An Auger and EELS study of oxygen adsorption on FeS$_2$

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Abstract. AES and EELS are used to study the effect of oxygen on the FeS$_2$ surface. The main Auger Fe M$_{2,3}$VV attenuates with increased oxygen exposures and shifts to lower kinetic energy while the high kinetic energy feature due to an 'autoionization process' remains unaltered in energy. The EELS spectra measured as a function of oxygen exposure clearly indicate the formation of iron oxide similar to that of α-Fe$_2$O$_3$. For the FeS$_2$ + O$_2$ system, we show that U_{eff} is negligibly small and is in good agreement with the estimated U_{eff} for Fe$_2$O$_3$. A slight change in the S L$_{2,3}$VV Auger peak is observed on adsorption of oxygen and the formation of sulphur oxides is ruled out.

1. Introduction

The iron sulphides form a class of chemical compounds which exhibit very interesting magnetic properties [1]. The iron disulphide, pyrite (FeS$_2$), is essentially a non-magnetic semiconductor (bandgap ~0.95 eV) with unusual electronic properties. The iron sulphides play an important role in coal liquefaction processes and FeS$_2$ has attracted interest in recent years as a promising candidate for future photovoltaic or photocatalytic material. With its high absorption coefficient, which exceeds 10^5 cm^{-1} at energies $h\nu > 1$ eV, FeS$_2$ would be suitable for application as absorber material in thin layer photovoltaic devices [2]. However, the property of this compound is strongly affected by the exact stoichiometry of its constituents, by impurity contamination, and by the preparation techniques [3]. Hence, any improved understanding of such materials will aid in the successful practical applications of this material mentioned above.

A number of spectroscopic measurements of FeS$_2$ have been made using a wide variety of techniques. Previously photoemission studies (UPS and XPS), AES and electron energy loss spectroscopy (EELS) studies have been done on FeS$_2$ and other α-iron surfaces [4–9].

Auger electrons carry a lot of information about the chemical environment of atoms in solid surfaces and the use of AES as a 'surface bonding probe' is experimentally well established [10, 11]. It is well known that core–valence–valence (CVV) Auger spectra provide information concerning the electronic structures of compounds, alloys and adsorbed elements [11]. EELS is a technique complimentary to XPS and UPS. It can be

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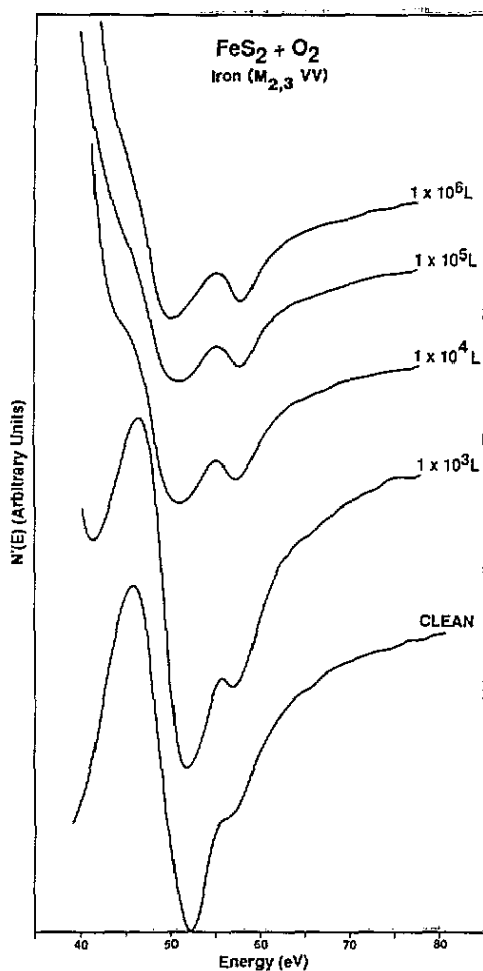
Figure 1. The Fe $M_{2,3}$vv Auger spectra, in the $N'(E)$ form, plotted as a function of oxygen exposure. All doses were cumulative and spectra were measured at room temperature.

used to study the transition energies of the valence and core electrons thus giving information about the empty states above the Fermi level.

