

## Experimental Procedure and Performance of Double-Edge DXAFS at BL-5

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The double-edge DXAFS (DE-DXAFS) system was developed at BL-5 of SR Center. The DE-DXAFS apparatus covers the XANES measurements for 13 combinations of 3d transition elements by using two Si(111) polychromators with the different curvature. The way to choose a set of polychromators, the setup procedure of the DE-DXAFS apparatus, and the measured XANES spectra for the standard metal foils are discussed to judge the performance.

### 1. Introduction

Dispersive XAFS (DXAFS) is a powerful tool to observe dynamically the chemical reactions. We developed a new DXAFS apparatus (Fig. 1) consists of two polychromators and a photodiode array (PDA) detector with 2048 sensing elements to monitor the chemical state of two elements simultaneously. The design and concept of the double-edge DXAFS (DE-DXAFS) apparatus has been previously reported [1]. In this paper, the experimental procedure and its performance at BL-5 of SR Center are described.

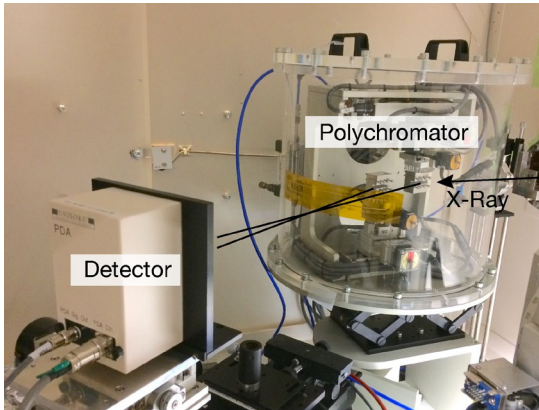


Fig. 1 Double-edge DXAFS apparatus of BL-5.

### 2. Selection of Polychromators

Roles of the polychromator (cylindrically bent crystal) in DXAFS are dispersion of X-ray wavelength and focusing the diffracted beam on the sample position. The incident angle of X-ray to the polychromator  $\theta$  is determined by the target X-ray energy, and the focal length  $q$  is given by the following equation,

$$q = \frac{Rp \sin \theta}{2p - R \sin \theta} \quad (1)$$

where  $p$  is the distance between the polychromator

and the light source, and  $R$  is the curvature radius of the polychromator. The angle  $\theta$  is equivalent to the Bragg angle in the case of the Bragg layout.

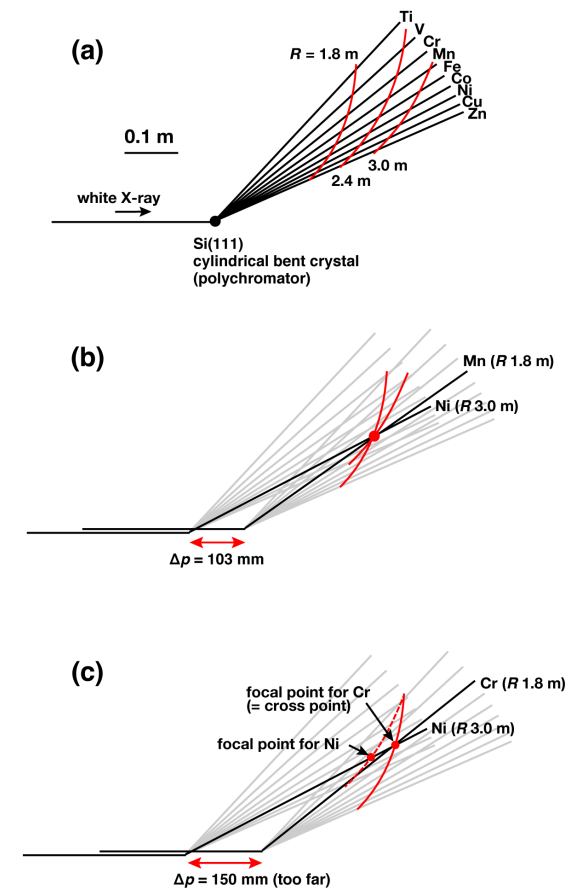


Fig. 2 X-Ray paths in DE-DXAFS arrangement. (a) Focal points (red lines) for three polychromators with the different curvature. In the DE-DXAFS arrangement with two polychromators, (b) a matched case for Mn and Ni K-edges and (c) a mismatched case for Cr and Ni K-edges.

