

Monday Evening, December 12, 2022

Charles S. Fadley Memorial Session

Room Naupaka Salon 4 - Session CF-MoE1

Charles S. Fadley Memorial Session I: Advances in X-ray Spectroscopy and Analysis

Moderators: Gregory S. Herman, Oregon State University, Boris Sinkovic, University of Connecticut

5:40pm **CF-MoE1-1 Pursuing Chuck Fadley's Ideas a Scientific Lifetime: Photoelectron Recording with Maximum Parallelization, Gerd Schönhense**, Institut für Physik, Johannes Gutenberg-Universität, Germany
INVITED

In 1988-89 the author had the great pleasure of doing postdoctoral work in the Fadley group. Experiencing the impressive work with an electron spectrometer with a multi-channel detector (VG ESCALAB5) [1] initiated decades of thinking about a further parallelization of photoelectron recording techniques. Today we find powerful implementations that extrapolate those early ideas that have resulted in orders of magnitude increased recording efficiency.

Thanks to the excellent time structure of modern photon sources such as lasers, HHG sources, Synchrotrons and FELs, time-of-flight (ToF) detectors can record a wide energy band in parallel. Additional full-field imaging of (k_x, k_y) momentum patterns has led to a novel ARPES technique, termed ToF momentum microscopy (ToF-MM). A fast delay-line detector records (x,y) position and ToF for each electron with count rates up to 8×10^6 cps. ToF-MM enabled new types of experiments, such as fast tomographic-like Fermi surface and -velocity mapping [2].

The developments had a dramatic impact on experiments with very low signal intensities. In particular, spin-resolved experiments suffer from the low figure-of-merit of spin detectors. Significant advances have been made with the advent of multichannel spin recording [3]. Bulk-sensitive photoemission using hard X-ray excitation suffers from low cross sections and enhanced phonon scattering. The ToF-MM approach was extended to energies >7 keV and an order of magnitude higher (E_B, k_x, k_y) phase-space acceptance. This led to new types of (H)ARPES [4] and X-ray photoelectron diffraction (XPD) experiments [5]. The large k-field-of-view provides 4D bulk spectral functions $\rho(E_B, \mathbf{k})$ in a single measurement without scanning the photon energy.

In fs time-resolved photoemission (tr-ARPES), weak signals of transient excited states are recorded with high efficiency, both for FELs [6] and HHG sources [7]. In parallel to the tracking of the electronic structure, rapid changes in the geometric structure can be observed using tr-XPD. Resolving the intrinsic time scale of ultrafast processes and further parameters like pump-laser fluence coined the term "multidimensional photoemission" for such experiments. For further reading, see current reviews [4,5,7].

[1] J. Osterwalder, C. S. Fadley et al., *J. Electron Spectrosc. Relat. Phenom.* **48**, 55 (1989); [2] K. Medjanik et al., *Nat. Mat.* **16**, 615 (2017) and *J. Synchr. Rad.* **26**, 1996 (2019); [3] M. Kolbe et al., *Phys. Rev. Lett.* **107**, 207601 (2012); [4] G. Schönhense, H.-J. Elmers, *J. Vac. Sci. Techn.* **A 40**, 020802 (2022); [5] O. Fedchenko et al., *J. Phys. Soc. Jpn.* **91**, 091006 (2022); [6] F. Pressacco et al., *Nat. Commun.* **12**, 5088 (2021); [7] O. Karni, I. Esin, K. M. Dani, *Advanced Materials* (2022), doi:10.1002/adma.202204120in print.

6:20pm **CF-MoE1-3 The State of Interpretation for Multiplet Splitting and Shake-Up Satellites in Transition Metal Compound XPS: Fe₂O₃ and NiO, Christopher R. Brundle**, C. R. Brundle and Associates; *B. Crist*, XPS Library; *P. Bagus*, University of North Texas

We discuss the understanding of multiplet splitting and shake-up satellite structure for transition metal compounds. Chuck Fadley was an early pioneer for the former (1).

