Valence-band *X*-Ray Emission Spectra of Manganese in Various Oxidation States

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The $K\alpha_{1,2}$, $K\beta_{1,3}$, $K\beta_{2,5}$, and $L\alpha_{1,2}$, $L\beta$ *X*-ray emission spectra of manganese in MnO, Mn_2O_3, MnO_2, $K[MnO_4]$, MnF_2, and $K_2[MnF_6]$ have been recorded. A knowledge of the $K\alpha_{1,2}$ energy enables the $K\beta$ and L emission spectra to be placed on a common energy scale thus revealing $4p$ and $3d$ ($+4s$) character in the molecular orbitals giving rise to the spectra. The changes in peak intensities and energies are rationalised using a simple molecular-orbital (ligand-field) approach.

X-RAY transitions involving the valence band of first-row transition-metal compounds can be observed in two distinct regions of the *X*-ray spectrum.[1] The higher-energy region, where peaks that result from transitions to a 1*s* (*K*) hole are found, ranges from 4 962 (Ti) to 8 977 eV (Cu), whilst the lower-energy region, in which peaks due to transitions to $2p$ ($L_{\text{II,III}}$) vacancies are observed, extends from 452 (Ti) to 930 eV (Cu).† The main peak in the higher-energy region is designated $K\beta_5$, which implies a $3d$–$1s$ transition. However, this nomenclature is based [2] on the false assumption that no electrons are to be found in orbitals with $4p$ character in the solid state. Furthermore, in this paper it will be demonstrated that when $K\beta_5$ peaks and L spectra (which manifestly do originate from orbitals with *d* character) are placed on a common energy scale they very rarely coincide, showing that *d* character is not responsible for the $K\beta_5$ peak. Since in all the models of bonding for transition-metal compounds [3] $3d$, $4s$, and $4p$ orbitals are all taken into consideration, it is reasonable to expect that some molecular orbitals will have some $4p$ character; it is from these orbitals that the valence-band *K* spectra may reasonably be expected to arise. A more reasonable nomenclature would therefore be $K\beta_2$ and the compromise $K\beta_{2,5}$ will be used in this paper. The other peaks that are sometimes observed in the *K* spectrum are $K\beta''$ to lower energy, and $K\beta'''$ to higher energy, of the $K\beta_{2,5}$ peak. The *L* spectra to be discussed here arise from the $3d\rightarrow2p$ transition. The $2p$ level is split by spin–orbit effects so that two *L* peaks are observed $L\alpha_{1,2}$ ($3d\rightarrow2p_{\frac{3}{2}}$) and $L\beta_1$ ($3d\rightarrow2p_{\frac{1}{2}}$). Since the $2p_{\frac{1}{2}}$ state is the more tightly bound, $L\beta_1$ lies at a higher energy than $L\alpha_{1,2}$. It should also be noted that 4*s* character in valence-band orbitals could also contribute to these transitions and that it is most unlikely, with the resolving power available, that distinct peaks due to orbitals with 3*d* or 4*s* character could be discerned.

Simple one-electron molecular-orbital models have been successfully used to interpret the *X*-ray emission spectra of main-group elements [4-7] and despite the obvious limitations of using such a theory for open-shell systems, such as are found in transition-metal compounds, it will be used in this paper in an attempt to rationalise the observed *K* and *L* spectra. The intensity of an *X*-ray emission peak [$I(\nu)$] of frequency ν is given [1,8] by $I \propto \nu^3(\int\psi_i\ \mathrm{P}\ \psi_f\ d\tau)^2$ where ψ_i and ψ_f are the wavefunctions for the initial and final states, and P denotes the transition operator which in the electric-dipole approximation may be set equal to *er*. Using the one-electron model, ψ_i and ψ_f may be approximated as hole-orbital wavefunction before transition and hole-orbital wavefunction after the transition. In *X*-ray valence-band spectra the former will be an atomic orbital (a.o.) (1*s* for *K* spectra and 2*p* for *L* spectra) and the latter will be a molecular orbital (m.o.). This orbital can then be expanded as a linear combination of atomic orbitals, thus, $\psi_f = \Sigma a_{rf}\phi_r$ where ϕ_r is the *r*th atomic orbital and a_{rf} is the coefficient describing the contribution of a.o. ϕ_r to the m.o. ψ_f.

