Electronic structure investigation of $Mg_{1-x}Fe_xS$ solid solution: X-ray absorption study

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X-ray absorption fine structure at the sulfur K edge in $Mg_{1-x}Fe_xS$ solid solution ($0 \le x \le 0.68$) has been measured at the Canadian Synchrotron Radiation Facility. It was shown that the S K-edge in MgS was formed by the multiple scattering of the photoelectron wave within a cluster of large size (containing 27 atoms and having radius about 4.5 Å). Comparison of experimental data with theoretical results allows study of the electronic structure of this system. The analysis of partial electronic density of s-, p- and d-states makes it possible to investigate the mutual influence of sulfur s-, p- and metal d- states in the conduction band. The study of changes in experimental S K-edges XANES of $Mg_{1-x}Fe_xS$ solid solution with variation of relative Fe-Mg concentration allows the extraction of the hypothetical cubic phase (B1) of FeS, and this is supported by theoretical simulation.

Keywords: X-ray, XANES, Electronic band structure.

1. Introduction.

Investigation of the X-ray absorption near edge structure (XANES) region probes information on the lower part of the conduction band of 3d transition metal sulfides (Sugiura, 1984). Generally the K-edge jump is assigned to the transition of core electrons to the lowest unoccupied p-states. The pre-peak feature in metal sulfides is often attributed to transition of 1s core electrons to unoccupied 3d states even though the transition is forbidden in cubic crystals by the dipole selection rules. The reason for this exclusion is hybridisation of S 3p σ^* antibonding and metal 3d states (Tossel 1977). This fact has been demonstrated in several S K-edge XANES studies on $Zn_{1-x}Fe_xS$ mixed crystals with the zincblende (B3) (Li et al. 1994) and $Mg_{1-x}Fe_xS$ (B1) (Farrell & Fleet 2000) structures. The mixed crystal medium was chosen because it allows study of the influence of progressive changes of 3d metal states, due to variation of Fe concentration, on XANES spectra.

In this report, we have measured the S K-edge XANES of $Mg_{1-x}Fe_xS$ and MgS at the Canadian Synchrotron Radiation facility and applied multiple scattering analysis in real space in order to study the fine structure of unoccupied electronic S p-states in the conduction band of this solid solution. The full multiple scattering analysis has been applied to interpret a large number of XAFS in various materials (Bianconi 1989) but no multiple scattering calculations in real space have been applied to the study of unoccupied states in $Mg_{1-x}Fe_xS$.

2. Experimental.

Samples were prepared by reaction of MgS and FeS in sealed silica glass tubes (Farrell & Fleet 2000). Sulfur K-edge XANES spectra were collected at the Canadian Synchrotron Radiation Facility (Aladdin storage ring; University of Wisconsin at Madison, Wisconsin) using a double crystal monochromator (DCM) beamline in both total electron yield (TEY; near surface sensitive) and fluorescence yield (FY; depth sensitive) modes (Yang et al. 1992). The DCM has an energy resolution of about 0.8 eV at 2460 eV. Samples were finely ground in air and uniformly distributed on double-sided conducting carbon tape affixed to clean stainless steel disks. The run conditions included a photon energy range of 2450-2525 eV, step size of 0.25 eV, count times determined by counting statistics (~3.3 s per step), and 2 scans per sample, giving a total run time of ~27 minutes per sample. All spectra were calibrated to the K-edge peak of native S at 2472.0 eV after removal of a linear pre-edge background.

3. Results and Discussion.

The algorithm of the full multiple scattering method we used in this study has been described earlier (Della Longa et al. 1995). We treated the spectrum of $Mg_{1-x}Fe_xS$ solid solution as a sum of two spectra of MgS and FeS (rocksalt crystal structure B1 with lattice constant 5.203 Å and 5.074 Å, respectively). Phase shifts were calculated in the crystal muffin-tin (MT) potential with touching MT spheres. The muffin-tin radii and the muffin-tin constants that we have obtained according to our procedure of the muffin-tin potential construction (Della Longa et al. 1995) are reported in Table 1. We have used the muffin-tin approximation according to the Mattheiss prescription with the exchange parameter equal to 1.0 while constructing the crystal potential. Atomic charge densities were obtained with the help of the self-consistent Dirac-Slater method.

Table 1
The muffin-tin radii R_{mt} of the atoms included and the muffin-tin constants V_0 of the potential vacuum level is set to zero used in the calculation.

	MgS	
Atom	R_{mt} (Å)	V_0 (eV)
S	1.3731	-14.51
Mg	1.2175	-14.44
	FeS	
Atom	R_{mt} (Å)	V_0 (eV)
S	1.2478	-15.96
Fe	1.0987	-16.05

In our calculation, we have included phase shifts with orbital momentum up to 3 because there is almost no change in the spectra in comparison with $l = 2$.

