Inorganica Chimica Acta, 139 (1987) 1–5

Lanthanides since 1839: From Crowded Elements to Quantum-chemical Rosetta Stone*

CHRISTIAN K. JØRGENSEN

Section de Chimie (Sciences II), University of Geneva, CH 1211 Geneva 4, Switzerland

Abstract

The lanthanides were separated between 1839 and 1907 by autonomous chemical methods; half of them were discovered between 1878 and 1886. The next year Crookes proposed avant-garde ideas of meta-elements (later shown to agree in uncanny ways with isotopes and their formation under extreme astrophysical conditions) but the nuclear charges $+Ze$ were not established as the criterion for elements before 1913. The reconciliation of electronic structure with the Periodic Table was made (as far as feasible) by Stoner in 1924. Chemists have learned much from the absorption and luminescence of J-levels of the partly filled 4f shell (and the concomitant high S values) and X-ray and photo-electron spectra of inner shells. Scarce nuclei having fractional Z values ($Z \pm \frac{1}{3}$) with comparable amounts of u, d and s quarks may occur in rare-earth minerals.

Johan Gadolin demonstrated in 1794 that a black mineral found in 1788 in the small village of Ytterby not far from Stockholm (now called gadolinite and known to be a beryllate–silicate with composition close to $Y_2FeBe_2Si_2O_{10}$ having some Y substituted by Yb, Er, Dy,... with relatively small ionic radii) contained a new earth with basicity between alumina and magnesia. This was called 'yttria' by Ekeberg in 1797, but its discovery marked not just the finding of one new element (like the contemporary titanium and strontium [1]) but a 'Pleiades' of indistinct elements which were to make foundations of inorganic theory shake like quicksand. In the same year (1803) as Klaproth discovered cerium, Berzelius and Hisinger showed this element to have two oxidation states, now known to be Ce(IV) and Ce(III). On the whole, solution chemistry and salts prepared from aqueous solutions gave almost exclusively the lower oxidation state of the other lanthanides (Ln), *i.e.*, Ln(III); the first Ln(II) (dark red $SmCl_2$) was prepared [2] in 1906. Berzelius remained convinced that yttria and ceria were mixtures of several rare earths, and persuaded Mosander to attempt their separation, starting in 1839 with lanthana. In 1843, Mosander confirmed the existence of six elements (lanthanum, cerium, didymium, terbium, yttrium and erbium) mentioned in order of increasing atomic weight A (except Y) and of decreasing basicity of the hydroxides (*i.e.*, decreasing solubilities and decreasing pH values for their incipient precipitation). In mixed oxides, didymium and terbium produce comparable, purple (in ThO_2), dark brown (in CeO_2 or Nd_2O_3) and orange (in Y_2O_3) colours which disappear on calcination in hydrogen, but return on heating in air. Auer von Welsbach separated didymium in 1885 into the (less abundant) praseodymium, which forms green Pr(III) salts, and neodymium, which has mauve to lilac Nd(III) salts. The dark-coloured didymia contains Pr(IV) and the sky-blue reduced didymia is coloured like the major constituent Nd_2O_3. The dark Ln(IV) colours and yellow Ce(IV) are due to electron transfer bands [3, 4] of the type known from chromate, Fe(III), Ir(IV), Pt(IV) and many other oxidizing transition-group central atoms. These bands are very intense, and it turns out [5] that the dark colour was due to minute traces of terbium(IV) in the original terbia, mainly consisting of adjacent Ln_2O_3 and of Y_2O_3.

The many versions of the Periodic Table [6] which appeared after the hypothesis of Avogadro ($PV = nRT$) were generally accepted at the congress in Karlsruhe in 1860, allowing equivalent weights (e.g., the amount of an element M bound to 35.45 g chlorine in binary MCl_z) to be multiplied by the oxidation number z for obtaining atomic weights A. Although the controversy about the normal z value for lanthanides being 2 or 3 continued long after 1880, Mendeleev considered in 1869 that Ln(III) was the lesser evil, because no other elements were known between $A = 138$ (Ba) and 181 (Ta); whereas the corollaries of Ln(II) are disastrous: $A = 59$ for Y, and the A from 93 (La) to 112 (Er) inserted between entirely differing elements. It was easy to accommodate Y, La and Er in column III and Ce in IV, and one might squeeze the notoriously non-stoichiometric didymium in V. Mendeleev was reluctant to accept more than the five lanthanides reported by Mosander in 1843. However, between 1878 and 1886, seven more lanthanides were dis-

