X-Ray Photoelectron Spectroscopy of Iron–Oxygen Systems

By **Geoffrey C. Allen,* Michael T. Curtis, Alan J. Hooper,** and **Philip M. Tucker,** Central Electricity Generating Board, Berkeley Nuclear Laboratories, Berkeley, Gloucestershire GL13 9PB

X-Ray photoelectron spectroscopy has been used to study a series of iron oxides. It has been shown that iron metal has a different ionisation energy from a number of iron(III) oxides. Small perturbations to the energy of the iron(III) $2p$ electrons can be attributed to changes in crystal structure. Multiplet splitting and shake-up in the iron oxides contributes to iron $2p$ peak widths. The chemisorption of water has a marked effect upon the observed peak profiles; the oxygen $1s$ peaks due to oxide, hydroxyl, and adsorbed water have been characterised.

A NUMBER of compounds containing iron and oxygen have been examined by *X*-ray photoelectron (*X*.p.e.) spectroscopy. The materials were chosen to reflect the change in electronic environment of atoms on going from simple binary oxides to ternary oxides incorporating various alkali metal atoms.

The difficulties of surface contamination due to chemisorption, particularly of water, experienced in an earlier study of chromium–oxygen systems [1] were again evident. Also, the resulting spectra were highly complex due to multiplet splitting effects which are characteristic of such iron compounds.

EXPERIMENTAL

Materials and Reagents.—Lithium ferrite was prepared in its face-centred cubic phase modification by the reaction of AnalaR lithium carbonate with Specpure Grade α-Fe_2O_3. The reaction mixture (having a $Li_2CO_3 : Fe_2O_3$ molar ratio of $1{\cdot}03 : 1$ rather than $1 : 1$ to compensate for vaporisation of Li_2O during the reaction) was ground intimately, compressed into pellet form, and fired in a platinum crucible at 900 K for 48 h in a stream of dry oxygen-free argon. The powder *X*-ray diffraction pattern for the reaction product was in excellent agreement with that given by Anderson and Schieber [2] and analyses for lithium and iron showed deviations within only 1% from the required $1 : 1$ atomic ratio.

Sodium ferrite was prepared in its hexagonal α-phase modification by the reaction of an intimate mixture of $NaOH : Fe_2O_3$ in $2 : 1$ molar ratio. The reactants were heated to 620 K (above the m.p. of NaOH) in a platinum crucible under a stream of dry oxygen-free argon.

$$2NaOH + Fe_2O_3 \longrightarrow 2NaFeO_2 + H_2O$$

The powder *X*-ray diffraction pattern given by the orange-brown reaction product was in excellent agreement with that published by Thèry and Collongues [3] for α-$NaFeO_2$.

The orthorhombic β-phase of sodium ferrite and face-centred cubic potassium ferrite were each prepared by the reaction of the corresponding alkali metal carbonate with Fe_2O_3. In both cases the reaction mixture, in pellet form, was fired in a nickel crucible at 1175 K for 48 h in a stream of dry oxygen-free argon. The product of each reaction gave a powder *X*-ray diffraction pattern in excellent agreement with data in the literature [Watanabe and Fukase [4] (for β-$NaFeO_2$) and Barth [5] (for $KFeO_2$)].

Wustite, ' FeO ', was prepared by the reaction of Fe_2O_3 with metallic iron and subsequent quenching as described by Addison, Barker, and Hooper.[6]

Samples of the minerals α-FeO(OH), Goethite; α-Fe_2O_3, Specular Haematite; Fe_3O_4, Magnetite were supplied by R. F. & D. Parkinson, Shepton Mallett, Somerset.

Specpure α-Fe_2O_3 was supplied by Johnson Matthey; Li_2CO_3, Na_2CO_3, NaOH, and K_2CO_3 were AnalaR Grade as supplied by British Drug Houses. 99·5% Pure reagent grade Fe_3O_4 was supplied by Hopkins and Williams. Iron metal foil of 0·125 mm thickness and purity 4N88 was supplied by Goodfellow Metals Limited.

X-*Ray Photoelectron Spectroscopic Measurements.*—Binding energies and chemical shifts were measured using a Vacuum Generators ESCA-2 *X*-ray photoelectron spectrometer with Al-K_α *X*-radiation (1486·6 eV). Samples of powders were ground to a particle size of <50 μm and pressed into a gold-plated mesh. To compensate for possible charging effects a thin layer of gold was deposited on the surface of the sample, after insertion into the spectrometer, according to the method of Hnatowich *et al.*,[7] and binding energies were measured relative to the $4f_{7/2}$ line at 84·0 eV given by the gold on the surface. An assessment of this technique has already been given.[1]

The observed binding energies, corrected for surface charging, for the electrons in the iron oxide species examined are listed in the Table.

