The Divalent State in Solid Rare Earth Metal Halides

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1 SUMMARY

Lanthanide compounds with the lanthanide in the +2 oxidation are known for chalcogenides and halides. Binary examples are EuO and TmS as well as LaI_2 and $NdCl_2$. Two cases of electronic configurations have to be distinguished, $[Xe]6s^0 5d^0 4f^n$ and $[Xe]6s^0 5d^1 4f^{n-1}$. The former with electrons occupying only 4f orbitals are salt-like insulators and their crystal chemical behavior is very similar to that of the respective alkaline-earth compounds. In the latter, there is one voluminous, outer-shell 5d orbital occupied. This 5d electron might be localized and involved in chemical bonding in cluster complexes (these are the subject of chapter *Rare Earth Metal Cluster Complexes*). It may also be delocalized into a 5d band causing semiconducting or metallic behavior. In this chapter, only halides of both classes of compounds are discussed.

2 INTRODUCTION

The lanthanides (R, lanthanum through lutetium) have, as atoms in the oxidation state ± 0, the general electronic configuration $[Xe]6s^2 5d^1 4f^n$ with $n = 0$ for La and $n = 14$ for Lu. In the trivalent state, as R^{3+} ions, their electronic configuration is, accordingly, $[Xe]6s^0 5d^0 4f^n$. In the divalent state, the $6s^0$ electrons are released but the electronic configuration may be $[Xe]6s^0 5d^0 4f^n$ or $[Xe]6s^0 5d^1 4f^{n-1}$. This phenomenon is called *(electronic) configuration crossover*; symbolically, the first configuration is addressed as R^{2+} and the second one as $R^{3+}(e^-)$. Structurally, lanthanides with the R^{2+} configuration act as pseudo alkaline-earth ions; Eu^{2+} has, for example, the same ionic radius as Sr^{2+}. The $R^{3+}(e^-)$ configuration leads to metallic or half-metallic compounds or to cluster complexes. The latter is discussed in *Rare Earth Metal Cluster Complexes*.

Halides of the lanthanides in the oxidation state +2 have been known since the early decades of the twentieth century. $EuCl_2$, $SmCl_2$, and $YbCl_2$ were the first to be reported.[1–5] For these 3 elements, all 12 possible halides are known. This is not the case for the elements thulium, dysprosium, and neodymium for which only the halides of the triad chlorine, bromine, and iodine have been synthesized and crystallographically characterized. They structurally bear close resemblance to the respective alkaline-earth metal halides.[6,7] The electronic configurations of the M^{2+} ions of these six elements are $6s^0 5d^0 4f^n$ with $n = 4$ (Nd), 6 (Sm), 7 (Eu), 10 (Dy), 13 (Tm), and 14 (Yb).

Diiodides RI_2 of the elements lanthanum, cerium, praseodymium, and gadolinium are also known. These were once called *metallic diiodides*;[8] in these the electronic configuration of the respective lanthanide is $[Xe]6s^0 5d^1 4f^{n-1}$ and the 5d electron is delocalized in a 5d band.[9–12]

Although scandium is not a lanthanide element, it belongs to the group of rare earth elements. Scandium diiodide should be mentioned in this connection. It is a special case as it is a scandium-deficient compound, $Sc_{0.9}I_2$. It does, however, qualify as a member of the $R^{3+}(e^-)$ group, at sufficiently high temperatures.[13,14]

All of the dihalides, insulators or metallic, are produced as solids either by comproportionation reactions[15,16] or by *Wöhler*'s metallothermic reduction from the trihalides with alkali metals.[7,17]

3   SYNTHESIS

3.1   Reduction Methods in General

The reduction of rare earth metal trihalides, RX_3, is in principle possible with all kinds of reducing agents as long as they have standard electrode potentials $E°$ that can overcome that of the respective potentials of $E°$ ($R^{3+} \rightarrow R^{2+}$). This is discussed below in more detail. Therefore, the classical reducing agents, nonmetals such as hydrogen or carbon, or like metals (comproportionation route) and unlike metals (metallothermic reduction) are all possible but (may) lead to different products. Cathodic reduction of appropriate melts is also an option.

Metal oxides or halides may be reduced to the respective metal by a number of reductants; hydrogen and carbon are the most easily available and are inexpensive for large scales. When pure compounds or even metals are desired, the use of carbon as reductant is disadvantageous because the rare earth metals form carbide halides and carbides. These are in fact metallic carbides with carbon atoms occupying octahedral or tetrahedral voids in the metal's lattice. Hydrogen is more advantageous, although hydrides are also ubiquitous with the rare earth metals. However, with sufficient care, hydrogen can be pumped off at elevated temperatures and, subsequently, the metals or compounds may be sublimed or distilled, whatever is possible and feasible.

Indeed, hydrogen has been used in the early days as a reductant, for example, for the trichlorides RCl_3, when the rare earth metals for comproportionation reactions were either not available or were too valuable. As it is a solid–gas reaction, temperature and surface blocking are always a big issue, as also time. Only for europium, ytterbium, and samarium, the dichlorides RCl_2 are stable enough and can be produced at reasonably low temperatures. At higher temperatures and with all the other trichlorides, the metals are produced, actually as hydrides, the hydrogen content depending upon hydrogen pressure and cooling procedures.

The comproportionation reaction is straightforward whenever the respective phase diagrams are known. One can also make use of a melt of some kind. If properly carried out, pure products will be obtained. This method can also be used to prepare ternary and quaternary compounds with the proper choice of starting materials. The only problem here is that the phase diagrams are in most cases not known. This research is, therefore, exploratory and rather serendipitous.

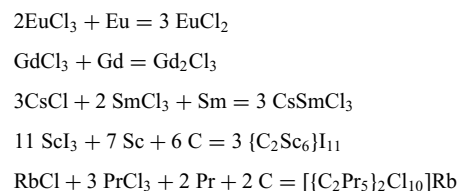The reduction of rare earth metal halides with unlike metals, Wöhler's metallothermic reduction, has originally

been used to produce the rare earth metals. When used properly, intermediates with oxidation states between $+3$ and 0 can be obtained.

Cathodic reduction of appropriate halide melts (mostly chlorides) is an important process to produce rare earth metals, unless in certain cases, lower-valent halides have not been obtained or did not form during the cooling process.

In the following sections, only the comproportionation route and the metallothermic reduction route are discussed as the two most commonly used synthetic methods.

3.2   The Comproportionation Route

The comproportionation route[15,16] is widely used and is very efficient when pure phases are desired, especially when the phase relationships are known. It led to a great variety of ''reduced'' rare earth halides, binary, ternary, and higher, simple and complex salts and such that incorporate metal clusters interstitially stabilized by a nonmetal atom or by a (transition) metal atom; for example,

$$2 EuCl_3 + Eu = 3 EuCl_2$$
$$GdCl_3 + Gd = Gd_2Cl_3$$
$$3 CsCl + 2 SmCl_3 + Sm = 3 CsSmCl_3$$
$$11 ScI_3 + 7 Sc + 6 C = 3 \{C_2Sc_6\}I_{11}$$
$$RbCl + 3 PrCl_3 + 2 Pr + 2 C = [\{C_2Pr_5\}_2Cl_{10}]Rb$$

One disadvantage of this route is the often high reaction temperatures and unknown phase equilibria. Especially when it comes to ''higher'' systems, phase diagrams are not known at all.

