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PREFACE

THE Editorial Board of Comprehensive Inorganic Chemistry planned the treatise to fill a gap in the literature. There was no work that provided more information than could be found in single volumes but was not so large as to put it out of reach of all but a few central libraries.

The Editorial Board drew up and incorporated in instructions to authors a scheme that would make the best possible use of about five thousand pages. It was envisaged that the treatise would be of service to a wide range of readers many of whom would not be professional chemists. Convenience for all classes of reader was of paramount importance so that if a conflict arose between brevity and ease of use, the latter was preferred. Nevertheless the arrangement of the treatise is so systematic that such conflicts rarely occurred. The convenience of the reader has been further ensured by the adoption of a consistent arrangement of material within the chapters on the elements. The editors have been very gratified to observe that authors have not found the imposed pattern unduly restrictive. It has certainly helped to keep the accounts coherent and to preserve the intended balance between the chapters. The editors are very sensible to the effort that authors have made to collaborate.

The section of the book devoted to the survey of topics, particularly those relating to the transition elements, was a special interest of Sir Ronald Nyholm, whose death after most chapters were in proof saddened many chemists. We hope that those chapters which bear repeated evidence of his intellectual influence will be judged to be one of the many worthy memorials that he left behind him.

A. F. TROTMAN-DICKENSON

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44. THE LANTHANIDES

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Arizona State University

INTRODUCTION

The lanthanides (Ce–Lu, atomic numbers 58–71) are unique among the elements, except for the closely similar actinides, in resembling each other so markedly both in the elemental state and in compounds that changes in properties for a given oxidation state with increasing atomic number are largely changes in degree rather than in kind. Typical examples are constancy of a particular thermodynamically stable oxidation state (+3) throughout the series, many instances of isomorphism when both oxidation state and anion are fixed, invariable co-occurrence in nature, the classically striking difficulty in separating one lanthanide from another, and small differences in the thermodynamic functions for particular reactions of lanthanide ions of a given charge type. Furthermore, both lanthanum (atomic number 57) and yttrium (atomic number 39), elements treated herein as members of Group IIIA, are broadly indistinguishable from the lanthanides in so many respects that they are operationally classifiable with the latter. It is, of course, the problems of explanation associated with these situations that prompted early difficulties in the periodic classification of the lanthanides.

ELECTRONIC CONFIGURATIONS AND THE CONSEQUENCES THEREOF

The problems of similarity and of difference in degree are, of course, most readily explicable in terms of the electronic configurations of the atoms and their derived ions. The elements scandium, yttrium, and lanthanum introduce, respectively, the first, second, and third *d*-transition series. The ground-state outer electronic configuration of an atom is in each instance of the type $(n-1)d^1ns^2$, where $n=1$ for Sc, 2 for Y, and 3 for La. The configuration of the neutral lanthanum atom thus amounts to an xenon core ($1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6$) with three electrons in the higher energy *5d* and *6s* orbitals. It has been shown that both the energy and the spatial extension of the *4f* orbitals decrease very abruptly as the nuclear charge increases beyond 57 (La)¹⁻³. For example, the nuclear binding energy of a single *4f* electron drops from -0.95 eV for the La atom to -5 eV for the Nd atom. Thus although the *4f* orbitals lie well outside the xenon structure in the La atom and are thus unoccupied, they lie within that structure in the Nd

¹ M. G. Mayer, *Phys. Rev.* **60** (1941) 184.

² R. Latter, *Phys. Rev.* **99** (1955) 510.

³ C. A. Coulson and C. S. Sharma, *Proc. Phys. Soc. (London)*, **79** (1962) 920.

atom and are occupied. It is the development of a deep potential energy well close to the nucleus that draws the $4f$ orbitals into the atom and permits, by occupancy of these orbitals, the existence of the lanthanide elements. Inasmuch as there are seven $4f$ orbitals, a total of 14 elements can be expected in this series.

Ground-state configurations for the atoms and cations are most commonly assigned in terms of emission spectral data⁴⁻⁶. The configurations listed for the atom (Ln^0) and gaseous ions Ln^{x+} in Table 1 are those most consistent with these and atomic beam

