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Valence Photoelectron Emission Spectra of Four Reduced Zirconium Chlorides and Inferences Regarding Their Metal–Metal Bonding

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Received May 9, 1980

Photoelectron emission spectra measured with both He I and monochromatic Al Kα radiation are reported for the valence regions of ZrCl, $ZrCl_2$ (3R-type), Zr_6Cl_{12}, and $ZrCl_3$. The metal-rich valence band observed in all phases at 1.1–1.5 eV is found to shrink and to move away from the Fermi level on oxidation. The results are compared with the implications regarding metal–metal bonding provided by the observed distances and the bond orders calculated therefrom, especially with regard to the evident absence of a strong metal–metal interaction in $ZrCl_3$.

Introduction

Binary halides of most of the 3d elements exhibit relatively large metal–metal separations compared with those in the metals themselves, and, since halide participation is generally small, the metal–metal interactions are characteristically weak and manifested only at low temperatures in such sensitive phenomena as magnetic coupling. Accordingly, the room-temperature phases can be fairly well described in terms of localized 3d valence electrons below E_F.[2] Although trends in valence photoelectron spectra of the halides of any 3d metal as a function of oxidation state have not been reported, these should manifest mainly localized electronic states.

In contrast, the lower halides of the first 3d element scandium together with those of groups 3–6 of the heavier transition elements and of many of the inner transition elements provide abundant examples of strong, even structure-dominating, metal–metal bonding,[3] the most remarkable and recently discovered of which occur in groups 3 and 4 and the rare earths.[4-9] Important questions regarding bandwidths and the relative binding energies of the electrons associated with the metal–metal bonding and their probable electrical properties (metallic, semiconducting, etc.) are conveniently explored via photoelectron emission spectroscopy, especially when the available samples are small, air sensitive, and powdered so that more conventional studies are not feasible. The present manuscript reports on the examination of the four reduced zirconium chlorides ZrCl, $ZrCl_2$, Zr_6Cl_{12}, and $ZrCl_3$, a series for which not only structural but also some electrical and magnetic data are available for comparison.[4-6,10-14] The behavior of the binding energy of the metal's valence electrons and of the interrelated metal–metal distances as a function of oxidation state is particularly interesting. Interpretation of metal–metal bonding in terms of bond lengths alone has been a classic approach, though a diversity of structure types, matrix effects, and other factors to be brought out in this article make this approach sometimes difficult or hazardous.

Experimental Section

The ZrCl, $ZrCl_2$, Zr_6Cl_{12}, and transported $ZrCl_3$ were prepared as previously described, by starting with sublimed $ZrCl_4$ and a high-purity zirconium sheet or turnings and using sealed tantalum containers.[5,11,12,14] All were handled only in the drybox and were identified by Guinier powder patterns.

Photoelectron emission spectra were obtained by using both X-ray (XPS, Al Kα) and ultraviolet (UPS, He I) sources with an AEI Model ES200B instrument coupled to a Nicolet 1180 minicomputer for data averaging and curve smoothing. Generally 2–11 and 20–500 scans were used with UV and X-ray sources, respectively, utilizing 512 channels, and the data were smoothed by a nine-channel running average. The valence spectra were referenced to the Fermi edge of silver, gold, or nickel metal. All XPS results reported were secured with the monochromater in operation. No evidence of charging was noted.

Samples for study were opened in a helium-filled drybox attached directly to the sample chamber of the spectrometer and maintained at <1 ppm O_2 and <0.5 ppm H_2O. The sample was pressed into a strip of indium mounted on the sample holder in a manner so as to generate fresh surface. The fibrous habit of $ZrCl_3$ made it difficult to cover the indium backing completely, but the substrate makes only a small and broad contribution in the valence region of interest. Samples were monitored by using Zr 3d and Cl 2p core spectra reported earlier[11] together with those of O 1s and C 1s impurities. The reference spectrum of zirconium metal was obtained from a sheet rolled from reactor grade, crystal bar metal which had first been cleaned outside the chamber and then argon ion etched until core levels for surface impurities (C, O) disappeared and the Fermi edge reached its maximum amplitude. The small changes seen in the XPS results during this process suggested the etching did not give an artificial result; on the other hand etching of particularly the di- and trichlorides gave severe peak broadening and evident decomposition.

