

Development of X-ray photoemission electron microscopy (X-PEEM) at the SRS

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The use of synchrotron radiation sources for X-ray spectroscopy is a well known and developed field. The majority of applications, however, have been limited to studies of materials containing only a single phase of the element of interest. Owing to limited availability of suitable instrumentation, the study of materials comprising intergrowths of different phases has presented difficulties in analysis. The majority of natural materials, including mineralogical samples, fall into this category. However, by applying the technique of photoemission electron microscopy (PEEM) to view the X-ray stimulated photoemission generated at an absorption edge, micro-area-selectable spectroscopy becomes possible. An instrument for X-ray PEEM (X-PEEM) is being developed at the Daresbury SRS and this paper shows how it can be used to obtain characteristic *L*-edge XANES spectra from finely intergrown iron oxide minerals.

Keywords: X-PEEM; mineralogy; XANES.

1. Introduction

It is well established that the use of X-ray absorption spectroscopy (XAS) can provide detailed chemical-state information from selected elements of interest within a sample. By using this technique in the sub-1 KeV energy range to collect $2p$ ($L_{2,3}$) spectra from the $3d$ transition metals, its effectiveness as a symmetry and valence-selective probe for mineralogical studies has been clearly demonstrated (Cressey *et al.*, 1993; Henderson *et al.*, 1995; Schofield *et al.*, 1995). Combining the experimentally derived spectra with theory (van der Laan & Kirkman, 1992) permits the interpretation of and yields analysis of the valence states, site symmetries and crystal-field parameters of the metal components.

In principle, multiple valence states within a material can be characterized from a single *L*-edge XAS spectrum. However, as area selectivity is not possible with the standard technique, this is limited to single-phase samples. The majority of real samples, and in particular minerals, contain many impurities intergrown on a variety of microscales which contribute their own spectra to that recorded.

Photoemission electron microscopy (PEEM) is a technique which has been used by the surface-science community to image the changes at a surface as a result of chemical reactions (*e.g.* Engel *et al.*, 1991; Ehsasi, 1994; Shidahara *et al.*, 1996). The standard method uses a laboratory UV source to excite photo-

electrons from areas with work functions lower than the energy of the lamp. X-ray stimulated photoemission electron microscopy (X-PEEM) (Tonner & Harp, 1988) is a new development of this technique and uses the intense monochromatic X-ray flux available from a synchrotron to excite photoelectrons from specific absorption edges. If X-PEEM is used to collect images from a multi-phase specimen while the energy of the incident X-ray beam is scanned across an absorption edge, then XAS spectra for the different phases can be extracted from the relevant areas in the resulting image set. The scope for measuring area-selectable XANES from inhomogeneous materials such as minerals, without the need to isolate physically the different phases first, makes X-PEEM a potentially powerful tool for many branches of materials science.

2. The instrument

We are developing an X-PEEM instrument for use on beamline 5U1 (Mythen *et al.*, 1992) at the Daresbury SRS. This follows a conventional design and comprises an electron-optics stage with objective and projector electrostatic lenses followed by an image intensifier using a microchannel plate (MCP) chevron and a phosphor screen. The image on the phosphor screen is viewed by a CCD camera and recorded using a frame-grabber card in a PC. The data-acquisition software on the PC communicates with the PC that drives the beamline monochromator *via* an RS232 connection. Sequences of images, each with the monochromator energy of the frame recorded in the header, are acquired as the monochromator is scanned through an edge of interest.

Accurate alignment of the sample within the X-PEEM instrument is critical in order to obtain focused and undistorted images. The sample is mounted on a manual manipulator which allows the position to be adjusted in three orthogonal lateral directions and about two rotational axes. The axes of rotation should be coincident with the sample surface as any slight misalignment here leads to difficulties in obtaining clear images, a consequence of the interdependence of all the degrees of freedom. We have recently added a 50 μm pinhole at the midpoint between the two electron lenses to minimize aberrations. Correct positioning of this pinhole is provided by external micrometer drives which add two further degrees of freedom to the setting up of the instrument.

We generally operate our X-PEEM instrument with lens and sample potentials of between 10 and 15 kV. Tests performed using fine nickel meshes have indicated a limiting spatial resolution of approximately 2 μm and a field of view of between 500 and 200 μm , depending on the projection magnification used. This resolution and field of view are suitable for the study of many mineralogical specimens.