If it is now assumed that a collection of peaks which differ only slightly in energy is to be discussed, then ν can be considered as constant and the intensity of an *X*-ray peak expressed as $\propto[a_{11}\int\psi_i\,.\,er\,.\,\phi_1 + a_{21}\int\psi_i\,.\,er\,.\,\phi_2,\ etc.]^2$ ($f = 1$). In a very simple m.o. where only two atomic orbitals are involved and ϕ_1 is on the same atom as ψ_i and ϕ_2 is a ligand orbital, then it can be shown [9] that the dominant term in the above equation arises from $\int\psi_i\,.\,er\,.\,\phi_1$ and that 'cross-over' terms involving ligand orbitals can be ignored. This is equivalent to saying that the ligand orbitals make no significant penetration into the electronic core of the central atom by comparison with valence-shell orbitals of the central atom. If one particular type of a.o. (*e.g.* ϕ_1) contributes to many valence-band molecular orbitals ($f = 1$—3, *etc.*) then the *X*-ray emissions that arise from those orbitals will have relative intensities $I_1 : I_2 : I_3$, *etc.* $= a_{11}^2 : a_{12}^2 : a_{13}^2$, *etc.* This result, in combination with the basic selection rule for electric-dipole transitions of $\Delta l = \pm 1$, enables transition-metal *K* and *L X*-ray spectra to be used to probe the amount of transition-metal *p* and *d* character present in valence-band molecular orbitals.

Experimentally, complications can arise which may cloud this simple interpretation of *X*-ray emission spectra.

K *Spectra*.—(*a*) Since in transition metals the 3*p* orbitals are only 30—70 eV more tightly bound than the

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† Thoughout this paper: 1 eV ≈ 1.60×10^{-19} J, 1 Torr = (101 325/760)Pa.

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valence-band molecular orbitals themselves, it is quite probable, and this has also been suggested by theoretical calculations,[10] that very little $3p$ character may be present together with $4p$ character in valence-shell orbitals (*i.e.* t_{1u} in O_h and t_2 in T_d). The presence of such $3p$ character will complicate the interpretation of $K\beta_{2,5}$ spectra because $\int\psi_{1s} . er . \psi_{3p} > \int\psi_{1s} . er . \psi_{4p}$, *i.e.* a little $3p$ character could go a long way! Two factors must be borne in mind: that this effect should be greatest for the most tightly bound of the valence-band K peaks, *i.e.* $K\beta''$, and that this effect should be most pronounced for Ti and V and become less important as the $3p$ ionisation energy increases, *i.e.* with increasing atomic number.

(*b*) High-energy satellites are clearly observed in the $K\alpha_{1,2}$ emission spectra of the lighter main-group elements. They arise from electronic-relaxation processes in doubly ionised atoms. If similar processes take place in transition-metal ions a comparable structure might be observed on the high-energy side of $K\alpha_{1,2}$ and also $K\beta_{1,3}$ emission peaks.[11,12] Such satellite peaks on the high-energy side of $K\beta_{1,3}$ peaks would compromise the observation of true $K\beta_{2,5}$ spectra.

(*c*) Self-absorption effects can complicate emission spectra especially if the absorption edge is only a few electronvolts removed in energy from the emission peak. In the K spectra discussed in this paper, however, p character is only expected in filled m.o. levels so that absorption and emission processes occur at significantly different energies.

L *Spectra*.—(*i*) Since the $3d$ level is only partially filled in most transition-metal compounds, severe self-absorption effects must, however, be anticipated in L spectra. For manganese the L_{III} absorption edge has an energy 2—3 eV higher than the $L\alpha_{1,2}$ emission energy. The $L_{II} - L_{III}$ energy separation is *ca.* 13 eV so that this edge will considerably affect the intensity of the higher-energy $L\beta_1$ ($3d \rightarrow L_{II}$) X-ray emission (*cf.* self-absorption effects in $L_{II,III}$ spectra of iron compounds [13]).

(*ii*) The relative intensities of the component peaks in the $3d \rightarrow 2p$ X-ray emission spectrum can be estimated, using the Burger–Dorgelo sum rules for closed shells,[1] as being $L\alpha_1 : L\alpha_2 : L\beta_1 = 9 : 1 : 5$. In systems with open shells, such as the compounds considered here, a much greater complexity of spin states arising from spin–orbit coupling can be anticipated,[14,15] which may in part explain the variations in the observed $L\alpha_{1,2} : L\beta_1$ peak intensity ratios.

