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Performance and Improved Design of the Log Spiral of Revolution Monochromator

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Abstract. We show that, whereas the present log spiral of revolution monochromator works well for Cr edges of 2.8% Cr_2O_3 in a V_2O_3 matrix, the device transmits noticeable V extended structure in the case of 0.365% Cr_2O_3 . We demonstrate that the transmitted V extended structure is due to the V K_β line which is unresolved by the monochromator. It is suggested that this limitation may be overcome by designing a log spiral detector for the Cr K_β line rather than the Cr K_α line. Aspects of the design of this modified log spiral are discussed.

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INTRODUCTION

The log spiral of revolution (LSR), highly oriented graphite (HOPG) monochromator has proven to be a useful apparatus for certain specialized problems in fluorescence detection XAFS. The devices are useful for detecting the XAFS signal from an element of atomic number Z in a matrix of atomic number Z-1, but without count pile up problems associated with energy dispersive detectors [1, 2]. The solid angle can be quite large, about 50% of the available 2π steradian for the Cr K_α line, and the devices can use a full 1 mm x 1 mm spot size with a resolution for Cr of order 200 eV. We report here limitations on these devices as presently used and suggest improvements. As part of this manuscript, we also discuss for the first time certain aspects of LSR design that we have found important to consider.

We have successfully used a LSR designed for Ti K_α radiation to remove Sc extended structure for 5% Ti in a matrix containing concentrated Sc [3]. We observed that the Sc extended structure oscillations were evident at the Ti K edge if the sample was off the LSR focal point, but these oscillations were removed at optimal adjustment. Despite this success, two problems with the present LSR are the following: (1) If the focal point of the LSR were to be sufficiently far from the HOPG surface to allow use with the most common sample refrigerator systems, the area of the LSR would scale up to be prohibitively expensive. (2) The V K_β line is only 12 eV from the Cr K_α line. This energy separation cannot be resolved by HOPG, and therefore, if one uses a LSR designed for Cr K_α , the rejection of the V XAFS relative to the Cr signal is limited to the factor of ten difference in intensity between the V K_α and V K_β lines.

EXPERIMENTAL RESULTS

Recently, we obtained excellent XANES and XAFS spectra of Cr for 2.85% Cr_2O_3 in 97.7% V_2O_3 [4]. However, similarly obtained data on a sample of 0.365% Cr_2O_3 in a V_2O_3 matrix showed evidence for interference between the Cr K edge and the extended structure of the V_2O_3 matrix. In Fig. 1 we show the XAFS of Cr for 0.365% Cr_2O_3 in a 99.635% V_2O_3 matrix for two orientations of the polarization vector relative to the c axis. The total time spent in scanning this portion of a full EXAFS scan is not known precisely, but is less than half an hour. It appears that V extended structure oscillations do interfere with the Cr XANES for the LSR data for this sample. During a subsequent beam line run, we attempted to separate the V K_β and Cr K_α lines for the 0.365 % Cr sample by using a Johansson ground and bent LiF monochroma-
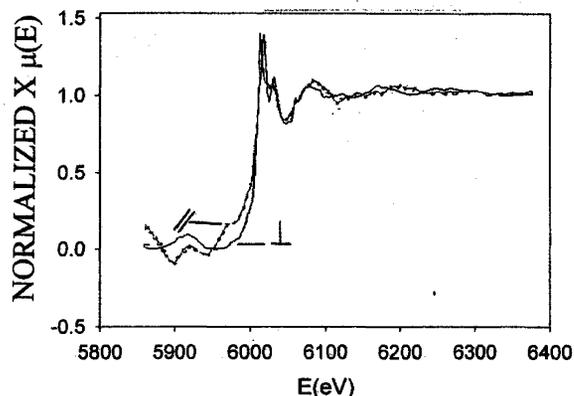
FIGURE 1. XAFS spectra of 0.365%Cr_2O_3 in V_2O_3 using LSR; E parallel and perpendicular to c axis.

tor adjusted to best transmit the Cr K_α line and reject the V K_β . This device is described by Cabri, et. al. [5] A set of XAFS data obtained using this monochromator is shown in Fig. 2.
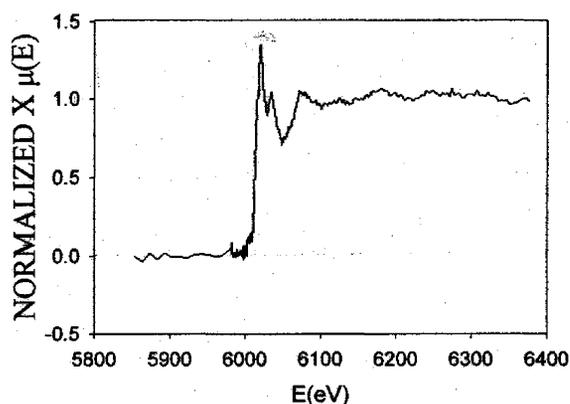

FIGURE 2. XAFS spectra of 0.365% Cr_2O_3 in V_2O_3 using the LiF monochromator.

In order to increase the energy resolution, the spot size on the sample was reduced with Kirkpatrick – Baez mirrors. Both sets of data, for Figs. 1 and 2, were obtained at the same 20 ID undulator beam line at the PNC /XOR of the APS. For the data of Fig. 2, about seven hours of scanning was required. (The c axis of the crystal was at an unknown orientation for this data.) The data in Fig. 2 is noisier than that of Fig. 1 despite the expenditure of more than fourteen times the beam time. On the other hand, the spurious pre-edge oscillations are almost removed in Fig. 2, demonstrating that indeed the pre edge structures in Fig. 1 are due to the contribution of V edge XAFS arising from the V K_β line fluorescence.

