ganization to fullerenes. Other 3-D nanostructural architectures can also be readily envisioned: reactions using polymer *dicarbanions* would be expected to yield networks having fullerene "cross-linkages"; reactions similar to those described here with carbon nanotubes[25] in place of fullerenes may yield novel, compatibilized reinforcements for polymer matrices. Our current efforts are focused on optimizing the synthesis[26] of $C_{60}(PS)_1$, anticipating that this soluble and fusible *mono*flagellene will exhibit minimally perturbed, intrinsic, fullerene characteristics. It is conceivable that some (nonlinear) properties of monoflagellenes might be enhanced if they nanophase-separate into a spatially delineated glass.

Acknowledgment. We thank Preston Snee for help with molecular modeling and Z. Guan for DSC analysis. This work was supported in part by the Wright Patterson Materials Lab under Air Force Prime Contract F3361-90-C-5813, a NSF Young Investigator Award (J.M.D.), and the University of North Carolina Department of Chemistry.

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Reviews

Unusual Valences in Rare-Earth Halides[†]

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The *valence* of an atom in a particular compound is considered *unusual* when there is a difference between the "localized" valence and the oxidation number. The degrees of delocalization of electrons may be different. Total delocalization gives rise to a conduction band. There may also be partial delocalization with multicenter or cluster bonding. With such a definition, reduced rare-earth halides such as metallic LaI_2 or semiconducting Pr_2Br_5 and Gd_2Cl_3 with $[Gd_6]$ clusters contain unusual valences but TmI_2 does not. In addition to the generalities of the synthesis and properties of reduced rare-earth halides, the electronic structures have been calculated making use of the extended Hückel algorithm. These calculations aim to yield a better understanding of bonding and the conductivity properties of these compounds.

Introduction

Valence determines the number of neighboring atoms with which an atom M can combine.[1] The *valence state* of this particular atom M is the arrangement of electron density around its core. The determination and theoretical description of the valence state in a discrete molecule are relatively easy tasks, even though bonding may be, although predominantly covalent, ionic or delocalized (as in the boranes or the fullerenes) to a certain degree. Molecular orbital calculations are a suitable method for the description and sometimes even understanding of bonding in molecules.

For solids with their three-dimensional infinite arrangement of atoms, the immediate problem is to determine where the neighborhood of atom M whose valence is under consideration ends. How many coordination spheres have to be taken into account: one, two, an infinite number? For predominantly ionic solids such as NaCl where the Coulomb (or Madelung) part of the lattice energy (MAPLE)[2] comes close to the total lattice energy, short-range order is much more important than long-range three-dimensional order, as a calculation for NaCl shows (Figure 1) where coordination number 1 (C.N.1) stands for a Na^+Cl^- molecule, C.N.2 for an infinite one-dimensional chain, C.N.3 for a double chain and, finally, C.N.6 for the three-dimensional network. Therefore, electron density is localized and the argument can only be how much covalency is involved in the bonding. For a complex compound such as $K_2[PtCl_6]$, there is nothing wrong with the ionic description $(K^+)_2[(Pt^{4+})(Cl^-)_6]$ as long as one takes into account that there is much covalency involved in the bonding of the complex anion $[PtCl_6]^{2-}$ and less in $K^+{\cdot\cdot}Cl^-$ bonding. The valence state of "Pt^{4+}" may be described as ligand field or molecular orbital theory have taught us. There is *nothing unusual* about its valence, however.

The same is true for the valence of Xe^{2+} in XeF_2[3] or In^+ in InCl.[4] Not even the valence of indium in In_5Br_7 is unusual. It is a mixed-valent bromide and contains according to a simple ionic formulation $(In^+)_3[(In_2)^{4+}(Br^-)_6](Br^-)$ mono- and divalent indium.[5] Divalent indium bound into the group $[In_2Br_6]^{2-}$ is characterized by a covalent σ bond (so-called metal–metal bond) as is the case with isoelectronic monovalent cadmium in $Cd_2(AlCl_4)_2$.[6]

[†] Dedicated to Professor Rudolf Hoppe on the occasion of his 70th birthday on October 29, 1992.

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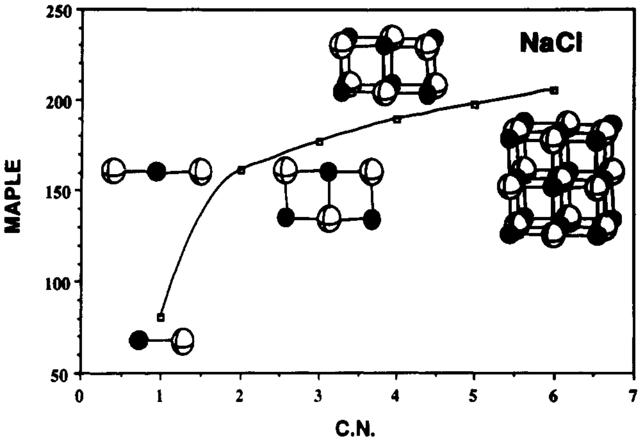

Figure 1. Variation of the Madelung part of the lattice energy, MAPLE (kcal/mol) for NaCl with different coordination numbers, C.N.

Nothing unusual again, although *uncommon*. Even monovalent iron as in $K_3[FeO_2]$, although highly uncommon, is not unusual because bonding is localized as may be judged from magnetic susceptibility data.[7]

So, what is an *unusual valence*? Let us consider valence being unusual when delocalization of electrons becomes involved. Examples are easy to detect because in such compounds the *oxidation number* (O) and the *valence* (V) have no longer much in common. A few examples may illustrate the problem:

(i) The oxidation number of indium in In_5Br_7 is $O = +1.4$. As it is a class I mixed-valent compound,[8] this is only an average as there are two types of indium atoms of which three have $V = +1$, i.e., the $(Kr)4d^{10}5s^2$ electronic configuration, and two have $V = +2$, i.e., the $(Kr)4d^{10}5s^1$ configuration with a $5s^1$–$5s^1$ σ bond. Nothing unusual.

(ii) Sodium cuprate(III), as one could address it, $NaCuO_2$, is not an oxide with trivalent copper. If it were, it would not be unusual, although highly oxidized and uncommon and hard to synthesize. Rather, it is unusual because it contains copper with the electronic configuration $(Ar)3d^9$, i.e., $V = +2$!, as X-ray absorption near-edge spectroscopy (XANES) clearly shows.[9] The electron that is needed for the "formal" reduction of copper from +3 to +2 comes from one of the oxygen atoms whose electronic configuration is then $(He)2s^22p^5$. It is an O^-, i.e., $V = -1$, or, as the physicist says, oxygen has a hole in the p band. However, everything is localized, and in a strict definition, $(Na^+)(Cu^{2+})(O^-)(O^{2-})$ does not contain an unusual valence.

(iii) The valence of neodymium in NdI_2 is unusual but only in the high-pressure modification (NdI_2-II).[10] According to crystal structure ($CuTi_2$ type structure) and, derived therefrom, ionic volume, neodymium has the valence +3, the electronic configuration is $(Xe)4f^35d^1$. Like LaI_2,[11] NdI_2-II is expected to be a metallic conductor arising from the $5d^1$ electron delocalized in a conduction band. In a simple picture, this electron does not contribute to the ionic volume, and the chemist uses the formulation $(Nd^{3+})(e^-)(I^-)_2$. Neodymium behaves for "bond" distances as if it were trivalent, hence like Nd^{3+} in NdI_3 with the $(Xe)4f^3$ configuration. Thus, in NdI_2-II the oxidation number is clearly $O = +2$ and the localized valence is $V_l = +3$. The difference beween O and V_l arises from the *delocalized* electron ($V_d = -1$). The *total valence* may therefore be written as $V = V_l/V_d$. For NdI_2-II one obtains $V = +3/-1$. Clearly, if we were to write $V = V_l + V_d$, we would obtain $V = O = +2$. When pressure is released, the delocalized 5d electron becomes localized and a structural phase transition to NdI_2-I ($SrBr_2$ structure type) occurs. With $V = +2/0$, neodymium is truly divalent, a usual but still not too common valence.

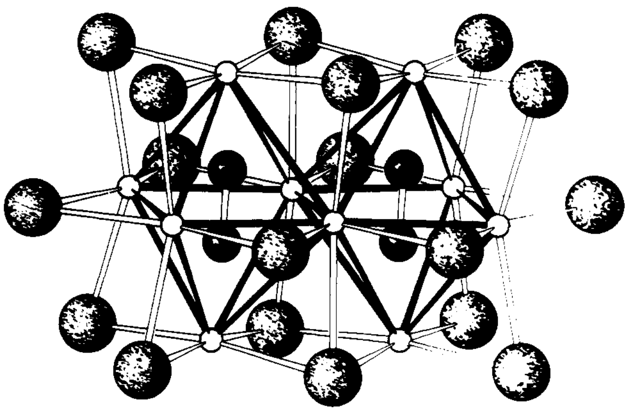

Figure 2. Dimeric $[Er_{10}(C_2)_2]$ unit in $Cs[Er_{10}(C_2)_2]I_{18}$.