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

0020-1693/87/$3.50

covered: ytterbium (1878) and gadolinium (1880) by Marignac [7]; holmium and thulium by Cleve in 1879; samarium (1879) and dysprosium (1886) by Lecoq de Boisbaudran (who found gallium in 1875); and Pr and Nd (1885) mentioned above. For Mendeleev, the column number was determined by the highest z value (excepting the highly electronegative oxygen and fluorine, and bromine of which BrO_4^- was prepared in 1968) although this was not necessarily a frequent oxidation state (*cf.* Mn and Bi). Since copper(II) and gold(III) were well known, Mendeleev originally introduced tetrades, such as iron, cobalt, nickel and copper as predominantly M(II), although this was not as invariant as Ln(III). The numerous lanthanides known after 1886 induced a vague sentiment that they constituted a kind of hypertetrade, but with the A value as the exclusive parameter characterizing an element, it was not possible to tell how many there were (although the A interval between 138 and 181 would suggest 13 or 14, one less than the actual number). The amount of patient and careful effort spent on separating genuine or (more than 10) spurious elements was extensive, and has been reviewed [1, 5, 8, 9].

William Crookes invented the high-voltage tube used for cathodoluminescence of solids, and hence colour television; this device allowed the characterization of the first elementary particle, the electron, in 1897, and also X-ray technology; he also discovered thallium in 1861 through its spectral lines. Crookes held a lecture in 1887 on 'The Genesis of the Elements' at the Royal Institution in London. The following year, Crookes [10, 11] elaborated a hypothesis of exceptional astrophysical conditions (exceedingly high temperatures, ...) allowing a primordial material (protyle) first to condense to hydrogen ($A = 1$) and subsequently to lithium ($A = 7$) and all heavier elements; only a very small amount (perhaps because the build-up becomes endothermic, or due to slow kinetics) gets beyond nickel ($A = 59$). Crookes assumed meta-elements of closely similar A values would show almost identical chemical properties (much like isotopes, of which the two first non-radioactive examples obtained were ^{206}Pb from uranium and ^{208}Pb from thorium minerals [12] in 1914). Crookes suspected that the rare earths were a huge number of meta-elements with unusually large chemical differences (much like ^1H and deuterium), rendering separation difficult but not impossible. Urbain [5] sharply criticized the idea that the lanthanides are meta-elements, but in many other ways this 100-year old hypothesis of Crookes agrees with uncanny similarity [9] with nucleosynthesis in modern astrophysics [13]. About 20 microseconds after the Big Bang, the protons and neutrons were produced from fractionally charged quarks (discussed at the end of this paper), and during the next four minutes [14] 23% of the total mass rearranged to the very stable helium isotope ^4He (also known as α-particles); amounts of a few times 10^{-5} formed ^2D and ^3He, and 10^{-9} formed lithium ^7Li (all heavier nuclei were much scarcer, and 77% remained as ^1H). The temperature varies roughly as 10^{10} K (10 gigakelvin) divided by the square-root of running time (in seconds). This, rather restricted, choice of nuclei does not change dramatically before galaxies, and then stars, are formed after 10^8 to 10^9 years. It is the business of normal stars (like our Sun, formed more recently, about 4700 million years ago) to transform a few percent more of ^1H to ^4He, but supernova explosions [13, 15] disperse huge amounts of carbon, nitrogen and oxygen, and also exponentially decreasing concentrations from neon to calcium. There is a second, smaller maximum around iron, with some Mn, Co and Ni, agreeing with thermodynamic equilibrium below 1 gigakelvin, and enhanced by the stability of ^{56}Ni having Maria Goeppert-Mayer closed-shell values of both the quantum numbers Z and N [16] like ^{208}Pb, but going through two stages (the half-life of 77 days of the intermediate ^{56}Co agrees with the luminosity curves of many supernovae [15], this phenomenon having been previously ascribed to spontaneous fission of californium ^{254}Cf) of positron radioactivity and/or electron capture, resulting in ^{56}Fe. In the solar atmosphere [13] there is less than 0.4 g/t (ppm) elements with Z above 36, among which 0.005 g/t is yttrium, and 0.04 g/t lanthanides (to be compared with 600 g/t magnesium and 1 kg/t of iron). Hence, the weight ratio between rare-earth elements and silicon [9] is 540 ppm for the outer crust of the Earth and only 60 ppm in the solar material. Not only organic chemists working with C, N, O but even more so, those inorganic chemists interested in Z values above 30, are highly indebted to supernova events.

