

Electronic Structure of Iron(II) and (III) Fluorides using X-ray Emission and X-ray Photoelectron Spectroscopies

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Iron(II) and (III) fluorides have been studied using X-ray emission (XE) and photoelectron (XP) spectroscopies. XE data enable the XP peaks to be identified unequivocally; in the iron(III) compound the F $2p$ and Fe $3d$ orbitals were shown to have almost identical energy. The F $K\alpha$ XE peak profile showed the Fe-F bond to be more covalent in ferric than ferrous fluoride. Whilst the F $1s$ binding energy was the same for both compounds a peak shift of 3.0–3.5 eV to higher binding energies was found for all iron orbitals upon oxidation. The rapid reduction of iron(III) to iron(II) by argon-ion bombardment was observed.

The electronic structures of the difluorides of the first row transition metals have been studied using X-ray photoelectron (XP) spectroscopy^{1, 2} and ultraviolet photoelectron spectroscopy.³ Further studies of other similar transition metal compounds, especially oxides, have shown that the valence band is complex since peaks due to both the ligands and to the transition metal have very similar ionisation energies.⁴ X-ray emission (XE) spectroscopy is often of great use in such circumstances because the different atoms in a complex will give rise to quite different spectra. Furthermore the simple electric dipole selection rule which dominates X-ray emission spectra ($\Delta l = \pm 1$) enables the bonding roles of specific orbitals on the constituent atoms to be identified.⁵ Thus a vacancy in a metal $1s$ orbital would attract transitions from outer p orbitals, *e.g.*, $2p \rightarrow 1s(K\alpha_{1,2})$, $3p \rightarrow 1s(K\beta_{1,3})$, $4p \rightarrow 1s(K\beta_2)$ *etc.*, and from the valence band, transitions from molecular orbitals with metal p character. The structure of the peaks that arise from transitions of this latter type will reflect the bonding role of the metal p orbitals since the relative intensities of the component peaks are proportional to the amount of metal p character in each molecular orbital.⁶ Similarly the bonding roles of s and d orbitals can be probed by a study of the X-rays that arise from electronic transitions between valence band and core p vacancies. Complementary spectra can also be measured for ligand atoms.

These X-ray spectra can all be related to a common energy scale if the ionisation energies of the initial states can be determined; this can be done directly by X-ray photoelectron spectroscopy. Even if the XP peaks are shifted due to sample charging this will not invalidate the XE-XP spectral correlations since all core and all valence band peaks will be displaced by an equal energy. In order to demonstrate the usefulness of X-ray emission spectroscopy in elucidating the structure of complex peaks in X-ray photoelectron spectra and in order to compare the bonding in di- and trivalent transition metal compounds, iron(II) and (III) fluorides were studied using combined X-ray emission and X-ray photoelectron spectroscopies. In both

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types of spectroscopy it is of course a positive ion and not the original molecule which is studied. Only if Koopmans' theorem⁷ is obeyed is it possible to relate the spectrum directly to the molecular orbitals of the electronic ground state of the substance under investigation. For simplicity in the discussion in this paper it will be assumed that Koopmans' theorem does hold.

EXPERIMENTAL

Samples of anhydrous iron(II) and (III) fluorides (purities > 98 %) from B.D.H. were used as supplied and without further purification. X-ray photoelectron spectra were measured in a Vacuum Generator ESCA 3 (mark I) spectrometer using unmonochromatised Al $K\alpha_{1,2}$ radiation (9 kV, 20 mA) under vacuum conditions of better than 10^{-8} Torr. The samples, as fine powders, were mounted at the end of the transfer mechanism probe with double sided sellotape. Attempts were made to reduce the surface contamination of the samples but this led, in the case of the iron(III) fluoride, to rapid reduction (see below), although the iron(II) fluoride seemed quite stable under similar conditions (3 min irradiation at 4 kV, 20 μ A with 3×10^{-6} Torr of argon). The spectra shown in the figures and the ionisation energies used in the alignment of the X-ray emission spectra were all measured