(iv) There are cases with unusual valences where no or only partial delocalization occurs. Later on, we will focus on praseodymium halides such as Pr_2Br_5 with $O = +2.5$ but with $V_l = +3$.[12,13] The additional electron per formula unit is localized in a three-center bond.[14] Halides with interstitially stabilized clusters also belong to this category. It is certainly not an easy task to decide "where the electrons are" in a compound such as $Cs[Er_{10}(C_2)_2]I_{18}$.[15] It contains two $[Er_6C_2]$ octahedra sharing one common edge (Figure 2). There are 29 electrons available for carbon–carbon, carbon–erbium, and, maybe, for erbium–erbium bonding. These electrons are localized within the $[Er_{10}(C_2)_2]$ building unit. A localized valence of $V_l = +3$ may be assigned to the erbium atoms even though the Er–Er distances are around 360 pm for the terminal cluster atoms and, therefore, considerably shorter than in $Cs_3[Er_2I_9]$[16] (401 pm) with $V = O = +3$ with two $[ErI_6]$ octahedra sharing one common face. Considerable erbium–erbium bonding must be involved in the common edge of $[Er_{10}(C_2)_2]$ where d(Er–Er) is only 316 pm. Certainly, one cannot speak of *the* valence of erbium in this cluster iodide. Only the localized valence must be regarded as $V_l = +3$; hence the electronic configuration of the "erbium" core is $(Xe)4f^{11}$. The above-mentioned 29 electrons are localized in covalent bonds or, maybe, "locally delocalized" or even three-dimensionally delocalized in a d band.

Therefore, we define the *unusual valence* of this article as follows: The valence of an atom in a particular compound is considered unusual when there is a difference between the "localized" valence V_l and the oxidation number O. The degrees of delocalization of electrons may be different. Total delocalization gives rise to a conduction

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band and metallic behavior. There may also be partial delocalization with multicenter or cluster bonding and semimetallic or even insulating behavior.

The scope of this review is to try to answer when one can expect delocalization, partial delocalization, or complete localization of electrons or, to put it in other words, under what circumstances does a *configuration crossover* in the valence region of lanthanide ions in halides occur?

The Three Classes of Reduced Rare-Earth Halides

An enormous wealth of halides of the rare-earth elements (M = Sc, Y, La, Ce–Lu) with an oxidation number of less than +3 (*reduced rare-earth halides*) has emerged after the early discovery of some dihalides through continuous research during the last 40 years.[17,18]

Milestones were as follows:

(i) The discovery that not only europium, ytterbium, samarium, and thulium would form dihalides but also neodymium and dysprosium and (although still somewhat mysteriously) maybe holmium (at least there is a mixed-valent compound known, Ho_5Cl_{11}).[19] These halides contain localized valences, their electronic configuration corresponds to (Xe)$4f^n5d^06s^0$ with $n = Z - 56$ (Z = atomic number). They are considered as divalent, i.e., $V = +2/0$, and will be symbolized as M^{2+}.

(ii) The discovery that there are metallic diiodides, MI_2, of lanthanum, cerium, praseodymium, and gadolinium[20] and of neodymium under high pressure (see above) that contain the unusual valence $V = +3/-1$, symbolized as $M^{3+}e^-$. The electronic configuration of the lanthanide atom in the diiodide is (Xe)$4f^{n-1}5d^16s^0$. The d electron is delocalized in a conduction band, but GdI_2 is also a two-dimensional ferromagnet.[21] Further below we will see that the "extra" electron may also be involved in multicenter bonding as in Pr_2Br_5 and, therefore, is weakly localized.

(iii) The discovery of Gd_2Cl_3,[22] the first cluster compound of such an electron-poor element resembling the early-transition-metal clusters with the basic $[Gd_6Cl_8]$ unit. This is "condensed" in a way that $[Gd_6]$ octahedra share two common edges to form an infinite chain. Still, the octahedra appear to be empty, it may be synthesized in high yield without an interstitial involved. The valence of gadolinium is $V = +3/-1.5$. The $[Gd_6]$ octahedron contains nine electrons for gadolinium–gadolinium bonding, but as the octahedron is not isolated, the bonding description is not easy.

(iv) The discovery that almost all of the reduced rare-earth halides with isolated and condensed octahedral clusters contain interstitials and will therefore be symbolized as $[M_6Z]$. The interstitial Z contributes to intracluster bonding through covalent Z–M bonding.[23] In some cases, there is also M–M bonding involved, and sometimes these compounds are conductors or semiconductors or exhibit interesting magnetic interactions, as far as one knows at the present time.

In conclusion, the three classes of reduced rare-earth halides are such that may be symbolized as M^{2+}, $M^{3+}e^-$, and $[M_6Z]$.

Synthesis

The principal synthetic route to reduced rare-earth halides is the conproportionation of a binary (or ternary) trivalent halide with the metal at temperatures around the melting point of the trihalide or the pseudobinary mixture, for example, via[24]

$$GdCl_3 + Gd = Gd_2Cl_3$$

$$3CsCl + 2TmCl_3 \text{ (or } Cs_3Tm_2Cl_9\text{)} + Tm = 3CsTmCl_3$$

Because of the corrosiveness of the rare-earth metals and the reduced halides against ceramics and many metals, a refractory metal such as niobium or tantalum needs to be used as the reaction container. This has become routine in a number of laboratories.

An alternative to the conproportionation route can be the metallothermic reduction with alkali metals,[25] for example

$$Cs + ErI_3 + C = Cs[Er_{10}(C_2)_2]I_{18} + \text{other products}$$

For exploratory research, this route has a number of advantages, especially for crystal growth. It is, however, not easy to obtain pure products except in simple cases such as

$$Cs + TmCl_3 = CsTmCl_3$$

The problem with these compounds is that a great deal of exploration, even serendipity, is still involved. This stems from the fact that we know almost nothing about the thermochemistry of these systems, and it appears clear that most of the interstitially stabilized cluster compounds cannot be the thermodynamically stable compounds in the system with respect to the neighboring phases. So, the general routes are clear, but each compound is a challenge!

Properties

Not too much is known about the properties of the three classes of reduced rare-earth halides as mentioned above. Most of these are only basically characterized, merely analyzed through crystal structure determinations. The general structural patterns were the subject of a number of reviews.[18,26,27] The particular crystal structures that are needed for the understanding of further physical properties and for the electronic structures will be discussed below. Most interesting are the $M^{3+}e^-$ and $[M_6Z]$ type halides with their unusual valences. Physical measurements that have been carried out to elucidate some of the properties of a few of the plethora of compounds include magnetic susceptibility and neutron diffraction for magnetic structures and location and occupation factors of light elements, conductivity measurements, and X-ray spectroscopy (especially XANES) to determine the localized valence(s). Extended Hückel calculations have been carried out in a number of cases to achieve an understanding of the physical properties through their electronic structures.

Electronic Structures: Generalities

The basic orbital interaction in three-dimensional solid state structures may be shown in an MO derived *solid-state interaction diagram*. For binary metal halide structures we have to consider interactions between metal f, d, s, and p orbitals and halide s and p orbitals. Considering the metal and the halide sublattices separately,

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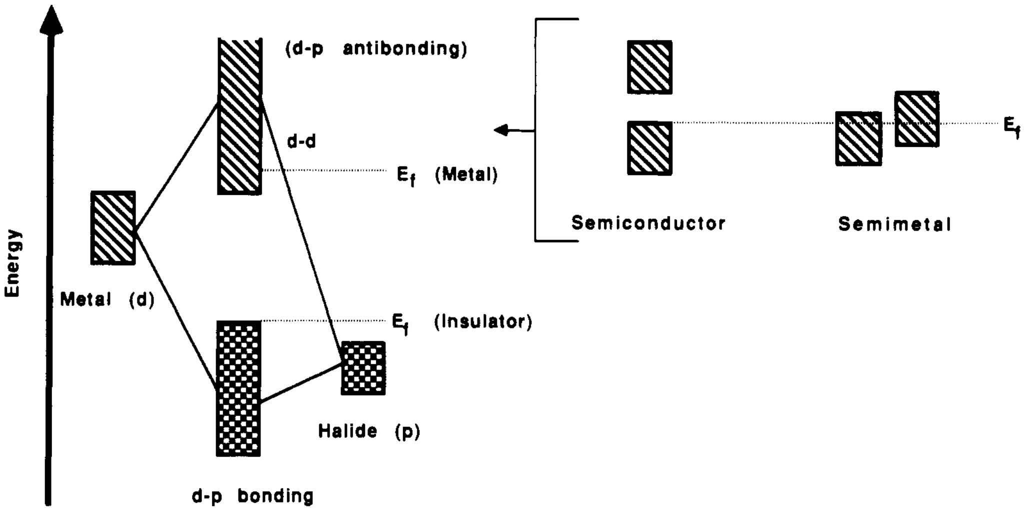

Figure 3. Solid-state interaction diagram for binary metal halides. The Fermi energy is marked for different electronic conditions as E_f.

their orbitals possess a finite width of allowed energy states, depending on their respective atom spacings and coordinations.

For d and f metals, we may restrict ourselves at first to the interactions of the d states with halide p states, to show in a simplified picture how these interactions may occur. A typical solid-state interaction diagram is shown in Figure 3. The metal (d)–halide (p) interactions yield basically two blocks. The lower block is formed predominantly of halide p orbitals with little admixture of metal d orbitals generating the metal–halide bonding interaction. The block located at higher energy is predominantly of metal d nature, with little admixture of halide p orbitals, containing the metal–halide antibonding combination.

The character of the main d block is critical to our analysis as well as the occupation of these states. For compounds with normal valences, i.e., $V = V_l/O$, the lower mainly p block is completely occupied with electrons, usually being well separated from the empty conduction block. Insulating behavior will be the result. Complex physical properties, however, may occur if there are electrons occupying the metal d states.