Gupta and Sen (2) expanded atomic multiplet splitting theory to include spin orbit coupling, providing predictions for the 2p XPS splitting features for TM cations. Such calculations do not include ligand-field or bonding effects in solids. Later semi-empirical approaches attempted to include such effects by scaling parameters and by invoking a charge transfer model to describe shake-up satellites. A free program, CTM4XAS (3), incorporates all this to simulate the cation 2p XPS spectrum.

Though CTM4XAS may roughly describe the BE spread in the cation 2p XPS, it completely disagrees with the description obtained from our full ab initio cluster calculations (Fe₂O₃ and NiO) of the electronic characteristics of the major features. The strong experimental satellite intensity for the Fe2p spectrum of Fe₂O₃ and other high spin Fe(III) compounds, at ~8.5 eV, has long been assigned to shake-up; and has been used to verify the presence of Fe(III) (4). Similarly, in the Ni2p spectrum of NiO, the satellite at ~6.5eV is

used to verify the presence of Ni(II). Our calculations confirm that these satellites do have a large amount of shake character, and that the leading edge of the "main" peak (lowest BE) is essentially "normal", ie it has no shake involvement (5, 6). CTM4XAS reverses these assignments, claiming that main peak is a shake state (charge transfer in their parlance) and the intense satellite represents the "normal" transition. Furthermore, our calculations show that once shake excitation is included, the intensity distribution of all structure in the 2p spectrum is highly modified, and there is no region, except the leading edge of the main 2p_{3/2} peak, that is 100% "normal" (5). Everywhere else there is significant mixing of "normal" and shake. We expect this mixing to hold for other TM compounds.

References

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5. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, N. Lahiri, and K. M. Rosso, *Phys. Chem. Chem. Phys.*, 2022, **24**, 4562-4575.
6. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, E. S. Ilton, N. Lahiri, and K. M. Rosso, *Inorganic Chemistry* in press.

6:40pm **CF-MoE1-4 Zinc and Cadmium: Chemical State Determination Through XPS Analyses of Standard Samples, Jeffrey D. Henderson, S. Buchanan, L. Grey, M. Biesinger**, Surface Science Western, Canada

Zinc, cadmium, and their related compounds have a myriad of applications, including, but not limited to, automotive manufacturing, batteries, photovoltaic devices, corrosion protection, and pigments. From a research perspective, the ability to accurately speciate different compounds is critical to understanding how surface chemistry can influence material properties. This ability allows for the advancement of our mechanistic understanding. It has been repeatedly demonstrated that X-ray photoelectron spectroscopy (XPS) is a powerful analytical tool for the study of changes in surface chemistry. Typically, speciation is achieved through the careful analysis of photoelectrons, and occasionally, Auger electrons. Since the main photoelectron binding energies of many zinc and cadmium compounds overlap, the modified Auger parameter must also be utilized to reliably detect chemical shifts. While the binding energies and Auger parameter data can be found in the literature for some zinc and cadmium compounds, in most cases, the available data lacks consistency, certainty, and reproducibility. Notably, Auger parameter data is often underreported in the existing literature, despite its proven utility. Additionally, many of these sources do not provide the variety of compounds needed to perform accurate chemical state analyses.

In this presentation, recent work to extend upon previously published XPS reference data and curve-fitting procedures will be detailed for a wide range of high-purity zinc- and cadmium-containing compounds. This will include a summary of literature data, carefully excluding those which contain issues related to reliability. Lastly, the applicability of peak fitting Auger lines will be explored for the analyses of mixed species systems.

