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Resonant Raman x-ray scattering at the S 2p edge of iron pyrite

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Abstract

The x-ray absorption and resonant inelastic x-ray spectra of iron pyrite (FeS₂) have been measured at the S 2p edge and compared with published electronic structure calculations. A minimum in the x-ray absorption intensity interpreted as indicating a gap in the unoccupied density of states is found from about 4 to 6 eV above the bottom of the conduction band, in agreement with some recent calculations. Resonant Raman scattering conditions were set up at the onset of S 2p_{3/2} absorption and a constant energy loss peak at 1.9 eV was observed. This is assigned to transitions from occupied t_g to unoccupied e_g states, both of which are predominantly of Fe 3d character but hybridized with the S valence states. This demonstrates that Fe dd excitations can be probed via S 2p resonant spectroscopy, as has been done recently at the O 1s edge for oxide materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In resonant inelastic x-ray scattering (RIXS), an incident photon is inelastically scattered from a target and a photon of lower energy is detected. Under resonant Raman conditions, this gives rise to loss features characteristic of excitations from the ground state to a valence excited state and is thus a powerful method for investigating low energy excitations of a wide range of materials [1, 2]. Since the final state of the system does not contain a core hole, the relaxation effects which can complicate core level photoemission are absent.

In this paper we have applied RIXS to the study of iron pyrite, FeS₂, at the sulfur 2p edge. This material is cubic, non-magnetic (in contrast with many other iron compounds, such as the

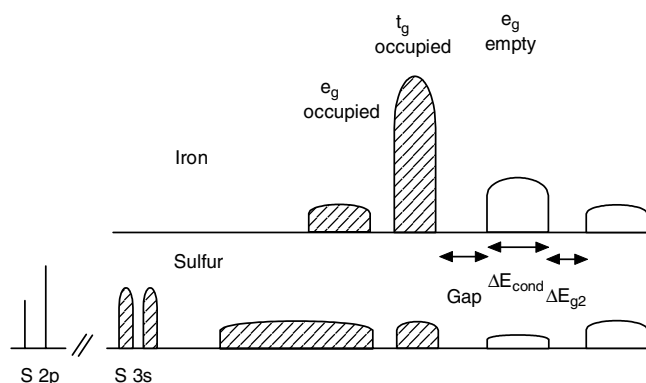


Figure 1. A schematic diagram of the density of states of FeS_2 . Only the valence states are shown for Fe. For S, the 3s outer core and 2p core levels are also shown. The empty states above the gap consist of a conduction band of width ΔE_{cond} , a gap of width ΔE_{g2} , and another empty band above this.

oxides), belongs to the space group $Pa\bar{3}$ (T_h^6), and has been widely studied both theoretically and experimentally. A previous x-ray emission study reported the resonant L edge emission spectra of this compound, but not resonant Raman scattering at the S 2p edge [3]. This appears to be the only soft x-ray scattering report for this material, which has otherwise been studied extensively by photoemission and other techniques. Many theoretical band structures have been reported [3–9], which agree in the general description of the electronic structure, which is summarized schematically in figure 1. Nesbitt *et al* [10] have recently reviewed valence band photoemission studies and their relation to the electronic structure. The top of the valence band is composed mainly of Fe 3d states of symmetry t_{2g} (this is the label in octahedral symmetry; more strictly it is t_g for the space group $Pa\bar{3}$), while the bottom of the conduction band is composed mostly of Fe 3d e_g states mixed with S 3p states. The upper valence band t_{2g} states have been interpreted as mostly Fe 3d non-bonding states by most authors, but Eyert *et al* [7] have emphasized the Fe–S π^* character of this part of the band. Theory confirms the experimental finding that the material is semiconducting; the experimental fundamental gap is 0.95 eV [11, 12]. The width of the conduction band is denoted by ΔE_{cond} in figure 1 and a second predicted gap is labelled with a width ΔE_{g2} . There are some differences in detail in theoretical calculations: Zhao *et al* obtain a width of about 7 eV for this second gap, while Zeng and Holzwarth and Muscat *et al* obtain values of about 3 eV. FeS_2 has also been studied by NEXAFS (near edge x-ray absorption spectroscopy) at the S L edge [13] and by Fe L edge NEXAFS [14–18].

