Chapter 3
Physical and Chemical Properties of the Rare Earths

Abstract This chapter discusses the chemical and physical properties of the lanthanides, some of which are in a certain way peculiar. It discusses the oxidation states of the REE, and the phenomenon called the **lanthanide contraction** (meaning that the atomic radius decreases with increasing atomic number in the series lanthanum–lutetium). It lists the isotopes known per element, and explains the radioactivity of promethium, the only element of the rare earths that has only radioactive isotopes and no stable isotopes. Magnetism and luminescence also are discussed.

3.1 Introduction

The rare earths are divided into the lanthanide group, and the elements scandium and yttrium. The lanthanides constitute a special group of elements that have an atomic structure different from the other elements, although they are somewhat akin to the actinide series. The lanthanides make up a group of elements ranging from atomic number 57 (lanthanum) to 71 (lutetium). They are all very similar to lanthanum, which is the reason for the name lanthanide. The other two rare earths, scandium and yttrium, are somewhat apart from the lanthanide series, and will be treated separately.

The similarity in characteristics of the lanthanides series includes:

- Similarity in physical properties throughout the series
- In crystalline compounds, they usually have the 3+ oxidation state, although some can also have a 2+ or 4+ oxidation state (Haire and Eyring 1994).
- Coordination numbers[1] in compounds are usually greater than 6.
- Across the series, the coordination number decreases.

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[1] Coordination number: this is in chemistry the number of the near neighbors of a central atom in a molecule.

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- They bind preferably with the strong electronegative elements such as oxygen or fluorine.

Common properties of the rare earths.

- The rare earths are silver, silvery-white, or grey metals.
- The metals have a high luster, but tarnish readily in air.
- The metals have high electrical conductivity.
- There are very small differences in solubility and complex formation between the rare earths.
- The rare earth metals naturally occur together in minerals.
- Rare earths are found with non-metals, usually in the 3+ oxidation state.

The similarity may be explained by the electronic configuration of the atoms. This is discussed later.

3.2 The Lanthanide Series

Theoretically, an atom may have the following electron shells: K, L, M, N, O, P, and Q; or 1, 2, 3, 4, 5, 6, and 7; where K (or 1) is the most inward and P (or 7) is the most outward. The electrons in the outer shells are most important for determining the chemical behavior, and how they behave as conductors.

Every shell has also subshells. These are composed of atomic orbitals. The electron subshells of an atom are labelled s, p, d, and f, which is short for: sharp, principal, diffuse, and fundamental (Jensen 2007). The first shell (K) has one subshell, called 1s. The second shell (L) has two subshells called 2s and 2p. The third shell (M) has 3 subshells (3s, 3p, 3d). The fourth shell (N) has 4 subshells (4s, 4p, 4d, 4f).

The numbers of possible electrons per orbital is given in Table 3.1.

The order in which these orbitals are filled is given by the n + ℓ rule (also known as the **Madelung rule** (Madelung 1943).

The **Madelung Rule**[2] is also called the **Aufbau principle** (from German "*Aufbau*" meaning *"build-up, fabric, structure"*). This describes electron configuration and the filling of atomic orbitals.

The rule states:

1. Energy increases with increasing $n + \ell$, where n = the principal quantum number, and ℓ = the azimuthal quantum number (orbital angular momentum quantum number).
2. For identical values of $n + \ell$, energy increases with increasing n.

Resulting from this, the following order of filling of orbitals (from left to right) emerges:

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[2] Named after Erwin Madelung (1881–1972), German physicist.

Table 3.1 Filling of the subshells

Subshell	Number of orbitals	Total number of possible electrons in each orbital
s	1	2
p	3	6
d	5	10
f	7	14

1s, ***2s***, ***2p***, ***3s***, ***3p***, ***4s***, ***3d***, ***4p***, ***5s***, ***4d***, ***5p***, ***6s***, ***4f***, ***5d***, ***6p***, ***7s***, ***5f***, ***6d***, ***7p***. Madelung's Rule is graphically depicted in Fig. 3.1:

This electronic configuration results in the following effects (Fig. 3.1). For the majority of the neutral lanthanide atoms, the electronic configuration can be given as $4f^{n+1,}$ $5s^2$, $5p^6$, $6s^2$. Loss of one 4f electron and two $6s^2$ electrons leads to the *characteristic 3+ cations.* In some cases, the energy difference between the 4f and 5d electrons is so small, that a 4f electron can be promoted to the 5d orbital. As a result, tetravalent ions form (e.g. Ce^{4+}). Also a 5d-electron may be transferred to a 4f orbital, which results in the formation of divalent atoms, for instance, Sm^{2+}, Eu^{2+}, and Yb^{2+} (Choppin and Rizkalla 1994).

