# CHAPTER 1

## **INTRODUCTION TO THE RARE EARTHS**

Ten billion years ago the rare-earth elements that we see on Earth today were born in a supernova explosion. They account for one hundredth of one percent of the mass of all the elements found in the Earth's crust. Although this may not sound much, bear in mind that this is many orders of magnitude greater than the sum of all of the precious metals. Throughout the aeons of the Earth's history, the rare earths have stayed together with unswerving loyalty. Despite billions of years of being subjected to the physical extremes of geological processes — repeated melting and resolidifying, mountain formation, erosion and immersion in sea water — the rare earths have not separated out into elemental minerals. This is a strong testament to the similarity of many of their physical and chemical properties.

Rock formations resulting from various geological processes can become enriched or depleted in some of the rare-earth elements, and analysis of their relative abundances can yield to geophysicists valuable information on the development of geological formations. It is also generally accepted that the relative abundances of the rare-earth elements in chondritic meteorites represent their overall abundance in the universe, and so this particular branch of rare-earth science is important for an understanding of the genesis of the chemical elements. Compared to such global-scale terrestrial and extra-terrestrial studies, the study of the atomic structure of the surfaces of the rare-earth metals may seem at first to be rather prosaic. It is our aim to show that this is definitely not the case, and that this research is prerequisite for an understanding of many of the properties of the rare-earth metals that are being investigated at present and will be exploited in the future.

### 1.1 What's in a Name?

The name *rare earth* has its origins in the history of the discovery of these elements. They are never found as free metals in the Earth's crust and pure minerals of individual rare earths do not exist. They are found as oxides which have proved to be particularly difficult to separate from each other, especially to  $18^{th}$  and  $19^{th}$  Century chemists. The early Greeks defined *earths* as materials that could not be changed further by sources of heat, and these oxides seemed to fit that definition. The *rare* part of their name refers to the difficulty in obtaining the pure elements, and not to their relative abundances in the Earth's crust; all of the rare–earth elements are actually more abundant than silver, and some are more abundant than lead. This also explains why the names of some of the rare–earth elements sound similar to each other — what was originally thought to be the earth of a single element was often found subsequently to be a mixture of two or more earths, requiring the hasty invention of more names derived from the original.

In this chapter we present some general background information about the rare earths that help to place the rare-earth metals in their proper context. This includes a brief account of the two-hundred-year history of their discovery, the realisation of their relationship to the other elements in the periodic table, and the uses to which they have been put.

### 1.2 Discovery of the Rare Earths

There are large deposits of rare earths in Scandinavia, South Africa, China and Australia, but the geographic distribution of 18<sup>th</sup> Century scientists was such that the Scandinavian deposits were the first to bear fruit. In 1794 the Finnish chemist Johan Gadolin, while investigating a rare mineral found near the town of Ytterby in Sweden, discovered a new earth. He gave it the name ytterbia, which was later shortened to yttria. (The name of Ytterby has been used in various guises to name four of the rare–earth elements, adding to the general confusion of their identities.) The mineral, later named gadolinite, yielded another earth in 1803 through the joint work of Jöns Berzelius and Wilhelm Hisinger and independently by Martin Klaproth. This earth was named ceria, after the asteroid Ceres that had been discovered only two years earlier. Since yttria and ceria had been discovered in a rare mineral, and they

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resembled closely other earths that were known at that time, they were referred to as rare earths. It was some years later that the English chemist Sir Humphry Davy demonstrated that earths were not elements, but compounds of metallic elements with oxygen. The elements of which yttria and ceria were the oxides were given the names yttrium and cerium. Four decades later it was shown by the Swedish chemist Carl Mosander (who was a student of Berzelius) from his work over the years 1839-43 that the earths then identified as yttria and ceria were in fact oxides of mixtures of elements. He reported that if solutions of the earths were subjected to a long series of fractional precipitations as various salts, then two new elemental substances could be separated from the main component of each of the oxides. The two new oxides found in yttria were named erbia and terbia (the names derived from Ytterby again), and those found in ceria were named lanthana and didymia (from the Greek meaning 'concealed' and 'twin'). Mosander was also the first to extract the rare-earth metals from their oxides, though only in a rather impure form.