Radioactivity was discovered in 1896, and through scattering of α-particles Rutherford established nuclei with densities close to 10^{14} g/cm^3 around 1911. This efficient separation of nuclear and chemical properties endowed chemists with the definition of the parameter Z behind the Periodic Table, the nuclear charge being $+Ze$ where e is the protonic charge. As discussed at length in ref. 9, the related problem of the electronic structure was resolved slowly and finally, with the spectroscopic version of the Periodic Table established by Stoner [17] in 1924. There had been two precursors giving 'Platonic' reasons for the intervals between two noble gases containing $2n^2$ elements. Thomsen [18] at first made this proposal before knowing about the noble gases, and established two vertical series of 7 elements each, two of 17, and one of 31. This system allowed a 'double allegiance' between the second 7-series Na, Mg, ..., Cl with the analogous member of both K, Ca, ..., Mn and Cu, Zn, ..., Br in the first 17-series. Although Thomsen did not give all the lanthanides nor exactly their order of present atomic weights, he insisted (like us) that there were two elements missing between ytterbium and tantalum, and the second of those is the only one to which a member (zirconium) of the second 17-series is connected by double allegiance, the other homolog being cerium. Rydberg [19] supposed in 1906 that each $2n^2$ is repeated once. The groups with 2, 2, 8, 8, 18, 18, 32,... members constituted an atomic number Z, but $Z = 2$ was ascribed to a gas (nebulium) known from emission lines of certain nebulae (it is mainly O^{2+}) and $Z = 3$ to coronium in the solar corona visible during total eclipses (Fe^{13+} and other high ionic charges) with the result that helium would have $Z = 4$, and all the subsequent elements would have the present Z values increased by two units. Already in 1914, Moseley insisted on $Z = 13$ for aluminium and $Z = 79$ for gold. Although this statement was abundantly confirmed later by nuclear physics, it must be said in all fairness [9] that the variation dI/dZ of ionization energy of 2p and 3d inner shells (involved in X-ray emission) is so non-monotonic, and the 1s absorption edges so broad, that Z might easily have been 1 or more units away from the values later firmly established. Early in 1922, Niels Bohr took up a justification of the Periodic Table (which he designed like Thomsen) with the $2n^2$ electrons for each 'principal' quantum number (the energy levels of one nucleus and one electron depend only on n) falling into n groups, containing (asymptotically, for high Z) $2n$ electrons each. Thus, the distribution of n-values of krypton (2, 8, 18, 8), xenon (2, 8, 18, 18, 8) and radon (2, 8, 18, 32, 18, 8) represent clear-cut intermediate steps of the evolution toward the asymptotic (2, 8, 18, 32, 50, ...) but the transition groups between these noble gases must undergo a rather enigmatic reorganization.