The possible oxidation states of the REEs are listed in Table 3.2.

As previously stated, the REEs are often divided into the light rare earth elements (LREEs) and the heavy rare earth elements (HREEs). This definition is based on the electron configuration of each rare earth element. The LREEs are defined as lanthanum, with atomic number 57 to gadolinium, with atomic number 64. The HREEs are defined as terbium with atomic number 65 to lutetium with atomic number 71, and also includes yttrium, with atomic number 39. The HREEs differ from the LREEs in that they have "paired electrons" (clockwise and

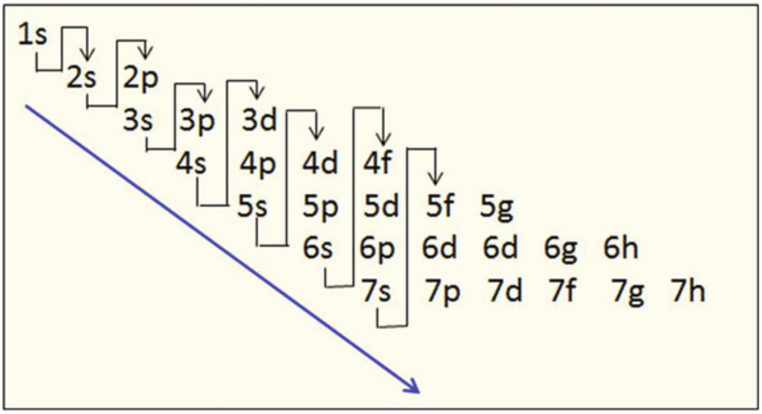

Fig. 3.1 Graphical depiction of the **Madelung Rule**, redrawn after (https://thespectrumofriemannium.wordpress.com/?s=Madelung). "Riemannium" is a fictional element, to describe the Madelung rule

Table 3.2 The oxidation states of the lanthanides

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		(2)	(2)		2	2			(2)	(2)		(2)	2	
3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	(4)					4	(4)					

Oxidation states in parentheses are unstable. The most common oxidation states are underlined (Choppin and Rizkalla 1994)

counter-clockwise spinning electrons). Yttrium is included in the HREE because of similarities in its ionic radius and similar chemical properties. Scandium is sufficiently different in properties to be not classified as either a LREE or a HREE, however, it is often (and also here) discussed together with REE (e.g. Beaudry and Geschneider 1978). See also Sect. 3.2.2. Sometimes also a medium group is identified, consisting of the elements samarium to dysprosium (Gupta and Krishnamurthy 2005).

It is observed that the abundance decreases with increasing atomic number Z: HREEs are much less abundant than LREEs. What's more, according to the Oddo-Harkins Rule,[3] elements with an even atomic number are more abundant than elements with an odd atomic number. For instance, cerium (Z = 58) is more abundant than lanthanum (Z = 57) and praseodymium (Z = 59). Cerium is the dominating rare earth in the LREE, whereas Y is the dominant rare earth in the HREE (Binnemans et al. 2013).

3.2.1 *Lanthanide Oxides*

For most lanthanides, the 3+ oxidation state is the most stable, and therefore almost all REE-oxides are presented as REE_2O_3. However, some of the lanthanides may have several valences in one and the same oxide, so formulas are given to express this phenomenon. Praseodymium oxide usually contains 3+ and 4+ praseodymium in a somewhat variable ratio, depending upon the conditions of formation. Its formula is rendered as Pr_6O_{11}. Similarly, Tb_4O_7, one of the main commercial terbium compounds, contains some Tb_{4+} along with the more stable Tb_{3+}. Ce has the 3+ state as most stable oxidation state, and the oxide is represented as Ce_2O_3.

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[3] The Oddo—Harkins rule states that elements with an even atomic number (such as carbon) are more common than elements with an odd atomic number (such as nitrogen). Reference: Wikipedia, https://en.wikipedia.org/wiki/Oddo–Harkins_rule See also Oddo (1914) and Harkins (1917).

3.2.2 Scandium and Yttrium

The electronic configuration of scandium can be expressed as [Ar] $3d^1$ $4s^2$ leading to oxidation states of 3+ (most common), 2+, and 1+. Its oxide is therefore given as Sc_2O_3. Scandium is considered a rare earth element, but this is firstly because it was discovered together with several other lanthanides. Secondly, scandium resembles yttrium and the rare earth elements more than it resembles aluminium or titanium (Hammond 2015). On the other hand, it also much resembles the ferromagnesian transition elements, although in aqueous systems it behaves more like the REE (see Chap. 1, and McLennan 2012).