3. Sample preparation

Minerals present particular difficulties as samples for X-PEEM. Many of them possess poor electrical conductivity and the surface charging which results prevents photoelectrons from being extracted by the X-PEEM instrument. The images obtained in these cases are therefore dim and can exhibit poor contrast. A common problem occurs in minerals which have highly conducting (relative to the matrix) intergrowths. We found that for these materials, little could be seen by X-PEEM in the regions between the intergrowths as localized surface charging binds

many photoelectrons to the sample. Only a few high-energy electrons are able to escape directly and consequently these areas remain dark in X-PEEM images. Although it is possible to extract spectra from these areas, the spectra are noisy because of the low photoelectron flux. Many of the photoelectrons produced in the insulating matrix migrate instead to the more conductive intergrowths and are then extracted by the X-PEEM instrument. Therefore, area-selected XANES from the intergrowths tend to combine spectra of the intergrowth and the matrix. To overcome this problem, we have experimented with applying different conductive coatings to mineral samples and have obtained good results using thin evaporated gold layers. Even nominally conductive minerals such as magnetite provide more stable images if they have been so treated.

Surface topography can yield similar effects. To prevent field emissions from high points or sharp edges, the samples must be polished flat. This is a standard mineralogical sample-preparation technique and is required for complimentary measurements made off-line using scanning electron microscopy (SEM). Owing to differences in the mechanical hardness of the component phases, there will generally be some residual topographic effects. The most obvious effect is the shadowing of low-lying regions and increased photoelectron production from their illuminated walls. A secondary effect is increased emission from any raised areas. This latter problem is evident even after coating, although the addition of a conductive layer does reduce the effect significantly. Lateral electron drift across the sample is reduced by increasing the acceleration voltage from the sample to the X-PEEM instrument. Minerals are also frequently full of cracks and holes which can trap electrons, which can accumulate before discharging. However, minor cracks in minerals do not seem to present problems, provided that the mineral surface is conductive.

4. X-PEEM measurements of magnetite

Because of the large number of degrees of freedom available in correctly positioning a sample with respect to the X-PEEM instrument, it is useful to be able to refer to identifiable features on its surface. Prior use of SEM is beneficial in identifying areas of interest. Fig. 1 shows a backscattered electron (BSE) image, of a magnetite surface cut and polished parallel to (111) and shows natural 'rusting' products of magnetite (Fe_3O_4). Combined information from X-ray powder diffraction, chemical analysis using an electron microprobe and the grey-level contrast in the BSE image indicates that three different iron oxide phases are present, intergrown on a micron scale. The intermediate grey is hematite (Fe_2O_3), the dark grey is goethite ($\text{FeO}\cdot\text{OH}$) and the lightest grey is the magnetite host. Oxidation of the magnetite to hematite has occurred along (111) planes of the magnetite; this oxidation is visible at the (111) polished surface of the magnetite as a series of intersecting thin lines of hematite in a triangular array parallel to the (111) planes of the magnetite. In places this alteration is more extensive and solid blocks of hematite have formed from the growing layers. The magnetite structure consists of cubic close-packed O atoms and interstitial octahedral and tetrahedral cations; the O-atom close-packed planes are parallel to (111). In the alteration texture the (111) planes of the magnetite are parallel to the (0001) close-packed O-atom planes of the hematite oxidation product. In hematite, the (0001) O-atom planes are stacked to form a hexagonal-close-packed structure. The goethite appears to fill dissolution voids in the magnetite and was probably precipitated later from solution.

We have used X-PEEM to view this same area and obtain Fe $L_{2,3}$ edge spectra from selected regions within it. These XANES spectra contain information about the valence states and site symmetries of the iron in the individual phases of the intergrowth. Fig. 2 shows the spectra obtained from the three key iron phases in this sample. The hematite and goethite spectra are both characteristic of octahedrally coordinated Fe^{3+} ; the subtle differences between these spectra correspond to the slightly different octahedral-site distortions in these two phases. The magnetite spectrum reflects the hybrid Fe electronic states resulting from delocalized electron hopping between Fe^{3+} and Fe^{2+} in adjacent edge-shared octahedral sites, plus the signature from tetrahedrally coordinated Fe^{3+} .