TABLE 1. GROUND-STATE "OUTER" ELECTRONIC CONFIGURATIONS

Atomic No.	Symbol	Configuration (spectroscopic term)			
		Ln^0	Ln^+	Ln^{2+}	Ln^{3+}
57	La	$5d^1 6s^2 (2D_{3/2})$	$5d^2 (3F_2)$	$5d^1 (2D_{3/2})$	$4f^0 (1S_0)$
58	Ce	$4f^1 5d^1 6s^2 (1G_4)$	$4f^1 5d^1 6s^1 (2G_{7/2})$	$4f^2 (3H_4)$	$4f^1 (2F_{5/2})$
59	Pr	$4f^3 6s^2 (4I_{9/2})$	$4f^3 6s^1 (5I_4)$	$4f^3 (4I_{9/2})$	$4f^2 (3H_4)$
60	Nd	$4f^4 6s^2 (5I_4)$	$4f^4 6s^1 (6I_{7/2})$	$4f^4 (5I_4)$	$4f^3 (4I_{9/2})$
61	Pm	$4f^5 6s^2 (6H_{5/2})$	$4f^5 6s^1 (7H_2)$	$4f^5 (6H_{5/2})$	$4f^4 (5I_4)$
62	Sm	$4f^6 6s^2 (7F_0)$	$4f^6 6s^1 (8F_{1/2})$	$4f^6 (7F_0)$	$4f^5 (6H_{5/2})$
63	Eu	$4f^7 6s^2 (8S_{7/2})$	$4f^7 6s^1 (9S_4)$	$4f^7 (8S_{7/2})$	$4f^6 (7F_0)$
64	Gd	$4f^7 5d^1 6s^2 (9D_2)$	$4f^7 5d^1 6s^1 (10D_{3/2})$	$4f^7 5d^1 (9D_2)$	$4f^7 (8S_{7/2})$
65*	Tb	$4f^9 6s^2 (6H_{15/2})$	$4f^9 6s^1 (7H_8)$	$4f^9 (6H_{15/2})$	$4f^8 (7F_6)$
66	Dy	$4f^{10} 6s^2 (5I_8)$	$4f^{10} 6s^1 (6I_{17/2})$	$4f^{10} (5I_8)$	$4f^9 (6H_{15/2})$
67	Ho	$4f^{11} 6s^2 (4I_{15/2})$	$4f^{11} 6s^1 (5I_8)$	$4f^{11} (4I_{15/2})$	$4f^{10} (5I_8)$
68	Er	$4f^{12} 6s^2 (3H_6)$	$4f^{12} 6s^1 (4H_{13/2})$	$4f^{12} (3H_6)$	$4f^{11} (4I_{15/2})$
69	Tm	$4f^{13} 6s^2 (2F_{7/2})$	$4f^{13} 6s^1 (3F_4)$	$4f^{13} (2F_{7/2})$	$4f^{12} (3H_6)$
70	Yb	$4f^{14} 6s^2 (1S_0)$	$4f^{14} 6s^1 (2S_{1/2})$	$4f^{14} (1S_0)$	$4f^{13} (2F_{7/2})$
71	Lu	$4f^{14} 5d^1 6s^2 (2D_{3/2})$	$4f^{14} 6s^2 (1S_0)$	$4f^{14} 6s^1 (2S_{1/2})$	$4f^{14} (1S_0)$

* Ground states of Tb^0 and Tb^+ may be $4f^8 5d^1 6s^2$ and $4f^8 5d^1 6s^1$ respectively.

resonance data⁷. The spectroscopic terms are included also for completeness. For the neutral atoms, the first $4f$ electron appears with cerium. There is not, however, a regular increase in occupancy of the $4f$ orbitals as atomic number decreases, and two types of configuration appear, namely $4f^n-15d^1 6s^2$ and $4f^n 6s^2$. Variation in the energy difference between these two types of configuration (Fig. 1)⁸ is such that the thermodynamic stability of the half-filled ($4f^7$) and filled ($4f^{14}$) subshell is emphasized. This same effect characterizes the uni- and bipoisitive ions⁹, but it disappears with the terpositive ions¹⁰, for which the regularly increasing $4f^n$ configuration is observed. Minor alterations in these configurations, e.g. for the Tb^0 and Tb^+ species, may result as methods of interpreting experimental data are refined.

⁴ W. F. Meggers, *Science*, **105** (1947) 514.

⁵ H. N. Russell and W. F. Meggers, *J. Research Natl. Bur. Standards*, **9** (1932) 625.

⁶ W. C. Martin, *J. Opt. Soc. Am.* **53** (1963) 1047.

⁷ B. B. Cunningham, in *Rare Earth Research* (E. V. Klieber, ed.), Macmillan, New York (1961), pp. 127-134.

⁸ M. Fred, in *Lanthanide/Actinide Chemistry*, Vol. 71, *Advances in Chemistry Series*, American Chemical Society, Washington (1967), pp. 200-201.

⁹ D. S. McClure and Z. Kiss, *J. Chem. Phys.* **39** (1963) 3251.

¹⁰ E. Loh, *Phys. Rev.* **147** (1966) 332.

Whether the ground-state configuration of a specific atom is $4f^{n-1}5d16s^2$ or $4f^n6s^2$ is of little consequence in determining the chemical behavior of that species, however, since other energy terms associated with a given reaction are more significant than the energy difference between these two states. The existence of a common +3 state of oxidation throughout the series does require in most instances that an f electron be removed in its formation. However, the $4f$ orbitals are sufficiently removed from the valency shell and sufficiently shielded by external shells as to be largely unavailable in other chemical

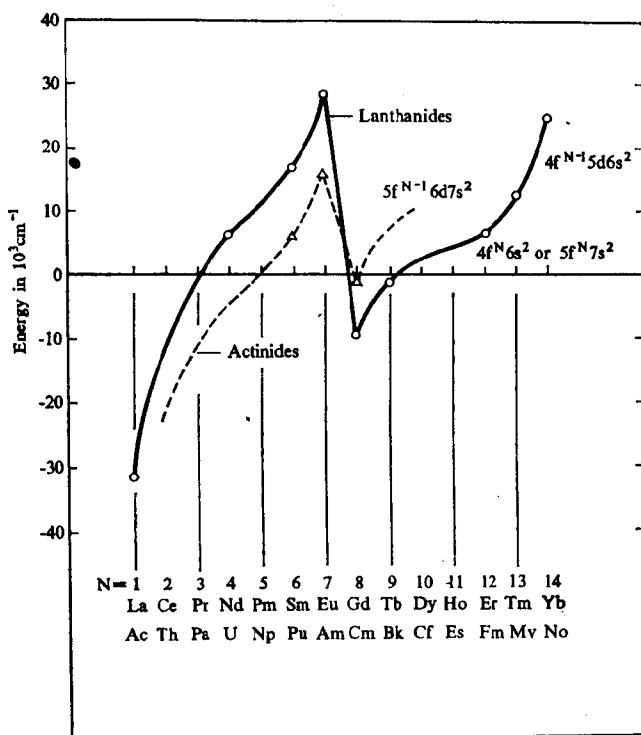


FIG. 1. Relative energy relationships between $f^n s^2$ and $f^{n-1} d 1 s^2$ ground-state electronic configurations. (Reproduced by permission from M. Fred in *Lanthanide/Actinide Chemistry*, Vol. 71, *Advances in Chemistry Series*, American Chemical Society, Washington, D.C. (1967), p. 200.)

reactions. Herein lies a significant difference from the d -transition species, the atoms and ions of which are characterized by d electrons in their valency shells. There is, therefore, a closer configurational similarity between the lanthanide ions and the Group Ia-IIIa cations than between the lanthanide ions and the d -transition metal ions. The presence of shielded $4f$ electrons in the lanthanide ions does not materially alter the noble-gas core that they present to incoming chemical groups. The exclusion of lanthanum from the lanthanide group is based solely upon the absence of $4f$ electrons.