The iron $2p_{3/2}$, oxygen $1s$, and the appropriate alkali metal level binding energies are listed for all the compounds together with other selected peaks.

Contamination of Surfaces by Chemisorption.—Most of the materials which were studied readily chemisorbed either water or oxygen. The dissociative chemisorption of water leads to a high surface concentration of hydroxyl groupings, and was characterised by broadening of the oxygen $1s$ peak to the high binding energy side as compared with the anhydrous oxide. The lower oxides of iron were subject to considerable surface oxidation effects.

It was necessary to dehydrate the samples which were contaminated by water, by controlled heating, within the spectrometer, in order to produce and maintain relatively anhydrous surfaces from which reproducible results could be obtained. During this process the changing profile of the oxygen $1s$ peak was observed, thus allowing the removal of water to be monitored.

The oxygen contaminated surface layer of the samples of Wustite, ' FeO ', and iron metal was removed using an Electrotech 5 kV argon ion gun within the spectrometer,

---

[1] G. C. Allen, M. T. Curtis, A. J. Hooper, and P. M. Tucker, *J.C.S. Dalton*, 1973, 1675.

[2] J. Anderson and T. Schieber, *J. Phys. and Chem. Solids*, 1964, **25**, 961.

[3] J. Thèry and R. Collongues, *Compt. rend.*, 1958, **247**, 2003.

[4] H. Watanabe and T. Fukase, *J. Phys. Soc. Japan*, 1961, **16**, 1181.

[5] T. F. W. Barth, *J. Chem. Phys.*, 1935, **3**, 324.

[6] C. C. Addison, M. G. Barker, and A. J. Hooper, *J.C.S. Dalton*, 1972, 1017.

[7] D. J. Hnatowich, J. Hindis, M. L. Perlman, and R. C. Ragaini, *J. Appl. Phys.*, 1971, **42**, 4883.

leaving a freshly exposed surface for analysis. Samples of the minerals Specular Haematite, α-Fe_2O_3, and Magnetite, Fe_3O_4, were also examined before and after argon-ion bombardment.

THEORETICAL CONSIDERATIONS

In the earlier study of chromium oxygen systems well defined pseudo-Gaussian peaks were obtained in the chromium $2p$ region, allowing easy measurement of peak position. However, in this study the iron $2p$ region of the X-ray p.e. spectra of the compounds did not yield to such ready analysis. The iron $2p$ region of the spectrum given by Wustite, ' FeO ', typifies the problem [see spectrum (a) in the Figure].

Binding energies for elements in various iron oxides

	Iron			Oxygen	Other	
	$2p_{3/2}$ (±0·2)	$2p_{1/2}$ (±0·2)	$2s$ (±0·2)	1s (±0·1)		
Fe metal	707·3	720·3				
Wustite,[a] ' FeO '	710·3	723·8		530·1		
α-Fe_2O_3	711·4	724·6	849·0	530·2		
Fe_3O_4	711·4	724·9		530·1		
Goethite, α-FeO(OH)	711·0	724·5		531·0 $\left\{\begin{matrix}530·1\\531·8\end{matrix}\right.$		
$LiFeO_2$	711·8	725·3		530·1	Li 1s [b]	
α-$NaFeO_2$	711·5	725·1		530·0	Na 1s	1073·1
β-$NaFeO_2$	711·8	725·4		530·0	Na 1s	1073·4
$KFeO_2$	711·3	724·6		530·1	K $2p_{3/2}$	287·5
					K $2p_{1/2}$	290·4

[a] Spectrum recorded after argon-ion bombardment. [b] Not measurable due to coincidence with Fe $3p$ and Au $5p$ levels.

The base-line climbs steeply in this region. In itself this would not normally present any experimental difficulty provided that the observed peaks were relatively sharp and well defined. Unfortunately, however, due to the multiplet splitting effects, the maxima assigned to Fe $2p_{3/2}$ and $2p_{1/2}$ each have a number of satellite peaks to the binding energy side, which combine to almost the height of the maxima in some cases.

The theory of multiplet splitting is now well known. The effect is caused by the presence of unpaired valence electrons, resulting in exchange interaction which affects differently the remaining spin-up or spin-down core electrons. In general multiplet splitting is greatest when both unfilled shells have the same principal quantum number, when there is a large number of unpaired valence electrons, and when the ligands around the atom of interest have no orbitals available for overlap which could lead to metal electron delocalisation through π bonding (*e.g.* oxygen and fluorine). Furthermore, if the core vacancy is in an s-shell, only two final states are possible, but when the vacancy occurs in an orbital of higher angular momentum, more complex final states result.