(*iii*) From simple orbital-ionisation-energy considerations it would be expected that, for elements in the range V or Cr to about Ge, $L_{II}(^2P_{\frac{1}{2}})$ holes could decay by an Auger $L_{II},L_{III},M_{IV,V}$ process.[16] The L_{III} vacancy in the remaining doubly ionised ion might be filled by radiative transitions from the $3d$ level. Such transitions (by analogy with the ' high-energy ' satellites $K\alpha_{3,4}$ observed in doubly ionised atoms of the light elements) would be expected to give rise to satellite peaks on the high-energy side of the main $L\alpha_{1,2}$ peak.[17] Much of the ' molecular-orbital ' structure of the $L\alpha_{1,2}$ peak is, however, anticipated on the low-energy side so that the presence of such satellite peaks should not interfere with the observation of bonding effects.

General.—The final problem is one common to all spectroscopies in which the final state is ionised, relative to the initial state, in that a correlation of the observed spectra with orbital-energy calculations for the initial state will only be possible if Koopmans' theory [18] is obeyed or if relaxation effects are the same for all the orbitals. (In this case all the calculated energies would be in error by the same amount, but the ordering of the orbitals would not be affected.) Creation of a core hole, as studied by X-ray photoelectron spectroscopy (X-p.e.) is frequently accompanied by shake-up and shake-off events of considerable intensity.[19,20] X-Rays emitted when such excited species relax will have different, usually higher, energies from normal. Apart from some discussion by Parratt,[21] these problems have not been considered in the context of X-ray emission spectroscopy, but have been extensively studied in X-p.e. spectroscopy.[22,23]

EXPERIMENTAL AND RESULTS

Of the compounds studied, Mn(metal), MnO, MnF_2, MnO_2, and $K[MnO_4]$ were bought commercially and used directly without further purification, while $K_2[MnF_6]$ and Mn_2O_3 were prepared by standard chemical techniques.[24] The compounds were each ground to a fine powder and compressed into disks (diameter 3.6 cm), with terephthalic acid as a binding agent, for presentation to the spectrometer.

The X-ray spectra were recorded using a Philips PW 1410 single flat-crystal spectrometer. For the L lines, the exciting radiation was the bremsstrahlung of a chromium X-ray tube, typically run at 50 mA and 50 kV. The X-rays emitted from the sample were first collimated by Soller slits (angular divergence $\pm 0.1°$, 2θ) and then dispersed with a Rb.A.P. (001) crystal. The overall resolution ($E/\Delta E$) under these conditions was probably *ca.* 400. The photons were detected with a conventional gas flow-proportional counter preceded by further collimation to reduce background radiation. The gas in the counter was methane, held at *ca.* 100 Torr. This arrangement increased the signal-to-noise ratio by at least a factor of two over the more usual P10 gas mixture (10% CH_4–90% argon) at atmospheric

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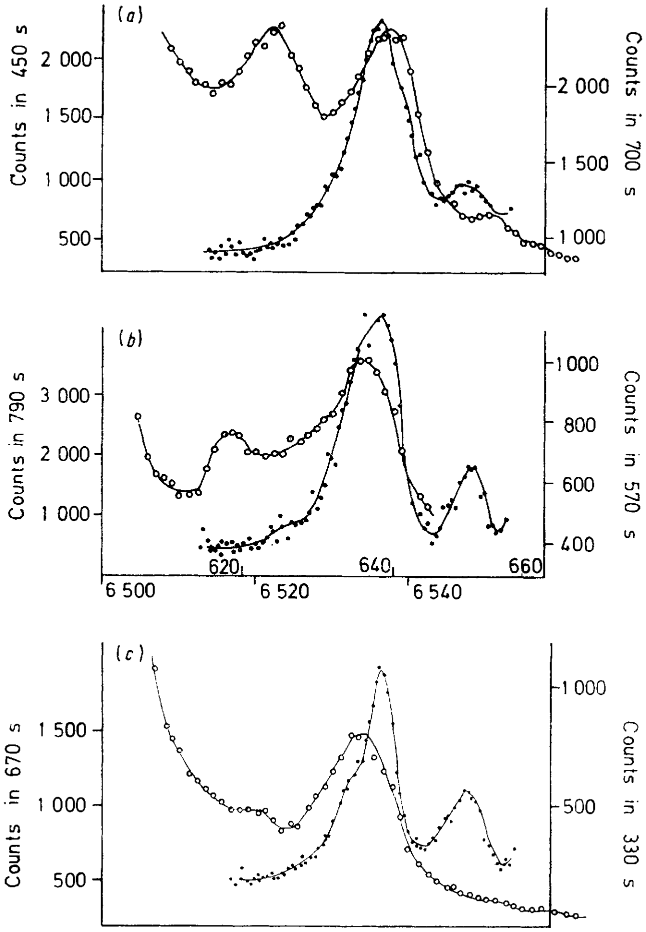
pressure. The spectra were recorded in a step-scanning mode, *i.e.* the number of counts in a given time was noted for intervals of 2θ corresponding to 0.5 eV. For spectra recorded with the flow counter the spectrometer was evacuated to *ca.* 0.01 Torr by means of a rotary pump together with a liquid-nitrogen cold trap.