The electronic configuration of yttrium can be expressed as [Kr] $4d^1$ $5s^2$ leading to an oxidation state of 3+. Its oxide is given as Y_2O_3

3.3 The Lanthanide Contraction

In the periodic system, the lanthanide group of elements also gives rise to a peculiar phenomenon, called the ***lanthanide contraction.*** This phenomenon is the important and progressive decrease in atomic radii and in radii of ions when going from lower to higher atomic numbers in the lanthanide series. Thus lanthanum has the largest atomic radius, and lutetium has the smallest. In Table 3.3, the ionic radii for the lanthanides are given, and the effect described above can be clearly seen in Fig. 3.2.

In the rows of the periodic system, the valence electrons always shield themselves in an imperfect way from the nuclear charge. This results in an increase in effective nuclear charge, when moving from left to right in a row in the periodic system. The lanthanides show contraction of the atomic and ionic radii, due to the imperfect shielding of the valence f-orbitals. Because there are 14 elements in this series, the effect is more pronounced than other rows of the periodic table. Because the 4f-orbitals are limited in size, the size of the lanthanide ions is defined by their 5s and 5p orbitals (Platt 2012).

The binding energy of an electron to its nucleus is proportional to its mass, so the electrons of the lanthanides are bound more strongly and thus the ionic size is reduced more strongly than would be expected from the increase in nuclear charge and orbital penetration[4] (Platt 2012).

Due to the restricted extension of the 4f orbitals, they cannot overlap with surrounding orbitals of other components. This means that covalent bonding for the lanthanides in their normal oxidation states virtually does not occur. Therefore, in general, the lanthanides are bonded by ionic/electrostatic interactions (Platt 2012).

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[4] Orbital penetration is a term that illustrates the proximity of electrons in an orbital to the nucleus. If the penetration for an electron is greater, it experiences less shielding, and therefore a larger effective nuclear charge.

Table 3.3 Ionic radii of the lanthanides in VI-coordination (Shannon 1976)

Element atomic number	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
2^+ ions						1.22	1.17						1.03	1.02	
3^+ *ions*	1.032	1.01	0.99	0.983	0.97	0.958	0.947	0.938	0.923	0.912	0.901	0.890	0.880	0.868	0.861
4^+ *ions*		0.87	0.85												

Values are given in Å

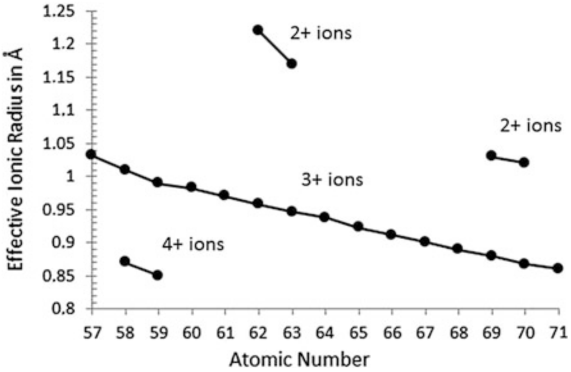

Fig. 3.2 Systematics of effective ionic radii of the lanthanides. The decrease from left to right is called the lanthanide contraction. Ionic radii are according to Table 3.3

Also as a result of the lanthanide contraction, yttrium has an ionic radius comparable to that of the heavier REE species in the holmium-erbium region. If the effective ionic radius (Shannon 1976) of Y^{3+} is plotted (0.90 Å)., it plots in between element 67 (Ho) and 68 (Er). Scandium (effective ionic radius is 0.745 Å), plots outside of the Lanthanide series. As also the outermost electronic arrangement of yttrium is similar to the heavy rare earths, the element behaves chemically like the heavy rare earths. It concentrates during (geo)chemical processes with the heavier REEs, and is difficult to separate from the heavy REEs. Scandium, on the other hand, has a much smaller atomic radius, and the trivalent ionic size is much smaller than that of the heavy rare earths. Therefore, scandium does not occur in rare earth minerals, and in general has a chemical behavior that is significantly different from the other rare earth elements (Gupta and Krishnamurthy 2005).

In sesquioxides (Ln_2O_3, Ln = lanthanide) the coordination number is six (Schweda and Kang 2004).

The lanthanide contraction, however, has also effects for the rest of the transition metals in the lower part of the periodic system. The lanthanide contraction is of sufficient magnitude to cause the elements which follow in the third transition series to have sizes very similar to those of the second row of transition elements. Due to this, for instance hafnium (Hf^{72}) has a 4^+-ionic radius similar to that of zirconium, leading to similar behavior of these elements. Likewise, the elements Nb and Ta and the elements Mo and W have nearly identical sizes. Ruthenium, rhodium and palladium have similar sizes to osmium iridium and platinum. They also have similar chemical properties and they are difficult to separate. The effect of the lanthanide contraction is noticeable up to platinum (Z[5] = 78), after which it no longer noticeable due to the so-called Inert Pair Effect (Encyclopedia Britannica 2015). The inert pair effect describes the preference of post-transition metals to form ions whose oxidation state is 2 less than the group valence.