In the present system two of these conditions which maximise multiplet splitting are present. First, many of the iron oxides contain iron having a formal oxidation number of three and all are high spin, giving the maximum number of five unpaired $3d$ electrons in these cases. Secondly, the ligand in all compounds studied is oxygen. Fadley and Shirley[8] have shown that for MnF_2 [another high spin $(3d)^5$ system] the $2p$ peaks are broadened by *ca.* 1·5 eV with respect to those given by systems for which little splitting is observed in the $3s$ region. Thus one would expect to observe broad Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks with half-widths $(\Delta_{\frac{1}{2}})$ of between 3·8 and 4·4 eV in the iron(III) oxides, but by analogy with the calculations for splittings in the $3p$ state of Mn^{2+} the most intense component should be that due to the high multiplicity P state occurring at high kinetic energy (low binding energy) relative to the other P state components. This is in good agreement with the peak shape observed in these present studies.

The multiple electron transitions producing shake-up processes are now similarly well understood although the magnitude of the separations (to the lower kinetic energy side) of the resultant satellites from the parent peak are not easily predicted. Novakov and Prins[9] have shown that the presence of an excess of oxygen atoms in the surface to the depth examined by X.p.e. spectroscopy in the form of oxygen itself or water, may greatly enhance shake-up. In other systems (*e.g.* NiO) it is suggested that intrinsic non-stoicheiometry will cause the process to occur, and a parallel study by Schön and Lundin[10] seems to substantiate this. In the well documented case of NiO, Novakov and Prins have tentatively assigned the satellites at low energy separations from the main photoelectron line to $d^8 \longrightarrow d^{8*}$ transitions whilst the satellites with larger energy separations may be due to $d^8 \longrightarrow d^7s$ and/or O $2p \longrightarrow$ Ni $4s$.

When applying these considerations to the present system, it should be noted that each of the components in the main photoelectron $2p_{3/2}$ or $2p_{1/2}$ response will give rise to a series of shake-up satellites which will have the same relative intensity with respect to the parent component. Since the compounds studied exhibit surfaces with an affinity for an excess of oxygen and also intrinsic non-stoicheiometry, shake-up processes would be expected to occur quite readily and overall the diffuse spectra observed in the iron $2p$ region are in agreement with those predicted from these theoretical considerations.

RESULTS

As in the case of our study of chromium oxygen systems[1] the spectra were strongly influenced by the susceptibility of the sample to dissociative chemisorption of water at the surface. The Fe $2p$ peaks were broadened as a consequence of the effects discussed above and did not permit the measurement of absolute binding energies. However, the use of the measured position of Fe $2p$ peak maxima in con-