The existence of these six new elements and their associated oxides were perplexing to many scientists. The elements appeared to belong to a group that was different from any known at the time. Each of the elements formed the same type of compounds with very similar properties, and the elements themselves could only be distinguished from each other by relatively small differences in the solubilities and molecular weights of the compounds that they formed. In the 1840s and 1850s there was considerable confusion and controversy over the results of further fractionation of the rare earths, with the names of the earths discovered varying from one laboratory to another. Indeed, the level of confusion over the naming of the rare earths was such that in 1860 it was decided, by general agreement of the scientists of the day, to interchange the names of erbia and terbia. From 1859 the use of the spectroscope resolved much of the confusion by providing an objective means to identify the constituent elements. The pattern of lines in the light emission or absorption spectrum of a substance were found to be characteristic of the elements present, and so the products of various fractionation processes could be identified without the ambiguity that characterised earlier attempts.

For much of the next one hundred years fractionation of the rare earths was investigated across Europe and North America. Didymia was shown to be a mixture of the oxides of samarium (1879), praseodymium (1885), neodymium (1885) and europium (1896). Terbia and erbia were

resolved into oxides of ytterbium (1878), holmium (1878), thulium (1879), dysprosium (1886) and lutetium (1907). The name lutetium (from the Latin name for Paris) was accepted by all scientists except those in Germany, who referred to it as cassiopeium until the 1950s, when the names were agreed internationally. Gadolinium was discovered, but not named, by Jean-Charles-Galinard de Marignac in 1880. He separated gadolinia from the mineral samarskite (not, as one might have guessed, gadolinite) and some years later Paul-Émile Lecoq de Boisbaudran produced a more pure form of the same earth. With Marignac's approval, he named it after the mineral gadolinite.

Over this period, many dozens of claims were made for the discovery of new rare-earth elements. Most of these were the result of impurities, often from transition metals, causing changes in the apparent molecular weight and emission spectra of their compounds. Without an understanding of the electronic structure of atoms, it was not possible to predict how many rare-earth elements there should be and hence refutation of claims for discoveries of new elements was not a simple matter. The development of the periodic classification of the elements in the late 1800s and early 1900s helped clarify the situation significantly.

### 1.2.1 The Periodic Table

When Dmitry Mendeleyev first proposed the periodic table of the elements in 1869 he left a blank at the location now occupied by scandium. He realised that an element yet to be discovered, which he called ekaboron, belonged at that location and in 1871 he predicted some of the properties that it would possess. The discovery of scandia in gadolinite by Lars Nilson in 1879, followed by the realisation by Per Cleve that scandium was the 'missing' element ekaboron, provided strong evidence of the validity of Mendeleyev's periodic table and contributed to its acceptance by the scientific community. Although scandium and yttrium now fitted into the periodic table, the placement of the remaining rare-earth elements was proving to be more problematic, as the table structure proposed by Mendeleyev could not accommodate them in any logical manner. Resolution of this puzzle would have to wait until an understanding of atomic structure had developed in the early 1900s.

The English physicist Henry Moseley studied elemental x-ray emission spectra over the years 1913-14 and discovered a relationship

Tb Dy Ho Er Tm Yb

Es Fm Md

Lu

Lr

between the x-ray frequencies and the atomic number of the element. This relationship made it possible to assign an unambiguous atomic number to any element and thus to verify its location in the periodic table. Moseley concluded that there are 92 elements from hydrogen to uranium and that there are 14 lanthanides with atomic numbers covering the range Z=58-71.

H											N						He
Li 3	Be 4											B 5	C 6	N 7	0	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Тс 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 72	Та 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	T1 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89															

Lanthanides	/	Ce 58	Pr 59	Nd 60	Pm 61	$\operatorname{Sm}_{_{62}}$	Eu <sub>63</sub>	G	
		Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	C	

Fig. 1.1 The periodic table of the ele	ements.
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95 96 97 98 99 100 101 102 103

Bk

Cf

At that time, all of the rare-earth elements were known with the exception of element 61. No stable isotopes of this element exist in nature and so it is found only as a by-product of nuclear reactions. Early investigators who mistakenly thought that they had found element 61 prematurely named it illinium and florentium, but it was not until 1947 that one of its radioactive isotopes was unambiguously identified in the fission products of a nuclear reactor. The element was then named promethium, after the Greek Titan who stole fire from the gods.