In this work we report on measurements of the electron excited Auger spectra in conjunction with EELS data as a function of oxygen exposure.

2. Experiment

The experiments were performed in an ion-pumped Varian UHV 12FE system with a base pressure in the 10^{-10} torr range. The Auger spectra were recorded in the first differential mode using a Varian LEED/Auger Optics as a retarding field analyzer (RFA) with a normal incidence gun. A resolution of about 1 eV could be achieved. Other experimental details have been published previously [12].

For this study a natural single crystal of FeS_2 from Valdenegrillos, Soria, Spain was used. Although the samples were naturally occurring single crystals, no attempt was made to align them into any particular crystallographic direction. They were cut at convenient angles so that they could be easily mounted in the sample holder.

The sample was cleaned *in-situ* by Ar^+ bombardment for 20 min with 400 eV Ar^+ ions (3 μA cm^{-2}). This was the minimum ion dose found necessary to remove all traces of C, H_2O, CO and any O_2. This was followed by annealing of the sample at 750 K for 30 min to 1 hr.

The sample was then exposed to high purity (99.998%, L'Air) oxygen after obtaining clean Auger spectra of iron and sulphur. All of the exposures were performed at laboratory temperature (300 K). The oxygen was introduced into the chamber via a high-precision variable leak valve. The gas-handling line was thoroughly baked prior to adsorption studies. For exposures in the range of 10^3–10^6 L, oxygen pressures were increased correspondingly over the range 10^{-8}–5×10^{-7} torr with appropriate time of exposure. All oxygen exposures were cumulative. During exposures the electron gun was switched off. It is well known that the presence of hot filaments affects the rates of adsorption of oxygen [13]. Hence the nude ionisation gauge located in close proximity to the specimen may be considered to produce excited oxygen.

In all the measurements, the Auger spectra were recorded at primary energies of 2 keV and an electron-beam current density of 10 μA cm^{-2} to minimize the beam/ adsorbate interactions.

3. Results

In view of the difficulty in accurately measuring the cross-over energies of the Fe Auger $M_{2,3}$VV after oxidation, we have taken the energies of the negative excursion in the Auger spectra recorded in the dN/dE [$N'(E)$] mode. For other CVV Auger signals, the energies given refer to the cross-over energies of the peaks. All the values given refer to the Fermi level of the sample.

The modulation amplitudes used in the present experiments are as follows:

$$\text{Fe } M_{2,3} \text{VV } (3 \text{ V}_{p-p}), \text{ S } L_{2,3} \text{VV } (3 \text{ V}_{p-p}) \text{ and O KLL } (6 \text{ V}_{p-p}).$$

Figures 1 and 2 show the Fe $M_{2,3}$VV and the S $L_{2,3}$VV Auger spectra, in the $N'(E)$ mode, as a function of oxygen exposure. Figure 3 shows the growth of oxygen KLL spectra. The O ($KL_{2,3}L_{2,3}$) peak-to-peak height ratio is a good indication of the amount of adsorbed oxygen as the major features in the shape of this line remain essentially unchanged in a wide coverage range.

The peak-to-peak intensities of the O ($KL_{2,3}L_{2,3}$), Fe ($M_{2,3}$VV) and S ($L_{2,3}$VV) Auger transitions are plotted in figure 4 as a function of oxygen exposure (logarithmic scale). We can discern from this figure that the substrate CVV signal amplitudes are considerably influenced by oxygen adsorption. The oxygen uptake curve for FeS₂ is similar to that of Fe metal [13]. Adsorption of oxygen results in a general attenuation of the CVV Auger signals, in particular the Fe Auger signal for which the high-energy peak becomes more prominent with insignificant energy shift.