A number of general properties that are either directly or indirectly consequences of the $4f$ electronic arrangement can now be discussed to advantage as a general prelude to the more specific topics covered in later sections.

Oxidation States

The +3 state of oxidation is characteristic of all the lanthanides both in solid compounds and in solutions in water and other solvents (Table 2). A few solid compounds exemplifying the +4 state have been prepared¹¹, but only tetrapositive cerium has a sufficiently long half-life with respect to reduction to be of importance in aqueous solution. Although all of the lanthanides have been obtained in the +2 state by trapping in solid alkaline earth halide matrices¹², dissolution in aqueous systems results in rapid oxidation to the +3 state of all the species except europium(II). Even europium(II) has only a comparatively short half-life with respect to oxidation in aqueous solution¹³. Solid compounds isolable

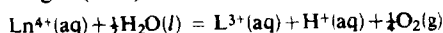
TABLE 2. DISTINGUISHING ELECTRONIC CONFIGURATIONS DESCRIBING BEST CHARACTERIZED OXIDATION STATES

Symbol	Configuration (examples)*			
	0	+2	+3	+4
La	5d ¹ 6s ²		4f ⁰ (La ³⁺)	
Ce	4f ¹ 5d ¹ 6s ²	4f ² (CeCl ₂)	4f ¹ (Ce ³⁺)	4f ⁰ (CeO ₂ , CeF ₄ , Ce ⁴⁺)
Pr	4f ³ 6s ²		4f ² (Pr ³⁺)	4f ¹ (PrO ₂ , PrF ₄ , K ₂ PrF ₆)
Nd	4f ⁴ 6s ²	4f ⁴ (NdI ₂)	4f ³ (Nd ³⁺)	4f ² (Cs ₃ NdF ₇)
Pm	4f ⁵ 6s ²		4f ⁴ (Pm ³⁺)	
Sm	4f ⁶ 6s ²	4f ⁶ (SmX ₂ , SmO)	4f ⁵ (Sm ³⁺)	
Eu	4f ⁷ 6s ²	4f ⁷ (Eu ²⁺)	4f ⁶ (Eu ³⁺)	
Gd	4f ⁷ 5d ¹ 6s ²		4f ⁷ (Gd ³⁺)	
Tb	4f ⁹ 6s ²		4f ⁸ (Tb ³⁺)	4f ⁷ (TbO ₂ , TbF ₄ , Cs ₃ TbF ₇)
Dy	4f ¹⁰ 6s ²		4f ⁹ (Dy ³⁺)	4f ⁸ (Cs ₃ DyF ₇)
Ho	4f ¹¹ 6s ²		4f ¹⁰ (Ho ³⁺)	
Er	4f ¹² 6s ²		4f ¹¹ (Er ³⁺)	
Tm	4f ¹³ 6s ²	4f ¹³ (TlI ₂)	4f ¹² (Tm ³⁺)	
Yb	4f ¹⁴ 6s ²	4f ¹⁴ (YbX ₂ , Yb ₂ ⁺)	4f ¹³ (Yb ³⁺)	
Lu	4f ¹⁴ 5d ¹ 6s ²		4f ¹⁴ (Lu ³⁺)	

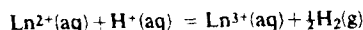
* Inclusion of formulas for ions implies that series of compounds are known both as solids and in aqueous solution (X = halogen atom).

in a state of purity are limited to derivatives of the ions Eu²⁺, Yb²⁺, Sm²⁺ and Tm²⁺¹¹. The metallic conduction shown by certain binary compounds of apparently bipositive stoichiometry (e.g. LnH₂, LnC₂, LnX₂; p. 76) precludes the presence of Ln²⁺ ions.

A direct correlation between observed oxidation state and the ground-state configuration of the parent atom appears to be fortuitous. Although the loss of electrons by the Ln³⁺ ions may well be minimized by the shielding of remaining 4f electrons by the kernels, the ubiquitous +3 state must owe its existence to factors other than this one. The terpositive ions can be expected to be thermodynamically stable in acidic aqueous medium only if the free energy changes (ΔG°) for the reactions described by the equations



and



¹¹ L. B. Asprey and B. B. Cunningham, in *Progress in Inorganic Chemistry*, Vol. II, Interscience Publishers, New York (1960), pp. 267-302.

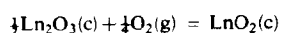
¹² P. N. Yocom, in *Lanthanide/Actinide Chemistry*, Vol. 71, Advances in Chemistry Series, American Chemical Society, Washington (1967), pp. 51-55.

¹³ G. R. Machlan, C. T. Stubblefield, and L. Eyring, *J. Am. Chem. Soc.* **77** (1955) 2975; C. T. Stubblefield and L. Eyring, *J. Am. Chem. Soc.* **77** (1955), 3004.

are simultaneously zero or less than zero (negative)¹⁴, i.e. only if the +4 state is reduced spontaneously by water and the +2 state oxidized spontaneously by hydrogen ion. More realistically, a change in free energy of *ca.* +25 kcal mole⁻¹ could be necessary in each case to establish stability of the +3 state since kinetic and mechanistic difficulties may allow otherwise unstable species to persist for measurable periods of time¹⁴.

