the intersystem crossing in solids to explore the relationship of Γ in (1) to the distribution of individual crystallite (or domain) size.[15]

Summary

A treatment of the thermodynamics of the intersystem crossing from the postulation of intermolecular enthalpies and entropies of interaction provides a basis for the definition of a cooperativity factor, $C = \Gamma_c/2RT_c$, and for the effects of lattice continuity (1) on transition completeness, (2) on T_c, and (3) on the sharpness of the intersystem crossing transition. The visually immediate diagnostics of "cooperativity", curve shape and position, are very sensitive functions of ΔH, ΔS, and Γ, and it is through the former that lattice continuity effects operate. The analytical expressions of these effects have yet to be subjected to quantitative experimental test but are of the correct qualitative form.

By investigating in detail the thermally induced intersystem crossing transitions in the $Fe(phen)_2(NCE)_2$ series with E = S, Se, BH_3, we have determined that comparable intermolecular interactions and lattice phonon contributions to the transitions are exhibited by all three compounds. The pronounced differences in cooperativities appear to be determined by the singlet/quintet energy gaps. For the BH_3 member, indications are that the intersystem crossing is effected on an individual molecule basis, in sharp contrast to the case for its S and Se analogues.

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Registry No. *cis*-$Fe(phen)_2(NCBH_3)_2$, 62561-27-7; *cis*-$Fe(phen)_2(NCBPh_3)_2$, 68581-81-7; *cis*-$Fe(phen)_2(NCS)_2$, 15319-93-4; *cis*-$Fe(phen)_2(NCSe)_2$, 53447-28-2.

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Core Photoelectron Emission Study of Binary and Ternary Indium Chlorides. Metal Binding Energy as a Function of Oxidation State and Other Parameters

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Binding energies for indium d and chlorine p core and valence levels are reported for $InCl_n$ (n = 1, 1.5, 1.8, 2, 3), $Cs_3In_2Cl_9$, PCl_4InCl_4, $Rb_2LiInCl_6$, $Cs_2InInCl_6$, and InY_2Cl_7. Data secured by using a C 1s calibrant from either the mounting tape or admixed graphite are consistent for the reduced phases but show variations of 1.5 eV in In 3d binding energy for $InCl_3$ and a 1.1-eV range among the indium(III) compounds mounted on tape. The spectra contain no evidence for the presence of mixed oxidation states, in spite of an apparent 2–3-eV increase in In binding energy within the binary chlorides. Differential charging of insulating phases with respect to tape or graphite standards (e.g., $InCl_3$ and $Cs_3In_2Cl_9$) together with unpredictable variations of the fundamental Fermi level reference appear responsible for most of the observed shifts and probably affect many other data in the literature. Some inferred Fermi level changes correlate well with differences in valence-band spectra, color, coordination number, and distances about indium(I), e.g., for InCl vs. InY_2Cl_7. The internally referenced binding energy In $3d_{5/2}$ − Cl $2p_{3/2}$ is essentially invariant (±0.3 eV) for all compounds studied, and similar results are obtained with published data for indium and antimony halides. This invariancy with oxidation state and the contrasting increases in metal binding energies in simple transition-metal systems appear to reflect the effect of both radius and Fermi level changes. In particular, a significantly greater decrease in metal radius on oxidation in some posttransition $d^{10}s^2/d^{10}$ systems is probably important in counteracting the expected increase in binding energy in most cases. Some instances of negative binding energy shifts on oxidation of s^1 or s^2 metals are also considered.

Introduction

The utility of core photoelectron spectroscopy[3-5] with X-ray excitation (XPS) in the characterization of inorganic compounds shows a marked dependence on both the state of the material and the nature of the element examined. The light and small non-metals with sizable ranges of oxidation states and inductive (polarization) effects in their compounds exhibit therewith relatively large chemical shifts. Furthermore, binding energies in individual compounds can often be measured particularly well in the gas phase where intermolecular effects are absent and referencing to the vacuum level is straightforward. Shifts in measured binding energies of core electrons then reflect changes in valence orbital and charge distributions, and significant correlations with other parameters or theory may be possible. Electronic relaxation elsewhere in the molecule in response to the creation of the core hole, reducing the ionization energy below that for the vertical process, may not be an important factor in many comparisons although it is still apt to be significant in an absolute sense.

On the other hand, metal ions are characteristically larger, and their core binding energies generally shift more slowly with charge or oxidation state. Moreover, the study of metal compounds often requires that the measurements be made on solids, and then additional factors must be recognized. The

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(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

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relaxation process may be quite a bit larger in the extended solid state, especially in metallic or otherwise delocalized systems. There may be a greater contribution and a complication from the electrostatic potential of the neighboring anions (and the whole lattice) about the point of ionization, from both the greater polarity and higher coordination numbers in solid compounds of the metals, or if we are considering a binding energy shift, appreciable changes in these potentials accompanying changes in oxidation state or structure or both. Equally or more important are new experimental problems associated with nonmetallic solids, the effective reference point of the observed binding energies and the calibration. Binding energies in solids are normally referenced to the Fermi level; for an insulator this is intrinsically located in the center of the band gap, but what in a chemical sense would be only traces of impurities may pin it elsewhere. And the calibration may be particularly vexing with an insulator since the photoionization event will probably generate a difference in charge between the sample and a macroscopic calibrant, and this will be accompanied by an unpredictable and perhaps unrecognized change in the apparent binding energy. These factors will be especially important in the present investigation where a series of compounds is of interest.

The prospect of distinguishing between oxidation states of metals in solid compounds by XPS means has been an important consideration for many years. The results have not been uniformly encouraging, even when the foregoing problems have evidently been surmounted. Several studies of a variety of coordination compounds, mainly of transition elements, led to the conclusion that core shifts associated with oxidation-state changes may be comparable to effects originating from electronic changes in the ligands and that trends may be discerned only in carefully selected series of closely allied compounds.[6-8] Measurements on such series of phosphine complexes of rhenium, osmium,[6] and platinum[9,10] and on gold ylides[11] have in fact revealed regular increases in metal binding energy on oxidation, ~1 eV per unit increase. A particularly simple view of the oxidation-state dependence of the core binding energy of a transition metal may be achieved from a series of binary compounds with a common anion, but the amount of available data is small and the results do not always show the expected parallel with oxidation state.[12,13] The most extensive set of data of this sort are for the series $ZrCl_n$ ($n = 0$–4), where there is a 4.3-eV increase in the Zr 3d levels over the series (relative to E_F).[14,15] The study of such a series is aided considerably by the metallic or at least high intrinsic conductivity of the compounds (except for $ZrCl_4$) so that charging does not occur and ready referencing to a pinned Fermi level is apparently achieved.