### **1.3 Defining the Rare Earths**

The rare-earth metals are, by definition, the Group IIIb elements Sc, Y, La and the 14 lanthanides Ce-Lu. The term 'rare earth' has often been applied in the more restricted sense as a synonym for the lanthanides, thus excluding Sc, Y and La. It is reasonable to consider the lanthanides as a group separate from the rest of the periodic table only if the principal interest in these elements is those properties that depend on the occupancy of the 4f electron shell, from 0 (La) to 14 (Lu). An important example can be found in the magnetic properties of the lanthanides - the complex, often exotic, magnetic structures observed in alloys and compounds containing these elements are intimately dependent on the lanthanide 4f electrons and are thus absent from Sc, Y and La. However, essential though the 4f electrons are in giving the lanthanides their character, the grouping together of the 17 rare-earth metals reminds us that they have analogous electronic configurations – the outer three electrons are  $(3d 4s)^3$  for Sc,  $(4d 5s)^3$  for Y and  $(5d 6s)^3$  for La and the trivalent lanthanides. As chemical interactions between atoms are dominated by their outer-electron configurations, this similarity is directly responsible for the rare-earth elements being difficult to separate from each other. Thus, the origin of the 'rare' part of the name lies not in the low abundance (indeed, many are more abundant in the Earth's crust than Pb), but in the difficulty with which any of the elements could be obtained in a pure state by chemical extraction.

Thus, in many respects, Sc and Y can be treated as 'prototype' lanthanides, sharing all of the properties of the lanthanides that are not dependent upon the 4f electrons. Playing devil's advocate, we can use the argument in the previous paragraph to extend the definition of 'rare-earth' to include all of the Group IIIb elements, *i.e.*, to include Ac and the actinides as well. Although this does have some logic behind it, including the actinides has two distinct disadvantages. Firstly, the total number of elements in the group reaches 32 (including the 14 lanthanides and 14 actinides), a rather unwieldy number to treat as a group. Secondly, it masks the fact that the character and properties of the lanthanide and actinide elements are quite different due to the differences in the spatial extents (and hence overlaps) of the 4f and 5f electron wavefunctions. In the lanthanides, the highly localised 4f electrons in one atom have essentially zero overlap with those of a neighbouring atom.

However, the same cannot be said of the 5f electrons in the actinides due to the greater spatial extent of their wavefunctions. In this respect, the actinides bear more resemblance to the *d*-block transition metals than they do to the lanthanides. Thus, treating the rare-earth elements as a group distinct from the rest of the Periodic Table is a reasonable practice.

### 1.4 Applications of the Rare Earths

Although scientific research is the principal destination for the rare earths that are subjected to the highest levels of purification, it is the industrial uses of rare—earth compounds or mixtures of the rare—earth metals that account for the bulk of the rare earths processed throughout the world.

### 1.4.1 Oxides

One of the principal industrial uses of the rare earths, involving millions of tons of raw material each year, is in the production of catalysts for the cracking of crude petroleum. They also catalyse various other organic reactions, including the hydrogenation of ketones to form secondary alcohols, the hydrogenation of olefins to form alkanes, the dehydrogenation of alcohols and butanes, and the formation of polyesters. The catalytic behaviour of the rare earths can be quite significant, but they are used only in situations where there is no alternative, and less expensive, material that will perform with comparable efficiency.

The rare-earth oxides have been used in various other applications. One of the most widespread uses, responsible for most of the production of ultrapure rare earths, is in the television industry. In the triad of red-green-blue phosphor dots that make up television and computer monitor screens, a mixture of europium and yttrium oxides provides a brilliant-red phosphor. Another large user, which employs rare earths in a number of different applications, is the glass industry. Cerium oxide is more efficient than rouge for polishing glass in the production of lenses for spectacles, cameras and binoculars. Glasses having a combination of low-dispersion and high-refractive index, of use in high quality lens components, can be created using lanthanum oxide. Doping glasses with rare earths can modify their absorption characteristics, making them suitable for use in welders' and glassblowers' goggles. In addition, various

compounds of the rare earths have found uses in high-power lasers (for cutting and welding), solid state microwave devices (for radar and communications systems), gas mantles, various electronic and optical devices, and in the ceramic, photographic and textile industries.