Depending on the spacing and the coordination environment of the metal atoms, the d block may be entirely metal–metal antibonding or gradually changing in character, from bonding to nonbonding to antibonding, with increasing energy. A calculation of the *crystal orbital overlap populations* (COOP)[28] may provide a useful tool to see if an occupation of d states is favoured up to a certain level, also if a compound is susceptible for oxidation.

If there are metal d states occupied with electrons, semiconductive to metallic properties may be regarded, depending on a present gap within the d block between occupied and empty d states. Another important criterion is the degree of localization of the electrons occupying the d states. A significant activation energy may be necessary to mobilize such localized electrons, even if the present bandgap separating occupied and unoccupied states is negligible. The highest occupied state (at 0 K) is referred to as the Fermi level, E_f (HOMO in the MO theory).

The extended Hückel[28] algorithm has proven to be a very useful tool to gain some understanding about the electronic conditions of solids. There are cases, however, where the result of a simple calculation does not appear to be very conclusive. There may be several reasons—several of them are considered. First of all, no theoretical approach is perfect, and, of course, a one-electron approach does not take electron–electron interactions into account. The effect of the f orbitals of the 5f and 6f elements appears to be somewhat uncertain as there are no reliable energy parameters for f orbitals, and thus, the occurrence of a f → d configuration crossover is not always clear. Also, adventitious impurities often have turned out to be a problem in synthesis, as well as in understanding the electronic properties of these compounds, as long as the impurity is undiscovered. However, a careful calculation of the electronic structure may lead to some helpful conclusion if an interstitial atom has to be considered, as we will show below, in an example of a lanthanide dihalide containing adventitious hydrogen as an interstitial.

In the following we will refer to MO interaction schemes, density of states (DOS), and band structure calculations to elucidate the electronic properties of a particular class of solids, i.e., those with unusual valences.

Configuration Crossover in the Lanthanide Series

The predominant ground state for most of the lanthanide atoms is $4f^n6s^25d^0$, but there are some well-known exceptions resulting from empty, half-filled, or filled f states (La, Gd, Lu). Thus, there are basically two valence electrons and at least one more electron is usually provided by the 4f orbitals that leads to the dominant trivalent state, $V_l = +3$ (except for Eu and Yb and a few more). As the ligand field is introduced, e.g., in $PrCl_3$, these three electrons are localized at the halide, in halide (p)–metal (d) bonding states, of the main p block. The f states are roughly located between the metal d and the halide p block in energy. Correspondingly, two f electrons are lowered in energy in the tetravalent state, for example, in CeF_4.

Unexpectedly, the trivalent state often remains preserved in compounds where a divalent state could be present, for example in LaI_2. The $f^nd^0 \rightarrow f^{n-1}d^1$ configuration crossover[29] occurs at the beginning of the series of the lanthanide elements, where the f bands are the highest in energy, and again for Gd to yield a half-filled $4f^7$ state.

Through the configuration crossover, one f electron is removed from the f orbitals to occupy metal–metal bonding d states. This may occur if metal–metal distances

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are sufficiently short. Increased d interactions lead to a broadening of the d block, which, in extreme, could then reach the f bands. But we have no reliable data to determine at what energy exactly the f bands are, and, thus, how far they are separated from the lowest d band in the respective compounds.

Critical to the analysis concerning the presence of a $f^nd^0 \rightarrow f^{n-1}d^1$ transition may be the volume reduction, that is associated with a decrease of the cationic radius, for example from EuF_2 to EuF_3 (21%).

In contrast to the iodides and bromides, the f → d excitation energies are increased in the lanthanide chlorides due to the enhanced ionicity (electronegativity of the ligand), following the nephelauxetic effect for the halides.

A configuration crossover is present in the dihalides LaI_2, CeI_2, and PrI_2 ($CuTi_2$-type structures); they possess a $f^{n-1}d^1$ configuration. The diiodides that follow in the lanthanide series tend to appear as d^0 systems (SmI_2, EuI_2), obviously because the f → d excitation energy increases gradually at the beginning of the series of lanthanide metals with increasing atomic number. NdI_2, however, was reported to appear in both, the f^4d^0 ($SrBr_2$-type structure) and f^3d^1 ($CuTi_2$-type structure) configuration, respectively. GdI_2 again exhibits a trivalent f^7d^1 state. Lanthanide dichlorides, as far as they exist ($NdCl_2$, $SmCl_2$, $EuCl_2$, $DyCl_2$, $TmCl_2$, $YbCl_2$) are considered in the nonmetallic f^nd^0 configuration because of ligand effects, as stated above. Most of the "dihalides" with MoS_2-type structures, surprisingly, have turned out to contain a significant amount of hydrogen, MX_2H_y ($y < 1$).[30] PrI_2 and GdI_2, however, may at present be considered as true binary MoS_2-type dihalides. Unusual electronic conditions with occupied d states, are also present in M_2X_5 (M = La, Ce, Pr; X = Br, I)[12,31,32] and in $Pr_{0.6}Pr_2Cl_6$.[33]

Praseodymium Halides

The largest structural variety of a lanthanide dihalide has been reported for PrI_2: the $CuTi_2(LaI_2)$-type structure, two MoS_2(2H,3R)-type structures, the $CdCl_2$-type structure, and the unusual $[Pr_4I_8]$ cluster. Although the MoS_2-type structures favorably contain hydrogen for most lanthanide dihalides, the MoS_2-like phases of PrI_2 seem to be stable without the presence of hydrogen. Other than this, there are the unusual compositions Pr_2X_5 (X = Br, I) and $Pr_{0.6}Pr_2Cl_6$ as noted above. The Pr present in these structures is considered to occur in the $4f^25d^1$ configuration (Pr^{3+}). The electronic situation in $Pr_{0.6}Pr_2Cl_6$, however, remains puzzling.

$PrCl_3$. We begin with $PrCl_3$—a typical "valence compound". $PrCl_3$ is a pale-green solid that adopts the UCl_3-type structure. Additional Pr can be incorporated in octahedral interstices to form a black solid of the unusual composition $Pr_{0.6}Pr_2Cl_6$ ($PrCl_{2.3}$) as shown in Figure 4. At this point one may ask why the composition is not $PrPr_2Cl_6$ (=$PrCl_2$)?

Having the structure of $PrCl_3$ in mind, there is an easy relationship with the structure of Pr_2Br_5 by removing two halide atoms from a Pr_4Cl_{12} superstructure of $PrCl_3$, accompanied with some geometrical adjustment. The calculated DOS of all these structures is shown in a simplified block diagram in Figure 5, containing the halide p block and the metal d block only. The f states are shown as a line at the relativistic energy near −10 eV. Their calculated width is not more than 0.3 eV. The electronic structure of $PrCl_3$ shows clearly an insulating band gap of about 7 eV between the fully occupied Cl-p block and the empty conduction block.

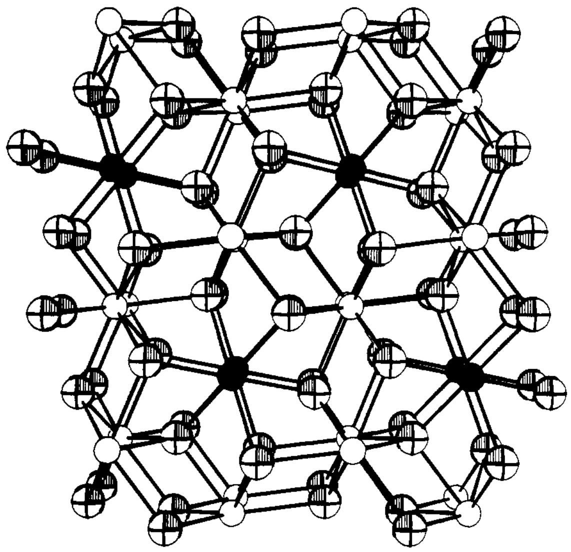

Figure 4. Structure of $Pr_{0.6}Pr_2Cl_6$, as derived from the UCl_3 type projected onto (001). Pr atoms of the $PrCl_3$ host are empty spheres. Statistically intercalated Pr atoms (black spheres) are considered in the origin of the unit cell ("$PrPr_2Cl_6$").

$Pr_{0.6}Pr_2Cl_6$. The additional $Pr_{0.6}$ statistically occupy trigonal-antiprismatic voids in the UCl_3-type structure of $PrCl_3$ to yield $Pr_{0.6}(Pr_2Cl_6)$. To prove the limits of the incorporation of praseodymium, the composition $Pr(Pr_2Cl_6)$ is considered first. The block diagram derived from the calculated DOS of $PrPr_2Cl_6$ naturally exhibits similarities with the DOS of $PrCl_3$, concerning the halide p block and the upper d block (Figure 5). The $PrPr_2Cl_6$ every second trigonal antiprismatic void of the $PrCl_3$ structure is occupied with additional Pr^{3+}, being stacked along the hexagonal c axis (at $d = c = 427$ pm). Thus, there are five extra d bands of which the "t_{2g} block" of the intercalated Pr atoms is located below the main d block. The upper and the lower part of this "t_{2g} block" is formed by d_{z^2} orbitals and the center block consists of $d_{x^2-y^2}$ and d_{xy} orbitals. Thus, there is one d_{z^2} band highly dispersive over an energy region of about 3.5 eV (along the $\Gamma \rightarrow A$ and $L \rightarrow M$ direction, parallel to the 6-fold axis), due to rather strong Pr–Pr interactions along the crystallographic c axis (Figure 6). With three electrons, these states would be half-filled. In "chemical" terms, this implies that the d_{z^2} band of Pr contains one electron, and, therefore, the $d_{x^2-y^2}$ and d_{xy} bands contain one electron each, because they are almost degenerate throughout the reciprocal space. Therefore electrons in the latter two bands are likely to be localized. On the other hand, the d_{z^2} band is extremely dispersive so that electrons in this band can be expected to be delocalized.

