Satellite Structure in the *X*-Ray Photoelectron Spectra of some Binary and Mixed Oxides of Lanthanum and Cerium

By **Peter Burroughs, Andrew Hamnett, Anthony F. Orchard,* and Geoffrey Thornton,** Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR

A study of the core-electron *X*-ray photoelectron (*X*-p.e.) spectra of the f^0 compounds La_2O_3, $LaMO_3$ (M = Fe and Co), CeO_2, and $BaCeO_3$ is described. Results on the chelate species $[La(tmhd)_3]$ and $[Ce(tmhd)_4]$ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionato) are included for comparison. Special precautions have been taken to ensure an optimal degree of surface purity of the samples. Satellite structure has been observed for the 4*p*, in addition to the 3*d* and 4*d*, signals in both the lanthanum(III) and cerium(IV) compounds. These satellites are discussed in terms of coexcitations of the charge-transfer type, principally O 2*p* $\longrightarrow$ metal 4*f* transitions. In the cerium(IV) oxides the satellites are apparently due to energy-gain (representing ' shake-down ') rather than energy-loss (shake-up) processes.

THERE has been continuing interest since 1970 in the many-electron satellite structure observed for the 3*d* and 4*d* ionisations in the *X*-ray photoelectron (*X*-p.e.) spectra of lanthanoid compounds.[1-13] This additional

---

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

[2] G. K. Wertheim, R. L. Cohen, A. Rosencwaig, and H. J. Guggenheim, in ' Electron Spectroscopy,' ed. D. A. Shirley, North Holland, Amsterdam, 1972, p. 813.

[3] R. L. Cohen, G. K. Wertheim, A. Rosencwaig, and H. J. Guggenheim, *Phys. Rev.*, 1972, **B5**, 1037.

[4] C. K. Jørgensen and H. Berthou, *Chem. Phys. Letters*, 1972, **13**, 186.

[5] C. Bonnelle, R. C. Karnatak, and C. K. Jørgensen, *Chem. Phys. Letters*, 1972, **14**, 145.

[6] I. Nagakura, T. Ishii, and T. Sagawa, *J. Phys. Soc. Japan*, 1972, **33**, 754.

[7] A. J. Signorelli and R. G. Hayes, *Phys. Rev.*, 1973, **B8**, 81.

[8] S. P. Kowalczyk, N. Edelstein, F. R. McFeely, L. Ley, and D. A. Shirley, *Chem. Phys. Letters*, 1974, **29**, 491.

[9] S. Suzuki, T. Ishii, and T. Sagawa, *J. Phys. Soc. Japan*, 1974, **37**, 1334.

[10] C. K. Jørgensen, *Structure and Bonding*, (*a*) 1973, **13**, 199; (*b*) 1975, **24**, 1.

[11] C. K. Jørgensen and H. Berthou, *Nat. fys. Medd. Danske Vidensk. Selskab.*, 1972, **38**, no. 15.

[12] W. C. Lang, B. D. Padalia, L. M. Watson, D. J. Fabian, and P. R. Norris, *Faraday Discuss. Chem. Soc.*, in the press.

[13] S. P. Kowalczyk, L. Ley, R. L. Martin, F. R. McFeely, and D. A. Shirley, *Faraday Discuss. Chem. Soc.*, in the press.

structure can be unusually intense and display many subtle features, even when the 4*f* subshell is unoccupied. When we began work on lanthanoid compounds in this laboratory the origin of these satellites was little understood but, since that time, it has been established [2,4,7] that the 3*d* satellites derive mainly (or entirely) from ligand to metal charge-transfer (c.t.) transitions (like the satellites observed in the 2*p* spectra of compounds of the first-row transition elements).[14-18] The situation regarding the 4*d* satellites is less clear, however: whilst electrostatic coupling [19,20] between the 4*d* core hole and the outer 4*f* electrons is undoubtedly important,[7,8] the extent of involvement of c.t. processes remains unknown.

Our present purpose is to examine in more detail the satellite structure accompanying the core electron signals in the *X*-p.e. spectra of binary and mixed lanthanoid oxides, especially those of lanthanum(III) and cerium(IV), and to explore further its chemical implications. We also investigate the possibility that the satellite structure might show a dependency on the nature of the cation site. We concentrate on oxide systems because only here can we have real confidence that we are making measurements on sufficiently pure samples. The more recent work on compounds of the lanthanoid elements relates mainly to halides,[7,9] where there can be severe problems in securing samples of adequate purity at the surface. Our approach is complementary to *X*-p.e. studies in progress elsewhere of surface oxide films on lanthanoid metals.[12] Here we deal mainly with oxides containing the f^0 cations, La^{III} and Ce^{IV}; the spectra of the open-shell oxides will be considered at length in a subsequent paper.[21]

EXPERIMENTAL

The measurements were made on commercial samples of at least 99.9% purity or on samples prepared from materials which were at least of this purity. The oxides $LaFeO_3$ and $LaCoO_3$ were made by a method described by Gallagher,[22] while $BaCeO_3$ was prepared by heating CeO_2 and $BaCO_3$ together in air at 1 000 °C. The oxide Pr_2O_3 was prepared by heating Pr_6O_{11} in hydrogen at 1 000 °C and the praseodymium(IV) compound, $BaPrO_3$, by heating the same oxide with $BaCO_3$ in oxygen, also at 1 000 °C. The purity of the samples prepared in this way was checked by monitoring weight changes and by *X*-ray diffraction measurements on the powdered materials.

The lanthanoid chelates $[Ln(tmhd)_3]$ and $[Ce(tmhd)_4]$ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionato) were obtained by a minor modification [23] of a preparative method described by Eisentraut and Sievers.[24] The purity of these compounds was checked by C and H analysis and by mass spectrometry.

X-Ray photoelectron spectra were recorded at room temperature using Al-K_α radiation ($h\nu$ = 1 487 eV) * on an A.E.I. ES 200B electron spectrometer. The volatile chelate compounds $[Ln(tmhd)_3]$ and $[Ce(tmhd)_4]$ were studied in the form of films sublimed on to a cooled sample probe, the ' bleed ' of vapour being maintained during the measurements. By adjusting the rate of condensation of sample one can ensure that its surface is free of contamination by water and hydrocarbons. We have found this to be the best method of dealing with volatile samples; [23] it has the advantage that *ultra*-high-vacuum (u.h.v.) conditions are not really necessary.

The oxide samples were studied as pressed pellets under u.h.v. conditions (main chamber pressure $\leqslant 10^{-9}$ Torr during the measurements). The oxide pellets were mounted by means of a tantalum clip on a special probe consisting essentially of a high-grade alumina former around which was wound a carbon-fibre heating element. The purpose of the heating element was to outgas H_2O and CO_2 adsorbed or incorporated by the samples. The probe carried no thermocouple and only a rough estimate of its temperature could be made, observing the sample through a view-port with an optical pyrometer. Where the risk of reduction (by oxygen loss) was slight, the oxide samples were heated at *ca.* 1 000 °C. Otherwise, the temperature was restricted to a value well below the decomposition temperature estimated from thermodynamic data (*e.g.* for CeO_2).[25] Oxygen loss as a result of heating could be guarded against by monitoring the $[O_2]^+$ and O^+ signals in a quadrupole mass spectrometer attached to the main chamber of the instrument, and by careful examination of changes in the *X*-p.e. spectra with time. It was recognised that there is always a risk in prolonged high-temperature treatment that trace impurities from the bulk may segregate at the surface of the sample.[26] (For example, we have observed the surface segregation of lead when CdO containing less than 1 p.p.m. was heated for some time.[27]) We could only guard against this problem by scrutinising the *X*-p.e. spectra for signals due to the more obvious impurity elements, and by checking carefully any signal that developed as a result of heating of a sample *in situ.*

The effectiveness of the heat treatment *in situ* was gauged by continuous observation of the oxygen and carbon 1*s* signals. The lanthanoid oxides adsorb water and CO_2 quite tenaciously and, even when the obvious precautions were taken, the oxygen 1*s* spectrum was apparently dominated by the peak due to water and $[CO_3]^{2-}$, and separate peaks due to carbonate and hydrocarbon were usually observed in the carbon 1*s* region of the initial spectra. The impurity O 1*s* signal decreased steadily on heating and could eventually be eliminated in most cases leaving a single sharp oxygen 1*s* band, often with a half-

---

* 1 eV ≈ 1.60×10^{-19} J, 1 Torr = (101 325/760) Pa, 1 atm = 101 325 Pa.

[14] B. Wallbank, C. E. Johnson, and I. G. Main, *J. Phys.*, 1973, **C6**, L340 and L493.

[15] T. A. Carlson, J. C. Carver, L. J. Saethre, F. Garcia Santibánez, and G. A. Vernon, *J. Electron Spectroscopy*, 1974, **5**, 247.

[16] B. Wallbank, I. G. Main, and C. E. Johnson, *J. Electron Spectroscopy*, 1974, **5**, 259.

[17] K. S. Kim and R. E. Davies, *J. Electron Spectroscopy*, 1972—1973, **1**, 253.

[18] S. Hüfner and G. K. Wertheim, *Phys. Rev.*, 1973, **B7**, 5086.

[19] C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, *Phys. Rev. Letters*, 1969, **23**, 1397.

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

[21] A. F. Orchard and G. Thornton, *J. Electron Spectroscopy*, in the press.

[22] P. K. Gallagher, *Mat. Res. Bull.*, 1968, **3**, 225.

[23] A. Hamnett, D.Phil. Thesis, Oxford, 1973.

[24] K. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, 1965, **87**, 5254.

[25] D. J. M. Bevan and J. Kordis, *J. Inorg. Nuclear Chem.*, 1964, **29**, 1509.