The observation of two oxidation states within a single mixed-valence phase is conceptually an even simpler problem, provided of course that the states involved show a sufficiently large difference. Obviously the prospects for resolution of two states are low when different oxidation states reside in crystallographically very similar sites, as in $Fe_{1-x}O$ and Fe_3O_4, where no evidence of mixed states has been seen. (Remember that even with care line widths are usually greater than 1 eV or more, largely because of the intrinsic breadth of the X-ray excitation.) At the other extreme, compounds containing two oxidation states in markedly different environments should present a much better opportunity for resolution. Still the number of successes is small, and these are usually associated with quite large differences in environments, e.g., $KCr^{III}(Cr^{VI}O_4)_2$[16] and $(Pt^{II}(NH_3)_4)(Pt^{IV}Cl_6)$.[17] (Final-state efforts may be misleading.[17])

The post transition metals with their well-known pairs of oxidation states based on ions with d^{10} and $d^{10}s^2$ configurations provide a large number of what would seem to be excellent prospects for separation of oxidation states of XPS means, but positive results are still scarce and only one clear resolution is known, $Cs_4(Sb^{III}Cl_6)(Sb^{V}Cl_6)$,[18] plus a few other cases showing a suggestive line broadening.[19] However, partial decomposition of a compound containing the higher valent (d^{10}) state by the X-ray beam may be a problem since these states are often relatively good oxidizing agents with low thermal or radiation stability. Thus, it has been suggested[17] that the absence of resolution with other good prospects, e.g., Sb_2O_4[19] and Pb_3O_4,[20] may have resulted because the irradiated surface had decomposed and contained only the lower oxidation state.

A similar study of chlorides in the indium(I, III) system appeared particularly attractive to us because of the substantially greater thermal stability associated with the higher oxidation state. Furthermore, the structures of several mixed-valent chlorides of indium have recently been elucidated as well as for some ternary inorganic derivatives,[21-26] the collection thus allowing the sampling of a range of oxidation states within a similar stoichiometry or structure, e.g., $Rb_2LiInCl_6$, $Cs_2In^{I}In^{III}Cl_6$, and $In^{I}{}_3In^{III}Cl_6$ in one case and the isostructural $Cs_3In^{III}{}_2Cl_9$ vs. $In^{I}{}_3In^{III}Cl_9$ in another. An earlier report of 3d binding energies for InX, InX_2, and InX_3 (X = Cl, Br, I) as well as for a number of quaternary ammonium salts of haloindium anions by Freeland, Habeeb, and Tuck[27] indicated shifts of about 1 eV between InX and InX_3, although McGuire et al.[28] had previously reported a binding energy shift twice as large among the chlorides, a more encouraging difference for the resolution of mixed-valent phases. However, some reinvestigation appeared in order as appreciable irregularities appear within the data from the former investigation, for example, $(Et_4N)InX_2$ phases (X = Br, I) with reported metal binding energies greater than those for all of the indium(III) compounds studied. Our original intent was also to study the valence XPS spectra of the reduced compounds as these can provide valuable information on the bonding in the form of a combination of the density of state and ionization cross-section functions. However, XPS data for the valence

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Table I. Core Binding Energies in Some Binary and Ternary Indium Chlorides (eV)[a]

compd	In $3d_{5/2}$	Cl $2p_{3/2}$	In 4d[b]	Cl $3p_{3/2}$
	Tape Standard[c]			
$InCl_3$	447.1 (1.4[d])	200.0	20.0	5.5
$(PCl_4)InCl_4$	446.8 (1.5[d])	199.8[e]	19.7	5.1
$Cs_3In_2Cl_9$	446.6 (1.7)	199.4	19.4	4.8
$Rb_2LiInCl_6$	446.0 (1.5)	198.8	19.4	4.4
$Cs_2InInCl_6$	446.0 (1.7)	199.1	18.8	4.6
$InCl_2$[f]	446.6 (2.0[d])	200.0	19.6	5.6
	446.8 (2.2)[g]	200.0		
In_5Cl_9	446.5 (1.7)	199.4	19.3	5.1
In_2Cl_3	445.6 (1.4)	198.8	18.8	4.9
InCl	445.3 (1.6)	198.3	18.4	$5._1$
InY_2Cl_7	446.2 (1.8)	199.4	18.9[d]	5.7
	446.3 (1.9)[g]	199.6		
	Graphite Standard[h]			
$InCl_3$[i]	448.6 (1.8)	201.5	21.8	7.5
	448.0	201.0		
	447.4	200.5		
$InCl_2$[e]	446.7 (2.2[d])	200.0	20.0	$6._0$
In_2Cl_3	445.6 (1.5)	198.3	18.2	$4._6$
InCl	445.0 (1.6)	198.1	18.4	...
In	443.9 (2.1)	...	17.2	...

[a] Some of the data for the indium(III) compounds are probably affected by charging; see text. [b] Maximum of unresolved doublet. [c] C 1s = 285.0 eV. [d] Minimum slit widths. [e] fwhm(Cl 2p) = 3.4 eV, compared with 2.7–3.1 eV for the remainder. [f] Sample consists of In_5Cl_9 and $InCl_3$. [g] Flood gun. [h] C 1s = 284.3 eV. [i] Listed in order of decreasing graphite content, C 1s:Cl 2s = 1.22:0.85:0.34 (the calculated cross-section ratio is 0.59: Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* 1976, *8*, 129).

regions of the indium monohalides were reported by Porte[29] after the present investigation was well under way, and so this aspect will not be emphasized.