Synthesis of Zr_6Cl_{12} in sufficient quantities and purity for this examination is best accomplished in the $ZrCl_2$–$ZrCl_3$ system at ≥650 °C.[12] However, samples with overall Cl:Zr ≥ 2.0 generate autogenous $ZrCl_4$ pressures of tens of atmospheres at these temperatures, and quenching such a system produces a coating of $ZrCl_4$(s) on the cluster phase. This is readily identified by the lower and higher binding energies of the Cl $2p_{3/2}$ and Zr $3d_{3/2}$ core levels,[11] respectively. Fortunately the $ZrCl_4$ layer does not contribute in the metal valence region (<5 eV) though it greatly reduces, but does not obliterate, the metal valence band of the substrate discernible with UV radiation (not shown). The same pertains to a lesser degree to some $ZrCl_3$ samples examined where a greater problem is the clear resolution of the small metal valence emission relative to that from Cl 3p (5.6% of the Cl peak for equal cross section, 4.3% observed). The range of stoichiometry of $ZrCl_3$[14] is not significant with respect to the sensitivity of the method. The Zr 3d spectra do suggest a multiplet splitting of ~1.8 eV.

Results and Discussion

The XPS and UPS data for the valence regions of Zr, ZrCl, $ZrCl_2$, Zr_6Cl_{12}, and $ZrCl_3$ are shown in Figures 1 and 2 while structural information on these phases is summarized in Table I. Peak positions for Zr 3d and Cl 2p core levels for this series have been summarized before.[11] The principal changes found there are increases in the zirconium 3d binding energies of

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[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 Assistant Secretary for Energy Research, Office of Basic Energy Sciences, WPAS-KC-02-03.

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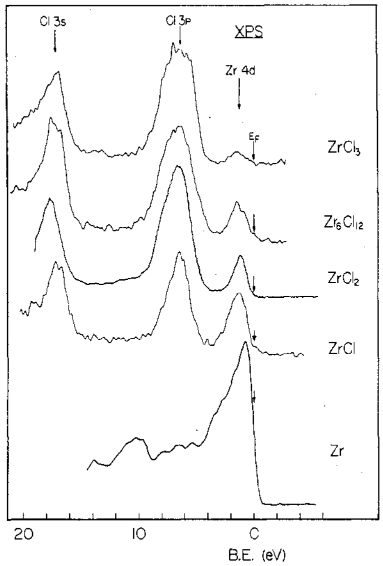

Figure 1. Valence photoemission spectra for the reduced zirconium chlorides and metal from an Al Kα source (monochromatized). The ordinate scale is arbitrary.

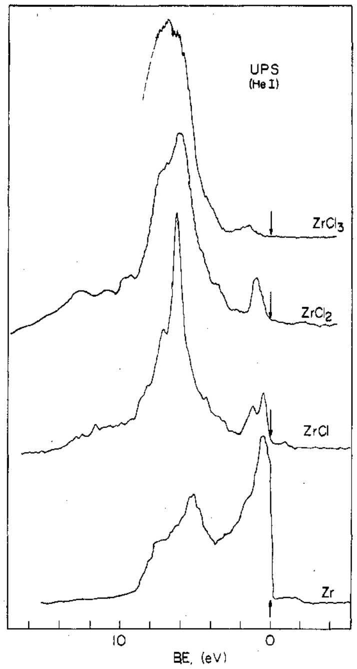

Figure 2. The He I valence photoemission spectra for three reduced zirconium chlorides and the metal.[16]

about 0.6 eV between metal and ZrCl, 0.5–0.9 eV between ZrCl and the dichlorides as a group, and 1.7–2.3 eV between the latter and $ZrCl_3$. Changes in Cl 2p levels are small save for a drop between $ZrCl_3$ and $ZrCl_4$.

Some oxygen contamination of one sample of $ZrCl_2$ is suggested by the high-energy shoulder observed on the "Cl 3p" peak in both the X-ray (not shown) and UV (Figure 2) scans. A similar result was obtained from another ZrCl sample known to have been contaminated by oxide at high temperatures. In neither case does the metal valence region seem to be measurably affected.

The two general features observed in the photoelectron emission spectra of the valence region as a whole on increase in oxidation state are (a) the appropriate shrinkage of the metal "4d" band near E_F relative to chlorine "3p" because of the changes in stoichiometry and (b) a lowering of the presumed metal-rich band below E_F. The binding energy of the metal-rich valence level at the maximum observed with X-rays increases from 1.1 eV with ZrCl to 1.2 eV for $ZrCl_2$ (3R-type), 1.3 eV with Zr_6Cl_{12} and 1.5–1.6 eV for $ZrCl_3$. The characteristically higher resolution obtained with UV radiation gives a better idea of shape of the metal valence band (cross section) and its narrowing on oxidation of ZrCl to $ZrCl_2$; on the other hand a layer of $ZrCl_4$ on Zr_6Cl_{12} as synthesized and the practical sensitivity limit for $ZrCl_3$ (see Experimental Section[16]) limited the quality of the UV spectra obtained for these. Therefore the metal valence band shown for $ZrCl_3$ is not believed to fairly represent the intrinsic bandwidth. The ratios of the apparent cross sections of the valence metal and chlorine levels to X-rays remain constant (±10%) on oxidation from ZrCl to $ZrCl_3$ while those for UV radiation appear to increase by a factor of 2 or more.

