Systematics in the optical and electronic properties of the binary lanthanide halide, chalcogenide and pnictide compounds: an overview

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Abstract. The basic optical, electrical and chemical properties of the binary divalent, trivalent and tetravalent lanthanide (Ln = La, . . . , Lu) halides (F, Cl, Br and I), chalcogenides (O, S, Se and Te) and pnictides (N, P, As and Sb) were studied using an empirical model that utilizes the systematic behaviour in the energy difference between the localized 4fⁿ-states, the 5d-derived conduction band and the mp-derived valence band (m = 2, . . . , 5) over the Lanthanide series. As the wide variety in the electrical and optical properties of Ln materials is to a large extent controlled by the energy of these states relative to each other, it is possible to simultaneously predict insulating, semiconducting or metallic behaviour, the nature and magnitude of bandgap energies and the chemical stability of Ln materials as well as valence and valence changes of Ln ions. It can thus be used to predict the basic electronic structure of materials for which no experimental data can be found, and may be a guideline for theoretical modelling.

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1. Introduction

The binary lanthanide compounds have been the subject of numerous theoretical and experimental investigations because they show a rich variation in electrical, optical and magnetic properties. The technological importance of lanthanide-based materials is apparent from a multitude of applications ranging from catalysts [1, 2] and magnets [3] to laser host crystals [4], transparent ceramics [5–9] and phosphors [9–13], while more recently binary materials such as CeBr$_3$ have shown the potential to become excellent scintillator materials for the detection of ionizing radiation [14–16]. They have also been considered for future applications based on spintronics [17, 18] or for high-density optical or magnetic data storage [19]. Binary lanthanide compounds also serve as precursors to the synthesis of more complex ternary or quaternary lanthanide materials that have found applications in a variety of photonic applications such as lasers [20], wide-bandgap electroluminescent devices [21], light-emitting diode phosphors [22] and scintillation detectors [23].

Scientifically, they have earned notoriety because of the unusual behaviour of certain materials such as CeN, which displays valence fluctuations [24], and SmS, which shows a first-order metal-to-insulator transition [25]. The Eu chalcogenides (O, S, Se and Te) were among the earliest known ferromagnetic insulators [26, 27] and EuO displays giant magnetoresistant behaviour [28, 29]. Also, the mixing of strongly correlated 4f electrons on the one hand, and delocalized 5d electrons on the other, constitutes a pronounced computational challenge and therefore the binary lanthanides have served as test cases for new computational methods [30, 31]. Outside of the binary lanthanides, Ln-based materials are the focus of solid-state research into a variety of fundamental phenomena such as metal–insulator transitions, colossal magnetoresistance and valence transitions or charge ordering [27, 32–35].

Ln ions have either an [Xe]4f$^n$ or an [Xe]4f$^{n-1}$5d$^1$ ground-state electron configuration. The 4f$^n$ configuration has $n$ strongly correlated and localized core-like 4f electrons. The 4f$^n$
energy levels are to a good approximation unaffected by the Ln-ion crystalline environment, but change strongly as a function of \( n \). The 5d electrons have an entirely different character. Their energy strongly depends on the crystalline environment but not on \( n \). In addition, the 5d orbitals are highly delocalized and form the conduction band (CB).

Despite the fact that the lanthanide ions are chemically very similar due to the well-shielded nature of the \( 4f^n \) valence electrons by filled \( 5p^6 \) and \( 6s^2 \) orbitals, Ln materials often show a strong change in behaviour when we move just one position in the periodic table. While TmS is a metal, YbS is a small-band-gap insulator \([36–38]\); \( \text{La}_2\text{O}_3 \) is a transparent insulator, whereas \( \text{Ce}_2\text{O}_3 \) is a yellow semiconductor; and while \( \text{CeF}_4 \) and \( \text{PrF}_4 \) are stable compounds, \( \text{NdF}_4 \) is not \([39]\).

Even when the lanthanide ion remains the same, material properties can vary considerably with the type of ligand. For example, \( \text{CeF}_4 \) is a stable compound, but the other Ce tetrahalides are not \([39]\), and while SmO is metallic, the other Sm monochalcogenides are semiconductors \([40, 41]\).

It would be very useful to have a universally applicable model that is able to explain all these variations in material properties in a systematic fashion. Many reviews have appeared that have attempted to do so for a subclass of lanthanide materials \([26, 42–44]\). Others reported systematic variation as a function of the type of lanthanide ion. For example, Hulliger’s review of the changes in conductivity behaviour of lanthanide compounds and Kim and Oishi’s work on the enthalpy of formation and stability of lanthanide dihalides both note that the systematic behaviour is related to the binding energy of the \( 4f \) electrons in the lanthanides \([45, 46]\).

Other work addresses the behaviour of a specific lanthanide such as Ce, Sm or Yb and describes the behaviour as a function of the type of ligand. For example, Cho \([47]\) compares the electronic structures of trivalent insulating Sm and Gd compounds such as \( \text{SmF}_3 \) and \( \text{GdF}_3 \), Wachter \([26]\) describes the optical properties of Eu chalcogenides, Weaver \([48]\) discusses \( 4f \) localization in Ce compounds and Temmerman \( et \ al \) \([49]\) consider the electronic configuration of Yb compounds. Recently, Petit \( et \ al \) \([50]\) used \textit{ab initio} methods to study the electronic structures of lanthanide monopnictides and monochalcogenides \( \text{LnX} \) (\( X = \text{N, P, As, Sb, Bi, O, S, Se, Te and Po} \)).

\textit{Ab initio} models, however, are computationally heavy and require a great deal of specialist knowledge before they can be applied. A model that can calculate the electronic structure of Ln compounds quickly and simply could be beneficial for the material sciences community. In a previous paper \([51]\), we showed that the change in the \( 4f^n \) ground-state energy with \( n \) (the type of lanthanide) appears to be independent of the type of compound, while the energy difference between the top of the \( mp \) valence band (\( mp\)-VB) and the bottom of the 5d-derived conduction band (5d-CB) appears to a good approximation to be independent of \( n \). It also appears that the wide variety in the electrical and optical properties of Ln materials is to a large extent controlled by the energies of these states relative to each other, meaning that in order to predict these properties for Ln materials, we need to establish the positions of the \( 4f, 5d\)-CB and \( mp\)-VB energies.

This universal behaviour was used to construct an empirical model that was applied to the well-known Ln oxides \( \text{LnO}, \text{Ln}_2\text{O}_3 \) and \( \text{LnO}_2 \), for which it correctly predicts insulating, semiconducting or metallic behaviour, the nature and magnitude of bandgap energies and the chemical stability of Ln materials, as well as valence and valence changes of Ln ions.

In this paper, we show that the same model can be used to systematically describe and predict these properties for all binary Ln halide, chalcogenide and pnictide compounds. The
paper is organized as follows. First we introduce the model before explaining the types of data used to construct the schemes and displaying the sources used. Then the Ln oxides are used as an example to explain how such data are used to construct our schemes before we present the modelled properties of the other binary Ln chalcogenides, halides and pnictides. Finally, various trends in properties such as Ln valence, optical bandgap and stability are discussed in relation to similar trends found in Ln-doped inorganic compounds.

2. Application of the empirical model

The method used to position the energy of the 4f ground state and the bottom of the 5d-CB of the lanthanide ions with respect to the top of the valence band in pure lanthanide compounds has evolved from an empirical method developed for lanthanide-doped inorganic compounds; see e.g. [52] and [53] and references therein. In previous work [51], two of us showed that the basic optical, electrical and some chemical properties of the binary lanthanide oxides and the lanthanide monosulfides are determined by the energy of the ligand mp-derived valence band (where \( m = 2 \) for F, O and N, \( m = 3 \) for Cl, S and P, \( m = 4 \) for Br, Se and As and \( m = 5 \) for I, Te and Sb), the lanthanide 5d-CB and the localized 4f\(^n\) ground states of the 2+, 3+ or 4+ lanthanides relative to each other. It was demonstrated that as soon as the energies of the \( m p\)-VB, 5d-CB and 4f\(^n\) states relative to each other are established experimentally for one specific Ln material (e.g. EuO), the energies of those states in all other compounds of that series, e.g. LnO (Ln = La, . . . , Yb), can be predicted using a simple empirical model. Within this model the energy difference between the top of the \( mp\)-VB and the bottom of the 5d-CB is assumed to be constant as a function of the type of Ln ion. It is also assumed that the energy of the 4f\(^n\) ground state as a function of the number of electrons \( n \) follows a characteristic double zigzag pattern that is independent of the type of compound. Figure 1 shows these energies and patterns for the 2+ and 3+ Ln ions as used in the 2006 paper [51] (square data symbols) and the energies used in this paper (circular data symbols) [53]. The differences between these two sets of energies are the result of including more and new experimental data. These changes have little impact on the properties predicted by the schemes in the original paper, with the exception of an improvement in the LnO\(_2\) scheme, which will be discussed further on in this paper. Thus, when reliable experimental data on a few crucial or pinning compounds are available, the \( mp\)-VB, 4f\(^n\) ground states and the 5d-CB energies can be plotted as a function of \( n \), which results in the typical schemes that were presented in our earlier work on the Ln oxides (LnO, Ln\(_2\)O\(_3\) and LnO\(_2\)) and which will be presented here for all of the other binary Ln halides, chalcogenides and pnictides (see figures 2–13). From here on, we will denote the zigzag curve that connects the lowest energy 4f\(^n\) level of the trivalent lanthanides in the level schemes as 4f(3+). Likewise the curve for the divalent lanthanides is denoted as 4f(2+).

Although several types of experimental data have been used to construct the schemes in figures 2–13, they can be divided into two categories: photoelectron emission and optical data. The experimental data used are compiled and referenced in table 1. Valence band x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were used to determine the energy difference between the \( mp\)-VB and the 4f\(^n\) ground states by using the difference between the lower-energy edges of the anion \( mp\) peak and the lanthanide 4f\(^n\) peak in XPS or UPS spectra. Examples of the data obtained using XPS are (i) the LnBr\(_3\) 4f(3+) ground
Figure 1. Variations in the divalent (top panel) and trivalent (bottom panel) $4f$ ground-state energies as a function of the type of lanthanide. Red and black curves indicate the difference between the 2006 version (black squares) [51] and the version used in this paper (red circles) [53].

