light brown, respectively. The cell constants of the high-pressure wolframite phase (space group *P*2/*c*) listed in Table I are in agreement with literature values.[8,10,20]

The Curie–Weiss plots for $NiMoO_4$ and $CoMoO_4$ before and after squeezing are given in Figures 3 and 4. The high-pressure phases show Curie–Weiss behavior in the temperature region between 100 and 300 K. The magnetic parameters are listed in Table II; a comparison of the Weiss constant before and after squeezing indicates that the antiferromagnetic interactions are stronger in the wolframite structure compared to the defect rock-salt structure. This same behavior has been reported in the high- and low-pressure polymorphs of $FeMoO_4$, where the values of the Weiss constant are given as −105 and +40 K, respectively.[9]

The existence, nature, and onset temperature of magnetic ordering depend in detail upon the topology of the exchange interactions present in the material.[21] The Weiss constant Θ, however, depends only on the average value of the arithmetic sum of all the magnetic-exchange interactions in which each ion participates. Thus, the dependence of Θ upon structure can readily be elucidated by the technique of path analysis.[22] Both high-spin cobalt $3d^7$ and nickel $3d^8$ possess half-filled e_g orbitals. Consequently, by the Goodenough–Kanamori rules, their $\{\sigma\sigma\}$ magnetic superexchange interactions will be strongly antiferromagnetic.[23–25] The t_{2g} orbitals are filled in nickel and more than three-quarters filled in cobalt. Hence, by the rules of superexchange, their $\{\sigma\pi\}$ and weaker $\{\pi\pi\}$ interactions will be ferromagnetic. In both the defect rock-salt and wolframite structures, the nearest-neighbor orbital overlaps are of the $\{\sigma\pi\}$ configuration and yield ferromagnetic interactions for cobalt and nickel. From the straightforward enumeration of interaction paths, it can be seen that each 3d ion has exactly 2 nearest neighbors in the wolframite structure but averages 2.5 in the defect rock salt. Similarly, each 3d ion participates in an average of 5 antiferromagnetic more-distant-neighbor $\{\sigma\Delta\sigma\}$ and 10.5 ferromagnetic $\{\sigma\Delta\pi\}$ interactions in the defect rock salt, compared with 20 antiferromagnetic more-distant-neighbor $\{\sigma'\Delta\sigma'\}$ interactions in the wolframite structure. (Here Δ denotes the anion–anion overlap of Mo ligands and σ' denotes a 135° e_g–anion bond.) This simplified path analysis suffices to show that the Weiss constant Θ should be more positive (ferromagnetic) for $CoMoO_4$ and $NiMoO_4$ with the defect rock-salt structure than with the wolframite, in agreement with experiment.

Conclusions

The divalent transition-metal molybdates of cobalt and nickel were prepared, and their magnetic susceptibilities were measured. The μ_{eff} values for the ambient temperature and pressure defect rock-salt phases of cobalt and nickel molybdate were consistent with high-spin Co(II) and Ni(II), and the small positive Θ values of 12 and 20 K, respectively, indicate that the antiferromagnetic interactions in the defect rock-salt structures are balanced by ferromagnetic interactions.

When the defect rock-salt phases of $NiMoO_4$ and $CoMoO_4$ were pressed at 50 kbar and 400 and 350 °C, respectively, the resulting product crystallized with the wolframite structure. The Θ values for the high-pressure phases were −102 K for $NiMoO_4$ and −105 K for $CoMoO_4$. The difference in the Θ values before and after pressing indicates a strengthening of antiferromagnetic interactions in the wolframite structure compared to the defect rock-salt structure. This is consistent with the results of a path analysis of the superexchange linkages present in the defect rock-salt and wolframite structures.

Acknowledgment. We acknowledge the Office of Naval Research, Arlington, VA, for the support of Kurt Sieber and Kirby Dwight. Acknowledgment is also made to the Materials Research Laboratory Program at Brown University, funded through the National Science Foundation.