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[5] Z = Atomic Number.

3.4 Radioactivity and Isotopes

Section 3.4 is devoted to the radioactivity and isotopes of the rare earth elements and provides the most important data for the different rare earths. For every element, the tables display the isotopes, their atomic masses, and their abundances.

The information below is taken from Audi et al. (2003). The "Table of Isotopic Masses and Natural Abundances" (www.chem.ualberta.ca/~massspec/atomic_mass_abund.pdf), which shows data from Audi and Wapstra (1993) and Audi and Wapstra (1995), is also used.

3.4.1 *Lanthanum (Element 57)*

Naturally occurring lanthanum (La) has one stable (^{139}La) and one radioactive (^{138}La) isotope. The stable isotope ^{139}La is the most abundant (99.91 % natural abundance). In total, 38 radioisotopes have been found. The most stable ones are ^{138}La with a half-life of 102×10^9 years, ^{137}La with a half-life of 60,000 years and ^{140}La with a half-life of 1.6781 days. The remaining radioactive isotopes have half-lives that are less than a day. The majority of the half-lives of these isotopes are less than 1 min (Table 3.4).

3.4.2 *Cerium (Element 58)*

Naturally occurring cerium (Ce) has 4 stable isotopes: ^{136}Ce, ^{138}Ce, ^{140}Ce, and ^{142}Ce. Of these, ^{140}Ce is the most abundant (88.48 % natural abundance). Other isotopes ^{119}Ce–^{135}Ce, ^{137}Ce, ^{139}Ce, ^{141}Ce, and ^{143}Ce–^{157}Ce are radioactive with half-lives varying from about 100 ns to about 137.6 days (Table 3.5).

3.4.3 *Praseodymium (Element 59)*

Naturally occurring praseodymium (Pr) has only one stable isotope, ^{141}Pr. Thirty-eight radioisotopes are known, of which ^{143}Pr is the most stable with a half-life of 13.57 days and ^{142}Pr with a half-life of 19.12 h. All other isotopes have half-lives shorter than 6 h and for many shorter than 33 s.

Table 3.4 Isotopes of La

Isotope	Atomic mass (u)	Abundance (%)
^{138}La	137.907107	0.090
^{139}La	138.906348	99.910

Table 3.5 Isotopes of Ce

Isotope	Atomic mass (u)	Abundance (%)
^{136}Ce	135.907144	0.185
^{138}Ce	137.905986	0.251
^{140}Ce	139.905434	88.450
^{142}Ce	141.909240	11.114

3.4.4 Neodymium (Element 60)

Naturally occurring neodymium (Nd) has 5 stable isotopes, ^{142}Nd, ^{143}Nd, ^{145}Nd, ^{146}Nd and ^{148}Nd. Of these, ^{142}Nd is the most abundant (27.2 % natural abundance). Two radioisotopes are known, ^{144}Nd and ^{150}Nd. Thirty three radioisotopes of Neodymium are known. The most stable of these are the naturally occurring ^{144}Nd (half-life of 2.29×10^{15} years) and ^{150}Nd (half-life of 7×10^{18} years). The remaining radioactive isotopes have half-lives that are less than 11 days (Table 3.6).

3.4.5 Promethium (Element 61)

This is the only lanthanide that has no stable or even any long-lived isotopes. This is explained below.

Promethium, like other elements with odd atomic numbers $Z^{odd} \geq 9$, should have one or two isotopes, which are stable towards beta decay (further called beta-stable isotopes), with odd atomic numbers M^{odd} having an intermediate value between M^{odd} for beta-stable isotopes for isotopes of neodymium and samarium. However, M^{odd} of beta-stable isotopes of neodymium and samarium follow each other successively: ^{143}Nd, ^{145}Nd, ^{147}Sm, ^{149}Sm. For beta-stable Pm-isotopes, there are no non-occupied numbers left. As a consequence, ^{145}Pm and ^{147}Pm are beta-unstable (Dr. Denis Bykov, TU Delft, RID, pers. comm. 2015). ^{145}Pm transforms by electron-capture decay into ^{145}Nd, and ^{147}Pm by β^--decay transforms into ^{147}Sm. The radioactivity of the synthetic (non-REE) element technetium can be explained in a similar way (Dr. Denis Bykov, TU Delft, RID, pers. comm. 2015).

Table 3.6 Isotopes of Nd

Isotope	Atomic mass (u)	Abundance (%)
^{142}Nd	141.907719	27.2
^{143}Nd	142.909810	12.2
^{144}Nd	143.910083	23.8
^{145}Nd	144.912569	8.3
^{146}Nd	145.913112	17.2
^{148}Nd	147.916889	5.7
^{150}Nd	149.920887	5.6

The explanation given above is also called the *Mattauch Isobar*[6]*Rule*[7] (Mattauch 1934).

