

4.5 HIGH-RESOLUTION SPECTROSCOPY BEAMLINES

LERIX

Due to improved light source brilliance and novel detector development in only the last 5 years, non-resonant x-ray Raman spectroscopy (XRS) has become a powerful tool for examining low-energy loss features with hard x-rays. XRS gives a bulk-sensitive alternative to UV, soft x-ray, or electron spectroscopies, especially for situations where those methods are not applicable because of complex sample environmental chambers. This technique has been widely used in high-pressure research to examine light elements, and more recent work at APS has given the first demonstration that XRS is extremely valuable for *in-situ* studies of metal oxide battery electrodes (Balasubramanian et al. 2007) (see fig 2.5.2), as was projected in the 2007 DOE report on Basic Research Needs in Electrical Energy Storage (BESAC 2007). Other work at the APS has shown that the momentum-transfer (q) dependence of XRS can characterize dipole-forbidden final states in transition metal, rare earth and actinide materials. Building on the success of the existing LERIX spectrometer at the APS Sector 20 (see fig. 2.5.2 background), we plan to develop a dedicated capability for high-throughput XRS measurements. The new station will have more analyzers for enhanced detection efficiency, and better capabilities for *in-situ* sample environments such as catalytic reactors and high pressure cells. As demonstrated by the battery studies, the *in-situ* capabilities will be essential in further enabling basic energy science studies relevant for electrical energy storage, fuel cell operation, catalysis, and next-generation nuclear fission fuels.

MERIX

MERIX, the medium resolution (~ 100 meV) inelastic x-ray scattering spectrometer at APS 30-ID (fig. 4.5.1), is dedicated for the study of collective valence electron excitations in correlated electron systems. The incident x-ray photon energy range of MERIX is 5-12 keV. MERIX offers a unique set of x-ray analyzers optimized for $3d$ and $4f$ resonances. Understanding the polarization dependence of the scattering at resonance is crucial. This is addressed by the ability of the MERIX spectrometer to scatter both vertically and horizontally. The MERIX instrument is equipped with x-ray mirrors, providing a micro-focused beam on the sample ($6 \times 45 \mu\text{m}^2$), enabling studies of small samples and samples under high pressure. The instrument has been working very well (Wakimoko et al. 2009), but the scientific impact would grow substantially with planned upgrades to increase the energy resolution, the throughput of the spectrometer, and the flux on the sample; to decrease the beam size on the sample to sub-micron size; and to add new and improved analyzers.



Fig. 4.5.1. MERIX: Picture of medium-energy resolution (~ 100 meV) inelastic x-ray spectrometer at 30-ID with focusing mirror and analyzer crystals.

HERIX

The HERIX spectrometer at 30ID is designed to study the phonon dispersion in crystals and the collective atomic excitations in disordered systems as a function of momentum and energy transfer. The HERIX spectrometer can from a micro-focused beam at the sample ($15 \times 34 \mu\text{m}^2$), which allows the study of samples under extreme thermodynamic conditions. Also, the HERIX spectrometer has a high-energy resolution (1.5 meV), which enables the study of collective excitations in soft matter (fig. 4.5.2). Another advantage of the HERIX spectrometer is the ability to measure the dynamical structure factor at high momentum transfer ($Q \sim 75 \text{ nm}^{-1}$), which is crucial to determine the phonon density of state in polycrystalline materials as demonstrated recently on pure δ -Pu and δ -Pu_{0.98}Ga_{0.02} at room temperature (Manley et al. 2009). A comparison of the phonon DOS of the two phases at room temperature allowed the conclusion that the heat capacity of α -Pu is accurately described in terms of the measured phonons and conventional electronic and thermal-expansion contributions. However, a comparison with the δ -phase demonstrates that most of the entropy stabilizing the δ -phase of plutonium at high temperature comes from unconventional sources, including electron correlations, intrinsic phonon softening, and possibly intrinsic localized modes. Options to increase

the energy resolution of HERIX are being explored. One direction, ultra-high resolution resonant inelastic scattering (UHRIX) would open the realm of inelastic neutron scattering and Brillouin light scattering to x-rays (Shvyd'ko et al. 2006). A more modest approach, but a big step forward is the next generation IX spectrometer (ANGIX), which significantly increases the measured solid-angle and momentum transfer range.

At present the MERIX and HERIX instruments split beamtime on sector 30 and, while performing very well, would benefit from tailored insertion devices and higher flux and brightness. Our plans consider the separation of these instruments into two dedicated beamlines, each with tailored insertion devices. For example, the HERIX instrument would be ideally suited for a superconducting insertion device, providing an order of magnitude higher flux at 25-35 kV, which is desired for the highest energy resolution.