Strangely enough, the intercalated Pr would carry its electrons in its "own" (about 95%) orbital states. The lower portion of the dispersive d_{z^2} band is strongly bonding, whereas the occupation of the remaining two bands involve nonbonding and antibonding interactions, respectively. A corresponding d^1 situation with "$Pr^{3+}(Pr^{2+})_2Cl_6$" would be strongly susceptible for electronic instability. The bonding portion of the d_{z^2} band is preserved if every third Pr atom along the c axis is removed, yielding pairs of Pr atoms (Figure 7). We may consider this as an indirect Peierls

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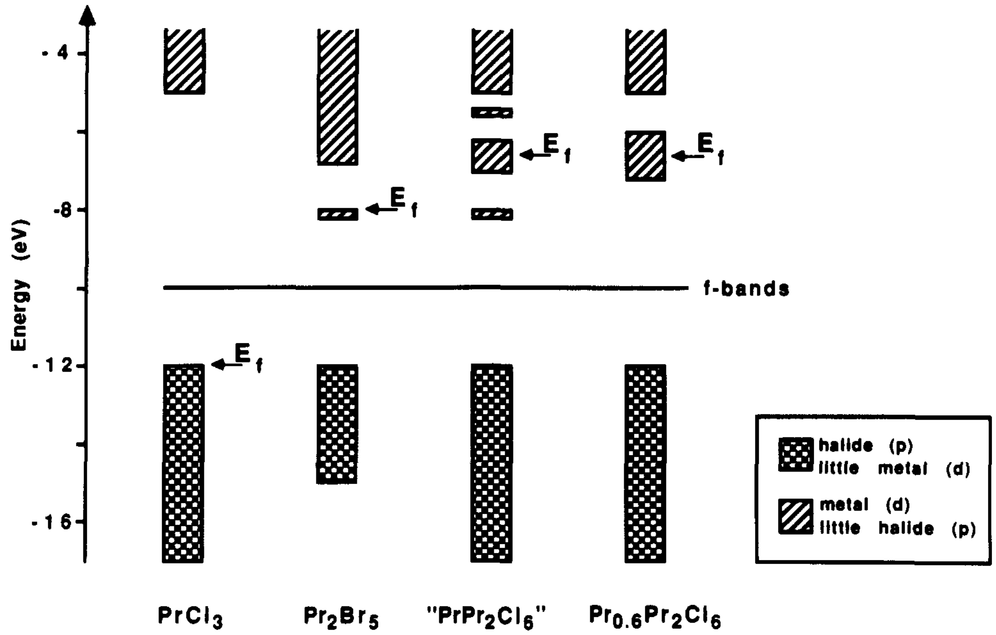

Figure 5. Block diagrams for praseodymium halides, showing the halide p block (at low energy) and the Pr d block (at high energy). Fermi levels are marked, considering all Pr as Pr^{3+}. The contracted f states are shown as a single line.

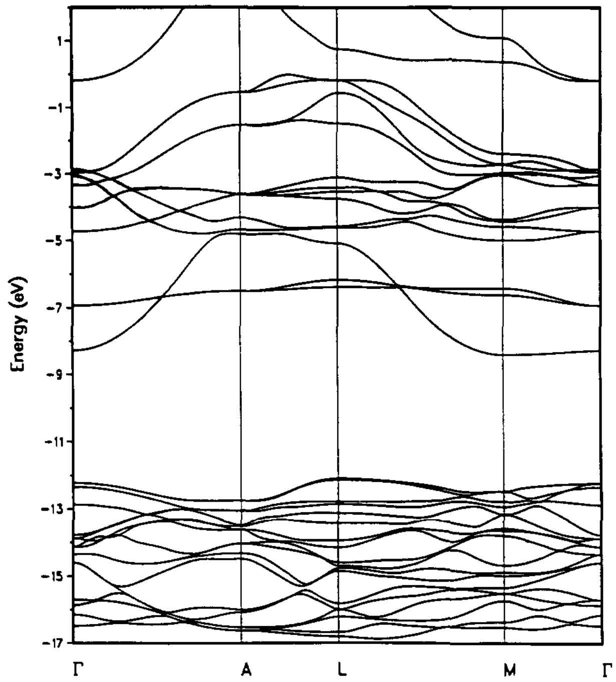

Figure 6. Band structure of $PrPr_2Cl_6$ ($\Gamma = 0,0,0$; $A = 0,0,c^*/2$; $L = a^*/2,0,c^*/2$; $M = a^*/2,0,0$). Three electrons occupy the lowest three d bands in the area around −7 eV (all Pr as Pr^{3+}). These three energy bands have almost pure d nature (95%) of the intercalated Pr atoms (t_{2g}-like block).

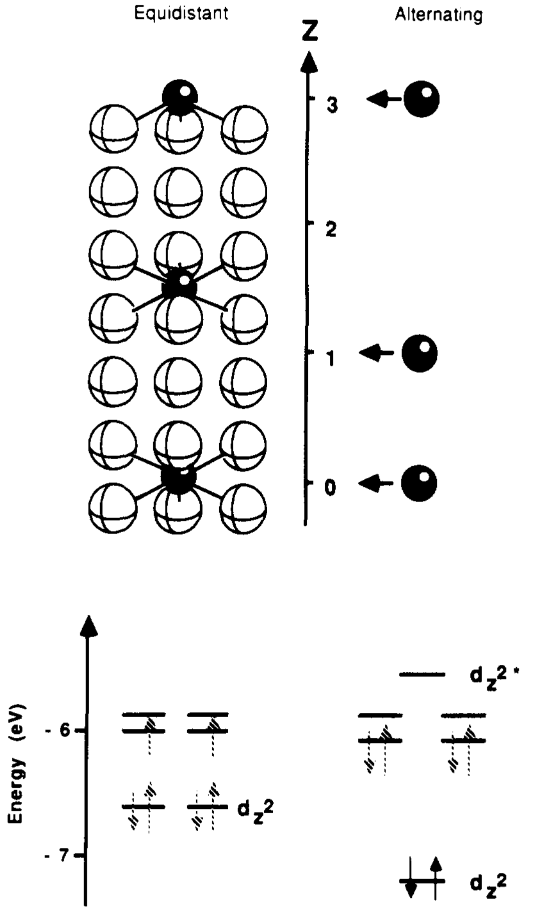

Figure 7. Two stacking models for the intercalation of Pr atoms into the $PrCl_3$ host lattice, with the corresponding crystal orbital energy levels for the t_{2g} block of the two intercalated Pr atoms in the tripled unit cell (along c) of Pr_2Cl_6: $Pr_2(Pr_6Cl_{18})$. Shaded arrows consider occupations of antibonding orbitals for all Pr in the trivalent state.

distortion, because an alternating removal of atoms is simply another way to distort a one-dimensional chain. As a result, the d_{z^2} band would split into a (fully occupied) bonding d_{z^2} level at low energy and an (empty) antiboding d_{z^2}* level at higher energy. This leads to localized bonding (Pr–Pr pairs) that is sufficiently described by an MO diagram (Figure 7). Thus, for the tripled unit cell, with $Pr_2(Pr_6Cl_{18})$, a d^2 state is stable (the Pr–Pr overlap population is 0.19), because the occupation of d_{xy} and $d_{x^2-y^2}$ leads to an increasing Pr–Pr antibonding overlap population (about −0.6 per additional electron). Therefore the $Pr_{0.6}$ in $Pr_{0.6}Pr_2Cl_6$ may be considered in the trivalent $4f^2d^1$ condition, and a residual 1.8 electrons will have to be compensated by a mixed valence state of the Pr of the Pr_2Cl_6 host. This view however conflicts with the absence of any volume expansion ($Pr^{3+} \rightarrow Pr^{2+}$) for the pair $PrCl_3/Pr_{0.3}PrCl_3$.

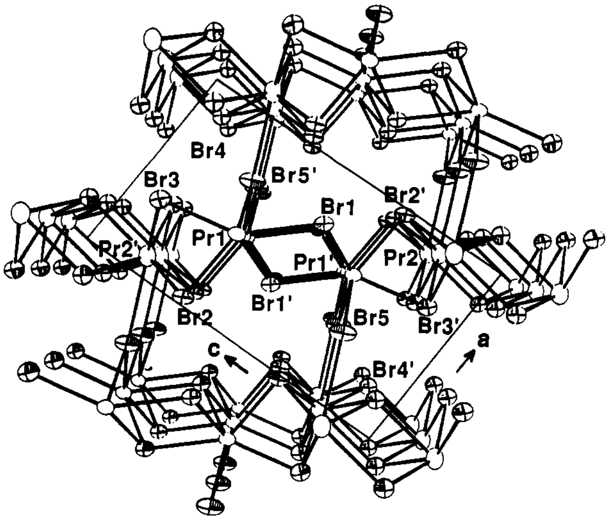

Figure 8. Perspective view of the Pr_2Br_5 structure along [010].