## 1.4.2 Metals

Since the early 1900s the primary commercial form of mixed rareearth metals has been misch metal, an alloy comprising 50% cerium, 25% lanthanum, 15% neodymium and 10% other rare-earth metals and iron. This metal has been used heavily by the metallurgy industry to improve the strength, malleability, corrosion and oxidation resistance and creep resistance of various alloys, especially steels and other iron-based alloys. In the manufacture of cathode ray tubes, misch metal acts as a getter to remove oxygen from the evacuated tubes. Other elemental rare earths are used as alloy additives — in particular, praseodymium is used in high-strength, low-creep magnesium alloys for jet engine parts. Precision castings of aluminium and magnesium have also been reported to be improved by the addition of other rare earths. The discovery by Auer von Welsbach that an alloy of cerium and iron emits sparks when struck started the flint industry, leading to the refinement of thousands of tons each year of the cerium-laden mineral monazite.

Considerable excitement in the scientific community was aroused by the discovery in the late 1980s of high-temperature superconductivity in compounds of rare earths (in particular, yttrium and lanthanum), copper and combinations of other transition metals. The common link between the various compounds discovered to have high critical temperatures was that they all adopted a crystal structure closely related to the oxide mineral perovskite. The initial fervour pushed up the price of the rare-earth metals yttrium and lanthanum in anticipation of the years ahead when there would be a huge increase in demand for the manufacture of large quantities of room-temperature superconductors. However, this situation was short-lived as subsequent years of intense study revealed that the superconducting properties of the compounds were determined by the behaviour of the atoms in the copper-oxygen planes, and that the role of the rare-earth atoms was secondary.

A significant industrial application of the rare–earth metals is in the production of strong permanent magnets for use in a wide range of electromechanical devices. An often-quoted example is the ultra-lightweight headphones that accompany personal cassette and compact disc players, as these are consumer products with which many individuals will have come into contact in everyday life. This is a rather trite example of a technology capable of producing very powerful and yet lightweight electric motors. When mixed with 'traditional' magnetic metals from the transition metal series, such as iron, cobalt or nickel, some rare-earth metals produce hybrid magnets with exceptional properties that cannot be matched by either rare-earth metals or transition metals alone. In particular, neodymium and samarium have been found to produce materials with highly desirable magnetic properties. The replacement of transition metals with rare-earth metals in permanent magnet materials has clear scientific and technological benefits in the manipulation of the magnetic characteristics of the materials, but the most powerful driving force behind these developments has been the reduction in costs associated with reducing the cobalt content of the materials, due to its high expense relative to other metals.

## 1.4.3 Elements

Although as yet no link has been made between the atomic structure of surfaces and the radioactive state of the nuclei within the atoms (and it seems unlikely that any will be found), for the sake of completeness we note the use of radioactive isotopes of the rare earth elements in a variety of disciplines — irradiated thulium produces x-rays that are used in portable units for medics, or archaeologists investigating metallic artefacts; yttrium is used in cancer therapy; the relative abundance of lutetium isotopes is used to date meteorites; and the soft  $\beta$ -radiation of promethium is converted to electricity in miniature batteries formed by sandwiches of promethium and silicon.

### 1.5 The Rare–Earth Metals

Belonging to a common group, it is not surprising to find that many of the rare-earth metals have similar properties. However, the similarities in their chemical properties that are a result of their atomic structure, and hence a part of their definition, are not necessarily reflected in other properties. Indeed, where differences between the individual metals do

exist, they can be quite striking. In the following sections some of the basic properties of the rare-earth metals are presented and discussed briefly.

## 1.5.1 Electronic Configurations

As an introduction to the properties of the rare–earth metals, Table 1.1 lists their electronic configurations, crystal structures and lattice constants. As the electronic configurations of the elements in the rare–earth series have a significant influence on their crystal structures, and hence their surface structures, it is important to consider the systematics of the filling of the outer electron subshells in the lanthanides. The outer electron configurations for the rare–earth elements Pr–Sm and Tb–Tm are different for the atomic and solid state – the divalent  $4f^{n+1} 6s^2$  atomic