Figure 2. Predicted electronic structures of the binary Ln oxides (Ln = La to Lu): (a) Ln monoxides (LnO): orange shading = metallic compounds; (b) Ln sesquioxides (Ln$_2$O$_3$): light green shading = optical band gap. Blue and red horizontal bars indicate the bandgaps measured by Borchardt [82] and White [101], respectively. (c) Ln dioxides (LnO$_2$): light blue vertical bands = stable compounds. In all figures, squares = 2p-VB, circles = 5d-CB and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

state that was positioned using data from the paper by Sato [54] on CeBr$_3$, (ii) the LnS-occupied $4f$(2+) ground state curve that was positioned using the data on SmS from the papers by Gudat et al and Chainani et al [55, 56] and (iii) the LnN-occupied $4f$(3+) curve that was positioned using data on CeN from the paper by Baer et al [57].
Table 1. Sources of the photoelectron (XPS, UPS) and optical (transmission, reflection, luminescence) experimental data for the 2+, 3+ and 4+ binary lanthanide compounds (halides, chalcogenides and pnictides) used in this work to construct the energy-level diagrams presented in figures 2–13. ‘?’ means that no information on that transition was available, ‘est.’ means that the transition was estimated, while ‘n/a’ means not applicable, indicating that the transition is not meaningful in that scheme.

| Ln“ (x =) | mp to 2+4f | mp to 3+4f | mp to 5d | 4f-5d |
|-----------|------------|------------|----------|-------|
| LnF₂      | 2          | n/a        | 10 eV est. | 3 eV EuF₂ [63] |
| LnCl₂     | 2          | n/a        | 6.2 eV est. | 3 eV SrCl₂ : Eu [64] |
| LnBr₂     | 2          | n/a        | 5.2 eV est. | 1.8 eV SmBr₂ [65] |
| LnI₂      | 2          | n/a        | 3.9 eV est. | 3.1 eV EuI₂ [66] |
| LnF₃      | 3          | 7.14 eV EuF₃ [67] | 4.5 eV CeF₃ [54, 68] | 10 eV LaF₃ [59, 60] |
| LnCl₃     | 3          | 3 eV LaCl₃ [70] | 1.5 eV CeCl₃ [54] | 6.2 eV LaCl₃ [58] |
| LnBr₃     | 3          | 4.96 eV PrBr₃ [71] | 1 eV CeBr₃ [54] | 5.2 eV LaBr₃ [58] |
| LnI₃      | 3          | 1.4 eV EuI₃ est. | 0.4 eV CeI₃ [72] | 3.9 eV LaI₃ [72] |
| LnF₄      | 4          | n/a        | 3.9 eV CeF₄ [74] | 8 eV CeF₄ [74] |
| LnCl₄     | 4          | n/a        | 1.5 eV CeCl₄ est.| 6.2 eV est. |
| LnBr₄     | 4          | n/a        | 1 eV CeBr₄ est. | 5.2 eV est. |
| LnI₄      | 4          | n/a        | 0.4 eV CeI₄ est. | 3.9 eV est. |
| LnO       | 2          | 3 eV EuO (average) [75–77] | n/a | 1.33 eV EuO [26] |
| LnS       | 2          | 2.95 eV SmS [55, 56] | n/a | 0.25 eV SmS [41] |
| LnSe      | 2          | 2.4 eV SmSe, 1.1 eV EuSe [78–80] | n/a | 1.62 eV EuSe [81] |
| LnTe      | 2          | 1.9 eV SmTe [79] | n/a | 0.82 eV SmTe [41] |
| LnO₂      | 3          | 4.1 eV Eu₂O₃ [82] | 3.4 eV Ce₂O₃ [83] | 5 eV La₂O₃ [82] |
| LnS₁      | 3          | 2.15 eV Sm₂S₃ [84] | –6 eV Gd₂S₃ [85, 86] | 2.7 eV La₂S₃, Dy₂S₃, Ho₂S₃ [87–89] |
| LnS₂      | 3          | 1.76 eV Sm₂Se₃ [91] | n/a | 2.3 eV La₂Se₃ [43] |
| LnTe₁      | 3          | 0.4 eV Eu₂Te₃ est. | 0.3 eV Ce₂Te₃ est. | 2.2 eV La₂Te₃ [92] |
| LnO₂      | 4          | n/a        | 3.1 eV Ce₂O₃ [93] | 5 eV est. |
| LnS₂      | 4          | n/a        | 0.6 eV Ce₂S₂ est.| 2.7 eV est. |
| LnSe₂      | 4          | n/a        | 0.45 eV Ce₂Se₂ est.| 2.3 eV est. |
| LnTe₂      | 4          | n/a        | 0.3 eV Ce₂Te₂ est.| 2.2 eV est. |
| LnN₂      | 2          | 2 eV Eu₂N₂ est. | n/a | 3 eV Eu₂N₂ est. |
| LnP₂      | 2          | n/a        | 2.2 eV Eu₂P₂ [94] | 1 eV Eu₂P₂ [94] |
| LnAs₂      | 2          | n/a        | 2 eV Eu₂As₂ [95] | 2 eV Eu₂As₂ [95] |
| LnSb₂      | 2          | 0.7 eV Eu₂Sb₂ est. | n/a | 1.9 eV Eu₂Sb₂ est. |
| LnN      | 3          | 1.7 eV YbN [96] | 1.4 eV CeN [57] | 1.5 eV DyN, HoN, ErN [97] |
| LnP      | 3          | 1.1 eV YbP [62] | 0.7 eV CeP [98] | 1.1 eV NdP, SmP, HoP [61, 62] |
| LnAs      | 3          | 1.05 eV YbAs [99] | 0.4 eV CeAs [98] | 1.05 average [99, 100] |
| LnSb      | 3          | 0.1 eV EuSb est. | 0 eV CeSb [57] | 0.55 eV PrSb, SmSb [99] |
| LnN₄      | 4          | n/a        | 1.4 eV Ce₄N₄ est.| 1.5 eV Ce₄N₄ est. |
| LnP₄      | 4          | n/a        | 0.7 eV Ce₄P₄ est.| 1.1 eV Ce₄P₄ est. |
| LnAs₄      | 4          | n/a        | 0.4 eV Ce₄As₄ est.| 1.05 eV Ce₄As₄ est. |
| LnSb₄      | 4          | n/a        | 0 eV Ce₄Sb₄ est.| 0.55 eV Ce₄Sb₄ est. |
Figure 3. Predicted electronic structures of the binary Ln fluorides (Ln = La to Lu): (a) Ln difluorides (LnF₂): orange shading = metallic compounds; (b) Ln trifluorides (LnF₃): light green shading = optical bandgap; (c) Ln tetrafluorides (LnF₄): light blue vertical bands = stable compounds. In all figures, squares = 2p-VB, circles = 5d–CB and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

Figure 4. Predicted electronic structures of the binary Ln chlorides (Ln = La to Lu): (a) Ln dichlorides (LnCl₂): orange shading = metallic compounds; (b) Ln trichlorides (LnCl₃): light green shading = optical bandgap; (c) Ln tetrachlorides (LnCl₄): light blue vertical bands = stable compounds. In all figures, squares = 3p-VB, circles = 5d-CB and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

Optical data were used to obtain the energy difference between occupied and unoccupied levels, in particular the transition energy from the 4f ground state to the 5d-CB, the transition energy from the mp-VB to the 5d-CB and the charge transfer (CT) energy from the mp-VB to a trivalent or tetravalent lanthanide. This latter transition has as a final state the 2+ or 3+ 4f
Figure 5. Predicted electronic structures of the binary Ln bromides (Ln = La to Lu): (a) Ln dibromides (LnBr$_2$): orange shading = metallic compounds; (b) Ln tribromides (LnBr$_3$): light green shading = optical bandgap; (c) Ln tetrabromides (LnBr$_4$): light blue vertical bands = stable compounds. In all figures, squares = 4p-VB, circles = 5d-CB and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

The ground state of that lanthanide and provides a pinning point for the respective 4f(2+) or 4f(3+) zigzag curves in our schemes. Luminescence excitation spectroscopy was of most use for wide-bandgap materials such as LnF$_3$ and LnCl$_3$ [58–60]. Because narrow-bandgap materials, such as EuS, do not luminesce, absorption, transmission or diffuse reflectance data were also used. For instance, the 4f$^n$–4f$^5$ 5d$^1$ transition energy of SmS as published by Batlogg et al [41] was used to position the LnS 5d-CB relative to the 4f(2+) curve. Diffuse reflectance was very useful in determining the bandgaps of narrow-bandgap powder samples. For example, for LnP the 3p-VB to 5d-CB bandgap was placed using data on the 3p to 5d-CB transitions of NdP, SmP and HoP from diffuse reflectance spectra measured by Meng and Ren [61, 62]. For all the optical measurements, we used the absorption edge to calculate the transition energy.

For cases where the 4f$^n$ to 5d-CB transition for all compounds in a series, for example the LnI$_2$ series, were unknown, the 4f$^n$ to 5d luminescence excitation energy of an isostructural Ln-doped inorganic compound such as SrI$_2$: Eu was used (see table 1 and references therein). In situations where the energy difference between the mp-VB and 5d-CB was not known for any compounds in a series (i.e. LnF$_2$), we used the energy difference known for the trivalent compounds (i.e. LnF$_3$). This is not necessarily correct but as will be apparent later, the precise location of the valence band does not affect the material properties of these types of compounds. For situations where no information on the 4f$^n$ to 5d-CB energy for either the compound or its doped equivalent could be found, e.g. Ln$_2$Te$_3$, trends seen in the decrease of the mp to 4f energy for the other series of compounds for that period of the periodic table (i.e. O, S, Se, . . .) were used to place the curves.