In the absence of overall thermodynamic data for either of these reaction types, a stepwise summation of a series of hypothetical processes, by means of which the gaseous Ln⁴⁺ or Ln²⁺ ion is converted ultimately to the aqueous Ln³⁺ ion and for which enthalpy changes are known or can be approximated reasonably, can be effected. If it is assumed that the free energy change is largely determined by the enthalpy change, two conclusions result¹⁴: (1) of the Ln⁴⁺ and Ln²⁺ ions, all are thermodynamically unstable with respect to the Ln³⁺ ion, the Ce⁴⁺ and Eu²⁺ ions being on the borderline and experimentally metastable only because of slow rates of conversion, and (2) the observed stability of the +3 state is primarily a consequence of a fortuitous balance between ionization and hydration energies of the ions.

Similar calculations can be made for pure solid compounds using crystal energies, ionization energies, and electron affinities¹⁴, but they are complicated by the changes in crystal structure that accompany many oxidation or reduction processes and the lack of data for anything except simple binary compounds. Cunningham finds that the conversion



should proceed in air if Ln = Ce, Pr, Tb, and Dy. Experimentally, the compounds CeO₂, Pr₆O₁₁(defect), and Tb₄O₇(defect) result, but no higher oxide of dysprosium forms. Among

TABLE 3. STANDARD OXIDATION POTENTIALS

Symbol	E_{298}° in volts ^a			
	$\text{Ln}(\text{c}) = \text{Ln}^{3+}(\text{aq}) + 3\text{e}^-$	$\text{Ln}(\text{c}) + 3\text{OH}^-(\text{aq}) = \text{Ln}(\text{OH})_3(\text{c}) + 3\text{e}^-$	$\text{Ln}^{2+}(\text{aq}) = \text{Ln}^{3+}(\text{aq}) + \text{e}^-$	$\text{Ln}^{3+}(\text{aq}) = \text{Ln}^{4+}(\text{aq}) + \text{e}^-$
La	+2.522	+2.90		
Ce	2.483	2.87		-1.74 ^b
Pr	2.462	2.85		<i>ca.</i> -2.86
Nd	2.431	2.84		
Pm	2.423	2.84		
Sm	2.414	2.83	+1.55	
Eu	2.407	2.83	0.43	
Gd	2.397	2.82		
Tb	2.391	2.79		
Dy	2.353	2.78		
Ho	2.319	2.77		
Er	2.296	2.75		
Tm	2.278	2.74		
Yb	2.267	2.73	1.15	
Lu	2.255	2.72		
Y	2.372	2.81		

^a Many values estimated.

^b In perchlorate solution.

the halides, LnX₄ compounds should be limited to the fluorides because of reduced electrostatic attractions between the Ln⁴⁺ and larger X⁻ ions. That the +4 and +2 states are

¹⁴ B. B. Cunningham, in *XVIIth International Congress of Pure and Applied Chemistry*, Munich 1959, Butterworths, London (1960), pp. 64-81.

more common in the solid state than in solution undoubtedly reflects also the isolation of the individual cations from each other and the enhanced difficulty of electron transfer. It appears, albeit far less definitively than for solutions, that a balance between crystal and ionization energies favors the +3 state as the common one.

The observed stability of the +3 state in aqueous systems is readily apparent from the oxidation-potential data summarized in Table 3^{15, 16}. Oxidation of each of the pure metals in acidic or alkaline medium proceeds preferentially to the +3 state with concomitant reduction of the hydrogen ion or water. The bipositive ions oxidize similarly in acidic medium. Cerium(IV), when in acidic perchlorate medium where complexing

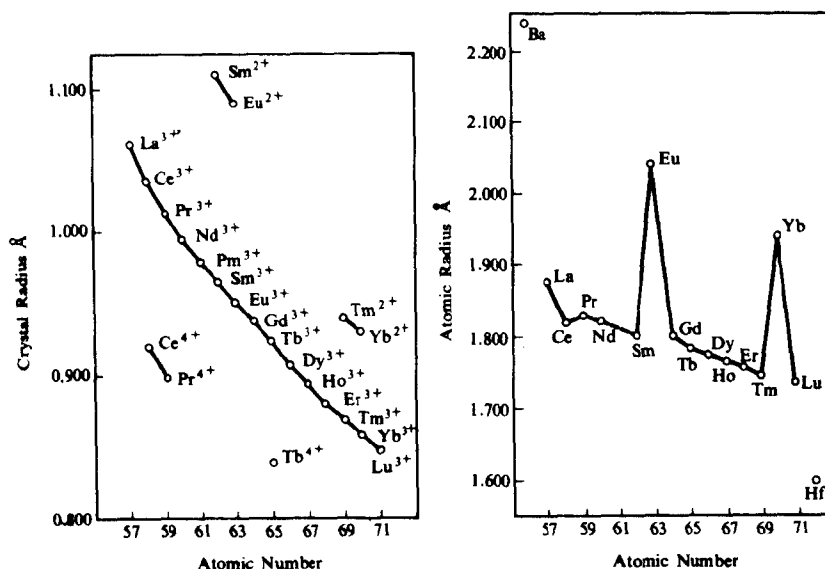


FIG. 2. Variations in atomic and crystal radii. (Reproduced by permission from T. Moeller, *The Chemistry of the Lanthanides*, Reinhold Book Corporation, New York (1963), pp. 21, 22.)

and polymerization are at a minimum (p. 98), is reduced slowly by water. In nitrate or sulfate medium, complexation renders cerium(IV) less susceptible to reduction to cerium(III). The estimated potential for the Pr(III)–Pr(IV) couple has no practical meaning since the Pr^{4+} ion has so short a half-life under these conditions that it has not been observed.