Our interest in the study of the electronic structure of this material stems partly from its practical importance in mineral science and solar cells, and partly in understanding whether resonant Raman conditions can be used to study it. As mentioned above, a previous study [3] did not find Raman scattering, although recently there have been several reports of this effect in transition metal compounds, all of which are oxides [19–23]. To date, dispersion of the loss features in the soft x-ray range has been observed mainly at metal and O 1s edges and we wished to determine whether this occurred for other anions, such as disulfide.

2. Experiment

The measurements were performed at the BACH beamline [24, 25], Elettra synchrotron radiation facility, Trieste, using the COMIXS spectrometer [26]. The total resolution for

x-ray emission, measured from the width of the elastic peak, was better than 0.4 eV, and the resolution for NEXAFS (measured in total yield mode, to maximize bulk sensitivity) was better than 0.1 eV. The scattering angle between the incident and emitted photons is 120° , corresponding to a momentum transfer of 0.05 \AA^{-1} , much smaller than a reciprocal lattice unit vector, $2\pi/5.416 = 1.16 \text{ \AA}^{-1}$. We therefore expect all transitions to be vertical. The emitted photon energy was calibrated to 148.5 eV for the maximum of the L_3M_1 emission peak [3] and the incident photon energy was calibrated to this value by observing the difference between the elastic and inelastic peaks. The incident light was p polarized, that is, linearly polarized in the horizontal plane with the sample surface in the vertical plane. The sample was prepared by scraping in air. Electron energy loss spectra (EELS) were measured in the Department of Physics, Osnabrück, using a PHI 5600 CI multi-technique spectrometer with a total energy resolution (incident electrons + analyser resolution) of 0.6 eV. For this measurement the sample was prepared by fracturing in vacuum.

3. Selection rules

As stated above, the space group of this material is $Pa\bar{3}$ and its point group is the cubic group T_h . Most discussions of the electronic structure of the Fe ions label the states using the irreducible representations (irreps) of the octahedral group, because the symmetry reduction between O_h and T_h is a small perturbation [7]. However, it is more correct, especially for the disulfide ions, to consider the true point group. The states can be labelled at the centre of the Brillouin zone by the irreps of the group T_h , which are a_g , a_u , e_g , e_u , t_g and t_u . The first two are one dimensional, the e irreps each consist of two degenerate (in the absence of a magnetic field) complex conjugate irreps, and the t irreps are three dimensional [27].

The electric vector belongs to the irrep t_u , as do the S core levels; the selection rules are deduced in the usual way from the Fermi golden rule. We are interested in the S states that bond with Fe, and these are the e_g and t_g states. We therefore need to evaluate the direct products $e_g \otimes t_u \otimes t_u$ and $t_g \otimes t_u \otimes t_u$. The multiplication tables have been given by Atkinson [28] and these products both contain the totally symmetric representation, and so transitions from core 2p levels are allowed to e_g and t_g states; similarly it can be shown that transitions to all states are allowed. Thus in both x-ray absorption and emission the selection rules are weak in our case. Since the resonant emission process consists of two dipole processes, we may have final states with a hole in any valence state and an electron in any previously empty state, independent of symmetry.

4. Results and discussion

The NEXAFS spectrum at the S L edge is shown in figure 2 and is similar to the spectrum of Li *et al* [13] except that the high energy features are more intense in the present spectrum. The Fe L edge spectrum [18] is shown for comparison and has been shifted to align the onsets. The NEXAFS spectrum shows four main features, labelled A to D in figure 2, of which the first two show clear spin-orbit splitting of the S $2p_{1/2}$ – $2p_{3/2}$ core levels. Li *et al* [13] assigned the states labelled A to ‘S 3s-like states’, and the states B to ‘the antibonding S 3s-like states at the conduction band minimum’. However the 3s states form an occupied bonding–antibonding pair at 13–15 eV binding energy, so it is unlikely that they participate in the conduction band. Possibly this was a misprint in their paper. We assign peak A to states at the minimum of the conduction band, and peak B to the second band above the conduction band. The character is indeed probably s like, but as stated above, the selection rules are weak.