The focal length is necessary to estimate the sample position for the standard DXAFS experiments using a single polychromator. For the DE-DXAFS experiment, the focal length of each polychromator is essential to achieve the proper setup. First, we should select curvatures of the polychromator for suitable and possible experimental layout.

Figure 2 is a schematic diagram of polychromatic X-rays reflected by two polychromators. Figure 2(a) shows X-ray paths and focal point for K edge of 3d transitional element for a Si(111) polychromator. The focal point moves to the downstream position with increasing  $R$  at a fixed Bragg angle. For a combination of two elements, Fig. 2(b) and 2(c) show the relationship of the focal points and the cross point of two polychromatic X-ray beams. The relative position of two polychromators are adjustable using their XY-stages. Figure 2(b) shows an ideal layout of two polychromator to overlap two

focal points for the Mn and Ni K edges. On the other hand, the case shown in Fig. 2(c) has two problems. One is a mismatch of two focal points, and the other problem is that the distance between two polychromators  $\Delta p$  is longer than the apparatus limit. For the present DE-DXAFS apparatus, the  $\Delta p$  value is limited from 45 mm to 130 mm because of the stage strokes and the conflict between the polychromators. Therefore, the combination of polychromators with  $R = 1.8$  m and 3.0 m is found to be unsuitable for the simultaneous measurement at the Cr and Ni K edges.

Table 1 lists the  $\Delta p$  values for the various combinations of the 3d transition elements to achieve the suitable layout as shown in Fig. 2(b). These values were calculated using  $R = 3.0$  m for lower Bragg angle and  $R = 1.8$  m for higher one. Table 2 shows the differences between the focal points for the same layout as Table 1. The value of zero means that two polychromatic X-rays have their focal

**Table 1.** Distances between two polychromators  $\Delta p$  (mm). The polychromator for elements shown in the first column is  $R = 3.0$  m, that for the first row is  $R = 1.8$  m. The acceptable  $\Delta p$  is from 45 mm to 130 mm.

	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>
<b>V</b>	55							
<b>Cr</b>	101	50						
<b>Mn</b>	149	89	46					
<b>Fe</b>	196	129	80	43				
<b>Co</b>	245	170	114	73	41			
<b>Ni</b>	295	212	150	103	67	40		
<b>Cu</b>	346	255	186	133	94	63	39	
<b>Zn</b>	399	300	224	166	121	87	60	39

**Table 2.** Differences between two focal points (mm) for the same layout for Table 1. The negative values mean that the focal point of lower angle element ( $R = 3.0$  m, shown in the first column) is located at more upstream side.

	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>
<b>V</b>	169							
<b>Cr</b>	77	151						
<b>Mn</b>	-10	70	135					
<b>Fe</b>	-92	-5	65	122				
<b>Co</b>	-171	-78	-2	59	109			
<b>Ni</b>	-247	-147	-66	0.2	54	99		
<b>Cu</b>	-322	-215	-127	-56	1.5	49	89	
<b>Zn</b>	-396	-281	-188	-112	-50	2	44	79

points at a same position. Although the combination of two polychromators with the fixed curvature cannot perfectly match the focal points for various elements, the difference of 10 mm, for example, is acceptable, because two focal points can be reasonably overlapped within their horizontal beam widths at the focal point.

The polychromator with an adjustable bending mechanism [2] is a solution to overcome these limitations. However, the bending mechanism is complex and too large to get the actual  $\Delta p$  value in the present DE-DXAFS apparatus. We have thus decided to use some polychromators with the fixed curvature. The polychromators of three different curvatures of  $R = 1.8, 2.4,$  and  $3.0$  m have been prepared, and they can cover the following 13 combinations of elements for their XANES measurements at the K edge.