The element promethium (Pm^{61}) has 38 radioisotopes. Among them are two relatively stable isotopes, ^{145}Pm, with an atomic weight of 144.9127 and a half-life of 17.7 year, and ^{147}Pm, with an atomic weight of 146.9151, and a half-life of 2.623 year (Wieser and Berglund 2006). Due to the rather short half-life of the two isotopes, promethium does not occur in nature. It can only be synthesized.

Most other isotopes of promethium have a half-life of less than a second. The shortest half- life is for ^{163}Pm, which is approximately 200 ms.

The primary decay products are neodymium and samarium isotopes. Promethium-146 decays to neodymium and samarium (^{146}Nd and ^{146}Sm), the lighter isotopes generally to neodymium via positron decay and electron capture, and the heavier isotopes to samarium via beta decay. Exceptions are ^{130}Pm and ^{131}Pm which give rise to Pr (^{129}Pr and ^{130}Pr respectively) via positron emission. The isotope ^{132}Pm decays to both ^{132}Nd and ^{131}Pr via positron emission, although the majority leads to ^{132}Nd (Oliveira 2011).

3.4.6 Samarium (Element 62)

Samarium has 7 isotopes: ^{144}Sm, ^{147}Sm, ^{148}Sm, ^{149}Sm, ^{150}Sm, ^{152}Sm, and ^{154}Sm. Of these, 4 isotopes are stable, ^{144}Sm, 150Sm, ^{152}Sm, and ^{154}Sm, and three are radioactive isotopes, which, however, are extremely long-lived (^{147}Sm, ^{148}Sm and ^{149}Sm, with half-lifes $>1.0 \times 10^{11}$ years) (Table 3.7).

3.4.7 Europium (Element 63)

Europium has two isotopes ^{151}Eu with an atomic mass of 150.919846 (u) and ^{153}Eu with an atomic mass of 152.921226 (u). The isotope ^{153}Eu is stable, whereas the other was recently found to unstable, but with an extremely long half-life (4.62×10^{18} years; Casali et al. 2014).

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[6] Isobars refers here to atoms (nuclides) of different chemical elements that have the same number of nucleons (particles in the nucleus, i.e. protons or neutrons). Correspondingly, isobars differ in atomic number (or number of protons) but have the same mass number.

[7] Josef Mattauch (1895–1976) was a German physicist known for his work on establishing the isotopic abundances by mass spectrometry.

Table 3.7 Isotopes of Sm

Isotope	Atomic mass (u)	Abundance (%)
^{144}Sm	143.911995	3.07
^{147}Sm	146.914893	14.99
^{148}Sm	147.914818	11.24
^{149}Sm	148.917180	13.82
^{150}Sm	149.917271	7.38
^{152}Sm	151.919728	26.75
^{154}Sm	153.922205	22.75

3.4.8 Gadolinium (Element 64)

Natural gadolinium consists of 6 stable isotopes, ^{154}Gd, ^{155}Gd, ^{156}Gd, ^{157}Gd, ^{158}Gd and ^{160}Gd, and 1 radioisotope, ^{152}Gd. Its half -life is 10^{12} year (Table 3.8).

3.4.9 Terbium (Element 65)

Naturally occurring terbium has one stable isotope ^{159}Tb with an atomic mass of 158.925343 (u). For terbium, 36 radioisotopes have been characterized. The most stable are ^{158}Tb with a half-life of 180 years, ^{157}Tb with a half-life of 71 years, and ^{160}Tb with a half-life of 72.3 days. All the others have half-lives shorter than 7 days.

3.4.10 Dysprosium (Element 66)

Dysprosium has 7 stable isotopes. There are 29 radioisotopes with the most stable being ^{154}Dy with a half-life of 3.0 million years, ^{159}Dy with a half-life of 144.4 days, and ^{166}Dy with a half-life of 81.6 h. All other radioactive isotopes have half-lives that are less than 10 h (Table 3.9).

Table 3.8 Isotopes of Gd

Isotope	Atomic mass (u)	Abundance (%)
^{152}Gd	151.919788	0.20
^{154}Gd	153.920862	2.18
^{155}Gd	154.922619	14.80
^{156}Gd	155.922120	20.47
^{157}Gd	156.923957	15.65
^{158}Gd	157.924101	24.84
^{160}Gd	159.927051	21.86

Table 3.9 Stable Isotopes of Dy

Isotope	Atomic mass (u)	Abundance (%)
^{156}Dy	155.924278	0.06
^{158}Dy	157.924405	0.10
^{160}Dy	159.925194	2.34
^{161}Dy	160.926930	18.91
^{162}Dy	161.926795	25.51
^{163}Dy	162.928728	24.90
^{164}Dy	163.929171	28.18

3.4.11 Holmium (Element 67)

Naturally occurring holmium has one stable isotope ^{165}Ho with an atomic mass of 164.930319 (u). There are 36 radioisotopes, with the most stable one being ^{163}Ho, with a half-life of 4,570 years. All other radioisotopes have half-lives shorter than 1.2 days.