Registry No. $NiMoO_4$, 14177-55-0; $CoMoO_4$, 13762-14-6; $TeCl_4$, 10026-07-0; $FeMoO_4$, 13718-70-2.

---

(20) Sleight, A. W. *Acta Crystallogr. Sect. B* **1972**, *B28*, 2899.
(21) Kaplan, T. A.; Stanley, H. E.; Dwight, K.; Menyuk, N. *J. Appl. Phys.* **1965**, *36*, 1129.
(22) Dwight, K.; Menyuk, N. *Phys. Rev.* **1967**, *163*, 435.
(23) Goodenough, J. B. *J. Phys. Chem. Solids* **1958**, *6*, 287.
(24) Kanamori, J. *J. Phys. Chem. Solids* **1959**, *10*, 87.
(25) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2.

Contribution from Ames Laboratory—DOE[1] and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Core Photoelectron Shifts in Reduced Zirconium Halides. Relaxation Effects and Delocalized Metal–Metal Bonding

JOHN D. CORBETT

Received January 21, 1983

Trends in binding energies of the zirconium $3d_{5/2}$ and chlorine $2p_{3/2}$ levels for Zr, $ZrCl_n$ (n = 1–4), ZrBr, $ZrXH_x$ (X = Cl, Br; x = 0.5, 1), and $ZrClO_{0.4}$ are considered as a function of oxidation state. The zirconium binding energy exhibits a regular and consistent increase on oxidation for all phases with formal oxidation states between 0 and +2, while those for $ZrCl_3$ and $ZrCl_4$ are displaced about 1.3 eV to higher binding energy. Structural and property data for the compounds suggest that the break in zirconium binding energy takes place at the point at which metal–metal bonding and the consequent valence-electron delocalization cease. This effect is considered in terms of the metal valence bands and the final-state relaxation processes that occur in response to the core hole. The apparent relaxation is otherwise remarkably insensitive to differences in valence bands and structure. The only change of significance seen in the chlorine data reflects the different Fermi level reference in $ZrCl_4$.

Introduction

The energies of core photoelectron emission events are well-known for their direct reflection of changes in valence-electron distributions that come about either through formal oxidation or reduction or by simple inductive (polarization) effects.[2–4] Although the changes are usually qualitatively predictable, the origins of the observed binding energies are quite complex. Part of this derives from the fact that the

---

(1) Operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

0020-1669/83/1322-2669$01.50/0

energy change realized is not for the vertical (frozen orbital) process but is a somewhate smaller quality because other electrons in the system simultaneously adjust to the appearance of a positive charge at the particular atom. One source of this is the intraatomic relaxation of the other electrons in the atom in question, reflecting the loss of electron–electron repulsions within the level in question and the descreening effect that the hole has on electrons outside the level sampled. This effect is substantially independent of the state of binding and therefore is relatively constant for that atom within a series of compounds. But the extraatomic response of the bonding and near-bonding levels in a molecule or an extended solid to creation of a core hole (beyond simple atom polarization) can provide evidenced on interesting chemical changes and differences. This relaxation is known to be 5–15 eV in some solids relative to the gaseous atoms.

Two extremes serve as examples. In the O_2 molecule, the creation of a positive 1s core hole in one atom is accompanied by extreme polarization of the less localized π and π^* levels, to the extent that calculations show that the positive charge created is overcompensated.[5] On the other hand, electrons at the Fermi level in metals can easily access empty states with large mean free paths and can thus readily move to screen the core hole or, in other terms, can react to the fact that the conduction band is bent downward in the immediate neighborhood of the localized defect, the ionized atom, and can alter the local electron population accordingly.

Information on the corresponding relaxation behavior of solid systems with intermediate degrees of delocalization, not necessarily in partly filled bands, appears much sparser. The photoelectron spectrea of the core levels in a series of zirconium halides and their derivatives, which span from metallic phases through narrow-band semiconductors to insulators, furnish interesting examples of both relaxation and ground-state effects within the particular structures provided. Although many of the compounds in this series are not completely characterized as to band and electronic props., some ancillary evidence regarding their valence levels is available from photoelectron spectra and, to a lesser degree, from electronic and optical properties and theory. In fact, these rather widely ranging compounds will be seen to react to the photoionization process in a remarkably uniform way that appears particularly sensitive to metal–metal bonding and the accompanying delocalization and insensitive to details of the structures.