It was a great thrust for reduced rare earth metal chemistry when it was discovered that sealed metal ampoules (mostly produced from niobium and tantalum tubing by He arc welding) were reaction containers inert enough to the corrosive molten salts to allow for pure products.[18] Still, all constituents of air need to be excluded, which is possible, thanks to modern dry box techniques. The unintended incorporation of ubiquitous hydrogen or carbon led to a whole new world of cluster complexes with endohedral atoms, mostly with extended structures, as in $\{H_xLu\}Cl$ or in $\{CLu_2\}Cl_2$ (see *Rare Earth Metal Cluster Complexes*).
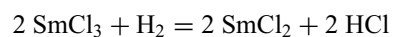
3.3   The Metallothermic Reduction Route

The metallothermic reduction of $SmCl_3$ designed for the preparation of samarium metal with an (apparently) insufficient quantity of sodium, resulting in the formation of $SmCl_2$,[5]

$$SmCl_3 + Na = SmCl_2 + NaCl$$
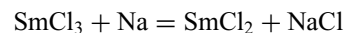
gave birth to a new approach to ''reduced'' rare earth metal halides that were previously synthesized only by the

comproportionation route or by reduction with hydrogen, namely,

$$2\,SmCl_3 + Sm = 3\,SmCl_2$$

$$2\,SmCl_3 + H_2 = 2\,SmCl_2 + 2\,HCl$$

In principle, the same experimental techniques as outlined above for the comproportionation route may be used for the reduction of rare earth metal halides with unlike metals, i.e., the metallothermic reduction route,[7,17] with low melting and highly electropositive metals, alkali, and alkaline-earth metals in particular. The low melting points of these metals are certainly an advantage, as the reaction temperatures may be much lower than for comparable comproportionation reactions. The most obvious disadvantage is that pure products are in most cases (but note the reaction $Cs + SmCl_3 = CsSmCl_3$) not available as one of the driving forces of this route is the production of high-lattice-energy alkali-metal halides.

The separation of the products is not easy, although not impossible. For the exploration of the respective systems and their phase contents, it is, however, often not necessary to obtain pure products because modern, fast X-ray crystallography is an easy means to analyze even multiproduct reactions. Afterwards, when the respective compounds are known, care has to be taken to produce the new compounds in pure phase by whatever route is desirable. One major advantage of the metallothermic reduction route is the fairly low reaction temperatures as these allow for the synthesis and crystal growth of compounds that decompose in the solid state, melt incongruently, or even form and decompose in the solid state at fairly low temperatures. Also, low-temperature modifications may be grown as single crystals below the transition temperature.

4 BINARY HALIDES

Dihalides of the rare earth elements became known shortly after the turn of the twentieth century. A first picture was completed in the late 1920s when it was thought that only the ''classical four,'' europium, ytterbium, samarium, and thulium, could be obtained in the divalent state. *Klemm*
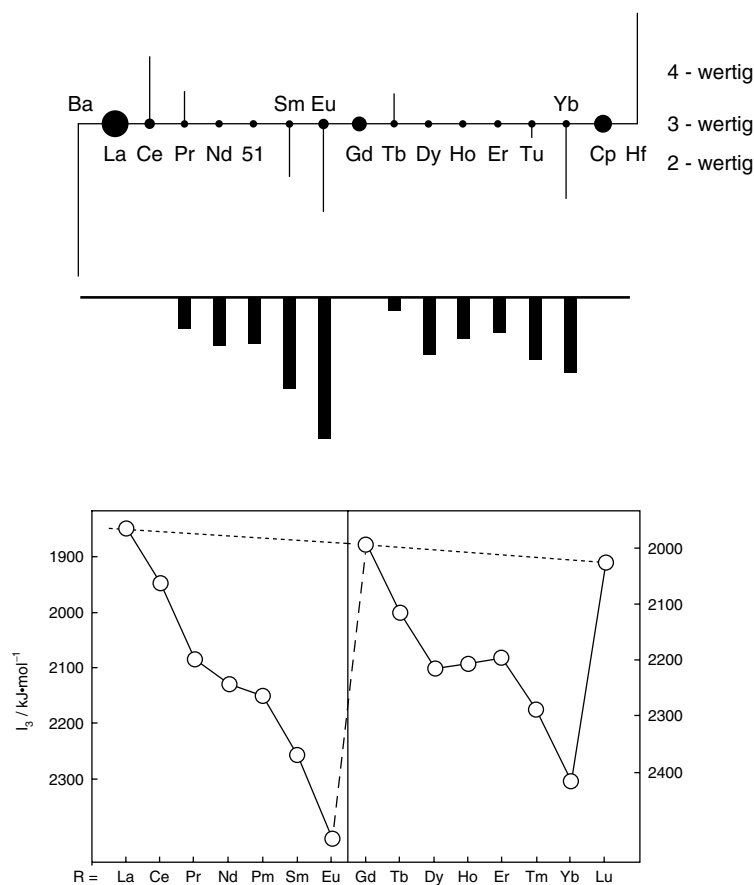

Figure 1 *Klemm*'s graph of 1929/1930 (top) exhibiting lanthanide elements with stable di- and tetravalent compounds; a modern version of this graph for the divalent state is shown in the middle: the difference $\Delta E° = E°\,(Gd^{3+}/Gd^{2+})$ -$E°\,(R^{3+}/R^{2+})$ is plotted to parallel *Klemm*'s graph. Bottom: The third ionization potentials of the lanthanides, $I_3 = \Delta H°\,(3)$, in $kJ\,mol^{-1}$

incorporated this knowledge in his famous graph, which is displayed in Figure 1.[19]

The picture became more complete (but also much more complicated) through the seminal phase diagram determinations by *Corbett* in the third quarter of the twentieth century. These made clear that in a number of other systems, dihalides can be thermodynamically stable under certain conditions; see Figure 2 for the system PrI_3/Pr. The picture

as of today, verified by X-ray crystallographic studies, is summarized in Table 1.

Corbett also discovered a number of other binary reduced lanthanide chlorides, bromides, and iodides through phase diagram determinations and through further exploratory research. For example, there is the scandium-deficient ''scandium diiodide,'' with a composition around $Sc_{0.89}I_2$, and the praseodymium excess $PrCl_{2.31} = Pr_{0.29}PrCl_3$, with
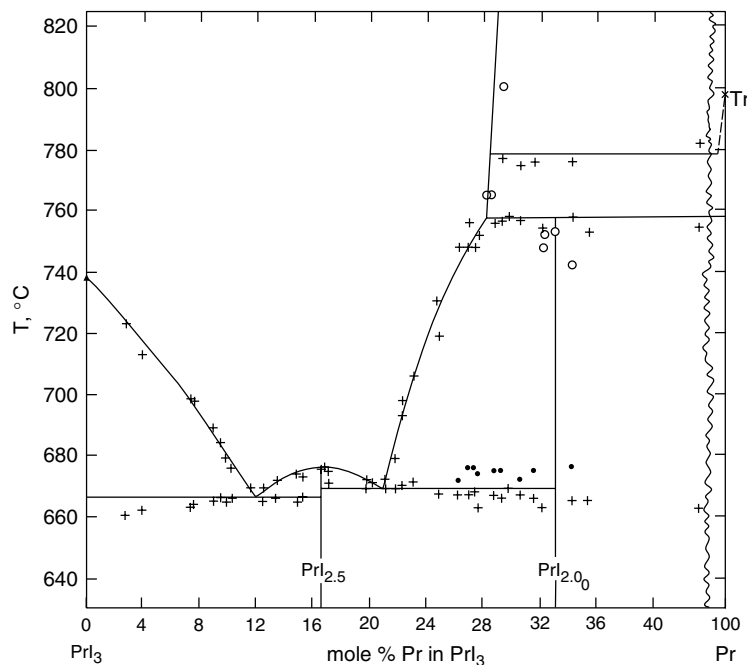

Figure 2   The temperature/composition phase diagram for the system PrI_3/Pr exhibiting the existence of two intermediate compounds, $PrI_{2.5} = Pr_2I_5$ and PrI_2, respectively. (Reprinted from Ref. 9. Reproduced by permission of The Royal Society of Chemistry. DOI: http://dx.doi.org/10.1039/DF9613200079.)