3.4.12 Erbium (Element 68)

Natural occurring erbium has 6 isotopes. There are 30 radioisotopes known, of which the most stable is ^{169}Er with a half-life of 9.4 days. The other radioisotopes have half-lives shorter than 50 h. The half-life of the majority of the radioisotopes is even shorter than 4 min (Table 3.10).

3.4.13 Thulium (Element 69)

Naturally occurring Thulium has one stable isotope ^{169}Tm with an atomic mass of 168.934211 (u). For thulium, 34 radioisotopes have been identified. Of these the most stable are ^{171}Tm with a half-life of 1.92 years, ^{170}Tm with a half-life of 128.6 days, ^{168}Tm with a half-life of 93.1 days, and ^{167}Tm with a half-life of 9.25 days. All the other radioactive isotopes have half-lives that are less than 64 h, and most of them have half-lives that are less than 2 min.

Table 3.10 Stable isotopes of Er

Isotope	Atomic mass (u)	Abundance (%)
^{162}Er	161.928775	0.14
^{164}Er	163.929197	1.61
^{166}Er	165.930290	33.61
^{167}Er	166.932045	22.93
^{168}Er	167.932368	26.78
^{170}Er	169.935460	14.93

Table 3.11 Stable isotopes of Yb

Isotope	Atomic mass (u)	Abundance (%)
^{168}Yb	167.933894	0.13
^{170}Yb	169.934759	3.04
^{171}Yb	170.936322	14.28
^{172}Yb	171.936378	21.83
^{173}Yb	172.938207	16.13
^{174}Yb	173.938858	31.83
^{176}Yb	175.942568	12.76

Table 3.12 The stable and the virtually stable isotopes of Lu

Isotope	Atomic mass (u)	Abundance (%)
^{175}Lu	174.940768	97.41
^{176}Lu	175.942682	2.59

3.4.14 Ytterbium (Element 70)

Ytterbium has 7 stable isotopes. There are 27 radioisotopes known. The most stable are ^{169}Yb with a half-life of 32.026 days, ^{175}Yb with a half-life of 4.185 days, and ^{166}Yb with a half-life of 56.7 h. All of the remaining radioactive isotopes have shorter half lives.

3.4.15 Lutetium (Element 71)

Natural lutetium consists of two isotopes: ^{175}Lu and ^{176}Lu (Tables 3.11 and 3.12). The latter is actually radioactive, but has an extremely long half-life of 3.78×10^{10} years. In total, 34 radioisotopes have been identified, of which, besides ^{176}Lu, the most stable are ^{174}Lu with a half-life of 3.31 years, and ^{173}Lu with a half-life of 1.37 years. All of the remaining radioactive isotopes have half-lives that are less than 9 days. Many half-lives are even less than half an hour.

3.5 Magnetism

For most of the lanthanide elements, their Curie-temperatures,[8] as far as they are known, are usually quite low, which results in the metals at room temperature generally displaying paramagnetism. An exception is gadolinium (Gd), which has a

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[8] Ferromagnetism is the magnetism commonly observed in iron, nickel and cobalt. The following types of magnetism are also recognized: ferrimagnetism, antiferromagnetism, and paramagnetism.

Table 3.13 Curie temperatures of the lanthanides. Data from Jensen and Mackintosh (1991)

	T_c (Curie-point) (K)	Type of magnetism
La	Not available	paramagnetic
Ce	Not available	paramagnetic
Pr	Not available	paramagnetic
Nd	Not available	paramagnetic
Pm	Not known	Not Known
Sm	Not available	paramagnetic
Eu	Not available	paramagnetic
Gd	293 K	ferromagnetic
Tb	220 K	paramagnetic
Dy	89 K	paramagnetic
Ho	20 K	paramagnetic
Er	20 K	paramagnetic
Tm	32 K	paramagnetic
Yb	Not available	paramagnetic
Lu	Not available	paramagnetic
Y	Not available	paramagnetic

Curie-temperature of 292 K (18.9 °C). It is ferromagnetic. The only other lanthanide with a (rather) high Curie-temperature is terbium, which has a Curie temperature of 222 K (−51.1 °C). The other known values are below 87 K (−186 °C). In Table 3.13, the known Curie-temperatures of the lanthanides are given.