Experimental Section

The compounds studied were all synthesized and characterized as described elsewhere.[21-26,30] The classical composition $InCl_2$ was also included for comparison with other works; this is now known to consist of $InCl_{1.8}$ ($In^I_3In^{III}_2Cl_9$) and $InCl_3$ in a 5:1 molar proportion.[25] The photoelectron emission spectra were obtained with the aid of Al Kα radiation and an AEI Model ES200B instrument coupled to a Nicolet 1180 minicomputer for data averaging. Generally 20–500 scans were made, utilizing 512 channels. Sealed containers of the compounds were opened only within the helium-filled drybox attached directly to the sample chamber of the spectrometer and maintained at <1 ppm of O_2 and <0.5 ppm of H_2O. Oxygen impurities as indicated by the O 1s line were very small throughout. Our experiences have shown that data pertinent to the bulk phase rather than surface impurities may be consistently obtained under these circumstances.[14,15,31,32]

Because of the obvious interference from an indium metal substrate, most samples were dusted and pressed onto a piece of double-sided cellophane tape (3M) mounted on the sample holder. Calibration of these was usually provided by the C 1s line that originates from the tape backing (plus adventitous carbon) and that has been measured in our laboratories as 285.0 eV relative to Au 4f. In other series of measurements, certain compounds were first ground with 20–60% graphite before being mounted in a like manner; in these cases the C 1s binding energy in graphite was taken to be 284.3 eV.[33] Vaporization of a thin layer of gold onto samples for calibration was not possible with this instrument for such low melting samples. The compound InY_2Cl_7 was observed to turn light tan after extensive radiation exposure, although no change in its core spectra was evident.

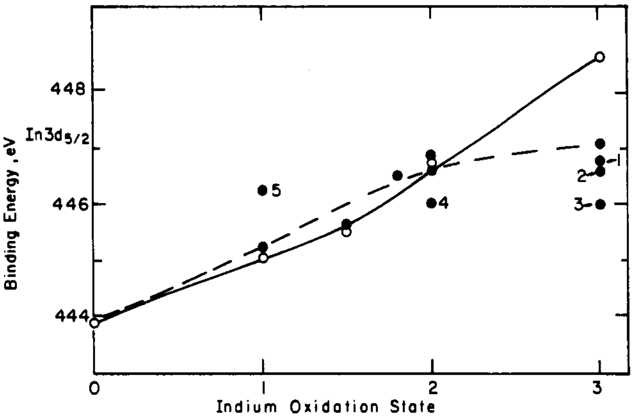

Figure 1. Binding energies of the In $3d_{5/2}$ core levels in indium chlorides as a function of oxidation state: ●, relative to C 1s in the mounting tape; ○, relative to C 1s in admixed graphite. Unlabeled points are for the binary chlorides: 1, $(PCl_4)InCl_4$; 2, $Cs_3In_2Cl_9$; 3, $Rb_2LiInCl_6$; 4, $Cs_2InInCl_6$; 5, InY_2Cl_7.

Some exploratory measurements of valence (XPS) spectra were made with minimum slits but without a monochromater because of the relative weakness of the emissions. This procedure leads to weak $K\alpha_3$ and $K\alpha_4$ shadows of the strong In 4d emission at −9.8 and −11.8 eV, that is, on the high-binding-energy side of Cl $3p_{3/2}$. These were subtracted when necessary. Correction of peak positions because of overlap was generally not pursued.

Results and Discussion

Binding energies for indium $3d_{5/2}$ and chlorine $2p_{3/2}$ core levels in the metal and the 10 chlorides studied as well as those for some of the In 4d and Cl 3p valence levels are listed in Table I where they are separated according to whether the standard was the backing cellophane tape or the admixed graphite. No split peaks that could be associated with distinguishable indium(I) and -(III) states were detected in the mixed-valent phases, and only the $InCl_2$ composition gave slightly broadened peaks (from ~1.5 to 2.1 eV fwhm). There was also no evidence for indium satellite peaks or skewing associated with attainment of other electronic states (shake-up processes) or relaxation in the ionized product state. This is probably normal for materials that would be classified either as moderate to large band gap semiconductors or as insulators with localized ground states, properties that are for the main part quite typical of halides, oxides, etc., of the post transition elements. All are colorless except for the yellow (α) monochloride and the very light yellow $CsIn_2InCl_6$.

The apparent indium $3d_{5/2}$ binding energies for these phases are plotted in Figure 1, with filled and open circles denoting calibration with cellophane tape and graphite, respectively. Somewhat fanciful curves describing just the binary chloride data have been fitted to each set. Both groups apparently show the classical increase in binding energy with an increase in oxidation state, and either one alone might be considered as acceptable and reasonable. However, the difference between the binary indium(I) and indium(III) chlorides implied by the end members in either set does not seem consistent with the lack of resolution or even a suggestion of two structurally distinctive oxidation states in the three mixed-valent phases. Factors other than an oxidation state dependence must then be responsible for the trend seen. In addition, although the results from the two methods show acceptable agreement for the low and intermediate chlorides (supporting the consistency of the two standards employed), a serious problem remains with differences of up to 1.5 eV obtained for the metal binding energy in $InCl_3$. In fact, results with mixtures of $InCl_3$ and a graphite calibrant were dependent on the relative amounts used (Table I and later discussion; only the largest value is shown in the figure). There is also a 1.1-eV range in metal

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binding energies amoung the indium(III) phases on tape and a surprising 1.0-eV difference between the results for InCl and InY_2Cl_7, not uncommon observations for which a popular rationalization has been individual differences in lattice potentials at indium.

Charging and Referencing Problems. In fact, two more fundamental problems associated with these measurements must be considered, charging and the question of the Fermi level reference.[33,34] We will return to the question of lattice potentials later on. Crystallites of a more-or-less insulating phase are apt to acquire some steady-state charge during the photoemission process relative to a similarly macrosized standard in contact with then at only a few points. It is conduction through the insulating sample not the calibrant (i.e., graphite or a metal substrate) that particularly matters. Were this to be general, the character of the trend with oxidation state of the halides seen in Figure 1 could be imagined to represent to some degree the steady-state potential differences acquired by the compounds relative to the standards inasmuch as band gaps and resistivities of such a series would reasonably be expected to increase with oxidation states as well, and increased positive charging relative to the standard gives a higher apparent binding energy. The greater differential charging implied by the higher binding energy found with $InCl_3$ and graphite is reasonable since the smaller band gap in this standard means the loss of fewer low-energy secondary electrons and thus less charging.