Finally in figure 5, we have plotted the EELS spectra of FeS₂ as a function of oxygen dose and compared them with the EELS spectrum from the Fe₂O₃ sample, in the $N'(E)$ mode. A primary energy of 400 eV and a modulation amplitude of 2–3 eV was used to measure these spectra.

4. Discussion

The clean Fe Auger signal, from figure 1, consists of a main peak (which is a super Coster–Kronig (SCK) transition) at about 52 eV (negative excursion) which is due to the
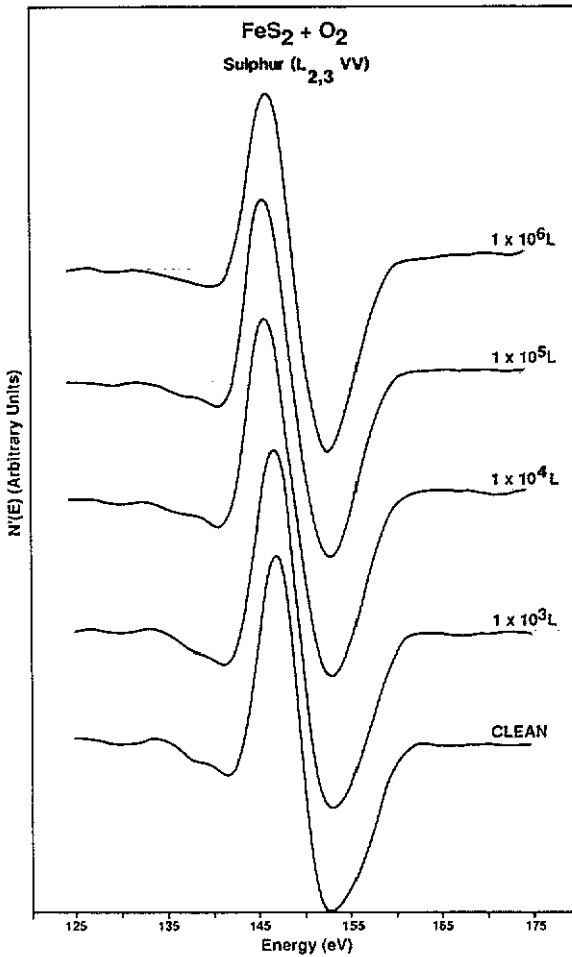
Figure 2. The S $L_{2,3}$vv Auger spectra, in the $N'(E)$ form, plotted as a function of oxygen exposure.