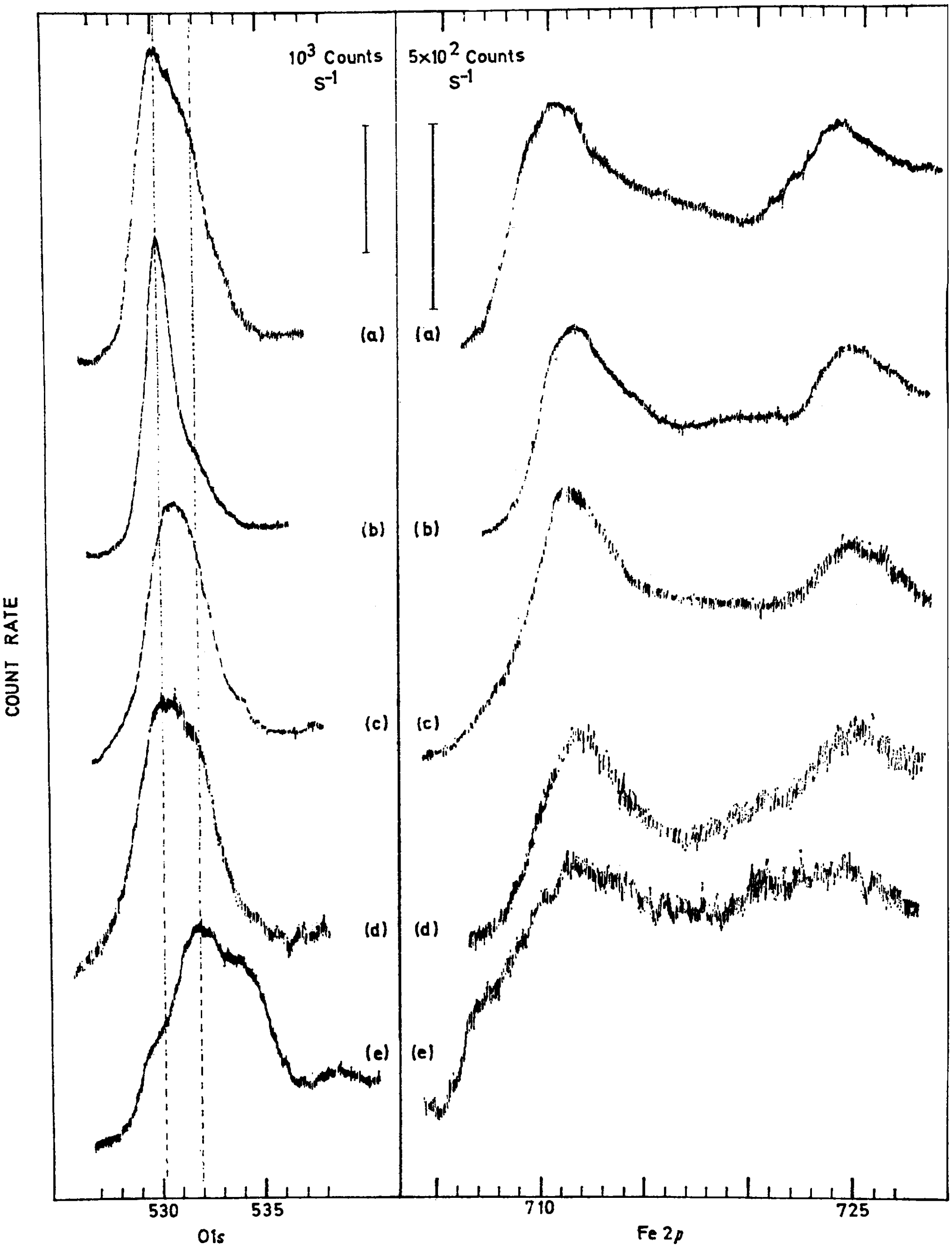
---

[8] C. S. Fadley and D. A. Shirley, *Phys. Rev.*, 1970, **A2**, 1109.

[9] T. Novakov and R. Prins, ' Electron Spectroscopy,' ed. D. A. Shirley, North-Holland, 1972, p. 821.

[10] G. Schön and S. T. Lundin, *J. Electron Spectroscopy*, 1972, **1**, 105.

junction with the measured O 1*s* binding energy provides a good characterisation of the sample.



Oxygen 1*s* and iron 2*p* photoelectron spectra of (a), Wustite, ' FeO,' after argon-ion bombardment; (b), freshly opened Specpure α-Fe_2O_3; (c), Goethite, α-FeO(OH); (d), α-$NaFeO_2$ after heat treatment; (e), α-$NaFeO_2$ prior to heat treatment

The oxygen 1*s* peak profile provides a good indication of the degree of chemisorption at the surface and the understanding of oxygen 1*s* spectra is increased by interpreting the spectra of (i), anhydrous α-Fe_2O_3 where oxygen atoms are present solely as oxide ion; (ii), α-FeO(OH) where oxygen atoms are present in two environments; and (iii), excessively hydrolysed species where oxygen is present at the sample surface in the form of physisorbed water.

Iron Metal.—Fadley [11] reported *X*-ray p.e. spectra from iron metal. The results reported here are in very close agreement with those of Fadley. The ' as received ' metal when placed in the spectrometer gave a well defined spectrum characteristic of α-Fe_2O_3 *vide infra* the Fe $2p_{3/2}$ and

---

[11] C. S. Fadley, ' Electron Spectroscopy,' ed. D. A. Shirley, North-Holland, 1972, p. 781.

Fe $2p_{1/2}$ maxima occurring at 711·4 and 725·0 eV respectively. After the sample had been subjected to argon-ion bombardment the iron peaks sharpened considerably and showed a marked shift to lower binding energy. The Fe $2p_{3/2}$ and Fe $2p_{1/2}$ now occurred at 707·3 and 720·3 eV respectively and the more intense Fe $2p_{3/2}$ peak showed a shoulder to the high binding energy side. Fadley's values are identical to these when referred to the Au $4f_{7/2}$ line taken at 84·0 eV.