The K lines, of much higher energy, were more efficiently excited with a tungsten X-ray tube typically operated at 45 mA and 60 kV. This tube, like the chromium tube, was evacuated, sealed, and water-cooled. Because of the geometry of the spectrometer (*i.e.* increased collimation) better resolution ($E/\Delta E \sim 1\,000$) was obtained if a scintillation counter, situated some distance behind the flow counter and outside the vacuum chamber, was used to detect the photons. The dispersing crystal was A.D.P. (101), and fourth-order reflections were required. The flow counter and its associated collimator could be removed when the scintillation counter was in use.

The combined $L\alpha$, $K\beta$ spectra for each compound are shown in Figure 1. In order to produce the combined spectra, the observed $K\alpha_1$ peak energy ($1s^+ \rightarrow 2p_{\frac{3}{2}}^+$) was added to the $L\alpha_{1,2}$ energy to give a ' $1s^+$–$3d^+$ ' energy separation. Hence both the ' $3d^+$ ' and ' $4p^+$ ' hole-state energies are known relative to the $1s^+$ state, and therefore they are known relative to each other. For all the three lines $K\alpha_1$, $K\beta_{2,5}$, and $L\alpha_{1,2}$ the observed spectra were calibrated against literature values for manganese metal.[25] The Table summarises peak position and intensity data. It should be noted that the $L\beta_1$ peaks are, as far as could be judged, the same shape as the $L\alpha_{1,2}$ peaks.