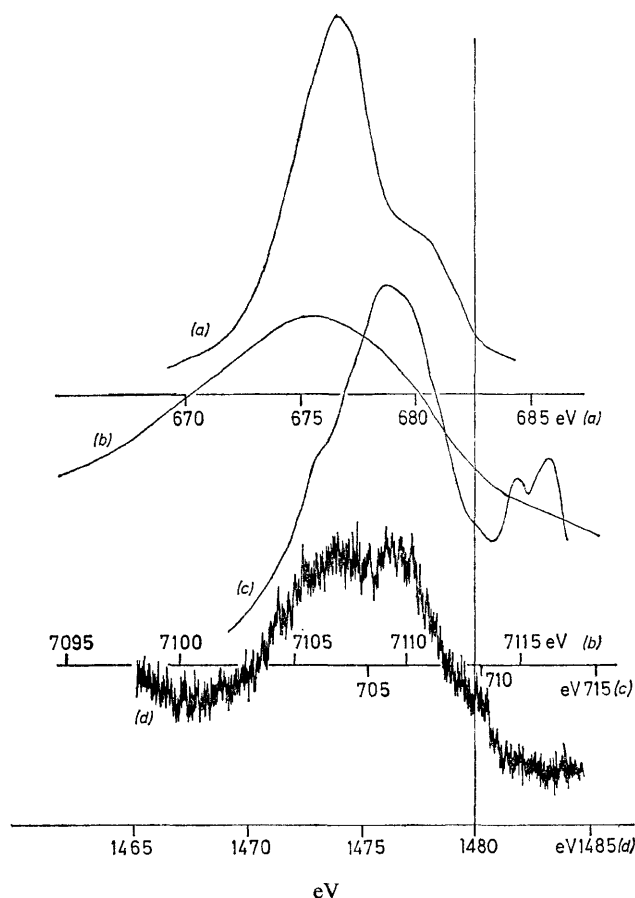


FIG. 1.—X-ray spectra for ferrous fluoride. (a) Fluorine $K\alpha$ X-ray emission; (b) iron $K\beta_{2,5}$ X-ray emission; (c) iron $L\alpha_{1,2}$ X-ray emission [doublet at 711–713 eV in (c) is due to ninth order Fe $K\alpha_{1,2}$]; (d) valence band X-ray photoelectron spectrum.

under identical conditions to avoid instrumental peak shifts. (Analyser setting, 50 V giving a minimum peak width of 1.5 eV, 3000 s scans of 25 eV range and a ratemeter time constant 3 s).

A Philips PW1410 X-ray fluorescence spectrometer was used to measure the fluorine $K\alpha$, iron $L\alpha_{1,2}$ and iron $K\beta_{2,5}$ spectra. The samples were made into discs backed with terephthalic acid and irradiated with X-rays from a chromium anode X-ray tube (50 kV, 50 mA). The characteristic X-rays emitted by the sample were diffracted using a rubidium acid phthalate ($2d = 2621$ pm) crystal for F $K\alpha$ and Fe $L\alpha_{1,2}$ and a germanium (111) ($2d = 655$ pm) crystal, operated in the third order for better resolution, for Fe $K\beta_{2,5}$. The diffracted F $K\alpha$ and Fe $L\alpha_{1,2}$ X-rays were detected in a gas-flow proportional counter (90 % argon, 10 % methane atmospheric pressure) fitted with a thin ($1\text{ }\mu\text{m}$) polypropylene window to reduce X-ray attenuation. For the harder Fe $K\beta$ X-rays a scintillation counter was used. In this case the additional collimation before the counter gave a higher overall resolution ($E/\Delta E \approx 1000$). The resolution for the softer X-rays was limited by the divergence of the primary "fine" collimator ($\approx \pm 0.1^\circ 2\theta$) and the rocking curve of the crystal giving a value of $E/\Delta E \approx 400$.