[ $R = 1.8$  m and  $3.0$  m]

V-Fe, Cr-Co, Mn-Ni, Fe-Cu, Co-Zn

[ $R = 2.4$  m and  $3.0$  m]

Ti-V, V-Cr, Cr-Mn, Mn-Fe, Fe-Co, Co-Ni,

Ni-Cu, Cu-Zn

In considering the X-ray transmittance, the accessible lowest X-ray energy is about 5 keV, corresponding to the K edge of Ti and  $L_3$  edge of Cs. The highest X-ray energy is limited the light spectrum of the X-ray source of the SR Center. The measurement at about 10 keV (the K edge of Zn and The  $L_3$  edge of W) is the limitation to get the reasonable quality of the spectrum.

### 3. Setup Procedure of DE-DXAFS System

The setup of the DE-DXAFS system is carried out by the following procedure.

- (1) Determine the curvature of polychromators by referring the information given in section 2. Set the polychromator in DE-DXAFS chambers and flow the He gas.
- (2) Set  $\Delta p$  between the polychromators to the calculated value.
- (3) Adjust the rotation center of two polychromators to the center of each incident X-ray beam (normally width of 5 mm). Set  $\theta$  to 0 degree so as the passed direct beam to the maximum intensity.
- (4) Rotate the polychromators to the target Bragg angles. Move the detector to the direction of  $2\theta$ .
- (5) Using reference metal foils, observe the absorption edge and adjust  $\theta$  to become the absorption edge to the suitable position in the available energy window.
- (6) Scanning the distance between the polychromator and the PDA detector, determine the crossing point position of two polychromatic beams and estimate the beam size at that point.

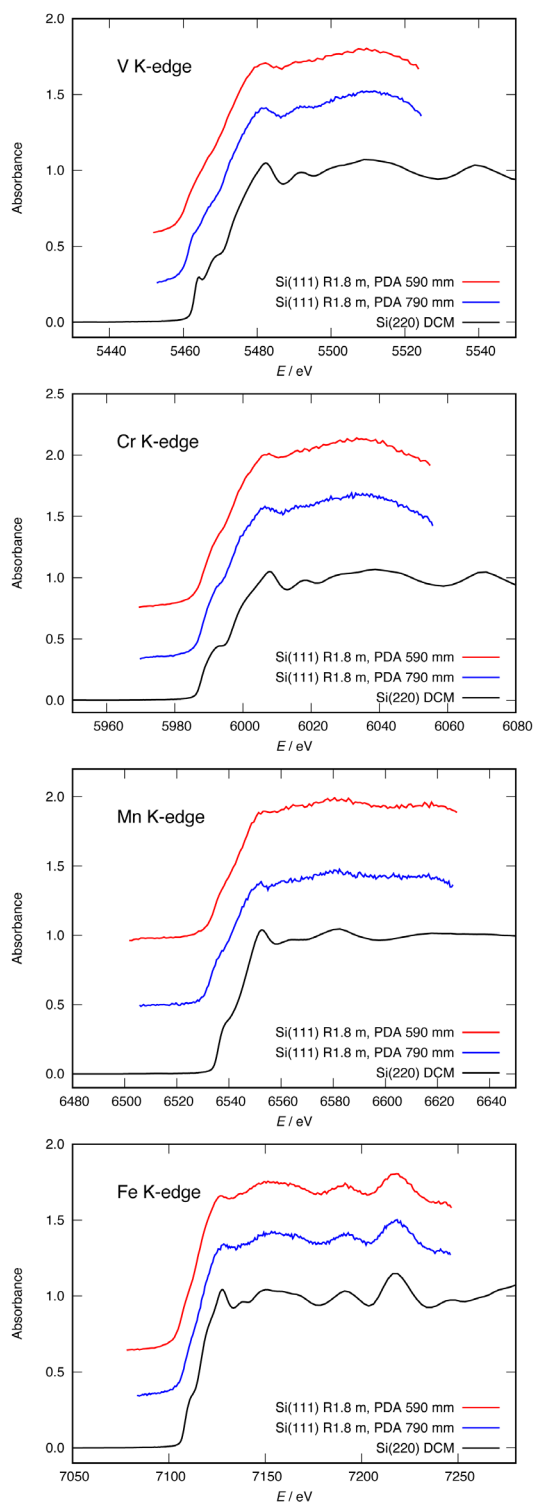
- (7) If necessary, precisely evaluate the focal points of two polychromatic beams. Place a slit in the white X-ray and observe the pathway of two polychromatic beams by moving the position of the PDA detector. Move the slit horizontally and get some beam pathways. The crossing point of the pathways corresponds to the focal point.
- (8) Place the PDA detector as far as possible from the polychromator within the limitation that two polychromatic beams are included in the observing area.
- (9) Set a sample to the crossing point position of two polychromatic beams. Put He paths around the sample. A suitable exposure time is estimated by measuring the spectra for the actual sample.