3.6 Chemical Behavior

The rare earth elements are very electropositive, and, as a consequence, they generally form ionic compounds. Mineralogically, the REEs therefore form oxides, halides, carbonates, phosphates and silicates, borates or arsenates, but not sulphides. (Henderson 1996). Their oxidation states are given in Table 3.2.

(Footnote 8 continued)

The first two occur only below the Curie-temperature, the last one only above. On heating. a ferromagnetic, ferrimagnetic or antiferromagnetic material will convert to a paramagnetic material at the Curie-temperature. A paramagnetic material is only magnetic when placed in a magnetic field. Antiferromagnetic substances are actually not magnetic at all. This is because of a special organization of electron spins with opposite sign, which carry the magnetic moments. The magnetic moments of these electron spins cancel each other out, contrary to ferrimagnetism, where they do not, resulting in the case of ferrimagnetism as an observable magnetism.

3.6.1 Air and Oxygen

At room temperature, not all the rare earth metals are affected by air in the same way. The light REEs tend to tarnish very quickly, especially europium, but also lanthanum and neodymium. When the air is moist, and at elevated temperatures, oxidation proceeds even more rapidly. Oxidation increases by a factor of ten when the relative humidity is increased from 1 to 75 % (Gupta and Krishnamurthy 2005). Rare earth oxides do not all have the same structure, and therefore some oxide coatings on fresh metal surfaces in contact with water vapor spall, exposing fresh surfaces, whereas others form a persistent tight layer, which prevents further oxidation. Rare earth oxides have a very large negative free energy of formation, even belonging among the most negative in the whole periodic system. As a consequence, the rare earth oxides are among the most stable in the periodic system (Gupta and Krishnamurthy 2005).

3.6.2 Nitrogen

The REEs also have a strong affinity with nitrogen. The mononitrides of the rare earths are very stable and comparable in stability to those of titanium or zirconium (Gupta and Krishnamurthy 2005). The reaction with nitrogen is, however, slow. High temperatures are needed for a reaction to proceed at a visible rate. The nitrides also form a stable layer on the surface, blocking any further nitridation. Solid solutions with nitrogen are also possible (Gupta and Krishnamurthy 2005).

3.6.3 Hydrogen

Rare earth metals readily form hydrides at temperatures of 400–600 °C. Several of them decompose and degas relatively easily (Gupta and Krishnamurthy 2005).

3.6.4 Carbon

All rare earths easily form dicarbides ($REEC_2$). Several of them (La–Sm and Gd–Ho) also form sesquicarbides (REE_2C_3). Solid solubility of carbon in rare earths also occurs easily. REE-carbides also form solid solutions with nitrogen and oxygen (Gupta and Krishnamurthy 2005).

3.6.5 Silicon

Silicon (Si) forms silicides and solid solutions with all REE. Silicides are generally disilicides, $REESi_2$ (Gupta and Krishnamurthy 2005).

3.6.6 Refractory Metals

Niobium, molybdenum tantalum and tungsten are refractory metals, i.e. the ones that show resistance against attack by liquid RE metals. These metals are usually listed in the literature in order of decreasing solubility in the liquid rare metals at high temperatures. Tungsten is the least soluble. However, tungsten is rather brittle and has poor mechanical properties compared to tantalum, which is the second best with respect to solubility. Tantalum containers are therefore used in purification of liquid rare element metals (Gupta and Krishnamurthy 2005).

3.6.7 Acids and Bases

The REE readily dissolve in dilute mineral acids. Concentrated sulphuric acid has a somewhat smaller effect on rare element metals. The metals resist attach by HF, because a thin layer of $REEF_3$ forms on the metal, preventing further dissolution (Gupta and Krishnamurthy 2005).

3.6.8 Water

The reactions of the rare earths with water varies, depending on the metal. LREE react with water slowly at room temperature and more strongly at higher temperatures. HREE react very slowly with water (Gupta and Krishnamurthy 2005).

In aqueous systems, the typically trivalent rare earths show strong ionic character. Ce (IV) is the only tetrapositive rare earth species that is stable in aqueous solution as well as in solids. The trivalent rare earths form salts with a large number of anions. There is a wide variability in solubility of such salts. Rare earths containing thermally unstable ions like OH-, CO_3^{2-}, or $C_2O_4^{2-}$, convert, when heated first, into the basic derivative, and finally into the oxide (Gupta and Krishnamurthy 2005). Chlorides, bromides, nitrates, bromates, and perchlorate salts of rare earths are all water soluble. When crystallizing as a result of evaporation, they all form hydrated crystalline salts (Gupta and Krishnamurthy 2005).