RESULTS

The spectroscopic results are presented graphically in fig. 1 and 2 using the core level XP data summarised in table 1. The valence band XP spectrum is very similar to that obtained by Wertheim¹ and shows, poorly resolved, the three main features

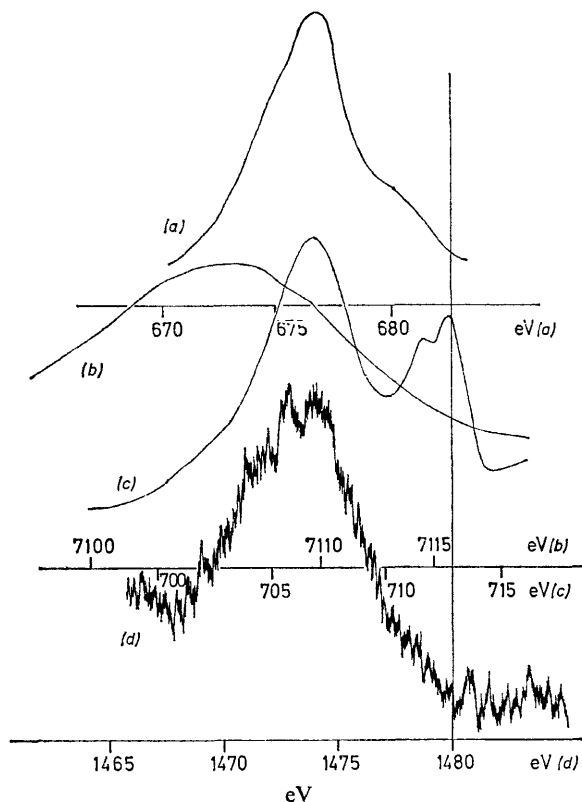


FIG. 2.—X-ray spectra for ferric fluoride. (a) Fluorine $K\alpha$ X-ray emission; (b) iron $K\beta_{2,5}$ X-ray emission; (c) iron $L\alpha_{1,2}$ X-ray emission [doublet at 711–713 eV in (c) is due to ninth order Fe $K\alpha_{1,2}$]; (d) valence band X-ray photoelectron spectrum.

seen by Shirley *et al.*² at much higher resolution, *i.e.*, two peaks of similar intensity separated by 3 eV and a weak peak at higher kinetic energy. This small peak is missing from the iron(III) fluoride XP spectrum and relative to both the carbon (contamination) 1s level and the fluorine 1s level the whole XP valence band spectrum is moved to lower kinetic energies, relative to iron(II) fluoride, by ≈ 2.5 V. No attempt was made either to measure or to dispel the charge which the samples acquired during the determination of XP spectra. The carbon 1s peak kinetic energy of 1197.5 eV suggests that both had a charge of $\approx +4$ V. Since the fluorine 1s energy was also found to be the same for both samples this provides a useful point of cross-reference.

TABLE 1.—KINETIC ENERGIES OF PHOTOELECTRON PEAKS FROM IRON FLUORIDES

	FeF ₂	FeF ₃
F 2s	1452.4	1452.0
Fe 3p	1426.0 ^a	1423.2 ^a
Fe 3s ^b	1388.0, 1382.0	1385.2, 1378.5
C 1s	1197.5	1197.5
F 1s	797.4	797.3
Fe 2p _{3/2}	$\sim 771.0^a$	$\sim 767.5^a$
Fe 2p _{1/2}	$\sim 757.5^a$	$\sim 754.0^a$

All kinetic energies have an estimated error of ± 0.1 eV.

^a These peaks showed strong asymmetry with a long tail to lower kinetic energies (see fig. 4 and 5 and text for Fe 2p_{3/2}). ^b This peak shows multiplet splitting; the lower kinetic energy component has about half the intensity of the higher energy peak. Carver *et al.*¹⁹ observed splittings of 6.0 and 6.5 eV for FeF₂ and FeF₃.

DISCUSSION

IRON(II) FLUORIDE

The clear separation (fig. 1) between the iron $L\alpha_{1,2}$ peak (Fe 3d character) and the fluorine $K\alpha$ peak (F 2p character) and their correlation with the main high kinetic and low kinetic energy peaks of the XP spectrum unequivocally identifies the nature of the electrons responsible for these peaks. This conclusion had already been arrived at by assuming that the F 2s–F 2p energy separation would be the same for iron(II) fluoride and for sodium fluoride (where it was found to be 21 eV).⁴ Further support for this identification of the XP peaks came from a study of the changes in their relative intensities as a function of the irradiation energy² and also from calculations based on a Born-model analysis.³ The X-ray emission data thus confirm the previously proposed peak identification. The weak ($^6A_{1g}$) peak at 1480 eV in the XP spectrum can be aligned with a poorly resolved low intensity shoulder in the iron $L\alpha_{1,2}$ spectrum. However, clear observation of this feature is hampered both by the presence of the high-order iron $K\alpha_{1,2}$ peak (which electronic pulse height selection was unable to remove) and of the Fe L_3 absorption edge.