### 4. DXAFS Spectra for Reference Metal Foils

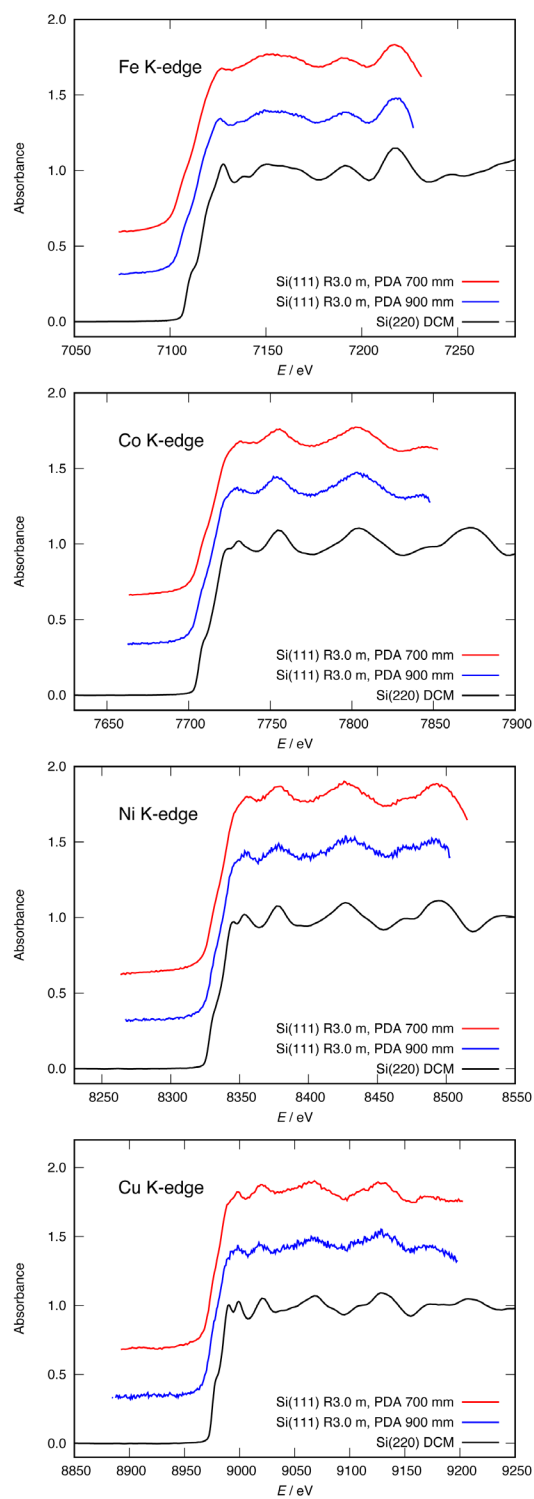
Figure 3 shows the XANES spectra of V, Cr, Mn, and Fe foils obtained using the polychromator with  $R = 1.8$  m and the exposure time of 10 s. Similarly, Fig. 4 shows the spectra of Fe, Co, Ni, and Cu foils using the polychromator with  $R = 3.0$  m. In these figures, the XANES spectra obtained at two detector positions from the polychromator (590 mm and 790 mm for Fig. 3, 700 mm and 900 mm for Fig. 4) are shown to compare together with that measured using a double crystal monochromator (DCM). The observed energy range is expanded when the detector approaches to the polychromator.