The data in Tables 2 and 3 emphasize the spectroscopically indicated and apparently real stabilities of the empty ($4f^0$), half-filled ($4f^7$), and filled ($4f^{14}$) f -subshell arrangements. Preference for these arrangements is shown by the number of species characterized by them and by the enhanced oxidizing (e.g. for Pr^{4+}) and reducing (e.g. for Sm^{2+}) strengths of non-terpositive ions that depart in electronic configurations from them.

Size Relationships

The data summarized in Table 4 and Fig. 2 indicate clearly that although there is the expected increase in the sizes of atoms and derived terpositive ions of the Group IIIA

¹⁵ A. J. de Bethune and N. A. S. Loud, in *The Encyclopedia of Electrochemistry* (C. A. Hampel, ed.), Reinhold Book Corp., New York (1964), pp. 414–426.

¹⁶ T. Moeller, *The Chemistry of the Lanthanides*, Reinhold Book Corp., New York (1963), Ch. 2.

elements (Sc to Y to La to Ac), an overall decrease occurs from lanthanum to lutetium. This decrease is the well-known *lanthanide contraction*. The lanthanide contraction is a result of the imperfect shielding of one $4f$ electron by another $4f$ electron¹⁷. As the nuclear charge, and thus the $4f$ electron population, increases, the imperfect shielding occasioned by the directed nature of these orbitals causes each $4f$ electron to experience added electrostatic attraction by the nucleus. The result is a decrease in the size of the entire $4f^n$ arrange-

TABLE 4. ATOMIC AND CRYSTAL RADII

Atomic No.	Symbol	Atomic radius* (Å)	Crystal radius (Å)		
			+2 ^b	+3 ^c	+4 ^b
21	Sc	1.641 (a)		0.68 ^b	
39	Y	1.801 (a)		0.88 ^b	
57	La	1.877 (a)		1.061	
58	Ce	1.824 (γ)		1.034	0.92
59	Pr	1.828 (a)		1.013	0.90
60	Nd	1.821		0.995	
61	Pm	(1.810) ^d		(0.979) ^d	
62	Sm	1.802 (a)	1.11	0.964	
63	Eu	2.042	1.09	0.950	
64	Gd	1.802 (a)		0.938	
65	Tb	1.782 (a)		0.923	0.84
66	Dy	1.773		0.908	
67	Ho	1.766		0.894	
68	Er	1.757		0.881	
69	Tm	1.746	0.94	0.869	
70	Yb	1.940 (a)	0.93	0.858	
71	Lu	1.734		0.848	
89	Ac	1.878		1.11 ^b	

* For coordination number = 12 and modification listed. Non-hexagonal crystal structures = γ-Ce, fcc; α-Sm, rhomb; Eu, bcc; α-Yb, fcc; Ac, fcc. (Data from A. H. Daane, in *The Rare Earths*, John Wiley, New York (1961), Ch. 13; K. A. Gschneider, *ibid.*, Ch. 14 (see Table 22).

^b W. H. Zachariasen in *The Actinide Elements*, McGraw-Hill, New York (1954), p. 775.

^c D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.* 76 (1954) 5237.

^d Estimated.

ment, and therefore in the sizes of atoms and ions, with increasing atomic number. The same effect is noted in each of the d -transition series, but is always less pronounced. There is, of course, a parallel *actinide contraction* among the $5f$ species (Chapter 45).

The contraction is shown most dramatically by the ions Ln^{3+} . The slight discontinuity at the Gd^{3+} ion (Fig. 2) is undoubtedly a reflection of the closed-shell configuration of that ion. To the extent that data are available for the Ln^{2+} and Ln^{4+} ions, parallel contractions occur. With the neutral atoms, however, striking discontinuities appear at europium and ytterbium and a more minor one at cerium. Inclusion of the divalent predecessor of the series, barium, and the tetravalent successor in Fig. 2 suggests, what is

¹⁷ C. Klixbüll Jørgensen, *J. Inorg. Nucl. Chem.* 1 (1955) 301.

confirmed by evaluation of metallic properties, that europium and ytterbium are divalent in the metallic state and that cerium tends toward quadrivalency, whereas the other lanthanides are trivalent. There is here a parallel to oxidation-state differences in compounds.

The atomic and ionic radii are important both with regard to their actual numerical magnitudes and the changes in magnitude with changing nuclear charge. Both the atoms and cations are large on a comparative basis¹⁶. That the elemental lanthanides are strong reducing agents (Table 3) and the compounds are quite generally ionic are direct consequences of large size. The bivalent ions compare in crystal radii with the calcium and strontium ions. The numerous recorded instances of isostructural compounds and similarities in solubility between europium(II) and ytterbium(II) compounds and those of these Group II elements are expected consequences of this size similarity. The trivalent lanthanide and actinide ions have sufficiently similar crystal radii to be closely parallel in many of their properties¹⁸. Cerium(IV) resembles thorium(IV) and the +4 actinide ions in general for the same reason¹⁸.

The lanthanide contraction is sufficient to cause differences in the *degree* to which some, but not all, of the properties associated with a given oxidation state are exhibited. Thus, considering only the trivalent ions, there are, parallel to decreasing crystal radius, many recorded examples of decrease in coordination number, decrease in basicity (as measured by increase in degree of hydrolysis of a particular salt type, increase in the thermodynamic stability of a given type of complex, decrease in the decomposition temperature of a solid compound with a given oxo anion, alteration of solubility), decrease in ionic character in solid binary compounds, and decrease in ease of oxidation (as measured by oxidation potential or ionization energy). On the other hand, there are cases of complete isomorphism throughout the entire or nearly entire series, e.g. among the compounds $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Ln}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$, where the differences in crystal radii are insufficient to produce change in crystal structure. It is, of course, these differences in degree that provide the basis for all procedures of fractional separation, whether they be the classical procedures of fractional crystallization or precipitation or the more modern procedures of ion exchange or solvent extraction.