Table 1   Salt-like and ''metallic'' (bold-type) dihalides of the rare earth elements

	Fluoride	Chloride	Bromide	Iodide
Scandium	—	—	—	**$Sc_{0.9}I_2$**
Yttrium	—	—	—	—
Lanthanum	—	—	—	**LaI_2**
Cerium	—	—	—	**CeI_2**
Praseodymium	—	—	—	**PrI_2**
Neodymium	—	$NdCl_2$	$NdBr_2$	NdI_2, **NdI_2**
Promethium	—	—	—	—
Samarium	SmF_2	$SmCl_2$	$SmBr_2$	SmI_2
Europium	EuF_2	$EuCl_2$	$EuBr_2$	EuI_2
Gadolinium	—	—	—	**GdI_2**
Terbium	—	—	—	—
Dysprosium	—	$DyCl_2$	$DyBr_2$	DyI_2
Holmium	—	—	—	—
Erbium	—	—	—	—
Thulium	—	$TmCl_2$	$TmBr_2$	TmI_2
Ytterbium	YbF_2	$YbCl_2$	$YbBr_2$	YbI_2
Lutetium	—	—	—	—

additional praseodymium atoms incorporated in voids of the UCl_3-type structure of $PrCl_3$.[20] A number of sesquichlorides were discovered following Gd_2Cl_3, the ''seventh wonder of the rare earth world,''[21,22] with scandium, yttrium, lanthanum, cerium, terbium, and erbium. And there are R_2X_5-type halides with R = La, Ce, Pr and X = Br, I which have interesting magnetic properties.[23] Finally, there are class I mixed-valence halides, i.e., with R^{2+} (large) and R^{3+} (smaller) ordered in defined positions in their crystal structures for the elements R = Nd, Sm, Eu, Dy, Ho, Tm, Yb, for example, $Dy_5Cl_{11} = (Dy^{2+})_4(Dy^{3+}) (Cl^-)_{11}$.[24]

Although this seems to be rather confusing, there are, of course, reasons. The relative stabilities of the di- and trivalent states of the respective lanthanides throughout the series follow, more or less, the third ionization potentials of the elements, $\Delta H°(3)$ (Figure 1). With a standard electrode potential of $E°(Eu^{2+}/Eu^{3+}) = -0.35$ V (which can be measured in aqueous solution), the ionization potentials or disproportionation enthalpies can be used to calculate standard electrode potentials $E°(R^{2+}/R^{3+})$ for the whole series. This work has essentially been put forward by *Johnson* and *Morss*.[25–27] These results may be summarized graphically as shown in Figure 1. It is evident that the standard electrode potentials perfectly parallel *Klemm*'s chemical intuition and observations. And, of course, the data explain why there are two further elements, neodymium and dysprosium, which form salt-like dihalides. In all of these halides, the rare earth ion R^{2+} has the electronic configuration $[Xe]6s^05d^04f^n$ with n = 4 (Nd^{2+}), 6 (Sm^{2+}), 7 (Eu^{2+}), 10 (Dy^{2+}), 13 (Tm^{2+}), and 14(Yb^{2+}).

These dihalides have crystal structures that are also observed for the respective alkaline-earth halides (see Table 2). Neodymium(II) iodide, NdI_2, undergoes a high-pressure phase transition from salt-like ($SrBr_2$ type of structure) to metallic ($CuTi_2$ type of structure) subject to the configuration crossover $4f^45d^0 \rightarrow 4f^35d^1$.[28] The 5d electron delocalizes into a 5d band with no volume such that the molar volume of $(Nd^{3+})(e^-)(I^-)_2$ is smaller than that of (Nd^{2+}) $(I^-)_2$, a transition which is triggered by pressure.

As can be seen from Table 2, most of the crystal structures that are observed for the rare earth metal dihalides are classical structure types which are known for salts, purely ionic or with some admixture of covalency, with coordination numbers of 9 ($PbCl_2$), 8 (CaF_2, $SrBr_2$), 7 (SrI_2, EuI_2), and 6 ($CdCl_2$, CdI_2). Halides crystallizing in these structure types are insulating salts. The 2H- and 3R-MoS_2 types of structure are intermediate as these layered compounds may generally be insulating or semiconducting and may have very special properties as seen in GdI_2. This is a ferromagnet with a Curie temperature of 313 K, and shows collosal magnetoresistance.[12] The structural chemistry of all of these halides is quite straightforward and classical and shall not be discussed further.

There are the four diiodides LaI_2, CeI_2, PrI_2-I, and HP-NdI_2 that crystallize with the $CuTi_2$ type of structure. These halides are two-dimensional metals that becomes obvious by an inspection of their crystal structure (Figure 3). It is built from 4^4 nets of metal atoms and of iodide ions which are stacked in the [001] direction of the tetragonal unit cell such that the metal atoms are eight-coordinate. R–R distances are between 393 and 386 pm (R = La $\rightarrow$ Pr) at ambient temperature. The metal atoms R, which are in

Table 2 Crystal structures of the rare earth metal dihalides, structure types (ST), coordination numbers (CN), and shortest R–R distances (wherever known)

Salt-like $(R^{2+})(X^-)_2$			''Metallic'' $(R^{3+})(e^-)(X^-)_2$		
RX_2	ST, CN	d(R–R)/pm	RX_2	ST, CN	d(R–R)/pm
$NdCl_2$	$PbCl_2$, 9	451	LaI_2	$CuTi_2$, 8	393.6(1)
$NdBr_2$	$PbCl_2$, 9	—	CeI_2	$CuTi_2$, 8	388.8(1)
SmF_2	CaF_2, 8	415	PrI_2-I	$CuTi_2$, 8	386.4(2)
$SmCl_2$	$PbCl_2$, 9	449	PrI_2-II	2H-MoS_2, 6	—
$SmBr_2$	$SrBr_2$, 8	—	PrI_2-III	3R-MoS_2, 6	—
SmI_2	EuI_2, 7	501	PrI_2-IV	$CdCl_2$, 6	426.5(1)
EuF_2	CaF_2, 8	413	PrI_2-V	own, 6	391.3(2)
$EuCl_2$	$PbCl_2$, 9	448	HP-NdI_2	$CuTi_2$, 8	384.3(1)
$EuBr_2$	$SrBr_2$, 8	—	GdI_2	2H-MoS_2, 6	407.5
EuI_2-I	own, 7	486	$Sc_{0.89}I_2$	CdI_2, 6	410.2(1)
EuI_2-II	SrI_2, 7	—	—	—	—
$DyCl_2$	$SrBr_2$, 8	—	—	—	—
$DyBr_2$	SrI_2, 7	457	—	—	—
DyI_2	$CdCl_2$, 6	462	—	—	—
$TmCl_2$	SrI_2, 7	432	—	—	—
$TmBr_2$	SrI_2, 7	—	—	—	—
TmI_2	CdI_2, 6	452	—	—	—
YbF_2	CaF_2, 8	396	—	—	—
$YbCl_2$	SrI_2, 7	432	—	—	—
$YbBr_2$	SrI_2, 7	437	—	—	—
YbI_2	CdI_2, 6	450	—	—	—

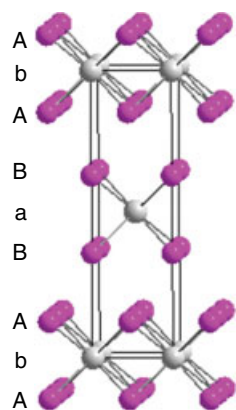**Figure 3** Crystal structure (tetragonal) of the rare earth metal diiodides LaI_2, CeI_2, PrI_2-I, and HP-NdI_2; projection approximately down [100]

the oxidation state $+2$, have the electronic configuration $[Xe]4f^n5d^1$ with $n = 0$ (La), 1 (Ce), 2 (Pr), and 3 (Nd). There is the paramagnetism of one to three core-like 4f electrons in CeI_2, PrI_2-I, and HP-NdI_2, respectively. The 5d electron is, however, not localized; rather it is delocalized in a two-dimensional 5d band which makes these compounds two-dimensional metals, similar to graphite. LaI_2 is a special case because here lanthanum has just one valence electron left. CeI_2 has one 4f and one 5d electron. It therefore is not only a metal but it also exhibits antiferromagnetism at temperatures below 10 K.[29]