$M_{2,3}$vv transition and the tiny peak at about 57.8 eV is due to an 'autoionization process' [14]. On exposure to oxygen, the main peak attenuates and shifts to lower kinetic energy while the autoionization feature remains relatively unaltered in energy. The latter feature now becomes the dominant peak due to continuous attenuation of the main Auger peak. At an exposure of 10^6 L, the $M_{2,3}$vv line is clearly split into two peaks at energies of 50.0 eV and 57.8 eV. The sharp changes in the $M_{2,3}$vv profile occur in the region of 10^3–10^4 L oxygen doses. The attenuation of the Auger feature may be due to a decrease in the number of d-band electrons as reflected in the photoemission results of Eastman and Freeouf [15] and Alvarado *et al* [16]. Ramsey and Russell [14] argue that the decrease in the Auger feature must be due to the bonding of the iron with the oxygen which results in a decrease of d-electrons available to take part in the Auger feature. In addition, according to Zajac *et al* [17], oxidation depopulates the d-band, which should act to enhance the autoionisation emission, as this process competes with the Auger process in the $M_{2,3}$ hole decay. Further, these authors [17] report the complex
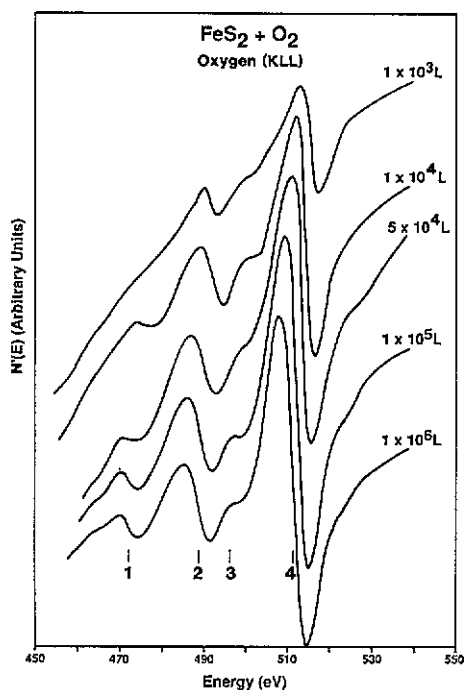
Figure 3. Growth of O KLLL Auger spectra, in the *N'(E)* form, with increased oxygen doses.
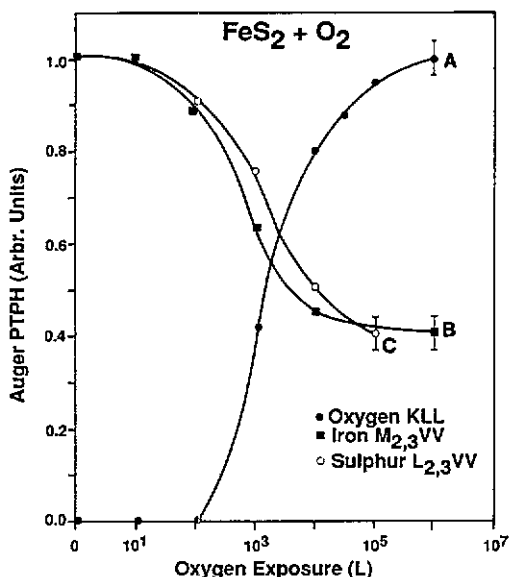

Figure 4. Rate of uptake of excited oxygen with exposure as judged by the Auger peak-to-peak height ratios of Fe M$_{2,3}$VV, S L$_{2,3}$VV and O KLL Auger spectra.

oxidation behaviour of Mn for which the Auger and autoionization features are merged into one feature before oxidation. After oxidation the Auger feature disappears leaving the autoionization feature pinned above the 3p binding energy. This situation is quite opposite to the FeS$_2$ + O$_2$ case. The behaviour of the autoionization emission upon oxidation has been earlier interpreted [14] as being due to a change in the excitation from 3p → 3d for the clean Fe surface to 3p → 4s in the oxidized Fe surface. However, such a phenomenon has been ruled out recently by McKay *et al* [18] in their EELS and resonant photoemission study on 3d metals and oxides. According to these authors the valence levels are, by definition, filled in the insulating oxides, hence a quasiatomic process such as 3p → 4s (valence) transition is not possible, which we believe to be true.

The Fe Auger M$_{2,3}$VV and the 'autoionization' feature are separated by about 7.8 eV upon oxidation, in our study. When a comparison is made with the same doublet separation for α-Fe$_2$O$_3$ and Fe$_3$O$_4$ [6], it is evident that the oxide formed in the present case is similar to that of α-Fe$_2$O$_3$. Seo *et al* [19] have investigated the M$_{2,3}$VV Auger profile of various iron oxides. They report a doublet separation of 7.5 eV for α-Fe$_2$O$_3$ and 8.0 eV for γ-Fe$_2$O$_3$. Again this agrees well with our results.