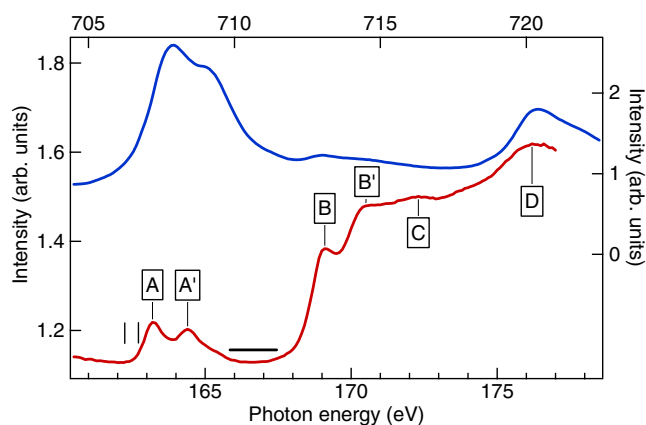


Figure 2. X-ray absorption spectra of FeS₂: lower curve, S L edge, left and lower axes; the vertical bars between 162 and 163 eV mark the photon energy range in which the spectra in figure 3 were taken. The horizontal bar indicates the energy over which the intensity is considered to be substantially constant, suggesting a gap. Upper curve: Fe L edge, right and upper axes.

Table 1. Theoretical and experimental values of the width of the conduction band (ΔE_{cond}) and the width of the second gap ($\Delta E_{\text{g}2}$) above the optical gap.

ΔE_{cond} (eV)	$\Delta E_{\text{g}2}$ (eV)	Reference
2.4	7.0	[5]
3.3	2.8	[6]
3.3		[7]
2.5		[3]
2.6	3.5	[9]
2.8		[8]
2.4 ± 0.2	3.0 ± 0.4	Present work, experimental

The low intensity between peaks A' and B, about equal to the intensity below threshold, suggests a substantial gap between the two bands. It is of course possible that this is due to a low density of empty states, but the existence of several calculations predicting a gap in this region imply that a gap is probably the correct interpretation. The spin-orbit splitting of the S 2p core levels means that the spectrum consists of the superposition of L₃ and L₂ spectra. Assuming that the two spectra have the same width and are shifted in energy by the spin-orbit splitting, we can estimate the width of the conduction band and second gap. The conduction band width is given by the measured width from the onset of the conduction band to the energy at which the intensity is minimum, minus the spin-orbit splitting. Similarly the gap is given by the energy interval from which the L₃ intensity is minimum (there is a continuum background which does not vary significantly) to the L₂ onset, plus the spin-orbit splitting. The experimental value of ΔE_{cond} is 2.4 ± 0.2 eV and the width $\Delta E_{\text{g}2}$ of the second gap above the fundamental gap is 3 ± 0.4 eV. These values are summarized in table 1 together with more recent theoretical estimates. Best agreement is found with the calculations of Zeng and Holzwarth [6] and Muscat *et al* [9]. The agreement must be treated with caution as it is well known that the local density approximation is not reliable for predicting values of gaps, but we provide these experimental data to allow comparison of calculated and measured values.

Comparison of sulfur NEXAFS with the Fe L₃ edge absorption spectrum in figure 2 shows that a shoulder also occurs at the same energy of about 7 eV above the onset of absorption

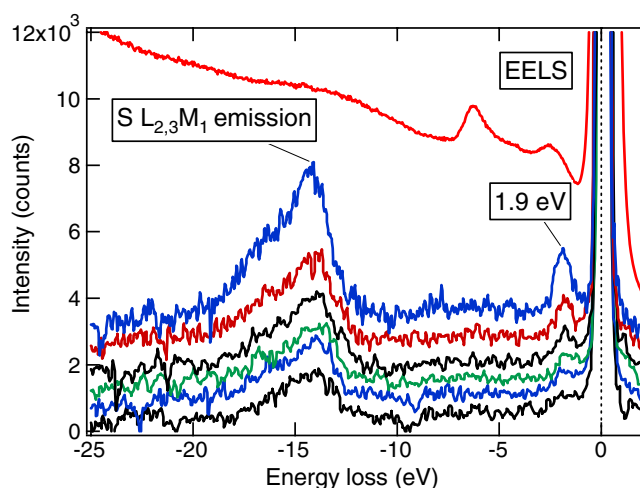


Figure 3. Resonant inelastic x-ray emission spectra of FeS₂ at the S L edge. Photon energy (from bottom to top): 162.3, 162.35, 162.4, 162.45, 162.5, 162.7 eV. Top curve: the inelastic electron energy loss spectrum (EELS) at 200 eV incident energy. A polynomial background (fitted to the low energy loss region) has been subtracted.

