

Use of the spindle stage for orientation of single crystals for microXAS: Isotropy and anisotropy in Fe-XANES spectra

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ABSTRACT

A new method has been developed to orient 50–100 μm size single crystals to obtain XANES or EXAFS spectra along any crystallographic orientation relative to a polarized synchrotron X-ray beam. The method uses a modified spindle stage and an X-ray goniometer head to hold a crystal and the glass fiber on which it is mounted. The orientation of the crystallographic axes within the crystal can be determined by X-ray diffraction in all cases or with the use of the polarizing light microscope if the minerals are biaxial. Once an optical orientation direction has been located, it can be oriented parallel to the polarization direction of the synchrotron source for spectral acquisition.

Mineral samples representing the three optical classes (i.e., isotropic, uniaxial, and biaxial) were oriented along their *a*, *b*, and *c* crystallographic axes, and Fe-XANES spectra were obtained. In all cases the interactions of polarized X-rays with the crystal structures are analogous to the interactions of visible light (e.g., as represented by refractive index). For the isotropic almandine sample the XANES spectra were similar at all orientations. For the uniaxial buergerite and scapolite samples the spectra were similar along the *a* and *b* axes and different along *c*. A detailed set of spectra acquired at multiple (known) optical orientations in the scapolite crystal demonstrates that spectral features vary in intensity as a function of orientation, with maxima and minima when the X-rays are polarized along optical orientations. For the biaxial fayalite sample, the XANES spectra differed along all three crystallographic axes, as expected by analogy to optical properties.

INTRODUCTION

Studies of minerals using polarized high energy X-rays from a synchrotron have long had the potential to provide information on directional bonding (Brown et al. 1988) but were hampered by the historically large beam sizes (>100 μm) relative to the size of available, optically homogeneous single mineral crystals. Furthermore, techniques for aligning single-crystal samples with respect to their crystallographic directions were not widely practiced. Thus, few researchers have had the opportunity to take full advantage of the polarization capability of most synchrotron facilities. In this letter, we show that application of the spindle stage to the synchrotron allows this potential to be fulfilled.

The technique is part of a larger, ongoing project by our group to characterize the extent of variation in Fe-XANES spectra of rock-forming minerals as a function of both composition and orientation (e.g., Delaney et al. 1996, 1998; Dyar et al. 1998a, 2001). The method described here was used to collect polarized XANES spectra along crystallographic orientations of a series of Fe-rich rock-forming minerals in the summer of

2001. Preliminary results from this work are presented in Gunter et al. (2002). The goal of this project was to develop a method to mount and orient small single crystals, 50–100 μm or less, so as to collect XANES spectra with the beam polarized along different directions within the same single crystal.

EXPERIMENTAL METHODS

Four mineral samples were chosen based on their optical classes: (1) almandine from Fort Wrangell, Alaska (Fe^{2+} garnet), which is optically isotropic; (2) buergerite from Mexquitic, San Luis Potosi, Mexico (Fe^{3+} tourmaline), and scapolite, which are optically uniaxial; and (3) Rockport fayalite (Fe^{2+} olivine), which is optically biaxial. The garnet, tourmaline, and olivine samples were previously studied by MDD and coworkers using Mössbauer spectroscopy, so they were already well characterized; their chemical analyses are reported in Dyar (1984), Dyar et al. (1998b), and Schaefer (1985), respectively. The scapolite sample was chosen for this study from M.E.G.'s personal collection; its composition is $\text{Na}_{2.79}\text{Ca}_{1.04}\text{K}_{0.27}\text{Fe}_{0.01}\text{Al}_{3.83}\text{Si}_{8.17}\text{O}_{24}(\text{SO}_{0.05}\text{Cl}_{0.91})$ (normalized to Si + Al = 12 cations, with no OH assumed in the analysis; JSD microanalysis at Rutgers University using standard operating conditions, cf. Dyar et al. 2002). Selection of crystals was constrained by the need for

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untwinned single crystals without inclusions with sizes $>30\ \mu\text{m}$ (Table 1).

The single crystals were mounted on $\sim 50\ \mu\text{m}$ diameter glass fibers with clear fingernail polish. Each sample was then mounted on its own goniometer head, which was then attached to an X-ray diffractometer or a microscope spindle stage, so that the orientation of the crystallographic axes could be determined.