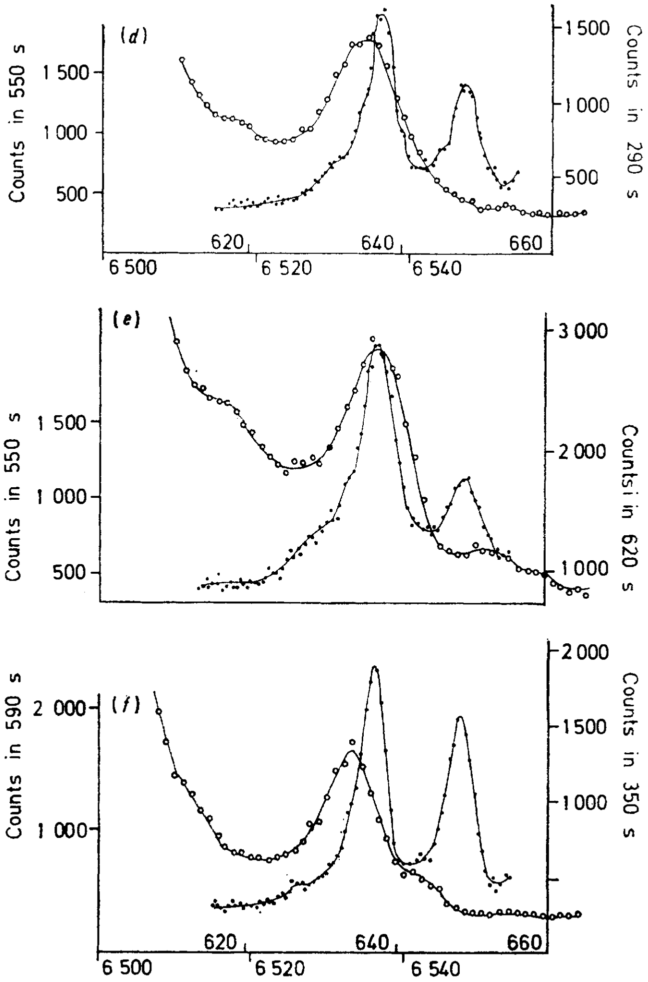


FIGURE 1 $K\beta_{2,5}$ (○) and $L\alpha_{1,2}$'$L\beta$ (●) manganese X-ray emission spectra for (*a*) K[MnO$_4$], (*b*) MnO$_2$, (*c*) Mn$_2$O$_3$, (*d*) MnO, (*e*) K$_2$[MnF$_6$], and (*f*) MnF$_2$. The ordinates give the number of disintegrations observed in a particular time interval for K spectra on the left and L spectra on the right. The upper abscissa is for L spectra, the lower for K spectra, the two scales being separated by the $K\alpha_1$ emission energy for the compound

DISCUSSION

The X-ray emission spectra shown in Figure 1 and nature of the chemical bond in the various compounds can most easily be discussed in terms of a simple m.o. energy-level diagram (Figure 2). The occupied orbitals in the valence band can be conveniently divided into three groups: A, mostly $3d$ in character; B, mostly ligand $2p$; and C, mostly ligand $2s$ in character. In the ionic limit of crystal-field theory A and B + C would, of course, be reduced respectively to transition-metal and ligand character only. The general trends shown by the spectra shed considerable light on the bonding in the compounds studied.

K *Spectra*.—In the $K\beta_{2,5}$ spectra of the oxides the

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Energies and relative intensities of manganese *X*-ray emission peaks

Compound	Peak positions (eV)				Relative peak intensities (%)		
	$K\alpha_1(2p_{\frac{3}{2}}\rightarrow 1s)$	$K\beta_{2,5}(4p\rightarrow 1s)$	$L\alpha_{1,2}(3d\rightarrow 2p_{\frac{3}{2}})$	$\Delta(3d - 4p)$	$L\beta_1 : L\alpha_{1,2}$	$K\beta'' : K\beta_{2,5}$	$(K\beta'' + K\beta_{2,5}) : K\beta_{1,3}$
MnF_2	5 899.1	6 533.6	637.6	3.0	77	*	1.2
MnO	5 899.2	6 534.6	637.6	2.0	62	6	1.3
Mn_2O_3	5 898.8	6 534.2	638.0	2.5	42	8	2.1
$K_2[MnF_6]$	5 898.5	6 536.8	638.7	0.5	43	13	2.3
MnO_2	5 898.6	6 535.2	638.0	1.5	19	29	2.2
$K[MnO_4]$	5 898.1	6 537.6	638.3	−1.0	17	63	3.7

* $K\beta''$ was very weak.

energy separation between $K\beta''$ and the main $K\beta_{2,5}$ peak was constant at 15 ± 1 eV, whilst for the two cases in which manganese is surrounded by fluoride ligands this energy difference was 20 eV. This is precisely the behaviour which would be expected[9] if these peaks were due to molecular orbitals which, whilst mostly ligand 2*p* and 2*s* in character respectively, also contained a small infusion of manganese 4*p* character; it is, however, unreasonable to expect such regular behaviour if $K\beta''$ and $K\beta_{2,5}$ are due to high-energy satellites of the $K\beta_{1,3}$ peak, a possibility considered in the introduction [(*b*)]. Furthermore, the wide fluctuation in the $K\beta'' : K\beta_{2,5}$ relative-intensity ratio (Table), increasing with the formal oxidation number from *ca.* 5% for MnO to > 60% in $[MnO_4]^-$, is in keeping with the increasingly covalent nature of the manganese–oxygen bond. A more direct measure of this covalency is to be had by considering the relative intensities of the $K\beta'' + K\beta_{2,5}$ peaks to the $K\beta_{1,3}$ peak. There are chemically induced perturbations[26,27] in the shape of the $K\beta_{1,3}$ peak, but the number of 3*p* electrons remains constant for all the chemical compounds of manganese. The intensity of the $K\beta_{1,3}$ peak can, therefore, be used as a reference to judge the relative amounts of 4*p* character present in the transition-metal–ligand bonds. As can be seen from the Table, $(K\beta'' + K\beta_5) : K\beta_{1,3}$ increases by a factor of three in going from bi- to hepta-valent manganese, indicating an increase in covalency. Whilst it seems reasonable to conclude that the peaks $K\beta''$ and $K\beta_{2,5}$ are due to Mn *p* character in orbitals of type A and B, it remains a more difficult problem to decide to what extent the intensities of these peaks are due to 4*p* and to what extent 3*p* character [see (*a*)]. The radial extent of both oxygen 2*s* and 2*p* orbitals is similar so that Mn 4*p* (or for that matter 3*p*) participation in A and B orbitals is probably primarily controlled by the differences in ionisation energies of the manganese and oxygen orbitals, rather than by overlap considerations. If this is so, then 3*p* character should always be present to a greater extent in A than in B orbitals; *i.e.* it should enhance the $K\beta''$ intensity more than $K\beta_{2,5}$. For the low valence states one can then conclude that the presence of 3*p* character in the valence-shell orbitals is of little importance but that it may play some role in explaining the extremely high $K\beta'' : K\beta_{2,5}$ intensity ratio observed for $[MnO_4]^-$.