Some of the breadth of the iron $L\alpha_{1,2}$ peak arises from the separation of the two possible quartet final states, 4E_g and $^4T_{2g}$, estimated to be ≈ 1 eV. There is,

however, further structure at ≈ 3 V less than the main peak which lines up with the low energy side of the fluorine $K\alpha$ peak. The iron $K\beta_{2,5}$ emission peak also lines up with the same region of the fluorine peak. In the simple ligand field model for bonding in iron(II) fluoride this coincidence of iron $3d$ and $4p$ character together with fluorine character should arise from molecular orbitals that are equivalent to bonds between iron and fluorine. In ferrous fluoride it is to be expected that these bonds would be quite ionic. The interaction of iron orbitals with fluorine $2p$ orbitals to make such bonds will not therefore cause a large perturbation from the fluorine $2p$ ionisation energy and extensive structure on the low energy side of the fluorine $K\alpha$ peak should therefore not be expected. That it is not observed confirms the ionic nature of the bonding in ferrous fluoride. It has also been observed that the intensity of the high energy satellite peaks ($K\alpha_{3,4}$) diminishes relative to the main ($K\alpha_{1,2}$) peak as the bonds to fluorine become more covalent.⁸ These peaks arise from transitions in doubly ionised systems, *i.e.*, (i) $1s^{-1} 2s^{-1} \rightarrow 2s^{-1} 2p^{-1}$ and (ii) $1s^{-1} 2p^{-1} \rightarrow 2p^{-2}$. The $1s$ and $2s$ holes can be regarded as localised on fluorine to a good approximation but the probability of the $2p$ spectator hole remaining on fluorine will be directly related to the covalency of the bands between fluorine and the adjacent atom. The greater the degree of covalence the less is the probability of (ii) taking place; a reduction in $\alpha_{3,4}$ satellite relative intensity is therefore an indication of increased covalency. In ferrous fluoride the F $K\alpha_{3,4}$ satellites are as strong as in sodium fluoride, indicative of the ionic nature of the $\text{Fe}^{\text{II}}\text{—F}$ bond.

IRON(III) FLUORIDE

A very different situation is found for ferric fluoride. The XP spectrum is less broad and the small peak at high kinetic energies is absent. Furthermore, the X-ray emission spectra show that the main iron $3d$ and fluorine $2p$ peaks are now almost coincident so that whilst the F $2s\text{—F } 2p$ energy difference method would locate fluorine $2p$ character there is no other feature in the XP spectrum to be identified with iron $3d$ orbitals. Also attempts to ascertain the location of F $2p$ and Fe $3d$ bands by varying the energy of the irradiating photons would be unsuccessful since the whole peak would slowly change intensity. In this case the unique advantages of X-ray emission spectra in elucidating the structure of XP peaks and in determining the location of specific orbitals is quite apparent.

The iron $L\alpha_{1,2}$ spectrum shows rather different low energy structure from the iron(II) case. The shoulder with an energy of 3 eV less than the peak is absent but a broader less intense feature is now observed as a low energy (699-704) tail at a greater energy separation from the main peak (707). This region corresponds to the low kinetic energy side of the XP peak and also to the pronounced low energy broadening of the fluorine $K\alpha$ peak. The iron $K\beta_{2,5}$ peak also aligns with this region. Since the main intensity of an X-ray emission peak for a halogen will come from transitions that originate from lone-pair orbitals it follows that low energy structure in such a peak will reflect participation by the halogen atom in bond formation.^{9, 10} The more covalent the bond the greater will be the separation of the new peak from the main peak but its intensity will diminish. That a distinct feature is observed on the low energy side of the F $K\alpha$ peak for iron(III) fluoride but not for the iron(II) compound shows that the bonds in the former are rather more covalent than in the latter. That these bonds are also more tightly bound in iron(III) than iron(II) fluoride relative to the fluorine $2p$ lone-pairs is shown by the greater F $K\alpha\text{—Fe } K\beta_{2,5}$ energy separation seen in the iron(III) case and also by the greater separation from the main peak of the low energy structure in the Fe $L\alpha_{1,2}$ spectrum for iron(III) fluoride. All the spectral

indications therefore confirm the anticipated increase in covalency of iron fluorine bonds with the increase in valency of the iron. It is interesting to note that the relative intensity of the $F K\alpha_{3,4}$ satellite peaks (to $F K\alpha_{1,2}$) is much less in FeF_3 than FeF_2 .