Unfortunately, PrI_2-I has never been obtained as a pure phase except for single crystals suitable for structure determination by X-ray diffraction. PrI_2-IV, which exists only at high temperatures, crystallizes in principle with the $CdCl_2$ structure and appears to incorporate an additional 10% of praseodymium atoms in octahedral voids between the layers which are empty in the parent structure. On cooling, the surplus metal can be released either from the additionally occupied voids or from regular interstices. The layers of 3^6 nets as found in all of the structures of PrI_2-II, -III, -D, -IV, and -V may be arranged differently. The transition from a 3^6 to a 4^4 net as observed in PrI_2-I is an easy task. Structurally, it is a shear process (see Figure 4).[11]

Nucleation probabilities and enthalpies for the transition from PrI_2-IV on cooling to all the others must be very similar. The temperatures for the beginning of the nucleation in equilibrium are not known. Therefore, when cooling PrI_2-IV from, say, 700 °C to ambient temperature, a mixture of I–V (except IV), depending on the cooling process, is always obtained. Hydrogen stabilizes PrI_2-D (D for disorder), which is a polytype of II and III. PrI_2-V is unique among the rare earth metal diiodides. It is a perfectly ordered variant of the $CdCl_2$ type of structure in which iodide layers are stacked in the cubic face-centered ...ABC... manner and octahedral holes between these layers are either all occupied

(1) or all empty (0). In PrI_2-V, they are filled to 0.75 and 0.25, and in α-ZrI_2, another derivative, the ratio is 0.5/0.5.[11]

The only rare earth metal diiodides that crystallize in the $CdCl_2$ type of structure are PrI_2-IV and DyI_2. Interestingly enough, the elements praseodymium and dysprosium are homologs (see Figure 5) with electronic configurations for Pr^{2+} of $[Xe]4f^35d^0$ or $[Xe]4f^25d^1$ and Dy^{2+} of $[Xe]4f^{10}5d^0$ (or $[Xe]4f^95d^1$).

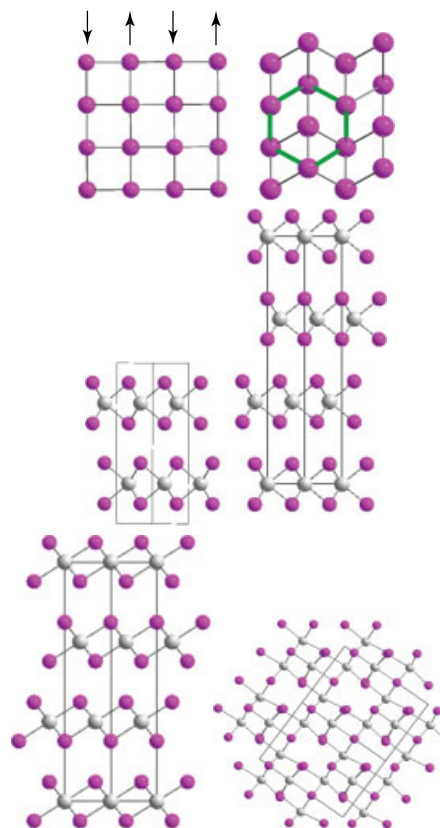An idea about the electronic structures of PrI_2 and DyI_2 can be obtained from band structure calculations.[30]

Figure 4 The shear transition from a 4^4 to a 3^6 net (above), the crystal structures of PrI_2-II and -III (middle), as well as of (bottom) PrI_2-IV and -V in equivalent projections showing the layer sequences

Figure 5 A periodic system of the rare earth elements, colored for the examples of the diiodides RI_2. Blue, $5d^04f^n$ configuration; red, $5d^14f^{n-1}$ configuration
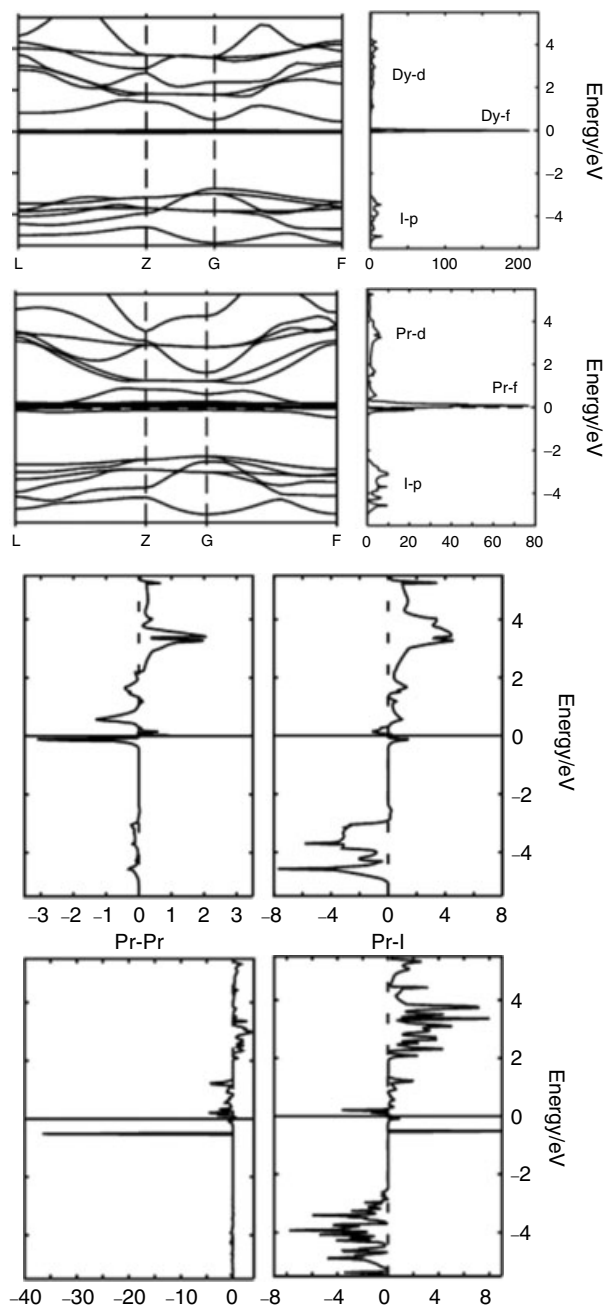
Figure 6 The electronic structures of DyI_2 and PrI_2-IV and -V. Shown are from top to bottom, the band structures of DyI_2 and PrI_2-IV and 5d densities of states (DOS) derived therefrom. Crystal overlap Hamiltonian population (COHP) curves for PrI_2-IV and -V) for Pr–Pr and Pr–I bonding (to the left, negative signs) and antibonding interactions (to the right) are exhibited

From these, the density of states (DOS) can be derived, either for the whole unit cell content or for certain atoms or atom types. This is shown in Figure 6. The DOS curves for the isostructural DyI_2 and PrI_2-IV show that the 4f and 5d states are much more separated for DyI_2; for PrI_2-IV, they

overlap and, more importantly, the 5d state is considerably lower in energy and touches the Fermi level. The crystal orbital Hamiltonian population (COHP) curves, also derived from band structure calculations, show furthermore that there are considerable Pr–Pr bonding interactions just below the Fermi level (lower left of Figure 6). They outweigh the Pr–I antibonding interactions that also appear in this energy region. Hence, for PrI_2-IV, the rather large 5d orbitals can interact and contribute further to the stabilization of the compound. This is apparently not possible for the smaller 5d orbitals in DyI_2 (seven additional protons). As a result, DyI_2 is a salt under ambient conditions. This result is also reflected in the R–R distances in PrI_2-IV (426 pm) and DyI_2 (462 pm), which are against the trend of the lanthanide contraction.

Further stabilization of PrI_2 is possible through the transition IV → V on cooling, which results in the formation of tetrahedral {Pr_4} clusters. This stabilization can be ''seen'' through the shrinkage of the Pr–Pr distances to 392 pm. In the COHP curves, bonding interactions are considerably lower in energy.