The spindle stage methods refined by Bloss (1981) for orientation and optical data collection were modified for this study. Two methods, described in Gunter and Twamley (2001), were used to orient the crystals: single-crystal X-ray diffraction (XRD) and the polarizing light microscope (PLM). For minerals belonging to the isotropic and uniaxial optical classes (i.e., the isometric and tetragonal and hexagonal crystal systems, respectively), the XRD method must be used. XRD data are collected and used to determine the orientation matrix for the reciprocal crystallographic axes, (a^* , b^* , c^*), from which the direct crystallographic axes (a , b , c) can be calculated. Optically biaxial minerals—those belonging to the orthorhombic, monoclinic, or triclinic crystal systems—can be oriented either by XRD or by PLM. With the PLM, the orientation of the optical indicatrix can be found with the computer program EXCALIBR (Bloss 1981; Gunter and Twamley 2001). With either method, the end result is that the crystallographic axes of each crystal are identified as unique positions on the goniometer head and spindle stage apparatus, which can then be transferred from the optical microscope or X-ray diffractometer to the synchrotron beamline. Any crystallographic direction can be made to coincide with the incident polarized X-ray beam of the synchrotron source.

XANES measurements were made at the synchrotron X-ray microprobe (beamline X26A at the National Synchrotron Light Source of Brookhaven National Laboratory, New York). A special beam geometry was used (Fig. 1). A spindle stage was mounted with the plane of rotation perpendicular to the path of the beam. This geometry is similar to that used in normal spindle stage measurements when the spindle stage is mounted on to a microscope stage (Bloss 1981; Gunter and Twamley 2001). This geometry allowed spectra to be acquired with the incident X-ray beam polarized directly parallel to the crystallographic axes, or parallel to any other direction.

The structure of the FeK-absorption edge was scanned in the near edge region. Incident beam energies from 50 eV below the main absorption edge energy (7111 eV for Fe) to about 60 eV above the main edge were used. Using mutually orthogonal Kirkpatrick-Baez mirrors, the beam was focused to a size of $20 \times 30\ \mu\text{m}$. The X-ray sampling depth is large, but $>90\%$ of the signal comes from the top $10\ \mu\text{m}$ of the sample. The incident beam energy was controlled by a Si(111) channel cut monochromator. The incident X-ray energy was incremented by 0.3 eV intervals over the most critical energy range of -10 to $+20$ eV relative to the main absorption energy. This provided detailed mapping of the relationship between the pre-edge peak and the main absorption edge. Between -50 and -10 eV and above $+20$ eV, the X-ray energy was incremented by larger intervals to reduce data collection times. Each energy interval was counted between 5 and 20 live seconds (depending on the intensity of the main edge signal) for a total XANES

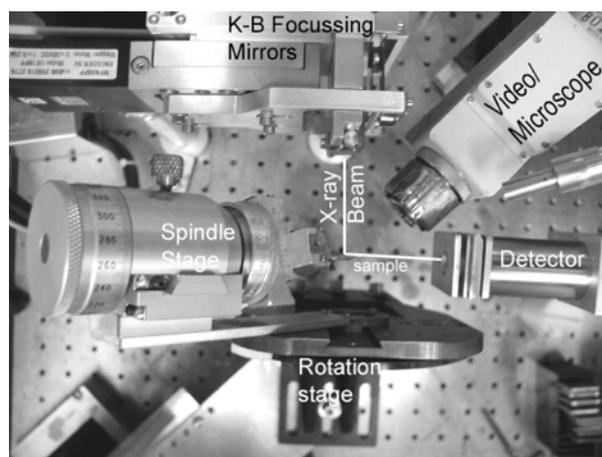


FIGURE 1. Plan-view photograph of experimental set-up at beamline X26A, National Synchrotron Light Source, Brookhaven National Laboratory. The photo shows a spindle stage and associated goniometer head with affixed single crystal, mounted in the X-ray beam path. The spindle stage is in turn mounted on a rotating stage similar to that found on a polarizing light microscope. Also shown are the incident X-ray beam path and the beam path into the detector (in white).

TABLE 1. Sizes of crystals

Mineral	Crystal dimensions
almandine	$60 \times 110 \times 120\ \mu\text{m}$
buergerite	$35 \times 40 \times 55\ \mu\text{m}$
scapolite	$70 \times 95 \times 105\ \mu\text{m}$
fayalite	$60 \times 70 \times 90\ \mu\text{m}$

spectrum acquisition time of about 20–30 minutes. Counting times were adjusted to obtain at least 10^4 counts per energy step at energies greater than the absorption edge.