[26] See, for example, C. A. Shell and J. C. Riviere, 'Analysis of Segregation of Phosphorus in Iron,' A.E.R.E. R7397, Harwell, 1973.

[27] G. Thornton and P. R. Young, unpublished work.

width of only 1.5 eV. The effect of heating (1 h) on the O 1*s* spectrum of Pr_2O_3 is shown in Figure 1. Initially the mass spectrometer indicated extensive outgassing of water followed, on raising the temperature above 400 °C, by evolution of CO_2 and further loss of water. The loss of chemisorbed and incorporated CO_2 was also evidenced by the eventual disappearance of one of the carbon 1*s* signals (that at lower electron kinetic energy). The heat treatment normally produced a significant improvement in resolution (compare, for example, the 3*d* spectra of La_2O_3 in Figures 2 and 3) and occasionally revealed detail that was not evident in the spectra of untreated samples.

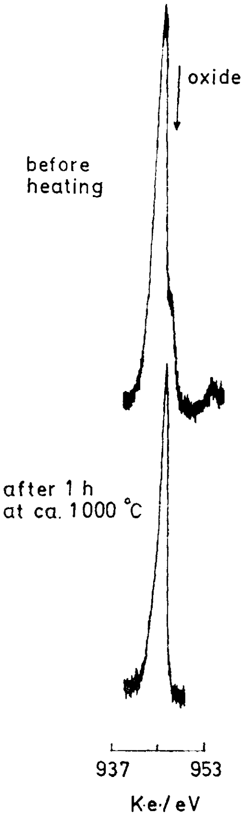

FIGURE 1 Oxygen 1*s* signal in the Al-$K\alpha$ p.e. spectrum of Pr_2O_3

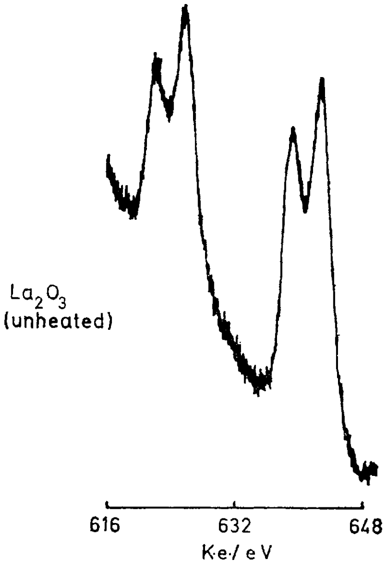

FIGURE 2 Lanthanum 3*d* signal in the Al-$K\alpha$ p.e. spectrum of uncleaned La_2O_3

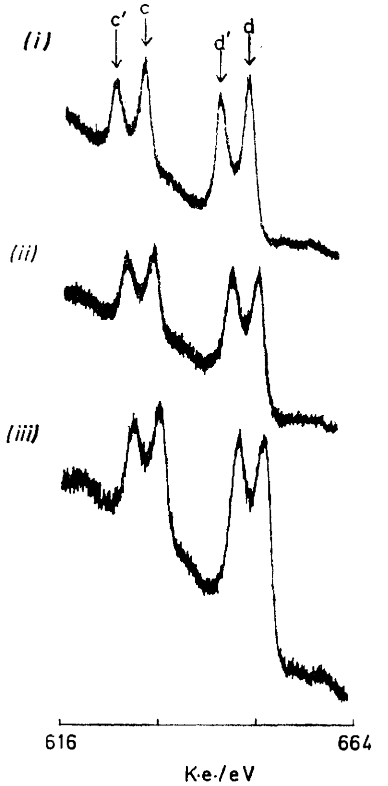

FIGURE 3 Lanthanum 3*d* signals in the Al-$K\alpha$ p.e. spectra of (*i*) La_2O_3, (*ii*) $LaFeO_3$, and (*iii*) $LaCoO_3$

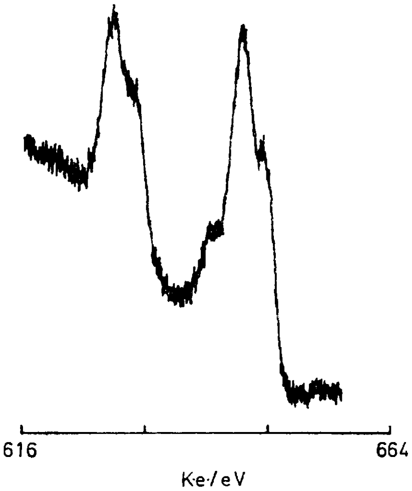

FIGURE 4 Lanthanum 3*d* signal in the Al-$K\alpha$ spectrum of $[La(tmhd)_3]$

The final core p.e. spectra are shown in Figures 3—16. The count rates obtained with the tmhd complexes were

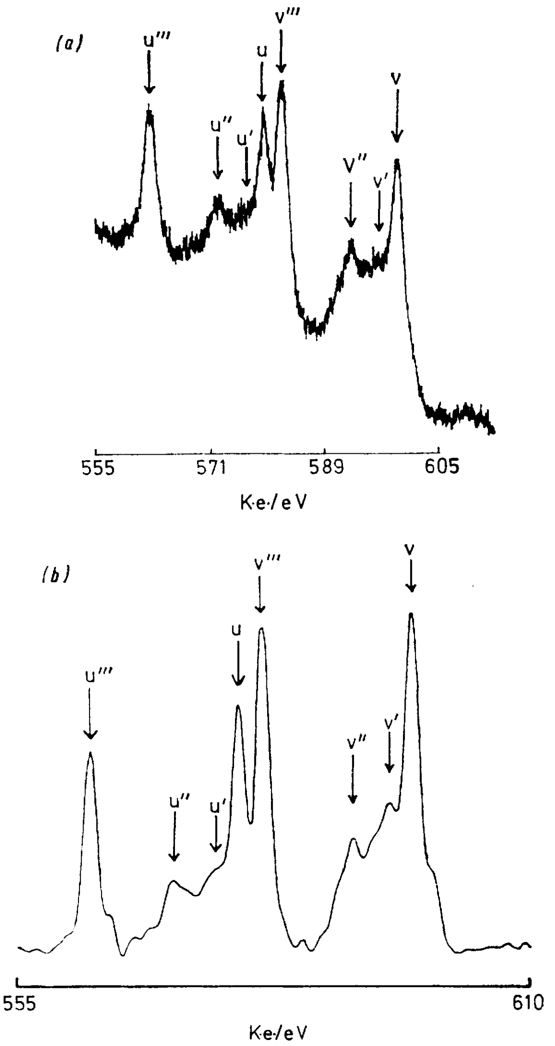

FIGURE 5 Cerium $3d$ signal in the p.e. spectrum of CeO_2: (*a*) raw Al-$K\alpha$ spectrum; (*b*) deconvoluted spectrum

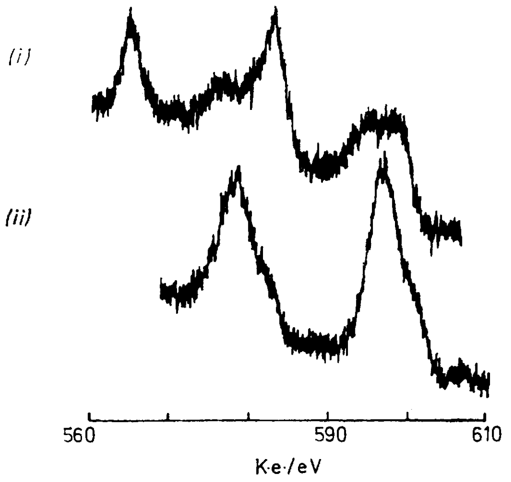

FIGURE 6 Cerium $3d$ signals in the Al-$K\alpha$ p.e. spectra of (*i*) [Ce(tmhd)$_4$] and (*ii*) [Ce(tmhd)$_3$]

unfortunately rather low (typically 300 counts s^{-1} for the stronger $3d$ signals) and the spectra are correspondingly less well defined than in the case of the oxides (where the $3d$ signal strengths were *ca.* 10^3 counts s^{-1}). Also reproduced in Figures 5, 13, and 15 are the results of deconvoluting

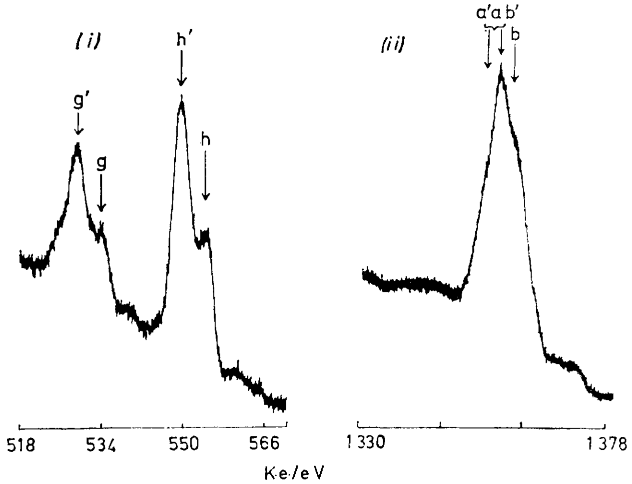

FIGURE 7 Praseodymium $3d$ (*i*) and $4d$ signals (*ii*) in the Al-$K\alpha$ p.e. spectrum of Pr_2O_3

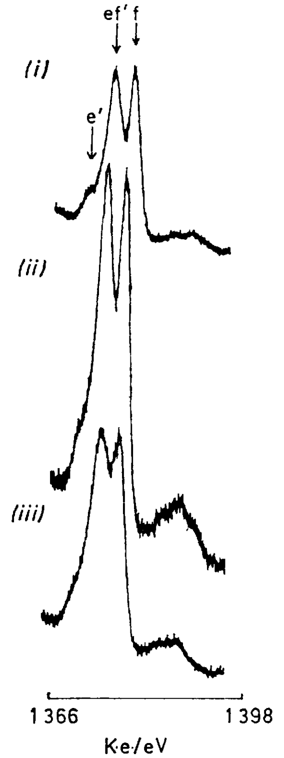

FIGURE 8 Lanthanum $4d$ signals in the Al-$K\alpha$ p.e. spectra of (*i*) La_2O_3, (*ii*) $LaFeO_3$, and (*iii*) $LaCoO_3$

certain spectra, after the removal of background due to secondary electrons and stripping away structure due to the Al-$K_{\alpha 3,4}$ satellite radiation, using a Fourier-transform technique developed in this laboratory.[28] This procedure

---

[28] N. Beatham and A. F. Orchard, *J. Electron Spectroscopy*, in the press.