The kinetic energy of a CVV Auger electron is given by

$$E_{KE} = E_B(c) - 2E_B(v) - U_{eff}$$

where $E_B(c)$ and $E_B(v)$ denote the binding energies of the core and valence electrons,
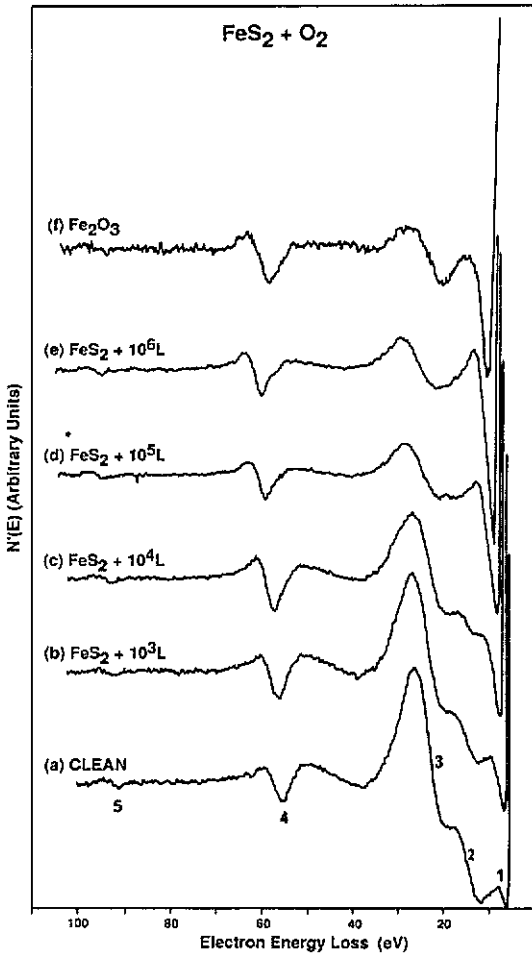
Figure 5. EELS spectra of FeS_2 measured as a function of oxygen exposure, in the $N'(E)$ mode. The spectrum (f) is measured on the F_2O_3 sample. ($E_p = 400$ eV, 2–3 V_{p-p}).

respectively. The term U_{eff} represents the effective Coulomb interaction [20–22]. The above equation can be written to calculate U_{eff} as follows:

$$U_{eff} = E_{3p} - 2E_d - E_{M_{2,3}VV}$$

now taking,

$E_{3p} = 58$ eV (Loss energy of peak 4 from figure 5(e))

$E_d = 4.5$ eV (for Fe_2O_3 from [23])

$E_{M_{2,3}VV} = 50.0$ eV (negative excursion of '10^6 L' Auger peak from figure 1)

gives $U_{eff} = -1.0$ eV.

However, U_{eff} cannot be a negative quantity which implies that either E_{3p} should increase or E_{3d} should decrease. The partial d-state intensities for FeO [15] and for

Fe_3O_4 [16, 24] suggest a maximum for the 3d band at binding energies around 4 eV and 5 eV, respectively. Lee and Montano [6] report a value of 4.2 eV for the 3d band from their EELS study of iron sulphides. Hence a binding energy of 4–5 eV for the 3d band is reasonable in the above calculations. Therefore, we suggest a slight increase in the 3p binding energy upon oxidation which agrees with a previous study [17] on oxidized iron. Thus it can be argued that in iron oxides, oxidized iron and iron sulphide surfaces, U_{eff} is negligibly small.

As seen in figure 4, the Fe $M_{2,3}vv$ Auger peak attenuates almost by 50% at an exposure of 10^4 L. The changes that occur in this line upon oxidation are relatively slow when compared with the oxidation of Fe metal [13]. This, we presume, may be due to the presence of elemental sulphur on the pyrite surfaces as noted by Lee and Montano [6]. Ar^+ bombardment is normally used for *in-situ* cleaning of the sample. Such a procedure will preferentially sputter S rather than Fe. One would expect that prolonged bombardment of the surface would produce areas of metallic Fe. However, given that the ion beam energy that we used was low (400 eV), we expect the initial bombardment would remove mainly the adsorbed layers of impurity species mentioned in section 2, leaving the surface relatively unchanged. Perhaps the O $(KL_{2,3}L_{2,3})$ peak is a better indicator of adsorption as proposed earlier. The oxygen uptake curve (see figure 4) suggests that hardly any oxygen sticks in the $1–10^2$ L region. However, the peak heights appear to increase rapidly with doses above 10^3 L.