DESIGN CONSIDERATIONS

One of the constraints on the solid angle obtainable with the LSR is pointed out in reference 1. Consider a lowest polar angle φ_{min}. The corresponding beam incident on the HOPG, when reflected, is in turn blocked by the HOPG at the point where an incident fluorescent beam corresponding to some largest possible polar angle φ_{max} strikes the HOPG. For the LSR designed for any particular wavelength, one can show that there is a constant value of $\Delta\varphi = \varphi_{max} - \varphi_{min}$. We have shown that the expression for $\Delta\varphi$ is given by the equation below:

1. $2\beta \cos (\Delta\varphi) - \beta^2 \sin (\Delta\varphi) + \sin(\Delta\varphi) = 2\beta e^{-\beta\Delta\varphi}$

where $\beta = \cot \theta_{Bragg}$. The equation of a log spiral is the following:

2. $R = C e^{\beta\varphi}$

where R and φ are the polar distance and angle, and C is a scaling factor which is one centimeter for the data shown in Fig. 1. From equations (1) and (2) above, the solid angle in steradians and the covering area for particular values of C and φ_{min} can then be determined. In Fig. 3 is plotted the available solid angle and the covering area for the Cr K_α LSR as a function of φ_{min}, assuming C = 1 cm. The greatest expense in manufacturing these devices is the covering cost of the HOPG deposition. It is evident from Fig. 3 that the cost divided by solid angle increases dramatically with φ_{min} for a constant value of scaling factor.
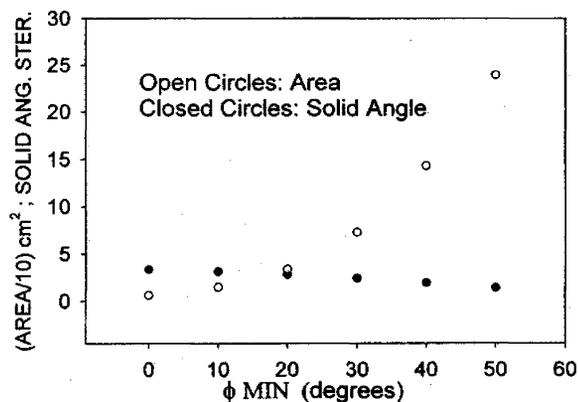

FIGURE 3. Area and solid angle versus minimum polar angle; LSR for Cr K_α.

We believe that one can remove the V K_β line from the Cr signal by utilizing a LSR designed for Cr K_β. The solid angle of the device is great enough to

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overcome the factor of ten loss of intensity relative to the Cr K_α. However, whereas the Cr K_α line is at an energy below the V K absorption edge, the Cr K_β line will be strongly absorbed by V. Therefore in this version of the LSR, it is desirable to increase φ_{min}, despite loss of solid angle, to lessen the self absorption of the Cr K_β line in the sample. In addition, if one increases φ_{min} to 50 degrees the distance between the LSR focus and the beam stop will be 1.1 cm using a scaling factor of S = 0.12 cm. The lessening of the scaling factor S, relative to the previous design value of approximately 1.0 centimeter, counteracts the increased covering area and increased cost associated with an increase in φ_{min}. By such a combination of parameters, however, one loses the advantage of the annular ion chamber detector, developed by Stern, for use with the LSR, which requires a scaling factor not much less than unity[3]. Without the annular ion chamber, an incident synchrotron beam angled, rather than normal to the sample, is necessary. We note also that the Cr K_β line will be close enough in energy to the elastically and inelastically scattered radiation that some scatter will not be removed by the LSR. The intensity of scattered radiation will be much less than that of the V K_β radiation, however, so that an advantage will still be gained by the envisioned approach. The energy dependence of the scatter background can be obtained by use of a pure V_2O_3 blank sample.

The proposed new geometry is illustrated in Fig. 4, and has the additional advantage of a 1.1cm offset from the focus to the HOPG covering.
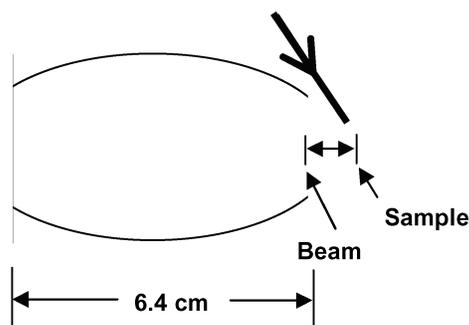

FIGURE 4. Schematic of LSR for Cr K_β. The distance from beam stop to sample focus is 1.1 cm.

Although a 1.1 cm offset of the focus from the HOPG will not be adequate for use with the most common commercial refrigerator systems, this offset is adequate for use with a commercial cryogenic stage cooled by liquid nitrogen, and such a cooling system is available at the PNC/XOR line. The temperature dependence of the XAFS for the $(Cr_2O_3)_x(V_2O_3)_{(100-x)}$ system can then be investigated. Finally, for the type of design shown in Fig. 4, the LSR Plexiglas HOPG substrate must be machined in two lengthwise cut sections that can be temporarily unbolted for application of the HOPG film.

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