Another possibility is an equidistant occupation of trigonal antiprismatic voids by Pr atoms at $d = 1.5z$. For this arrangement two d_{z^2} levels are located below two d_{xy} and $d_{x^2-y^2}$ levels (Figure 7) for the tripled unit cell with $Pr_2(Pr_6Cl_{18})$. Now all states are slightly antibonding. The corresponding block scheme is provided at right in Figure 5.

We are not sure what the correct occupation of these states looks like at this point for the possible intercalation models of Pr. Although the metallic d states are rather high in energy to receive f electrons, the electrons may be "frozen" in d states, because the compound is obtained only through rapid quenching!

It is important to note that an incorporation of Pr into the $PrCl_3$ structure increases the energy of the system (especially if all Pr present is Pr^{3+}!) and the metal sites in the $PrCl_3$ host of the $Pr_{0.6}Pr_2Cl_6$ lattice are fully occupied, according to the crystal structure refinement. The latter does not appear in the valence compounds "$NaM_{1.66}Cl_6$" (M = La, Ce, Pr).[34]

In contrast, $NaNd_2Cl_6$ was reported to be a mixed-valence compound with $4f^4$ (Nd^{2+}) and $4f^3$ (Nd^{3+}) states, that cannot be assigned to lattice sites because there is only one crystallographic Nd site.[35] This mixed-valence situation is not indicated for $NaPr_2Cl_6$ by comparison of the volume expansion of the two pairs MCl_3/NaM_2Cl_6 (M = Nd, Pr). This comparison, however, may be subtle because Na seems to occupy nine-coordinate sites in $NaNd_2Cl_6$ and 6-fold sites in $NaPr_2Cl_6$. We believe that the Pr(d) states in $NaPr_2Cl_6$ are too high in energy to be occupied by the single electron provided by the Na atom (see the $PrCl_3$ block scheme, at left in Figure 5), and thus the electronic point of view again clearly favors mixed valence.

Pr_2Br_5. The metal atoms in Pr_2Br_5 form puckered layers which may be considered as being derived from a hexagonal close-packed layer.[12] Shortest metal–metal distances are obtained along the *b* repeat (416.6 pm) and between the two crystallographically distinct Pr atoms (421.0 pm). These layers are sandwiched and interconnected by Br atoms (Figure 8).

Praseodymium in Pr_2Br_5 again is Pr^{3+}, and thus there are two electrons per $(Pr_2Br_5)_2$ unit to be put into the d bands. The low-lying d block that is split off below the main d block is formed by two bands (Figure 9). Thus, this block would be half-filled, so that the two electrons could occupy one band. Considering the fact that these bands are very narrow, the electron–electron repulsion should lead to a high-spin configuration, with one electron occupying one band. An analysis of the overlap populations shows that there are metal–metal bonding interactions for some short metal–metal contacts, i.e., between Pr1 and Pr1 (but not between Pr2 and Pr2) in the direction of the *b* axis. Additional bonding interactions occur between the Pr1 and Pr2 atoms (Figure 10). These bonding interactions are limited to the low-lying portion of the d block (two energy bands). Thus, bonding interactions exclusively occur in the non-halide-capped corner-sharing Pr triangles, running along the *b* axis forming double chains. The electrons are supposed to be situated in semilocalized (three-center one-electron) bonds within these Pr triangles. We note that the incorporation of some hydrogen into the trigonal interstices would introduce a significant stabilization, similar to the situation of some lanthanide dihalide hydrides, such as $LaBr_2H_x$ (see below).

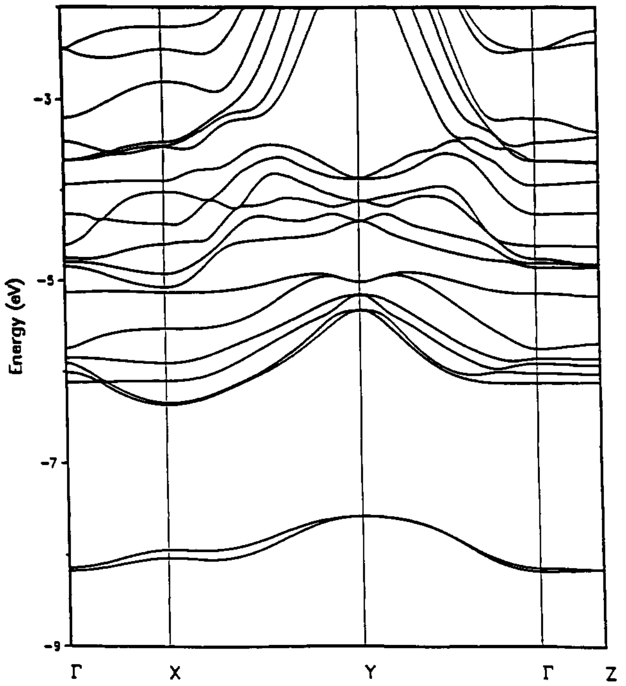

Figure 9. Band structure for Pr_2Br_5 (Γ = 0,0,0; $X = a^*/2,0,0$; $Y = 0,b^*/2,0$; $Z = 0,0,c^*/2$). Two electrons occupy the two lowest d bands.

Localized Electrons

The first recognition of the unusual properties of materials now known as Mott[36] insulators occurred for oxides such as MnO, CoO, NiO, and Cr_2O_3.[37] By simply counting the number of electrons, one may judge the presence of d electrons as contributors to metallic conductivity if a significant band gap is absent. But there are conditions where electrons tend to be localized on lattice sites and an insulating or semiconductive behavior is obtained instead of metallic behavior. Such conditions resulting from partially filled bands are referred to as Mott localized states. One basic argument for localized states is the appearance of large lattice spacings between atoms.

For a widely spaced system, as for a collection of quasi-isolated atoms, electrons should be assigned to lattice sites. An insulating state is the result. Thus, if there is a large distance between neighboring cation sites, a sig-

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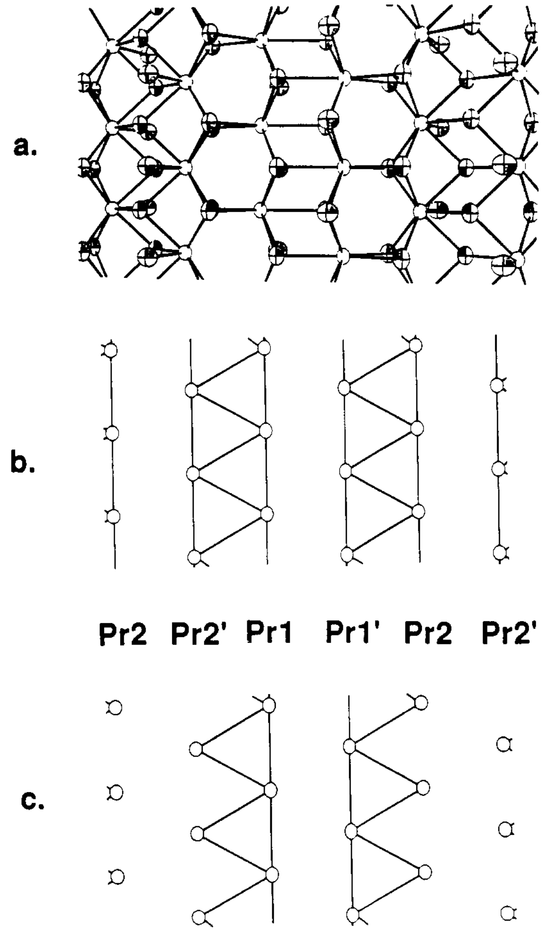

Figure 10. (a) Perspective projection onto the (101) plane of a section of one layer in the Pr_2Br_5 structure. (b) Metal part of the layer only. Metal–metal distances less than 430 pm are outlined. (c) Metal part of the layer only. All positive overlap populations are outlined.

nificant barrier for tunneling of the electrons will be present. In most cases, it seems to be important that a structure can provide preferred sites for electron localization.

The general correlation between the curvature of a band structure and the atomic distance is well-known. If we consider a one-dimensional equally spaced chain of atoms, i.e., along the *c* direction, the dispersion of the d_{z^2} band will behave in accordance with the interatomic distance. This relationship can be transferred to three-dimensional space. For strong metal–metal interactions (short interatomic distances) the bands representing the direct metal–metal interactions will be very broad, with energetically well separated bonding and antibonding proportions. Such a system, with a half-filled band will be susceptible to a Peierls distortion rather than electron localization. If metal–metal interactions are rather weak, bands will be flat throughout the reciprocal space representing relatively nonbonding behavior, and localized states are possible.

Of course there are no general rules as to where to place the electrons because it depends very much on the structure type. For Pr_2Br_5, an assumption was made, as to where they may be localized. Again, in Pr_2Br_5 two bands are split off below the main d block being half-filled with electrons (Figure 9). This electronic situation fits the above criteria of electron localization, because the bands remain flat throughout the reciprocal space. Accordingly, the compound appears to be weakly semiconducting. With the lower band filled with two electrons, the upper band would be empty (and consequently allow electronic conductivity although the mobility of the electrons is very limited). As the present gap between both bands is sufficiently small compared with the on-site electron repulsion, a high-spin state is likely to be present. This would lead to a situation with one electron occupying one band. This state is insulating in nature because electron hopping from one site to another leads to a situation where two electrons reside on a single site thereby causing on-site repulsion. Thus, the weakly semiconducting behavior should be represented by electrons overcoming the 1.6-eV barrier to the main d block. According to the calculated overlap populations, the electrons are suggested to be located in three-center bonds of the halide uncapped Pr triangles (Figure 10). Below T_N = 50 and 25 K, Pr_2Br_5 orders antiferromagnetically[13] (Figure 11), and electrons in one metal double chain running along the *b* axis are spin-up and those in the adjacent double chain are spin-down.