Shaking for action

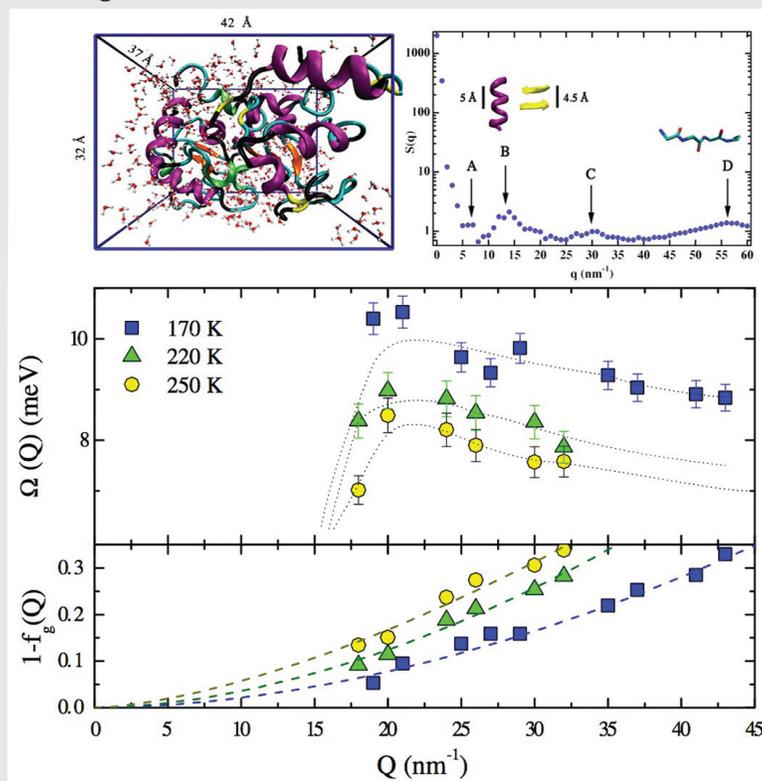


Fig. 4.5.2. HERIX spectra reveal a fascinating correlation between the temperature onset of biochemical activity of a protein and intramolecular vibrations (Liu et al. 2008).

X-RAY EMISSION SPECTROSCOPY

X-ray emission spectroscopy (XES) of the photons generated when valence electrons, or electrons in weakly bound orbitals, fill deep core holes is an experimentally versatile and reliable way to characterize the occupied local electronic states of a targeted atomic species. For example, the $K\beta$ and $K\beta'$ features for $3d$ transition metals often provide unique insight into the spin, valence, ligand species, and ligand bonding. Such information could be of critical importance for studies of bulk and nanophase transition metal oxides used in numerous energy science applications. In contrast, XANES is most directly sensitive to the unoccupied final density of states. Unfortunately,

few XANES studies at hard x-ray energies are accompanied by XES measurements with resolution comparable to the core-hole lifetimes (e.g., 0.5-2 eV for $3d$ transition metals), even though many such studies would vastly benefit from the complementary information provided by XES. This neglect is due to the complexity, cost, and lack of portability of large-scale x-ray spectrometers based on spherically bent crystal analyzers. Recent work at the APS has successfully demonstrated a new type of “miniature” x-ray spectrometer (miniXS) that overcomes many of these issues, while also providing up to 50x improvements in measurements times compared to the existing APS apparatus (fig. 4.5.3). We plan to develop a portable x-ray emission spectrometer for operation at 3-10 keV. This energy range is of high scientific importance, as it spans the K -emission for $3d$ transition metals, the L -emission for lanthanides, and the M -emission for actinides. The spectrometer will be compatible with the beam characteristics of numerous APS beamlines, while also being easily integrated with important experimental apparatus, such as diamond anvil cells, laser systems for pump/probe studies, cryostats, furnaces, and x-ray compatible chambers for *in-situ* electrochemical or chemical studies.

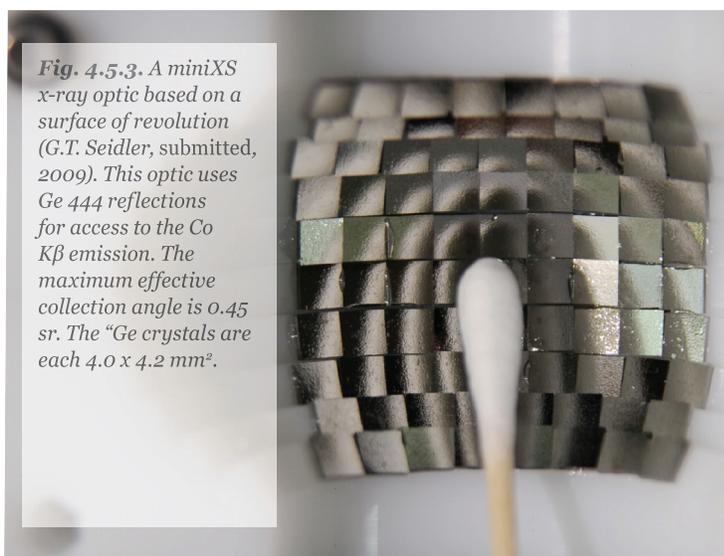


Fig. 4.5.3. A miniXS x-ray optic based on a surface of revolution (G.T. Seidler, submitted, 2009). This optic uses Ge 444 reflections for access to the Co $K\beta$ emission. The maximum effective collection angle is 0.45 sr. The “Ge crystals are each $4.0 \times 4.2 \text{ mm}^2$.”