

Study of Complex Materials and NanoStructures Using Hard X-ray Photoemission Spectroscopy

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Science

The U. S. Department of Energy (DOE) has identified five key areas in materials research that are grand challenges for the continued exploitation of materials resources[1]. A Hard X-ray Photoelectron Spectroscopy (HAXPES) beamline is directly applicable to many of the five challenges that have been identified. Photoelectron spectroscopy (PES)[2] has been used to develop much of our current understanding of the physics and chemistry of materials. Notably, PES has been responsible for our understanding of the valence electronic structure of semiconductors, high-temperature superconductors, spintronic materials, and other functionalized materials. The strengths of photoelectron spectroscopy allow it to answer questions in each of the following areas identified by the DOE: controlling materials processes at the level of electrons; designing materials with tailored properties; understanding complex correlations of electrons; and mastering the nanoscale. Another way of looking at these areas is to combine them in terms of the complexity of materials. Over the past 30 years, materials science has transitioned from the study of bulk elemental materials, such as silicon and germanium, to systems with either complex unit cells (ie. multiple atoms) without unit cells (nanoparticles) or with complex nanoscale layered structures.

Scientists and engineers are turning to complex materials or nanostructures in order to synthesize solutions to problems in data storage, energy production and transport, and drug delivery. Multilayer giant magnetoresistive (GMR) or tunnel magnetoresistive (TMR) nanostructures have been used to reduce the size of storage bits in magnetic storage devices. As one example of a new class of complex material with potential in spintronics, Figure 1 shows Mn 2p HAXPES spectra from the colossal magnetoresistive (CMR) material $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. Beyond this, lanthanates and titanates are used in clean energy production. High- T_c cuprates have the potential to revolutionize the transport of energy. Layered shell structures or controlled growth nanoparticles show promise as methods of drug delivery or disease detection. The important properties of these materials are all governed by their electronic structure. An understanding of the electronic structure of these complex materials is required to improve devices or to find new materials that may have better characteristics than those now known.

Even though understanding these complex materials has become the focus of research[1], measurements of the electronic structure of these novel materials have proven to be difficult. Many variables can affect measurements of the electronic structure of materials using photoelectron spectroscopy. One of the biggest issues with using photoelectron spectroscopy is that it has been inherently a surface sensitive technique. This is due to the short escape depths of photoelectrons excited by photons with energies below 1000 eV, which are of the order of 1-2 nm or less. If the electronic structure of the surface is different from that of the bulk material, photoemission measurements can lead to incorrect interpretations[3]. The complex materials listed above, as well as any kind of layered nanostructure, have been difficult to study precisely because of the problems involved in removing surface effects from photoemission spectra. HAXPES mitigates the typical surface sensitivity of photoelectron spectroscopy by measuring the photoelectrons at high kinetic energies that are on the order of a factor of 10 less surface sensitive than corresponding low-kinetic energy photoelectrons. It is thus possible to study true bulk electronic structure.

Hard x-ray photoelectron spectroscopy is not a replacement for standard vacuum ultraviolet (VUV) photoemission. It is a complementary technique. Even though HAXPES is still a relatively new technique, an overview of what is

expected from it is available [4a], and a number of papers have by now appeared, mostly from Japanese or European groups [4b]. Here we will detail the main differences between HAXPES and standard VUV photoemission. At the high energies, the momentum of the incident photon may not be neglected; this is in fact a slight breakdown of the dipole approximation. Beyond this, the angular averaging of approximately 0.5 degrees due to the acceptance cone of the lens, together with phonon creation/annihilation during photoexcitation, leads to a valence spectrum that is nearly independent of electron momentum (wave vector conservation) effects. The measured valence band spectra will thus be an average over the Brillouin zone (BZ) and as such will be a measure of the matrix-element weighted density of states. Also, because of the greater escape depths of photoelectrons at high kinetic energy, the density of states (DOS) will be a better representation of the intrinsic DOS of a material. These two features make the valence band spectra collected at high kinetic energy much easier to compare with theoretical calculations of the DOS of a material. Once matrix-element effects are allowed for, spectral differences between low- and high-energy measurements then are likely due the effects of surface reconstruction or effects of poorly averaged electron momentum.