Table 1 presents all the data used to construct the energy-level schemes presented in figures 2–13. Energies that were estimated have also been compiled in the table.
Figure 6. Predicted electronic structures of the binary Ln iodides (Ln = La to Lu): (a) Ln diiodides (LnI₂): orange shading = metallic compounds; (b) Ln triiodides (LnI₃): light-green shading = optical bandgap; (c) Ln tetraiodides (LnI₄): light blue vertical bands = stable compounds. In all figures, squares = 5p-VB, circles = 5d-CB, and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

Figure 7. Predicted electronic structures of the binary Ln sulfides (Ln = La to Lu): (a) Ln monosulfides (LnS): orange shading = metallic compounds; (b) Ln sesquisulfides (Ln₂S₃): light green shading = optical bandgap; (c) Ln disulfides (LnS₂): light blue vertical bands = stable compounds. In all figures, squares = 3p-VB, circles = 5d-CB and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

Before presenting the results for all 516 binary lanthanide compounds in figures 2–13 below, we will first explain how the results will be presented and how the presented schemes should be interpreted. In each of the energy-level schemes presented in figures 2–13 below, the mp-VB is plotted using square data symbols, while the 5d-CB is represented by round
Figure 8. Predicted electronic structures of the binary Ln selenides (Ln = La to Lu): (a) Ln monoselenides (LnSe): orange shading = metallic compounds; (b) Ln sesquiselenides (Ln2Se3): light green shading = optical bandgap; (c) Ln diselenides (LnSe2): light blue vertical bands = stable compounds. In all figures, squares = 4p–VB, circles = 5d–CB, and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

Figure 9. Predicted electronic structures of the binary Ln tellurides (Ln = La to Lu): (a) Ln monotellurides (LnTe): orange shading = metallic compounds; (b) Ln sesquitellurides (Ln2Te3): light green shading = optical bandgap; (c) Ln ditellurides (LnTe2): light blue vertical bands = stable compounds. In all figures, squares = 5p–VB, circles = 5d–CB and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

data symbols. 4f$^n$ ground-state levels are represented by triangular data symbols. Generally, occupied states (donor states) are represented by solid data symbols, while unoccupied states (acceptor states) are represented by empty data symbols. The data symbols as a function of $n$ will
Figure 10. Predicted electronic structures of the binary Ln nitrides (Ln = La to Lu): (a) \( \text{Ln}_3\text{N}_2 \): orange shading = metallic compounds; (b) Ln mononitrides (LnN): light green shading = optical bandgap; (c) \( \text{Ln}_3\text{N}_4 \): light blue vertical bands = stable compounds. In all figures, squares = 2p-VB, circles = 5d-CB and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

Figure 11. Predicted electronic structures of the binary Ln phosphides (Ln = La to Lu): (a) \( \text{Ln}_3\text{P}_2 \): orange shading = metallic compounds; (b) Ln monophosphides (LnP): light green shading = optical bandgap; (c) \( \text{Ln}_3\text{P}_4 \): light blue vertical bands = stable compounds. In all figures, squares = 3p-VB, circles = 5d-CB, and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

be connected with solid lines, as shown in figure 1. Both the resulting 4f(2+) and 4f(3+) curves make a characteristic double zigzag pattern. The experimental data used to position the 4f(2+) and 4f(3+) curves relative to the VB curve and/or CB curve are represented by star-shaped data symbols, with an arrow indicating the corresponding transition.
Figure 12. Predicted electronic structures of the binary Ln arsenides (Ln = La to Lu): (a) Ln$_3$As$_2$: orange shading = metallic compounds; (b) Ln monoarsenides (LnAs): light green shading = optical bandgap; (c) Ln$_3$As$_4$: light blue vertical bands = stable compounds. In all figures, squares = 4p-VB, circles = 5d-CB and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

As an example, the energy-level scheme of the binary Ln oxides that have 2+ Ln ions (from here on, referred to as a divalent scheme) shows the data symbols pertaining to the mp-VB, 4f(2+) ground state and the 5d-CB energy for each of the compounds in the lanthanide monoxide series (see figure 2(a)). When the 4f(2+) ground state is below the CB, it will be occupied and denoted as a solid triangle in our schemes, while the 5d-CB states are unoccupied (open circle) so that consequently the compound is insulating or semiconducting with the electronic configuration 4f$^n$5d$^0$. This is the case for EuO and YbO in figure 2(a). When the 4f(2+) ground state is above the bottom of the CB, the 4f electron is donated to the CB. The 4f(2+) data symbol will, in this case, be shown as an open triangle and the 5d-CB data symbol as a solid circle. The lanthanide ion becomes trivalent and the material becomes metallic with the electronic configuration 4f$^{n-1}$5d$^1$. When compounds are metallic this is indicated in the schemes by vertical orange bands. Apart from EuO and YbO this is the case for all LnO compounds; see figure 2(a). Some materials have the 4f(2+) ground-state level lying just below or overlapping with the bottom of the CB. We consider these materials to be critical as they show unique properties and the correct prediction of these properties provides an indication of the accuracy of our model. When the 4f(2+) ground state lies just below the 5d-CB, as is seen for SmS and TmTe, the material is usually switchable in the sense that a small perturbation, such as pressure, is enough to shift the bottom of the 5d-CB to below the 4f levels leading to metallic behaviour. The other situation leads to a mixed valence compound such as TmSe or SmO. In this case, the 4f$^n$ levels lie so close above the bottom of the 5d band leading to interconfigurational valence behaviour where lanthanide ions fluctuate rapidly between a 2+ and a 3+ configuration, so that the valence appears to be somewhere between 2+ and 3+.

The energy-level scheme of the binary Ln oxides that have 3+ Ln ions (from here on, referred to as trivalent schemes) such as the one for Ln$_2$O$_3$ shown in figure 2(b) shows curves
Figure 13. Predicted electronic structures of the binary Ln antimonides (Ln = La to Lu): (a) Ln₃Sb₂: orange shading = metallic compounds; (b) Ln monoantimonides (LnSb): light green shading = optical bandgap; (c) Ln₃Sb₄: light blue vertical bands = stable compounds. In all figures, squares = 5p-VB, circles = 5d-CB and triangles = 4f ground state. Filled symbols indicate an occupied band. Stars and arrows indicate the experimental data used.

that connect the data symbols of the mp-VB (solid squares), the 4f(3+) ground state (solid triangles), the position of the divalent 4f(2+) ground state (open triangles) and the 5d-CB (open circles). One obvious property that can be derived from trivalent compounds such as Ln₂O₃ is the change in bandgap energy when going through the series from La to Lu. The bandgap energy is in this case that of the lowest dipole-allowed transition, i.e. mp-VB to the 5d-CB, mp-VB to the 4f(2+) ground state or from the 4f(3+) ground state to the 5d-CB. Light green shading has been used to indicate what levels determine the optical bandgap of each compound in a series. Figure 2(b) shows that 2p-VB to 5d-CB transitions determine the bandgap for La₂O₃, Nd₂O₃, Pm₂O₃, Sm₂O₃, Gd₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃ and Lu₂O₃, while 4f(3+) ground state to 5d-CB transitions apply for Ce₂O₃, Pr₂O₃, Tb₂O₃ and Dy₂O₃, and finally mp-VB to 4f(2+) ground state transitions apply for Eu₂O₃ and Yb₂O₃.

Finally, the energy-level scheme of the binary Ln oxides that have 4+ Ln ions (from here on, referred to as tetravalent schemes) shows curves corresponding to a filled mp-VB (solid squares), an empty 4f(3+) ground state (open triangles) and a 5d-CB (open circles); see figure 2(c). For these compounds the schemes can be used to predict whether a compound can in principle be stable. An unoccupied 4f(3+) acceptor state below the filled mp-VB is energetically impossible because it will capture an electron from the higher-energy mp-VB. Those compounds therefore do not exist. In addition, we conclude that the closer the empty 4f(3+) ground state is above the valence band, the less stable the compound will be. Those compounds that energetically can exist are indicated by vertical light blue bands in the schemes.

Although the mp-VB to 5d-CB energy difference is considered constant as a function of n, there are some exceptions. We noticed that compounds with the 4fⁿ ground state located between the mp-VB and the 5d-CB showed a different mp-VB to 5d-CB energy, depending on which method was used to determine it. The energy can be derived from the sum of the mp-VB to 4fⁿ energy obtained for one lanthanide compound and the 4f–5d transition energy estimated.

New Journal of Physics 13 (2011) 093038 (http://www.njp.org/)
from another lanthanide compound of the same series. It can also be obtained from the directly measured mp-VB to 5d-CB of one specific lanthanide compound of the series. For example, if an electron is excited from the 2p-VB to the 5d-CB as in La$_2$O$_3$, the energy difference is 5 eV, and this difference to first approximation holds in figure 2(b) for all Ln$_2$O$_3$ compounds. If we next consider Ce$_2$O$_3$, the energy difference between the 2p-VB and the 4f$^{1}$ Ce$^{3+}$ ground state is 3.4 eV. With the 4f(3+) curve we then predict a 2p-VB to 4f$^{2}$ Pr$^{3+}$ ground-state energy difference of 1.7 eV. From data on Pr$_2$O$_3$ the energy difference between the 4f$^{2}$Pr$^{3+}$ ground state and the 5d-CB is 3.6 eV and we then get a 5.3 eV energy difference between the 2p-VB and 5d-CB for Pr$_2$O$_3$. We believe that the 0.3 eV difference between the value of 5.0 eV based on La$_2$O$_3$ and the value of 5.3 eV found indirectly for Pr$_2$O$_3$ is due to lattice relaxation after an optical transition has taken place.