Table 1.1 Structural and electronic	properties (from Bea	udry and Gschneidner 1978)
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				Electron	Radi	us / pm	Crystal	Lattic	e Parame	eters
Element		Z	Α	Config	Ionic	Metallic	Structure	a / pm	c / pm	c / a
Scandium	Sc	21	45	$(3d4s)^3$	78.5	164.1	hcp	330.9	526.8	1.592
Yttrium	Y	39	89	$(4d5s)^{3}$	88.0	180.1	hcp	364.8	573.2	1.571
Lanthanum	La	57	139	$4f^{0}(5d6s)^{3}$	106.1	187.9	dhcp	377.4	1217.1	3.225
Cerium	Ce	58	140	$4f^{1}(5d6s)^{3}$	103.4	182.5	fcc	516.1	_	_
Praseodymium	$\mathbf{Pr}$	59	141	$4f^2 (5d6s)^3$	101.3	182.8	dhcp	367.2	1183.3	3.222
Neodymium	Nd	60	144	$4f^{3}(5d6s)^{3}$	99.5	182.1	dhcp	365.8	1179.7	3.225
Promethium	Pm	61	145	$4f^4 (5d6s)^3$	97.9	181.1	dhcp	365	1165	3.19
Samarium	$\operatorname{Sm}$	62	150	$4f^5 (5d6s)^3$	96.4	180.4	rhom	362.9	2620.7	7.222
Europium	Eu	63	152	$4f^{7} (5d6s)^{2}$	95.0	204.2	bcc	458.3	_	_
Gadolinium	Gd	64	157	$4f^{7} (5d6s)^{3}$	93.8	180.1	hcp	363.4	578.1	1.591
Terbium	Tb	65	159	$4f^{8} (5d6s)^{3}$	92.3	178.3	hcp	360.6	569.7	1.580
Dysprosium	Dy	66	163	$4f^{9} (5d6s)^{3}$	80.8	177.4	hcp	359.2	565.0	1.573
Holmium	Ho	67	165	$4f^{10}(5d6s)^3$	89.4	176.6	hcp	357.8	561.8	1.570
Erbium	Er	68	167	$4f^{11}(5d6s)^3$	88.1	175.7	hcp	355.9	558.5	1.569
Thulium	Tm	69	169	$4f^{12}(5d6s)^3$	86.9	174.6	hcp	353.8	555.4	1.570
Ytterbium	Yb	70	173	$4f^{14}(5d6s)^2$	85.8	193.9	fcc	548.5	_	_
Lutetium	Lu	71	175	$4f^{14}(5d6s)^3$	84.8	173.5	hcp	350.5	554.9	1.583

configurations become trivalent  $4f^n (5d 6s)^3$  in the solid state (where n = 2-5 and 8-12, respectively). Ce is a special case, as a precise value for the 4f occupancy and the resultant valency can not be determined uniquely. For the other rare-earth elements, the atomic valency is unchanged upon forming a solid. Along with praseodymium and terbium, cerium is different from the other trivalent rare-earths in that it forms compounds in which it is tetravalent; it is the only rare earth that exhibits a +4 oxidation state in solution.

Surface studies of Pm are conspicuous by their absence as the most stable Pm isotope is radioactive with a half-life of 18 years. Unless the elemental metal or one of its alloys or compounds proves to (or is predicted to) exhibit interesting properties that are absent from those of its neighbours Nd and Sm, this situation is not likely to change in the near future.

## 1.5.2 Crystal Structures

As can be seen from the table above, the 17 rare-earth metals exist in one of five crystal structures. At room temperature, nine exist in the hexagonal close-packed (hcp) structure, four in the double c-axis hcp (dhcp) structure, two in the face-centred cubic (fcc), and one in each of the body-centred cubic (bcc) and rhombic (Sm-type) structures. This distribution changes with temperature and pressure as many of the elements go through a number of structural phase transitions. The changes with elevated temperature are particularly relevant to the growth of single-crystal samples and will be discussed further in Chapter 4. All of the crystal structures, with the exception of bcc, are close-packed (*i.e.*, the number of nearest neighbours, or coordination number, has its maximum possible value of 12). The close-packed structures can be defined by the stacking sequence of the layers of close-packed atoms, as shown in Fig. 1.2. If the three inequivalent sites on a two-dimensional hexagonal lattice are labelled A, B and C, then the hcp structure is defined by a stacking sequence of ABAB..., dhcp is ABAC..., fcc is ABC... and the eponymous Sm-type is ABABCBCAC... Ideal close packing in the hcp structure is characterised by a lattice parameter ratio of  $c_a = \sqrt{(8_3)} \approx 1.633$ . As can be seen from Table 1.1, the ratios for the hcp rare-earth metals fall into the range 1.57–1.59, indicating that the atoms in the basal (hexagonal) plane are dilated by  $\sim 3\%$  with respect to ideal close packing. The corresponding