Measuring core-level spectra will benefit from the larger escape depths. Photoemission Spectroscopy (PES) is widely used in surface and interface studies because it is very sensitive to the electronic environment of the element under study. Therefore, both, the electronic structure of the interface and chemical reactions that occur at the interface can be studied. One way to view the photoemission process is through the three-step-model proposed by Spicer[5]: excitation, transport, and escape. It is in the transportation process where observations at high kinetic energies are an improvement as the photoelectrons are less likely to undergo inelastic scattering. In general, the probability that an electron excited will reach the surface is $\exp(-x/l)$, where l is escape depth of the electron and x is the distance from the emitting atom to the surface. Thus, a larger escape depth results in a greater probability of measuring a photoelectron from greater depths. The measured core level spectrum is dependent upon Fermi level position, screening of the final state core hole, magnetic state, and chemical environment. A chemical shift occurs when the measured kinetic energy of the photoelectron is modified due to the chemical environment of the emitting atom. Often chemical shifts are the result of charge transfer. A simple way to look at chemical shifts is to focus on the difference in the potential field that the core electrons are exposed to in the different chemical environments. Chemically-shifted components in core level photoemission measurements allow one to determine direct chemical bonding information. The larger escape depths at high kinetic energy allow us to determine the intrinsic properties from buried layers and interfaces and samples that can not be prepared under UHV conditions[4b]. The HAXPES system that will allow the measurements described above must be developed with two main components, a high-resolution x-ray monochromator and a UHV photoemission chamber with an analyzer capable of detecting high kinetic energy electrons.

Added Value of the Mid-Term Upgrade

The proposed facility is complementary to the Intermediate Energy X-ray (IEX) beamline currently under construction. The IEX facility is designed to probe valence electronic states. It has an energy range (1000 – 3000 eV) that allows for more bulk-like measurements than possible at most Vacuum Ultra-Violet (VUV) synchrotrons. This facility will be very successful as escape depths at these energies are a factor of 3 to 5 greater than at conventional VUV energies. Given the recent work of Plucinski, *et al.*, [6] at the Advanced Light Source, it is clear that band structure measurements will be possible at this facility. The HAXPES facility proposed here will provide complementary measurements of bulk valence band density of states and also bulk core-level photoemission described above. The proposed HAXPES beamline would be the first high-resolution, hard x-ray photoelectron spectroscopy system on a third-generation light source in the U. S. The U. S. is currently playing catch-up in this area as HAXPES beam lines are currently operational at synchrotrons in Europe and Asia, with more in the planning stage [4b].

Expected User Community

It is expected that a diverse user community will fill all the available time at a Hard X-ray Photoelectron Spectroscopy Beamline. As discussed above, HAXPES has many applications in diverse areas of materials physics and chemistry. The supporting users listed below are from a variety of backgrounds including physics, chemistry, engineering, and industry. Once the facility becomes operational, it is expected that the user community will attract many more users who apply HAXPES to complex materials, nanostructures of relevance to semiconductor technology and spintronics, radioactive and environmental materials, functionalized nanosensors, and biomaterial interfaces.

Enabling Technology and Infrastructure

A HAXPES facility requires a standard pre-monochromator (pre-mono) followed by a high-resolution monochromator, and an electron energy analyzer. The pre-mono will be used to monochromate the x-ray beam before moving toward the high-resolution monochromator. The premono is used to so only a relatively low heat load is placed on the high-resolution monochromator. This project also requires three components not commonly found at high-energy synchrotrons. The undulator will be an Elliptical Polarized Undulator (EPU). An EPU produces high-fluence x-ray beams that can be circularly polarized or can be rotated to any linear polarization vector. Either circular or linear dichroism measurements can be performed with the light from an EPU. A high-resolution monochromator is used to provide the energy resolution necessary for photoelectron spectroscopy. The high-resolution monochromator described below is designed to allow a tunable range with moderate-resolution and a fixed energy with high-resolution. Finally, a high-energy hemispherical energy analyzer will detect the ejected photoelectrons.