7:00pm **CF-MoE1-5 X-Ray Spectroscopic Identification of Strain and Structure-Based Resonances in a Series of Saturated Carbon-Cage Molecules: Adamantane, Twistane, Octahedrane, and Cubane, Trevor Willey, J. Lee**, Lawrence Livermore National Laboratory; *D. Brehmer, O. Paredes Mellone*, SLAC National Accelerator Laboratory; *L. Landt*, Lawrence Livermore National Laboratory; *P. Schriener, A. Fokin, B. Tkachenko*, Institute of Organic Chemistry, Justus Liebig University, Germany; *A. de Meijere, S. Kozhushkov*, Institute for Organic and Biomolecular Chemistry, Georg-August-University, Germany; *T. van Buuren*, Lawrence Livermore National Laboratory

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. Along with chemical functionalization, geometrical constraints (such as extreme curvature in nanotubes, or defects within or at the surfaces of diamond nanoparticles) significantly alter the electronic states of the nanocarbon material. Understanding the effects of steric strain on electronic structure is critical to developing nanoelectronic applications based on these materials. This paper presents a fundamental study of how strain affects electronic structure in a benchmark series of some

Monday Evening, December 12, 2022

fundamental saturated carbon cage compounds. Adamantane, C₁₀H₁₆, the smallest diamondoid, and arguably the smallest nanodiamond crystallite, has carbon atoms essentially commensurate with diamond lattice positions and possesses by far the least bond strain of this series. Twistane also is a C₁₀H₁₆ isomer but the fixed cyclohexane twist conformation of the central ring introduces some strain into the cage. Octahedrane, (CH)₁₂, and cubane, (CH)₈, are considerably much more strained, culminating in cubane where carbon-carbon bonds lie either parallel, or orthogonal to one another. Using gas-phase near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to probe the unoccupied electronic states, we observe two major progressions across this series. First, a broad C-C σ^* resonance in the absorption splits into two more narrow and intense resonances with increasing strain. Second, the first manifold of states previously associated with tertiary C-H σ^* in the diamondoid series appears to broaden and shift to lower energy. This feature is more than twice as intense in cubane as in octahedrane, even though these two molecules have only tertiary carbons, with chemical formula (CH)_x. The spectral differences are entirely due to the shape of the molecules; in particular, in cubane, the features arise from a high degree of p-p interaction between parallel C-C bonds. In contrast to the conventional wisdom that near-edge X-ray absorption is primarily an atomically localized spectroscopy, molecular shape and associated bond strain lead to the dominant features in spectra acquired from this fundamental series of carbon cage structures.

Charles S. Fadley Memorial Session Room Naupaka Salon 4 - Session CF-MoE2

Charles S. Fadley Memorial Session II: Ambient-Pressure X-ray Photoelectron Spectroscopy

Moderators: Christopher R. Brundle, C.R. Brundle and Associates, Alexander Gray, Temple University

7:40pm CF-MoE2-7 **Catching a Wave: From Quantum Materials to Liquid Chemistry**, Slavomir Nemsak, Lawrence Berkeley National Laboratory, USA
INVITED

Standing-wave photoelectron spectroscopy of multi-layer structures, as pioneered by Prof. Chuck Fadley and his group in the past two decades, proved to be a very powerful technique for probing solid/solid, but also solid/liquid and solid/gas interfaces. Its superior depth selectivity and non-destructive nature were crucial to answer key questions in problems spread over several scientific fields, such as emergent phenomena at complex oxide interfaces [1], artificial multiferroics [2], adsorption mechanisms in liquids [3], corrosion [4], and electrocatalysis [5]. These achievements were only possible thanks to innovative approaches both in experiments and analyses, including development of X-ray optical simulations package [6] and its coupling with the black-box optimizer [7]. In this talk I will introduce these tools and highlight their applications to answer diverse scientific problems.