In this paper, we have decided to show those different values in our schemes. If the 4f levels lie below the mp-VB or above the 5d-CB, the mp-VB to 5d-CB energy is used to place the 5d-CB. If the 4f levels lie above the mp-VB and below the 5d-CB the summation of the mp to 4f energy and the 4f to 5d-CB energy is used to place the 5d-CB. This can be seen in figure 2(b), where the 5d-CBs of Ce$_2$O$_3$, Pr$_2$O$_3$, Tb$_2$O$_3$ and Dy$_2$O$_3$ are shown at higher energy than the 5d-CBs of the other Ln sesquioxides.

As this model is empirical and therefore relies on experimental data, most errors arise from experimental errors or the ambiguity of the interpretation. For example, by using the absorption edge to establish an energy value, errors can be introduced due to the presence of impurities and therefore change from sample to sample. From our comprehensive analysis of experimental data, we estimate the error to be in the range of 0.3 eV.

In addition, as we use data collected by different methods such as x-ray photoelectron spectroscopy and luminescence excitation spectroscopy, systematic errors may be present too. Throughout this work we have tried to use as much as possible the same experimental technique for a specific p–f, f–d or p–d transition. In order to be consistent we have used the absorption edge of band features to derive energy values for our schemes.

3. Results

By presenting the energy-level schemes for the binary lanthanide oxides in figure 2, we introduced how the schemes should be interpreted. The schemes show occupied and unoccupied states by means of solid and open data symbols. Transitions between them determine the size and nature of the bandgap of the material. Whether or not the 4f$^{n}$ or the 4f$^{n-1}$5d state is occupied determines if the compound will be insulating/semiconducting or metallic. In situations where unoccupied states are found below the valence band, materials energetically cannot exist. By means of the introduced colouring a rapid overview of the main properties of the materials can be observed. In the following, we present schemes for the other binary lanthanide compounds in the same fashion as used for the Ln oxides above. Each time we will briefly indicate the main sources of experimental data used and the characteristics derived from the presented schemes.

3.1. Lanthanide halides

The lanthanide halides have properties that range from those of wide-bandgap insulators such as LaF$_3$, through semiconductors such as SmBr$_2$, to metals such as LaI$_2$. Because of their wide
bandgaps, which range from about 10 eV for LaF$_3$ to 3.9 eV for LnI$_3$, the trivalent lanthanide trihalides have been used as scintillators and laser crystals. The lanthanide dihalides form both semiconducting compounds such as EuF$_2$, SmCl$_2$, NdBr$_2$ and DyI$_2$ and metallic compounds such as LaBr$_2$ and CeI$_2$. However, the only tetravalent halides observed are CeF$_4$, PrF$_4$ and TbF$_4$.

3.1.1. Lanthanide fluorides. Lanthanide ions in binary lanthanide fluoride compounds exist in a divalent, a trivalent and a tetravalent form. The energy-level scheme for the lanthanide difluorides LnF$_2$ is plotted in figure 3(a). The only usable experimental data available for the difluorides is the 4f$^7$ to 5d-CB energy of EuF$_2$. This energy, listed in table 1, was used to position the 4f(2+) zigzag curve of the Ln$^{2+}$ ions relative to the 5d-CB, as shown in figure 3(a). As no data on the 2p-VB to 5d-CB transition energy could be found, that energy was assumed to be the same as that of LaF$_3$. The resulting energy scheme predicts semiconducting behaviour for NdF$_2$, PmF$_2$, SmF$_2$, EuF$_2$, DyF$_2$, HoF$_2$, ErF$_2$, TmF$_2$ and YbF$_2$. Today only SmF$_2$, EuF$_2$ and YbF$_2$ are known to exist [39, 102, 103]. The other LnF$_2$ compounds, LaF$_2$, CeF$_2$, PrF$_2$, GdF$_2$ and TbF$_2$, are predicted to be metallic, although they have not yet been synthesized.

The energy-level scheme for the lanthanide trifluoride compounds (LnF$_3$) is shown in figure 3(b). The lanthanide trifluorides are all wide-bandgap insulators. The optical gap for La, Gd and LuF$_3$ is determined by the 2p-VB to a 5d-CB transition, while for Ce, Pr, Nd, Pm, Sm, Tb and Dy, Ho, Er, and TbF$_3$ the transition is controlled by a 4f$^n$ to 5d-CB transition and for Eu and YbF$_3$ a 2p-VB to 4f$^{n+1}$ transition is predicted, as can be seen in figure 3(b), where the variation in the optical bandgap is coloured light green. It is also possible that SmF$_3$ and TmF$_3$ could show an inter-lanthanide charge transfer, i.e. Sm$^{3+}$ + Sm$^{3+}$ → Sm$^{4+}$Sm$^{2+}$. The vertical arrows indicate the available experimental data from table 1 that were used to construct the energy-level scheme.

Figure 3(c) shows the energy-level scheme for the tetravalent lanthanide fluoride compounds, LnF$_4$. As indicated by the arrow at $j = 0$, data on CeF$_4$ was used to construct the level schemes. Figure 3(c) predicts that CeF$_4$, PrF$_4$ NdF$_4$, PmF$_4$, TbF$_4$ and DyF$_4$ have a 4f-ground state above the VB and could therefore in principle exist as stable compounds, indicated by blue vertical bands in the scheme. Of the LnF$_4$ compounds CeF$_4$, PrF$_4$ and TbF$_4$ are known to exist [39]. The scheme predicts that the energies of the unoccupied trivalent 4f states of NdF$_4$, PmF$_4$ and DyF$_4$ lie less than 1 eV from the top of the valence band. In such cases, it is easy to reduce Ln$^{4+}$ to the trivalent charge state, suggesting that such compounds are unstable and difficult or even impossible to synthesize.

3.1.2. Lanthanide chlorides. In contrast to the lanthanide fluoride compounds, the lanthanide chloride compounds are only reported to exist in a divalent and a trivalent form. Semiconducting NdCl$_2$, SmCl$_2$, EuCl$_2$, DyCl$_2$, TmCl$_2$ and YbCl$_2$ have been prepared [39, 104]. However, no relevant data on the electronic structure could be found, so the level scheme in figure 4(a) was made using the 4f(2+) ground state to 5d-CB transition energy estimated from the excitation spectrum of Eu$^{2+}$-doped SrCl$_2$ (see table 1 and references therein). The scheme predicts that, if they can be prepared, PrCl$_2$, PmCl$_2$, HoCl$_2$ and ErCl$_2$ should also be semiconducting, while La, Ce, Gd and TbCl$_2$ would be metallic.

In figure 4(b), the energy-level scheme for the lanthanide trichlorides (LnCl$_3$) has been plotted. Contrary to what is observed for the trifluorides, where the optical gap is most often controlled by a 4f(3+) ground state to 5d-CB transition, the optical gap for most trichlorides is
determined by a 3p-VB to 4f(2+) transition. Only for CeCl$_3$ is the bandgap energy determined by a 4f to 5d-CB transition, while a 3p-VB to a 5d-CB transition is indicated for La, Gd and LuCl$_3$.

No lanthanide tetrachlorides are known to exist. Lanza and Fragalá [105] conclude from an *ab initio* study that CeCl$_4$ should thermodynamically be far less stable than CeF$_4$. A scheme has been predicted by assuming that the positions of the 4f levels in the tetravalent chlorides have similar energies to those of trivalent LnCl$_3$ (figure 4(c)). This can be assumed because this behaviour is also observed for the tetravalent oxides and fluorides. From this scheme we can see that of all the compounds in this series, only CeCl$_4$ might be stable. However, the 4f(3+) ground state lies about 1.5 eV above the 3p-VB, whereas for CeF$_4$ the energy difference is 4 eV. This suggests, similarly to Lanza and Fragalá, that CeCl$_4$ will be much less stable than CeF$_4$.

3.1.3. Lanthanide bromides. In figure 5(a), the level scheme for the lanthanide dibromides (LnBr$_2$) is shown. As for the chlorides, usable experimental information on the electronic structure is scarce. The 4f(2+) ground-state curve was placed using information from a lanthanide-doped inorganic compound, in this case SrBr$_2$:Eu. The 5d-CB was placed relative to the VB by assuming that this energy difference is similar to the 4p-VB to 5d-CB energy of LaBr$_3$, NdBr$_2$, SmBr$_2$, EuBr$_2$, DyBr$_2$, TmBr$_2$ and YbBr$_2$ are all known to be semiconducting [65, 106–110], as is indeed predicted by our level scheme. Figure 5(a) also predicts that PrBr$_2$, HoBr$_2$ and ErBr$_2$ could be prepared as semiconducting compounds. Metallic behaviour is predicted for LaBr$_2$, CeBr$_2$, GdBr$_2$ and TbBr$_2$. Of these, only metallic LaBr$_2$ has been successfully prepared according to the literature [39, 111].

The level scheme for the lanthanide tribromides (LnBr$_3$) is shown in figure 5(b). The scheme is quite similar to that of the trichlorides, albeit with a shift to lower energies of the divalent and trivalent 4f ground-state energies and the 5d-CB energy, relative to the top of the 4p-VB.

No lanthanide tetrabromides are known to exist. If the same assumptions are made for the tetrabromides as were made for LnCl$_4$, figure 5(c) can be drawn. As seen for the tetrachlorides, only CeBr$_4$ with the empty 4f$^1$ state 1 eV above the 4p-VB could possibly exist, although CeBr$_4$ would be even less stable than CeCl$_4$.

3.1.4. Lanthanide iodides. The lanthanide iodides exist in both a divalent and a trivalent form. The energy-level scheme for the lanthanide diiodides (LnI$_2$) is shown in figure 6(a). The 4f(2+) ground state to 5d-CB energy was taken from optical data on EuI$_2$, as indicated by the vertical arrow at $k = 7$. Using this value gives a scheme in figure 6(a) that predicts NdI$_2$, SmI$_2$, EuI$_2$, DyI$_2$, TmI$_2$ and YbI$_2$ to be semiconducting materials, and this agrees with what has been observed experimentally [39, 112].