Although the inevitable adventitious carbon in equilibrium with the surface of the emitting indium compounds would possibly make a better standard, its emission will be admixed with that from the tape backing because of unavoidable gaps in the coverage, and these will appear at different energies if significant charging occurs. (Peak heights of C 1s signals from samples on tape were observed to be 30–80% of the adjoining Cl 2s emission, depending on how the sample was applied, or typically 15–50% of the relative emission obtained with admixed graphite.) It should be noted that sample peak broadening, which has sometimes been taken to be diagnostic of charging, was not observed except perhaps with the two-phase composition $InCl_2$. Although measurements relative to a thin layer of a standard such as gold[33] deposited directly on the sample surface should eliminate any errors in binding energies originating from charging, standardization of binding energy measurements on insulators via carbon in the mounting tape or by core emission from some admixed phase is much more common in the literature. In any case, the fundamental problem of the Fermi level reference energy and its unpredictable change from one phase to the next still remains.

The existence of charging in some of these systems was subsequently confirmed by the application of a flood of electrons to irradiated samples. This increased the relative kinetic energy of the sample emissions by 0.7 and 0.3 eV for $InCl_3$ and $Cs_3In_2Cl_9$, respectively, both with graphite, while neither the flood gun nor changes in X-ray tube power had any effect on the results for $InCl_2$ or InY_2Cl_7 on tape. In addition, $InCl_3$ mixed with Pt black and mounted on tape yielded an apparent indium binding energy that was 0.8 eV lower when calibrated with Pt $4f_{7/2}$ emission (71.0 eV[33]) than the usual value obtained from carbon in the backing, the former evidently exhibiting less charging relative to $InCl_3$. The presence of a charging problem but only with the indium(III) compounds was also indicated by the carbon 1s spectra found with samples on tape. All of these were asymmetric to the low binding energy side, often with a discernible shoulder (one $PCl_4(InCl_4)$ sample exhibited a double peak, $\Delta = 0.8$ eV). The tape emission could be the source of the latter feature since the backing might be expected to suffer from lower charging. Samples mixed with small amounts of graphite exhibited a clear shoulder on the lower energy side, presumably from lower charging of the graphite or tape, while the C 1s peak developed a pronounced high-energy asymmetry at high loading, this presumably now representing the signal from adventitious carbon that, of course, overlays both the sample and the graphite.

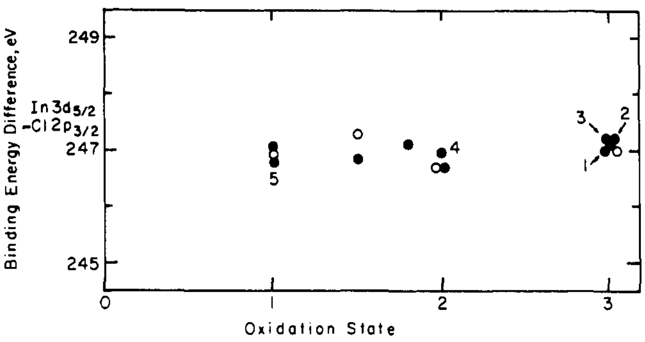

Figure 2. The In $3d_{5/2}$ quantity internally referenced to the Cl $2p_{3/2}$ core binding energy as a function of oxidation state. The identification of the compounds and the energy scale are the same as in Figure 1.

A solution to the problems both of charging and of a meaningful reference for the data that also provides some striking evidence regarding the source of the differences in Figure 1 comes from the observation that the indium and chlorine binding energies move essentially in parallel across the entire series and that their differences exhibit considerably greater consistency among related compounds, say all of the indium(III) phases. Thus, a much simplified view of the system is obtained when chlorine is used as a common *internal* reference, eliminating both the need to have a standard in equilibrium with each sample and obvious uncertainties about variations in the position of E_F. Figure 2 shows these In $3d_{5/2}$ – Cl $2p_{3/2}$ binding energy differences plotted on the same ordinate scale as before. All values are now the same within ±0.3 eV, and the apparent range among the indium(III) compounds on tape has been reduced to about 20% of that seen before, basically the experimental uncertainties. Certainly there is now no significant evidence for a dependence on oxidation state, supporting the experimental inseparability of indium(I) and indium(III) states by XPS core shifts. The indium Auger data give the same result.[35]

Fermi Levels and Structure. Although charging seems to have been of some importance with the indium(III) compounds, the elimination of its effect is certainly not responsible for much of the smoothing accomplished by the use of a chlorine internal standard. Furthermore, it is certainly difficult to imagine how lattice potential variations could produce the differences between Figures 1 and 2 since these are expected to affect indium and chlorine in opposite directions.[34] Instead, an attractive explanation for the behavior seen in Figure 1 relative to that in Figure 2 is in terms of differences in the intrinsic or extrinsic Fermi levels to which the measured binding energies are referenced.

A general increase in E_F with oxidation state would be expected, following a parallel increase in band gap. But more

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Table II. Structures and Coordination Characteristics of Indium in the Chlorides Studied

			chlorine polyhedra				
			In^{I}		In^{III}		
compd	$\text{In}^{\text{I}}:\text{In}^{\text{III}}$	struct type	coord no.	*d*/Å	coord no.	*d*/Å	ref
InCl_3	0:100	YCl_3			6	~2.50[a]	37
$\text{PCl}_4\text{InCl}_4$ (1)	0:100	unknown			4[b]	~2.35[b]	30
$\text{Cs}_3\text{In}_2\text{Cl}_9$ (2)	0:100	$\text{Cs}_3\text{Tl}_2\text{Cl}_9$			6	2.42, 2.65/2.53[c]	21
$\text{Rb}_2\text{LiInCl}_6$ (3)	0:100	K_2NaAlF_6			6	~2.49[d]	22
$\text{Cs}_2\text{InInCl}_6$ (4)	50:50	K_2NaAlF_6[e]	6	~2.92[f]	6	~2.53[f]	23
$\text{In}_3\text{In}_2\text{Cl}_9$	60:40	$\text{Cs}_3\text{Tl}_2\text{Cl}_9$	12	3.48-3.70/3.59[c]	6	2.46, 2.62/2.54	25
In_3InCl_6	75:25	α-Tl_2Cl_3	7	3.08-3.70/3.29	6	2.45-2.57/2.51	24
			8 (2×)	3.11-3.85/3.36			
			9	3.15-3.75/3.37			
			10	3.12-3.97/3.48			
			11	3.35-4.08/3.59			
InY_2Cl_7 (5)	100:0	DyY_2Cl_7[g]	10	3.36-3.66/3.50[h]			26
InCl (α)	100:0	NaCl[i]	6	2.90-3.56/3.22			38