The energy resolution of the XANES spectrum is naturally lower than that measured with the DCM, because some factors of the DXAFS optics affect the energy resolution, *i.e.*, the horizontal width of the X-ray source, the spatial resolution of the detector element, the intrinsic angular width of the diffraction X-ray at the polychromator crystal, and the penetration depth of X-rays into the polychromator crystal. The spatial resolution of the detector is the most important factor to determine the energy resolution and is dependent on the detector position from the polychromator. For all absorption edges, the energy resolution is apparently improved by separating the PDA detector from the polychromator. However, the S/N ratio of the XANES spectrum decreases at the same time because of the decrease of the acceptance of the polychromatic X-ray for one detector pixel. As described later, the S/N ratio is recovered by the elongation of the exposure time and/or by the increase in the number of repetitions to accumulate the obtained data.

For all XANES spectra of the reference metal foils, the spectral fine structure (the top, the shoulder, and the bottom of the oscillation) is perfectly in agreement with that of the corresponding spectrum measured with the DCM by the conventional step-scanning procedure. This fact demonstrates that the cylindrical curvature is not deformed for the



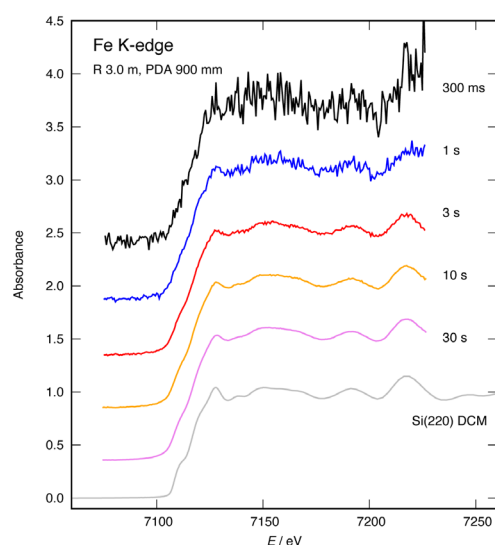
**Fig. 3** XANES spectra for reference metal foils obtained using a Si(111) polychromator with  $R = 1.8$  m. The distance between the polychromator and the detector was set to 590 mm (red line) and 790 mm (blue line). Exposure time was 10 s.



**Fig. 4** XANES spectra for reference metal foils obtained using a Si(111) polychromator with  $R = 3.0$  m. The distance between the polychromator and the detector was set to 700 mm (red line) and 900 mm (blue line). Exposure time was 10 s.

prepared polychromators. The characteristic spectral features at the absorption edge are correctly reproduced in the XANES spectra obtained using the DE-DXAFS apparatus.

Figure 5 shows the XANES spectra of Fe foil obtained by changing the exposure time from 300 ms to 30 s. The absorption edge can be observed by the single-shot measurement with the exposure time less than 1 s, and it is reasonable to adjust the DE-DXAFS system. The measurement under the longer exposure time such as 3 s has a sufficient quality to analyze the XANES spectrum. In addition to the



**Fig. 5** XANES spectra of Fe foil obtained at various exposure times.

elongation of the exposure time, the increase in the number of the accumulation time also improves the S/N ratio. However, the quality of the XANES spectrum measured by a single shot with the exposure time of 30 s exceeds the corresponding one obtained by the accumulation of 30 spectra measured with the exposure time of 1 s, because the scanning noise of the PDA detector is contained for all scans with almost the constant level, which is emphasized by the accumulation.

## 5. Conclusion

The experimental procedure and the quality of XANES spectra for reference metal foils were presented to help preparing the DE-DXAFS system. The possible combinations of the target elements are essential to the further application of the DE-DXAFS technique, and they can expand by adding the polychromator with the other curvatures. The time resolution is also an important factor in the DXAFS experiment. The exposure time of 3 s for the XANES measurement is sufficiently short in comparison to

the standard measurement time by the conventional scanning method at the SR Center. It should be also noted that the DE-DXAFS apparatus provides the simultaneous measurements of two XANES spectra at the different absorption edges. The present spectral quality indicates the valuable possibility to analyze dynamically the chemical states of two elements in the functional materials.

## References

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- [2] K. Kato, T. Irie, T. Uruga, K. Uera, and M. Kawase, *J. Phys. Conf. Ser.*, **2016**, *712*, 012025.