Log Spiral of Revolution HOPG Monochromator for Fluorescence XAFS

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Introduction

The x-ray background contribution is an experimental problems that arises when one obtains x-ray absorption edge fine structure (XAFS) of dilute atomic species using the fluorescence technique. Particularly troublesome are scattered radiation, diffraction peaks, or fluorescence emission from elements other than the element of interest. In addition, fluorescence from (Z-1) elements cannot be diminished by filters without seriously decreasing the signal from the desired element (Z), so that the standard ion chamber-filter-slit combination[1] cannot be used. Therefore, for dilute samples, the ion chamber-filter combination is sometimes replaced by a multidetecting element, energy-dispersive detector. For energy-dispersive detectors, however, the total count rate one may obtain is limited due to count pile-up effects (saturation). We have as an alternative developed a log spiral[2] of revolution (LSR), oriented graphite monochromator.

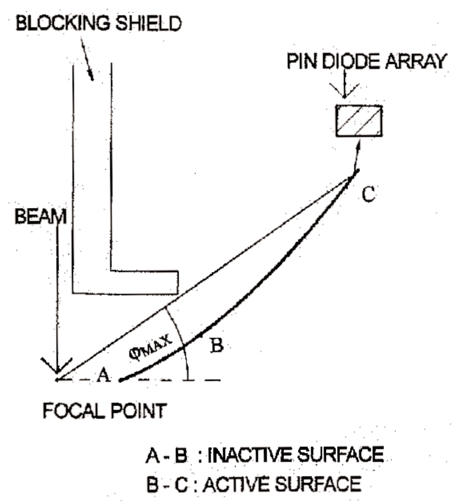

FIG. 1. Log spiral schematic.

Methods and Materials

A logarithmic spiral has the defining characteristic that all rays from a focal point meet the spiral at the same angle. In principle, one can therefore imagine a log spiral of revolution designed to monochromatize the fluorescence radiation emanating from a point focus in a fluorescence XAFS experiment. The ray bundle is concentrated into a region where photons can be detected by a non-energy-dispersive detector, such as an ion chamber or an array of (PIN) diodes. Because of a process recently developed in Russia whereby films of highly oriented pyrolytic graphite (HOPG) can be economically deposited on smooth surfaces,[3] such a monochromator becomes practical. The solid angle obtainable using a log spiral of revolution significantly exceeds that obtainable with practical Johann crystal arrangements or Johannson bent crystals. For our prototype LSR, we have chosen the shape for detection of Cr K_α radiation. Cr is an important environmental pollutant, and vanadium oxides doped with Cr are of particular interest for studies of metal-insulator transitions.[4] The characteristics of the HOPG deposition process are such that thin layers (factor of two of 0.2 mm) can be molded onto smooth surfaces and will maintain a highly oriented, or low mosaic spread, configuration. For Cr K_α radiation normally incident onto carbon, one absorption length is ~ 1 mm. However, in practice, the effective penetration distance d is related to Bragg angle and total path length through the carbon such that for an absorption length of 1 mm, one has an attenuation length normal to the reflecting surface, d, of 0.17 mm. Thus, the manufacturing process is capable of applying HOPG layers, which are highly oriented and of adequate thickness to give good intensity.

Figure 1 represents half of a two-dimensional slice through a log spiral of revolution with the Bragg angle chosen to reflect Cr fluorescence. The maximum solid angle depends on the minimum polar angle φ_{MIN} at which the active area, covered with HOPG, begins. For the log spiral we have tested, the active area begins at zero polar angle. For this choice of minimum polar angle, the maximum polar angle φ_{MAX} is about 30 degrees. This limit is set by the fact that the ray leaving the sample at zero polar angle and then diffracted by the HOPG is blocked by that HOPG surface, which diffracts the ~30 degree polar angle ray. This angular range, for a log spiral of revolution, corresponds to a solid angle of one third 2π or 17% of 4π. The distance from the focal point to point A in our prototype LSR is 1.5 cm. Our analysis shows that the prototype LSR described here satisfies the Bragg condition well for the 0.5-mm-diameter beam spot available at the insertion device line at PNC-CAT.[5]

Results

Tests were done on a series of $V_{(1-x)}Cr_x$ alloys[5] and a $Cr_{80}Mn_{20}$ alloy.[5,6] The alloys were melted in an arc melter and polished flat. We first obtained XAFS of the combined V and Cr absorption edges of a $V_{.99}Cr_{.01}$ sample, using an ion chamber and the X-11 beamline at the National Synchrotron Light Source (NSLS). We demonstrated that, for data obtained under these conditions, the XAFS oscillations of V were sufficiently intense at the Cr edge as to render the Cr XAFS unusable. We then obtained good quality Cr XAFS for $V_{(1-x)}Cr_x$ alloys for x values of .01, 0.1 and 0.5 using the LSR and the insertion device line at PNC-CAT. All data at the PNC-CAT line were obtained using an unfocused beam passing through a pinhole with 0.5 mm diameter and aligned onto the LSR

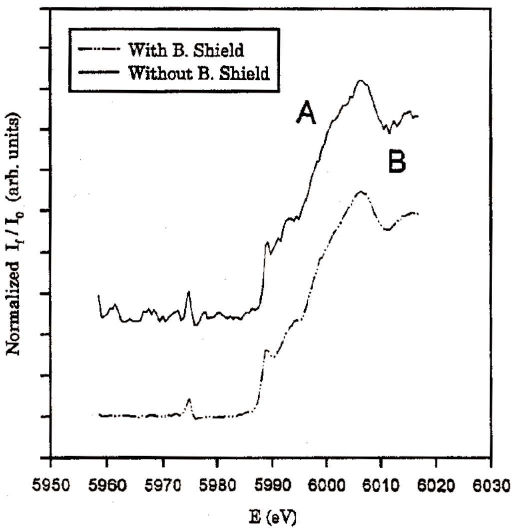

FIG. 2. Cr XAFS V.99Cr.01 - with shield (bottom), without shield (top).

sample focus. Figure 2 shows a comparison of Cr fluorescence from a 1% Cr in V alloy, background subtracted, for blocking shield in versus out conditions. Identical beam conditions at the APS are used, on identical samples, by averaging 10 scans. The data obtained with the blocking shield out results from fluorescence, some of which is monochromatized by the log spiral and some of which reaches the PIN diodes directly. The data obtained with the blocking shield in is due to fluorescence, all of which is monochromatized by the log spiral. It is evident that use of the log spiral to monochromatize the data results in a significant improvement in data quality and reduced distortion. Finally, we obtained data on a $Cr_{.80}Mn_{.20}$ sample at the focused X-16 line at the NSLS. Since the Mn K_β line does not interfere with the Cr K_α line, in principle, the LSR should be able to remove essentially all the Mn XAFS for this sample. We were able to tune the sample plane position so that we observed a "negative absorption jump" in the Cr edge at the position of the onset of the Mn edge. The negative edge jump is due to removal of photons from the Cr fluorescence channel due to the absorption of the Mn. We then detuned the sample plane position so as to deliberately allow some Mn fluorescence to be accepted. We were able by this means to nearly cancel the negative absorption, at least as could be seen by eye. These results are shown in references 5 and 6. Since the energy of the Mn edge is approximately that of scattered radiation if one excites the Cr edge at threshold, our experiments indicate that the LSR could be effective in removing scatter background in experiments involving dilute environmental samples.

Acknowledgments

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