Stoner [17] said in 1924 that each of the n distinct nl-shells (with n larger than l) can accommodate at most $(4l + 2)$ electrons (using the modern symbols, such as l for the one-electron quantum number of orbital angular momentum). Hence, the length of the transition groups is related to the ten possible d and 14 possible f electrons in a given shell. It may be noted that the letters s (sharp), p (principal), d (diffuse) and f (fundamental), derived from the names of spectral series of alkali-metal atoms, described by the Rydberg (1895) formula, were not explicitly used by Stoner before 1925, but this was still a year before the equation of Schrödinger [9]. It is sometimes argued that Main Smith [20] has the priority in this matter. It is true that his 1924 paper was both submitted and published four months before the paper by Stoner, but Main Smith based chemical arguments on the fact (derived from X-ray spectra) (involving inner shells) that the $2n^2$ electrons of Bohr should be distributed on $(2n - 1)$ groups having $(2, 2, 4, 4, 6, \ldots, 2n)$ sites available (with modern symbols, each corresponding to $(2j + 1)$ electrons). Giving semicolons for complete n-manifolds, carbon is said to be (2; 2, 2, 0) and sodium (2; 2, 2, 4; 1) in spite of the spin-orbit splitting of ^3P of the carbon atom being only 43 cm^{-1}, one-fifth of kT at room temperature (and 0.08% of the heat of vaporization of diamond) and the yellow sodium lines (specifically mentioned by Main Smith) being separated by only 17 cm^{-1}. The extension to the iron group provides the expectation of 4 electrons being considerably more stable than the last 6; in the lanthanides 6 below the group of 8 electrons. In both cases, isoelectronic gaseous ions (such as Mn^{2+} and Fe^{3+}; Mo^{2+} and Ru^{4+}; Sm^{2+} and Eu^{3+}; Pt^{2+} and Au^{3+}) are ascribed differing distributions [20] of electrons on the $(2j + 1)$ groups with apparently arbitrary choices.

It is important for chemists that the approximate Aufbau principle (having 20 exceptions between hydrogen and einsteinium) for the electron configuration to which the groundstate of the neutral gaseous atom belongs [21–23] is not nearly as relevant as the order of consecutive filling of nl-shells in gaseous M^{2+} (with the exception of M = La, Gd, Lu, Ac and Th) and all known instances of the ionic charges +3, +4, +5 and +6. For these higher z values, the Kossel numbers $K = (Z - z) = 18, 36, 54$ and 86 isoelectronic with noble gases are immediately followed by the shell 3d, 4d, 4f and 5f, respectively (and $K = 68$ not being a closed-shell system in the erbium atom and Tm^+, but a closed-shell from Yb^{2+} to far beyond $Z = 100$, is immediately followed by the 5d shell):

$$1s \ll 2s < 2p \ll 3s < 3p \ll 3d < 4s < 4p \ll 4d < 5s < 5p \ll 4f < 5d < 6s < 6p \ll 5f < \ldots$$

As far as the lanthanides go, all compounds having a well-defined oxidation state [9, 21, 24] are either M(II) with $q = (Z - 56)$ electrons in the 4f shell; or M(III) with $q = (Z - 57)$; or M(IV) with $q = (Z - 58)$. The integer q can be used safely as a definition of the oxidation state in lanthanide compounds. The main argument for a definite q value is the characteristic distribution of J-levels [25, 26] from $q = 2$ in Pr(III) to $q = 13$ in Yb(III). They are situated at distances less than 4% below the few J-levels known of gaseous Pr^{3+}, Tb^{3+} and Yb^{3+} and their positions vary by less than 3% (and normally well below 1%) between different compounds of the same Ln(III). The separation of the $(2J + 1)$ states belonging to a given J-level is nearly always below 800 cm^{-1} (or 0.1 eV), *i.e.*, the same order of magnitude as the total spreading between the seven 4f one-electron energies. This spreading is essentially due to the operator of kinetic energy acting on weakly anti-bonding orbitals, as treated in the angular overlap model [27, 28] but to a much smaller extent than the energy differences (typically 1 to 4 eV) in compounds containing a partly filled 3d, 4d or 5d shell [21].

Physical properties, such as magnetic behaviour, molar volumes and photo-electron spectra, can be used to evaluate conditional oxidation states [9, 29] from definite $q = (Z - 54 - z)$ for $z = 2$ in Ln[II] and 3 in Ln[III], even in metallic elements and alloys, and in black non-metallic compounds. It is also feasible to define a similar conditional oxidation state (written with Roman numerals in rectangular brackets) for gaseous atoms and ions. It is a striking example of the difference between the chemical and the spectroscopic versions of the Periodic Table [23] that the groundstates of 11 lanthanide atoms indicate Ln[II] 'barides' and that only La, Ce, Gd and Lu have the additional 5d electron rendering them Ln[III]. Ytterbium atoms are spectroscopic alkaline earths like helium, zinc, cadmium and mercury. The quantitative energy difference between the lowest J-level of Ln[III] and the lowest J-level of Ln[II] when varying Ln in a series of the same ionic charge (or the same type of compound) can be rationalized by the refined spin-pairing energy treatment [9, 29–32] using the parameters of the Slater–Condon–Shortley or the Racah treatment, otherwise normally restricted to monatomic entities. Johnson [33] and the author [31, 32] independently pointed out that the tendency to increase the conditional oxidation state from Ln[II] to Ln[III] is a regular function of *decreasing* Ln–Ln internuclear distance:

$$Ln^0(g) < LnI_2 < LnTe < LnSe < LnS < LnB_6 < Ln(s) < LnO$$

In a way, Ln(II) dispersed in low concentrations in fluorite crystals $Ca_{1-x}Ln_xF_2$ is intermediate between gaseous atoms and crystalline LnI_2; electron paramagnetic resonance shows ten Ln(II), including Pr, Dy, Ho and Er. Among the di-iodides, NdI_2, SmI_2, EuI_2, (probably DyI_2), TmI_2 and YbI_2 are non-metallic Ln(II). Photo-electron spectra [31, 32, 34] of the NaCl-type TmTe show comparable concentrations of Tm[III] and Tm[II] on an instantaneous picture, whereas SmTe, EuTe and YbTe are clear-cut Ln(II). The same three cases occur for the NaCl-type sulphides. The cubic hexaborides and the solid metals (excepting one cubic modification of cerium) are Eu[II] and Yb[II], and otherwise Ln[III]. There is nothing exceptional in metallic NdO and SmO having shorter Ln–Ln distances than the metallic elements; this is also true for NaCl-type CsF compared with metallic caesium. Some high-density alloys of ytterbium (such as $YbNi_5$) contain Yb[III], and a few europium alloys contain Eu[III]. Other ytterbium and europium alloys contain simultaneously Ln[II] and Ln[III] on an instantaneous picture.

Some non-metallic Ln(III) and Ln(II) have a feature in common with the spherical symmetry of gaseous ions. The J-levels may fluoresce, and in fortunate cases of weakly competing processes of non-radiative de-excitation [25], cascading may take place from one J-level to another down to a third, finally reaching the groundstate. Fluoride glasses are particularly apt at this cascading, and eight J-levels of holmium(III) are indeed luminescent [26, 35, 36].

For the chemist, another unexpected analogy to atomic spectroscopy is the pronounced stability of highly positive S values. Thus, the octet ($S = 7/2$) groundstate of all europium(II), gadolinium(III) and terbium(IV) compounds is the highest total spin quantum number (S) known for one partly filled shell in any system. The stability of these three oxidation states should not be immediately ascribed to the half-filled shell ($q = 7$), the quantitative aspects of the refined spin-pairing energy treatment [9, 29–32, 37] are equally apt to rationalize the preparation of praseodymium(IV) ($q = 1$) and samarium(II) ($q = 6$).

The background parameters (to which spin-pairing effects are added) are the weak linear stabilization of 4f electrons going from $q = 1$ to 14 (this stabilization is not at all linear [24, 38] at the end of the 3d group) and the huge difference (of the order of 8 eV) between the ionization energy and the electron affinity of a partly filled 4f shell in compounds (such differences sometimes almost vanish in d-group compounds which have a high propensity towards disproportionation). These distinctions correspond to the 4f shell behaving much more like an inner shell in compounds than do d shells. This can be seen even from the comparable average radii of 4d and 4f in lanthanides. The reason why 4d shells then have ionization energies 100 to 180 eV higher, and are objects for X-ray and photo-electron spectra, is that the 4f angular part [21, 28] of the kinetic energy $6\langle r^{-2}\rangle$ hartree/bohr^2 under equal circumstances is twice as large as for d electrons, where the factor is 3. Actually, Watson has calculated this expression to be 540 eV per 4f electron in Gd^{3+} Hartree–Fock functions, to be compared with $I_4 = 44$ eV for gaseous Gd^{3+} and values between 11 and 15 eV for typical Gd(III) compounds; the two extreme values represent the metallic element and solid GdF_3 [29, 31].