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- [5] C. Baeumer et al., *Nature Materials* **20**, 674 (2021).
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8:20pm CF-MoE2-9 **High Pressure Hard X-ray XPS Studies of Operando Catalytic Reactions for CO₂ and N₂ Reduction**, Anders Nilsson, Stockholm University, Sweden

Charles Fadley was a pioneer in the field of x-ray photoelectron spectroscopy (XPS) for over 5 decades and I had the pleasure to interact with him frequently since my time at Uppsala University in the 1980s. In the last part of his scientific life he brought forward hard x-ray XPS as an important tool to investigate interfaces. In the following contribution, I would like to honor him with a new direction of hard x-ray XPS that can play an important role for the development of a sustainable society to address climate change and in particular to mitigate CO₂ emissions.

Some of the most essential catalytic reactions for our energy society is to reduce CO₂ to hydrocarbons and alcohols to be used as fuels and base chemicals for the chemical industry. In order to convert a fossil dependent chemical industry and instead use sustainable hydrogen as a feedstock we

need to develop new catalysts. Furthermore, the catalytic reduction of N₂ to ammonia has been considered as one of the most important discoveries during the 20th century to produce fertilizers for a growing population. Despite an enormous effort in studying these catalytic reactions we are still lacking experimental information about the chemical state of the catalytic surface and the adsorbates existing as the reaction is turning over.

X-ray photoelectron spectroscopy (XPS) is a powerful surface sensitive technique that can provide almost all essential chemical information and it has been developed to operate also in a few mbar of pressure with great success for probing oxidation catalytic reactions. Unfortunately, this pressure regime is too low for the hydrogenation reactions to turn over. However, utilizing the hard x-ray XPS technique can bring the pressure up by many orders of magnitude in a unique instrumentation¹.

Here I will present how Fischer-Tropsch, methanol and ammonia synthesis reactions on single crystal metal surfaces have been probed during operando conditions in the pressure range 100 mbar-1 bar using the new XPS system built at Stockholm University¹ and permanently located at the PETRA III synchrotron in Hamburg. The instrument can vary the incidence angle of the X-rays allowing it to be either surface or bulk sensitive.

¹P. Amann, D. Degerman, M. T. Lee, J. D. Alexander, M. Shipilin, H. Y. Wang, F. Cavalca, M. Weston, J. Gladh, M. Blom, M. Björkhage, P. Löfgren, C. Schlueter, P. Loemker, K. Ederer, W. Drube, H. Noei, J. Zehetner, H. Wentzel, J. Ålund and A. Nilsson, *Rev. Sci. Instrum.* **90**, 103102 (2019).

8:40pm CF-MoE2-10 **Initial Oxidation of Ternary Amorphous Metal Alloy Surfaces Under Ambient Oxygen Pressures**, Gregory Herman, Oregon State University; P. Alzaga, HP Inc.; T. Diulus, R. Addou, Oregon State University; W. Stickle, HP Inc.; J. Jenkins, R. Elzein, Oregon State University

The oxidation of complex alloys is governed by both thermodynamics and kinetics. The formation of a surface oxide influences a range of surface properties, including catalysis, corrosion resistance, tribology, and others. Further, the structure of ternary alloys can influence oxidation properties, where grain boundaries in polycrystalline samples can provide fast diffusional pathways for oxygen or metal ions/atoms. Amorphous metal thin films (AMTFs) do not have grain boundaries and as a result can have both unique mechanical properties and chemical stability. AMTFs are typically structurally unstable at high temperatures, where they are found to crystallize. Recent studies have developed AMTFs with high thermal stability, including Ta₅₄W₂₇Si₁₉. The present research is focused on the characterization of the chemical stability of Ta₅₄W₂₇Si₁₉, a ternary AMTF, using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). AP-XPS allows the surface composition and oxidation states of the growing oxide layer to be measured in situ as the AMTFs are heated over a range of temperatures and O₂ partial pressures. Typical experiments were performed at 1 mbar O₂ partial pressure with temperatures ranging from 25 to 300° C. AP-XPS data was obtained with relatively short time intervals and the spectra were modeled using the Simulation of Electron Spectra for Surface Analysis (SESSA) software package. This analysis made it possible to determine the rate of oxide growth for the conditions studied, as well as the oxide film composition. Spectral analysis of the AP-XPS data indicated that Ta in Ta₅₄W₂₇Si₁₉ films was preferentially oxidized, thus forming primarily a tantalum pentoxide (Ta₂O₅) layer on the surface. Experiments were also performed on elemental Ta, W, and Si samples, and the results were compared to Ta₅₄W₂₇Si₁₉. Analysis of the data indicated that the apparent activation energies for the formation of Ta₂O₅ films on polycrystalline Ta and amorphous Ta₅₄W₂₇Si₁₉ films were very similar. However, we found that the oxidation of polycrystalline W and amorphous Ta₅₄W₂₇Si₁₉ films were distinctly different. We will discuss these results based on thermodynamic considerations and competitive reactions in the ternary alloys.