[a] Estimated with atom parameters of YCl_3. [b] Based on unpublished vibrational spectra and the data for *n*-$\text{Bu}_4\text{NInCl}_4$ (Khan, M. A.; Tuck, D. G. *Acta Crystallogr., Sect. B* **1982,** *B38,* 803). [c] Average value. [d] For *x*(Cl) = 0.245. [e] Above 188 °C, with tetragonal and orthorhombic structures arising at lower temperature from octahedral tilting.[23] [f] Estimated for the cubic parent structure. [g] Meyer, G. *Z. Anorg. Allg. Chem.* **1982,** *491,* 217. [h] 3.59 Å when two more neighbors at 4.04 Å are included. [i] Severely deformed.

convincing evidence can be found in a correlation of some of the larger binding energy differences in Figure 1 with structure and valence spectra and what these mean as far as the placement of E_F. The structures of the phases studied are summarized in Table II. The most striking comparison is found between the two indium(I) compounds InCl and InY_2Cl_7 for which charging is not important and the monochloride exhibits a In $3d_{5/2}$ binding energy 1.0 eV smaller. The monochloride has a severely deformed version of the rock salt structure, with the metal displaced from the center of the nominal chlorine octahedron to give In–Cl distances that fall mainly in two groups, 2.90–2.96 Å and 3.42–3.56 Å, with an average of 3.22 Å. In contrast, the structure of the colorless InY_2Cl_7 is dominated by Y_2Cl_7 sheets, and indium(I) occurs in larger cavities with 10 chlorine neighbors between 3.36 and 3.66 Å at an average distance of 3.50 Å. Since there is no real difference between these two phases in relative core binding energies (Figure 2), the potential terms for the two elements are presumably structurally invariant, perhaps those for indium being compensated by greater covalency associated with the lower coordination numbers. On the other hand, the yellow color of InCl necessarily means a smaller band gap. The highest valence level of all of these compounds is more or less fixed in the neighborhood of chlorine $3p_{3/2}$ ~ indium $4s^2$, and the lower observed binding energy for InCl must mean the conduction band and hence E_F have come down (presuming the behavior is still instrinsic). Further evidence regarding this differentiation between InCl and InY_2Cl_7 will be described shortly in connection with their valence spectra, where the bonding in InCl also results in clear changes in the nominal chlorine 3p bands. Thus, a smaller coordination number and accompanying stronger In–Cl interactions in InCl are mainly associated with changes in the neighborhood of the gap and in the Fermi level, not in relative core levels. The sesquichloride, which has a binding energy similar to that for InCl (Figure 1), appears to have a similar bonding. In this case there are five different indium(I) atoms, but the one with the strongest interactions, seven chlorine neighbors at distances averaging 3.29 Å, should logically generate the highest valence band and predominate in fixing the position of E_F.

The pair $\text{In}_3\text{In}_2\text{Cl}_9$ and $\text{Cs}_2\text{InInCl}_6$ appear analogous to InCl and InY_2Cl_7 as regards the indium(I) environments. Here, it is now the ternary compound that contains the smaller coordination polyhedra, which for the high-temperature structure is a regular trigonal antiprism with In^{I}–Cl distances estimated to be around 2.92 Å, whereas In_5Cl_9 has one type of 12-coordinate indium(I) with much longer distances that average 3.59 Å. Again, $\text{CsIn}_2\text{InCl}_6$ has the short distances, a very light lemon yellow color and a binding energy 0.5 eV lower (Figure 1), likewise indicating a somewhat lower E_F.

A similar consideration of indium(III) compounds is precluded by uncertainties in charging. The range of binding energy differences among these in Figure 2 is sufficiently small that it is not at all clear that there are any significant variations in local lattice potentials. However, we shall see later that lattice potential effects do appear to be important in the lack of any resolution of two indium oxidation states in the mixed phases.

Valence Spectra. The XPS spectra for the valence region of some phases containing indium(I) seem strange at first sight since there are three peaks, all intrinsic to the sample, in the region of 2–7 eV below E_F in addition to the expected In 4d pair near 19 eV. These have been measured and discussed by Porte for the three indium monochlorides,[29] and the details will not be repeated here. Briefly, the three nearly degenerate bands normally contributing to the chlorine 3p peak near 5 eV are split by covalent interactions with indium 4s through mixing with In 4p, basically of a σ type, to give an indium 4s (+In 4p, Cl 3p) band at slightly higher binding energy (with increased cross section relative to In $4s^2$) and a filled chlorine 3p (+In 4s, 4p) band closer to the E_F. The latter is particularly clear in our measurements. For In_2Cl_3 we find the two new emissions at ~6.6 and 3.2 eV bracketing the larger remaining chlorine 3p peak at 4.9 eV. Neither these nor the chlorine core peaks appear significantly broadened in spite of the wide range of chlorine environments about different indium(I) atoms in the structure,[24] but this is usual.[20,39] The principal difference on going to InCl that accompanies the onset of a visible color is the shift of the least-bound XPS peak by about 0.7 eV toward E_F relative to that in In_2Cl_3; the same is particularly well resolved in the He I spectrum at ~3.4 eV.

The correlations found in differences between InY_2Cl_7 and InCl in binding energies (Figure 1), structures (Table II), and colors together with the implication of a drop of E_F are nicely consistent with differences observed in the valence spectra. The larger and less asymmetric chlorine polyhedron about indium(I) in InY_2Cl_7 produces *no* visible splitting of the chlorine 3p band but rather only a slight broadening (fwhm = 3.5 eV, 10–15% greater than normal). (There is of course a substantial increase in Cl:In, too.) The reduced and asymmetric bond distances, lower binding energy, and color in InCl are all

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(39) Tricker, M. J. *Inorg. Chem.* **1974,** *13,* 742.

associated with narrowing of the band gap. This change also gives rise to a clearly visible valence band displaced to lower binding energies, although on balance there must be a net downward motion of the conduction band and E_F as the valence band remains pinned near chlorine 3p. In a similar manner, lower binding energies may also be associated with decreased distances in $Cs_2In_2Cl_6$ vs. $In_3In_2Cl_9$ (vide supra) and, likewise, there is good evidence for the lower energy band in $Cs_2In_2Cl_6$ at 2.8–3.0 eV, while XPS data for In_5Cl_9 show only a hint of an inflection on the tail of the chlorine emission at ~3.4 eV.