PrI$_2$ is known to exist in five different crystal modifications. In four of these, PrI$_2$ appears to be semiconducting, while in one modification it appears metallic [113, 114]. The close proximity of the 4f$^3$ ground state to the 5d-CB, which is predicted for PrI$_2$ by our scheme, corresponds well to such behaviour. Apparently, in most modifications the 5d-CB is just above the 4f ground state, whereas in one modification it is below it. It is likely that the semiconducting phases of PrI$_2$ will show metal–insulator switching behaviour under pressure.

NdI$_2$ and DyI$_2$ are also predicted to be switchable materials because their 4f(2+) ground state energies are located just below the 5d-CB. Indeed, NdI$_2$ is known to switch continuously from a semiconductor to a metal under pressure between 10 and 20 kbar [115]. HoI$_2$ and ErI$_2$
are predicted to exist as semiconductors, but no information could be found on the existence of these compounds. Metallic LaI$_2$, CeI$_2$ and GdI$_2$ have also been reported [113, 116, 117] and the level schemes indeed predict these compounds to be metallic, with the 4f ground state lying inside the 5d-CB. TbI$_2$, which we also predict to be metallic, has not been synthesized yet as far as we know.

The energy-level scheme of the lanthanide triiodides (LnI$_3$) is shown in figure 6(b). The results are similar to those of the lanthanide trichlorides and tribromides, albeit with a further shift of the 4f(2+) and the 4f(3+) ground state curves and the 5d-CB to lower energies relative to the mp-VB. The energy-level scheme for the lanthanide tetraiodides shown in figure 6(c) has been predicted using the same assumption as that made for the LnCl$_4$ and LnBr$_4$ compounds. The unoccupied 4f(3+) ground state of CeI$_4$ is 0.4 eV above the 5p-VB, which will make the compound extremely unstable. We are not surprised that no reports on CeI$_4$ were found in the archived literature.

### 3.2. Lanthanide chalcogenides

The lanthanide chalcogenides range from wide-bandgap semiconductors such as La$_2$O$_3$ to metallic compounds such as CeS. From our literature survey we found that the trivalent lanthanide oxides are the materials that have undergone the most diverse optical investigations. These oxides, along with the tetravalent LnO$_2$ and divalent LnO and LnS compounds, were the subject of a previous investigation [51] and are revisited in this paper using the updated 4f(2+) and 4f(3+) ground-state curves, as explained in section 2.

#### 3.2.1. Lanthanide oxides

The energy-level schemes of the three lanthanide oxides (LnO, Ln$_2$O$_3$ and LnO$_2$) were introduced in section 2 in figures 2(a)–(c). Figure 2(a) shows the energy-level scheme for the divalent lanthanide monoxides LnO. Optical data for EuO (see table 1 and references therein) were used to position the 4f ground state with respect to the 5d-CB and the 2p-VB. The resulting scheme suggests that apart from EuO, only YbO can exist as a semiconducting compound, and this prediction agrees with what has been observed elsewhere [26, 118]. All other lanthanide monoxides are predicted to be metallic, which is also what is found in practice [119–121]. Even in the case of SmO, where the 4f(2+) ground-state level is only 0.05 eV from the bottom of the 5d-CB, the scheme correctly predicts the metallic phase [40].

The trivalent lanthanide sesquioxides presented in figure 2(b) are the most studied of all the binary lanthanide compounds. The optical bandgap values predicted by our level scheme are all within 0.3 eV of the values derived from diffuse reflectance spectra in the papers by Borchardt and White [82, 101]. Their experimental data are indicated in figure 2(b) by blue and red horizontal bars.

The scheme for the tetravalent lanthanide dioxides is shown in figure 2(c). The only experimental data available is the energy of the VB to 4f transition of CeO$_2$. In our earlier paper we predicted that both NdO$_2$ and DyO$_2$ should exist, although no reports confirming their existence had been found [51]. However, when we apply the refined curves from figure 1, the unoccupied 4f(3+) ground states of these compounds are predicted at or below the top of the valence band, suggesting that rather than being too unstable to synthesize, these compounds are actually non-existent.
3.2.2. Lanthanide sulfides. The energy-level scheme for the divalent lanthanide monosulfides (LnS) is shown in figure 7(a). When experimental data on SmS (see table 1 and references therein) are used to construct the scheme, the model correctly predicts semiconducting or metallic behaviour as a function of the number of electrons in 4f. Like the monoxides EuO and YbO, EuS and YbS are semiconducting [26, 118]. SmS is well known for its semiconductor-to-metal phase transition at relatively low pressures. In our scheme its 4f(2+) ground state energy is 0.25 eV below the 5d-CB, making it indeed semiconducting in ambient conditions. TmS is the heavy lanthanide analogue to SmS and has its 4f(2+) ground-state level lying 0.2 eV above the 5d-CB, which leads us to predict metallic behaviour. Both observations agree with what has been observed experimentally [41, 122].

The energy-level scheme for the trivalent lanthanide sesquisulfides (Ln$_2$S$_3$) is shown in figure 7(b). The sesquisulfides have all been synthesized, with the exception of Pm$_2$S$_3$ and Eu$_2$S$_3$ [123]. The schemes suggest that Eu$_2$S$_3$ should exist, but the location of the unoccupied 4f(2+) ground-state level only 0.9 eV above the valence band is probably the reason why it is difficult or even impossible to prepare.

No reports on the synthesis of tetravalent lanthanide disulfides were found. If we assume that the unoccupied 4f(3+) ground-state levels of the lanthanide disulfides are at approximately the same energy as the occupied 4f(3+) ground-state energies in the Ln$_2$S$_3$ scheme, then only CeS$_2$ might exist, as is shown in figure 7(c). However, an energy difference of only 0.6 eV between the unoccupied 4f(3+) ground-state energy and the 3p-VB would reduce the 4+ valence of Ce very easily to the 3+ valency and our scheme then suggests that CeS$_2$ cannot be prepared. Interestingly, the existence of layered compounds with the formula LnS$_2$ (Ln = La, . . ., Nd, Gd) has been reported [124–127]. The crystal structure of these compounds consists of layers of Ln$^{3+}$S$^{2-}$ alternating with layers of covalently bonded S$_2^{2-}$ sulfur complexes. Similar types of compound were reported for the diselenides and ditellurides [125, 126]. This suggests that tetravalent CeS$_2$ will be difficult to prepare because of the more stable CeS$_2$ layered compound alternative containing trivalent Ce.

3.2.3. Lanthanide selenides. The energy-level scheme for the divalent lanthanide monoselenides (LnSe) is shown in figure 8(a). The constructed energy-level scheme presents a consistent picture in which only SmSe, EuSe and YbSe are predicted to be semiconducting, which is confirmed by the experimental data found for these compounds [26, 41, 128]. Indeed, while the 1.64 eV 4f(2+) to 5d-CB transition of EuSe is used to position the 5d-CB with respect to the 4f(2+) ground state, the model correctly predicts the 4f to 5d bandgaps of SmSe and YbSe to within 0.3 eV [41, 129, 130]. All the other lanthanide monoselenides are metallic. Even the intermediate valence behaviour of TmSe [79, 122, 131], where the Tm ion fluctuates between a 2+ and a 3+ charge state due to the close proximity of the 4f(2+) ground state energy to the 5d-CB, is predicted correctly by our model. The energy-level scheme for trivalent lanthanide sesquiselenides is shown in figure 8(b). As the energy-level locations are practically identical to those of the sesquisulfides they are not further discussed.

If it is assumed that the position of the unoccupied 4f(3+) ground-state levels of LnSe$_2$ are at approximately the same energy as the occupied 4f(3+) ground state in Ln$_2$Se$_3$ with respect to the top of the VB, then it follows that only CeSe$_2$ may exist, as is shown in figure 8(c). As is the case with the sulfides, the 0.45 eV energy difference between the unoccupied cerium 4f(3+) ground state and the top of the valence band suggests that this compound is very unstable. Similarly to the lanthanide disulfides, layered polyselenides with the formula LnSe$_2$...
(Ln = La, . . . , Nd) consisting of layers of LnSe alternating with layers of Se$_2^{2-}$ molecular complexes have been synthesized [125, 126, 132]. Therefore, it can be suggested that tetravalent CeSe$_2$ will be difficult to prepare because of the more stable layered CeSe$_2$ compound, which contains Ce$^{3+}$ rather than Ce$^{4+}$ ions.

3.2.4. Lanthanide tellurides. The energy-level scheme for the divalent lanthanide monotelurides is shown in figure 9(a). The overall pattern is similar to that of the monoselenides and SmTe, EuTe and YbTe are predicted to be semiconducting [26, 133]. There are slight differences due to a somewhat lower energy of the 4f(2+) ground-state energies with respect to the 5d-CB energy. As a result, TmTe is a semiconducting compound that can be switched to its metallic phase by the application of pressure [122]. The other LnTe compounds are predicted to be metallic.

The energy-level scheme for the lanthanide sesquitellurides is shown in figure 9(b). Unfortunately, no data were found that could be used to position the 4f(2+) and 4f(3+) ground-state energy curves. Instead we estimate the relative positions of these curves using trends in the position of the curves for the other sesquichalcogenides and for the lanthanide monochalcogenides. The schemes of figures 2(b), 7(b) and 8(b) show that the 4f(2+) and 4f(3+) curves of the lanthanide sesquichalcogenides move closer to or deeper inside the VB when the anion changes from O, to S, to Se. The same trend is observed for the 4f(2+) curve of the lanthanide monochalcogenides; see figures 2(a), 7(a), 8(a) and 9(a). By combining these two trends, we estimated the location of the 4f(2+) and 4f(3+) curves in figure 9(b) for Ln$_2$Te$_3$. The scheme, and therefore also the properties predicted for the sesquitellurides, is very similar to those of the sesquiselenides.