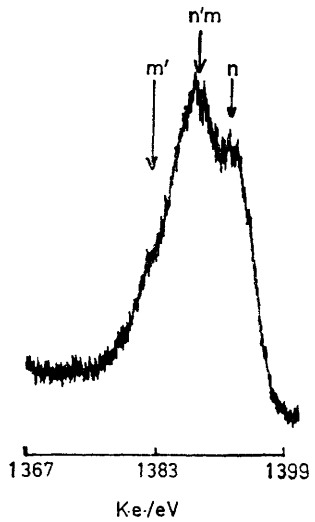

FIGURE 9 Lanthanum $4d$ signal in the Al-$K\alpha$ p.e. spectrum of [La(tmhd)$_3$]

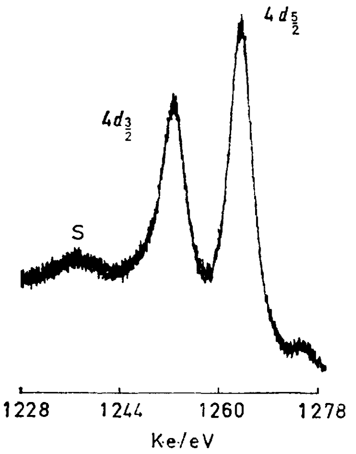

FIGURE 10 Hafnium $4d$ signal in the Al-$K\alpha$ p.e. spectrum of HfO$_2$

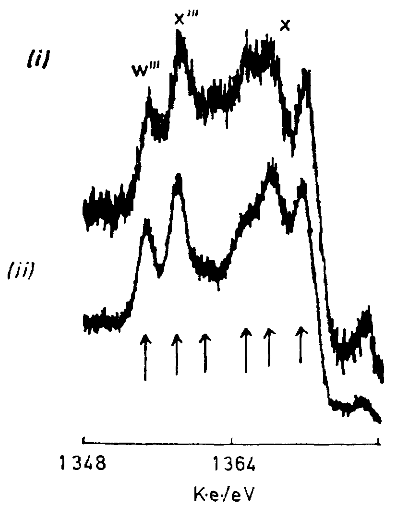

FIGURE 11 Cerium $4d$ signals in the Al-$K\alpha$ p.e. spectra of (*i*) BaCeO$_3$ and (*ii*) CeO$_2$

permits a degree of resolution enhancement limited by the signal-to-noise characteristics of the raw spectra.

No attempt was made to calibrate the spectra and extract core-electron ionisation energies (binding energies); our purpose did not require it. The kinetic energy (k.e.) scale in the Figures is thus not corrected for charging effects or for the work function of the sample. The p.e. peak positions in Table 1 are given relative to prominent neighbouring peaks.

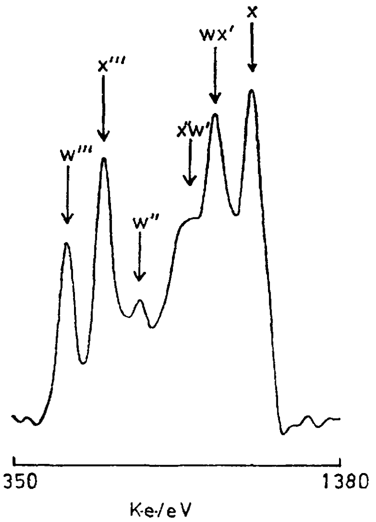

FIGURE 12 Deconvoluted $4d$ spectrum of CeO$_2$ (*cf.* Figure 11)

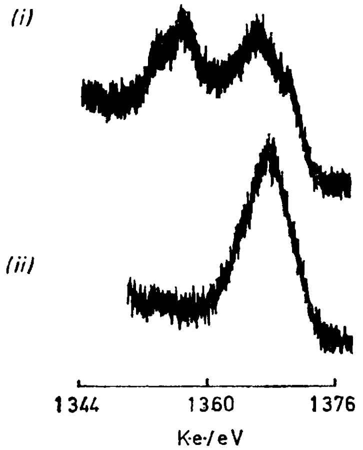

FIGURE 13 Cerium $4d$ signals in the Al-$K\alpha$ p.e. spectra of (*i*) [Ce(tmhd)$_4$] and (*ii*) [Ce(tmhd)$_3$]

X-Ray photoelectron spectra of La$_2$O$_3$ and CeO$_2$ have been measured before,^{4,6,7,9,10} but the spectra reproduced here are of a higher quality, especially as regards resolution, and show certain significant detail (see below) not apparent in the earlier spectra. Particular care was exercised in the case of CeO$_2$ to avoid decomposition through excessive heating. The same *X*-p.e. spectra were obtained for CeO$_2$ whether it was preheated in 1 atm of oxygen or in a vacuum of 10^{-9} Torr. (Heating in 1 atm of H$_2$ at 700 °C also had no significant effect on the spectra.) The consistent form of the cerium core p.e. signals in the spectra of CeO$_2$, [Ce(tmhd)$_4$], and the perovskite BaCeO$_3$ tend to confirm that the CeO$_2$ sample suffered no significant oxygen loss.

DISCUSSION

3d *Spectra.—Lanthanum*(III) *compounds.*—The remarkably intense satellite structure evident in the 3d X-p.e. spectrum of La_2O_3 (Figure 3) and other lanthanum compounds [2,4,7,9] has been assigned, reliably we think, to shake-up processes in which an electron is promoted from the filled oxygen 2p band to the empty metal 4f band.[2,4] Figuratively, we might say that the creation of a 3d core hole in $\mathrm{La^{III}}$ by primary photoionisation, which leads to a sudden increase of nearly one unit in the effective nuclear charge experienced by the valence electrons, can 'trigger' an O $2p \longrightarrow$ La $4f$ c.t. transition. The alternative possibility that the satellite structure is due to intra-atomic transitions $5p \longrightarrow 4f$ may be discounted on energy grounds: energy-level tables given by Bearden and Burr [29] indicate that the energies of

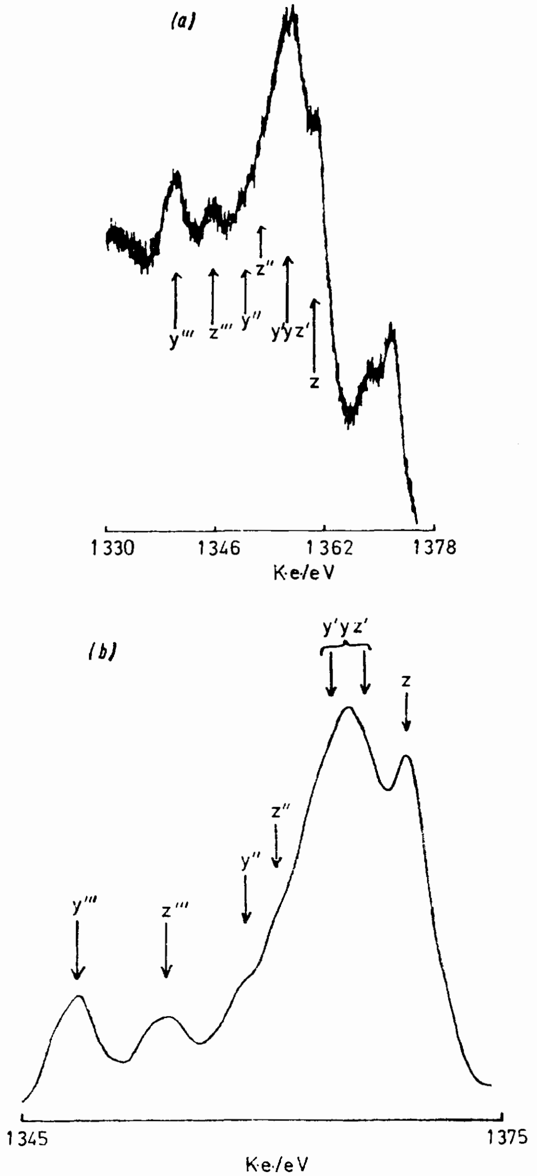

FIGURE 14 Praseodymium 4d signal in the p.e. spectrum of $BaPrO_3$: (a) raw Al-K_α spectrum; (b) deconvoluted spectrum

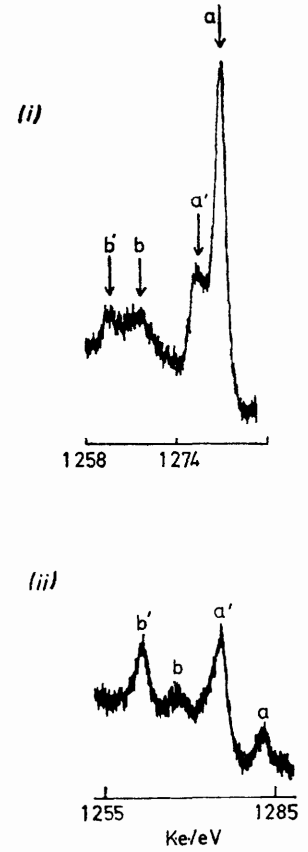

FIGURE 15 Lanthanum 4p signals in the Al-$K\alpha$ p.e. spectra of (i) La_2O_3 and (ii) CeO_2