These splittings offer dramatic proof of the noninertness of the $5s^2$ pair in these indium compounds and of the indium(I)–chlorine covalent interactions that are only suggested by the low-symmetry structures. Similar interactions are suggested by the XPS spectral and theoretical studies of the thallium monohalides.[40] A systematic high-resolution XPS and UPS study of the valence features of these and other compounds promises to be extremely useful and informative.

Literature Data. Unfortunately the methods utilized here for mounting and calibration of XPS measurements on more-or-less insulating crystallites have been widely used, sometimes with little consideration of differential charging relative to the standard and often with no thought as to the character of the reference level to which the measurements apply. Much of the "absolute" binding energy data published for insulating materials where a distinctive calibrant was not shown to be in equilibrium with the emitting surface appear to be of questionable usefulness. The proported use of adventitious carbon on the surface as a standard, which may in itself be satisfactory when the source is known and reproducible,[33] may be unreliable when the sample is mounted on cellophane tape since the latter can provide a substantial C 1s signal and may develop a significantly different charge than the surface of the sample exposed to the X-ray beam. Admixed standards generally should offer little improvement on studies of insulating phases, and the same obviously applies to dispersion of such samples on a metallic backing. The supposition that data free of charging effects are secured if samples are admixed with graphite until the apparent binding energies cease to increase[41] is in general unjustified and may even be seriously in error judging from the exactly opposite behavior of $InCl_3$ (Table I).

These are not entirely new concerns;[33,34] indeed the problem led one pair of reviewers[42] to describe charging as the bete noir of XPS. However, the unpredictable and probably irregular positioning of the Fermi reference may be every bit as serious, even for a common oxidation state within a structurally diverse series. The present results recall a little used but apparently effective means to avoid both standard and reference problems and to recover useful information, an internal reference of a common atom that is fairly inert chemically. Of course, we have no firm assurance that chlorine is precisely inert in the series studied here. However, binding energy differentiation of simple anions even in structures containing widely different types of those atoms is evidently not found.[20,39]

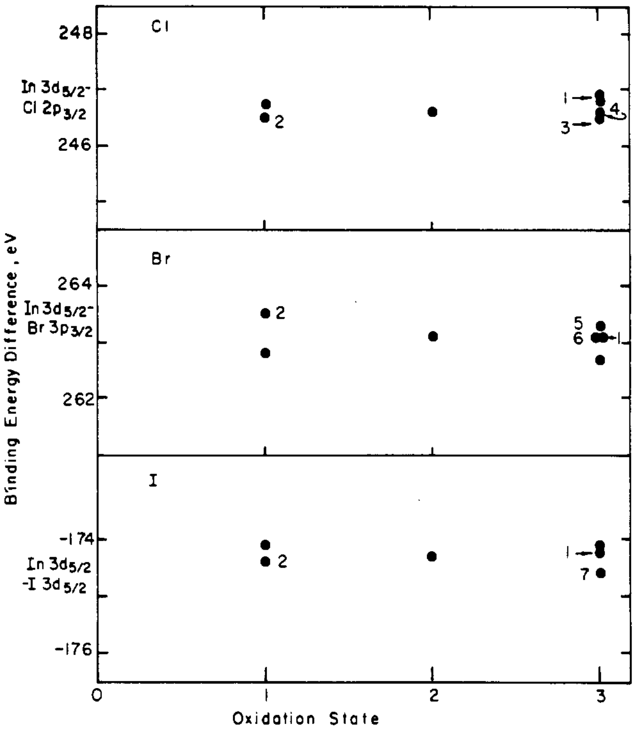

Figure 3. In $3d_{5/2}$ binding energies relative to those of the Cl $2p_{3/2}$, Br $3p_{3/2}$, or I $3d_{5/2}$ levels in binary halides (unlabeled): 1, (n-Pr_4N)InX_4; 2, (Et_4N)InX_2; 3, (Me_3NH)$_3InCl_6$; 4, (Et_4N)$InCl_4$; 5, (Me_4N)$_2InBr_5$, 6, (Me_4N)$InBr_4$; 7, (Me_2diphos)InI_3 (from ref 26). (The scale is the same as in previous figures.)

Some better understanding of earlier measurements of indium halides can now be obtained. The usual calibrant employed by Freeland et al.[27] was a core line from the platinum sheet on which the powdered samples were smeared, while the earlier study of McGuire and co-workers[28] employed the tape calibrant. The latter gave an In $3d_{5/2}$ binding energy in $InCl_3$ 1 eV higher and in agreement with our result. Both of these studies were undoubtedly troubled with both differential charging and irregularities in Fermi reference levels, so much so in the later study[27] that systematics are difficult to find over the wide range of compounds studied, which included a considerable number of quaternary ammonium haloindate salts. All of these results are again much more uniform and independent of oxidation state when the indium $3d_{5/2}$ binding energy is not considered absolute but rather relative to an internal reference, Cl $2p_{3/2}$, Br $3p_{3/2}$, or I $3d_{5/2}$ (as far as data for these were reported). Figure 3 shows these differences using the same ordinate scale as before. The use of such an internal reference decreases the range of reported shifts from 1.0 to 0.4 eV among all of the chlorides, from 1.1 to 0.7 eV for the bromides, and from 2.2 to 0.5 eV for the iodides, supporting the assessment. The near invariancy of the chloride values with oxidation state (±0.2 eV) is now even somewhat better than shown in Figure 2 and about 0.4 eV lower in magnitude, presumably because of instrumental differences.