α-Iron(III) *Oxide*, α-Fe_2O_3.—The spectroscopic study of α-Fe_2O_3 showed many similarities to that previously carried out for its isostructural analogue in the chromium oxygen system, Cr_2O_3.[1] The spectrum obtained was highly dependent upon the pretreatment of the sample, extremely broad peaks being observed when the sample had undergone prolonged exposure to the atmosphere, which allowed surface contamination by the dissociative chemisorption of water. As in the case of Cr_2O_3, the fresh Specpure material gave a spectrum with relatively narrow well defined peaks (see Figure) the oxygen 1*s* peak having $\Delta_{\frac{1}{2}} = 1{\cdot}6$ eV. The Fe $2p_{3/2}$ binding energy recorded (711·4 eV) for this sample was in good agreement with the value of 711·5 eV reported by Carver, Schweitzer, and Carlson.[12] Samples which were subject to prolonged grinding in air but no subsequent heat-treatment within the spectrometer gave oxygen 1*s* peaks broadened to give $\Delta_{\frac{1}{2}} = 4{\cdot}8$ eV in the most extreme case. The broadening was caused by the growth of a second oxygen 1*s* peak at 531·8 eV due to the more positive oxygen atoms in the surface hydroxyl groups, *vide infra*.

A sample of Specular Haematite gave an identical spectrum to that obtained for α-Fe_2O_3.

Tri-iron Tetra-oxide, Fe_3O_4.—The room temperature spectrum of Fe_3O_4 was indistinguishable from many of those obtained for Fe_2O_3 at room temperature. Identical Fe $2p_{3/2}$ peak profiles were obtained with the maximum occurring at 711·4 eV. The oxygen 1*s* spectrum, however, was dominated by the peak at 531·8 eV rather than by that due to oxide oxygen. It would appear therefore that the sample surface consisted of hydrated Fe_2O_3 rather than Fe_3O_4. From standard thermodynamic data[13] the free energy of formation for the reaction

$$Fe_3O_4 + \tfrac{1}{4}O_{2(air)} \rightleftharpoons 3/2Fe_2O_3 \qquad (1)$$

may be obtained. The value for ΔG_{298} of $-95{\cdot}9$ kJ mol^{-1} Fe_3O_4 reflects the susceptibility of Fe_3O_4 to air oxidation to Fe_2O_3. Although the kinetics of the reaction preclude a short-term bulk reaction at room temperature, *X*.p.e. spectroscopy clearly demonstrates that surface oxidation does occur to a depth at least as great as the spatial limit for *X*.p.e. spectroscopy detection (*ca.* 2—3 nm).

This point was further substantiated by heating the Fe_3O_4 sample in the spectrometer. At temperatures above 900 K the maximum in the $2p_{3/2}$ region began to give a lower count rate and the peak envelope began to broaden appreciably to the low binding energy side. This behaviour was ascribed to the formation of iron having a lower oxidation state, namely the formally denoted Fe^{2+} centres in Fe_3O_4. The maximum of the envelope was in the same position of 711·4 eV as prior to the heat treatment (within experimental error) and the complex peak shape prevented deconvolution to yield the position of the underlying second peak corresponding to the iron in a lower oxidation state. It was of interest to note that even at these elevated temperatures the oxygen 1*s* spectrum still contained an appreciable (30—40%) contribution from hydroxyl oxygen.

Further consideration of the equilibrium represented in (1) yields an expression for the partial pressure of oxygen (p_{O_2}) when $\Delta G_T = 0$.

$$\text{Log}\, p_{O_2}\,(\text{Nm}^{-2}) = -\frac{26\,700}{T} + 19{\cdot}87 \qquad (2)$$

Thus one would expect the decomposition of Fe_2O_3 to occur at temperatures around 1000 K when heated in a vacuum in the pressure range 10^{-7} to 10^{-6} Nm^{-2} typical of the working pressure in the ESCA-2 sample preparation chamber. These calculations should be modified to include the mutual solid solution behaviour of Fe_2O_3 and Fe_3O_4, which would therefore result in a lowering of the chemical activities of the two phases from the assumed standard state values of unity. The calculation may, however, be used to substantiate the hypothesis that the Fe_3O_4 sample was initially contaminated with Fe_2O_3 at the surface and that the spectroscopic changes observed on heating under vacuum are due to the decomposition of this surface layer of Fe_2O_3, to give Fe_3O_4.

The mineral Magnetite in a very pure form was also investigated. The mineral was cut to expose a freshly cleaved surface and a spectrum was immediately recorded. This spectrum closely resembled that previously recorded for Fe_3O_4. On argon-ion bombardment the spectrum sharpened and the Fe $2p_{3/2}$ peak showed a small shift to lower binding energy ($-0{\cdot}4$ eV). In an attempt to further resolve the Fe $2p$ spectrum the sample was cooled to liquid nitrogen temperature. No further sharpening occurred and no evidence for discrete Fe^{II} and Fe^{III} oxidation states in the octahedral sites could be evinced at this temperature.[14] However it should be emphasised that the Fe $2p_{3/2}$ peaks are complex in these systems (*vide supra*) and if the resolution of the spectrometer is taken into account together with the relatively small shifts observed between the Fe $2p_{3/2}$ levels in Wustite, 'FeO', and α-Fe_2O_3 it is not surprising that no evidence for the discrete oxidation states could be obtained.