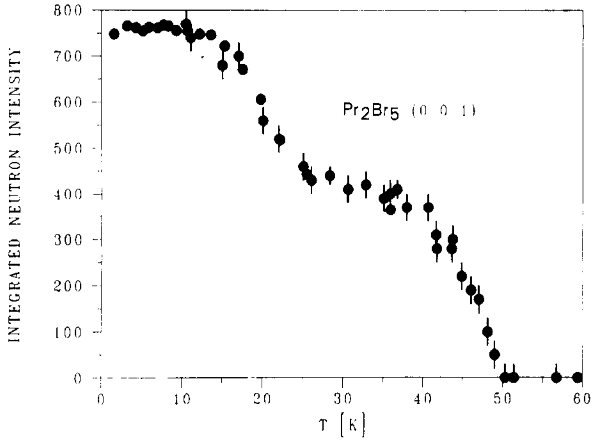

Figure 11. Temperature dependence of the (001) magnetic peak of Pr_2Br_5.

Lanthanide Dihalides

PrI_2-V = Pr_4I_8. The Pr_4I_8 structure[38] provides the most unusual feature of the lanthanide dihalides. The cubic structure contains $[Pr_4]$ tetrahedra (d_{Pr-Pr} = 387.4 pm) with 4 face-capping and 12 exo iodine atoms, interconnecting three adjacent clusters each. From a simple MO calculation of a $[Pr_4I_4]I_{12}^{8-}$ cluster (symmetry group T_d), an a_1 below e below t_2 ordering is obtained for the lowest metal d levels (Figure 12). The a_1 combination points inward, toward the center of the cluster. The bonding characteristics of the e orbitals are concentrated along the edges of the cluster. The t_2 orbital allows bonding along the edges and face centers of the cluster. These three sets of a_1, e, and t_2 assemble the metal–metal bonding orbitals, providing states for 12 metal electrons, representing six metal–metal bonds. Clusters containing less than 12 metal electrons will have an incompletely filled set of metal–metal bonding orbitals and may have different metal–metal distances. This is certainly apparent for a local $[Pr_4I_4]I_{12}^{8-}$ cluster and in other examples of tetrahedral clusters containing four metal electrons. The expected deformation pattern is a separation of two opposite vertices of the $[Pr_4]$ cluster, yielding two short Pr–Pr distances with two localized bonds (idealized symmetry group D_{2d}), a diamagnetic cluster.

The deformation, however, is not apparent in the present (extended) Pr_4I_8 structure. Two reasons may be considered that would avoid such a type of Jahn–Teller distortion. The first and most unlikely possibility is the

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[38] Warkentin, E.; Bärnighausen, H. *Z. Anorg. Allg. Chem.* **1979**, *459*, 187.

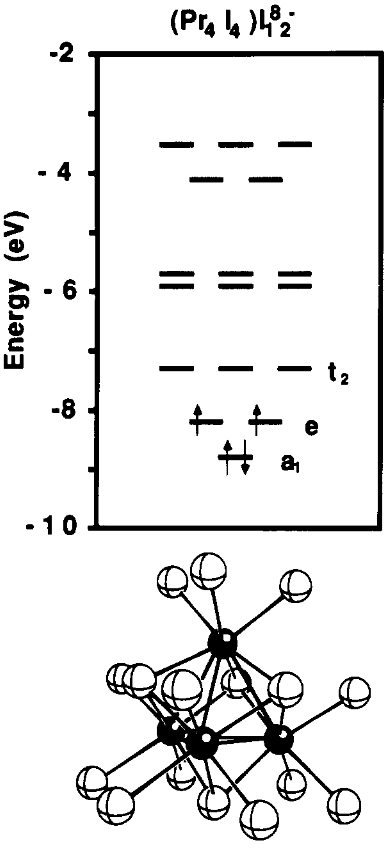

Figure 12. Schematic d block splitting diagram for the low-lying d states of a $[Pr_4I_4]I_{12}^{8-}$ cluster subunit (T_d symmetry), with the geometry adapted from the Pr_4I_8 structure.

presence of an interstitial atom that would change the number of electrons in metal–metal bonding states. The second possibility is that there are interactions with neighboring clusters in the structure. Interestingly, in the extended structure, the e level is slightly below the a level at Γ (Figure 13), showing that, indeed, there is metal–metal interaction between neighboring clusters (at $d_{Pr-Pr(inter)}$ = 486.5 pm). If we include the nearest 12 Pr neighbors in the MO calculation of the $[Pr_4I_4]I_{12}^{8-}$ cluster, the energy of the e level drops by about 0.5 eV. Similarly, if we increase the spacings between the clusters in the three-dimensional calculation, the e-derived bands are raised in energy at Γ. There is no interaction along certain directions of the reciprocal space where bands are dispersionless (along X–W–L). The weakly bonding interactions between metal atoms of adjacent clusters take place along all the extended edges of the tetrahedra, where bonding is marked by the e levels. Therefore we note a band dispersion for those directions, mainly along Γ–X. As in the MO, bonding interactions decrease in the order $a_1 > e > t_2$. Therefore, several tetrahedral clusters often exhibit electron counts with less than 12 metal electrons. The present e-derived bands appear to be slightly bonding and the t_2-derived bands are nonbonding. Significant bonding is marked by the a_1 orbitals inside the cluster. The half-filled e orbitals contribute to intracluster bonding but also to some weak intercluster interactions. Thus, they ascertain electronic mobility which, however, is limited by the present bandgap around −8 eV. The partial occupancy of bands (see E_f) leads to a nesting behavior of electrons and thus to an electron Fermi surface around Γ. Indeed, it is remarkable that no CDW instability follows. But Pr_4I_8 may be susceptible to a phase transition which has not yet been studied, as the compound has been obtained in small yields only.

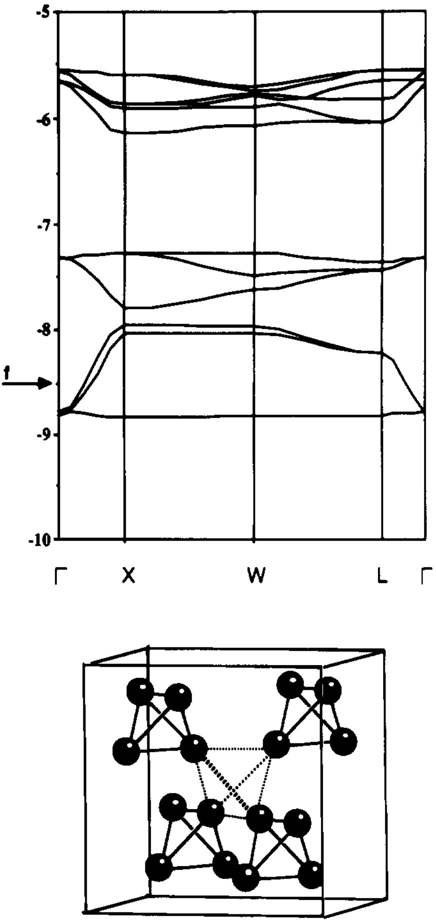

Figure 13. Band structure of Pr_4I_8 (Γ = 0,0,0; $X = a^*/2,b^*/2,0$; $W = a^*/2,b^*/4,3c^*/2$; $L = a^*/2,b^*/2,c^*/2$).

LaI_2 (PrI_2) Structure. LaI_2[11,20] and PrI_2[39] form layer structures of two-dimensional halide bridged $MI_{8/4}$ cubes, stacked along the tetragonal *c* axis in an AbA... fashion ($CuTi_2$ structure). A detailed study of the electronic properties of LaI_2 has been reported.[11] An MO calculation of an $[LaI_8]$ polyhedron yields two low-lying states (d_{z^2}, $d_{x^2-y^2}$) pointing through the faces of the $[LaI_8]$ cube, below three levels. The slight compression along the C_4 axis causes a slight splitting of states. Thus, the d_{z^2} is less than 0.1 eV below the $d_{x^2-y^2}$ molecular level (and the d_{xy} is slightly above the d_{xy}, d_{yz} levels). The lowest d level contains one electron. In the band structure, conditions similar to those found in the MO occur. The low-lying d_{z^2} and the $d_{x^2-y^2}$ bands, however, are allowed to mix in the absence of the zone centre (Γ). The metal–metal interactions within the *a–b* plane (at d_{La-La} = 392 pm) introduce significant band dispersion, causing band crossings, most importantly for the lowest band, and, therefore, allow electronic conductivity. Thus, LaI_2 may be regarded as a "delocalized material", as electrons are mobile through different energy bands. There is no preferred lattice site where the electrons may be located. This is indicated also by the nearly cubic metal atom coordination in each of the well-separated sandwich slabs in the structure.

GdI_2. GdI_2 crystallizes with the (2H-)MoS_2 structure, but was not reported to incorporate hydrogen. Thus, the electronic structure matches the conditions described below for "$LaBr_2$". Magnetic studies revealed ferromagnetic ordering within the hexagonal Gd layers below 313 K,

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(39) Hulliger, F. *Structural Chemistry of Layer-type Phases, Physics and Chemistry of Materials with Layered Structures*; Levy, F., Ed.; Dordrecht: Reidel, 1976; Vol. 5.