The first step in the multiple scattering analysis of XAFS data is to determine the size of a representative cluster of neighbor atoms around the absorbing S atom which will reproduce fully all of the fine structure of unoccupied electronic states in the conduction band of both MgS and FeS. An analysis of the dependence of the main structures in the XANES spectrum of FeS (NaCl-type; B1 structure) on cluster size shows that convergence is reached for a cluster with 3 shells. Further addition of shells results only in variation of relative intensity. Clearly, 3 shells is large enough for XANES calculation.

In Figure 1 we present a comparison of experimental and theoretical S K-edge XANES of MgS. The theoretical spectra were calculated taking into account the broadening factors and the Fermi distribution. As one can see the agreement of theoretical results with experimental data is satisfactory for the multiple scattering of the photoelectron wave within clusters of a large size (containing at least 27 atoms and having a radius about 4.5 Å). This fact and other calculations (Stekhin et al. 1995) let us assume that our technique for the B1 crystal structure works well, permitting calculations for the hypothetical cubic (B1) phase of FeS can be carried out. We assume that the 7 shell cluster used for cubic (B1) MgS is adequate to describe multiple scattering in cubic (B1) FeS because these compounds are very similar. The S K-edge XANES of the latter (hypothetical) compound was extracted from the experimental S K-edge XANES of B1 structure Mg$_{1-x}$Fe$_x$S solid solution ($0 \le x \le 0.68$) in Farrell and Fleet (2000). Changes in the S K-edge XANES spectra of these solid solutions were progressive and near-linear with increase in *x*. Therefore, the XANES spectrum of cubic (B1) FeS was derived from the spectrum for $x = 0.625$ by assuming linear contributions from 0.625 FeS (B1) and 0.375 MgS (B1) (see Fig. 1). This experimentally derived S K-edge XANES of FeS (B1) is compared with the theoretical simulation in Figure 1, showing satisfactory agreement. We also have compared the XANES spectra of FeS in B1 and B8 phases in Figure 1, which highlights the great influence of the symmetry of neighbour atoms.

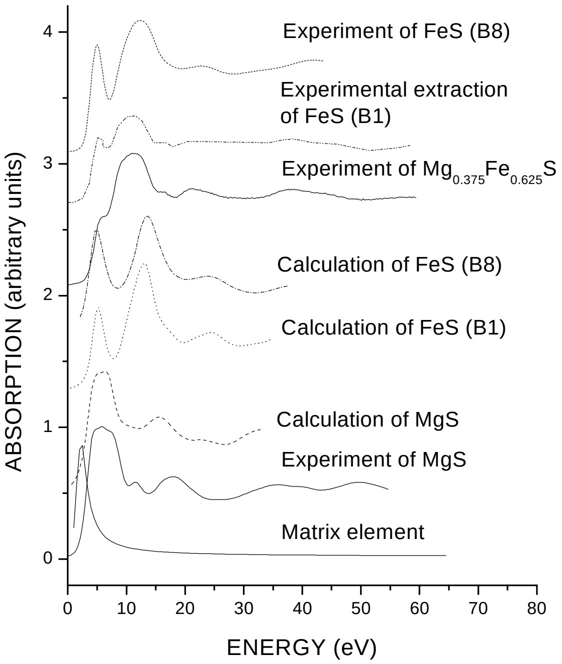

Figure 1
Comparison of S K edges of MgS (B1) and FeS (B8) experimental data and X-ray absorption coefficient for S K-edge of FeS calculated for both B1 and B8 crystal structures. We also show the experimentally-derived XANES of FeS (B1) from Farrell & Fleet (2000). The squared dipole transition matrix element for FeS (B1) is plotted below the XANES spectra.

An important factor that determines the XANES in the multiple scattering formalism is the transition matrix element, which influences the relative intensity of XANES features. As is well known the K-edge x-ray absorption in the dipole approximation is proportional to the partial density of unoccupied S p-states in the conduction band of the compound. So, if the coefficient of proportionality (namely, the dipole matrix element) is not a very sharp function of energy one can to a first approximation study the details of the partial density of states, averaged in real space, by analyzing the fine structure of the x-ray absorption spectra. In Figure 1 we also present the squared dipole transition matrix element of FeS (B1) as a function of energy for the ground state potential. As one can see in the energy interval close to the absorption threshold (above 10 eV) the squared dipole transition matrix element shows an absence of sharp energy dependence. Thus one can use experimental XANES to study the partial density of unoccupied S p-states in the conduction band of the compound.

The analysis of partial electronic density of states shows that d-states of the metal push away p-states of sulfur (the energy position of d-state maximum is the same as for minimum of p-state). So, one can says that there is mutual influence of p-states of sulfur and d-states of metal (Fe and Mg).

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