The diiodides of thulium and ytterbium, TmI_2 and YbI_2, crystallize with the CdI_2 type of structure and are salts. Scandium diiodide crystallizes also with this structure but is scandium deficient, Sc_xI_2 ($x = 0.87$, 0.93 from different structure determinations; we refer to it with a $Sc_{0.89}I_2$ in the following).[14] $Sc_{0.89}I_2$ is interesting because 4f electrons cannot be involved. It is the first 3d element, and the 3d orbitals are the most expanded in the fourth period. $Sc_{0.89}I_2$ is a metal above about 100 K, hence the electronic configurations are $[Ar]4s^0 3d^1$ and $[Ar]4s^0 3d^0$, above and below 100 K. According to the formulation $Sc_{0.89}I_2 \times 9 = Sc_8I_{18} = (Sc^{3+})_8(e^-)_6(I^-)_{18}$ (see Figure 7), there are only six electrons for eight scandium atoms which occupy

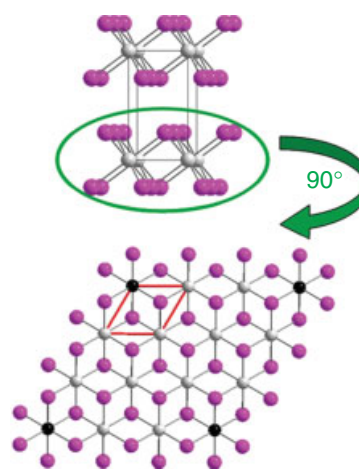**Figure 7** Crystal structure of $Sc_{0.89}I_2$. (a) CdI_2 type of structure. (b) A model for the under-occupation of one out of nine octahedral voids, leading, in principle, to a 3×3 larger unit cell

statistically the nine octahedral holes provided in the CdI_2-like structure of $Sc_{0.89}I_2$. At temperatures above 100 K, these electrons delocalize and (partly) fill the 3d band. The under-occupation of the scandium sites lowers the Fermi level and thereby appears to stabilize the whole structure (fighting the antibonding Sc–I interactions around the Fermi level). Below 100 K, the six electrons localize and $Sc_{0.89}I_2$ becomes an insulating, paramagnetic, mixed valent iodide according to $(Sc^{2+})_6(Sc^{3+})_2(I^-)_{18}$.

5   TERNARY HALIDES

Complex halides are generally obtained from the binary components; for example,

$$CsCl + TmCl_2 = CsTmCl_3$$
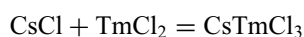
To avoid the tedious production of thulium(II) chloride, $TmCl_2$, by the comproportionation reaction

$$2TmCl_3 + Tm = 3TmCl_2$$

a ''one-pot'' reaction can also be carried out.

$$Cs + TmCl_3 = CsTmCl_3$$
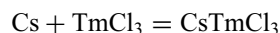
This works in principle for the rare earth elements R = Nd, Sm, Eu, Dy, Tm, and Yb. In the case of the other rare earth elements which have much higher third ionization potentials I_3, partial reduction to the metals and the formation of ternary rare earth metal(III) halides is observed; for example,

$$3\,Li + 4\,GdCl_3 = 3\,GdLiCl_4 + Gd$$
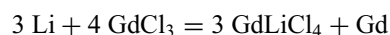
The structural chemistry of $GdLiCl_4$ and other ternary lanthanide(III) halides such as Na_3GdCl_6 is not the subject of this chapter, but is discussed in a handbook article.[31] There are a few reduced ternary compounds, however, with R = La, Ce, Pr, which have similar behavior as the respective dihalides.

The metallothermic reduction with sodium appears to be special, as Na^+ has an ionic radius very similar to that of the large trivalent lanthanides, R^{3+}. Therefore, the reduction of all of the trichlorides RCl_3 that crystallize with the UCl_3 type of structure with sodium produces stuffed derivatives of this structure, $Na_{0.5}RCl_3$ or NaR_2Cl_6. These have been crystallographically characterized for R = Ce, Pr, Nd, Sm, Eu (see Figure 8).[5] Two classes need to be considered: Those with R = Ce, Pr are one-dimensional metals, in accord with the formulation $(Na^+)(R^{3+})_2(e^-)(Cl^-)_6$. The others with R = Nd, Sm, Eu are mixed-valent chlorides, $(Na^+)(R^{2+})(R^{3+})(Cl^-)_6$.
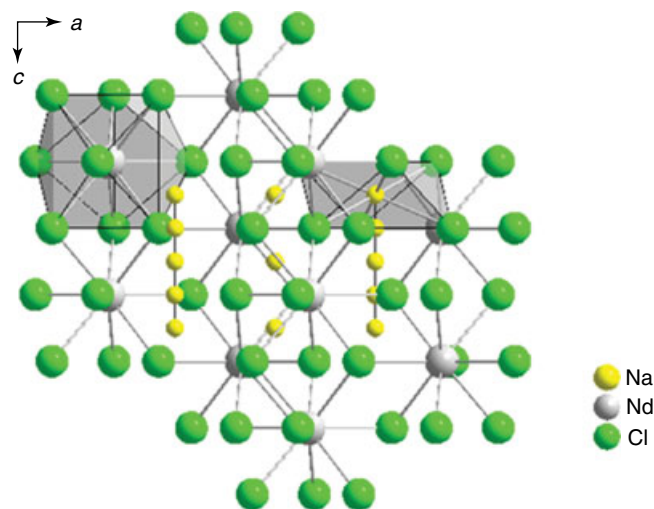

Figure 8   Crystal structure of the stuffed derivatives of the UCl_3 type of structure: additional (yellow) sites along the hexagonal c axis are occupied statistically by Na^+ in NaR_2Cl_6 and by Pr^{3+} in $PrCl_{2.31}$ (= $Pr_{0.58}Pr_2Cl_6$)
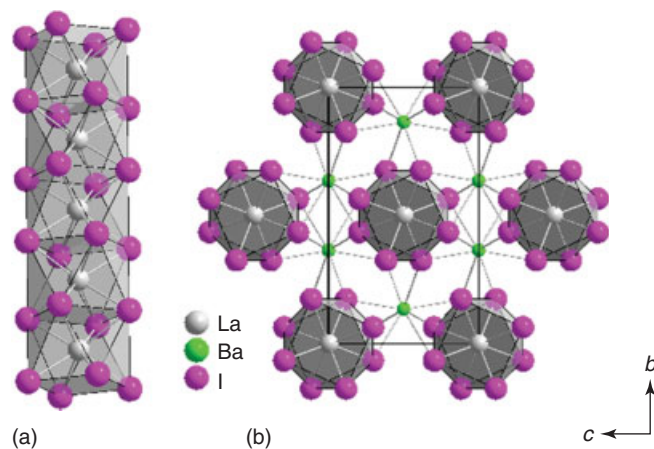

Figure 9   Crystal structure of ARI_4-type iodides exhibiting chains of face-sharing $[RI_{8/2}]$ square antiprisms (a) and their connection via A^{2+} cations (b), A = Sr, Ba, Nd, Sm, Eu; R = La, Ce

The enigmatic black $PrCl_{2.31}$ falls in the first class too, i.e., $(Pr^{3+})_{0.58}(Pr^{3+})_2(e^-)_{1.74}(Cl^-)_6$, with 58% of the additional sites occupied.[20]

