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The advantages of soft X-rays and cryogenic spectrometers for measuring chemical speciation by X-ray spectroscopy

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Abstract

We have built a 36-pixel high-resolution superconducting tunnel junction (STJ) soft X-ray spectrometer for chemical analysis of dilute metals by fluorescence-detected X-ray absorption spectroscopy (XAS) at the Advanced Light Source synchrotron. Soft X-ray absorption edges are preferred over traditional hard X-ray spectroscopy at the K-edges, since they have narrower natural linewidths and exhibit stronger chemical shifts. STJ detectors are preferred in the soft X-ray band over traditional Ge or grating spectrometers, since they have sufficient energy resolution to resolve transition metal L and M lines from light element K emission, and sufficient detection efficiency to measure the weak lines of dilute specimens within an acceptable time. We demonstrate the capabilities of our STJ spectrometer for chemical analysis with soft XAS measurements of molybdenum speciation on the Mo $M_{4,5}$-edges.

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Keywords: High-resolution X-ray spectrometer; Superconducting tunnel junction; Soft X-ray absorption spectroscopy; Mo speciation

1. X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is used to analyze the chemical environment of elements by scanning a monochromatic synchrotron beam with sub-eV resolution through their absorption edges, thus probing atomic energy levels. The valence shell energy levels of the central atom are sensitive to its chemical state and the geometry of the surrounding atoms that form the ligand environment. Changes in ligand environment cause chemical shifts of the energy levels on the order of 1 eV. These changes are most sensitively measured using low-energy soft X-ray transitions into these levels, since they have very narrow natural linewidths [1].

For concentrated samples, the X-ray absorption is typically measured by total electron yield. For dilute samples, the background can be greatly reduced and the sensitivity can be enhanced by measuring the corresponding fluorescence instead, if an X-ray detector is used that can separate the fluorescence of interest from that of the matrix background [2]. STJ spectrometers offer an advantage over conventional detectors in the soft X-ray region below ~1 keV. Semiconductor detectors lack the resolution to separate overlapping lines, and grating spectrometers lack the detection efficiency to collect enough signal counts within an acceptable time [3].

We have built a high resolution soft X-ray spectrometer based on four 3×3 Nb(165 nm)–Al(50 nm)–AlOx–Al(50 nm)–Nb(265 nm) STJ arrays measuring $0.6\times0.6\,\mathrm{mm}^2$ each. Every junction can acquire soft X-rays below 1 keV with an energy resolution of $\Delta E_{\mathrm{FWHM}}\approx10$–20 eV at a rate of 30,000 cts/s, for a total maximum count rate of $\sim10^6$ cts/s. The STJs are mounted in a UHV chamber at the end of a 40 cm long cold finger within 12 mm of a room temperature sample and cover a solid angle $\Omega/4\pi\approx5\times10^{-4}$ [4].

We use fluorescence-detected XAS to study the role of metals as catalyst in biological systems [5]. Our interest in

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Mo arises from its role in nitrogen fixation in the nitrogenase protein [6]. Here, we use Mo M-edge spectroscopy as a representative example to discuss the enhancement in chemical sensitivity over conventional K and L-edge spectroscopy that our STJ spectrometer provides.

2. Molybdenum speciation measurements

Fig. 1 shows the soft X-ray fluorescence from different Mo compounds. The ~15 eV FWHM energy resolution of the STJ is sufficient to resolve the Mo $M_{\xi1,2}$ and other Mo M emission lines of interest from light element K X-rays. Note that for weak lines, spectral artifacts can increase the background at the Mo M lines and limit the spectrometer sensitivity.

Fluorescence-detected X-ray absorption spectra are taken at beam line 4.0.2 at the ALS synchrotron. The excitation energy of the monochromatic X-ray beam is scanned through the Mo $M_{4,5}$ absorption edges, which correspond to the binding energy of the Mo $3d_{3/2,5/2}$ electrons, in 0.1 eV increments. Fluorescence spectra are recorded over 10 s with each STJ for each excitation energy, and a window is defined around the Mo $M_{\xi1,2}$ line for each STJ. The absorption spectrum then consists of the total number of Mo $M_{\xi1,2}$ fluorescence counts in these windows as a function of excitation energy, normalized by the incident flux and with a constant spectral background subtracted (Fig. 2). There is a clear and significant shift in the energy of the absorption edge for three Mo compounds with different oxidation states.

The Mo(0) metal film, capped by ~20 Å of Si to prevent oxidation shows the Mo $M_{4,5}$ absorption edges at $E = \sim 228$ and 232 eV as expected [1]. The edges are shifted to higher energies for the Mo(II)Acetate and the NaMo(VI)O_4 samples because at higher oxidation states the number of screening electrons is reduced, leading to tighter binding of the core electrons. Note that the natural linewidth of ~0.7 eV FWHM for the $M_{4,5}$ edges is significantly narrower than the ~4.5 and ~2 eV FWHM linewidth at the Mo K and L-edges, respectively [1].