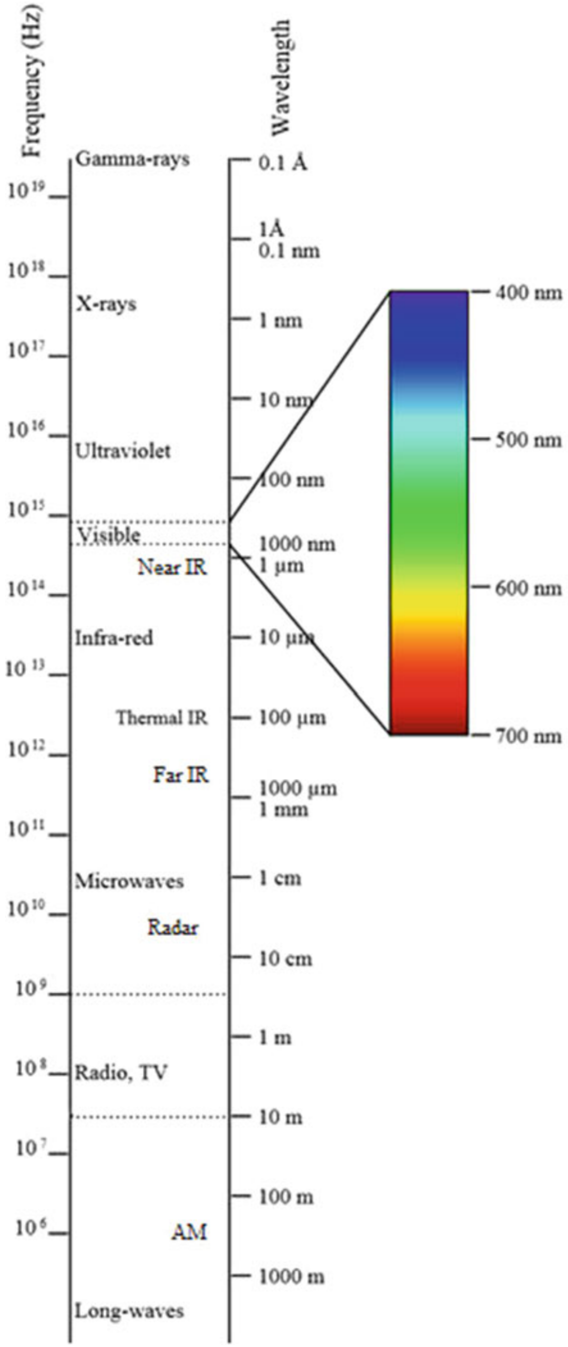

Fig. 3.3 Frequency and wavelength range

Table 3.14 Summary of the main visible emissions of lanthanide ions, and typical intensities of their visible emission (Andres and Chauvin 2012)

Trivalent lanthanide ion	Colour of visible luminescence	Intensity of the emission
Eu	Red or red-orange	Strong
Tb	Green	Strong
Dy	Yellow	Medium
Sm	Orange-red	Medium
Pr	Red	Weak
Er	Green	Weak
Ho	Red	Weak
Tm	Blue	Weak

3.7 Luminescence

The emission of light by a body can result from heat: for instance iron may glow red-yellow when heated to high temperatures. This is called incandescence. Luminescence is the emission of light by a substance which is not the result of heating. It is a type of cold-body radiation.

The lanthanides display luminescence in the spectral range from ultraviolet (UV) to near infrared (NIR). The spectral ranges are displayed in Fig. 3.3. The near infrared is a subsection of the infrared spectrum, ranging in wavelength from 0.75–1.4 µm.

Many lanthanide ***ions*** have unique spectral characteristics in the visible region of the electromagnetic spectrum, which results in their having distinct luminescent colors (Andres and Chauvin 2012). Many applications are based on these characteristic emissions for color reproduction and lighting. Among them are phosphors and LEDs. Another intensively studied application is energy conversion. The lanthanide ion converts one type of excitation energy (UV or IR) into visible energy that can be easily be absorbed by a photosensitive instrument, for instance a solar cell (Andres and Chauvin 2012).

With respect to luminescence, the most used lanthanides are europium and terbium. They have red (europium) and green (terbium) emissions. They are applied in additive color synthesis where all colors are reproduced by combinations of red, green and blue. Dysprosium (yellow) and samarium (orange) are also interesting for their luminescence, but the emissions are weaker than for europium and terbium. Other REEs exhibiting luminescence are thulium (red, blue, NIR), and praseodymium, but they have not been fully investigated (Andres and Chauvin 2012).

In the NIR part of the spectrum, the best lanthanides are ytterbium, erbium and neodymium. Holmium has been less investigated, but shows an emission spectrum with a peak in the red and a peak in the IR.

Finally, divalent europium exhibits luminescence in the blue part of the visible spectrum (Andres and Chauvin 2012).

The colors of the emissions and their intensities are summarized in Table 3.14.

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