Fig. 1.2 Conventional unit cells for the crystal structures based on the hexagonal lattice.

values for the dhcp and rhombic metals, taking into account the extra atoms in the unit cell, indicate a similar dilation.

If Ce and the divalent metals Eu and Yb are notionally removed from the 17 rare-earth metals, then the remaining 14 can be divided into two major sub-groups: (i) the heavy rare-earth metals Gd-Lu, with the exception of Yb and the addition of Sc and Y, and (ii) the light rare-earth metals La-Sm, with the exception of Ce and Eu. Within each group, the chemical properties of the elements are very similar, with the result that they are almost always found together in mineral deposits (the latter group together with Ce compounds). It is quite common for the terms 'heavy' and 'light' to be applied to the rare-earth elements in the context of these two groups rather than the more usual reference to the atomic number. The adjectives 'yttric' and 'ceric' are also used to describe the heavy and light elements, respectively.

All the heavy rare-earth metals adopt the hexagonal close-packed (hcp) crystal structure and all the light rare-earth metals, with the exception of Sm, adopt the double *c*-axis hcp (dhcp) structure. The rhombic crystal structure of Sm (Sm-type) can be viewed as a rather exotic mixture

of one part fcc and two parts hcp (just as the dhcp structure can be viewed as an equal mix of fcc and hcp). Considering only the close-packed crystal structures, there is a systematic variation of the room temperature structures along the lanthanide series as the hcp structure gradually takes over from the fcc:

lanthanide elements	La–Ce		La–Pm		$\operatorname{Sm}$		Gd–Lu
fcc:hcp ratio	1:0	$\rightarrow$	$1_{2}: 1_{2}$	$\rightarrow$	$1_{/3}$ : $2_{/3}$	$\rightarrow$	0:1
crystal structure	fcc		dhcp		Sm-type		hcp

La and Ce have been included in both the fcc and dhcp categories as they both have a dhcp-fcc transformation close to room temperature. The application of high pressure causes the elements to revert to the previous structure in the series – Gd and Tb adopt the Sm-type structure, Sm becomes dhcp and La, Pr and Nd become fcc. The reason for this behaviour lies with the electronic structures of the rare-earth metals. Skriver (1982) suggested that the sequence of crystal structures could be entirely explained by the variation in *d*-band occupancy across the series, supporting his argument with bandstructure calculations that showed a systematic decrease in the *d*-band occupancy for the trivalent lanthanides. Other theories have involved the changing *f* occupancy across the lanthanide series, but the observation of the pressure-induced hcp  $\rightarrow$  Sm-type  $\rightarrow$  dhcp  $\rightarrow$  fcc sequence for Y (Grosshans *et al* 1982) clearly rules out the direct involvement of *f* electrons.

All but three of the studies of rare–earth single–crystal surfaces have used samples with crystal structures based on the hexagonal lattice – either bulk hcp or dhcp crystal structures or thin films of close–packed hexagonal layers with an unspecified stacking sequence. The exceptions are the photoemission studies of fcc  $\gamma$ –Ce (Jensen and Wieliczka 1984, Rosina *et al* 1985,1986) which investigated the valence band features of the (100) surface.

As the hcp structure is common to so many studies of rare-earth metal surfaces, it is worth taking a closer look at this crystal structure. It is assumed that the reader is familiar with the Miller index notation used to label crystallographic planes and directions, and in particular the fourindex notation that is often used for crystals that have hexagonal symmetry (undergraduate text books on solid state physics, such as

Blakemore 1992 or Kittel 1996, cover the definitions). Note that such familiarity is not essential, as the Miller indices can be treated simply as labels that define the crystal planes and surfaces. As we will be considering only a limited number of planes and directions, in crystals with either hexagonal and cubic symmetry, then the origins of the Miller indices are not strictly required.



