

Tests of Energy-dispersive Detectors, a Johansson Bent LiF Monochromator, and an LSR HOPG Detector for Fluorescence XAFS of a Model Catalyst

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Introduction

A common problem in fluorescence x-ray absorption fine structure (XAFS) is interference between absorption edges corresponding to different elements in the same material. For neighboring transition metal absorption edges, the competing emission lines are separated in energy by several hundred eV, and one edge can be discriminated from another by using a relatively low-resolution monochromator. Examples include energy-dispersive detectors, multilayer arrays, and a log spiral of resolution (LSR) covered with highly oriented pyrolytic graphite (HOPG) [1, 2]. On the other hand, it is not that uncommon to deal with competing absorption edges that correspond to emission lines separated by tens of eV. In such cases, the low-resolution monochromators fail. One recent example of a useful high-resolution monochromator is a bent silicon Laue device with a quoted resolution of 20 eV at 6 keV [3]. On the other hand, Gordon et al. [4] previously used a commercially available Johansson bent LiF monochromator, with a quoted resolution at the gold L edge (9.7 keV) of 20 eV. Since a given angular resolution translates into improved energy resolution as the x-ray energy is lowered, a comparison suggests that the LiF bent crystal device could have an even better resolution at 6 keV than the bent Laue silicon monochromator, although perhaps with poorer intensity.

We decided to test the performance of the LiF ground and bent crystal monochromatic in an application for obtaining V XAFS from a model catalyst in the presence of competing La peaks. As far as the LSR HOPG monochromator is concerned, it was clear at the outset that a monochromator that uses the full width of the HOPG rocking curve would not have adequate energy resolution to discriminate the fluorescence lines we deal with in the present study. Nevertheless, tests using the LSR were carried out in order to learn more about the LSR as applied to different kinds of samples.

Methods and Materials

Test samples of a LaO_x oxide powder mixed with Al₂O₃ (sample A) and then a 50-50 mixture of LaO_x/Al₂O₃ and VO_x/Al₂O₃ (sample B) were packed into a sample holder

and sealed with Kapton® tape. Both mixtures contained nominal 2 wt% lanthanum or vanadium. Sample B is a model for a class of catalysts of potential industrial significance. Experiments on samples A and B that used energy-dispersive detectors were carried out at the National Synchrotron Light Source (NSLS). Then, by using the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT) insertion device beamline of the APS, the same spectra were measured by using a bent crystal spectrometer.

Results

For the first x-ray experiments, samples A and B were irradiated, and the resulting emission spectra were measured at the NSLS. The energy chosen for the irradiating x-rays was 6465 eV, which is 1000 volts past the onset of the V K edge. Spectra were obtained by using two different models of energy-dispersive detectors, with the better-resolved spectrum corresponding to one selected element of a modern 30-element detector, and the more poorly resolved spectra corresponding to an older 13-element array. In a later set of experiments, these samples were irradiated at the same energy by using the insertion device PNC-CAT line at the APS. The emitted spectra were measured by using an Oxford WDX-600 wavelength-dispersive spectrometer. This device uses a Johansson ground and bent LiF crystal as a monochromator. To attain the best resolution, it was necessary to limit the angular width of the x-rays leaving the beam spot by receiving slits. A comparison between the results for the two energy-dispersive spectrometers and the bent crystal device for samples A and B is shown in Figs. 1 and 2. It can be seen that neither energy-dispersive detector can separate the V K_α lines from the La_{β1} peak. On the other hand, the LiF monochromator readily obtains peak separation for the V K_α line. The full width at half-maximum (FWHM) of the La L_{α1, α2} doublet, as measured with the bent LiF device, is 27 eV. The reported inherent energy separation of these peaks is about 16 eV, implying excellent resolution of the LiF monochromator.

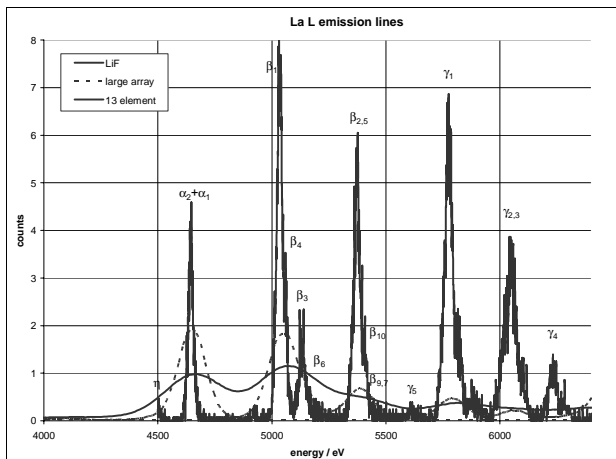


FIG. 1. Emission spectra from two energy-dispersive detectors and the ground and bent LiF crystal, for LaO_x in an Al_2O_3 matrix.