Data were collected in fluorescence mode for this study because the measurements were done with a micro-beam in order to simulate conditions for analysis of minerals in thin section. Although simultaneous transmission mode spectra could also have been acquired, it is unclear (1) if count rates would have been high enough for the transmission spectra to be viable, and (2) how variations in sample thickness for the same crystal acquired at various orientations would have affected our results. In future work we plan to collect simultaneous transmission and fluorescence mode spectra using crystals ground to spheres so that sample thickness will be constant. Such work was obviously beyond the scope of the current, exploratory project.

The measured FeK α fluorescence line intensities were normalized to the ion chamber current and corrected for dead time. For this study, the data for each crystal were normalized to the same number of counts (Fig. 2). This step was necessary to highlight the similarities and differences among spectra acquired for different orientations of the same sample. Unfortunately it also obscures the real first-order differences in peak intensities that occur due to the transitions being studied here. However, because the crystals used in this study were angular, the path length followed by the X-ray beam and the resultant

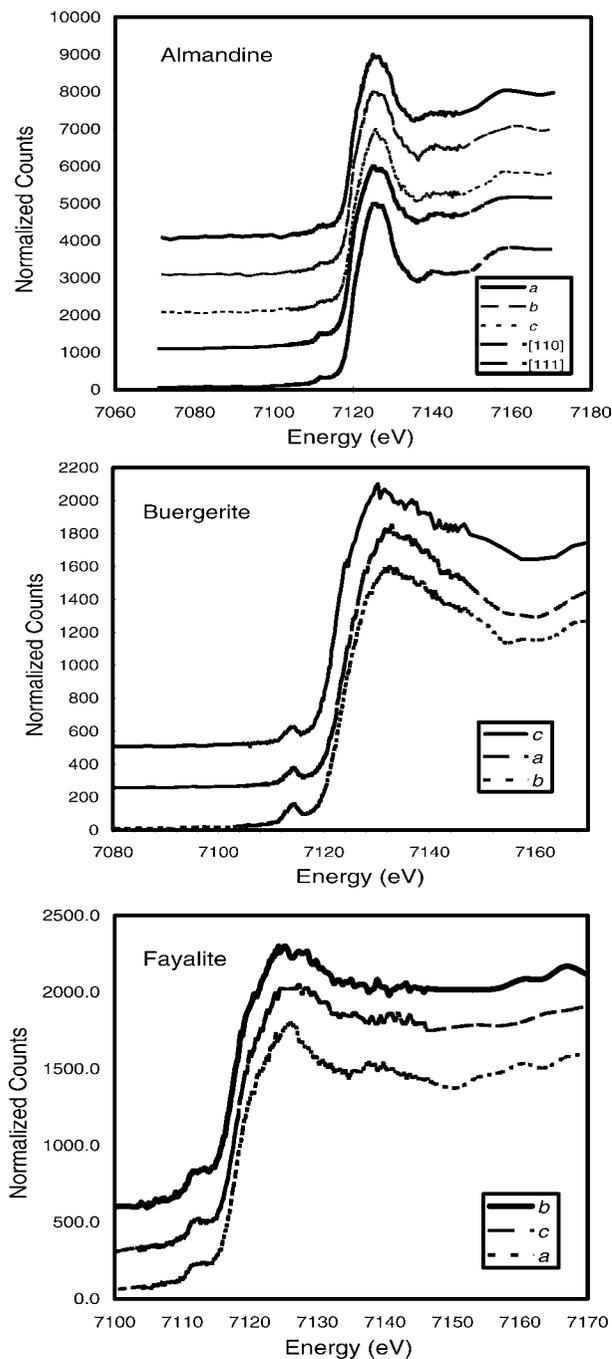


FIGURE 2. XANES spectra collected for an isotropic mineral (almandine), a uniaxial mineral (buergerite), and a biaxial mineral (fayalite) with the X-ray beam polarized along major crystallographic axes. For the garnet, all five spectra are similar. For the tourmaline, the *a* and *b* spectra are predictably similar and distinct from *c*, and for olivine, each spectrum is unique.

fluorescing X-rays was not always the same at different orientations, so different amounts of self-absorption and excitation are evident in the spectra unless the data are normalized. Although this is probably a second-order effect, it justifies displaying the spectra in this paper in a normalized format. We

note that future studies of this type would do well to use spherical grains (advice we intend to follow ourselves!).