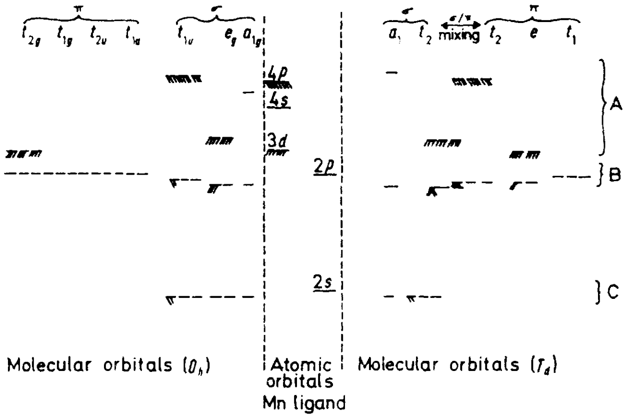

FIGURE 2 Qualitative molecular-orbital energy-level diagram for a transition metal in either an octahedral (O_h) or tetrahedral (T_d) ligand environment. An indication of 4*p* and 3*d* character is given (\\\\ and //). Electron occupancy is not shown.

L *Spectra*.—The *L* spectra exhibited interesting variations both in the relative intensities of the $L\alpha_{1,2}$ and $L\beta_1$ peaks and in peak shape (most easily observed in $L\beta_{1,2}$). As far as one can tell it would appear that $L\beta_1$ has a similar shape and structure to the corresponding $L\alpha_{1,2}$ peak. The relative intensities of the $L\alpha_{1,2}$ and $L\beta_1$ peaks seem to be a function of the valency of the manganese, $L\alpha_{1,2} : L\beta_1$ increasing with the formal oxidation number. Whilst a variety of possible factors was considered in the introduction [(*i*) and (*ii*)], the simplest explanation of this observation would seem to be self absorption, the higher-energy $L\beta_1$ line being more readily absorbed when A orbitals are empty and increasing in relative intensity as the number of *d* electrons permanently lodged in these orbitals increases. Even so it must be admitted that the $L\alpha_{1,2} : L\beta_1$ intensity ratio of less than 2, observed for MnO and MnF_2, is quite anomalous and not easily explained by any of the possible factors considered above.

For the most part the high-energy edge of the $L\alpha_{1,2}$ peak was devoid of structure indicating that high-energy satellites, which might be observed from doubly ionised atoms following Auger processes[16] [(*iii*) above], do not play a distinctive role in these spectra. Low-energy structure was, however, observed for the lower-valency compounds as would be expected for peaks which reflect 3*d* character in both A and B orbitals. It is most interesting to observe the absence of any distinctive feature analogous to $K\beta''$ in the *L* spectra. This is perhaps in

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keeping with the more localised nature of $3d$ orbitals. In the band structure of the metallic elements, for example, $3d$ character is usually confined to quite a narrow band of energies whilst $4s$ and $4p$ character is spread over a much wider range. Whatever the reason this observation is in accord with the predictions of Connor *et al.*[10] for permanganate. Peak $K\beta''$ was calculated to have 80% of the intensity of $K\beta_{2,5}$, but the corresponding feature in the L spectrum to have only 5% of the intensity of the main $L\alpha_{1,2}$ peak.