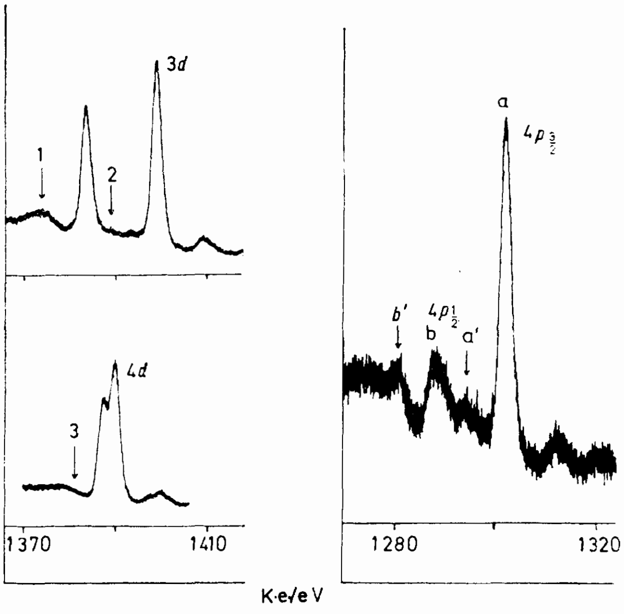

FIGURE 16 Barium core-electron signals in the Al-K_α p.e. spectrum of BaO

---

[29] J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.*, **1967**, **39**, 125.

such processes are far too high. (The naïve interpretation of the La_2O_3 3*d* spectrum as arising from two sets of chemically inequivalent La^{III} atoms is negated by the markedly different form of the 4*d* and 4*p* spectra, see below.) *

Unfortunately, we have not been able to confirm the c.t. interpretation by the obvious expedient, a comparative study of the f^{14} systems Lu_2O_3 and HfO_2 (which should not show 3*d* satellites). The metal 3*d* electrons are too tightly bound (the ionisation energies being 1 589 and 1 640 eV in lutetium, according to Siegbahn *et al.*)[31] to be ionised by Al-K_α photons, the most energetic we have at our disposal. However, despite certain superficial problems regarding assignment, the 3*d* satellite structure we have observed for both lanthanum(III) and cerium(IV) compounds proves to be consistent with the c.t. mechanism.

TABLE 1

Ionisation-energy data (eV)[a] for the 3*d*, 4*d*, and 4*p* core electrons of lanthanum and cerium in the lanthanum(III) and cerium(IV) oxide systems[b]

	La_2O_3	$LaFeO_3$	$LaCoO_3$		
3*d*	0	0	0	d	$3d_{\frac{5}{2}}$
	4.47	4.16	4.2	d′	
	16.8	17.0	17.0	c	$3d_{\frac{3}{2}}$
	21.37	21.25	21.2	c′	
	CeO_2	$BaCeO_3$			
3*d*	0	0		v	$3d_{\frac{5}{2}}$
	6.3			v″	
	16.2	16.5		v‴	
	18.8	*ca.* 19.0		u	$3d_{\frac{3}{2}}$
	25.1	24.5		u″	
	34.8	35.0		u‴	
	La_2O_3	$LaFeO_3$	$LaCoO_3$		
4*d*	0	0	0	f	$4d_{\frac{5}{2}}$ $4d_{\frac{3}{2}}$
	3.0	3.0	2.8	e f′	
	(6.6)	(5.8)	(5.6)	e′	
	CeO_2	$BaCeO_3$			
4*d*	0	0		x	$4d_{\frac{5}{2}}$ $4d_{\frac{3}{2}}$
	3.15	3.9		w x′	
	(5.7)	(5.8)		x′ w′	
	13.5	13.4		x‴	
	16.7	16.8		w‴	
	La_2O_3	CeO_2	BaO		
4*p*	0	0	0	a	$4p_{\frac{3}{2}}$ $4p_{\frac{1}{2}}$
	4.0	7.6	8.0	a′	
	14.4	15.2	14.4	b	
	19.6	23.2	21.2	b′	

[a] For each region of the *X*-p.e. spectra (3*d*, 4*d*, or 4*p*) the ionisation energies are expressed relative to the initial (highest k.e.) peak. The data for the sharper peaks should be accurate to ±0.25 eV, but for the more amorphous features the accuracy can be no better than ±0.6 eV. [b] The labels appearing on the right-hand side of the Table are those that occur in the Figures.

It is to be noted, first of all, that the form of the lanthanum 3*d* p.e. signals in the mixed oxides $LaFeO_3$ and $LaCoO_3$ (both essentially perovskite lattices)[32-34] is closely similar to that in La_2O_3 (Figure 3). This observation suggests that the satellites are the result of relatively localised excitations essentially confined to the La^{III} atom or to the LaO_n clusters. It is unlikely that the secondary transitions can involve the conduction band, since its structure must be significantly influenced by the partner M^{III} transition-metal atoms. However, on the c.t. hypothesis it is surprising that the energy and probability of shake-up should be sensibly independent of the La^{III} site symmetry (low-symmetry seven-co-ordination in the La_2O_3 A-type lattice as compared with cubic twelve-co-ordination in the perovskite lattice).[34]

Secondly, we note that the 3*d* satellite structure in the *X*-p.e. spectrum of $[La(tmhd)_3]$ (Figure 4) is qualitatively quite different from that observed in the case of oxide lattices.† It is instead very like the satellite structure reported for $LaCl_3$[9] and $LaBr_3$,[7,9] the higher kinetic-energy component of both the $3d_{\frac{3}{2}}$ and $3d_{\frac{5}{2}}$ doublet signals being very distinctly the weaker. The customary interpretation of core p.e. satellites in terms of energy-loss processes[35] might lead one to observe that the satellites are more intense than the parent peaks. However, for reasons elaborated below, we prefer the view that the stronger p.e. signals correspond to the primary 3*d* photoemission while the weaker (higher k.e.) signals are satellites representing energy-gain processes or, to coin a term, ' shake-down.'

We have our reservations concerning the reliability of the *X*-p.e. measurements on $LaCl_3$ and $LaBr_3$,[7,9] but consider that the ideas on which Signorelli and Hayes[7] based their assignments are essentially correct. Photoemission from the lanthanum 3*d* subshell yields a species La^{4+} $(3d^{-1})$ which, in view of the highly efficient screening of nuclear charge expected of the 3*d* electrons, should chemically be very like Ce^{4+}.[4] Electron transfer from the ligands in the ionised system produces La^{3+} $(3d^{-1}$ $4f^{-1})$ which ought correspondingly to resemble Ce^{3+}. To a good approximation the energy differences between the one-electron (*a*) and two-electron processes (*b*) depicted in Figure 17, that is the shake-up energy E_s, may thus be identified with the average ligand-to-4*f* optical c.t. energies in comparable cerium(IV) compounds. There is of course a catch in the word comparable since strictly one needs to refer to optical c.t. data for a cerium(IV) compound in which the ligand co-ordination number and equilibrium metal–ligand dis-

---

* Shake-up structure observed for the core *d* ionisations in xenon and Cs^+ (CsI), both of which are of course isoelectronic with La^{3+}, is extremely weak, and can be interpreted solely on the basis of $5p \rightarrow np$ and $5s \rightarrow ns$ excitations.[30] The *X*-p.e. spectra of lanthanum and cerium metals also lack intense satellite structure.[6]

† The weak structure labelled X in the 3*d* spectrum of $[La(tmhd)_3]$ (Figure 4) may be the $K_{\alpha 3,4}$ ' shadow ' satellite of the $3d_{\frac{3}{2}}$ signal.

[30] U. Gelius, *J. Electron Spectroscopy*, 1974, **5**, 985.

[31] K. Siegbahn, C. N. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, ' ESCA—Atomic, Molecular, and Solid State Structure studied by Means of Electron Spectroscopy,' Amqvist and Wiksells, Uppsala, 1967.

[32] M. Marezio and P. D. Dernier, *Mat. Res. Bull.*, 1971, **6**, 23.

[33] N. Menyuk, K. Dwight, and P. M. Raccah, *J. Phys. and Chem. Solids*, 1967, **28**, 549.

[34] A. F. Wells, ' Structural Inorganic Chemistry,' 3rd edn., Oxford University Press, 1962.

[35] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, ' ESCA Applied to Free Molecules,' North Holland, Amsterdam, 1969.

tances are the same as in the compound of La$^{\mathrm{III}}$ whose X-p.e. spectrum is under scrutiny. Such data are not available, of course, but the difference in site potentials between compounds of La$^{\mathrm{III}}$ and Ce$^{\mathrm{IV}}$ can easily be allowed for in a simple ionic description of the problem.

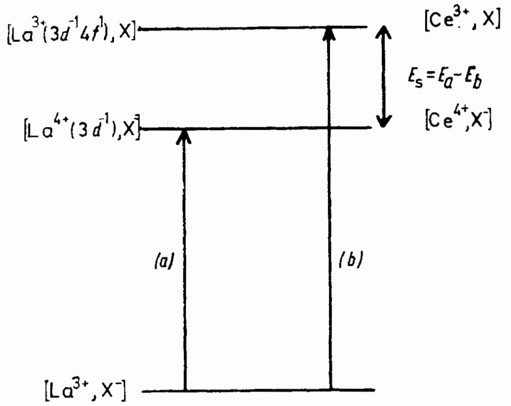

FIGURE 17 Energy levels accessible by photoionisation in compounds of La$^{\mathrm{III}}$

TABLE 2

Satellite displacements or ' shake-up ' energies (E_s/eV) reported for the $3d$ ionisations in La_2O_3, LaF_3, and $LaBr_3$

La_2O_3	LaF_3	$LaBr_3$	Ref.
2.8	3.2	2.4	7
	4.3 [a]		2
3.7	*ca.* 4		4
	4.4 [a]	3.1 [a]	9
4.5			*b*

[a] Estimated from spectra reproduced by the authors. [b] This work.

