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High-resolution Sulfur K-edge XANES of Sulfide Minerals

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Introduction

High-resolution XANES measurements have been recorded for the sulfide minerals listed in Table 1. The experiments were carried out at beamline 11B of the Photon Factory. Spectra were recorded in both fluorescence and total electron yield, using a Ge (111) monochromator crystal.

Results

A summary of the main features in the spectrum of each mineral is given in Table 1. The spectra were all aligned to zero by subtracting the energy of the S $2p_{3/2}$ photoelectron (listed in Table 1) and the S K_α X-ray emission (2307.8 eV). The positions of the peaks listed in Table 1 are referenced to this zero point.

In general, the spectrum of each iron-containing mineral comprised a sharp peak near 1 eV and a broad peak in the region 8–11 eV. The absorbance edge of sphalerite (ZnS) appeared at 3.2 ± 0.2 eV and contained a number of peaks superimposed on the high-energy side (Figure 1).

Strict adherence to the $\Delta l = \pm 1$ selection rule means that the S 1s electron is promoted to an empty S p-orbital after excitation. Thus, the structure of the near-edge region is expected to resemble the density of states (DOS) of S p-orbitals in the conduction band. This has been investigated by a first-principles calculation of these states for sphalerite. As shown in Figure 1, the DOS of the empty S p-orbitals is in good agreement with the XANES spectrum of this mineral. Similar DOS calculations for the other minerals listed in Table 1 are now in progress.

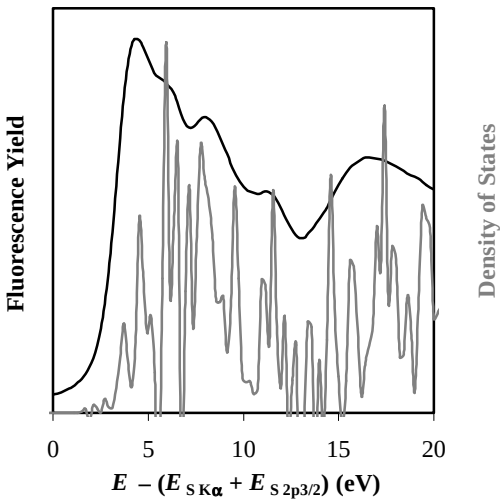

Figure 1: S K-edge XANES spectrum of sphalerite (thick line) and a plot of the S p-orbital density of states (DOS) from a first-principles calculation (thin line).

References

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Table 1: Main features of the S K-edge XANES of several sulfide minerals. ΔE is the energy after subtraction of the S K_α X-ray emission (2307.8 eV) and the S $2p_{3/2}$ binding energy measured by XPS (column 3). sh: shoulder; br: broad.

Mineral	Formula	S $2p_{3/2}$ Binding Energy (eV)	ΔE (eV) ± 0.2 eV
Pyrite	FeS_2	162.4 [1]	1.6, 7.6(sh), 9.8(br)
Marcasite	FeS_2	162.4 [2]	1.4, 8.0(sh), 11.4(br)
Troilite	FeS	161.1 [3]	2.1, 8.1(sh), 9.1(br)
Arsenopyrite	FeAsS	162.2 [4]	1.4, 2.8(sh), 9.2(sh), 10.4(br)
Chalcopyrite	$CuFeS_2$	161.1 [5]	1.1, 6.3(sh), 7.5, 8.9(sh)
Pentlandite	$(Fe,Ni)_8S_9$	162.2 [6]	1.0, 7.6(br), 9.2(sh)
Sphalerite	ZnS	161.4 [7]	4.4, 6.0(sh), 8.0, 11.2

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