REDUCTION OF IRON(III) TO IRON(II) BY ARGON-ION BOMBARDMENT

That argon-ion bombardment can cause chemical reduction has been appreciated for some time.¹¹ In many systems however, the effects of reduction might not easily be observed, *e.g.*, due to peak overlap⁴ or to the speed of reduction of the

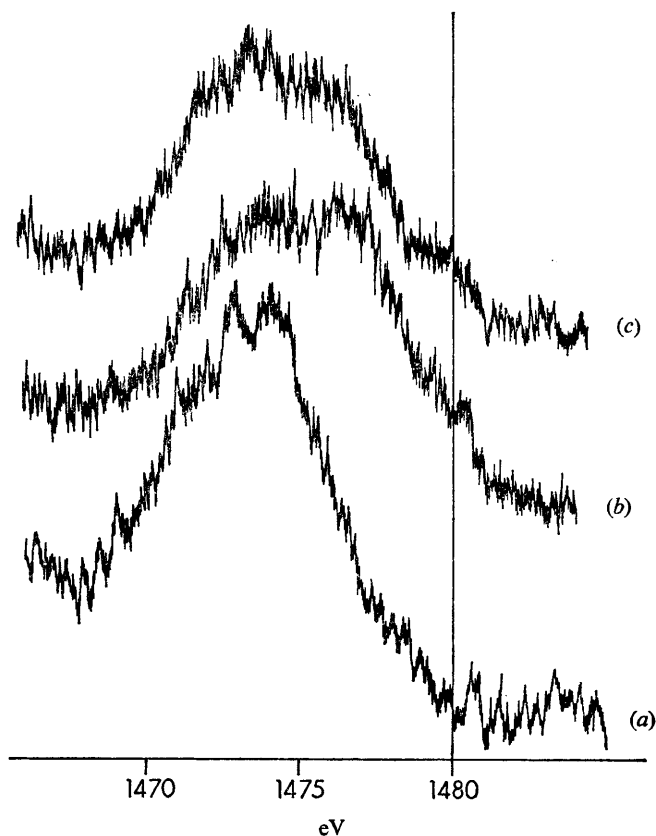


FIG. 3.—Valence band X-ray photoelectron spectra: (a) lower: iron(III) fluoride before argon-ion bombardment; (b) middle: iron(II) fluoride; (c) upper: iron(III) fluoride after argon ion bombardment. The spectra have been placed on a common energy scale using the following photoelectron kinetic energies, carbon $1s$, 1197.5 eV and fluorine $1s$, 797.4 eV.

surface layer being too rapid. Since the Fe^{III} and Fe^{II} fluoride spectra are quite distinctive in the valence band and show large core level shifts the reduction in this system could easily be observed, as is shown in fig. 3 and 4. Spectrum 3(c), FeF_3 after bombardment, exhibits those features that are uniquely characteristic of ferrous iron [fig. 3(b)] and quite different from the original [fig. 3(a)]. Similar changes are found in core levels, as is shown in fig. 4, associated with the peak shift $Fe^{III}-Fe^{II}$ of ≈ 3 V. Bombardment of iron(III) fluoride has caused the growth of a new peak at the energy characteristic of photoelectrons from iron(II) but the unsymmetric peak

shapes preclude the resolution of the peak into its components. Both fig. 3 and 4 show that after a brief bombardment with argon ions the majority of iron in the surface layers is in the ferrous state.