Results and Discussion

Figure 1 shows the data of particular interest, the emission energy maxima for zirconium $3d_{5/2}$ and chlorine $2p_{3/2}$ core levels in a variety of zirconium halide compounds as a function of oxidation state or d-electron count. Data for the metal,[6,7] ZrCl,[8] ZrBr,[9,10] the metal in $ZrCl_4$,[6] and the hydride[10] and oxide[11] derivatives of the monohalides are all referenced to adventitious carbon 1s at 285.0 eV. The $ZrCl_2$, Zr_6Cl_{12}, and $ZrCl_3$ data[8,12] were measured relative to the $3d_{5/2}$ level of Ag metal mounted on the sample probe, which was taken to be 368.2 eV.[13] Core levels of both elements in $ZrCl_4$ have also been measured relative to the $4f_{7/2}$ level of overlaid gold.[9] All phases were handled and mounted in a drybox attached directly to the spectrometer. The XPS results were generally reproducible to ±0.1 eV, ±0.2 eV at the outside, some for measurements spread over a period of several years.

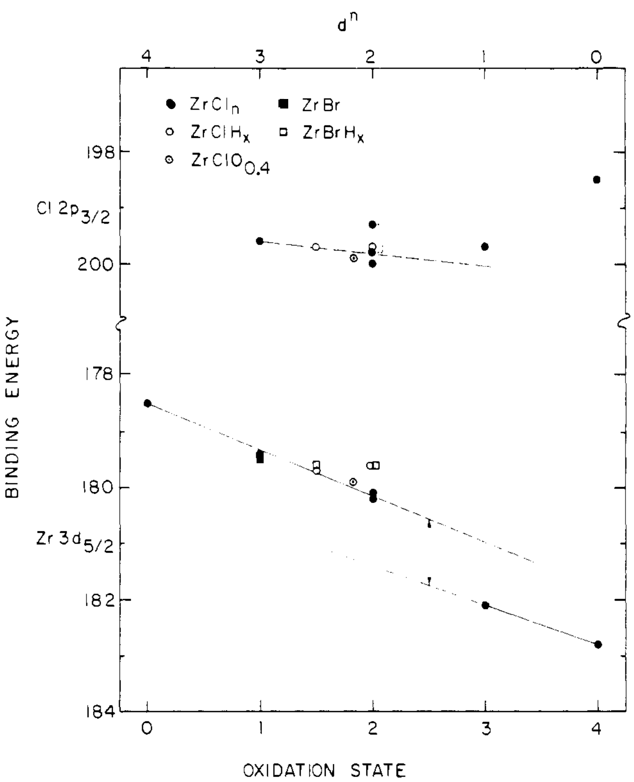

Figure 1. Zr $3d_{5/2}$ and Cl $2p_{3/2}$ binding energies (eV) in zirconium halides and their derivatives as a function of oxidation state.

As usual, the chloride data for the reduced phases reveal little in terms of oxidation state, let alone more subtle effects. This is reasonable since involvement of chlorine orbitals in the metal–metal bonding is quite small. In addition, even in a wide series of metal chlorides the charge on chlorine might be expected to vary in the extreme from 1− to a value approaching zero as the oxidation state of the metal increases, thereby producing a small increase in binding energy across the series. However, the actual binding energy change in these particular compounds should be much less since ZrX, their derivatives, and $ZrCl_2$ are all layered and only small charges on and small changes in the adjacent chlorine layers in such structures are to be expected, presumably reflecting appreciable Zr–X covalency. Changes in the electrostatic potential term at the metal across the series are expected to be small for the same reason. The contrary behavior of $ZrCl_4$ seen in Figure 1 will be considered later.