A recent publication by Droubay *et al.* (1997) demonstrates further the effectiveness of the X-PEEM technique for isolating the Fe-centred chemistry of another iron-rich mineral, ilmenite (FeTiO_3), intergrown with magnetite. The ability to extract area-selected XANES from an X-PEEM image set can be used as a contrast mechanism to highlight particular phases within the field of view. From Fig. 2, a difference

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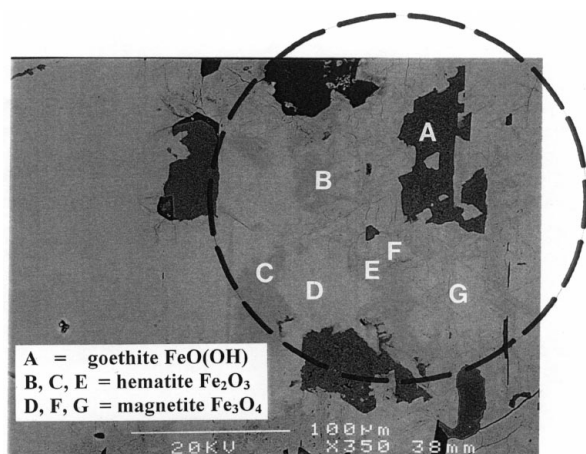


Figure 1

Backscattered electron image obtained by SEM of a magnetite sample subsequently imaged using X-PEEM.

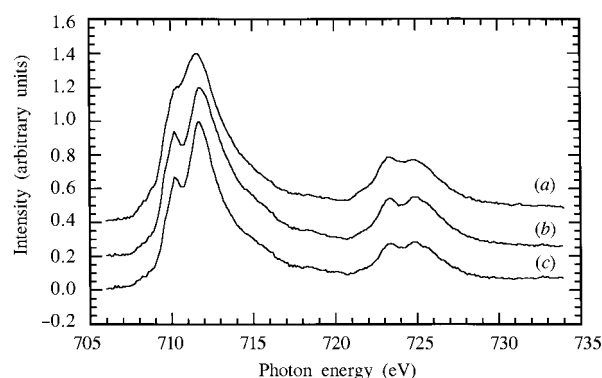


Figure 2

Fe $L_{2,3}$ XANES spectra obtained using X-PEEM from the three key iron phases prevalent in Fig. 1: (a) magnetite (Fe_3O_4) from areas D, F and G; (b) goethite [$\text{FeO}(\text{OH})$] from area A; (c) hematite (Fe_2O_3) from areas B, C and E.

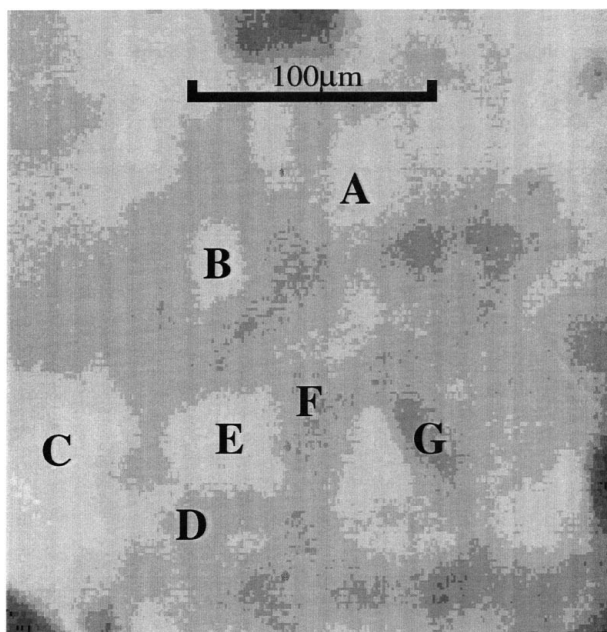


Figure 3

A contrast image obtained from X-PEEM showing the hematite/goethite regions as a lighter grey than the magnetite host.

can be determined in the ratio of the minimum between the Fe^{3+} and Fe^{2+} resonances (710.8 eV) to the maximum of the Fe^{3+}

feature (711.8 eV) in the Fe L_3 line. The ratio of the X-PEEM images collected at these two energies is shown in Fig. 3; this can be compared with the BSE image shown in Fig. 1 and shows the hematite/goethite regions as being a lighter grey than the magnetite regions.

Using X-PEEM, we have obtained area-selected XAS spectra of comparable quality to those previously recorded from bulk samples. We are currently working on a better understanding of our electron optics to improve the spatial clarity.

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