Fig. 1.3 Principal planes of the hcp crystal structure.

The principal planes of the hcp crystal structure and their corresponding Miller indices are shown in Fig. 1.3. Clearly, the  $(11\overline{2}0)$  and  $(10\overline{1}0)$ planes are less densely packed than the (0001) basal plane (with relative packing densities of 61% and 50%, respectively, assuming ideal close packing). Note that the  $(10\overline{1}0)$  plane shown does not cut through any of the atoms in the middle of the hcp unit cell, but the  $(11\overline{2}0)$  plane does. The crystallographic structure of surfaces created by cutting the hcp crystal parallel to these planes will be discussed in Chapter 2.

### 1.5.3 Electronic Structure

On taking a cursory scan through the period table, it may seem that the electronic structure of the lanthanides should be analogous to the transition metal series. In both cases, one of the electronic shells are filling across the series. For the transition metals this is either the 3d, 4dor 5d shell, whereas for the lanthanides it is the 4f shell. The potential experienced by each electron is determined by the charge densities, and hence the wavefunctions, of all the other electrons in the metal. Clearly, approximations are required to make this a tractable problem, so the many-electron system is treated as a set of soluble one-electron systems. Although producing an enormous simplification to the mathematics of the solution, most of the important physics is retained. The potentials are fed in to the Schrödinger equation and computers solve the equation numerically to give the wavefunctions of the electrons. These wavefunctions can then be used to recalculate the charge densities and potentials. Thus there is a cycle involving

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potentials V \rightarrow wavefunctions \Psi \rightarrow charge densities \rho \rightarrow potentials V
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that must be self-consistent if the solutions are to have any meaning at all. Using the potentials for a free atom as a reasonable first guess, the cycle can be started and the calculations continued until self-consistency is achieved to within the desired tolerances.

Within such schemes, the electronic structure of extended, or delocalised, valence band states is reasonably well understood, as are the localised core electron states with large binding energies. However, for the lanthanides there is a complication that has impeded calculations of their electronic structures. The 4f electrons of the lanthanides have a character that is very different from the s, p and d valence electrons of any other atoms. Spatially, the 4f electron wavefunctions bear greater resemblance to core electrons than to valence electrons, and yet energetically they are degenerate with the valence electrons as they have binding energies below  $\sim 12$  eV. This degeneracy of highly localised 'core-like' electrons with the delocalised 'band-like' s and d valence electrons is the problem. Treating the 4f electrons as valence electrons in calculations of the electronic structure does not take proper account of their limited spatial extent, and treating them as core electrons does not take account of their interaction with the other valence electrons. Attempts to break this stalemate have been made (see, for instance, Temmerman et al 1993) but the rate of progress over the past four decades is a reflection of the difficulty of the problem. The rare–earth metals that have no 4f electrons (Sc, Y and La) thus serve as prototypes for the lanthanides, allowing the calculation of electronic structures that can act as benchmarks for all of the rare-earth metals.

Most of the rare-earth metals undergo a transformation of crystal structure at elevated temperatures, which will be discussed further in Chapter 4 in the discussion of crystal growth, but one of the rare-earth metals has a rather unusual transformation that is driven by changes in

its electronic structure — the isostructural transformation of Ce between the  $\gamma$  and  $\alpha$  phases. Both phases are fcc, but have lattice constants that differ by ~6%. Thus, the phase transformation from  $\gamma$  to  $\alpha$  on cooling is manifested as a collapse of the crystal structure. A desire to understand the driving force behind this transformation prompted many theoretical studies of the electronic structure of Ce, and it is now accepted that a change in the relative *d* and *f* occupancy of the valence band is responsible for the crystal transformation (see the reviews by Liu 1978 and Lynch and Weaver 1987, and more recent studies by Gu *et al* 1991, Weschke *et al* 1991, Laubschat *et al* 1992 and Liu *et al* 1992).

### 1.5.4 Magnetic Structure

Some of the magnetic structures exhibited by the heavy rare-earth metals are shown schematically as a function of temperature in Fig. 1.4. Whilst not presenting the subtlety of the spin alignments in some of the more exotic magnetic structures, it does show some of the diversity of the magnetic phases displayed by some of the metals in the rare-earth series.