Trends in the core binding energy for zirconium shown in Figure 1 are much more interesting, not just for their regularity but especially because of the clear break that occurs between oxidation states +2 and +3. However, the analysis and interpretation of these results first require some information of the structural features of the phases and what is known or may be inferred about their valence electronic structures. These

---

(2) Carlson, T. A. "Photoelectron and Auger Spectroscopy"; Plenum Press: New York, 1975; Chapter 5.

(3) Fadley, C. S. In "Electron Spectroscopy. Theory, Techniques and Applications"; Brundle, C. R., Baker, A. D., Eds.; Academic Press: London, 1978; Vol. 2, p 1.

(4) Martin, R. L.; Shirley D. A. In "Electron Spectroscopy. Theory, Techniques and Applications"; Brundle, C. R., Baker, A. D., Eds.; Academic Press: London, 1977, Vol. 1, p 98.

(5) Haas, C. In "Current Topics in Materials Science"; Kaldis, E., Ed.; North-Holland Publishing Co.: Amsterdam, 1979; Vol. 3, p 1.

(6) Nefedov, V. I.; Salyn', Y. V.; Chertkov, A. A.; Padurets, L. N. *Zh. Neorg. Khim.* **1974**, *19*, 1443.

(7) Nguyen, T.-H; Franzen, H.; Harmon, B. N. *J. Chem. Phys.* **1980**, *73*, 425.

(8) Cisar, A.; Corbett, J. D.; Daake, R. L. *Inorg. Chem.* **1979**, *18*, 836.

(9) Daake, R. L.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2029.

(10) Corbett, J. D.; Marek, H. S. *Inorg. Chem.*, in press.

(11) Seaverson, L. M.; Corbett, J. D. *Inorg. Chem.*, in press.

(12) The dichloride with (slightly) higher Zr binding energy in Figure 1 is $ZrCl_2$, and the lower, Zr_6Cl_{12}. The latter shows two energies for chloride since half are only two-coordinate to metal, and the rest, three, the latter presumably exhibiting the larger binding energy.

(13) Bird, R. J.; Swift, P. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *21*, 227.

Table I. Structural and Electronic Properties of Zirconium Halides and Their Derivatives

				metal valence band	
	d^n	structure[a]	electronic properties[a]	fwhm, eV	energy,[b] eV
Zr	d^4	hcp	metal	2.0	1.1
ZrCl	d^3	ccp layers X–Zr–Zr–X	metallic,[c] low DOS at E_F	1.3	2.0
ZrBr				1.2	2.0
$ZrClH_{0.5}$	$d^{2.5}$	distorted ZrX; H in $^1/_2$ tetrahedral (Zr_4) holes	metallic, larger DOS	2.4	1.3
$ZrBrH_{0.5}$				1.9	1.6
$ZrClO_{0.4}$	$d^{2.2}$	ZrCl, O in tetrahedral holes	metallic	1.2	1.8
ZrClH	d^2	hcp layers X–Zr–Zr–X; H in all tetrahedral holes	colored, metallic with low DOS or semiconductor	0.9	1.8
ZrBrX				0.9	1.5
$ZrCl_2$	d^2	layered; Cl–Zr–Cl (3R-NbS_2 type)	semiconductor, $E_g \sim 0.3$ eV[d]	0.9	1.2
Zr_6Cl_{12}	d^2	cluster, $\bar{3}$ symmetry	semiconductor based on structure	<1.6 (0.9[e])	1.9
$ZrCl_3$	d^1	hcp chlorine, chains of Zr in $^1/_3$ of octahedra	poor semiconductor ($\sigma \sim 1.6 \times 10^{-5}$ Ω^{-1} cm^{-1}; $E_g \sim 0.3$ eV), magnetic[f]	(≤0.7[e])	1.9
$ZrCl_4$	d^0	$ZrCl_2Cl_{4/2}$	insulator		

[a] Summarized in ref 9, 11, 14 and 15. [b] Midpoint of the principal feature in the He I spectrum, thereby excluding lower DOS regions.[10,11,14] [c] References 9 and 16. [d] Reference 8. [e] Half-width at 75% height in X-ray spectrum (with monochromator), a measure which fits XPS vs. UPS emissions from ZrCl and $ZrCl_2$. [f] References 17 and 18.