The presence of similar troubles in other XPS studies on insulating phases is also suggested by the substantially reduced variations in reported binding energy shifts achieved when these can be referenced to some internal non-metal level. For example, a 4.8-eV range of antimony chemical shifts was found by Birchall and co-workers[19] among 31 diverse compounds, the solids again being mounted on tape and calibrated by C 1s, this signal possibly originating from the tape at least for the 50% of the phases that contained no bound carbon. In any case, a markedly lower range is found among subsets of these relative to a common non-metal; viz., a 2.90-eV range in antimony binding energies among seven chlorides falls to 0.8 eV with a chlorine reference and, likewise, there is a decrease from 4.2 eV to 1.5 eV among eight fluorides, six of which contained no carbon. (An irregularity is still found within this group for SbF_5 in graphite.) An the reported 1.4-eV difference between Hg $4f_{7/2}$ energies for $HgCl_2$ and Hg_2Cl_2[43] becomes only ~0.5 eV relative to internal chloride,

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(40) Porte, L. *J. Chem. Phys.* **1980**, *73*, 1104.
(41) Murtha, D. P.; Walton, R. A. *Inorg. Chem.* **1973**, *12*, 368.
(42) Hercules, D.; Carver, J. C. *Anal. Chem.* **1976**, *48*, 296R.
(43) Seals, R. D.; Alexander, R.; Taylor, L. T.; Dillard, J. G. *Inorg. Chem.* **1973**, *12*, 2485.

the sublimed or precipitated samples having been calibrated by underlying gold plate on the probe. On the other hand, some *transition*-metal systems so referenced do show appreciable changes on oxidation. Three studies that evidently employed good internal standards are those of platinum complexes (vs. carbon in PPh_3, Cl 2p, or K 2p)[9,10] and gold(I, II, III) (vs. bound carbon in the ylide).[11] Here regular *increases* in the metal binding energies of about 1.2 eV per oxidation state are observed within the ylide, $Pt-(PPh_3)_2PtCl_2-(PPh_3)_2PtCl_4$ and $Pt-K_2PtCl_4-K_2PtCl_6$ series (presuming the calibrations are correct). The contrast in the binding energy shift found between these and post-transition-metal systems in general will receive further consideration later.

In the very simplest view (and neglecting the reference problem), the binding energy of core levels in simple anions might be expected either to remain essentially constant while core binding energies for the metal increase with oxidation state or to increase slightly with increasing covalency. Of course, changes in the anion potential at the cation sites add a less obvious factor that tends to counter the trend on oxidation, and in actual fact the behavior of the effective Fermi level reference within a series of insulators is unclear. In any case, the anion change just described is sometimes found experimentally for conducting or semiconducting compounds of the transition elements,[15] but it is not universal. One instance in which contrary variations of both the cation and anion core levels on oxidation of an insulating compound are known is from the careful study by Thomas and Tricker[20] of the series PbO (two forms), Pb_3O_4, and PbO_2 in which evaporated gold was used for calibration to the Fermi level. The binding of the Pb 4f levels was actually found to *decrease* by ~1.5 eV relative to E_F on oxidation from PbO to PbO_2, substantially all in the first step, while the oxide changed in the same direction by ~1.0 eV. Thus, the binding energy of lead relative to oxygen really decreased but only by ~0.5 eV. When C 1s signals from the surface were used for calibration, the apparent shift of both the oxide levels and of the lead–oxygen difference on oxidation were greater but in the same direction, −2.3 and −1.7 eV, respectively. They also noted that in the ionic limit there was a factor of about 2 difference in the magnitude of the potential of the surrounding lattice about the lead ions that oppose (and evidently effectively cancels) the anticipated increase in metal binding energy on oxidation. The effect of lattice potentials has also been considered for mixed antimony systems.[19] In any case this leveling appears to be general in many $d^{10}/d^{10}s^2$ systems.

Binding Energies, Oxidation States, and Radii. The near invariancy of metal binding energies to oxidation state in the indium chlorides, in lead oxides, and by implication, for many other post transition elements is in considerable contrast with the significant changes in absolute or relative binding energies found in many transition-metal systems under similar circumstances. The notable changes in some platinum(0–IV) and gold(I–III) series were noted in the second paragraph above. Data for zirconium chlorides and some of their interstitial derivatives, which cover the oxidation state range of +1 to +4, are shown in Figure 4 as the Zr $3d_{5/2}$ − Cl $2p_{3/2}$ binding energy difference and with the same scales as before. (This behavior was not evident in the earlier presentation.[15]) The separate zirconium and chloride data[15] indicate that the binding energy differences for compounds with oxidation states +1 through +2 are displaced downward by ~1.2 eV in Figure 4, evidently because of additional electronic relaxation that occurs in the delocalized metal–metal-bonded system in response to the creation of a zirconium core hole. The Fermi levels for the lower states through $ZrCl_3$ are pinned within the 4d states, but it is naturally higher for $ZrCl_4$. The rate of increase of binding energy for the higher oxidation states, 2 eV/state, is striking relative to even that in the platinum and gold series and is again in great contrast to the behavior of indium and its neighbors.

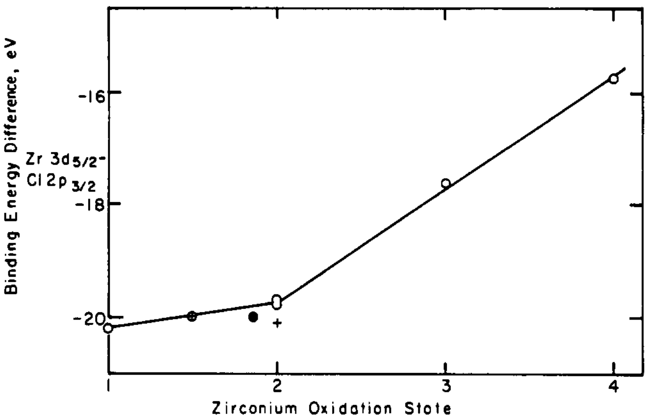

Figure 4. Binding energy difference Zr $3d_{5/2}$ − Cl $2p_{3/2}$ in solid zirconium halides as a function of oxidation state: ○, binary chlorides; +, $ZrClH_n$ ($n = 0.5, 1$); ●, $ZrClO_{0.43}$ (data from ref 15).