Figure 9(c) shows our predicted scheme for the lanthanide ditellurides. It is more or less a copy of the Ln$_2$Te$_3$ scheme where the occupied 4f(3+) levels have been changed into unoccupied ones. The scheme suggests that only CeTe$_2$ could energetically be stable, although it would be even less stable than CeSe$_2$ because the empty 4f(3+) state of Ce$^{3+}$ is predicted to be 0.15 eV closer to the top of the valence band. As for the disulfides and diselenides, the tetravalent ditellurides have never been synthesized; instead layered LnTe$_2$ (Ln = La, . . . , Pr, Sm, Gd) compounds are formed [126, 134–137] involving Te$_2^{2-}$ complexes. Of these, LaTe$_2$ and CeTe$_2$ are the most widely investigated, as they are charge density wave compounds [138].

3.3. Lanthanide pnictides

Of all the binary lanthanide compounds, the fewest experimental data were found for the pnictides. Only examples of the trivalent monopnictides (LnN, LnP, LnAs and LnSb) and divalent Ln$_3$P$_2$ and Ln$_3$As$_2$ are known to exist. The divalent europium pnictides Eu$_3$P$_2$ and Eu$_3$As$_2$ are semiconductors, while the properties of the trivalent pnictides range from narrow-band semiconductors such as LaN to semimetals such as the lanthanide antimonides.

3.3.1. Lanthanide nitrides. Figure 10 shows the energy-level scheme for the lanthanide nitrides. Of all the possible binary lanthanide nitrides only data on compounds of the form LnN have been published. The corresponding energy-level scheme, shown in figure 10(b), was constructed using XPS data that define the energy of the Ce 4f(3+) ground state relative to the N 2p-VB. The 2p-VB to 5d-CB energy of DyN, HoN and ErN were used to place the 5d-CB relative to the valence band. The 4f(2+) curve was positioned using data on YbN. The energy
of the Ce 4f\(^{3+}\) ground state, which lies less than 0.1 eV below the bottom of the 5d-CB in the scheme, explains why CeN is a metallic intermediate valence compound, as demonstrated by Baer et al [57].

Figure 10(a) gives an educated guess at the electronic structures of Ln\(_3\)N\(_2\) compounds that have not yet been synthesized. The energy-level scheme was predicted as follows. First the schemes for the trivalent Ln monopnictides LnN, LnP and LnAs in figures 10(b), 11(b) and 12(b) and the schemes for the divalent Ln\(_3\)P\(_2\) and Ln\(_3\)As\(_2\) compounds in figures 11(a) and 12(a) were constructed based on available experimental data. The trends found in the energy difference between the 4f(2+) curves and the \(m_p\)-VB for these compounds were then used to estimate the 4f(2+) curve location in the Ln\(_3\)N\(_2\) compounds. A similar method was used to estimate the \(m_p\)-VB to 5d-CB energy difference of 3 eV.

No tetravalent lanthanide nitrides of the form Ln\(_3\)N\(_4\) have been reported. Therefore, a level scheme was again estimated by assuming that the energy-level position of the unoccupied 4f\(^{3+}\) ground state is at approximately the same energy as the occupied 4f\(^{3+}\) ground state of the LnN compounds. Basically, we copied the scheme for the LnN compounds and changed the occupied 4f\(^{3+}\) levels into unoccupied ones. This is shown in figure 10(c). Apart from the energy of the 5d-CB, the scheme resembles that of LnCl\(_4\). Like CeCl\(_4\), Ce\(_3\)N\(_4\) is the only compound in this series that is predicted to be stable. However, neither compound has been synthesized yet.

3.3.2. Lanthanide phosphides. Figure 11(a) shows the energy-level scheme for Ln\(_3\)P\(_2\) compounds, constructed using the 3p-VB to 5d-CB and the 4f(2+) ground state to 5d-CB transition energies of Eu\(_3\)P\(_2\). The scheme predicts that like Eu\(_3\)P\(_2\), Yb\(_3\)P\(_2\) should also be semiconducting. However, no data on Yb\(_3\)P\(_2\) were found, nor were there any published data on metallic Ln\(_3\)P\(_2\) compounds.

Figure 11(b) shows the energy-level scheme proposed for the lanthanide monopnictides (LnP). Of all the pnictides most experimental data are available for the monophosphides, as can be seen from the arrows in figure 11(b).

Figure 11(c) shows the predicted energy-level scheme for Ln\(_3\)P\(_4\). We copied the scheme for the LnP compounds and changed the occupied 4f\(^{3+}\) levels into unoccupied ones. Only Ce\(_3\)P\(_4\) is predicted to exist, but since the unoccupied 4f\(^{3+}\) ground-state level is only 0.7 eV above the 3p-VB it is likely that Ce\(^{4+}\) is unstable against reduction to Ce\(^{3+}\) and the compound therefore cannot be synthesized.

3.3.3. Lanthanide arsenides. The energy-level scheme for lanthanide arsenides of the form Ln\(_3\)As\(_2\) is shown in figure 12(a). The scheme is very similar to that of the Ln\(_3\)P\(_2\) compounds. Like Eu\(_3\)P\(_2\), only Eu\(_3\)As\(_2\) is known to exist [95]. The 4f(2+) ground state of Eu is 1.2 eV below the 5d-CB and the compound is semiconducting.

The energy-level scheme for the lanthanide monoarsenides LnAs is shown in figure 12(b). The scheme predicts that EuAs should exist as a semiconducting Ln\(^{3+}\) compound, as is the case for EuN and EuP, and EuAs indeed does exist, but the Eu appears to be present as a 2+ ion rather than a 3+ ion. In addition EuAs has a Na\(_2\)O\(_2\) (hexagonal) structure rather than the face-centred cubic (FCC) NaCl rock salt structure generally observed for the Ln monopnictides. Iandelli and Franceschi [139] suggested that in EuAs two As ions form As\(_4^{2-}\) complexes. Therefore, in this case Eu is divalent and it is better to write the compound as Eu\(_2\)(As\(_2\)).

Figure 12(c) shows the predicted energy scheme for Ln\(_3\)As\(_4\) obtained by copying the scheme for the LnAs compounds and changing the occupied 4f(3+) levels into unoccupied ones.
Only $\text{Ce}_3\text{As}_4$ is predicted to exist, but since the unoccupied 4f(3+) ground state is only 0.4 eV above the valence band $\text{Ce}^{3+}$ will be very prone to reduction and the material will therefore be extremely unstable.

### 3.3.4. Lanthanide antimonides

No published data on any $\text{Ln}_3\text{Sb}_2$ compound were found. Therefore, the scheme in figure 13(a) is an educated guess based on trends observed for the pnictides and the chalcogenide compounds. Our energy-level scheme suggests that $\text{Eu}_3\text{Sb}_2$ and $\text{Yb}_3\text{Sb}_2$ are both small-bandgap semiconductors.

The energy-level scheme for the mono-antimonides ($\text{LnSb}$) is shown in figure 13(b). The unoccupied 4f(2+) ground-state energy of $\text{Eu}^{2+}$ is calculated to be about 0.1 eV above the top of the valence band by using the 0.55 eV $5p$-VB to 4f(2+) transition of YbN to place the 4f(2+) curve. Such a small energy difference makes Eu very susceptible to reduction to the divalent state. Like EuAs, EuSb does not contain Eu$^{3+}$ but Eu$^{2+}$, and like the As in EuAS, the Sb in EuSb forms Sb$^{4-}$ units that form a bond with divalent europium [139].

Figure 13(c) shows the predicted energy scheme for $\text{Ln}_3\text{Sb}_4$. We simply copied the scheme for the $\text{LnSb}$ compounds and changed the occupied 4f(3+) levels into unoccupied ones. Since all these unoccupied states are below the filled valence band, none of the $\text{Ln}_3\text{Sb}_4$ compounds, including $\text{Ce}_3\text{Sb}_4$, can be energetically stable and are therefore non-existent.

### 4. Observed trends in the level schemes

The universal behaviour of the ground-state energies as a function of the number of electrons in the 4f orbital, i.e. the 4f(2+) and 4f(3+) curves from figure 1, forms the basis with which to construct the level schemes in figures 2–13. In addition to these clear trends as a function of the type of lanthanide ion, we occasionally mentioned trends with changing type of anion or with changing lanthanide valency when discussing the schemes in figures 2–13. Several of those trends were used to predict schemes in cases where no experimental data were available. We will analyse these trends further below.

Figure 14 shows trends in the behaviour of the divalent lanthanide compounds that have an occupied Ln 4f(2+) ground state, such as $\text{LnCl}_2$, $\text{LnS}$ and $\text{Ln}_3\text{P}_2$. Because the energy of the 4f(2+) ground state of Eu$^{2+}$ is usually located between the $m^-\text{VB}$ and the 5d-CB, the binary divalent europium compounds (i.e. EuF$_2$) have been selected to quantify the trends. Figure 14(a) shows the energy of the 5d-CB with respect to the top of the $m^-\text{VB}$. The halides are represented by black squares, the chalcogenides by red circles and the pnictides by green triangles. The data on the halides and on $\text{Eu}_3\text{N}_2$ and $\text{Eu}_3\text{Sb}_2$ are estimated values. The bandgap decreases in a regular fashion with an increase in the period ($m$) of the periodic table to which the anion belongs. It also decreases in going from halides to chalcogenides to pnictides.

Figure 14(b) shows the energy of the 4f(2+) ground state of the Eu$^{2+}$ ion above the top of the $m^-\text{VB}$ for the halides, chalcogenides and pnictides and as a function of the period ($m$). We observe similar trends to those seen in figure 14(a). Figure 14(c) shows the 4f(2+) to 5d-CB energy difference of the Eu compound predicted for halides, chalcogenides and pnictides. Note that these results can be derived from figures 14(a) and (b).

Figure 15 shows trends derived from energy-level schemes 2b–13b for compounds that have an occupied Ln 4f(3+) ground state. Because the optical properties of Ce compounds are most frequently studied and tend to have 4f levels lying above the $m^-\text{VB}$, data on Ce compounds are used to illustrate these trends. Figure 15(a) shows the position of the La (filled
Figure 14. Trends found in the schemes for the divalent compounds: (a) $mp$-VB $\rightarrow$ 5d-CB energy difference, (b) $mp$-VB $\rightarrow$ 4f($2^+$) energy difference, (c) 4f($2^+$) ground state $\rightarrow$ 5d-CB energy difference, black squares = halides, red circles = chalcogenides and green triangles = pnictides. Unfilled symbols indicate estimated values.