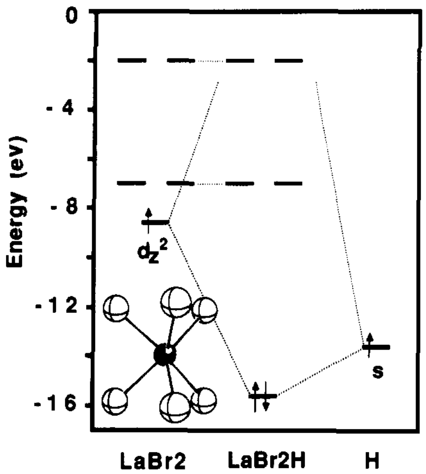

Figure 14. MO interaction diagram of the d states of a [$LaBr_6$] fragment, adapted from the $LaBr_2H$ structure, with a hydrogen (1s) orbital.

marked by a strong increase of the zero-field ac susceptibility.[40] Alternating layers are supposed to order antiferromagnetically. If we consider the electrons to occupy three-center bonds, with one electron occupying every second metal triangle (the halide uncapped ones), they are all spin-up within one layer.

Hydrogen Incorporation in Lanthanide Dihalides ($LaBr_2H$) with MoS_2/NbS_2-Type Structures

Hydrogen provides a serious problem for solid-state chemists since it normally cannot be localized by X-ray crystal structure refinement. Lanthanide metals are almost impossible to dehydride, once hydrogen is used to produce the metal powder, for example, from rods. Most of the lanthanide "dihalides" adopting the MoS_2- or NbS_2-type structures have recently been found to contain previously unexpected hydrogen contamination, i.e., $LaBr_2H_x$ ($x \leq 1$).[41]

The coordination environment around the La atoms is trigonal prismatic. A simple MO calculation for a local [$LaBr_6$] polyhedron yields a one-below-two-below-two level splitting as shown at left in Figure 14. The local coordinate system contains z along the 3-fold axis, resulting in the lowest level being d_{z^2} and the degenerate $d_{x^2-y^2}$, d_{xy} orbitals slightly higher in energy. The remaining degenerate d_{xy}, d_{yz} levels are destabilized by the local Br ligand field.

In the extended structure, similar electronic features may be expected because the La atoms are relatively far from each other. Any interaction between the La atoms, however, will affect the local ligand field splitting and introduce additional orbital mixing (La–La distances are at 409.9 pm). The DOS of the extended structure of "$LaBr_2$" is shown at left in Figure 15. The ordering of the states is Br s, Br p (with some La d (s,p) contribution) and La d (with some Br p (s) contribution) with increasing energy. One d block is split off below the main d block, being half-filled with one electron. The corresponding low-lying single band does not show a significant dispersion throughout the reciprocal space and also no band crossings. It appears to be the weakly metal–metal bonding combination, mainly formed by d_{z^2}, $d_{x^2-y^2}$, d_{xy} orbitals, as they are allowed to mix in the absence of the zone center.

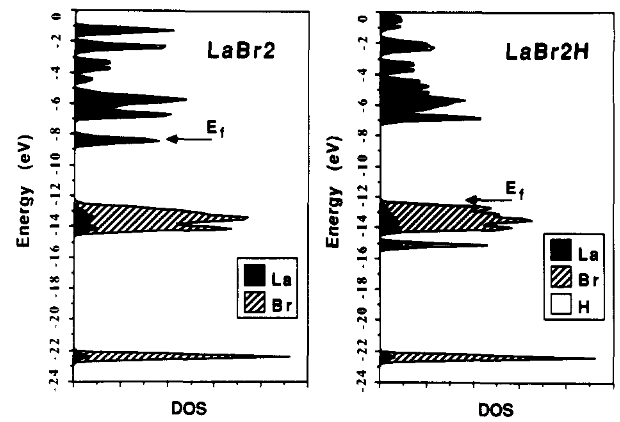

Figure 15. DOS (density of states) projections of the "$LaBr_2$" and the $LaBr_2H$ structures. Fermi levels are indicated as E_f.

Occupation with only one electron instead of two appears to be rather unusual. This energy splitting favors a d^2 system, especially if one notes that this low-lying block is La–La bonding as a whole. Therefore, one may expect a susceptibility for oxidation. Indeed the compound contains hydrogen, presumably located in the triangular centers of the metal layers where we would consider the metal electrons to be located, in three-center one-electron bonds, which then become four-center two-electron bonds with the presence of hydrogen.

A general interaction scheme with hydrogen is provided in the MO diagram in Figure 14. The d_{z^2} orbitals are allowed to mix with the hydrogen 1s orbital to form the bonding combination located at low energy. The antibonding combination is pushed way up in energy.

In the extended structure we must consider the same basic interaction as in the MO, but in addition the $d_{x^2-y^2}$ and d_{xy} orbitals are allowed to mix with the d_{z^2} orbitals. The former low-lying metal–metal bonding d block ("$LaBr_2$") is converted into a metal–hydrogen, metal–metal bonding block ($LaBr_2H$). Electrons in these states are located predominantly in hydrogen orbitals ($H^{0.6-}$). Since the hydrogen content in $LaBr_2H$ seems to be somewhat less than unity, the "real" electronic situation appears to be in between the two DOS curves shown in Figure 15. We conclude that for $LaBr_2H_x$ with $x < 1$ not all of the low-lying d states of "$LaBr_2$" are involved to interact with hydrogen 1s orbitals, providing remaining d states just below the main d block. Thus, for the composition $LaBr_2H$ insulating behavior would be expected with the Fermi level located at the upper edge of the Br p block (4-eV bandgap); whereas for $LaBr_2H_x$ ($x < 1$), a semiconducting behavior should be obtained, depending on the degree of localization of electrons in non-hydrogen-centered metal triangles in three-center one-electron bonds. Similar electronic conditions have been described for the TaS_2H_x (MoS_2 type)[42] and $YSeH_x$ (WC type)[43] structures.

The incorporation of hydrogen in halide-uncapped hexagonal metal arrangements, with typical M–H distances around 230 pm, seems to be unique for many compounds if a structure cannot provide the preferred tetrahedral or less-preferred octahedral voids.

Hydrogen Intercalated Monohalides

Of the originally suggested binary metal monohalides of the transition and rare-earth metals, only ZrCl and ZrBr[44] have been realized, although both incorporate hy-

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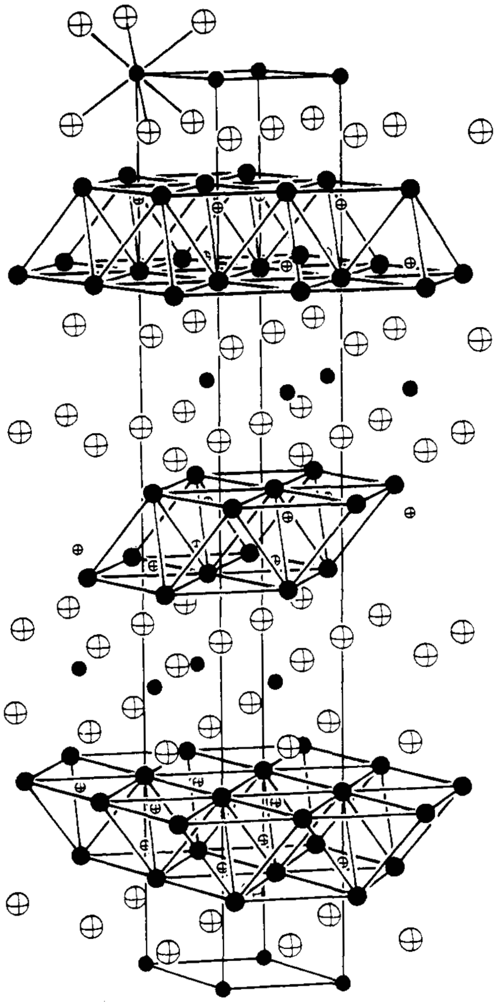

Figure 16. Perspective view of the crystal structure of $Li_{0.15}YClD_{0.65}$ with deuterium in tetrahedral interstices between double layers of yttrium. Lithium occupies octahedral holes between chloride layers.

drogen under mild conditions to form ZrXH.[45] In these structures two hydrogen atoms are located in one $[Zr_6]$ octahedron, capping two opposite triangular faces. The stacking sequence of halide and zirconium layers changes from AbcA in ZrX to AbaB in ZrXH. The D–D distances in ZrBrD are relatively short (220 pm).[46] As a result, the electronic structure (DOS) exhibits two low-lying Zr–H bonding states: the in-phase and the out-of-phase H–H interaction which, of course, are fully occupied with electrons (nonbonding H–H). Such conditions have been outlined previously and are known as the "Switendick" criterion:[47] when a H–H separation is forced to be lower than 210 pm, fully occupied hydrogen states become significantly antibonding and the structure is destabilized. This may be the reason that the intercalation of hydrogen in ZrXH occurs very easily (50 Torr, 400 °C). The remaining two electrons of the d^2 system (ZrXH) occupy the lowest portion of the d block that is slightly split off below the conduction block.