are summarized and referenced in Table I where UPS-derived bandwidths and positions are used to provide something of a universal overview of the metal valence structures. The lower halides ZrX (X = Cl, Br), $ZrXH_{0.5}$, ZrXH, and $ZrClO_{0.4}$ are all layered and contain double metal layers with strong Zr–Zr bonding between and within these (d(Zr–Zr) = 3.09 and 3.43 Å, respectively, in ZrCl). This serves to generate good approximations to two-dimensional metals with fairly narrow bands in most cases. Hydrogen fills tetrahedral interstices between the metal layers, withdrawing electrons (and d orbitals) from the conduction band to form a hydride "anion" with appreciable covalent bonding to zirconium,[10] and the oxide $ZrClO_{0.4}$ is similar. The monohalides are known by theory and experiment to be metallic with a clear but small density of states (DOS) at the Fermi level E_F. A higher DOS develops in the hemihydrides according to UPS data (though what is seen for the band probably includes to some degree the contribution of hydrogen with its higher cross section). The ZrXH phases show a narrow metal valence band and are either poor metals (low DOS) or small-gap semiconductors (no electrical data are available). The $ZrCl_2$ contains only a single metal layer and is a small-gap semiconductor analogous to the isoelectronic MoS_2 but with notably narrower valence bands and less evidence of metal–nonmetal mixing. (This last feature is common to all of these halides relative to sulfides and selenides.) The band shape of Zr_6Cl_{12} is similar to that in 3R-$ZrCl_2$, and a low conductivity seems likely in view of the separation of the individual clusters.[19] The trichloride appears to possess a much more localized and magnetically coupled $4d^1$ state rather than collective bonding properties of the compounds just described. The confacial $ZrCl_6$ units in this are distorted so as to suggest repulsion between the zirconium atoms that are only 3.07 Å apart in well-separated chains of single metal atoms. (An earlier UPS study[14] of $ZrCl_3$ was not able to define the metal 4d levels adequately but the XPS data suggest a narrow band—Table I).

The zirconium core data shown in Figure 1 show a remarkably smooth and consistent trend for those phases with oxidation states of +2 or less even though the compounds span a considerable range of electronic properties and their structures range from the hcp metal to phases with single or double metal layers.[20] Equally striking is the substantial (~1.3 eV) break between these and the $ZrCl_4$ data at the point that corresponds to the loss of significant communication between and delocation of (mainly) zirconium 4d valence states. The inflection can also be described as a manifestation of an abrupt increase in the electron correlation energy for zirconium(III) relative to that in lower oxidation states. In hindsight, it appears that a break of this sort could probably have been used to predict such a transition in the bonding. Other examples have evidently not been reported.

Inquiry as to the possible valence-state (bonding) effects that could contribute to such a sizable deviation is useful. Of course, the observed transition may involve changes both in ground-state bonding, the nature of which may be inferred to some degree from the physical properties (including the valence photoemission spectra where more delocalized holes are usually generated), and in the less certain product state in which the system has responded to the localized core hole therein. As far as the ground state is concerned, the most obvious effect that delocalization could have on the 3d core-level energies would be through general participation of the more penetrating 5s (and 5p) orbitals in the bands and the additional screening of the nuclear charge this would provide. But an effect as uniform as implied by Figure 1 would seem unusual.

Final-state effects of the character generally described as "relaxation" are known to be large and varied in the solid state. However, the cases at hand are structurally more diverse and their relaxation behaviors possibly more complex than present in simple metals or semiconductors so that their treatment can only be highly inferential. Some of the best studied effects accompany the creation of a core hole in metallic phases where the conduction band is relatively wide compared with the core-hole–valence-electron interaction. Theory and experiment are in agreement in many respects; the general shift caused by screening of the core charge is accompanied by a pronounced tailing or skewing on the high-binding-energy side of the otherwise symmetric profile of the core-electron peak.[21] The peak maximum corresponds to ionization to the optimal relaxed or screened configuration while the other transitions comprising the tail include the results of many simultaneous

---

(14) Corbett, J. D.; Anderegg, J. W. *Inorg. Chem.* **1980**, *19*, 3822.