The inorganic chemists had great luck in finding 120 g/t lanthanides, on average, in rocks. The minerals having provided these rather paradoxical elements (which happened all to be separated by autonomous chemical methods) may still hide some surprises [9] of importance for our understanding of matter. Quarks were introduced by Gell-Mann in 1964; e.g., u(up) quarks with +2e/3, and d(down) and s(strange) quarks both with charge −e/3. In recent years [16, 39, 40] protons and neutrons have lost their status as ultimate 'elementary' particles, and the nucleus characterized by the quantum numbers Z and $N = (A - Z)$ is a system with $(2Z + N)$ u-quarks and $(Z + 2N)$ d-quarks, having strong correlations of three quarks keeping together, but perceptible percolation. Fractionally charged nuclei (being unsaturated by containing a number of quarks not divisible by 3) are almost certain to be at least 20 amu heavier than conventional nuclei, an excess that may attenuate with higher A values. When the primordial quark soup coagulated to protons (and other baryons) 20 microseconds after the Big Bang (by cooling below 2 terakelvin) about 1 unsaturated system per 10^{20} amu (*i.e.*, 6000/g) may have survived. We know that the chemical properties of the unsaturated quark agglutinate are essentially determined [9] by $Z = 0.33 \ldots, 0.66 \ldots, 1.33 \ldots, 1.66 \ldots, \ldots, (Z + \frac{1}{3}), (Z + \frac{2}{3}), \ldots$ of the heavy centre. Negative Z values are expected rapidly to become permanently attached to adjacent usual nuclei, producing positive, fractional Z values.

For many years, there have been suggestions that a denser form (say 10^{15} g/cm^3) of nuclear matter may be metastable, or even more stable (but hopefully not too contagious) such as a manifold constructed from comparable numbers of u, d and s quarks called *uds*-matter, or in larger chunks, 'nuclearites' or 'quark nuggets' [41–43]. Besides probably replacing 'neutron stars' with A above 2×10^{57} (3×10^{33} g) and conceivably representing a substantial part of matter (with positive rest-mass) in the Universe, they have also other astrophysical implications [44, 45]. It seems now that they also represent the most appealing possibility of unsaturated quarks [9] such as $(A + \delta - \epsilon)$ u-quarks, $(A + \epsilon)$ d-quarks and $(A - \delta - 1)$ s-quarks, having the moderate $Z = (\delta - \epsilon + \frac{1}{3})$, perhaps hundreds of times smaller than A. The (roughly Z) electrons bound to such a system prevent (risky) contacts with conventional nuclei, and for A values below 10^{11} (10^{-13} g) they may remain suspended for quite some time in the oceans before fixing in manganese nodules on the sea floor. The geochemical fractionation may readily concentrate such species in rare-earth minerals, and we may still see a quark-rush this millennium.

Acknowledgements

The author is grateful for extensive collaboration with Professor Renata Reisfeld, that is rendered possible by 2.820-0.85 and previous grants from the Swiss National Science Foundation.