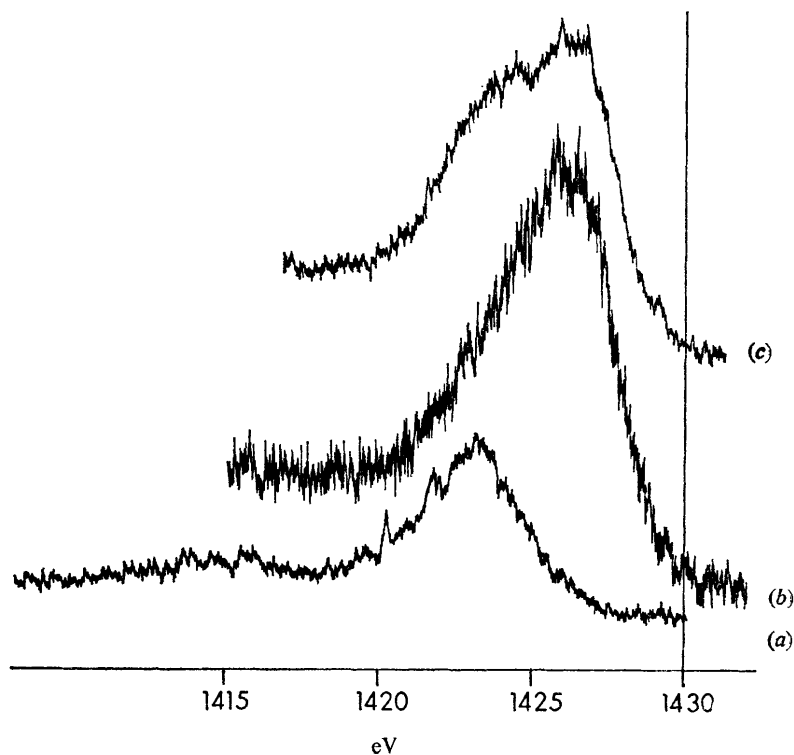


FIG. 4.—X-ray photoelectron spectra for iron 3*p*, (see caption fig. 3 for alignment): (a) lower: iron(III) fluoride before bombardment; (b) middle: iron(II) fluoride; (c) upper: iron(III) fluoride after bombardment.

XP SPECTRA: PEAK SHIFTS

Kinetic energies of photoelectrons ejected from various core orbitals in iron(II) and (III) fluorides are listed in table 1. Relative to the carbon 1*s* peak, the fluorine 1*s* ionisation energy is the same in both fluorides. Previous XP investigations of ionic substances have attempted^{12, 13} to interpret the chemical shifts in orbital binding energies of anions and cations by considering not only the effective charge on the ion itself but also the potential induced by neighbouring charges (Madelung potential).¹⁴ Calculations of this type predicted shifts that were much too large, although better correlations with experiment were achieved when polarisation effects were taken into account. Since the M—F bond must become progressively more covalent as the valency of M increases, the effective negative charge at fluorine must decrease, yet the F 1*s* binding energy is the same, for example, for NaF and for UF₄.¹³ Indeed, for many fluorides, where the valency of M varies from one to four, F 1*s* binding energies are all within the range 685.9 ± 0.7 eV. Clearly shifts, or their absence, in F 1*s* binding energies cannot be directly related to the effective charge of a fluoride ion. The fact that identical binding energies are observed for fluorine in

FeF_2 and FeF_3 is, therefore, not surprising. Since this result does not imply that the charge at fluorine is the same in both compounds, it in no way contradicts the qualitative conclusion from the XE spectra that the iron fluorine bond is more covalent in iron(III) than iron(II) fluoride.

In contrast to fluorine large shifts are observed for the core orbitals of iron of the order of 3.5 eV. Since the Madelung constant does not vary greatly for different crystal structures¹² and since the potential due to neighbouring ions does not seem to be the major factor in determining core orbital binding energies it is probably reasonable to conclude that the observed shifts in iron orbital energies are largely due to changes in the formal valence of the iron. In the valence band oxidation also causes the $\text{Fe } 3d$ orbitals to become more tightly bound, by 3 eV. It is this shift which accounts for the dramatic difference in the XP valence band spectra of the fluorides. Comparison with the iso-electronic manganese(II) fluoride² also suggests that it is the increased charge on the iron which causes the spectral shift since the XP spectrum of MnF_2 has two distinct peaks, just like FeF_2 . Brundle *et al.*¹⁵ have recently examined the XP spectra of iron oxides and shown that the chemical shift upon oxidation (specifically for $\text{Fe } 2p_{3/2}$) is only 1.5 V, *i.e.*, much less than observed here for the fluorides. This reduction could be due to the greater polarisability of oxygen, resulting in reduced formal changes at iron in the oxides, by comparison with the fluorides. Experimental determination of the absolute $\text{Fe } 2p_{3/2}$ ionisation energies supports this idea; FeF_3 , 714.2 eV; FeF_2 , 710.2 eV and Fe_2O_3 , 711.2 eV; FeO , 709.7 eV (C 1s, 284.0 eV). Whilst some error (possibly as much as ± 0.3 eV) must be attached to the measurements for the fluorides because of the shape of the peaks, the trends between fluorides and oxides are apparent.