'FeO', *Wustite*.—As in the case of Fe_3O_4, the room temperature spectra of Wustite indicated that air oxidation had occurred to a sufficient extent to convert the surface region examined by *X*.p.e. spectroscopy entirely to Fe_2O_3. Again this would be predicted from thermodynamic data since for

$$\text{'FeO'} + \tfrac{1}{4}O_2(\text{air}) \rightleftharpoons \tfrac{1}{2}Fe_2O_3 \qquad (3)$$

the value for ΔG_{298} of $-124{\cdot}4$ kJ mol^{-1} 'FeO' is obtained. The oxygen 1*s* region of the room temperature spectra was consistently dominated by a high binding energy peak which in this case occurred with binding energy valued in the range 531·8 to 532·2 eV and may well have been produced by adsorbed oxygen rather than water.

Samples of Wustite which had been ground more vigorously prior to examination gave rather different spectra to those described above. The iron $2p_{3/2}$ peak was considerably broadened to the low binding energy side such that the maximum occurred at 711·0 eV. It seemed

---

[12] J. C. Carver, G. K. Schweitzer, and T. A. Carlson, *J. Chem. Phys.*, 1972, **57**, 973.

[13] C. E. Wicks and F. E. Block, Bureau of Mines Bulletin 605, 1963.

[14] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 302.

reasonable to assume that some iron atoms having a lower oxidation state were now present in the fresh sample surfaces and that since the maximum no longer occurred at the familiar value for Fe^{3+} in Fe_2O_3 or Fe_3O_4, these atoms were in Wustite. Whereas the oxygen 1*s* region had previously been resolved into two distinct peaks, the more vigorously ground samples gave an unresolved combination of the original oxide oxygen 1*s* peak (which had binding energy 350·1 eV) and a higher binding energy peak occurring *ca.* 531·5 eV.

Spectroscopic changes of the type developed by grinding samples to produce fresh Wustite surfaces (which were not completely oxidised to Fe_2O_3 subsequently) were observed to a greater extent when samples, irrespective of pre-treatment, were subjected to argon-ion bombardment in the sample preparation chamber of the spectrometer. The high binding energy side of the iron $2p_{3/2}$ peak was considerably diminished and a somewhat narrower peak with a maximum at 710·3 eV was obtained (see Figure). This observation indicated that the oxidised surface of the sample had been stripped away sufficiently for a spectrum representative of Wustite to be obtained. (It appeared that the oxygen partial pressure in the spectrometer was too low to completely reoxidise the exposed Wustite in the time required for the spectroscopic examination although it is possible that different sputtering rates for iron and oxygen occurred casting some doubt on the precise composition of the sample surface.) The decontaminating effect of argon-ion bombardment was further emphasised by the oxygen 1*s* spectrum corresponding to the best resolved Fe $2p_{3/2}$ spectrum (see Figure). Although the peak obtained was non-Gaussian, the $\Delta_{\frac{1}{2}}$ value had been reduced to 2·9 eV and the oxide oxygen component was 70—75% of the total peak area with the higher binding energy response, due to chemisorbed species, making up the remainder.

α-FeO(OH), *Goethite*.—Spectra obtained at room temperature were surprisingly stable during prolonged exposure of the sample to the vacuum system of the spectrometer, considering that the bulk decomposition of α-FeO(OH) occurs at 403 K in air:

$$FeO(OH) \longrightarrow \tfrac{1}{2}Fe_2O_3 + \tfrac{1}{2}H_2O \qquad (4)$$

The maximum in the iron $2p_{3/2}$ region of the spectrum occurred at a binding energy of 711·0 eV. This value is some 0·4 eV lower than the consistently recorded value for iron in α-Fe_2O_3 and suggests that the iron atoms in α-FeO(OH) have a slightly lower atomic charge. This is not easily rationalised on the basis of the structures of the two compounds α-FeO(OH) and α-Fe_2O_3 since both may be described as almost perfect hexagonal close packings of oxygen atoms with iron situated in octahedral sites. But the marginally shorter Fe–O bond lengths in α-FeO(OH) may be an indication of an increase in covalent character. The oxygen 1*s* spectrum almost invariably consisted of a broad ($\Delta_{\frac{1}{2}} \simeq 3·5$ eV), symmetrical, flat-topped peak centred *ca.* 531·0 eV (see Figure). A spectrum of this nature was obtained irrespective of sample pre-treatment (grinding procedure, exposure to air). This broad peak may be easily deconvoluted to show the presence of two pseudo-Gaussian peaks (each with $\Delta_{\frac{1}{2}} \simeq 1·7$ eV) occurring at 530·1 eV and 531·8 eV. This observation is consistent with the crystal structure,[15] which shows that two types of oxygen environment are present in α-FeO(OH). The presence of asymmetric hydrogen bridging as in the isostructural Diaspore,[16] α-AlO(OH), leads to oxide-like and hydroxide-like oxygen atoms but it is not possible to regard either form as discrete, *viz.*, $Fe—O^{I}——H—O^{II}—Fe$.