Lanthanum and **cerium** triiodide, LaI_3 and CeI_3, when reduced with strontium or barium or with the *pseudo* alkaline-earth metals neodymium, samarium, and europium, yield ARI_4-type iodides, A = Sr, Ba, Nd, Sm, Eu; R = La, Ce.[32] These are built from square-antiprismatic $[MI_8]$ polyhedra sharing common faces to columns running parallel [100] (Figure 9). Although these iodides have one excess electron per formula unit, e.g., $(Ba^{2+})(La^{3+})(e^-)(I^-)_4$,
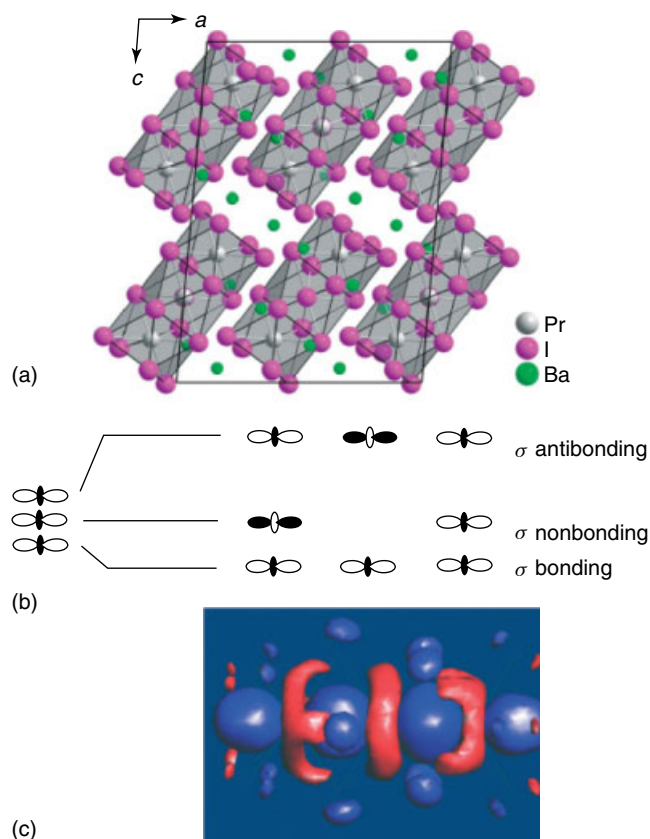
Figure 10 Crystal structure of $Ba_6Pr_3I_{19}$ (a) and the interaction scheme of three linearly oriented d_{z2} orbitals as well as the σ bonding three-center-two-electron orbital (b)

a *Peierls* distortion could not be detected, perhaps subject to matrix constraints. The structures are one-dimensional derivatives of the $CuTi_2$-type rare earth diiodides RI_2 (R = La, Ce) where $[RI_8]$ cubes are connected via four common faces to layers (see Figure 9).

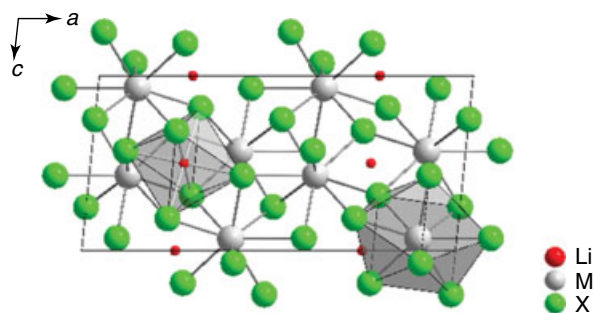Surprisingly, with *praseodymium*, an analogous iodide could not be synthesized. Rather, $Ba_6Pr_3I_{19}$ was

Figure 11 Crystal structure of LiR_2X_5 (R = Dy, Tm, Yb; X = Cl, Br)

obtained as single crystals from a reduction of PrI_3 with barium. This compound contains linear trimers, $[Pr_3I_{16}]$, consisting of three PrI_8 square antiprisms sharing two common faces (Figure 10). According to $(Ba^{2+})_6(Pr^{3+})_3(e^-)_2(I^-)_{19}$, there are two electrons available for an open two-electron-three-center bond.[33]

With the smaller, harder rare earth elements (Gd through Lu), such compounds have never been seen, except for *scandium* where scandium-deficient hexagonal perovskites, ASc_xX_3 (A = Rb, Cs; X = Cl, Br, I), have been observed.[14] These are discussed together with the perovskite-type halides of R = Sm, Eu, Dy, Tm, Yb below. All other complex halides with reduced rare earth metals contain clusters and are discussed in *Rare Earth Metal Cluster Complexes*.

Divalent *europium, ytterbium, samarium, thulium, dysprosium, and neodymium* can be incorporated in ternary AX/RX_2 compounds.[6,24,31] With the larger rare earth elements, R = Nd, Sm, Eu, mixed-valent $Na[R_2Cl_6]$ chlorides are obtained, which crystallize with a stuffed UCl_3-type structure, as described above. In the systems LiX/RX_2 with the smaller rare earth elements R = Dy, Tm, Yb, the ternary halides LiR_2Cl_5 and $LiDy_2Br_5$ are obtained as single crystals. In this crystal structure, which is known also from FeU_2S_5, R^{2+} is eight-coordinate (bicapped trigonal prism) and the polyhedra are connected to a three-dimensional network (Figure 11).

With the larger alkali metals, potassium, rubidium, and cesium, the perovskite-type structure with its variants plays an important role.[6,31,34] The usual concepts, radius ratios including *Goldschmidt*'s tolerance factor, structure field diagrams, or volume considerations derived from *Biltz*'s concept of volume increments may be used to classify these compounds and their behavior at different temperatures.[34] For example, $CsTmCl_3$ crystallizes with *the* (cubic) perovskite type of structure (Figure 12); $CsTmBr_3$ and $CsTmI_3$ with tetragonal and orthorhombic variants with octahedral tilts; and $CsSc_{0.71}Cl_3$ with the so-called hexagonal perovskite structure (Figure 12), isostructural with, for example, $CsNiCl_3$. In the ''perovskites,'' the R^{2+} cations are surrounded octahedrally by halide ions (in the variants symmetry elements as the four- and the threefold axes are given up), and common vertices or faces are shared to ensure the *Niggli* notation $A[RX_{6/2}]$. Variants with edge-sharing octahedra were also observed; $KTmI_3$ ($FeUS_3$ type) and $RbTmI_3$ (NH_4CdCl_3 type) are examples (Figure 12). Isolated octahedra occur in $Rb_4[YbI_6]$, K_4CdCl_6 type of structure, which is the only example of that kind in rare earth halide chemistry.