The Scienta R4000 hemispherical energy analyzer is currently able to detect photoelectrons up to 10,000 keV with good angular resolution. The minimum energy resolution of the detector is better than 12.4 meV. This resolution is a good match to that of the monochromator described below. This detector has been used to measure photoelectrons with kinetic energy up to 9000 eV. The R4000 HE has been in use since 2002 on a HAXPES beam line at SPring-8 [4b]. The R4000 will be equipped with a spin polarimeter that can operate on photoelectrons up to 8 keV in energy. Both a multichannel plate and the spin polarimeter are in the analyzer at all times. The control software can switch between detectors. This allows for standard photoemission and spin-polarized photoemission to be performed on the same sample.

The second key component of the HAXPES beamline will be the high-resolution X-ray monochromator (HRXM). Figure 2 shows our proposed design for the double beam monochromator. In order to match the resolution of the electron analyzer an x-ray resolving power of 10^6 is required, or about 10 meV at 10 keV. This required resolution is at least a factor of 10 better than most high-heat-load monochromators. Therefore, a pre-monochromator (double-crystal monochromator, or DCM) will be used to attenuate the incident x-ray beam power. The HRXM will be located downstream of the DCM and their motions will be synchronized through software control. The HRXM we propose will be based on a pair of channel-cut silicon (or germanium) blocks in the + - +, or dispersive geometry, both to achieve a fixed exit as well as to improve the energy resolution over a wide range compared with a single channel-cut block [7-9].

We require at least two resolutions and energy ranges in the HRXM. This requires at least two different monochromatization schemes. The lower resolution beam will be on the order of 40 meV but will be tunable over a relatively large energy range. This can be accomplished in the four-bounce mode, using the (333) reflection for symmetric channel-cut silicon blocks. The potential energy range of this arrangement will be from 6 keV to beyond 10 keV. The second x-ray beam will be high-resolution (15 meV), high-fluence beam that is only available at a single energy near 10 keV. This may be accomplished with a double bounce (555) reflection in back-scattering geometry, using only one channel-cut crystal [10]. The monochromator tanks will be large enough to accommodate crystal blocks as large as 20 cm long, if necessary. The photon flux at 9.90 keV possible from this arrangement should be greater than 1×10^{11} ph/sec with an energy resolution of about 15 meV (undulator fundamental, 100mA ring current, 7GeV ring energy). This beam will be utilized for the highest kinetic energy and therefore, most bulk-like measurements with the highest resolution and fluence available at these photon energies. With $\theta_B = 86.9$ degrees, the acceptance of the back-reflection monochromator nearly matches the vertical beam divergence. This compares quite favorably to a four-bounce Si(444) monochromator that has a bandwidth of 50 meV at 10 keV, but provides only the same flux of 1×10^{11} ph/sec. If in the future other high-resolution modes are needed, they can be easily added to this system. At the high precision required for selecting the monochromatic energy, the effects of thermal fluctuations must be minimized in order to maintain long-term stability in the beam intensity as well as the beam energy. The HRXM will be housed in its own temperature-controlled hutch, rather than installing the HXRm into the experimental hutch.

Finally, the undulator is required to be an Elliptical Polarized Undulator (EPU). There are many designs for hard x-ray EPUs but they are not commonly in use. The hybrid APPLE design [11] which can provide 100% circularly polarized radiation may be the perfect undulator for use at the proposed HAXPES facility.

Partnerships and User Interest

The following users have expressed interest utilizing the proposed facility:

Juan Campuzano, Professor of Physics, University of Illinois, Chicago
 Elio Vescovo, Staff Scientist, Brookhaven National Laboratory
 Joe Woicik, Senior Scientist, National Institute of Standards and Technology
 Daniel Fischer, Staff Scientist, National Institute of Standards and Technology
 Piero Pianetta, Professor of Electrical Engineering, Stanford University
 Ken Czerwinski, Professor of Chemistry, University of Nevada, Las Vegas
 Sandra Bishnoi, Professor of Chemistry, Illinois Institute of Technology
 See-Hun Yang, Staff Scientist, IBM Almaden
 Giuseppina Conti, Staff Scientist, Applied Materials
 Scott Chambers, Staff Scientist, Pacific Northwest National Laboratory

Industry and Technology Transfer

None expected at this time.