The lanthanide contraction is sufficiently large that the size of the Y^{3+} ion is reached in the Ho^{3+} – Er^{3+} region (Table 4). The heavier Ln^{3+} ions are then smaller than the Y^{3+} ion, but never as small as the Sc^{3+} ion. The invariable cooccurrence in nature of yttrium with the heavier lanthanides, the observed concentration of yttrium with these elements in most procedures of fractional separation, the enhanced difficulty of effecting a final separation of yttrium from the heavier—as opposed to the lighter—lanthanides, and the close similarity between compounds of yttrium and these heavier ions in all properties that are determined by cation charge-cation size relationships (e.g. crystal structure, degree of covalency, stability of complex species) are reasonable consequences of this circumstance. Yttrium, even though it is a true member of the preceding periodic series, is thus usefully considered to be a lanthanide. Indeed, the greater crustal abundance of yttrium (p. 44) and the fact that yttrium chemistry often establishes aspects of the chemistries of less abundant lanthanides prompt characterization of the heavier lanthanides (Gd–Lu) as *yttrium earths*. No such direct parallels between scandium and the lanthanides are either expected or observed.

Although unrelated to the lanthanides themselves, the remarkable parallels between

¹⁸ W. H. Zachariasen, in *The Actinide Elements*, McGraw-Hill, New York (1954), Ch. 18.

the elements that follow the lanthanides in nuclear charge and their congeners in the preceding periodic series, e.g. between Hf and Zr, Ta and Nb, W and Mo, Re and Tc, etc., are also consequences of the lanthanide contraction.

Electronic Energy States

The effective shielding of $4f$ electrons from external fields by the $5s^25p^6$ arrangement causes the electronic energy states that arise from the $4f^n$ configurations to be only minimally affected by the surroundings in which the Ln^{3+} ions find themselves and thus to be essentially the same for a given ion in nearly all of its compounds, both in crystals and in solution¹⁹. Inasmuch as the energy states of the $4f^n$ configurations are usefully approximated by the Russell-Saunders scheme and spin-orbit coupling constants are

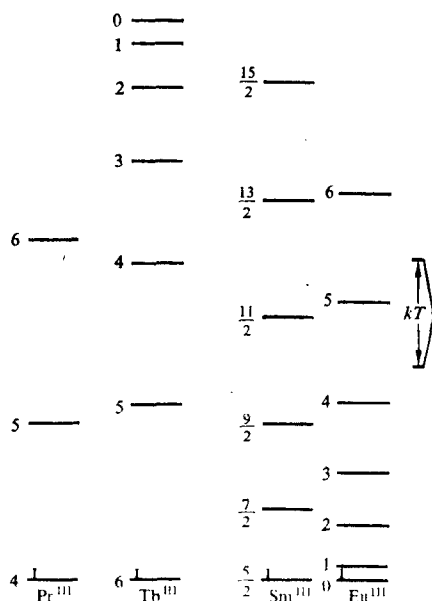


FIG. 3. J states for selected trivalent lanthanide ions. (Reproduced by permission from F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience Publishers, New York (1966), 2nd edn., p. 1057.)

comparatively large, nearly every one of the trivalent ions is characterized by a ground state with a single value of resultant total angular momentum J and a first excited state at an energy larger by a number of times the quantity kT . The net effect is that for each of these ions the first excited state is essentially unpopulated by electrons except at very high temperatures. This situation is indicated in terms of a number of examples in Fig. 3. The Sm^{3+} and Eu^{3+} ions, however, differ from the others in that the first excited state in each lies sufficiently close to the ground state to be somewhat populated even at room temperature. Indeed, with the Eu^{3+} ion, even the second and third excited states can be so populated. The Sm^{3+} and Eu^{3+} ions may be expected to differ somewhat from the other Ln^{3+} ions in properties that depend upon population of the J states.

¹⁹ B. G. Wybourne, *Spectroscopic Properties of the Rare Earths*, Interscience Publishers, New York (1965).

The two properties that depend most directly upon electronic energy states are *magnetic susceptibility* (or permanent moment) and *radiant energy absorption or emission*.

Magnetic Properties

The ions La^{3+} and Lu^{3+} , together with Y^{3+} , are diamagnetic, as may be expected from their closed-shell electronic configurations and concomitant absence of unpaired electrons. The other Ln^{3+} ions, containing unpaired $4f$ electrons, are all paramagnetic and impart paramagnetism both to their solid compounds and to solutions thereof (Table 5). It is immediately apparent from experimentally determined values of the permanent magnetic moment μ or molar susceptibility χ_M that the $4f^7$ species, Gd^{3+} , with the maximum number of unpaired electrons is not the most strongly paramagnetic. There is thus a difference from the ions of the first d -transition series where maximum moment is characteristic of the $3d^5$ species, and moment is closely related to the spin-only formulation

$$\mu_B = 2\sqrt{[S(S+1)]} = \sqrt{[n(n+2)]}, \quad (1)$$

where S represents the spin states, n the number of unpaired electrons, and μ_B the moment in Bohr magnetons. The difference resides, of course, in the fact that since the $3d$ electrons are in the valency shell their orbital contributions to magnetic moment are essentially quenched, whereas the shielding of the $4f$ electrons by the $5s^25p^6$ arrangement is sufficient to allow significant orbital contribution in all except the Gd^{3+} ion²⁰.

The first generally successful attempt to derive magnetic moments in terms of both spin and orbital considerations made use of the early quantum mechanical expression

$$\chi_M = \frac{Ng^2\beta^2J(J+1)}{3kT} \quad (2)$$

where N is Avogadro's number, g is the Landé splitting factor, β is the Bohr magneton, J is the vector sum of orbital L and spin S states, k is the Boltzmann constant, and T is the temperature in degrees Kelvin²¹. Agreement between values so calculated and those determined experimentally is satisfactory for all the terpositive ions except Sm^{3+} and Eu^{3+} (Table 5) when due allowance is made for lack of correction for the underlying diamagnetism in each paramagnetic ion.