Let V_M and V_X be the electrostatic site potentials of the metal cations M (La^{3+} or Ce^{4+}) and the anions X^{z-}, respectively. (If there are inequivalent cation or anion sites, then V_M or V_X denote the average site potentials.) The transition energy for optical charge transfer in a cerium(IV) compound may then be expressed as (1)

$$E_{ct} = (E + eV_X) - (I + eV_{Ce}) - (e^2/4\pi\varepsilon_0)\left\langle \frac{1}{r_{CeX}} \right\rangle \quad (1)$$

(*cf.* refs. 36 and 37, for example) where I is the ionisation energy $Ce^{3+} \longrightarrow Ce^{4+}$ and $-E$ is the enthalpy of the process $X^{(z-1)-} + e \longrightarrow X^{z-}$ (*i.e.* E is the ionisation energy of X^{z-}); $\langle 1/r_{CeX} \rangle$ is the average inverse metal–ligand distance, and the term in question gives the interaction energy between the excited electron and the hole it leaves behind. At the same level of approximation, the $3d$ shake-up energy in the lanthanum(III) compound with the same anion X^{z-} is as in (2) where

$$E_s = (E + eV_X') - (I' + eV_{La}) \quad (2)$$

$I' \approx I$ (see above). The prime in V_X' serves to distinguish this anion site potential in the lattice of the lanthanum(III) compound from the site potential V_X in the cerium(IV) compound. Combining (1) and (2), we obtain (3).

$$E_s \approx E_{ct} - e(V_{La} - V_{Ce}) + e(V_X' - V_X) + (e^2/4\pi\varepsilon_0)\left\langle \frac{1}{r_{CeX}} \right\rangle \quad (3)$$

It is instructive to apply this model to the particular case of the molecular species, trigonal-planar LaL_3 and tetrahedral CeL_4 (corresponding to $X = L^-$). Putting $e^2/4\pi\varepsilon_0 = C$, we have (4) and (5), and hence (6). But

$$\begin{aligned} LaL_3 : E_s &= (E - I) + (6C/r_{LaL}) - (2C/r_{LL}) \\ &= (E - I) + (4.85C/r_{LaL}) \ (\text{since } r_{LL} = 3^{\frac{1}{2}} r_{LaL}) \end{aligned} \quad (4)$$

$$\begin{aligned} CeL_4 : E_{ct} &= (E - I) + (7C/r_{CeL}) - (3C/r_{LL}) \\ &= (E - I) + (5.16C/r_{CeL}) \\ &\qquad (\text{since } r_{LL} = \frac{2^{\frac{1}{2}}}{3^{\frac{1}{2}}} r_{CeL}) \end{aligned} \quad (5)$$

$$E_s \approx E_{ct} - C[(5.16/r_{CeL}) - (4.85/r_{LaL})] \quad (6)$$

normally $r_{LaL} > r_{CeL}$, and therefore $E_s < E_{ct}$. This may well be the case for solids also. Thus evaluation of the site potentials in La_2O_3 and CeO_2 (*cf.* Table 3), assuming perfect ionic lattices, leads to the estimates $E_{ct} = 10.3$ eV in CeO_2 and $E_s = 9.2$ eV in La_2O_3.

However, the results of such calculations will be considerably in error through covalency effects. Some idea of the errors involved may be gained by comparing calculated E_{ct} values for cerium(IV) compounds with data derived from electronic-absorption spectroscopy. For example, Ce$^{\mathrm{IV}}$ doped into ZrO_2 is reported to have its first c.t. absorption band at *ca.* 4.5 eV photon energy;[38] a calculation of the site potentials in ZrO_2 (which yields $\langle V_{Zr} \rangle = -41.635$ eV and $\langle V_O \rangle = 22.69$ eV) leads to the estimate $E_{ct} = 12.7$ eV. It seems likely that, in general, calculations based on the simple ionic model will tend to overestimate both E_{ct} and E_s. In the hope that the point-charge model might nonetheless assist the interpretation of the trends in E_{ct} and E_s values from compound to compound, we calculated the site potentials for a variety of relevant materials. Some simple estimates of E_s thereby obtained are given in Table 3.

Our assignment of the $3d$ spectrum of $[La(tmhd)_3]$ is such that the satellite bands (S) represent energy gain relative to the primary p.e. bands. In other words, it is assumed that the two-electron process (*b*) in Figure 17 requires less energy than the one-electron process (*a*) (when E_s is negative), the ground state of the ionised system being the Ce$^{\mathrm{III}}$-like c.t. states symbolised $[La^{3+}(3d^{-1}4f^{1}),X]$. This interpretation parallels that advanced in connection with $LaBr_3$ by Signorelli and Hayes,[7] who pointed to the corroborative fact that the corresponding compound $CeBr_4$ is apparently intrinsically unstable.[39] (The same remarks could be made concerning the $3d$ spectrum of $LaCl_3$ reported by Suzuki *et al.*,[9]

---

[36] E. Rabinowitch, *Rev. Mod. Phys.*, 1942, **14**, 112.

[37] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[38] N. Van Vugt, T. Wigmans, and G. Blasse, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2601.

[39] D. Brown, ' Halides of the Lanthanides and Actinides,' Wiley–Interscience, 1968.

and the alleged instability of $CeCl_4$.*) The somewhat paradoxical fact that [Ce(tmhd)$_4$] is quite stable can be attributed to the Madelung terms that must be considered when comparing charge transfer in an ionised lanthanum(III) compound with that occurring in the cerium(IV) analogue (see above).

TABLE 3

Cation and anion electrostatic site potentials, V_M and V_X, in some compounds of La^{III} and Ce^{IV}, and in BaO, calculated on the basis of the simple ionic model.[a] Charge-transfer (shake-up) energies in the $3d^{-1}$ ionised states, estimated from equation (2),[b] are also included

			E_s/eV	
Lattice	V_M/V	V_X/V	Calc.	Expt.
La_2O_3 [c]	−31.98	24.25 21.16	4.8 (9.2)	±4.5 (av)
$LaFeO_3$ [d]	−28.16	22.17 22.19	0.5 (4.9)	±4.2 (av)
LaF_3 [c]	−27.20	10.75 9.50	−0.3 (4.05)	3.2 [e]
CeO_2 [c]	−40.26	21.66	−10.1	−16.0 (av)
$BaCeO_3$ [f]	−39.59	21.20 21.10	−11.1	−16.1 (av)
BaO [c]	−15.07	15.07	0.02	

[a] The site-potential calculations were carried out by the method of W. Van Gool and A. G. Piken, *J. Mat. Sci.*, 1969, **4**, 95. [b] We used the values $E(O^{2-}) = -8.75$ eV and $E(F^-) = 3.45$ eV. The ionisation energies $I'(3d^{-1}4f^1 \rightarrow 3d^{-1})$ needed in equation (2) were estimated by separate state ('ΔSCF') calculations in the non-relativistic Hartree–Fock approximation, using a computer program developed by D. F. Mayers of the Oxford University Computing Laboratory. The ionisation energies so calculated were: $Ba^{2+} \longrightarrow Ba^{3+}$ 21.37; $La^{3+} \longrightarrow La^{4+}$ 41.09; and $Ce^{4+} \longrightarrow Ce^{5+}$ 63.29 eV. In the case of the lanthanum(III) compounds, E_s was also calculated by assuming that $I' = I(Ce^{3+} \longrightarrow Ce^{4+}) = 36.72$ eV (see text). The estimates thus obtained are given in parentheses in the Table. [c] Ref. 33. [d] Ref. 31. [e] Ref. 7. [f] A. J. Jacobson, B. C. Tofield, and B. E. F. Fender, *Acta Cryst.*, 1972, **B28**, 956.

Interestingly, the $3d$ satellite structure reported [2] in the X-p.e. spectrum of LaF_3 is of the more familiar kind, that is each of the $3d_{\frac{3}{2}}$ and $3d_{\frac{5}{2}}$ signals shows a relatively weak satellite at lower electron k.e. Here the obvious interpretation is that the ground state of the ionised system is predominantly $[La^{4+}(3d^{-1}),X^-]$ (that is, Ce^{IV}-like), a view that is consistent with the known stability of CeF_4.[39] (The tetrafluoride and CeO_2 are of course the only known binary compounds of Ce^{IV}.) Curiously, the shake-up energy, E_s, in LaF_3 appears to be roughly equal to, or perhaps slightly smaller than, the value we find for La_2O_3 (see Table 1). But this observation appears to be consistent with the simple ionic model of charge transfer (Table 3).