The spectral observations of the valence region are in good accord with the physical data. ZrCl is metallic not only by this criterion[5] but by preliminary conductivity measurements[17] and by band calculations.[18] The UPS data for ZrCl in fact exhibit an ionization profile for the conduction band (primarily Zr 4d[18]) which is remarkably similar to the calculated band shape. On the other hand $ZrCl_2$ would probably (but not conclusively) be judged a semiconductor on the basis of the photoelectron data, a circumstance which has been established by direct measurement of an electrical band gap of ca. 0.3 eV.[11] This makes 3R-$ZrCl_2$ quite analogous to the isoelectronic MoS_2. However the chloride band is noticeably narrower and its separation from the more metal-dominated valence level substantially greater than for the first two bands in MoS_2[19] (5.4 vs. 1.4 eV peak to peak). The $ZrCl_2$ spectrum thus suggests there is substantially less mixing of metal d and nonmetal p functions in the first two valence bands than in the more covalent disulfide, a general feature[3] which is known to apply to the parentage of the first two bands in the ZrCl according to band theory. The same in essence applies to its polymorph, the clustered Zr_6Cl_{12} where the metal valence level may have a slightly higher binding energy; otherwise it exhibits no significant difference from the layered structure at the resolution achieved with monochromatized X-rays.

Zirconium trichloride provides the greatest contrast between an expectation of metal–metal bonding according to structure alone and the properties deduced by measurement. In spite of the 3.07-Å approach of the metal atoms (Table I) $ZrCl_3$ is not metallic;[20] rather it is a poor conductor ($\sigma \approx 1.6 \times 10^{-5}$ Ω^{-1} cm^{-1}, $E_g \approx 0.33$ eV) and apparently a weak ferromagnet.[21] The photoelectron data support the absence of a band at or near E_F, more or less in accord with the expected trend from metallic to insulating phases on oxidation. In effect a gap opens up within the d bands for $ZrCl_3$ (and $ZrCl_2$) as ligand field effects appear to dominate. The contrast provided by the short metal–metal distances in $ZrCl_3$ is worthy of further consideration.

The structure adopted by each phase in this zirconium chloride series is not easily explained let alone predicted, but the metal–metal distances contained within the structures provided do offer a worthwhile lesson on metal–metal bonding. The Zr–Zr distances given in Table I for the chlorides are striking in two respects—the close 3.09-Å approach of three metal atoms in the adjacent layer in the metallic ZrCl and an equally noteworthy separation of 3.07 Å for two neighbors

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(16) The shape and energy of the chlorine 3p emission from $ZrCl_3$ obtained with UV radiation are somewhat distorted by a spurious magnetic field.

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Table I. Structural Data for the Reduced Zirconium Chlorides and Zirconium Metal

	formal d state	structure type	metal distribution	metal environment	metal–metal bond order per electron[a]	ref
Zr	d^4	hcp		6 Zr at 3.232 Å,[b] 6 Zr at 3.179 Å (D_{3h})	(1.00)	15
ZrCl	d^3	ZrCl	infinite double metal sheets between double halogen sheets (Cl–Zr–Zr–Cl, ccp)	3 Zr at 3.087 (5) Å, 6 Zr at 3.423 (1) Å,[b] 3 Cl at 2.629 (6) Å	0.82	4
$ZrCl_2$	d^2	3R-NbS_2	infinite single metal sheets, sequenced Cl–Zr–Cl	6 Zr at 3.3819 (3) Å, 6 Cl at 2.600 (4) Å (D_{3h})	0.51	10, 11
Zr_6Cl_{12}	d^2	Zr_6I_{12}	isolated metal octahedra edge-bridged by halide	2 Zr at 3.178 (1) Å,[c] 2 Zr at 3.224 (1) Å, 4 Cl at 2.54–2.57 Å, 1 Cl at 2.77 Å	0.68	6, 12
$ZrCl_3$	d^1	β-$TiCl_3$	infinite chains perpendicular to hcp chloride layers	2 Zr at 3.0670 (3) Å, 6 Cl at 2.54 Å (D_{3d})	1.13	13, 14