A more sophisticated quantum mechanical treatment²² indicates that eq. (2) assumes that differences between adjacent J states are large compared to kT (p. 9). The general Van Vleck expression

$$\chi_M = N \left(\frac{\beta^2 \mu_B^2 + \bar{\alpha}}{3kT} \right) \quad (3)$$

where μ_B is the low-frequency magnetic moment vector in Bohr magnetons as weightedly average² over the normal J states and $\bar{\alpha}$ is a combination of the temperature-independent high-frequency component and the diamagnetic contribution, reduces for this case to

$$\chi_M = N \left(\frac{g^2 \beta^2 J(J+1) + \bar{\alpha}}{3kT} \right). \quad (4)$$

The first term of eq. (4) is thus eq. (2). For the Eu^{3+} and Sm^{3+} ions, where the separation

²⁰ P. W. Selwood, *Magnetochemistry*, 2nd ed., Interscience Publishers, New York (1956), Ch. VIII.

²¹ F. Hund, *Z. Physik*, **33** (1925) 855.

²² J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press (1932), Ch. IX.

TABLE 5. PERMANENT MAGNETIC MOMENTS AT 20–30°C

Ln ³⁺	Calculated		Measured				
	Hund ^a	Van Vleck and Frank ^b	Ln ₂ (SO ₄) ₃ ·8H ₂ O ^c	Ln ₂ O ₃ ^d	[Ln(EDTA)] ^{–e}	[Ln(HEDTA)] ^{–e}	[Ln(DCTA)] ^e
							Ln(C ₅ H ₅) ₃ ^f
La ³⁺	0.00	0.00	2.37	3.71	3.6	3.3	3.47
Ce ³⁺	2.54	2.56	3.47	3.71	3.6	—	3.52
Pr ³⁺	3.58	3.62	3.52	—	—	—	—
Nd ³⁺	3.62	3.68	—	—	—	—	—
Pm ³⁺	2.68	2.83	—	—	—	—	—
Sm ³⁺	0.84	1.55–1.65	1.53	1.50	1.7	1.4	1.58
Eu ³⁺	0.00	3.40–3.51	—	3.32	3.6	3.1	3.54
Gd ³⁺	7.94	7.94	7.81	7.9	7.9	7.9	7.9
Tb ³⁺	9.7	9.7	9.4	—	—	—	9.6
Dy ³⁺	10.6	10.6	—	10.5	—	—	10.3
Ho ³⁺	10.6	10.6	10.3	10.5	—	—	10.4
Er ³⁺	9.6	9.6	9.6	9.5	—	—	9.4
Tm ³⁺	7.6	7.6	—	7.2	—	—	7.0
Yb ³⁺	4.5	4.5	4.4	4.5	—	—	4.3
Lu ³⁺	0.00	0.00	diam.	—	—	—	—

^a F. Hund, *Z. Physik*, **33** (1925) 855.^b J. H. Van Vleck and Frank, *Phys. Rev.* **34** (1929) 1494, 1625.^c J. Zernicke and C. James, *J. Am. Chem. Soc.* **48** (1926) 2827.^d From Cabrera and Dupretier, *Compt. rend.* **188** (1929) 1640, as recalculated by Van Vleck.^e T. Moeller and E. P. Horwitz, *J. Inorg. Nucl. Chem.* **12** (1959) 49. (See pp. 29, 31 for meaning of abbreviations used.)^f G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.* **76** (1954) 6210; **78** (1956) 42. (C₅H₅[–] = cyclopentadienide ion.)

of J states is comparable to kT (Fig. 3), an involved summation of contributions in terms of the J states in terms of the population of each as determined by the Boltzmann temperature factor is essential to calculation of the permanent moments²². The validity of Van Vleck's method is indicated by a comparison of values in Table 5 and Fig. 4.

The Gd^{3+} ion is in an S spectroscopic state with each $4f$ orbital singly occupied. The spin-only calculation for $n = 7$ is thus applicable and yields 7.94 B.M. for the permanent

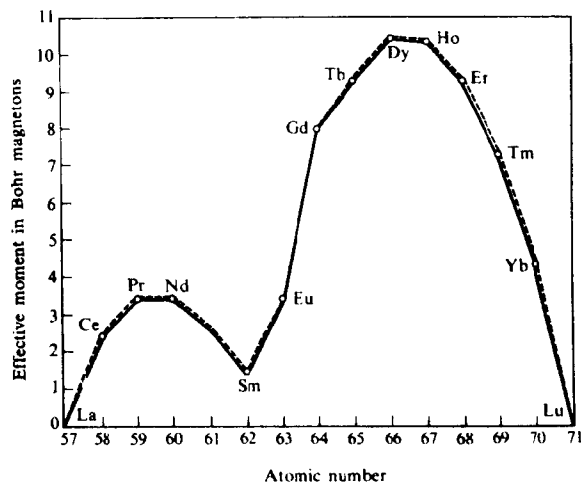


FIG. 4. Effective magnetic moments of trivalent lanthanide ions at room temperature. Broken line shows theoretical values as calculated from equations of Van Vleck. (Reproduced by permission from P. W. Selwood, *Magnetochemistry*, Interscience Publishers, New York, N.Y. (1956), 2nd edn., p. 142.)

moment, in good agreement with experimentally determined values. All of the Ln^{3+} ions except Sm^{3+} and Eu^{3+} obey the Curie law

$$\chi_M = C/T \quad (5)$$

where C is a constant, except for the small deviations caused by the high-frequency component. The Boltzmann distribution of electrons among the various states characteristic of the Sm^{3+} and Eu^{3+} ions causes these species to depart significantly from the Curie relationship in their magnetic behaviour.