References

1 M. E. Weeks, 'Discovery of the Elements', 7th edn., J. Chem. Educ. Publishers, Easton, Penn., 1968.
2 C. Matignon and E. Cazes, *Ann. Chim. Phys. (Paris)*, *8*, 417 (1906).
3 C. K. Jørgensen, *Prog. Inorg. Chem.*, *12*, 101 (1970).
4 H. E. Hoefdraad, *J. Inorg. Nucl. Chem.*, *37*, 1917 (1975).
5 G. Urbain, *Chem. Rev.*, *1*, 143 (1925).
6 J. W. Van Spronsen, 'The Periodic System of Elements', Elsevier, Amsterdam, 1969.
7 C. K. Jørgensen, *Chimia*, *32*, 89 (1978); *34*, 381 (1980).
8 F. Szabadvary, in K. A. Gschneidner and L. Eyring (eds.), 'Handbook on the Physics and Chemistry of Rare Earths', Vol. 13, North-Holland, Amsterdam, in press.
9 C. K. Jørgensen, in K. A. Gschneidner and L. Eyring (eds.), 'Handbook on the Physics and Chemistry of Rare Earths', Vol. 13, North-Holland, Amsterdam, in press.
10 W. Crookes, *J. Chem. Soc.*, *53*, 487 (1888).
11 W. Crookes, 'Die Genesis der Elemente, zweite deutsche Auflage von W. Preyer', Friedrich Vieweg, Braunschweig, 1895.
12 G. B. Kauffman, *J. Chem. Educ.*, *59*, 3 and 119 (1982).
13 V. Trimble, *Rev. Mod. Phys.*, *47*, 877 (1975).
14 S. Weinberg, 'The First Three Minutes', Bantam Books, New York, 1979.
15 V. Trimble, *Rev. Mod. Phys.*, *54*, 1183 (1982); *55*, 511 (1983).
16 C. K. Jørgensen, *Struct. Bonding (Berlin)*, *43*, 1 (1981).
17 E. C. Stoner, *Phil. Mag.*, *48*, 719 (1924); *49*, 1289 (1925).
18 J. Thomsen, *Z. Anorg. Chem.*, *9*, 190 and 283 (1895).
19 J. R. Rydberg, *J. Chim. Phys.*, *12*, 585 (1914).
20 J. D. M. Smith, *Chem. Ind.*, *43*, 323 (1924); *44*, 944 (1925).
21 C. K. Jørgensen, 'Oxidation Numbers and Oxidation States', Springer, Berlin, 1969.
22 J. Katriel and C. K. Jørgensen, *Chem. Phys. Lett.*, *87*, 315 (1982).
23 C. K. Jørgensen, *Radiochim. Acta*, *32*, 1 (1983).
24 C. K. Jørgensen, *Z. Anorg. Allg. Chem.*, *540*, 91 (1986).
25 R. Reisfeld and C. K. Jørgensen, 'Lasers and Excited States of Rare Earths', Springer, Berlin, 1977.
26 R. Reisfeld and C. K. Jørgensen, in K. A. Gschneidner and L. Eyring (eds.), 'Handbook on the Physics and Chemistry of Rare Earths', Vol. 9, North-Holland, Amsterdam, 1987, p. 1.
27 C. K. Jørgensen, R. Pappalardo and H. H. Schmidtke, *J. Chem. Phys.*, *39*, 1422 (1963).
28 C. K. Jørgensen, M. Faucher and D. Garcia, *Chem. Phys. Lett.*, *128*, 250 (1986).
29 C. K. Jørgensen, *J. Less-Common Met.*, *112*, 141 (1985).
30 C. K. Jørgensen, *Mol. Phys.*, *5*, 271 (1962).
31 C. K. Jørgensen, 'Gmelin Handbuch der anorganischen Chemie, Seltenerd-Elemente', Vol. 39 B 1, Springer, Berlin, 1976, p. 17.
32 C. K. Jørgensen, in K. A. Gschneidner and L. Eyring (eds.), 'Handbook on the Physics and Chemistry of Rare Earths', Vol. 3, North-Holland, Amsterdam, 1979, p. 111.
33 D. A. Johnson, *Adv. Inorg. Chem. Radiochem.*, *20*, 1 (1977).
34 M. Campagna, G. K. Wertheim and E. Bucher, *Struct. Bonding (Berlin)*, *30*, 99 (1976).
35 C. K. Jørgensen, R. Reisfeld and M. Eyal, *J. Electrochem. Soc.*, *133*, 1961 (1986).
36 C. K. Jørgensen, R. Reisfeld and M. Eyal, *J. Less-Common Met.*, *126*, 181 (1986).
37 L. J. Nugent, R. D. Baybarz, J. L. Burnett and J. L. Ryan, *J. Phys. Chem.*, *77*, 1528 (1973).
38 C. K. Jørgensen, *Chimia*, *28*, 6 (1974).
39 C. K. Jørgensen, *Naturwissenschaften*, *69*, 420 (1982); *71*, 151 (1984).
40 C. K. Jørgensen, *Nature (London)*, *305*, 787 (1983).
41 E. Witten, *Phys. Rev.*, *D 30*, 272 (1984).
42 A. De Rújula and S. L. Glashow, *Nature (London)*, *312*, 734 (1984).
43 E. Farhi and R. L. Jaffe, *Phys. Rev.*, *D 30*, 2379 (1984).
44 J. Madsen, H. Heiselberg and K. Riisager, *Phys. Rev.*, *D 34*, 2947 (1986).
45 C. Alcock, E. Farhi and A. Olinto, *Phys. Rev. Lett.*, *57*, 2088 (1986).