Charles S. Fadley Memorial Session

Room Naupaka Salon 5-7 - Session CF-TuM1

Charles S. Fadley Memorial Session III: Hard X-ray Photoelectron Spectroscopy

Moderators: Gerd Schönhense, Johannes Gutenberg-Universität, Trevor Willey, Lawrence Livermore Laboratory

8:00am **CF-TuM1-1 Probing Quantum Materials Interfaces with HAXPES at the GALAXIES Beamline, SOLEIL Synchrotron, Jean-Pascal Rueff, Synchrotron SOLEIL, France** **INVITED**

We will review recent HAXPES results obtained at the GALAXIES beamline, SOLEIL Synchrotron [1] regarding interfacial properties of metal oxides specially when combined to standing waves. This approach started at GALAXIES in collaboration with C.S. Fadley in CCMO [2] and continues today in different systems including CMO / YCO superlattices [3]. The functionality of novel quantum materials derives from the competition between the internal degrees of freedom (electrons, spin, orbital, topology, spin-orbit coupling) most notably observed at interfaces. An intense research activity has been set off for fabricating and manipulating interfacial properties of quantum materials leading to a frenzy of scientific discoveries including 2DEG, interfacial superconductivity, etc. HAXPES appears as a major probe of electronic interfacial behavior due to its superior probing depth and sensitivity to the local atomic properties. Extension of this work to investigating materials properties in operando conditions or characterizing ultrafast charge dynamics as recently obtained in GeSe [4] will be discussed. These results will be put in the context of the 4th generation (DLSR) synchrotron sources with much reduced H source size which offer new possibilities for in-depth interfacial characterization.

References

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- [3] L. Cambou *et al.*, *J. of Vacuum Science & Technology A* **39**, no. 5, 053204 (2021)
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8:40am **CF-TuM1-3 Hard X-ray Photoemission Spectroscopy (HAXPES) at the Advanced Photon Source: A Legacy of Charles S. Fadley, Jeff Terry, Illinois Institute of Technology**

Over my career few scientists have helped me as much as Charles S. (Chuck) Fadley. He was always willing to provide advice, analysis code, and a pep talk when needed. Unfortunately, we were only able to put together one document out of all of our shared interests. This document, “**Study of Complex Materials and Nanostructures Using Hard X-ray Photoemission Spectroscopy**,” has played an important role at the Advanced Photon Source (APS). The APS had no hard x-ray photoemission facilities dedicated to photoemission measurements prior to our writing this document. The APS now has 3 HAXPES instruments and one intermediate energy PES system of which 3 of are used primarily for photoemission, one is utilized more for detection of x-ray standing wave measurements. In this talk, I will highlight some of the measurements performed using HAXPES at the APS and discuss how Chuck’s passion and dedication to the development of HAXPES within the US will continue to shape the future of photoemission for the foreseeable future.