With the larger lanthanides, with neodymium, samarium, and europium, a structure type was observed which may envelope many different compositions as K_2SmCl_5, KSm_2Cl_5, $K_3Nd_3Br_{10}$, and $K_8Nd_7I_{25}$.[31] The parent crystal structures are $U_3Se_5/PbU_2S_5/Y_2HfS_5/K_2PrCl_5$ and $TlPb_2Cl_5/NH_4Pb_2Cl_5$. They have unit cells of the same shape. However, the first are orthorhombic (*Pnma*) and the latter monoclinic (*$P2_1/c$*, with a β angle very close
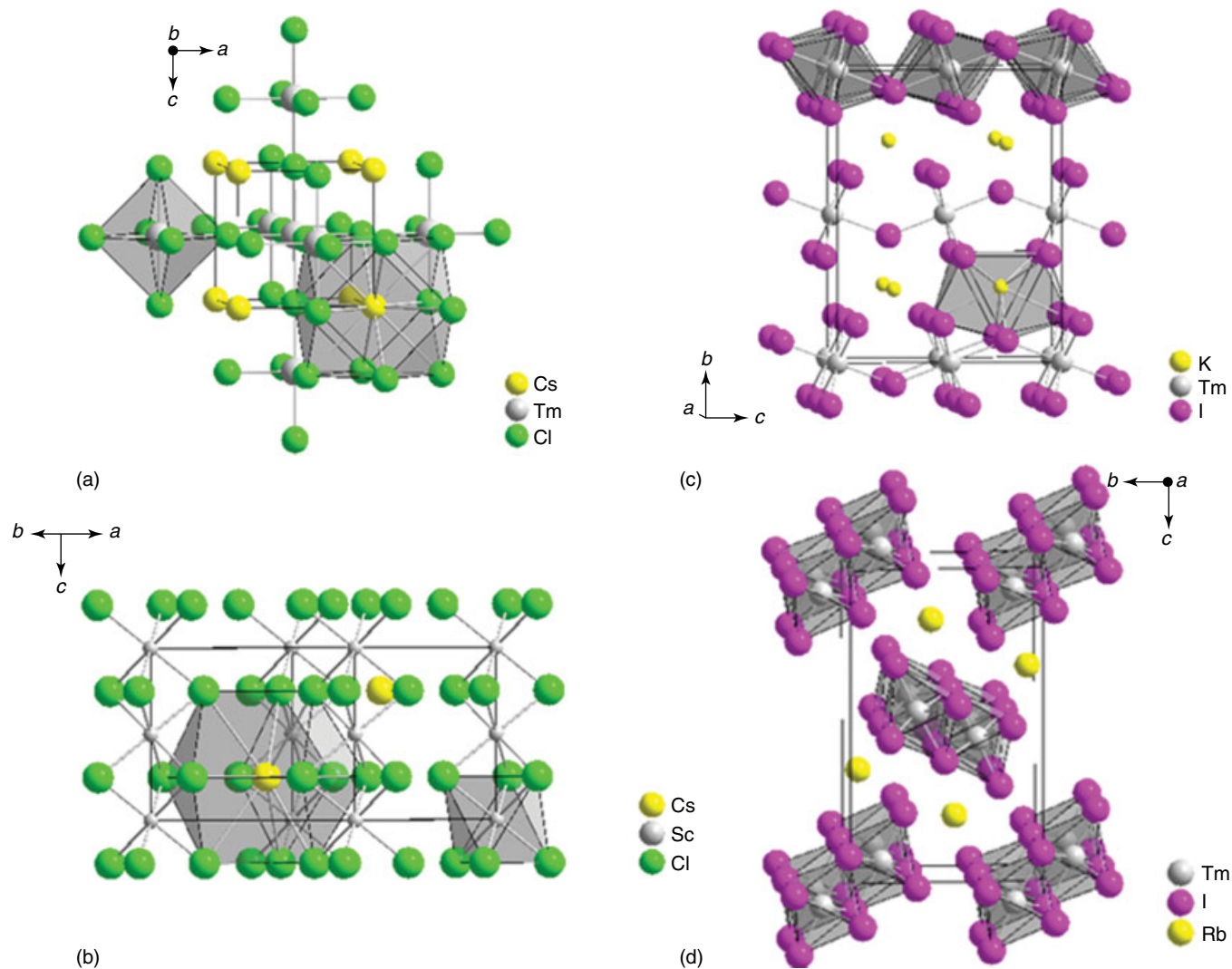
Figure 12   Crystal structures of AMX_3-type compounds. (a–d) The cubic perovskite type of structure, e.g., $CsTmCl_3$; the so-called hexagonal perovskite, e.g., $CsSc_{0.71}Cl_3$; the stuffed $PuBr_3$ or $FeUS_3$ type of structure, e.g., $KTmI_3$; the NH_4CdCl_3 type of structure, e.g., $RbTmI_3$

to 90°) by symmetry. For a general formula $ABRX_5$, the A_2RX_5 type is generated with A = B, eight- and seven-coordinate, and with B = R, the AR_2X_5 type with A and one R eight-coordinate and the other R seven-coordinate. The $RX_5 = RX_{3/1}X_{4/2}$ part of the structure is built from monocapped trigonal prisms that are edge-connected to chains (see Figure 13). For $K_8Nd_7I_{25}$, for example, a mixed-valent iodide, the formula must be understood as follows: $K_{1.6}Nd^{II}_{0.4}[Nd^{II}_{0.2}Nd^{III}_{0.8}I_5]$. Needless to say that many other compositions are possible because neodymium(II) and -(III) can afford both coordination numbers, seven and eight, in these halides.

Another interesting structure was found in the AX/RX_3 (A = K, Rb; X = Br, I) systems with dysprosium and thulium for the composition $A_5R_3X_{12}$. These
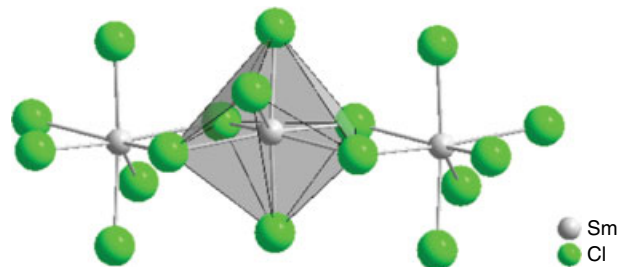

Figure 13   Part of the $RX_5 = RX_{3/1}X_{4/2}$ chain of trans edge-connected monocapped trigonal prisms as an important structural feature of the A_2RX_5/AR_2X_5 family

are mixed-valent halides, too; for example, $K_5Dy_3I_{12} = (K^+)_5(Dy^{2+})_2(Dy^{3+})(I^-)_{12}$. The anionic structure consists

of chains of edge-sharing octahedra, $Dy_3I_{12} = DyI_4 = DyI_{2/1}I_{4/2}$ (Figure 14) in which the Dy^{II}/Dy^{III} cations are statistically distributed. Antiferromagnetic coupling is observed at low temperatures.[35]

6 OXIDE HALIDES

Accidental oxide ''impurities'' or the deliberate addition of rare earths, R_2O_3, with europium, samarium, and ytterbium leads to the formation of $\{OR_4\}X_6$-type oxide halides with isolated oxide-centered R^{2+} tetrahedra (Figure 15). This structure type was first observed with the rare earth metals europium and ytterbium, as $\{OEu_4\}Cl_6$ and $\{OYb_4\}Cl_6$, and is the antitype of K_6HgS_4/Na_6ZnO_4. The oxide chlorides $\{OR_4\}Cl_6$ are now all known with Ae, R = Ca, Sr, Ba, Sm, Eu, Yb, for $\{OR_4\}Br_6$ (R = Sm, Eu) as well as for $\{OR_4\}I_6$ (Ae, R = Sr, Ba, Sm, Eu).[36] Isostructural compounds with neodymium, dysprosium, and thulium are elusive. This cannot be a size effect. If it is not an experimental disability, it must have thermodynamic reasons. Indeed, in systems where such $\{OR_4\}X_6$ compounds are usually obtained, for example, in the system $Na/EuCl_3/Eu_2O_3$, elements with higher reduction potentials form oxide chlorides such as NdOCl or even oxides such as Sc_2O_3 as single crystals under reducing conditions.[37,38]

In an attempt to prepare a large sample of $\{OEu_4\}Br_6$ and during the reduction of a mixture of EuI_2 and $\{OEu_4\}I_6$ with barium metal, two new oxide halides of europium