The measured FeK α fluorescence line intensities were normalized to the ion chamber current and corrected for dead time. A computer program was written for data analysis to extract the pre-edge from the background and determine the centroid of the pre-edge so comparisons could be made among spectra. The program requires input of two points; one of which has to be on the low side of the peak of interest and the other on the high side of the peak. This part of the spectrum is fitted to a second order polynomial (background) plus a Gaussian function (peak). The centroid of the peak is reproducible to within 1% if the peak of interest is the highest in the chosen part of the spectrum. A fit of a Lorentzian function did not give as good a result as that of the Gaussian function. Further details of the iterative fitting process and its effect on peak centroid positions are given in Bajt et al. (1994). In brief, at least five independent fits to each spectrum were made and the results were averaged to result in a final peak position. Typical standard deviations on these fits were <0.1 eV, so the baseline subtraction approach and fitting method do not appear to greatly affect the fitted value of the peak centroid. Absolute peak energies were determined by correcting all spectra relative to the position of features in the spectrum of magnetite. For additional details, see Delaney et al. (1996).

RESULTS AND DISCUSSION

Our working hypothesis was that the polarized X-rays would interact with the minerals in a qualitatively similar manner to visible light. This assumption was made based on the symmetry rules that govern the interaction of visible light with crystalline materials, and through analogy with the optical indicatrix. It was also assumed that X-rays, being one form of electromagnetic radiation, would behave in a similar manner to other forms of electromagnetic radiation such as visible light. For example, in isotropic minerals belonging to the isometric crystal system, the XANES spectra should be the same regardless of orientation. For uniaxial minerals belonging to the hexagonal and tetragonal crystal systems, the XANES spectra would be similar along the symmetrically related *a* and *b* crystallographic axes and differ from those along the *c* axes. Lastly, for biaxial minerals belonging to the orthorhombic, monoclinic, and triclinic crystal systems, XANES spectra would be distinctive along the three crystallographic directions, *a*, *b*, and *c*.

Figure 2 shows the three sets of XANES spectra collected for the almandine, buergerite, and fayalite samples. Based on observation of the spectra our assumptions are correct: the XANES spectra are a function of orientation in anisotropic minerals, and are thus symmetry-controlled. For the almandine sample, the spectra are similar along the *a*, *b*, and *c* directions, as well as along the [110] and [111] directions; all five main-edge spectra are identical within our current analytical resolution (Fig. 2).

For the uniaxial crystals, the spectra along the *a* and *b* axes are similar (Figs. 2 and 3). These directions would correspond to the ω refractive index. These spectra differ from those acquired with the beam polarized along *c*, which would correspond to the ϵ refractive index value.

More specifically, in buergerite the maxima of the main edges are at ~ 7132.4 , ~ 7132.8 , and ~ 7129.8 eV for the *a*, *b*, and *c* orientations; this peak shift is well within our experimental resolution. The pre-edge centroids lie at ~ 7113.90 , ~ 7113.84 , and ~ 7113.72 eV for the *a*, *b*, and *c* orientations, so there is a suggestion that spectra acquired with the *c* orientation are shifted to lower energies. In scapolite, the pre-edge peaks are identical within our resolution: maxima occur at ~ 7114.0 eV (for *a*), ~ 7112.6 and ~ 7113.0 eV (*b*), and ~ 7113.5 eV (*c*). However, the main edge features in scapolite change dramatically between the *a/b* orientations, which are the same in a uniaxial system, and the *c* orientation. In particular, we noted that there is a conspicuous band at ~ 7126 eV that is present in the *c* spectra and absent in the *a* spectrum.

Therefore, for the scapolite sample we also collected spectra at 15° increments in the *a-c* plane. These spectra (Fig. 3) differ from each other and would represent the ϵ' values in the uniaxial optical indicatrix. The intensity of each of the many overlapping peaks varies systematically as a function of orientation. As noted by Libowitzky and Rossman (1996), these intensities can be mathematically determined once the maximum and minimum for each peak (corresponding to the extinction positions in visible light) are known. Once these two points are known, every other point can be computed from the physical principles that govern the interaction of polarized waves with crystals. To check for experimental problems, we compared the experimentally determined intensity of the prominent 7126 eV peak in the scapolite spectra (Table 2) with the theoretically predicted intensities based on our peak maxima and minima. There were no deviations from a smooth curve (such as minor secondary lobes), suggesting that the experimental data are of high quality.