(162.5 eV in the S spectrum), but is much weaker. We have argued elsewhere [18] that this indicates that the peak in the Fe spectrum is not a satellite due for instance to two-hole or multiplet excitations [14], but is a feature of the density of states. It is clear that feature B has only very weak Fe character, and much stronger S character: it is predicted to have either mainly Fe s character [5], or mainly S p character [6], or mainly S 3d character [9].

Peaks C and D were assigned by Li *et al* [13] to empty S 3d-like states of e_g and t_{2g} symmetry. They are not observed in the Fe L edge spectrum: peak C is in any case very weak, while peak D overlaps and is obscured by the Fe L₂ edge.

Emission spectra were taken across the absorption resonance at energies above the onset. The spectral features had constant emission energy and in general were similar to those of Kurmaev *et al* [3] and so are not shown here. Resonant spectra taken close to the onset of absorption, figure 3, showed different behaviour. The spectra are plotted on an energy loss scale, and the elastic scattering peak is very strong at this incident energy. Elastic scattering is in this case mostly due to diffuse scattering associated with surface roughness, that is, microfacets that are aligned at the specular angle. The scattering angle in the present experiment is 60°, far from the Brewster angle (scattering angle about 91°), at which the reflectivity is zero for p polarized light. In their study, Kurmaev *et al* [3] used a scattering angle of 90° so that the elastic peak was very weak.

A weak inelastic loss peak can be distinguished near each elastic peak. The energy loss is constant over a range of 0.3–0.4 eV of the incident beam energy; that is, the loss peak disperses with the elastic peak, while at higher incident energy the emitted photon energy is constant. There is a peak close to the elastic peak with a loss energy of 1.9 eV and a width of 0.9 eV, and a loss peak at about 14 eV due to L_{2,3}M₁ emission. The latter is very broad so it is difficult to observe small energy changes, but it does not appear to show a constant energy loss; that is, it is due to incoherent scattering. Figure 3 also displays an inelastic electron energy loss spectrum (EELS).

The present results show that resonant Raman conditions can be established in a narrow energy range close to the S 2p_{3/2} threshold. At lower energy, there is insufficient intensity

for observing the loss peak, while at higher energy the peak is stationary in energy. We identify this peak by comparison with available band structure calculations. All calculations which explicitly show the band structure (and not just the density of states) predict that the conduction band minimum is located at the Γ point [5–8]. This band has S sp character—indeed its parabolic shape and dispersion suggest an s-like band. We assign the weak x-ray absorption at the onset of 2p absorption to transitions from 2p states to these states at the bottom of the conduction band. Emission is then assigned to final states with a hole in the flat t_g band and an electron in the previously unoccupied e_g band. This picture implies that the system is correlated as this one-electron final state does not correspond to the one-electron intermediate state with an electron in the sp band. Muscat *et al* [9] have recently drawn attention to the importance of correlation in this system.

The calculations of Zeng and Holzwarth predict that the occupied t_g band is overwhelmingly (about 90%) of Fe d character while the unoccupied e_g band is predicted to be mainly (about 75%) of Fe character. However, since we observe a loss peak, the density of states at the S 2p site is significant. The binding energy of the t_g band extends from the top of the valence band to about 1 eV, while the e_g band is centred at about 1.5 eV. Thus the sum of the one-electron energies, 1.5–2.5 eV, covers the experimental value of 1.9 eV and the width of 0.9 eV is approximately as expected. We conclude that excitonic energy shifts are not strong and that the final state, if not the scattering process, can be described with reference to a one-electron band picture.

In a resonant inelastic x-ray scattering study of graphite [29] it was possible to extract band structure information, but this does not appear to be the case for FeS₂. If the behaviour were similar, the present results imply that there exist roughly parallel valence and conduction bands of S character, which would explain the constant energy loss. However, such bands cannot be distinguished in published band structure calculations. Rather, the difference appears to be due to the fundamentally different electronic structures. Graphite has strongly delocalized valence and conduction bands, and under resonant x-ray scattering conditions, the spectral peaks show clear dispersion. Pyrite has a more complicated electronic structure in which the S states are more delocalized and the Fe states more localized. It appears that the existence of correlation has the effect of masking one-electron behaviour. If this is generally true, and many more studies are needed to test this idea, then it means that the technique reported in [29] may be restricted to wide band materials.