It has been shown that the O (KLL) line shape provides important chemical information and exhibits a 'quasiatomic' behaviour [25, 26]. When oxygen atoms are close to a 'neon-like' electronic configuration, the spin–orbit coupling theory predicts five main features. Four peaks can easily be seen in the oxygen Auger profile (see figure 3). The main peak $[O (KL_{2,3}L_{2,3})]$ shifts from 512 eV to 511 eV between $10^5–10^6$ L exposures. This is consistent with the results of Bendorff *et al* [27] for the oxidation of the Ni (110) surface.

The main sulphur $L_{2,3}vv$ Auger line remains relatively unchanged in energy upon oxidation. Only slight changes can be seen on the low kinetic energy side of the peak. This region in the clean spectrum consists of two small features which are associated with 1p, 3p components of the $L_{2,3}M_1M_{2,3}$ Auger transition [7]. The 3p component almost disappears at 10^6 L exposure and the main line $(L_{2,3}vv)$ attenuates by about 60% (see figure 4).

The attenuation of the Fe and S signal is clearly due to an overlayer forming of iron oxide. The principal effect is to reduce the intensity of the sulphur signal coming from the substrate as the inelastic mean free path (IMFP) of sulphur Auger electrons is about 5 Å [28]. There may be further effects due to changes in the ratio of Fe to S in the oxide that is forming, but these are small compared with the loss of signal from the substrate. In fact, one can see that in all spectra, expect for the last point, the S is more intense than the Fe (compared to the clean surface), suggesting that the S is migrating to the surface. Furthermore, the S signal is certainly changing in shape with oxidation. The small features to the left of the main Auger line are changing with oxidation, indicating a change in the chemical environment. Hence, we suggest the formation of iron oxides and rule out any formation of sulphur oxides as this would have resulted in marked changes in the S Auger line, unlike the P Auger line in InP and Zn_3P_2 [29].

The clean EELS spectrum for the clean FeS_2 surface, as shown in figure 5, is in excellent agreement with that of Panzner and Egert [7]. They use a primary energy of 200 eV, 1 V_{p-p} modulation amplitude. They collected their data using a 180° hemispherical analyser. In comparison with their earlier energy loss spectra of clean Fe [30], they

observe an additional loss feature with a loss energy of 6.6 eV in FeS_2. This feature is just visible in our spectrum and has been interpreted as an 'interband transition' from the S 3p level into an empty state above E_F. The feature 2 with a loss energy of 14.8 eV can be assigned to a volume plasmon [6]. The feature 3 with a loss energy of about 22.3 eV may be assigned to a volume plasmon. The features 4 and 5 are due to transitions involving the Fe 3p ($M_{2,3}$) and 3s (M_1) electrons. The peak 4 at about 57 eV is due to Fe $3p_{3/2}$ and Fe $3p_{1/2}$ levels which are not clearly resolved.

On adsorption of oxygen, the peaks 1 and 2 gradually decrease in intensity and for an exposure of 10^5 L, the peak 2 shifts slightly to lower energy. We find that the $M_{2,3}$ core loss shifts down by about 1 eV and the M_1 core loss remains unchanged in energy. We assign the peak 2 in figure 5(*e*), with a loss energy of around 6.5 eV to O 2p level. This assignment agrees well with the similar EELS spectrum from our Fe_2O_3 sample (figure 5(*f*)). This is a clear indication that the oxide that is forming on FeS_2 upon oxidation is closer in composition to Fe_2O_3.

5. Conclusion

When FeS_2 is exposed to up to 10^6 L oxygen, the only major change observed is in the Fe Auger doublet. The main Auger peak attenuates while the 'autoionization' feature remains unaltered. The attenuation of the main peak is due to a decrease in the number of d-electrons, resulting in a bonding of these electrons with the oxygen 2p electrons. We have shown that U_{eff} is negligibly small for the $FeS_2 + O_2$ system.

No significant change in the S $L_{2,3}VV$ Auger line is observed and the EELS spectra indicate that the oxide that is formed on the FeS_2 surface is closer in composition to Fe_2O_3. This study shows that we can monitor the formation of oxide species on the iron sulphide surfaces.

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