Figure 15. Trends found in the schemes for the trivalent compounds: (a) $mp$-VB $\rightarrow$ 5d-CB energy difference, (b) $mp$-VB $\rightarrow$ 4f($3^+$) energy difference, (c) 4f($3^+$) ground state $\rightarrow$ 5d-CB energy difference, black squares = halides, red circles = chalcogenides and green triangles = pnictides. Unfilled symbols indicate estimated values and half-filled symbols indicate the $mp$ to 5d energy difference of compounds where the 4f($3^+$) ground state lies above the $mp$ band.

symbols) and Ce (half-filled symbols) 5d-CB levels above the top of the $mp$-VB as predicted by the model for the halides (black squares), chalcogenides (red circles) and pnictides (green triangles). The La and Ce values are shown in this figure due to the differences between the $mp$-VB to 5d-CB energies measured directly for La compounds and calculated from the sum of the $mp$-VB to 4f($3^+$) energy difference and the 4f($3^+$) to 5d-CB energy observed for Ce compounds. Similar trends to those found in figure 14(a) are observed.
Figure 15(b) shows the position of the Ce 4f(3+) ground-state level above the top of the mp-VB for the lanthanide halides, chalcogenides and pnictides. Figure 15(c) shows the 4f(3+) ground state to 5d-CB transition energy of the binary cerium compounds.

5. Discussion

5.1. Discussion of trends in the level schemes

For both the divalent and trivalent Ln ions, the 5d–CB, 4f(2+) and 4f(3+) energies decrease with respect to the top of the mp-VB not only when we go horizontally in the periodic table from halides to chalcogenides to pnictides, but also when we go vertically, i.e. from F to Cl to Br to I. This is related to the electronegativity of the anions, which decreases in the same sequence. Pauling’s electronegativity is 3.98, 3.44 and 3.04 for F, O and N, respectively, and it is 3.98, 3.16, 2.96 and 2.66 for F, Cl, Br and I, respectively [140]. The 4f and 5d energy differences in figures 14(c) and 15(c) are determined by the crystal field interaction and the covalence of the compound. These aspects have been studied in detail for lanthanide-activated compounds [141–145] and will not be further addressed in this paper.

This work reveals that the binary lanthanide compounds display simple systematic behaviour in electronic structure over the Ln series (La, Ce, Pr, . . ., Lu). The simplicity originates from two important aspects of Ln compounds. The first is the double zigzag curves of the variation in 4f ground-state energy with the type of lanthanide as presented in figure 1. They are universal in the sense that they do not change with the type of Ln material. The second is the invariance of the 5d energy with changing lanthanide ion. This causes the mp-VB to 5d-CB to be constant as a function of the type of Ln ion.

There also appears to be much similarity between the divalent-, trivalent- and tetravalent-level schemes within a compound series such as LnO–Ln₂O₃–LnO₂ or LnI₂–LnI₃–LnI₄. On the one hand, the energies of the mp-VB, the 5d-CB and the 4f ground state with respect to each other are different for each series of lanthanide compounds and have to be established using experimental data. On the other hand, these energies appear surprisingly similar within a series of compounds. For example, the schemes in figure 2 for LnO, Ln₂O₃ and LnO₂ all appear similar, the only difference between them being whether lanthanide states are occupied or not.

For LnO₂ the 4f(3+) states are empty. The scheme for Ln₂O₃ is practically the same as that of LnO₂ but with occupied 4f(3+) states. Going to the scheme of LnO, an extra electron is added to the lanthanides and either the 4f(2+) state or the 5d-CB is being occupied, but again the energies of the mp-VB, the 5d-CB and the 4f(2+) and/or 4f(3+) ground state with respect to each other appear similar to the other Ln oxides. In predicting level schemes, particularly for the pnictides where very little or no experimental data were available for some compounds, we frequently made use of these similarities.

5.2. The stability of some binary lanthanide materials

Many possible binary Ln compounds do not as yet exist. Our schemes predict that trivalent compounds such as EuI₃, Eu₂S₃, Eu₂Se₃, Eu₂Te₃, Yb₂Te₃, EuAs and EuSb can exist based on energy-level considerations, but no reports were found on their existence. One reason for this could be the presence of more favourable alternatives. Europium sulfides, selenides and tellurides (figures 7(b), 8(b) and 9(b)) form divalent EuX or mixed valence EuₓX₄ compounds.
rather than trivalent Eu\(_2\)X\(_3\) (X = S, Se, Te), while EuAs and EuSb form divalent compounds of the form Eu\(_{3+}\)X\(_2^{2-}\) (X = As, Sb) where there is a covalent bond between two As or Sb ions (figures 12(b) and 13(b)) rather than the trivalent rock salt structures found for the other Ln monopnictides.

However, there appears to be a trend in the existence/non-existence of trivalent Ln compounds. Looking at the non-existing compounds EuI\(_3\), Eu\(_2\)S\(_3\), Eu\(_2\)Se\(_3\), Eu\(_2\)Te\(_3\), Yb\(_2\)Te\(_3\), EuAs and EuSb, we note that with the exception of EuAs, the energies of the unoccupied 4f\(^{2+}\) states are located at less than 40\% of the mp-VB to 5d-CB bandgap above the mp-VB in our schemes, which in absolute terms means that they are all located less than 1.4 eV above the valence band. Apparently, under such conditions the 3+ valence state is not stable against reduction to 2+ during synthesis of the compound and the 3+ lanthanide compound is not formed.

Almost all tetravalent lanthanide compounds are predicted by our model to not exist. Exceptions are several compounds within the lanthanide tetrafluoride (LnF\(_4\)) and dioxide (LnO\(_2\)) families as can be derived from figures 3(c) and 2(c), respectively. All the lanthanide dioxides that we predict to be stable do indeed exist. The use of the refined 4f\(^{2+}\) and 4f\(^{3+}\) curves (see figure 1) in the level schemes of this work clears up an issue from our previous work, where, in addition to CeO\(_2\), PrO\(_2\) and TbO\(_2\), the model predicted that the non-existent NdO\(_2\) and DyO\(_2\) would be stable [51].

The divalent lanthanide monochalcogenides are the most complete of all the series studied regarding their stability. With the exception of the Pm monochalcogenides, all of the monosulfides, monoselenides and monotellurides have been prepared (figures 7(a), 8(a) and 9(a)) and most of the lanthanide monoxides (figure 2(a)) have also been prepared. These compounds include semiconductors such as EuO, mixed valence compounds such as TmSe and metallic compounds such as GdS, and the nature of these compounds, whether they are semiconducting, mixed valence or metallic, has been correctly modelled by our schemes. TbO, HoO and TmO have not been reported in the literature, but there is no reason to believe that with the proper synthesis conditions they would not exist as FCC metals like the other isostructural metallic monoxides.

The situation for the lanthanide dihalide materials is more complex than that observed for the monochalcogenides. Figures 3(a), 4(a), 5(a) and 6(a) predict that compounds such as NdF\(_2\), LaCl\(_2\), PrBr\(_2\) and HoI\(_2\) should exist as semiconductors if we only take into consideration the positions of their energy levels. However, reports that they have been prepared were not found. This suggests that aspects other than energy-level location also determine whether a compound can be synthesized or not. One such aspect might be the crystal structure, which should be energetically stable. The lanthanide monochalcogenides all exhibit the same face-centred cubic NaCl-type structure, but the lanthanide dihalides show a great deal of variety of crystal structure. Several of the dihalide compounds are polymorphic and PrI\(_2\) has five different crystal structures, one of which corresponds to a metallic phase [113, 114]. With the exception of the difluorides, which are all isostructural, the semiconducting dihalides can be divided into light and heavy lanthanide compounds. The light lanthanide compounds from NdX\(_2\) to EuX\(_2\) have crystal structures with a larger anion co-ordination number around the lanthanide ion than that seen for the heavier DyX\(_2\) to YbX\(_2\) compounds. In addition, while both the monochalcogenide and dihalide series contain materials that undergo semiconductor-to-metal phase transitions under pressure, switchable monochalcogenides undergo an isostructural transition to a metallic
phase, whereas switchable NdI$_2$ undergoes a structural change during its semiconductor-to-metal transition [115]. All this suggests that the crystal structure and therefore the co-ordination number of the cations complicate the chemical behaviour of the dihalide series compared to that of the lanthanide monochalcogenides.

It is interesting to note that the metallic di-bromides, chlorides and fluorides do not exist, whereas most metallic monochalcogenides do. This is probably due to the highly oxidizing behaviour of the anion, leading to the far higher stability of the trivalent LnX$_3$ compound compared to its LnX$_2$ counterpart. Clearly this is not considered by our model, which is primarily designed to predict the electronic structure.

Of the lanthanide dihalides the diiodides (figure 6(a)) are probably the most interesting to consider when regarding the existence or non-existence of nominally divalent compounds. Although there are little spectroscopic data available for the diiodides, there is a wealth of crystallographic and electrical data available on both semiconducting and metallic compounds and these data match well with what is expected on the basis of the energy-level scheme shown in figure 6(a). However, no experimental data could be found on TbI$_2$, HoI$_2$ or ErI$_2$ and no explanation for their non-existence can be found from our model. We predict TbI$_2$ to be metallic, while HoI$_2$ and ErI$_2$ are suggested to be semiconductors. Our model shows several lighter lanthanide compounds with similar electronic properties: CeI$_2$, PrI$_2$ and NdI$_2$, respectively, and these have been prepared. Sadly then, the mystery behind the current non-existence of these materials is beyond the scope of this model.

