Applied Surface Science Division
Room 320 - Session AS+LS+RE+SS-TuM

Synchrotron-Based Photoelectron Spectroscopy Studies of Technologically Important Materials: in Memory of David Shirley

Moderators: James G. Tobin, University of Wisconsin-Oshkosh, **Eric L. Shirley**, National Institute of Standard and Technology

8:20am **AS+LS+RE+SS-TuM-2 Limitations in the Structural Determination of a Close-Packed Overlayer*, JG Tobin,*** U. Wisconsin-Oshkosh

The close-packed metal overlayer system c(10x2)Ag/Cu(001) has been the subject of extensive electronic structure studies. These include the examination of the two dimensional behavior at low coverages, the development from two- to three-dimensionality and the convergence to three-dimensional dispersion as in Ag(111). It would be of use to have a firmer picture of the placement of the first monolayer Ag atoms ($d_\perp$) versus the Cu(001) substrate. However, it will be demonstrated with FEFF that there are fundamental limitations to the extraction of that information with photon-induced electron diffraction. [1,2]

1. Part of the JVSTA Commemorative Volume of the Career of David A. Shirley

2**.** J. G. Tobin**,** "Limitations in the Structural Determination of a Close-Packed Overlayer,"J. Vac. Sci. Tech. A **39**, 063203 (2021), https://doi.org/10.1116/6.0001320.

8:40am **AS+LS+RE+SS-TuM-3 Sub-Micron Chemical Speciation Mapping of Uranium Dioxide Aged Under Humid Conditions*, David Shuh,*** *A. Ditter, J. Pacold,* Lawrence Berkeley National Laboratory (LBNL)*; Z. Dai, L. Davison,* Lawrence Livermore National Laboratory*; D. Vine,* Lawrence Berkeley National Laboratory (LBNL)*; S. Donald, B. Chung,* Lawrence Livermore National Laboratory **INVITED**

The oxidation of uranium is a critically important process across a variety of fields. It is a key component to understanding the nuclear fuel cycle, the fate and transport of uranium in the environment, and important signatures for nuclear forensics investigations. At room temperature, the humidity of the environment is more important to oxidation than the oxygen content of the atmosphere, so understanding the uranium oxidation can offer important insights into the provenance of a specimen. The scanning transmission X-ray microscope (STXM) at Advanced Light Source (ALS) Beamline 11.0.2 is an instrument capable of chemical speciation mapping below the micron scale. Uranium oxide powder was allowed to age and agglomerate at 98% relative humidity for 378 days, then a focused ion beam (FIB) was used to section a thin slice of this agglomeration for study at the ALS STXM. Results at the oxygen K-edge and uranium N_5-edge identify a bulk, UO_2 phase and an interfacial, schoepite phase, located in distinct regions of the sample. A modified non-negative matrix factorization (NMF) method was used to separate out the primary spectral components and identify these two phases, along with a surface phase which is suspected to be water adsorbed to the surface of the sample. Use of the STXM to identify uranium phases, particularly when coupled with FIB sectioning and NMF analysis is a promising method for uranium analysis going forward.

9:20am **AS+LS+RE+SS-TuM-5 On Photoelectron Spectroscopy and the Shirley Background*, Eric L. Shirley,*** NIST **INVITED**

Photoelectron spectroscopy and allied spectroscopies, electron-yield and Auger, provide rich information about occupied and unoccupied electron states in solids. Photoelectron spectroscopy and momentum-resolved photoemission allow one to probe band structure. However, photoemission is also plagued by inelastic losses, which occur because creation of additional excitations in the sample lowers a photoelectron's kinetic energy, usually manifested in the form of "satellite peaks." This can be a nuisance in some cases, because complicated interpretation is required when analyzing photoelectron spectra, but it also affords insight into the additional excitations. Background subtraction, such as is done using, say the "Shirley background," is one method used distill spectral features. Measuring electron-yield versus photon energy can be an excellent method for obtaining x-ray absorption spectra, and this can be accomplished using the same electron analyzers as for photoemission. Auger spectroscopy is also feasible using such analyzers, and the small angular acceptance of many current analyzers at hard-x-ray photoelectron spectroscopy (HAXPES) beamlines provides Auger spectroscopy with additional insight into unoccupied states, as will be shown. In this talk, we will survey theoretical treatments applied in connection with many of the above spectroscopies, discussing both insights gained and the treatments' limitations.

11:00am **AS+LS+RE+SS-TuM-10 Origin of the Complex Main and Satellite Features in Oxides*, Paul S. Bagus,*** University of North Texas*; C. Nelin, C. Brundle, B. Crist,* Consultant*; N. Lahiri, K. Rosso,* PNNL **INVITED**

The assignment of the complex XPS features of the cations in ionic compounds has been the subject of extensive theoretical work. However, there are strong disagreements, even for the origin of the main peaks, [1-2] and the agreement with experimental observations remains insufficient for unambiguous interpretation. In particular, previous cluster model treatments were not able to properly describe the satellite features for the cation XPS. Here we present a rigorous *ab inito* treatment of the main and satellite features in the cation 2p XPS of Fe_2O_3 and NiO which resolves this problem and provides a comparable treatment of both main and satellite features. This has been possible based on a new method for the selection of orbitals that are used to form the ionic wavefunctions. This method is a state averaging of the optimized orbitals over a mixture of normal and shake configurations. The normal configurations have only an electron removed from the cation 2p shell and the shake configurations include, in addition, an electron moved from orbitals of dominantly O(2p) character into the partly filled orbitals of dominantly cation 3d character. Previous cluster model XPS studies had used orbitals optimized only for the normal configuration. [1-2] Thus, for the first time, it is possible to have a set of orbitals that can describe, with comparable accuracy, both the normal and shake configurations. [3] This is especially important since, both in the states for the main and for the satellite XPS features, the normal and shake configurations can, and often do, mix. Thus, comparable accuracy is necessary to have proper descriptions of the ionic final states. It is also important that the character of the ionic states in terms of the occupations of the open shell core and valence orbitals and of the contributions of $2p_{1/2}$ and $2p_{3/2}$ ionization to the XPS intensities have been also determined. Thus, we are able to resolve the ongoing disagreement for the assignment of some regions of the spectra to normal configurations and other regions to shake, or charge transfer, configurations. This is possible because the theoretical treatment, based on cluster models of the oxides, allows us to obtain a detailed level of information about the character of the ionic configurations.

1. P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. **68**, 273 (2013).

2. P. S. Bagus, E. S. Ilton, and C. J. Nelin, Catal. Lett. **148**, 1785 (2018).

3. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, N. Lahiri, and K. M. Rosso, Phys. Chem. Chem. Phys. **24**, 4562 (2022).

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