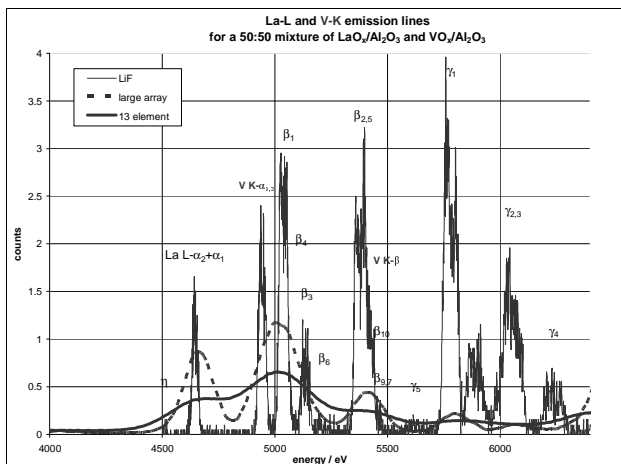


FIG. 2. Emission spectra from two energy-dispersive detectors and the ground and bent LiF crystal, for a 50-50 mixture of LaO_x and VO_x in an Al_2O_3 matrix.

The LiF Johansson monochromator was then used to measure the V K-edge XAFS in sample B. These results are shown in Fig. 3. A beam focused to about 1 mm on the sample, Si(111) monochromator crystals, and an incident flux estimated to be between 10^{12} and 10^{13} photons per second, were used. The results of nine averaged scans are shown. Although the La edges are removed, the V edge data appear to be noisy. However, the fact that narrow receiving slits were necessary to obtain optimal resolution means that intensity was lost because of a spot size that exceeded the acceptance conditions of the LiF monochromator. Since this experiment was performed, by using Kirkpatrick-Baez (K-B) mirrors, the incident beam

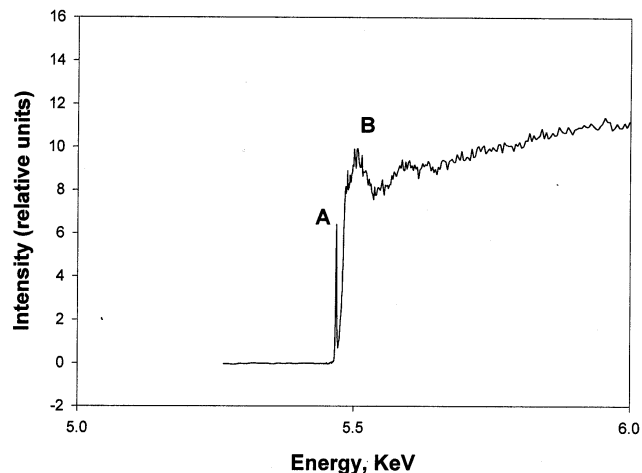


FIG. 3. XAFS spectra for the V K edge for a 50-50 mixture of LaO_x and VO_x in an Al_2O_3 matrix. Nine scans were averaged.

spot diameter at nearly full flux available at this beamline has decreased by a factor of nearly 10. Therefore, we infer that the intensity at optimal resolution of this monochromator would be significantly enhanced if a corresponding experiment were repeated by using the K-B mirrors.

Finally, we investigated using the LSR monochromator to study these systems. The LSR device available was manufactured to detect the Cr K_α line rather than the V K_α line. However, the V K_β line is at an energy that lies within the acceptance of this LSR. Although the energy resolution of HOPG, using the FWHM reflection, is not adequate for separating the V K_α peak for these samples, we expected to observe V edges with excellent intensity. In a previous study, by using an unfocussed beam at the PNC-CAT line, we measured clean Cr XAFS for 1% Cr in the presence of a background of 99% V, in a flat, self-supporting alloy [3]. In that experiment, an incident beam intensity in the ~ 1 -mm-diameter spot used was on the order of 10^{11} photons per second.

In the present experiment, one deals with a factor of ~ 10 loss in intensity due to the fact that the K_β intensity is about a factor of 10 less than the K_α intensity. However, the beam used was estimated to be between one and two orders of magnitude more intense than that used in the study of the $\text{Cr}_{0.1}\text{V}_{0.9}$ alloy. The increased beam intensity made up for the use of the K_β rather than the K_α line of V. The concentration of V in sample C, as a fraction of metal atoms present, is comparable to the concentration of Cr in the $\text{Cr}_{0.1}\text{V}_{0.9}$. Furthermore, sample B does not produce an intense fluorescence background comparable to the V background in the alloy. However, for sample B, we could barely observe a V edge by using the LSR. We suspect

that our experimental problem had to do with the fact that the sample was a powder held in a recess by tape. The large solid angle ($\sim 25\%$ of 4π) of this LSR comes about because of the detection of fluorescence that leaves the sample at angles between glancing and 30° . The closest portions of the LSR are only 1.5 cm from the incident beam spot, and the furthest portions of the LSR are less than 6 cm from the spot. If the surface of the powder is irregular to, say, 0.1 mm, then the HOPG surface 3 cm away sees a spread in emergent angles that is about the half width at half-maximum (HWHM) of good HOPG. An irregularity of ~ 1 mm in the powder surface would be expected to wipe out the signal. These problems are possibly exacerbated by the fact that to the glancing emergent rays, the tape approaches infinite thickness, and even at 10° emergence, the effective tape thickness is enhanced by a factor of six because of the small angle of emergence.

Discussion

We have shown that the resolution of a commercially available ground and bent LiF monochromator is excellent at removing La edge interference from the V XAFS for catalyst samples on the basis of the model systems studied. If the K-B focusing that is now available were to be used, the intensity would increase, and there would be an option of using a larger monochromator crystal. The

resolution is superior to that of a bent Laue silicon device for comparable x-ray energies, and it appears to be adequate to remove the K_β line from a Z-1 element such as Ti from the K_α line of a Z element such as V. This excellent resolution could be important in some applications.

Acknowledgments

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