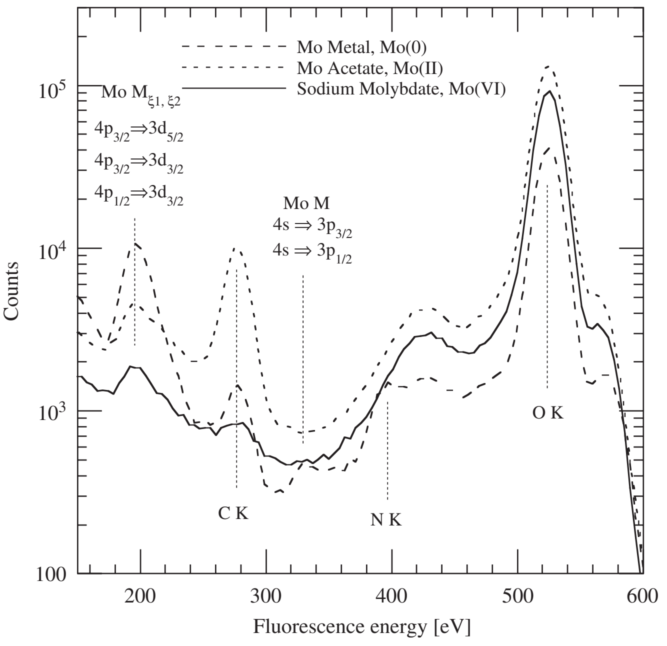

Fig. 1. Soft X-ray emission spectra of different Mo compounds taken with the STJ spectrometer at constant excitation energy.

The narrow linewidth of the M-edges is the basis for the high chemical sensitivity of soft X-ray XAS. Fig. 3

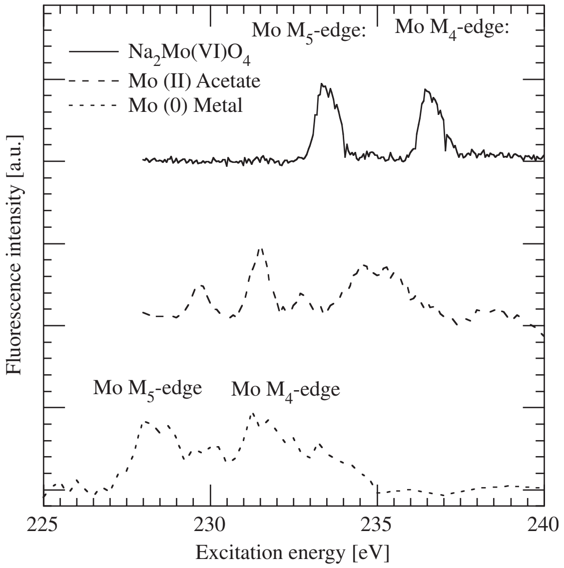

Fig. 2. Fluorescence-detected Mo M_4 and M_5 edges for Mo(0) metal, Mo(II) acetate, and $Na_2Mo(VI)O_4$. The chemical shifts are around ~1 eV per change in oxidation state.

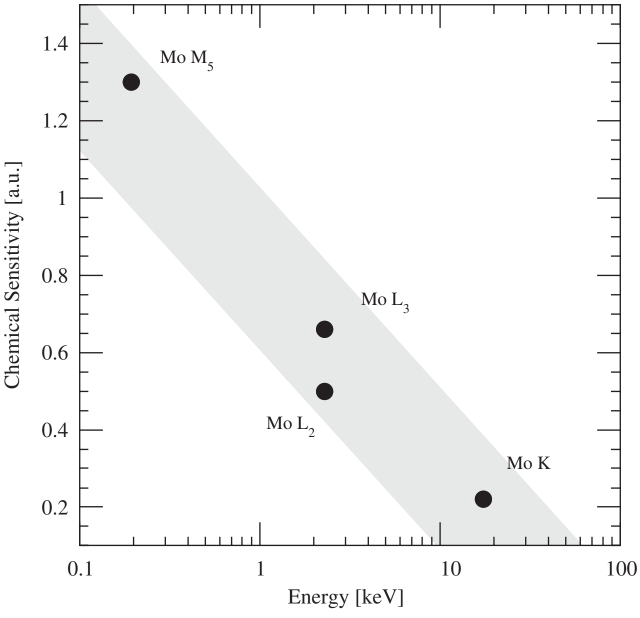

Fig. 3. The chemical sensitivity, defined as the shift per oxidation state divided by the natural linewidth of the transition, increases significantly for low energy X-ray transitions.

displays the trend of increasing chemical sensitivity, defined as the shift in the energy per oxidation state divided by the natural linewidth of the transition, for low energy transitions. These more sensitive edges require spectrometers like STJs capable of distinguishing the various fluorescence lines in the crowded soft X-ray region.

In summary, we have built a 36-channel STJ spectrometer for synchrotron-based fluorescence-detected X-ray absorption spectroscopy. It offers an energy resolution between 10 and 20 eV FWHM in the soft X-ray band below 1 keV, and can be operated at a total count rate of $\sim 10^6$ counts/s. We are using the high-energy resolution and high count rate of the STJ spectrometer, and the high chemical sensitivity of soft X-ray transitions to understand role of metals as catalysts in biological systems.

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