9:00am **CF-TuM1-4 Bulk Sensitive PhotoElectron Spectroscopy on Metal Hydrides, G. Panaccione, IOM- Consiglio Nazionale delle Ricerche (CNR), Italy; Curran Kalha, A. Regoutz, University College London, UK; L. Ratcliff, University of Bristol, UK; F. Offi, Università Roma III, Italy; C. Schlueter, A. Gloskovskii, DESY, Germany; J. Osterwalder, University of Zurich, Switzerland; G. Colombi, Technical University of Delft - TU Delft, Netherlands**

Efficient hydrogen storage is a key process for energy, transport and electrochemistry technology and metal hydrides have demonstrated high capacity of reversible storage, tuneable diffusion rate, and thermodynamic stability [1]. In terms of electronic structure, the identification of the electronic character vs. thickness and the hybridization between hydrogen and the metal host are fundamental values to be known, and a number of Photoelectron Spectroscopy works captured many relevant characteristics of the metal-hydrides properties, such as i) the high reactivity of the

surface and formation of more or less stable intrinsic oxides (influencing catalytic properties), and ii) the changes in the electronic character of the extended valence states upon formation of the hydrides (influencing the (semi)-metallic or semiconducting behaviour) [2-6]. Though, these results have been mainly obtained with a strong surface sensitivity in the VUV or soft X-ray region. As the hydrides are extremely reactive and their surfaces easily oxidize under ambient conditions, a precise determination of H-related features was difficult, leaving significant uncertainties in the understanding of hydrides both experimentally and theoretically

In this work, we exploit the bulk-sensitivity of Hard X-ray PhotoElectron Spectroscopy (HAXPES) to probe the electronic structure of metal-hydrogen states of two technologically relevant metal hydrides titanium (TiH_x) and yttrium hydride (YH_x). By means of energy dependent core level peak analysis we are able to disentangle the hydride, the main oxide and hydroxide spectral line shapes, and precisely determine their thicknesses and their chemical shifts (related to their valence oxidation number) (Fig.1). Analysis of valence band spectra and comparison with model calculations allow to attribute the metal-hydrogen states, as well as to identify the d vs sp contribution in the electronic states near the Fermi level, thus providing estimate of the charge-transfer between the metal and H, a value strongly affecting the conductivity of the system.

References

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- [6] A. Fujimori and L. Schlappbach *J. Phys. C: Solid State Phys.* **17**, 341 (1984)

9:20am **CF-TuM1-5 Synergies between Synchrotron and Lab-Based X-Ray Techniques for the Studies of Complex Materials and Interfaces, Alexander Gray, Temple University** **INVITED**

X-ray photoelectron spectroscopy, or photoemission, is a powerful and well-established experimental technique for probing the electronic structure and chemical composition of matter. Since the pioneering measurements in the 1950s, to the most recent angle-, spin-, and time-resolved studies, photoemission had and continues to have major impacts on condensed-matter physics in emerging fields, such as the studies of topological phenomena, strong electronic correlations, high-temperature superconductivity, and 2D materials. In this talk, I will describe several new directions in the field of photoemission that were pioneered by the Fadley Group, with a particular focus on the enhancement and control of the depth sensitivity and selectivity of the measurements through high-energy excitation and the use of standing waves. I will further discuss some of the latest studies that utilize hard x-ray and standing-wave photoemission in synergy with complementary synchrotron and lab-based x-ray spectroscopic and electron imaging techniques.

10:20am **CF-TuM1-8 In Situ Observation of Electrochemical Lithiation and Delithiation in Silicon Electrodes in All-solid-state Battery Configuration, Takuya Masuda, National Institute for Materials Science, Japan**

We have developed an in-situ/operando XPS apparatus equipped with a bias application system and investigated electrochemical lithiation/delithiation reactions of a silicon electrode in contact with a solid electrolyte in an all-solid-state battery configuration. Not only lithium silicides but also lithium oxides, lithium silicates and lithium carbonates are formed due to the lithiation of silicon and native oxide, followed by undesired side reactions with residual oxygen and carbon dioxide in the chamber. Lithium silicides reversibly respond to the successive lithiation/delithiation cycles. However, lithium oxides, lithium silicates and lithium carbonates are remained at the surface as irreversible species. The lithium silicide peak drastically shifts during the successive delithiation after preceding lithiation up to certain level. This is attributed to the phase transition of a crystalline lithium silicide to an amorphous phase. The effect of this phase transition on the cycle performance will be discussed on the basis of nanomechanical aspect.