The $3d$ spectra of LaF_3, La_2O_3, [La(tmhd)$_3$], and $LaBr_3$ present an intriguing series in which the relative intensity of the satellite band apparently passes through a maximum (approximately at La_2O_3) as the ground state of the system changes in character from essentially $[La^{4+}(3d^{-1}),X^-]$ to $[La^{3+}(3d^{-1}4f^1),X]$. This phenomenon can be rationalised in terms of a simple c.t. picture of covalency. Using a familiar notation that originates with Mulliken,[41] the ground state of the neutral system $[La^{3+},X^-]$ may be denoted as in (7) where D (the donor

$$|0\rangle = (1 - \lambda_0^2)^{\frac{1}{2}}\,|D, A\rangle + \lambda_0\,|D^+{-}A^-\rangle \qquad (7)$$

species) represents the anions X^- and A (the acceptor species) represents La^{3+}. The coefficient λ_0 specifying the degree of mixing of $|D,A\rangle$, the ionic ground state, with the c.t. state $|D^+{-}A^-\rangle$ is assumed, for our present purposes, to be sufficiently small that the overlap term arising in normalisation may be neglected.† The states of the ionised system are correspondingly (8) and (9).

$$|i\rangle = (1 - \lambda^2)^{\frac{1}{2}}|D,A^+\rangle + \lambda|D^+{-}A\rangle\ (\sim Ce^{4+}) \qquad (8)$$

$$|f\rangle = \lambda|D,A^+\rangle - (1 - \lambda^2)^{\frac{1}{2}}|D^+{-}A\rangle\ (\sim Ce^{3+}) \qquad (9)$$

The ionised system is likely to be more covalent than the neutral system so that $\lambda > \lambda_0$ (although we assume that λ is still small). Now, invoking the sudden approximation [42] (which will be most reliable when relaxation in the ionised system is slight), photoionisation of a lanthanum $3d$ electron creates a non-stationary state (10)

$$|K\rangle = (1 - \lambda_0^2)^{\frac{1}{2}}|D,A^+\rangle + \lambda_0|D^+{-}A\rangle \qquad (10)$$

which we call the Koopmans' state.[43] The ratio of the probabilities of reaching the two different states of the ionised system is then (11) which for small λ and λ_0

$$P_f/P_i = |\langle K|f\rangle|^2/|\langle K|i\rangle|^2 \qquad (11)$$

approximates to (12) where $\Delta\lambda = \lambda - \lambda_0$. In reality

$$P_f/P_i = \Delta\lambda^2/(1 - \Delta\lambda^2) \qquad (12)$$

$|f\rangle$, the Ce^{III}-like state, represents more than one state of the ionised system, so that equation (12) must be modified by the inclusion of a weighting factor W [equation (13)].‡

$$P_f/P_i = W[\Delta\lambda^2/(1 - \Delta\lambda^2)] \qquad (13)$$

In the sudden approximation (or in an equivalent configuration-interaction model) the states $|f\rangle$ must of course be of the same symmetry as the state $|i\rangle$, namely $^1\Gamma_1$ (totally symmetric orbital representation) if one ignores the $3d$ hole. On this basis W should be the number of $^1\Gamma_1$ c.t. states of the LaX_n cluster arising from coupling of a metal F state with the p-type hole states of the surrounding anions. If the cluster has no symmetry elements, but roughly equidistant anions, then $W = 7 \times 3n$; symmetrical clusters will have lower weighting factors in equation (13). The application of

---

* It should be noted, however, that the complex anions $[CeCl_6^{2-}]$ and $[CeBr_6^{2-}]$ have been characterised in the solid state;[39] they show c.t. spectra commencing with absorption bands at *ca.* 3.3 and 2.4 eV, respectively.[40]

† The same ultimate conclusions are reached if one makes the weaker assumption that the overlaps $\langle D,A\ D^+{-}A^-\rangle$ and $\langle D,A^+\ D^+{-}A\rangle$ are approximately equal. With this assumption one finds that, for small overlap $P_f/P_i = W[(\lambda - \lambda_0)^2/(1 + \lambda\lambda_0)^2]$ which has essentially the same properties as (13).

‡ A related formula $P_f/P_i = 7\lambda^2/(1 - \lambda^2)$, which involves the neglect of covalency in the neutral lanthanum(III) compound, was suggested by Signorelli and Hayes,[7] who based their arguments on molecular-orbital theory.

[40] J. L. Ryan and C. K. Jørgensen, *J. Phys. Chem.*, 1966, **70**, 2845.

[41] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801; *cf.* J. N. Murrell, *Quart. Rev.*, 1961, **15**, 191.

[42] R. Manne and T. Åberg, *Chem. Phys. Letters*, 1970, **7**, 282.

[43] T. Koopmans, *Physica*, 1934, **1**, 104.

this model is however much confused by ambiguities regarding the specification of the LaX_n clusters since in its binary compounds La^{III} usually has a very complicated anion environment.[34] Thus in La_2O_3 the immediate environment of the metal atom consists of three oxygens at 2.38 Å, one at 2.45 Å, and three more at 2.72 Å; in the LaF_3 lattice there are five equidistant fluorine atoms at 2.36 Å and six at 2.70 Å.[34] If for La_2O_3 we consider the asymmetric cluster LaO_7, and neglect the variation in La–O distance, we have $W = 147$. The experimental ratio $P_f/P_i \approx 1$ (Figure 3) then implies $\Delta\lambda = 0.08$. If, on the other hand, we consider only the three nearest-neighbour oxygen atoms, $W = 63$ and $\Delta\lambda = 0.125$. Thus the near equality in intensity of the primary and secondary *3d* signals in La_2O_3 can be understood in terms of a change of *ca.* 0.1 in the covalency parameter λ on going from La^{III} to Ce^{IV}-like La^{III} $(3d^{-1})$. This is an intuitively reasonable figure.

The variation in the intensity ratio P_f/P_i in the series LaF_3, La_2O_3, and $[La(tmhd)_3]$, which is roughly 1 : 5, 1 : 1, and 1 : 5, probably reflects the expected trend of increasing covalency modified by irregular changes in the weighting factor W. If we could reasonably assume that W was essentially constant then it would be possible to compare the covalency parameters $\Delta\lambda$. For $W = 100$ the intensity ratios 1 : 5 and 1 : 1 require $\Delta\lambda$ values of 0.045 and 0.100, respectively, while for $W = 10$, $\Delta\lambda =$ 0.140 or 0.301. Comparing LaF_3 and La_2O_3, these figures imply sensible covalency trends in the individual parameters λ_0 and λ. The anomalous position of $[La(tmhd)_3]$ is presumably due to a very low value of W, a supposition consistent with the relatively high La^{III} site symmetry (D_3). (Similarly, the considerably lower P_f/P_i ratio in LaF_3 as compared with La_2O_3 may be in part a reflection of the somewhat higher La^{III} site symmetry.) It should be said, however, that one cannot entirely rule out the possibility that P_f/P_i is actually greater than unity in $[La(tmhd)_3]$, which would correspond to a reassignment of its *3d* spectrum. There is nothing in the c.t. description we have used that precludes this, although the simple equations (12) and (13) are really inappropriate unless $P_f/P_i \ll 1$.

The similarity of the observed P_f/P_i values in $LaFeO_3$ and $LaCoO_3$ to that in La_3O_3 (Figure 3) is somewhat surprising at first sight since we might have expected both $\Delta\lambda$ and W to be significantly smaller in the perovskite lattices, where the La^{III} atoms occupy a cubic twelve-co-ordinate site.[34] But in fact the crystal structures of the $LaMO_3$ compounds show considerable distortions from the ideal cubic symmetry [32,33] and these may have the effect of increasing W and $\Delta\lambda$ such that the product $W\Delta\lambda^2$ is close to that in La_2O_3. That E_s is of similar magnitude in La_2O_3 and in the $LaMO_3$ systems is also surprising in the light of the point-charge calculations (Table 3). Perhaps the discrepancy is due to greater covalency in La_2O_3. Alternatively, it may be that E_s is negative in La_2O_3, but positive in $LaFeO_3$ and $LaCoO_3$.

Cerium(IV) *compounds*. The *3d* spectra of CeO_2 [Figure 5(*a*)] and $[Ce(tmhd)_4]$ (Figure 6) are qualitatively quite different from, and more complicated than, those of their lanthanum(III) analogues, but are themselves not dissimilar. The cerium *3d* spectrum of $BaCeO_3$ is unfortunately overlapped by relatively strong barium Auger structure [44] and is therefore less informative. However, the discernible cerium *3d* structure resembles that in the CeO_2 spectrum.*

In the light of the foregoing discussion of lanthanum(III) compounds, and the results of the point-charge calculations for CeO_2 and $BaCeO_3$ (Table 3), we would expect the *3d* spectra of cerium(IV) compounds to show only satellites of the 'shake-down' type. The ionised species $Ce^{5+}(3d^{-1})$ should resemble Pr^{5+}, but praseodymium(V) compounds are unknown. The chemical evidence indicates therefore that, for any crystal lattice, the state $[Ce^{4+}(3d^{-1}4f^1),X]$ is distinctly more stable than the Koopmans' state $[Ce^{5+}(3d^{-1}),X^-]$ so that the lower-energy ionisation processes will be essentially two-electron transitions (with $E_s < 0$) leading to a Pr^{IV}-like state of the ionised system. The complex *3d* spectrum of CeO_2 may be interpreted on this basis. As indicated in Table 1, we consider that the bands labelled v collectivily represent the $3d_{\frac{5}{2}}$ ionisation while the similar group of bands labelled u represent the $3d_{\frac{3}{2}}$ ionisation. This assignment implies a *3d* multiplet splitting (u — v or u‴ — v‴) of 18.7 eV as compared with 16.8 eV in the case of La_2O_3. The two bands with unprimed labels, u and v, correspond to production of the Pr^{IV}-like state of the ionised system, while those labelled v‴ and u‴ represent the Pr^{V}-like excited state lying some 16.0 eV above the ground state.

The CeO_2 *3d* spectrum also shows two sets of weaker bands (v′, v″ and u′, u″) which are more clearly defined in the deconvoluted spectrum [Figure 5(*b*)]. There appear to be two conceivable explanations for this additional structure: either, it arises from *3d*–*4f* coupling effects in the $Ce^{4+}(3d^{-1}4f^1)$ final state, or it must be due to production of excited states of the ionised system such as $Ce^{4+}(3d^{-1}5d^1)$. The first hypothesis can be discarded on the grounds that the *3d*–*4f* coupling energies are probably too small. The coupling effect in question can after all occur in $La^{3+}(3d^{-1}4f^1)$, but in the *3d* spectrum of La_2O_3 the doublet components (c,c′ or d,d′) of the *3d* signals have approximately the same half-width. The alternative explanation is much more convincing in the light of what is known about the excited energy levels of lanthanoid ions,† and it seems likely that the weak bands

---

* The cerium *3d* spectrum of $BaCeO_3$ excited by Mg–K_α radiation, which is free of overlapping Auger signals, is indeed very similar to the Al–K_α spectrum of CeO_2 [Figure 5(*a*)]. The Mg–K_α spectrum was kindly measured by Dr. S. Evans of the University College of Wales, Aberystwyth.