As the formal valency of manganese increased, the structure observed on the low-energy side of the $L\alpha_{1,2}$ peak decreased in clarity but the main peak became somewhat broader. The energy separation (Δ in the Table) of the $K\beta_{2,5}$ and $L\alpha_{1,2}$ peaks decreased until, in the case of $K[MnO_4]$, $K\beta_{2,5} > L\alpha_{1,2}$ In all the cases except $[MnO_4]$, the $L\alpha_{1,2}$ spectrum reflects $3d$ electron character in both the B and A orbitals whereas the $K\beta_{2,5}$ peak is indicative of $4p$ character in the B orbitals. Since B orbitals will be more tightly bound than the non-bonding $3d$ type A orbitals, it is most reasonable to expect that the $K\beta_{2,5}$ peak should overlap the low-energy side of the $L\alpha_{1,2}$ peak. As the formal valency of manganese increases, so does the covalency of the bonds formed. Thus a high electron population in orbitals of type A will be associated with very little $3d$ character in B orbitals, and as the number of $3d$ electrons in A orbitals decreases the $3d$ character in B orbitals will increase. These trends were clearly seen in the $L\alpha_{1,2}$ spectra, the lower-energy structure ($3d$ character in B orbitals) increasing in intensity relative to the main peak as the formal valency increased, so that the low-energy features seen in the MnO spectrum as weak shoulders were of comparable intensity with the ' main ' $L\alpha_{1,2}$ peak in MnO_2, giving rise to a much broader overall peak.

It is interesting to compare the low-energy structure of the Mn $L\alpha_{1,2}$ spectra when a manganese ion of the same formal valency is surrounded by ligands of different electronegativity. For Mn^{II} and Mn^{IV} such a comparison is possible using the spectra for MnO and MnF_2 and for MnO_2 and $K_2[MnF_6]$. In both cases the relative intensity of the low-energy features to the main peak was much greater for oxygen than for fluorine ligands. This shows that more $3d$ character is present in B orbitals (relative to A) for oxygen than for fluorine ligands, *i.e.* that the manganese–ligand bonds are more ionic when fluorine is a ligand than when oxygen is a ligand. Calculations by Basch *et al.*,[28] who found that the charge on manganese in manganese-(VII), -(VI), and -(V) oxo-anions was +0.68 whilst for the fluoro-species $[MnF_6]^{2-}$ and $[MnF_6]^{4-}$ the manganese charges were +1.00 and +0.85 respectively, also suggest that more ionic bonds should be associated with fluorine rather than oxygen ligands. An examination of the relative intensities of the peaks in the Mn $L\alpha_{1,2}$ spectra thus provides experimental confirmation both of theoretical calculations and notions of bond ionicity based on chemical intuition.

In the case of permanganate the absence of $3d$ electrons in A orbitals means that the whole of the $L\alpha_{1,2}$ spectrum arises from $3d$ character in type B orbitals. It is interesting to observe that there is a high-energy shoulder in the $L\alpha_{1,2}$ spectrum which lines up well with the $K\beta_{2,5}$ peak. Calculations [10] suggest that π as well as σ bonding is significant in $[MnO_4]^-$. If the main $L\alpha_{1,2}$ peak can be identified with $3d$ character in σ orbitals, then the high-energy shoulder would be due to $3d$ character in π orbitals. The correlation between $K\beta_{2,5}$ and L spectra then indicates that Mn $4p$ orbitals make a greater contribution to π than to σ bonds.

As the formal valence of manganese increases it is reasonable to expect that the ionisation energies of the valence-shell orbitals ($3d$, $4s$, and $4p$) should also increase whilst those of the ligand $2s$ and $2p$ orbitals should be more nearly constant. This will have the effect of reducing the energy difference between type A and B orbitals, an effect most clearly seen experimentally by observing the energy difference between the $K\beta_{2,5}$ peak and the main $L\alpha_{1,2}$ peak for all the compounds except $K[MnO_4]$. The same effect can also be observed in charge-transfer spectra, in which an electron is excited from a ligand lone-pair orbital (*i.e.* of comparable energy with B orbitals) to a central-atom orbital (type A): both calculation [28] and experiment [29] show that the wavelength of the charge-transfer band increases with the formal valence of the transition-metal ion, *i.e.* the energy of the transition decreases.

Conclusions.—A study of the K and L emission spectra of a series of manganese oxides and fluorides shows that the changing role of manganese valence-shell orbitals, in bond formation, as a function of the formal valence state can be qualitatively monitored. The changes in relative peak intensities and energies can be rationalised using simple molecular-orbital and ligand-field theory.

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