Lastly for biaxial fayalite, the spectra differ along the *a*, *b*, and *c* crystallographic axes, as would be expected. The pre-edge peak for the *c* orientation has a distinctive narrow shape relative to the pre-edges of *a* and *b*. In the main-edge region, the *a* spectrum has a prominent sharp peak around ~ 7126 eV, which is shifted to ~ 7127 eV in the *c* orientation; the *b* orientation has two peaks at ~ 7125 and ~ 7128 eV. However, these main-edge features are muted in fayalite because its high FeO content ($\sim 69\%$) results in a very strong "dampening" influence of X-ray self-absorption. Comparable spectra for a low-Fe olivine (1–5% FeO) should show more dramatic differences as a function of orientation, and use of a higher resolution crystal may lead to better understanding of the pre-edge features. Variation of the relative height of the first main-edge peak would be expected to affect the apparent pre-edge peak positions used for other compositional measurements.

Prior researchers have postulated that XANES spectra may be orientationally dependent and provided demonstrations for structures with strong site asymmetry (e.g., gillespite, Waychunas and Brown 1990; PbTiO₃, Kraizman et al. 1995). Our work confirms that these spectral shapes in minerals are indeed a function of orientation. The X-ray indicatrix of each crystal follows the basic rules of optical indicatrix symmetry for the appropriate crystal system. This variation in spectra must be taken into account when quantitative interpretations are applied. We intend to use this new method in higher resolution

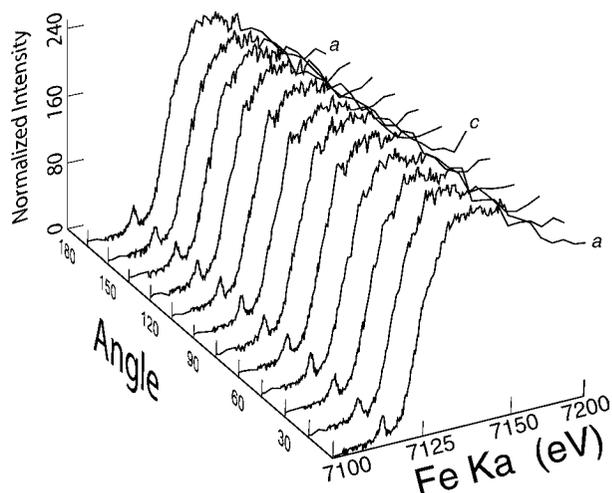


FIGURE 3. XANES spectra of a single scapolite crystal systematically acquired at 15° increments in the *a-c* plane, starting at $a = 0^\circ$ and $a = 180^\circ$ and $c = 90^\circ$. Note the appearance of the small shoulder on the main edge increasing in intensity from *a* to *c* (i.e., $0-90^\circ$), and then its symmetrical disappearance going from *c* to *a* (i.e., $90-180^\circ$). Data intensities are arbitrarily normalized to a maximum of 250 counts to factor out differences in the X-ray path length. Note the change in intensity around, for example, 7126 eV.

TABLE 2. Intensity of the 7126 eV peak in scapolite

Rotation angle ($a = 0^\circ$ and $c = 90^\circ$) as in Fig. 3	Peak Intensity (in normalized counts)
0	179.28
15	185.28
30	192.97
45	195.34
60	201.19
75	202.19
90	208.75
105	203.42
120	206.69
135	198.07
150	181.41
165	174.25

studies of lower Fe content specimens of key anisotropic minerals using spherical single crystals.

ACKNOWLEDGMENTS

This work was supported by NSF grants EAR-9806182, EAR-9909587, EAR-9909588, NAG5-8820, NAG5-9528, NAG5-10424, and DOE-Geosciences DE-FG02-92ER14244. We acknowledge helpful discussions with M.L. Brigatti and A. Mottana regarding orientation problems with XANES work, G. Rossman for ever-thoughtful spectroscopic input, two anonymous reviewers for helpful reviews, and C. Francis and the Harvard Mineralogical Museum for the use of the buergerite (no. 43293).

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MANUSCRIPT RECEIVED MARCH 11, 2002

MANUSCRIPT ACCEPTED MAY 13, 2002

MANUSCRIPT HANDLED BY LEE A. GROAT