(15) Marek, H. S.; Corbett, J. D.; Daake, R. L. *J. Less-Common Met.* **1983**, *89*, 243.

(16) Troyanov, S. I. *Vestn. Mosk. Univ., Ser. 2: Khim.* **1973**, *28*, 369.

(17) Clemmer, R. G. Ph.D. Thesis, University of Wisconsin—Madison, 1977; *Diss. Abst. B* **1977**, *38B*, 674.

(18) Feldman, C. D. Ph.D. Thesis, University of Wisconsin—Madison, 1979; *Diss. Abst. B* **1980**, *40B*, 5661.

(19) Guthrie, D. G.; Corbett, J. D. *Inorg. Chem.* **1982**, *21*, 3290.

(20) There is of course no reason for the dependence to be linear. The somewhat lower Zr binding energies for the ZrXH phases could easily be explained by an electronegativity or inductive effect from greater covalency of hydride; ZrH_2 lies still lower in binding energy.[16]

(21) Wertheim, G. K.; Citrin, P. H. *Top. Appl. Phys.* **1978**, *26*, 197.

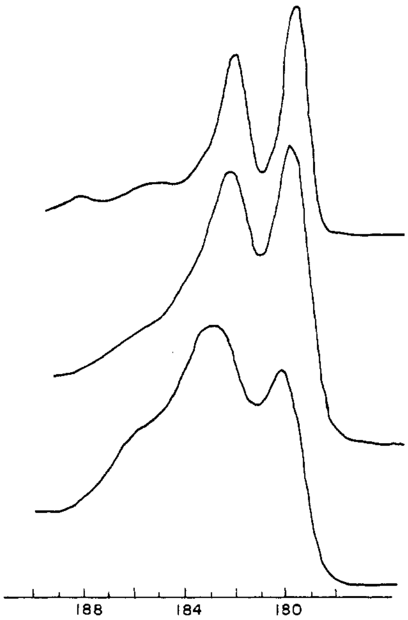

Figure 2. Zirconium $3d_{5/2}$ and $3d_{3/2}$ spectra of ZrCl (top), $ZrClH_{0.5}$ (middle), and Zr_6Cl_{12} (bottom). The $3d_{5/2}$ component has the lower binding energy (eV).

electron–hole pair excitations in the conduction band. In this instance, the hole can be viewed as hardly perturbing the band system. With larger core hole–electron interactions or narrower bands one or more sets of local, impurity-like levels are often generated. The lowest may or may not be occupied, giving rise to the main peak of lowest binding energy plus one or more weaker "shake-up" peaks at higher energy. (The simple and somewhat analogous case for Li_2^+ has been modeled.[22]) Such satellites can be seen as long as the valence electron–hole interaction exceeds the band gap while in the large-gap extreme a single symmetric peak is found.

A simple description of the probable process in the clustered Zr_6Cl_{12} aids in understanding the general concept. The sudden creation of a core hole in the nominal metal octahedron is substantially equivalent in its effect on the valence levels to the substitution of an isoelectroonic Nb^+ ion at that point. A significant redistribution of the atomic orbitals among the molecular orbitals of that particular cluster takes place in response to the "new" atom and the lower symmetry, and this involves all, not just the occupied, levels. In molecular terms, the system's ability to respond to this particular perturbation and to lower the energy of the cluster and thence the binding energy should vary qualitatively as the number of atoms and orbitals involved, i.e., the degree of delocalization, and inversely with the energy separation between filled and empty states, i.e., the gap. Again, this possibility appears to disappear at $ZrCl_3$. In addition, excited states corresponding to less screening of the "new" atom may also be seen in the form of satellites at higher binding energies. In the simple cases such as O_2 and Li_2^+, these correspond to a core hole that does not trap a valence electron. In the sudden approximation, skewing with or without satellites is to be expected when extraatomic relaxation occurs.