Experimental evidence indicates that this structure does not readily chemisorb water vapour and that the 1 : 1 ratio of oxide-to-hydroxide bound oxygen atoms is stable in the α-FeO(OH) structure. Indeed it seems probable that a similar structure is produced on most of these iron oxide systems following the chemisorption of water vapour.

On this basis the peak at 530·1 eV is assigned to the O^{I} (oxide-like) oxygens and that at 531·8 eV to the O^{II} (hydroxide-like) oxygens in these compounds.

Lithium Dioxoferrate(III), $LiFeO_2$.—The room temperature oxygen 1*s* spectrum of $LiFeO_2$ showed the sample surface to be almost free of contamination by chemisorbed oxygen-containing molecules since a well resolved peak was obtained showing only slight broadening to the high binding energy side. The peak position corresponded to a binding energy of 530·1 eV which has been established as characteristic of oxide oxygen in this system. The Fe $2p_{3/2}$ spectrum showed little evidence of the satellites produced by chemisorption of water to the high binding energy side of the main peak, compared with previous spectra, and the maximum at binding energy 711·8 eV was well defined.

This higher value for the binding energy of Fe $2p_{3/2}$ electrons, compared with other oxides containing iron with an oxidation state of three, indicates a larger atomic charge for the iron atoms in $LiFeO_2$. This could be attributed to the cubic $LiFeO_2$. However, the reported low temperature form could not be obtained despite numerous attempted preparations, whilst the high temperature form could not be prepared completely free of the cubic phase. The ideal method of preparing the high temperature form would have been to anneal the sample in the spectrometer but in the pressure ranges used the evolution of Li_2O at the required temperature (843 K) was found to preclude this.

α-*Sodium Dioxoferrate*(III), α-$NaFeO_2$.—Initial spectroscopic studies of α-$NaFeO_2$ at room temperature revealed numerous similarities to the isostructural chromium analogue $NaCrO_2$.[1] This was particularly true for the oxygen 1*s* spectrum which consisted of a broad peak with a shoulder either side of the maximum at binding energy 530·5 eV, having $\Delta_{\frac{1}{2}} = 5·5$ eV (see Figure). The corresponding Fe $2p_{3/2}$ peak was ill defined and although the maximum occurred in the region 711—712 eV it was considered impossible to define a value with the same accuracy accorded to values for Fe $2p_{3/2}$ binding energies for previous compounds.

Leaving the finely ground sample to stand in air prior to the spectroscopic study resulted in an oxygen 1*s* spectrum dominated by the peak due to chemisorbed species (occurring at 531·9 eV in this case). A 'shake-off peak' was also observed in this spectrum at 538·6 eV.

These experimental observations are in accordance with the theory put forward for the oxygen 1*s* spectrum of $NaCrO_2$, that the shape of the oxygen envelope is determined by surface adsorption effects rather than structural aspects of the compound.

A detailed spectroscopic study of $NaFeO_2$ was then conducted at elevated temperatures to determine the

---

[15] S. Goldsztaub, *Bull. Soc. Franc. Mineral*, 1935, **58**, 6.

[16] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1958, **11**, 798.

nature of the oxygen species present. A freshly prepared sample was mounted in the spectrometer with minimal exposure to air and immediately heated to 473 K. The familiar oxygen 1*s* spectrum (taken as soon as the sample had attained 473 K) of a broad peak with two shoulders was again observed although the position of the maximum had shifted to higher binding energy. Prolonged heating at 473 K resulted in a reduction of the high binding energy side of the oxygen 1*s* envelope such that after 21 h there was no longer a well defined shoulder in this region. Just prior to this observation (after 20 h) the two shoulders on the peak had been obtained with maximum definition and there could be little doubt that three distinct oxygen species were present, giving three pseudo-Gaussian peaks each with $\Delta_{\frac{1}{2}} \simeq 2{\cdot}0$ eV. The reduction of the high binding energy side could be reversed rapidly by reducing the efficiency of the spectrometer's cold traps. This final observation, in conjunction with the low temperature required to remove the relevant oxygen-containing species and the high binding energy of the associated oxygen atoms, indicates the species to be physisorbed water, present in addition to chemisorbed water.