Hydrogen in tetrahedral interstices has been reported for rare-earth halides MXH_n (M = Sc, Y, La, Gd, Tb; X = Cl (Br)) in which n varies between about 0.6 and 0.9. An upper phase boundary of $n = 2$ leads to valence compounds such as $TbBrD_2$[48] and $GdClH_2$ where octahedral and tetrahedral voids of the metal arrangement are occupied by hydrogen. The electronic preferences in these and the above ZrX(H) structures have been discussed by Burdett and Miller.[49]

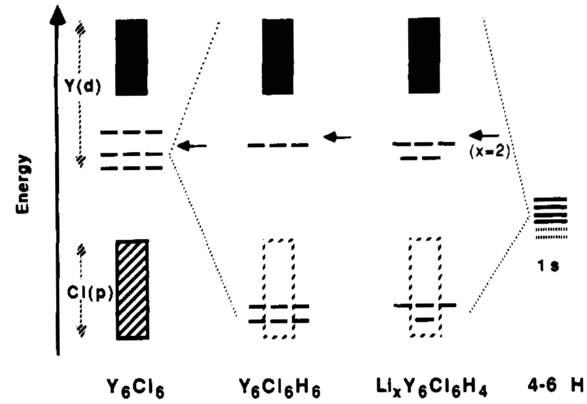

Figure 17. Crystal orbital interaction diagram of $[Y_6Cl_6]$ ("YCl") with four and six hydrogen atoms, respectively. Fermi levels are indicated by an arrow for 12 d electrons (Y_6Cl_6), 18 d-1s electrons ($Y_6Cl_6H_6$), and 18 d-1s electrons ($Li_xY_6Cl_6H_4$).

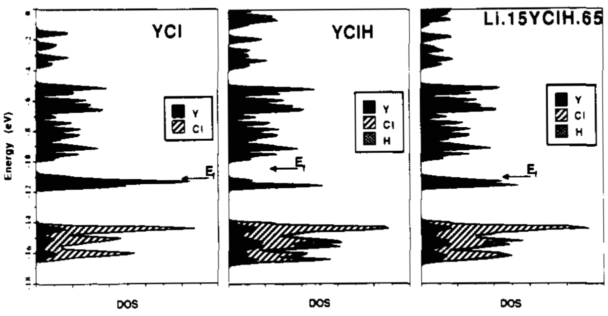

Figure 18. DOS of "YCl", YClH and $Li_{0.15}YClH_{0.65}$. Fermi levels are indicated as E_f.

Lithium and Hydrogen Intercalated Yttrium Monochloride

The structure of Li_zYClH_x consists of ZrBr-like slabs (AbcA) that are arrayed in a three-slab rhombohedral cell. The composition $Li_{0.15}YClD_{0.65}$ has been verified by neutron diffraction.[50] Hydrogen occupies tetrahedral interstices of the metal arrangement and Li interconnects the halide double layers, being situated in an octahedral coordination environment (Figure 16).

The electronic structure of $[Y_6Cl_6]$ exhibits nine low-lying d states (three states for $[Y_2Cl_2]$), as shown in the crystal orbital interaction diagram in Figure 17. These d levels contain twelve electrons for $[Y_6Cl_6]$. Six out of the nine low-lying metal levels are of appropriate symmetry (at Γ: $4d_{z^2}$, 5s, $5p_z$) to interact with six hydrogen 1s orbitals. Because of orbital interactions with hydrogen 1s orbitals, these levels split, whereas the Y–H bonding combinations are lowered in energy, being located within the Cl(p)–Y bonding block. The Y–H antibonding combination is pushed way up in energy.

For the composition $Y_6Cl_6H_6$, three levels remain pure Y–Y bonding states, now containing six electrons, because of the six electrons provided by hydrogen. For the composition $Li_{0.9}Y_6Cl_6H_4$ ($=Li_{0.15}YClH_{0.66}$) only four instead of six d levels are lowered in energy by the interaction with

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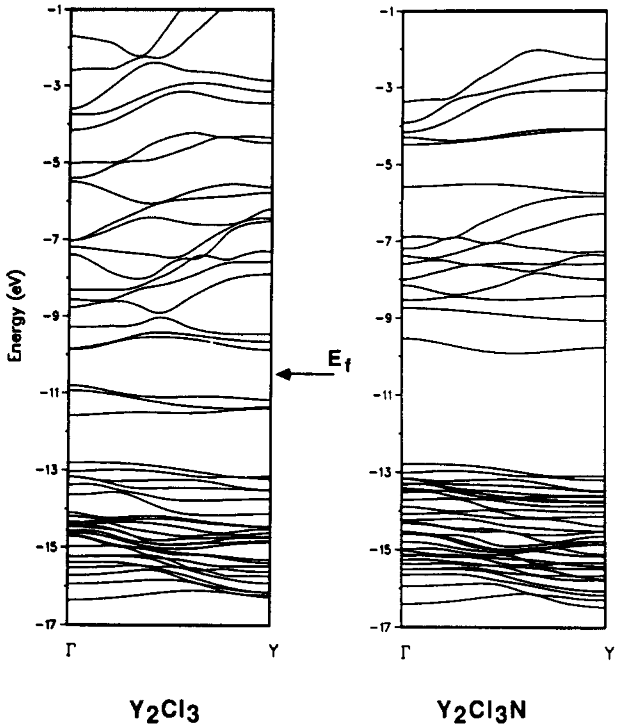

Figure 19. Band structures of Y_2Cl_3 and β-Y_2Cl_3N (two formula units each). The Fermi level is indicated for the d^6 count in Y_2Cl_3.

hydrogen, leaving five pure d states being occupied by eight electrons. Approximately one more electron is provided by the Li ($2s^1$) orbital that is located significantly higher in energy than the bottom of the d block. Therefore, there is a total of nine electrons occupying the lower portion of the Y d block. Although this block, with the Fermi level close to its upper edge, is separated by a 0.7 eV trough from the main d states (Figure 18) there falls a small but nonzero density of states into this gap. This is caused by a semimetallic band shape without crossings of bands in this region. Thus, electronic mobility is expected to be very limited and semiconductive properties may prevail to the expected ionic conductivity of the Li atoms.

Yttrium Sesquichloride and Yttrium Sesquichloride Nitride

Y_2Cl_3 forms an unusual structure containing infinite chains of metal octahedra sharing opposite edges.[51] Chlorine atoms are located over triangular faces of the octahedra and as bridges between the chains of octahedra. Several isostructural sesquihalides have been described (Gd_2Cl_3, Gd_2Br_3, Tb_2Cl_3),[52] of which Gd_2Cl_3 has been shown to be a semiconductor. Similar semiconductive behavior should occur for Y_2Cl_3.

The calculated band structure for two formula units of Y_2Cl_3 shows three metal-based bands located around −11 eV above the main Cl(p) bands and below the main Y(d) bands (Figure 19). These three bands are completely filled with six electrons being separated from the conduction bands by a 0.9-eV bandgap.

Two yttrium sesquichloride nitrides have been described, β-Y_2Cl_3N and (α-)Y_2Cl_3N[53] (also β-Gd_2Cl_3N[53] and (α-)Gd_2Cl_3N),[54] of which the α-type structure contains nitrogen-centered Y_4 tetrahedra that are linked via opposite edges to form infinite chains. (α-)Y_2Cl_3N and (α-)Gd_2Cl_3N are saltlike insulators with a bandgap of about 4 eV.[55]

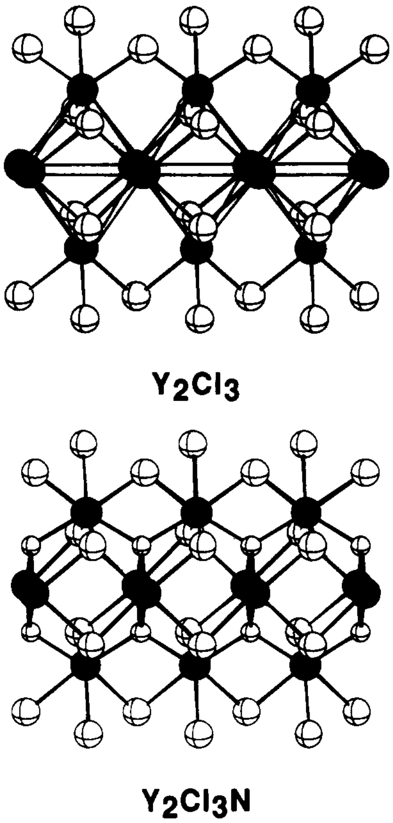

Figure 20. Section of an infinite chain in the structure of Y_2Cl_3 and β-Y_2Cl_3N. Y atoms are solid black, N atoms are small spheres.

β-Y_2Cl_3N and β-Gd_2Cl_3N (Figure 20) are isostructural with Y_2Cl_3. Nitrogen atoms occupy tetrahedral interstices between the $[Y_6]$ octrahedra above and below the shared cluster edges that define the infinite chains. The nitrogen content in these compounds is thought to be slightly deficient ("$Y_2Cl_3N_{0.8}$"), according to the X-ray structure refinement.

The band structure of β-Y_2Cl_3N is shown in Figure 19. Because of orbital mixing of Y(d) orbitals with N(s,p) orbitals, two of the formerly three low-lying d bands in Y_2Cl_3 are pushed up in energy. Thus, one d band remains to be located below the d band core that is empty for the composition Y_2Cl_3N. The bonding Y–N interactions are located at lower energy, within the main Cl(p) block. Due to nitrogen deficiency ("$Y_2Cl_3N_{0.8}$"), the single d band is occupied with a small residue of less than one electron depending on the exact composition. In fact, a small fraction of metal states also adds to this band with decreasing N content. This leads to weak metal–metal bonding along the shared edge of the chains of octahedra and may prevent the breakdown of the structure.

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