Budget

This project will require the construction of a new beamline at the Advanced Photon Source. The budget includes an estimate of the costs of a Hard X-ray Elliptical Polarized Undulator (EPU) of \$6M, a HAXPES photoemission endstation \$1.5M, a standard-resolution monochromator \$1M, a high-resolution monochromator \$1M, and necessary hutches and equipment for the beamline \$2.6M. Effort is computed at the IIT Rate of \$500K for 3.5 FTE

	Year 1	Year 2	Year 3	Year 4	Total
Effort (IIT rates)	\$500K	\$525K	\$550K	\$170K	\$1745K
M&S	\$100K	\$200K	\$200K	\$100K	\$600K
Capital	\$6000K	\$5000K	\$1000K	\$100K	\$12100K
Total	\$6600K	\$5725K	\$1750K	\$370K	\$14445K

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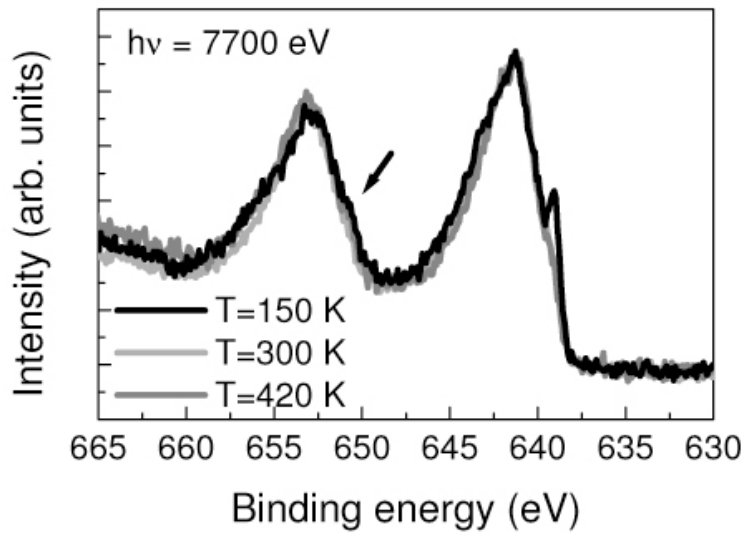


Figure 1: Mn 2p photoelectron spectra from $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ excited with a photon energy of 7700 eV and for several temperatures below and above the Curie temperature of 370 K. The arrow highlights a small shoulder on the $2p_{1/2}$ peak.

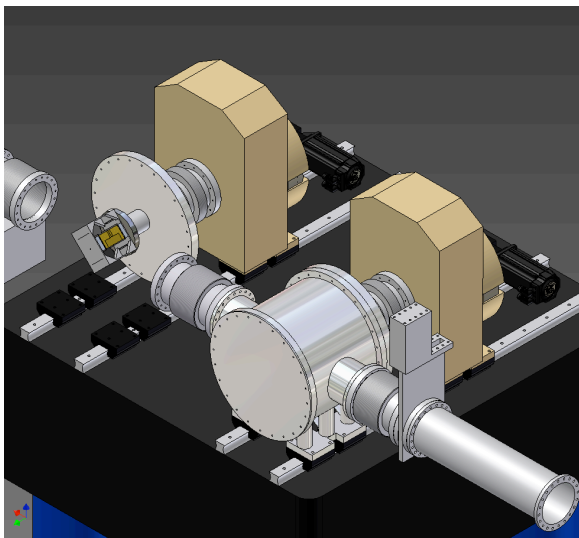


Figure 2: Schematic representation of four-bounce, high-resolution monochromator on synchrotron plinth, showing triple channel mounting arrangement for two high-resolution modes and a pass through for low-resolution from the pre-monochromator.