Finally, we look at the divalent lanthanide pnictides. Here only two ioniically bonded compounds are known to exist, Eu$_3$P$_2$ and Eu$_3$As$_2$. However, mixed valence Sm, Eu and Yb compounds, which are not covered in this paper, are found in the Ln–LnX (X = As, Sb) series and the review by Hulliger gives a good overview of these [100]. Because little information is available, we cannot say for certain whether or not the other ioniically bonded divalent pnictides are possible. As the trivalent LnX phase is so stable, only the semiconducting Eu and Yb versions such as Eu$_3$N$_2$ are likely to be possible.

5.3. The relationship between lanthanide-activated and binary lanthanide compounds

The method used in this work to construct level schemes such as those in figures 2–13 is derived from the method developed for lanthanide-doped inorganic compounds and many of the features and trends observed are similar too. Figure 14(b) shows the location of the Eu$^{2+}$ 4f(2+) ground-state energy above the top of the $m$-p-VB. In Eu$^{3+}$-doped compounds this location is obtained from the so-called CT band in the excitation spectrum of Eu$^{3+}$ emission. Here an electron is excited from the top of the anion $m$-p-VB to the Eu$^{3+}$ ion, so that the final state of the Eu ion is Eu$^{2+}$ and there is a hole in the valence band. A compilation on CT energies in [146] comprises almost 200 different halide, chalcogenide and nitride compounds. The trend in the $m$-p-VB $\rightarrow$ Eu$^{3+}$ CT energy with the type of anion in the compounds reported there is basically the same as that we observe in figure 14(b).

The energy differences between the 4f and 5d-CB states of Eu$^{2+}$ or Ce$^{3+}$ binary lanthanide compounds summarized in figures 14(c) and 15(c) show the same trends and patterns as those observed for Eu$^{2+}$-doped [147] and Ce$^{3+}$-doped [144, 145] inorganic compounds. The 4f to 5d–CB energy difference is determined by the splitting of the 5d states due to the crystal field interaction plus the shift of the average energy of the 5d configuration relative to that of the free (gaseous) lanthanide ions. The splitting and shift in turn depend on the size and shape of the...
Figure 16. The Coulomb correlation energy $U_{ff}(\text{Eu})$ of the binary europium compounds. Black squares = halides (EuX$_3$), red circles = chalcogenides (Eu$_2$X$_3$), green triangles = pnictides (EuX). Empty symbols are estimated values.

anion coordination polyhedron around the lanthanide and on the amount of covalency between the lanthanide and its neighbouring anion ligands, respectively. The details are very compound specific. For example, the increase in $4f^{(2+)} \rightarrow 5d$-CB energy of Eu$^{2+}$ with the period $(m)$ for EuO, EuS, EuSe and EuTe in figure 14(c) is also observed for Eu$^{2+}$ doped in CaO, CaS, CaSe and in SrO, SrS and SrSe [147]. It was attributed to the increasingly large size of the anion in going from O to S to Se to Te. This leads to a decrease in the crystal field splitting of the 5d states and consequently a larger $4f^{(2+)} \rightarrow 5d$ energy.

Inspecting the schemes in figures 2–13, one may notice that the energy difference between the $4f^n$ ground state of Ln$^{3+}$ and that of the $4f^{n+1}$ ground state of Ln$^{2+}$ is about 8 eV for the fluoride compounds, but appears significantly smaller for the chalcogenide and pnictide compounds. This is further illustrated in figure 16 for all of the binary Eu compounds. The europium halides are represented by black squares, the chalcogenides by red circles and the pnictides by green triangles. Values that were estimated are represented by unfilled symbols.

The energy difference is known as the Coulomb correlation or Coulomb interaction energy $U_{ff}$ between two $4f$ electrons [148, 149]. It is determined by the Coulomb repulsion between the two electrons in the same orbital at the same cation site. For free (or gaseous) Eu ions, $U_{ff}(\text{Eu})$ is the same as the difference between the third and fourth ionization potentials of Eu and it amounts to about 18 eV [150, 151]. In Eu metal $U_{ff}$ reduces to a value of about 5.4 eV. This large reduction has been attributed to electronic screening and ionic relaxation in the metal phase [148, 149]. From the work on lanthanide-doped inorganic compounds it was found that $U_{ff}(\text{Eu})$ depends on the type of compound. For our most thoroughly studied compound YPO$_4$, $U_{ff}(\text{Eu})$ appears to be 7.0 eV [152]. For the poorly polarizable fluoride compounds there are strong indications that $U_{ff}(\text{Eu})$ is larger at about 7.5–8 eV, whereas it decreases to values around 6 eV in strongly polarizable compounds such as LaBr$_3$ and CaGa$_2$S$_4$. Figure 16 illustrates that the same trend appears to apply for the binary lanthanide compounds shown in the schemes in figures 2–13.
Figure 16 shows that $U_{\text{ff}}(\text{Eu})$ for the halides and chalcogenides decreases with the period ($m$). Clearly the larger polarizability of the anion with an increase of $m$ leads to larger screening effects and the reduction of the correlation energy $U_{\text{ff}}(\text{Eu})$. The same applies when going from the halides to the chalcogenides, i.e. an $\text{O}^{2-}$ anion is more strongly polarizable and provides stronger screening than an $\text{F}^{-}$ anion. For the pnictides we observe a somewhat reversed behaviour, i.e. $U_{\text{ff}}(\text{Eu})$ tends to increase from N to P to As to Sb. However, the errors involved in the schemes especially for this family of compounds may well be of the order of 0.5 eV and therefore the observed trend is not significant. Interestingly, $U_{\text{ff}}(\text{Eu})$ for the most polarizable ($m = 4$ and 5) chalcogenides and pnictides in figure 16 approaches the same value of around 5.5 eV for Eu metal. It suggests that the effects of screening in those compounds on $U_{\text{ff}}$ are similar. We regard the observed trends in $U_{\text{ff}}(\text{Eu})$ and the quantitative correspondence with $U_{\text{ff}}$ in Eu metal and Eu-doped inorganic compounds as strong support for the schemes presented in figures 2–13.

5.4. **Comparison with ab initio methods**

Finally, we should consider how this method compares with others used to calculate the electronic structures of Ln compounds. In a recent publication by Petit et al [50], the electronic structures of Ln monochalcogenides and monopnictides, $\text{LnX}$ ($\text{X} = \text{O, S, Se, Te, Po, N, P, As, Sb, Bi}$), were calculated using *ab initio* methods. It is interesting to compare their results with those presented here as the two methods are so different. While Petit et al use an *ab initio* method, the self-interaction corrected local spin density (SIC-LSD) energy functional, our method relies on experimental data. Both models can successfully predict the valencies of binary Ln compounds, but there are differences regarding the predicted bandgaps and the semiconducting/metallic nature of some compounds. However, the model presented in this paper has been shown to be able to accurately predict the bandgap of binary Ln compounds. It can also be easily applied to compounds with different crystal environments within minutes, as long as appropriate experimental data are available. Therefore, while *ab initio* methods are more elegant than our empirical method, our method is able to give quite accurate results very quickly and, at this stage, is more suitable for use in the search for new Ln-based materials.

6. **Conclusion and outlook**

This work involves the implementation of an empirical model or technique based on previously collected experimental data, which is able to organize in a consistent way a huge body of scattered experimental data. These compounds vary from wide-bandgap insulators, through semiconductors, to metallic compounds, showing that the model can be successfully applied to predict and explain a wide range of materials.

The application of the model explicitly reveals that the wide variety of properties seen for the binary lanthanide compounds can be reproduced with great accuracy by applying two simple empirical rules: (i) the mp-VB to 5d-CB energy is constant over the lanthanide series and (ii) the lanthanide 4f ground state energy follows a material-independent double-seated shaped curve over the lanthanide series, as shown in figure 1. These empirical rules result in the observed systematic and universal behaviour of the optical, electrical and chemical properties of binary lanthanide materials as a function of the Ln ion.
The relative energies of the mp-VB, 5d-CB and 4f ground state observed as a function of the type of ligand follow a clear trend that was noted before for smaller subgroups of materials such as the Ce pnictides, but are now presented for all binary lanthanides. These trends can be explained to a first approximation by the Pauling electronegativity of the ligands and the crystal field splitting of the 5d-CB. These trends have successfully been used to predict the electronic structure of those binary Ln materials for which no experimental data were available.

The presented data on the binary Ln materials convincingly reveal that methods for Ln-ion-doped materials, recently developed by one of us in the field of luminescence, can be used to understand and predict electrical and optical properties of fully concentrated lanthanide materials. It is also possible to work in the other direction, using knowledge of concentrated lanthanide materials to predict the luminescence properties of Ln ions as dopants in materials.

Our energy-level schemes also reveal that the relative energies of the mp-VB, 5d-CB and 4f ground state do not change significantly when the stoichiometry of a certain material (i.e. LnO, Ln$_2$O$_3$, LnO$_2$) changes. The difference between stoichiometries is in the filling of either the 4f or 5d-CB of the 2+, 3+ or 4+ Ln energy levels. This allows one to predict the properties of, for example, a tetravalent Ln material such as CeO$_2$ from the optical gap of a trivalent material such as Pr$_2$O$_3$.

We have strong indications that the approach presented here for the binary Ln materials is also applicable to ternary materials with the general formula Ln$_x$M$_y$L$_z$ (Ln = lanthanide, M = closed shell cation and L = pnictides, chalcogenide or halide ligands) as long as the cations are optically inactive, which is the case for monovalent Li, Na, K, . . . , divalent Mg, Ca, Sr, . . . , or trivalent Sc or Y. This is also the case for trivalent ions such as B, Al and Ga; tetravalent ions such as C, Si and Ge; pentavalent ions such as P, As and Sb; or hexavalent ions such as S.

The model may serve as a reliable tool for material scientists to accelerate the design of Ln materials with deliberately chosen properties. Unlike ab initio-based models, this empirical model can be applied immediately, without any further specialist knowledge, by other material scientists to explain and predict the properties of their favourite Ln materials.

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