This distinction between transition and posttransition systems can apparently be traced back to marked contrasts in the fundamental rate of decrease of the metal radius (and coordination number) on oxidation of the two types of elements and the consequent contrast in the rate of change in lattice potential for the surrounding lattice (or covalency) that presumably accompanies this. For simplicity we will limit the consideration to the contribution of the nearest neighbors. In the structures of the compounds investigated here (Table II), all indium(III) atoms are six-coordinate in regular, distorted, or confacial chlorine octahedra (except for PCl_4InCl_4 of course) with average In–Cl distances of 2.49–2.54 Å. On the other hand the environment of indium(I) is usually much more distorted and variable. The structures exhibit the same or, more often, a higher effective coordination number about indium(I), viz., 6 in InCl and 7–12 in the remainder, though, as we have seen, this change has little to no effect on core binding energies. More striking are the much larger In–Cl distances that average from 3.22 Å (InCl) to nearly 3.60 Å in the remainder. At fixed CN6 the decrease in the average metal radius on oxidation is thus a remarkable 0.7 Å or 45% of that deduced for indium(I), 1.55 Å, according to the crystal radius of chloride. Shannon's[44] crystal radii (CN6) also contain differences of 0.62 Å for the Tl(I–III) pair and 0.41 Å for Pb(II–IV) based on crystal data for oxides, fluorides, etc. Clearly, the large increase in local site potential from the surrounding anions (or covalency) that would accompany such a large reduction in radius would be more effective in countering the expected increase in binding energy with oxidation, the (negative) potential at the ionized site being relatively low for the large indium(I) compared with that at indium(III). The large polarizability of the $5s^2$ core in indium(I)[45] should contribute in the same direction. On this basis, such post-transition-element pairs with ions based on $d^{10}s^2$ and d^{10} configurations justifiably provide particularly poor examples with which to demonstrate, or separate, chemical shifts as a function of oxidation state.

Whether separation of mixed oxidation states in antimony(III–V) systems can be regularly accomplished or whether it will be generally beset by the difficulties found for indium and lead components requires a more systematic study of diverse and preferably structurally known compounds. Success has been reported for $Cs_4Sb_2Cl_{12}$,[18] Sb_2O_4, and SbF_4,[19] the

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(44) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32A*, 751.

(45) Van der Vorst, C. P. J. M.; Maaskant, W. J. A. *J. Solid State Chem.* **1980**, *34*, 301.

latter two giving only significant line broadening, while exploratory measurements that led to negative results may not have been reported. One can imagine that two of the compounds showing positive results may represent structural extremes. Although the structure of the ternary chloride appears to be unknown in detail, the evidently isostructural $M^{I}_4Sb_2Br_{12}$ phases are slightly distorted versions of the K_2PtCl_6 type with a small differentiation between the $SbBr_6^{3-}$ and $SbBr_6^{-}$ octahedra that varies with cation.[46] On the other hand, β-Sb_2O_4 exhibits an unusual square-pyramidal configuration for $Sb^{III}O_4$ with more regular octahedra about antimony(V).[47] The average radii in the latter are quite normal ($\Delta R = 0.16$ Å[44]).

Implicit in the above conclusion is the existence of a significantly smaller dependence of radius on oxidation state with transition elements. Although there are few +1–+3 pairs with which to compare indium, the listed six-coordinate crystal radii for the +2 and +4 oxidation states for platinum, iron, and titanium differ by only 0.18–0.25 Å[44] or no more than 25% of the radius of the larger ion. The radii characteristics in many compounds of the heavier transition elements are in fact distinctly different. In these cases the differentiating electrons do not appear to screen the metal core–non-metal interaction significantly so that the metal–non-metal separations do not show the traditional increase on reduction but remain relatively constant.[48] For example, in the zirconium chloride series (Figure 4) the reduction sequence from $ZrCl_4$ to ZrCl involves the replacement of half of the chlorine neighbors by the same or a greater number of bonded zirconium neighbors, but this is accompanied by only a 0.09-Å increase in average Zr–Cl distances, some of which presumably originates with the increase in chlorine coordination number.[31] Other series of simple transition-metal compounds that appear to show binding energy trends on oxidation similar to that seen in Figure 4, including likewise lower rates of change with the metallic examples, are Ti–TiO–TiO_2 (successive metal binding energy differences of 0.9 and 3.7 eV), W–WO_2–WO_3 (1.6, ~2.8 eV),[36] Nb–NbO–NbO_2–Nb_2O_5 (1.3, 2.4, ~2.0 eV[49]), and Sc–ScS–Sc_2S_3 (0.2, 2.7 eV[50]). (Anion reference values have often not been reported so more regarding the sources of the trends can not be diagnosed.) In general, the simple reduced compounds of the transition metals appear to present more favorable prospects for the exploitation of changes in metal bining energies with oxidation state, changes that may also reflect fundamental changes in the Fermi reference point as well as effects of delocalization.

Negative Shifts. Finally there remains a particular group of elements for which reported binding energy data indicate a *negative* or very small positive shift that occurs on oxidation of the metal to simple compounds in the lowest oxidation state, namely, for sodium, copper, silver, cadmium, and mercury and, to a lesser extent, for zinc.[36,42] Two factors appear relevant to such a behavior in this part of the periodic table, both pertaining to properties of these particular metals. The above examples all involve atoms with s^1 or s^2 valence states for which E_F in the metal will be located relatively high on a broad conduction band of largely s character. For example, the $5s^2$ band in cadmium is 5 eV wide at half-height.[51] This band is emptied on oxidation to the salts, and now the highest valence level belongs to the added anion. These particular metals would thus appear to present some of the better prospects for a decrease, or a minimal increase, in E_F on oxidation to a typical salt. This trend will be enhanced if there is also a smaller loss of extraatomic electronic relaxation of the sort that is particularly significant with metallic (or otherwise delocalized) systems and that acts to reduce the binding energy in the metal from that of the vertical process by screening of the core hole. It is well-known that this relaxation (relative to free-atom values) decreases abruptly and substantially at the end of the transition series at the point at which the d band becomes filled, by about 8 eV between nickel and copper, for example.[4] Although this is a final-state effect, it will give the appearance of abruptly increasing the Fermi-referenced core binding energies of the s-band metals. Thus, both of these relationships appear to be maximal for just the elements listed, thereby providing the best chances for observation of a minimal or even negative core shift on oxidation.

Oxidation in transition-metal systems of the sorts described earlier instead often leads first to metallic products that retain significant relaxation effects while the Fermi level remains pinned within a d band of some sort. A third type of behavior occurs on oxidation of the ns^2–np^x post transition metals. Here, a more normal increase in binding energy appears on oxidation of a p-band element to an insulating or semiconducting compound in which the ns^2 configuration is retained somewhere near the anion valence level.

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Registry No. InCl, 13465-10-6; $InCl_{1.5}$, 12167-90-7; $InCl_n$, 12672-70-7; $InCl_2$, 13465-11-7; $InCl_3$, 10025-82-8; $Cs_3In_2Cl_9$, 12709-85-2; PCl_4InCl_4, 23041-98-7; $Rb_2LiInCl_6$, 72267-80-2; $Cs_2InInCl_6$, 73644-27-6; InY_2Cl_7, 90188-64-0.

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