References

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Tuesday Morning, December 13, 2022

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10:40am **CF-TuM1-9 Structural Investigation of Ruthenium Silicide Si 2p Core Level Surface States Using X-Ray Photoelectron Diffraction, Jonathan Denlinger**, Lawrence Berkeley National Laboratory

The Si 2p core-level photoemission spectra of URu₂Si₂, a heavy-fermion superconductor with a famous unexplained ‘hidden’-order transition at 17.5K, provides a distinct signature of the (001) cleaved-surface termination, which is important for the interpretation of valence band electronic structure studies. The Si-terminated surface, in particular, exhibits multiple distinct Si 2p peaks shifted to lower binding energy than the bulk component. Density functional theory calculations of the core-level spectra predict an unexpected structural site assignment and energy ordering of the top surface dangling bond surface state relative to a sub-surface Si site. Structural investigation with these surface states is explored using photon- and angle-dependent measurements of the Si 2p x-ray photoelectron diffraction intensities in comparison to EDAC scattering simulations.

Author Index

Bold page numbers indicate presenter

— A —

Addou, R.: CF-MoE2-10, 2

Alzaga, P.: CF-MoE2-10, 2

— B —

Bagus, P.: CF-MoE1-3, 1

Biesinger, M.: CF-MoE1-4, 1

Brehmer, D.: CF-MoE1-5, 1

Brundle, C.: CF-MoE1-3, 1

Buchanan, S.: CF-MoE1-4, 1

— C —

Colombi, G.: CF-TuM1-4, 3

Crist, B.: CF-MoE1-3, 1

— D —

de Meijere, A.: CF-MoE1-5, 1

Denlinger, J.: CF-TuM1-9, **4**

Diulus, T.: CF-MoE2-10, 2

— E —

Elzein, R.: CF-MoE2-10, 2

— F —

Fokin, A.: CF-MoE1-5, 1

— G —

Gloskovskij, A.: CF-TuM1-4, 3

Gray, A.: CF-TuM1-5, **3**

Grey, L.: CF-MoE1-4, 1

— H —

Henderson, J.: CF-MoE1-4, **1**

Herman, G.: CF-MoE2-10, **2**

— J —

Jenkins, J.: CF-MoE2-10, 2

— K —

Kalha, C.: CF-TuM1-4, **3**

Kozhushkov, S.: CF-MoE1-5, 1

— L —

Landt, L.: CF-MoE1-5, 1

Lee, J.: CF-MoE1-5, 1

— M —

Masuda, T.: CF-TuM1-8, **3**

— N —

Nemsak, S.: CF-MoE2-7, **2**

Nilsson, A.: CF-MoE2-9, **2**

— O —

Offi, F.: CF-TuM1-4, 3

Osterwalder, J.: CF-TuM1-4, 3

— P —

Panaccione, G.: CF-TuM1-4, 3

Paredes Mellone, O.: CF-MoE1-5, 1

— R —

Ratcliff, L.: CF-TuM1-4, 3

Regoutz, A.: CF-TuM1-4, 3

Rueff, J.: CF-TuM1-1, **3**

— S —

Schlueter, C.: CF-TuM1-4, 3

Schönhense, G.: CF-MoE1-1, **1**

Schriener, P.: CF-MoE1-5, 1

Stickle, W.: CF-MoE2-10, 2

— T —

Terry, J.: CF-TuM1-3, **3**

Tkachenko, B.: CF-MoE1-5, 1

— V —

van Buuren, T.: CF-MoE1-5, 1

— W —

Willey, T.: CF-MoE1-5, **1**