figure 1. Chemical structure of the molecule C8-BTBT (left), in-situ X-ray reflectivity at decreasing temperature of a multilayer film crossing the phase transition temperature from the smectic A phase to the crystalline state (middle) and an atomic force microscopy image of a bilayer film with the height distribution image as an inset (right).



ganic films is investigated by temperature dependent in-situ methods using atomic force microscopy, X-ray reflectivity and grazing incidence X-ray diffraction. Already at temperatures few degrees below the phase transition from the crystalline state to the smectic A state ($T = 381.5$ K) the formation of a single monolayer is observed (for thin films). The molecular rearrangement is slow and it takes 30 minutes until the monolayer formation is completed. In case of thick films, an increase of the temperature induces discrete monolayer formation whereby bi-layer, triple-layer, ... up to 5-monolayer structures form. The re-

versibility of the discrete layer formation strongly indicate that thermodynamic equilibrium states are the reason for this behaviour. Using rapid cooling, also non-equilibrium structures can be observed and are stabilised by the substrate surface. Explanation of these observations are given in terms of classical film formation models involving surface energy differences of the silicon oxide surfaces and the C8-BTBT-C8 molecules whereby the later changes concretely on temperature variation.

C33

UNCOVERING THREE-DIMENSIONAL GRADIENTS IN FIBRILLAR ORIENTATION IN AN IMPACT-RESISTANT BIOLOGICAL ARMOUR

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The architecture of the mineralized cuticle of arthropods like the mantis shrimp (stomatopod) may serve as examples of natural structural materials for bioinspired materials design [1-4]. The stomatopod telson is a defensive shield at the tail of the animal, used to resist blows during intra-species fights [2]. As such, it requires strong impact resistance, to resist the high loading rate blows inflicted by the dactyl club of other stomatopods [1, 4] without damage to structural integrity, and its architecture will provide insight into, for example, design of new armour materials. At the molecular- and supramolecular level, cuticle comprises a fibrous composite of chitin fibrils, calcium carbonate mineral and proteins [3, 5]. However the architecture and functional gradients in this composite at the meso- and microscale, including in fibril and mineral composition, are less investigated. The extraction of 3D orientation distributions of mineralized fibril as well as the quantitative information is technically challenging due to the anisotropic feature inside telson and the presence of both in-plane and out plane fibres. Here, we report the three-dimensional chitin-fibril orientation across the central carinae of the stomatopod telson and tergite, using a combination of microfocuss synchrotron wide-angle X-ray diffraction (WAXD) together with a model for localized three-dimensional diffraction reconstruction. We identify two separate families of in-plane and out-plane fibrils, corresponding to

the fibres in the lamellae and perpendicular pore-canals running through the cuticle. The 3D orientation of these two different fibril families and their quantitative ratios are mapped across the telson cuticle. We find gradients in fibril orientation in both groups and that the relative amounts of the two fibrils varies across the telson cross-section. Higher proportions of out-plane fibrils in the centre of the telson are identified, which may enable higher resistance to impact loads during natural use. We propose a simple two-phase fibre-buckling model to understand how the telson resists high-impact loading. Further, the 3D fibrillar orientation extraction methodology presented here can be applied to a range of other graded microtextured fibre composites to provide insights into structure-function correlations at multiple hierarchical levels.

1. J. C. Weaver et al, *Science* **336**:127-1279 (2012) .
2. J.R.A. Taylor and S.N. Patek, *J. Exp. Biol.*, **213**: 3496-3504 (2010).
3. A. C. Neville, *Biology of the Arthropod Cuticle*, Berlin: Springer (1975).
4. S. Amini et al, *Nat Mater*, advance online publication (2015).
5. C. Sachs et al, *J Mater Res* **21** (8), 1987-1995 (2006)