† In free Pr^{3+}, for example, the $4f5d$, $4f6s$, and $4f6p$ configurations lie *ca.* 6, 8.5, and 11 eV, respectively, above the $4f^2$ ground configuration.[45]

[44] P. W. Palmberg, G. E. Riach, R. E. Weber, and N. C. MacDonald, 'Handbook of Auger Electron Spectroscopy,' Physical Electronics Ind., Inc., Edina, Minnesota 55435, U.S.A.

[45] G. H. Dieke, 'Spectra and Energy Levels of Rare Earth Ions in Crystals,' eds. H. M. Crosswhite and H. Crosswhite, Interscience, 1968.

represent closely spaced states derived from the $3d^{-1}5d^{1}$, $3d^{-1}6s^{1}$, and $3d^{-1}6p^{1}$ configurations of Ce^{4+}. The absence of similar structure in the spectrum of La_2O_3 (Figure 3) may be due to smaller overlap of outer orbitals such as La $5d$ with oxygen $2p$ (the average La–O distance in La_2O_3 is greater than the Ce-O distance in CeO_2); or, if the $La^{3+}(3d^{-1}4f^{1})$ state is represented by bands d and c, such structure might be present but be obscured by the $La^{4+}(3d^{-1})$ bands d′ and c′.

Our interpretation of the CeO_2 $3d$ spectrum is thus such that the ratio P_f/P_i defined earlier is clearly greater than one, and this despite the fact that the weighting factor W should be very much smaller in cubic CeO_2 (fluorite lattice) [34] than in La_2O_3. But, as remarked earlier, the enormous degree of relaxation so implied may invalidate equation (12).

The $3d$ spectrum of $[Ce(tmhd)_4]$ (Figure 6) is less well resolved than that of CeO_2, but is clearly of the same essential form. This is of course in marked contrast to our observations concerning $[La(tmhd)_3]$ and La_2O_3, which show $3d$ spectra of a quite different kind. If the ideas underlying the assignment of the CeO_2 spectrum are correct then other cerium(IV) compounds should show qualitatively similar spectra. However, Signorelli and Hayes [7] reproduced a $3d$ spectrum of CeF_4 which is of a quite simple form, rather like that of LaF_3. We are inclined to doubt the veracity of this spectrum, and note that it is very similar to $3d$ spectra of CeF_3 that have been published.[2,9] Ionisation-energy data reported for $CeF_4{\cdot}H_2O$ by Jørgensen [10a] suggest a spectrum more in line with our general expectations.

Cerium(III) *and praseodymium*(III) *compounds*. Our $3d$ spectra of the compounds M_2O_3 and $[M(tmhd)_3]$ ($M = Ce$ or Pr) (*e.g.* Figures 6 and 7) are essentially of the $[La(tmhd)_3]$ type; that is the higher kinetic k.e. component (*e.g.* h or g in Figure 7) is the weaker for both the $3d_{\frac{3}{2}}$ and $3d_{\frac{5}{2}}$ signals. This is again consistent with the chemical facts, *viz.* that Pr^{IV} and Nd^{IV} are stable only in oxide or fluoride lattices offering particularly high site potentials. The *X*-p.e. results (Table 1) in fact bear out the expectation that, for an isostructural series of compounds of La^{III}, Ce^{III}, and Pr^{III}, the $M^{3+}(3d^{-1}4f^{n+1})$ state of the ionised system gains stability relative to the $M^{4+}(3d^{-1}4f^{n})$ state. The only evidence for additional final-state structure is a weak shoulder on the low k.e. side of band g′ in the Pr_2O_3 spectrum (Figure 7). If this feature is genuine it presumably has the same origin as the additional detail observed in the CeO_2 $3d$ spectrum. Of course, for the lanthanoid elements proper, with the $4f$ subshell occupied in the ground state, there exists the possibility of observing ‘ fine structure ’ due to coupling effects in the $M^{3+}(3d^{-1}4f^{n+1})$ final states, but this is unlikely to influence the appearance of spectra of compounds of Ce^{III} ($4f^{1}$) and Pr^{III} ($4f^{2}$).

4d *Spectra*.—Close examination of the detail in the $4d$ spectra of the lanthanum(III) and cerium(IV) compounds suggests that the satellite structure is also due to charge transfer in the final states. However, relaxation effects are apparently less dramatic for $4d$ than for $3d$ core–hole states, which is only reasonable since the inner $4d$ electrons do not provide comparable screening of the nuclear charge from the outer electrons. On simple models for charge transfer one would accordingly anticipate both higher shake-up energies and lower λ values (less covalency) in the final states. For the most part such expectations are realised. Otherwise the differences between the $3d$ and $4d$ *X*-p.e. spectra are attributable simply to the reduced spin–orbit coupling in the $4d^{-1}$ core–hole states.

Lanthanum(III) *compounds*. The improved resolution in our $4d$ spectrum of La_2O_3, as compared with earlier spectra,[7,9] permits the unambiguous identification of a satellite band e′ and demonstrates clearly that the main peaks (labelled ef′ and f in Figure 8) have an intensity ratio quite different from that expected of a simple spin–orbit doublet (namely 2 : 3). The $4d$ spectra of $LaFeO_3$ and $LaCoO_3$ are very similar (Figure 8). The spacing of the principal $4d$ bands is 3.0 eV. This should be compared with a $4d_{\frac{3}{2}} - 4d_{\frac{5}{2}}$ separation of 2.85 eV in the *X*-p.e. spectrum of lanthanum metal, which shows a ‘ clean ’ $4d$ spin–orbit doublet with the theoretical intensity ratio. In agreement with previous workers,[5,12] we find that Lu_2O_3 and HfO_2, both $4f^{14}$ compounds, also have simple $4d$ spectra devoid of strong satellites. The weak feature marked S in our HfO_2 spectrum (Figure 10) may be due merely to inelastically scattered, secondary, electrons. Its separation from the principal $4d$ signal ($S - 4d_{\frac{3}{2}} = 16$ eV) is too large for it to be assigned to O $2p$ to metal $5d$ shake-up analogous to the O $2p$ to metal $3d$ shake-up processes evident in the $2p$ spectrum of TiO_2.[14–16]

The additional structure in the $4d$ spectra of the lanthanum(III) oxides apparently consists of two bands, one of which (f′) coincides with the $3d_{\frac{3}{2}}$ band (e). The evidence points clearly to these satellites being due to shake-up of the c.t. type leading to final states $[La^{3+}(4d^{-1}4f),X]$. Their diminished intensity compared with the satellites in the $3d$ spectra is in line with the expectation of reduced covalency in the ionised system, *i.e.* with lower values of λ, and hence $\Delta\lambda$ [*cf.* equation (13)]. The effective nuclear charge experienced by an outer electron (*e.g.* $4f$) should be considerably smaller in $La^{4+}(4d^{-1})$ than in $La^{4+}(3d^{-1})$, and the electron affinities of the cations are then such that the final states of the system ought to be less covalent than those produced by ionisation of the $3d$ subshell. However, the c.t. energies in the final state, E_s (*cf.* Figure 17), deduced from the $4d$ and $3d$ spectra of the lanthanum(III) oxides, do not immediately fit the general hypothesis. The $4d$ spectra in Figure 8 indicate a c.t. energy of 3.0—3.5 eV while, for the $3d$ ionisations (see above) the separation of the satellite band from the primary band is 4.0—4.5 eV: the trend in E_s values is thus the reverse of that expected on the basis of equation (2). It may be that covalency effects are sufficiently large to confuse the issue when E_s is small or, conceivably, the $3d$ spectra in Figure 3 represent a negative value of E_s, in which case there is no inconsistency.

The $4d$ spectrum of [La(tmhd)$_3$] (Figure 9) is broadly similar to that of La_2O_3. Such differences as are apparent may be attributed to lower resolution and a slight change in the shake-up energy E_s.

Cerium(IV) *compounds*.—The oxides CeO_2 and $BaCeO_3$ have closely similar $4d$ spectra (Figure 11), each showing six bands. The weaker features (in particular, the band w‴) are more evident in the deconvoluted spectrum of CeO_2 (Figure 12). Our measurements confirm and improve on a CeO_2 $4d$ spectrum reported by Suzuki *et al.*,[9] who did not hazard an assignment. (Strangely, the Japanese workers did not describe the $3d$ spectrum of CeO_2.) Actually, the detail in the $4d$ spectrum of CeO_2 appears to parallel that observed in the $3d$ spectrum (see above), and is susceptible to an interpretation along similar lines (see Table 1). This assignment is such that both the $4d_{\frac{5}{2}}$ and $4d_{\frac{3}{2}}$ signals comprise four bands, there being an overlap of two pairs of bands (w, x′, and w′, x″). The multiplet splitting (w — x) is *ca.* 3.2 eV, and the relative intensities of bands x‴ and w‴ are consistent with the 3 : 2 ratio expected on the basis of J multiplicities. Our interpretation implies of course that, in contrast to the situation prevailing in the lanthanum(III) oxides and [La(tmhd)$_3$], the increase in effective nuclear charge on ionising the $4d$ subshell in CeO_2 or $BaCeO_3$ is sufficient to make a c.t. state of the ionised system the ground state; in other words, bands x and w (figure 12) represent the [$Ce^{4+}(4d^{-1}4f)$,X] states while x‴ and w‴ correspond to the states [$Ce^{5+}(4d^{-1})$,-X^-]. The separation of the 'ionic' and c.t. states (x‴ — x = 13.5 eV) is noticeably less than the separation of the [$Ce^{5+}(3d^{-1})$, X^-] and [$Ce^{4+}(3d^{-1}4f)$,X] states (*ca.* 16.0 eV, see above); E_s being negative, this is consistent with the simplest expectations. The integrated probability of the two electron processes is somewhat greater (see Figure 12, in particular) than the probability of the primary one-electron ionisation, as is the case with the $3d$ ionisations.