With regard to the transition from resonant Raman to normal (incoherent) fluorescence, we explain this within the time dependent scattering model of Luo *et al* [1]. Resonant scattering occurs only if the lifetime of the excited electron is longer than the lifetime of the core hole: if it de-excites or delocalizes before the core hole de-excites, then the fluorescence is incoherent. In general terms one expects the lifetime of a conduction band electron to be longer if it is closer to the band edge, and this indeed appears to be the case here. For excitations to the lower part of the band (of largely S character) the scattering is coherent; at just a few tenths of an electronvolt higher, where we expect excitations to many different bands, the fluorescence energy is constant—that is, it corresponds to the decay of a S 2p hole in the absence of an excited electron.

In comparison the EELS spectrum in figure 3 shows losses at 2.6 and 6.25 eV, with a weak structure at 4.3 eV. EELS measures electronic transitions without restrictions due to momentum conservation or site selectivity. The first loss peak is at higher energy than the loss peak observed in RIXS and is likely to be dominated by Fe dd transitions, as these constitute the highest joint density of states. However, other transitions may be present, such as non- k -conserving transitions that shift the centre of gravity of the peak. The advantage of RIXS in terms of selectivity is clear.

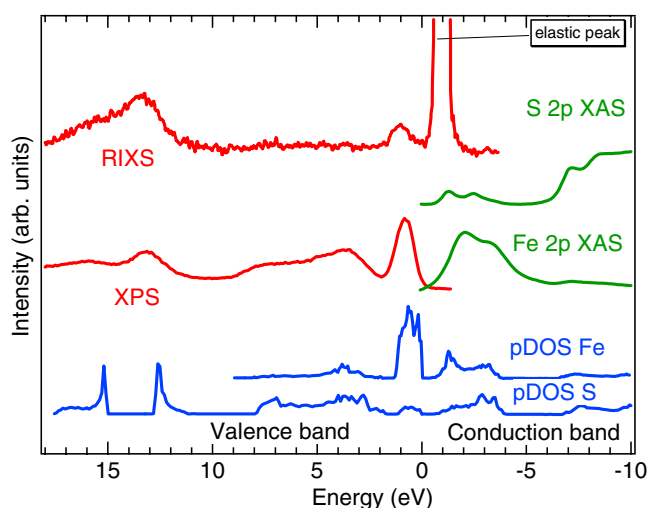


Figure 4. A summary of the electronic structure. From bottom to top: pDOS: the calculated partial density of Fe and S states, after Zeng and Holzwarth [6]; the XPS spectrum of the valence band; XAS: Fe 2p and S 2p x-ray absorption spectra; RIXS: the resonant inelastic x-ray scattering spectrum at the S 2p edge, 162.7 eV.

The electronic structure data are summarized in figure 4, where the digitized calculated density of states of Zeng and Holzwarth [6] is compared with spectroscopic measurements of the density of occupied (XPS) and unoccupied (NEXAFS) states. The zero of the energy scale is the top of the valence band, and the empty state spectra and elastic peak of RIXS have been aligned to -1 eV, that is, the bottom of the conduction band. The inelastic loss correlates well with the main peak seen in XPS, although in XPS the peak is due mainly to Fe d states. The calculation of the density of states shows that the Fe d bands and S 3p states overlap and are strongly hybridized, that is, they contribute to the same band. Thus the S 2p RIXS spectra are effectively probing the Fe dd transitions. This is analogous to the case of O 1s RIXS reported by Duda *et al* [20] and discussed by Okada and Kotani [22]: details of transition metal dd excitations can be probed via chalcogen (oxygen or sulfur) core level spectroscopy. This is important as it is in principle possible, though more difficult, to resolve these transitions via scattering from the deeper Fe 2p core level. We have recently reported a study with a resolution of 1.6 eV where a shoulder on the elastic peak was observed but it was not possible to determine the energy of the loss [18].

5. Conclusions

In summary, by setting up resonant Raman conditions over a narrow energy range near the S 2p threshold we are able to probe Fe dd excitations between the valence and conduction band, via the hybridization of the Fe states with sulfur states. The results, and the S 2p edge NEXAFS, can be interpreted in the light of published electronic structure calculations.

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