The lack of absolute dependence of the magnetic moment on the number of unpaired $4f$ electrons is particularly evident from Fig. 4. The presence of two maxima represents a balance among the factors outlined above. It is not, as has been suggested by the existence of an essentially parallel variation among appropriately selected $5f$ -type ions²³, a characteristic of f -electron ions. By careful choice of compounds, one can plot a very similar curve for the magnetic moments of $3d$ -transition metal ions²⁰.

Magnetic moment (or susceptibility) data for the Ln^{3+} species are best compared for dilute solutions or for magnetically dilute solids to minimize the effect one paramagnetic ion may have on the behavior of another in close proximity. Magnetically dilute solids result where strong complexation by water or other ligand effectively shields each cation.

²³ J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, John Wiley, New York (1957), p. 447.

The hydrated sulfates, $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, are cases in point. However, even for compounds that are not magnetically dilute, deviations among observed values are not major, suggesting that the 4f shell is not substantially affected by the environment of the cation. To the extent that the magnetic moments of the ions have been measured in solid chelated complexes at room temperature²⁴, the relatively small differences from the calculated values of Van Vleck and Frank suggest either minor or no involvement of the 4f orbitals in bonding. On the other hand, deviations in the temperature range 1.3–20°K for the compounds $[\text{Ln}(\text{CH}_3\text{COCH}=\text{COCH}_3)_3 \cdot \text{H}_2\text{O}]$ and $\text{Na}[\text{Ln}(\text{EDTA})] \cdot 8\text{H}_2\text{O}$ ^{25, 26} do indicate that the lowest states are mixtures of two or more *J* states and that the magnetic behaviors of the lanthanides in these complexes are more involved than for the simple ions.

It may be expected that the magnetic moment of a non-terpositive lanthanide ion should be the same or nearly the same as that of the isoelectronic terpositive ion^{27, 28}. Thus the Ce^{4+} ion should be diamagnetic like the La^{3+} ion. The carefully corrected molar magnetic susceptibility of this ion in the salt $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is 22×10^{-6} c.g.s. units²⁹. This slight paramagnetism is parallel to that once reported for pure lanthanum oxide as a surface paramagnetism³⁰ and to values observed for certain transition-metal ion with the noble-gas atom structures²⁰, but it is insufficient to characterize the Ce^{4+} ion as truly paramagnetic. The magnetic moment of the Pr^{4+} ion in the stoichiometric oxide PrO_2 is 2.48 B.M., in good agreement with the Van Vleck value of 2.56 B.M. for the isoelectronic Ce^{3+} ion³¹. The molar susceptibility of the Eu^{2+} ion in its sulfate ($25,800 \times 10^{-6}$ c.g.s. units at 20°C) is nearly identical with that of the Gd^{3+} ion (*ca.* $25,700 \times 10^{-6}$ c.g.s. at room temperature), and the magnetic properties of the Eu^{2+} ion, like those of the Gd^{3+} ion but unlike those of the Eu^{3+} ion, follow the Curie law^{32, 33}. Furthermore, the permanent moment of the Eu^{2+} ion in its solid chloride, bromide, and iodide is 7.9 B.M., the same as that of the Gd^{3+} ion³⁴. Variations in the magnetic moments with temperature of the ions Sm^{2+} and Eu^{3+} are nearly identical³³, and the Yb^{2+} ion is either diamagnetic like the Lu^{3+} ion or has only a very small temperature-independent paramagnetism³². These data support the ground-state electronic configurations listed in Table 1.

Absorption of Radiant Energy

The ions Sc^{3+} , Y^{3+} , La^{3+} , Lu^{3+} , and Ac^{3+} have no absorption bands in the wavelength range 2000–10,000 Å, as may be expected from their closed-shell electronic configurations and the absence of unpaired electrons. All of the other Ln^{3+} ions have characteristic absorption bands in this region. The ions Ce^{3+} , Eu^{3+} , Gd^{3+} , and Tb^{3+} absorb either entirely or very largely in the ultraviolet region and are thus colorless^{34a}. The Yb^{3+} ion absorbs only in the near infrared region and is also colorless. The remaining ions absorb significantly in the visible region and are colored, sometimes beautifully so (e.g. Pr^{3+} , Nd^{3+} , Er^{3+}).

²⁴ T. Moeller and E. P. Horwitz, *J. Inorg. Nucl. Chem.* **12** (1959) 49.

²⁵ J. J. Fritz, I. Grenthe, P. E. Field and W. C. Fernelius, *J. Am. Chem. Soc.* **82** (1960), 6200.

²⁶ J. J. Fritz, P. E. Field and I. Grenthe, *J. Phys. Chem.* **65** (1961) 2070.

²⁷ D. W. Pearce, *Chem. Rev.* **16** (1935) 121.

²⁸ D. W. Pearce and P. W. Selwood, *J. Chem. Ed.* **13** (1936) 224.

²⁹ G. Föex, *Compt. rend.* **208** (1939) 738.

³⁰ R. B. Haller and P. W. Selwood, *J. Am. Chem. Soc.* **61** (1939) 85.

³¹ S. W. Rabideau, *J. Chem. Phys.* **19** (1951) 874.

³² G. W. Hughes and D. W. Pearce, *J. Am. Chem. Soc.* **55** (1933) 3277.

³³ P. W. Selwood, *J. Am. Chem. Soc.* **55** (1933) 4869.

³⁴ W. Klemm and W. Döll, *Z. anorg. u. allgem. Chem.* **241** (1939) 233.

^{34a} Terbium(III) salts may be faintly pink in the crystalline state or in very concentrated solutions.