The $4d$ spectrum of [Ce(tmhd)$_4$] (Figure 13), like its $3d$ spectrum, is rather poorly resolved, but it is consistent with the spectra of CeO_2 and $BaCeO_3$.

f^1 *and* f^2 *Compounds*. The $4d$ spectrum of [Ce(tmhd)$_3$] is rather amorphous, but is not unlike that of [La(tmhd)$_3$] (see above). It is consistent also with $4d$ spectra reported for $CeCl_3$ and $CeBr_3$. (The $4d$ spectrum of CeF_3 is more like that of La_2O_3.) The $4d$ spectrum of $BaPrO_3$ (also an f^1 compound) is however distinguished by the presence of quite prominent structure (labelled y‴ and z‴ in Figure 14) on the low k.e. side of the main signal. A detailed assignment of this spectrum cannot confidently be made but we note that, superficially, it shows some resemblance to the $4d$ spectra of $BaCeO_3$ and CeO_2, the low k.e. bands y‴ and z‴ in the $BaPrO_3$ spectrum being much less intense than their apparent counterparts w‴ and x‴ in the spectra of the cerium(IV) oxides. The differences between the $4d$ spectra of $BaPrO_3$ and $BaCeO_3$ may be due to a greater degree of relaxation in the former, and to a broadening effect due to additional unresolved structure arising from $4d$–$4f$ coupling in the final states. The electrostatic coupling of an outer $4f^n$ configuration with the $4d$ core hole is expected to be stronger than its coupling with a $3d$ core hole, and the effects of this coupling are indeed evident in the $4d$ spectra of the lanthanoid metals.[8] The high-resolution $4d$ spectrum of cerium metal indicates that the splittings due to $4d$–$4f$ coupling might exceed 3 eV.[8]

These coupling effects also presumably contribute to the somewhat diffuse nature of the spectrum of Pr_2O_3 (Figure 16) as compared with that of La_2O_3. {The $4d$ spectrum of [Pr(tmhd)$_3$], which is not reproduced here, is very like that of the praseodymium(III) oxide.} The spectrum of Pr_2O_3 is otherwise quite similar to that of [La(tmhd)$_3$].

4p *Spectra*.—The $4p$ spectra of both La_2O_3 and CeO_2 also display satellite structure (Figure 15). For La_2O_3 this is of the more familiar kind attributable to some shake-up process. Both the $4p_{\frac{3}{2}}$ (a) and $4p_{\frac{1}{2}}$ (b) signals appear to have a satellite (a′ and b′, respectively) and for the better defined $4p_{\frac{3}{2}}$ signal, the lower k.e. component is clearly the weaker. The shake-up energy is 4.5 ± 0.3 eV. Curiously, the previous workers did not report any satellite structure in the $4p$ region for any lanthanum compounds. Indeed, Wertheim *et al.*[2] invoked the absence of $4p$ satellites in the case of LaF_3 as evidence that the $3d$ satellites cannot be due to surface reduction of the sample. It seems likely however that the $4p$ doublet they described is in fact merely the $4p_{\frac{3}{2}}$ structure. According to Bearden and Burr,[29] the $4p$ multiplet splitting should be *ca.* 14 eV; the figure we deduce from the $4p$ spectrum of La_2O_3 is 14.5 ± 0.5 eV.

The $4p$ satellites observed for La_2O_3 presumably have the same origin as those observed in the $3d$ and $4d$ spectra. That they are of an intermediate intensity (measured relative to the primary peaks) lends support to the c.t. interpretation since the increase in effective nuclear charge sensed by the outer electrons on creation of a $4p$ hole is expected to be much less than that occasioned by a $3d$ ionisation, but somewhat larger than that following ionisation of a $4d$ electron. However, the trend in E_s values (*viz.* $3d$ ± 4.5 eV, $4p$ 4.5 eV, $4d$ *ca.* 3.0 eV) is difficult to understand.

The $4p$ spectrum of CeO_2 (Figure 15) adds to the confusion. The satellite structure is here apparently of the shake-down type (with E_s −7.6 eV), an interpretation which itself fits in with our assignments of the $3d$ and $4d$ spectra of the compound. But the pattern of E_s values deduced from the CeO_2 X-p.e. spectrum ($3d$ −16.0 eV, $4p$ − 7.6 eV, $4d$ − 13.5 eV) is qualitatively different from that inferred from the La_2O_3 spectrum, and equally puzzling. It should be said that the cerium $4p$ spectrum of $BaCeO_3$ (not reproduced here) is not altogether consistent with that of CeO_2, but its interpretation is much confused by overlapping barium $4p$ signals.

Thus the $4p$ satellites in the X-p.e. spectra of La_2O_3 and CeO_2 have somewhat anomalous characteristics. It should be noted, at the same time, that the intensity ratio of the $4p_{\frac{3}{2}}$ and $4p_{\frac{1}{2}}$ structure is remote from that expected on the basis of spin–orbital degeneracies

(Figure 15), especially in the case of La_2O_3. It seems likely that these anomalies are due to the collective resonance effects discussed by Gelius [30] in connection with xenon in particular. These effects, which are associated with the proximity of a continuum of shake-off states,[30] should be relatively more important in the case of Ba^{2+}.

The $4p$ spectrum of BaO (Figure 16) is consistent with a spectrum of $Ba[NO_3]_2$ reported by Gelius [30] (although the latter spectrum, excited by monochromatised *X*-rays, has better resolution), and apparently contains weak satellites with a separation of *ca.* 8 eV from the primary peaks. The $4p$ shake-up energy thus decreases progressively in the series BaO, La_2O_3, and CeO_2 (average E_s 7.5, 4.0, and —7.8 eV, respectively), while the relative intensity of the satellites increases. Both trends are consistent with the expectations of the simple c.t. model for the satellite structure. In agreement with previous workers, we could find no convincing evidence for satellite structure in the $3d$ and $4d$ spectra of BaO (Figure 16). The weak secondary structure that we do see (in $BaCeO_3$, as well as in BaO) may simply be due to inelastically scattered electrons or, in the case of the $3d$ ionisations, to the weak barium Auger signals expected in this region.[44]

Oxygen 1s *Spectra.*—With careful heat treatment, each of the oxide samples ultimately gave quite sharp, symmetrical, oxygen 1*s* signals. Remarkably, the full widths at half-maximum (f.w.h.m.) observed for the sesquioxides (1.8 eV for La_2O_3, 1.6 eV for Pr_2O_3), which are known to contain two crystallographically inequivalent sets of oxygen atoms (*cf.* Table 3), are not significantly greater than the O 1*s* half-widths found for $LaFeO_3$, $BaCeO_3$, and CeO_2 (all 1.6 eV) where the oxygen atoms occupy essentially equivalent sites. Yet the site potentials V_O, calculated with the assumption of full ionicity, differ by *ca.* 3 eV (Table 3). This question has arisen previously in connection with the F 1*s* signals in a variety of metal fluorides (in LaF_3, for example, the F 1*s* signal has a mere 1.3 eV half-width) [46] and with the O 1*s* signals of Pb_3O_4.[47-49] This virtual coincidence of *X*-p.e. signals from inequivalent anion species must be largely due to a reduction in the site-potential differences through covalency, supplemented perhaps by a differential-covalency effect.

Conclusions.—The satellite structure observed to accompany the $3d$, $4d$, and $4p$ signals in the *X*-p.e. spectra of oxides of La^{III} and Ce^{IV} can in each case be understood in terms of coupled excitations of the O $2p$ to metal charge-transfer type. The interpretation of the more complex satellite structure encountered in the case of lanthanoid ions having a partly occupied $4f$ sub-shell must therefore take into account not only electrostatic coupling effects (between the core hole and the $4f$ electrons) but also c.t. co-excitations. It may be however that the latter diminish in importance as one crosses the lanthanoid series.[10b]

The interpretation of the c.t. satellites observed for the $3d$ ionisations has intriguing chemical import. Where satellite structure of this kind can be identified, certain information concerning the energetics of hitherto unknown metal oxidation states might be deduced. Thus the additional structure observed in the metal $3d$ region of the CeO_2 *X*-p.e. spectrum tells us something about Pr^V, namely that in an oxide lattice having the fluorite structure and with the dimensions appropriate to CeO_2 the ' chemical ' energy difference between Pr^V and Pr^{IV} is *ca.* 16 eV probably less than half the $Pr^{4+} \longrightarrow Pr^{5+}$ ionisation energy. Such information might occasionally prove useful in guiding attempts to prepare compounds involving unusual oxidation states.

We thank Dr. A. J. Jacobson for his generous advice on a number of matters, and Neil Beatham for his help with the deconvolution of spectra, and the S.R.C. for their support (including a studentship to G. T.).

[6/309 *Received, 13th February,* 1976]

---

[46] R. G. Hayes and N. Edelstein, ' Electron Spectroscopy,' ed. D. A. Shirley, North Holland, Amsterdam, 1972, p. 711.

[47] J. M .Thomas and M. J. Tricker, *J.C.S. Faraday II*, 1975, 336.

[48] D. E. Parry and M. J. Tricker, *Chem. Phys. Letters*, 1973, **20**, 124.

[49] D. E. Parry, *J.C.S. Faraday II*, 1975, 344.