In fact, the nature of excited states accompanying the ionization of the present collection of zirconium compounds appears diverse and not readily interpretable in spite of the very considerable regularity in the net energy of the process. Three examples are shown in Figure 2. A ready measure of peak skewing is the deviation in the relative heights of the $3d_{5/2}$ and $3d_{3/2}$ zirconium peaks ($\Delta \sim 2.4$ eV) from the expected ratio $R = 3{:}2$. Sharp peaks and substantially no deviation in R are found with ZrCl and $ZrCl_4$ although a small tailing and perhaps a weak satellite or two are evident in the former. (Overlap of Zr 3d and Br 3p core levels prevents this comparison in bromides in general.) Substantial skewing ($R \sim 1.1$) is observed for $ZrClH_{0.5}$, ZrClH, and $ZrClO_{0.4}$ while $ZrCl_2$ gives a normal ratio but satellites at 1.5–2.5 eV above the $3d_{3/2}$ level. Obvious changes in the intensities ($R < 1$) and satellites are found for Zr_6Cl_{12} and $ZrCl_3$ (at ~3 and 1.8 eV, respectively); of course, unresolved satellites with small displacement could also be responsible for deviations found in relative peak heights. A multiplet structure is to be expected for $ZrCl_3$ because of its (uninterpreted) magnetism. (Not all of these spectra were run with a monochromator, however.) In all cases the same effects are seen in the zirconium 3p but not in the chlorine 2p spectra, substantiating the small contribution of chlorine to the metal bands. Several examples of the use of line shapes to distinguish among contributing orbitals are given by Folmer and deBoer.[23]

In retrospect, the regularity ultimately found in the metal core shifts for this variety of compounds and structures with formal oxidation states of +2 or less is quite surprising when the observed complexities of relaxation are considered. The quite regular trends suggest that delocalization may in effect be a major factor and that the degree of relaxation achieved is remarkably consistent. Other circumstances seem less important, such as whether the compounds are small DOS metals or small-gap semiconductors in the ground state, the details of the particular structural arrangement, and any satellite structure observed for the product state. Further theoretical consideration would be highly desirable.

Finally, the seemingly errant value for chlorine $3p_{3/2}$ binding energy for $ZrCl_4$ (Figure 1) doubtlessly originates with a change in the Fermi level reference. In the other compounds E_F either is defined by uppermost electrons in a largely 4d conduction band or lies midway between filled and empty bands within the 4d manifold. In principle, this drops to the midpoint between the empty 4d and the chlorine 3p bands in $ZrCl_4$ (although impurities may pin it at the bottom of the conduction band), and the apparent binding energy for chlorine 2p drops accordingly. For $ZrCl_3$, the reference in practice may be at the top of the fairly isolated d states rather than midway in the gap. But in neither case does this alter the previous conclusions. The relative binding energy of the zirconium 3d levels in $ZrCl_3$ and $ZrCl_4$ would be increased even further relative to those for the more reduced phases if either chlorine 2p or chlorine 3p levels were instead used for the reference point, by roughly 0.5 and 1.5 eV, respectively. This would serve only to enhance what are deduced to be relaxation effects derived from delocalized bonding in the more reduced compounds.

Acknowledgment. The author is indebted to both P. A. Cox and J. C. W. Folmer for helpful and informative discussions. James W. Anderegg is in large part responsible for the high quality of the core data.

Registry No. Zr, 7440-67-7; ZrCl, 14989-34-5; $ZrCl_2$, 13762-26-0; $ZrCl_3$, 10241-03-9; $ZrCl_4$, 10026-11-6; ZrBr, 31483-18-8; chlorine, 7782-50-5; zirconium chloride oxide, 7699-43-6; zirconium bromide oxide, 33712-61-7.

---

(22) Sawatsky, G. A.; Lenselink, A. *J. Chem. Phys.* **1980**, *72*, 3748.

(23) Folmer, J. C. W.; deBoer, D. K. G. *Solid State Commun.* **1981**, *38*, 1135.