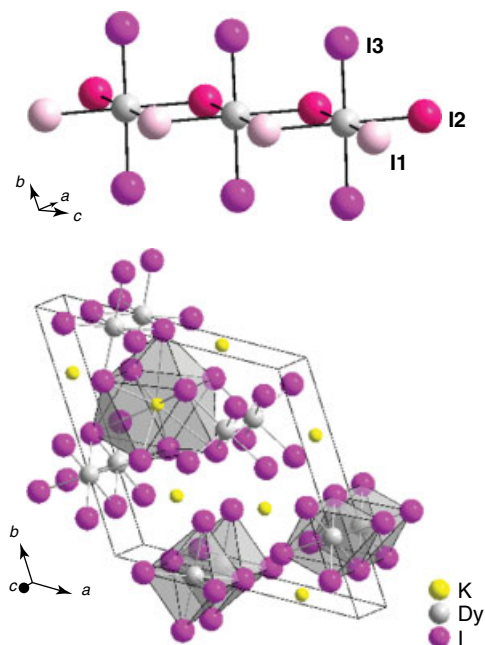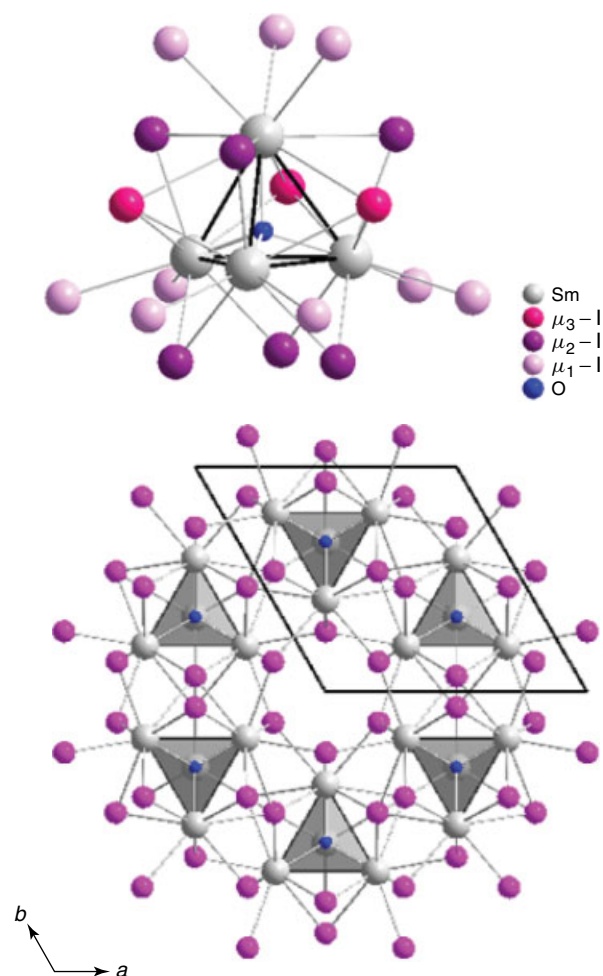**Figure 15** Crystal structure of $\{OSm_4\}I_6$ as an example of $\{OR_4\}X_6$-type oxide halides
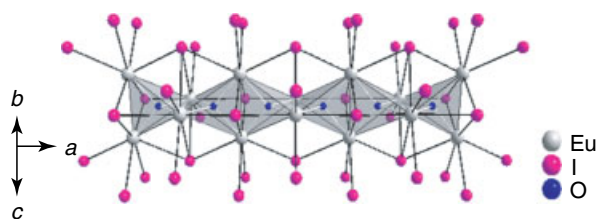
Figure 16 A chain of trans-edge-connected $\{OEu_{4/2}\}$ chains in the crystal structure of Eu_2OI_2

Figure 14 Crystal structure of $K_5Dy_3I_{12}$. (a) Part of the trans-edge connected $DyI_{4/2}I_{2/1}$ chains; (b) a projection down the chains

were obtained, the mixed-valent $Eu_2O_2Br = (Eu^{2+})\ (Eu^{3+})\ (O^{2-})_2(Br^-)$ and the Eu(II) oxide iodide Eu_2OI_2.[39,40] In both $\{OEu_4\}$ tetrahedra occur. They are edge-connected, just as in SiS_2, in $Eu_2OI_2 = \{OEu_{4/2}\}I_2$, surrounded by and connected through iodide anions (Figure 16). In Eu_2O_2Br, the $\{OEu_4\}$ tetrahedra are connected to two kinds of chains that combine to corrugated layers $[O_2Eu_2]^+$ and sheath likewise corrugated

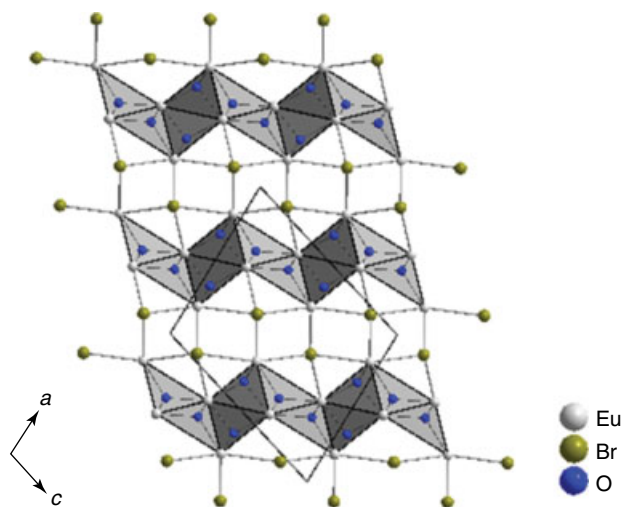**Figure 17** Corrugated layers built from two types of edge-connected chains $\{OEu_{4/4}\}$ in the crystal structure of Eu_2O_2Br

layers of Br^- ions (Figure 17). The Eu^{2+} and Eu^{3+} cations can be clearly distinguished in the crystal structure of Eu_2O_2Br, likewise in the isostructural Sm_2O_2I.[41]

7   GLOSSARY

Band structure: k-space-dependent energy level diagram for an extended solid, similar to the molecular orbital diagram at the gamma point

Binary halides: Compounds of two elements, one typically a metal and the other a halogen

Cathodic reduction: Electrochemical reduction at the cathode

Configuration crossover: Transition from one electronic configuration to another

Comproportionation: Compounds with higher and lower oxidation states of one element react to a compound with an oxidation state in between

Coordination number (CN):   The number of atoms surrounding a central (metal) atom in a coordination complex

Cluster: According to Cotton, ''a group of two or more metal atoms in which there are substantial and direct bonds between the metal atoms'', put in waved brackets {...} in this chapter

Cluster complex: A cluster surrounded by ligands, $\{R_x\}X_z$

Crystal orbital Hamiltonian population (COHP):   From the density of states of band structure calculations, showing the degree of bonding and antibonding interactions between atom types in a solid

Density of states (DOS):   Number of states per interval of energy at each energy level that are available to be occupied by electrons in a solid

Electronic configuration: Energy levels in the shell of an atom which are occupied with electrons; symbolized by quantum numbers

Endohedral atom: Atom Z in the center of a cluster, $\{ZR_x\}X_z$

Extended structures: Crystal structures with polyhedra connected to a one-, two-, or three-dimensional arrangement

Fermi level: Highest occupied energy level in a solid

Incongruent melting: A compound decomposes at an elevated temperature yielding at least one liquid phase

Lanthanides: The elements La, Ce–Lu

Metallothermic reduction: Reduction of a metal oxide or halide with a highly reductive metal

Mixed valence halide: A metal halide in which the metal atoms are in two different oxidation states (class I: the oxidation states can be clearly distinguished)

Nucleation: Process of forming a crystal nucleus

Oxidation state (... number):   According to Pauling (1949), the ''number which represents the electrical charge which an atom would have if the electrons in a compound were assigned to the atoms''

Peierls distortion: Distortion that occurs to break the symmetry in order to avoid a degeneracy of states at the Fermi level, similar to the Jahn–Teller distortion in molecular compounds

rare earth elements (metals):   The elements Sc, Y, La, and the lanthanoids Ce through Lu

Rare earths: Oxides of the rare earth elements, in most cases of the composition R_2O_3

Ternary halides: Compounds of three elements, of which two are metals and the third a halogen

Valence: According to Pauling (1949) ''the number of other atoms with which an atom of a certain element can combine''

Valence electron(s):   Electron(s) constituting the valence shell beyond the core (usually a noble gas configuration)

8   ABBREVIATIONS AND ACRONYMS

[. . .] = square brackets indicate a Werner-type complex; {. . .} = waved brackets indicate a cluster; A = alkali metal atom; Ae = alkaline-earth metal atom; [Ar] = electronic configuration of an argon atom; °C = degrees Celsius; temperature scale after Celsius; CN = coordination number; COHP = crystal orbital Hamiltonian population; d = distance (between the nuclei of two atoms); DOS = density of states; $E°$ = standard electrode potential (in V); $\Delta H°(3)$ = third ionization potential (in kJ mol^{-1}); HP = high pressure; I_3 = third ionization potential (in eV or kJ mol^{-1}); K = Kelvin; absolute temperature scale; pm = picometer, 10^{-12} m; R = rare-earth and lanthanide element (Sc, Y, La, Ce–Lu); ST = structure type; X = halogen atom, X$^-$ halide ion; [Xe] = electronic configuration of a xenon atom; V = Volt; unit of voltage.

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