Fig. 1.4 Some of the magnetic phases of the heavy rare—earth metals. For each magnetic phase, the arrows represent the changing magnitudes and directions of the components of magnetic moments relative to the basal planes (circles) from one atomic plane to the next.

The magnetic moments of the rare-earth metals are dominated by the spin contribution from the highly localised 4f electrons, and are thus good examples of local-moment ferromagnets. As the 4f electron shell can accommodate 14 electrons, a half-filled shell has seven electrons with

parallel spins (according to Hunds' rule, the empirical rule in atomic physics that states that in general parallel spins are a lower-energy configuration than anti-parallel spins). Thus, the 4*f* electrons contribute  $7\mu_{\rm B}$  to the total magnetic moment of Gd (~7.6 $\mu_{\rm B}$ ), and similarly large contributions to the total moments for the other magnetic rare-earth metals. In contrast to the situation with itinerant ferromagnets (based on the magnetic transition metals), the valence electrons contribute a small fraction of the overall magnetic moment per atom — in the case of Gd, the 5*d* 6*s* valence electrons contribute 0.6  $\mu_{\rm B}$ , less than 10% of the total moment. The magnetic structures of the rare-earth metals and many rare-earth-based compounds are well understood as the result of many decades of experimental study and the development of the local spin-density approximation in calculations of the valence electronic structures of solids.

# 1.6 Rare-Earth Metal Surfaces

Interest in the surfaces of the rare-earth metals has gone through something of a renaissance over the past ten years, due principally to the discovery of novel magnetic properties of the elemental metal surfaces. Prior to this, surface studies could be categorised as more chemistry than physics.

## 1.6.1 Early Surface Studies

Over the period 1960–1980 most rare-earth surface studies tended to focus on the chemical properties of the metals and their compounds. These included studies of the adsorption of molecules onto metallic and oxide surfaces, with emphasis on their chemical reactivity and catalytic properties. Many studies involved semiconductor substrates, and in particular Si. The interest here was in the formation of rare-earth silicides at the interface with Si, producing metal-semiconductor contacts with low Schottky barrier heights. Like so many other areas of research related to (or a subset of) rare-earth surface science, the study of rare-earth silicides could justify a book dedicated to that field alone. The scope of this book encompasses the surfaces of rare-earth metals but not those of rare-earth compounds (unless the latter have some bearing on the former) and so studies of rare-earth silicides will not be described

here in any detail.

## 1.6.2 Surface Magnetism

The effect of the presence of a surface on the magnetic properties of metals is currently a very active topic of research. The atomic structure and morphology of a surface influences the behaviour of the valence electrons and hence the magnetic properties of the system. Even in a local-moment system such as a rare-earth-based metal or compound, the behaviour of the valence electrons is crucial as it is these electrons that mediate the exchange interaction between neighbouring magnetic moments localised on the parent atoms. Thus the surface can be thought of as a perturbation to an infinite three-dimensional crystal, which in turn perturbs the electronic structure, which in turn perturbs the magnetic structure. This form of linear thinking is rather restrictive. A more realistic approach is to consider how a redistribution of the electrons near the surface of a material may result in a lowering of the total electronic energy or a change in the magnetic interaction between moments that drives the surface to change its structure. The true picture of a surface, if such a concept can be realised, involves a complex interplay between geometric structure (atomic positions and surface morphology) and electronic/ magnetic structure (the behaviour of atomically localised and itinerant electrons). The desire to understand this interplay is the prime mover behind most, if not all, of the studies of rare-earth metal surfaces.

We are not there yet, but the studies described in this book represent some pieces of the jigsaw. More studies will be carried out and more books will be written to provide the remaining pieces. When, or if, we have the complete picture of the relationships and correlations between surface structure and electronic/magnetic properties, then we will have the opportunity to manipulate surfaces to provide materials with the desired properties — surface engineering at an atomic scale.

# Further Reading

For those readers who wish to find out more about the physics and chemistry of the rare earths, one of the most comprehensive sources of information is the *Handbook on the Physics and Chemistry of Rare Earths*. Covering all aspects of the rare earths — atomic properties; structural, electronic, magnetic and optical properties of the elemental metals and

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their compounds, alloys and intermetallics; technological and industrial applications — the handbook now comprises more than 20 volumes.