At higher temperatures (>573 K) dehydration proceeded rapidly and the oxygenated 1*s* envelope clearly consisted of two components having binding energies respectively at *ca.* 532·0 and 530·0 eV. Significantly the corresponding Fe $2p_{3/2}$ peak was considerably improved in definition and the maximum could be placed accurately at 711·5 eV (see Figure). This observation reflects the importance of an excess of oxygen for production of shake-up satellites and infers that the species with oxygen having a binding energy *ca.* 532·0 eV is stoicheiometrically chemically bonded to iron nuclei. Also the shake-off peak in the oxygen 1*s* spectrum appeared at the same energy as before.

Heating at temperatures in the region 773—823 K did not alter the definition of the Fe $2p_{3/2}$ maximum nor its binding energy value, but did affect the oxygen 1*s* spectrum in which the low binding energy peak assigned to oxide oxygen atoms was very slowly enhanced at the expense of the higher binding energy peak. Treatment at higher temperatures to effect complete removal of the chemisorbed species within a few days was precluded since the α-$NaFeO_2$ would be converted to the β-phase modification.[17]

The strong retention of this chemisorbed species by α-$NaFeO_2$ is identical to the behaviour observed for the isostructural compound $NaCrO_2$. It would appear that the hexagonal structure and related electronic band structure associated with these materials allows them to chemisorb some species very strongly.

β-*Sodium Dioxoferrate*(III), β-$NaFeO_2$.—The room temperature spectra of β-$NaFeO_2$ showed many similarities to those recorded for α-$NaFeO_2$. An extremely broad irregular peak was observed in the oxygen 1*s* region and the Fe $2p_{3/2}$ maximum was ill defined. However, heating the sample to temperatures in the range 393—423 K resulted in an oxygen 1*s* spectrum, which clearly consisted of the familar peaks at 530·0 and 531·9 eV, and a correspondingly well defined maximum in the Fe $2p_{3/2}$ region. This maximum occurred at rather higher binding energy (711·8 eV) than that observed for α-$NaFeO_2$. β-$NaFeO_2$ is a rather unusual transition metal oxide in that it incorporates tetrahedral co-ordination of oxygen atoms around the iron atoms. This change in co-ordination number (and thus in associated effects) on going from α- to β-$NaFeO_2$ results in a small increase in the binding energies of the iron electrons.

In contrast to α-$NaFeO_2$, the peak at binding energy 531·9 eV in the oxygen 1*s* spectrum of β-$NaFeO_2$ diminished rapidly at temperatures above 573 K with accompanying enhancement of the peak at 530·0 eV, assigned to oxide oxygen atoms.

Potassium Dioxoferrate(III).—As in the case of β-$NaFeO_2$ the room temperature spectra recorded for $KFeO_2$ showed ample evidence of the presence of chemisorbed oxygen-containing species at the surface, Mild heat treatment at about 573 K resulted in a spectrum with only one major oxygen 1*s* peak, occurring at 530·1 eV, and a well defined maximum in the Fe $2p_{3/2}$ region at 711·3 eV. The Fe $2p_{3/2}$ peak might have been expected to occur at a value similar to that for β-$NaFeO_2$ since the iron atoms in $KFeO_2$ are also tetrahedrally co-ordinated by oxygen atoms but the different crystal structure of $KFeO_2$ and the different alkali metal cation involved do not produce a similar increase in the binding energies of iron electrons.

CONCLUSION

(1) The Fe 2*p* peaks in the *X*-ray p.e. spectra of iron(II) and iron(III) oxides are considerably broadened by multiplet-splitting effects and their shape is further determined by shake-up processes.

(2) When suitably corrected for surface charging effects the measured maxima in the Fe $2p_{3/2}$ region of spectra from the series of iron(III) oxides showed only a small dependence upon parameters such as crystal structure or incorporation of different alkali metal cations.

(3) The oxygen 1*s* peaks observed in low-temperature spectra could invariably be resolved into a peak due to oxide oxygen atoms and a second peak due to chemically bonded hydroxide groupings. With the exception of Goethite [FeO(OH)], these hydroxide groupings resulted from chemisorption processes. In the case of α-$NaFeO_2$ chemisorption was found to occur particularly strongly.

(4) The 1*s* electrons in oxygen atoms which are present as oxide have a constant binding energy of 530·1 ± 0·1 eV.

(5) The 1*s* electrons in oxygen atoms which are present as hydroxide have a constant binding energy of 531·9 ± 0·1 eV.

This paper is published by permission of the Central Electricity Generating Board.

[4/075 *Received*, 16*th January*, 1974]

---

[17] A. J. Hooper, Ph.D. Thesis, University of Nottingham, 1971.