[a] $d(1) = 2.919$ Å. [b] Within the metal layers. [c] Based on the closely related $Zr_6Cl_{12}\cdot K_2ZrCl_6$.[10]

to each metal along the chains in the semiconducting $ZrCl_3$. These distances compare with an average of 3.21 Å in the 12-coordinate metal and 2.92 Å for the "single bond" distance.[15] Matrix effects—separations dictated or limited by chloride–chloride interactions—are doubtlessly present in all three structures, particularly in the repeat distances within the sheets in both ZrCl and $ZrCl_2$ and along the chains of confacial octahedra in $ZrCl_3$. The increased proportion of halide to metal accompanying oxidation naturally accentuates anion–anion effects, making the particular choice for the $ZrCl_3$ structure even more remarkable. Even so, the chains of face-shared $ZrCl_{6/2}$ groups (D_{3d}) are actually *elongated* along the chain rather than compressed, as revealed either by Cl–Cl distances of 3.53 Å in the shared face compared with 3.68 Å along the chain or by a Cl–Zr–Cl angle along the chain of 92°.[22] As also independently noted by Clemmer,[21] this elongation requires revision of the prediction of a half-filled "d_{z^2}" metal band along the chain[13] since it places e_g ($d_{x^2-y^2}$, d_{xy}) lower in energy, putting the one valence electron more or less localized in an orbital perpendicular to the chain, the antithesis of the effect promised by the 3.07-Å Zr–Zr distances. Evidently any d_{z^2} band must be relatively narrow so it does not overlap these localized levels, probably with relatively little mixing with chlorine 3p.[23]

Indeed it is a bit of a puzzle why $ZrCl_3$ should choose to adopt this particular structure in the first place rather than that of $CrCl_3$ (YCl_3) where the d^1 ions would occur in pairs with an ideal separation of about 3.4 Å (d_{Cl-Cl}). The octahedra there would likely be elongated along the $\bar{3}$ axis as well, again placing the odd electron in orbitals directed between the sheets. The β-$TiCl_3$ structure type appears to represent a means of *avoiding* metal–metal interactions and still gaining crystal field stabilization energy. Either spin–orbit coupling or a local distortion would remove the ideal degeneracy of the half-filled e_g level. Similar effects may also be demonstrated by $CsScCl_3$ (d_{Sc-Sc} = 3.02 Å)[24] where a similar distortion of chains of face-sharing octahedra is a logical consequence of the structure type.

A simple means of summarizing and comparing diverse metal–metal distances and possible bonding in different phases is through the Pauling bond orders when these are summed over all metal–metal distances and divided by the number of electrons available, thus utilizing the metal itself as a calibration.[25] The resultant value of 0.82 for ZrCl (Table I) is reasonable comparable with that in the metal itself (1.0) and presumably represents something of the similar degree of metal–metal bonding possible between the metal sheets within which the period is limited by chloride packing. Lower values of this quantity, especially in the layered dichloride, presumably arise from substantial matrix effects, though the valence bands observed and the configuration of the Zr_6X_{12} cluster make it clear that metal–metal bonding occurs with this oxidation state. On the other hand, the bond order sum of 1.13 for $ZrCl_3$ based on the metal reference suggests strong bonding, contrary to fact, and illustrates the hazards of inferring metal–metal bonding from distances alone. The procedure ignores two factors: (1) the radial part of the 4d function (for the free ion) must shrink appreciably during oxidation as the interelectron Coulomb repulsions between the 4d electrons diminish, and (2) this orbital shrinkage will be exacerbated by loss of screening which is provided by s and p contributions to metal bands of the sort which are evident in ZrCl and $ZrCl_2$. The sharp increase in the binding energy of the zirconium 3d levels found on transition from $ZrCl_2$ to $ZrCl_3$[11] presumably also reflects loss of screening and a collective behavior, and an increased zirconium–chlorine covalency in $ZrCl_3$ does not appear sufficient to counteract this. Notwithstanding, the Pauling bond-order comparisons do give some remarkable correlations when oxidation states and matrix effects are low.[25]

Acknowledgment. The authors are indebted to Drs. Hideo Imoto, Alan Cisar, and Richard Daake for the preparation of the chlorides studied and to Dr. Thuy Nguyen for the XPS data for the metal. Professor B. N. Harmon made some pertinent and helpful observations regarding some of the principles. The instrument on which the spectra were measured was made available by a grant from the National Science Foundation to the Department of Chemistry, Iowa State University.

Registry No. $ZrCl_3$, 10241-03-9; $ZrCl_2$, 13762-26-0; ZrCl, 14989-34-5; Zr, 7440-67-7.

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(23) Local distortions, pairing, ordering, etc. in $ZrCl_3$ on a scale which would give rise only to diffuse X-ray scattering could also be responsible for some of the observed properties. A superstructure has been found for β-TiI_3 (Schnering, H.-G. *Naturwissenschaften* **1966**, *53*, 359) and diffuse scattering has been seen in other halides with the same structure but with more valence electrons (von Schnering, H.-G., private communication, 1979). However, $ZrCl_3$ and $ZrBr_3$ do not seem to show evidence for similar defects by high-resolution (Guinier) powder diffraction, although a weak and very broad band for the forbidden 001 reflection (removing the restriction of equal spaced metal atoms) is seen in substoichiometric trichloride ($ZrCl_{2.94}$) only.[14]

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