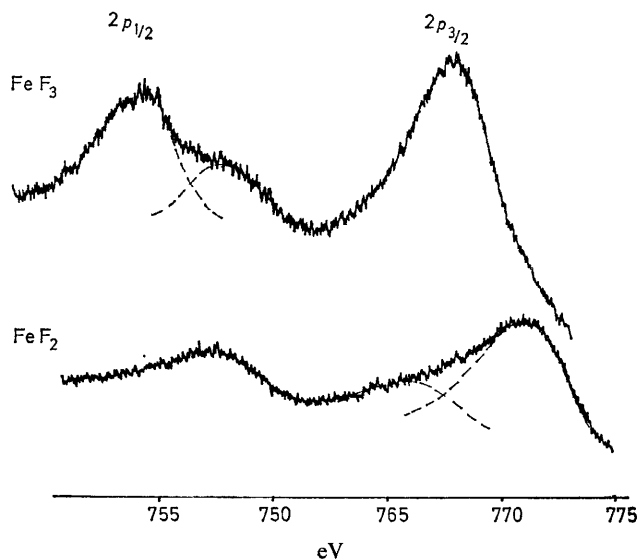


FIG. 5.—XP spectra for iron(II) and (III) fluorides in the $\text{Fe } 2p_{3/2}, 2p_{1/2}$ region.

The $\text{Fe } 2p_{3/2}, 2p_{1/2}$ XP peaks for the iron fluorides are shown in fig. 5 in order that the positions of the "shake-up" satellites can be observed. In the ferrous case the separation, satellite-main peak, has been variously quoted as 5.4 eV¹⁶ and 6.4 eV,¹⁷ from fig. 5 this separation can be estimated as 6 eV. A similar value was found

for iron(II) oxide.¹⁵ In the ferric case much greater separations were observed, ≈ 9.5 eV for the fluoride but only 8.5 eV¹⁵ or less¹⁶ for the oxide. It is therefore reasonable to conclude that these splittings can be used to differentiate the valence state of the iron as has been suggested,¹⁵ but that small ligand perturbations do occur. Similar but relatively much less intense shake-up structure was also observed for the iron 3*p* level in FeF₃ but with a separation of only 8.0 ± 0.5 eV. In the ferrous compound no satellite structure was resolved but the Fe 3*p* peak was strongly distorted. If this distortion is due to an unresolved satellite then the separation is 3.2 ± 0.5 eV. In neither case was there any evidence for a satellite of ≈ 15 eV less than the Fe 3*p* peak which could correlate with the *K* β' peak observed in the X-ray emission spectra. (For both FeF₂ and FeF₃ the X-ray spectrum shows a *K* β' peak of $\approx 30\%$ the intensity of the main *K* $\beta_{1,3}$ peak.) If multiplet splitting in the final state after the 3*p* \rightarrow 1*s* transition were the cause for the *K* $\beta_{1,3}$, *K* β' structure then such final state effects should also manifest themselves in XP spectra.¹⁸ Their absence in the XP spectra discussed here once again raises the question of the origin of the *K* β' peaks in first row transition metal X-ray emission spectra.

CONCLUSIONS

The data presented for iron(II) and (III) fluorides show that X-ray emission spectra can be used to identify X-ray photoelectron peaks and to resolve complex and overlapping structures in XP spectra. X-ray emission spectra also show that the Fe—F bond is more ionic to Fe^{II} than to Fe^{III}.

The distinctive nature of the iron(II) and iron(III) XP spectra enable the reduction of the latter to the former by argon-ion bombardment to be easily detected.

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