

THE LANTHANIDE (4f) GROUP

THE rare earth or 'lanthanide' series forms a distinctive group whose chemical properties are remarkably similar. The valency is usually 3, with occasional values of 2 or 4 which occur mostly for ions that thereby achieve an empty, half-full, or full shell. The significant feature of the lanthanide group is the filling of the 4f shell, apart from some exceptional cases where an electron enters the 5d rather than the 4f shell. The closed shells of electrons correspond to an xenon 'core' $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$, which is the spectroscopic state of La^{3+} and Ce^{4+} . In the following ions electrons are added successively into the 4f shell, until this is full with fourteen electrons at Yb^{2+} and Lu^{3+} . Table 5.1 gives the basic information about the ground configuration of the tripositive ions.

A striking feature of the lanthanides is that most compounds exhibit sharp lines in their optical spectra, particularly at low temperatures, and much detailed information has been obtained for both ground and

TABLE 5.1

Ionic radii (in nanometres) and values of $\langle r^2 \rangle$, $\langle r^4 \rangle$, and $\langle r^6 \rangle$ (in atomic units). The ionic radii are from Evans (1964) and the other data from Freeman and Watson (1962)

<i>Z</i>	Ion	State	Ionic radius (nm)	$\langle r^2 \rangle$ (a.u.)	$\langle r^4 \rangle$ (a.u.)	$\langle r^6 \rangle$ (a.u.)
57	La^{3+}	$4f^0$	0.115			
58	Ce^{3+}	$4f^1$	0.102	1.200	3.455	21.226
59	Pr^{3+}	$4f^2$	0.100	1.086	2.822	15.726
60	Nd^{3+}	$4f^3$	0.099	1.001	2.401	12.396
61	Pm^{3+}	$4f^4$	0.098			
62	Sm^{3+}	$4f^5$	0.097	0.883	1.897	8.775
63	Eu^{3+}	$4f^6$	0.097			
64	Gd^{3+}	$4f^7$	0.097	0.785	1.515	6.281
65	Tb^{3+}	$4f^8$	0.100			
66	Dy^{3+}	$4f^9$	0.099	0.726	1.322	5.102
67	Ho^{3+}	$4f^{10}$	0.097			
68	Er^{3+}	$4f^{11}$	0.096	0.666	1.126	3.978
69	Tm^{3+}	$4f^{12}$	0.095			
70	Yb^{3+}	$4f^{13}$	0.094	0.613	0.860	3.104
71	Lu^{3+}	$4f^{14}$	0.093			
63	Eu^{2+}	$4f^7$		0.938	2.273	11.670

excited states by high resolution spectroscopy. An extensive discussion of the theory of the spectroscopic properties is given by Wybourne (1965), much of which is relevant to the paramagnetic resonance properties with which this chapter is concerned.

5.1. Lanthanide compounds

Lanthanide ions enter many chemical compounds but we shall confine discussion to a few types of compound where the local symmetry is at least axial and in which a wide range of lanthanide ions have been studied. The first of these is the series of lanthanide ethylsulphates, $\text{Ln}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, whose X-ray crystallography was investigated by Ketelaar (1937) and more recently by Fitzwater and Rundle (1959), who examined the compounds of Pr, Er, and Y. The latter workers show that all heavy atoms are found in the space group $P6_3/m$, and that probably the hydrogen positions also conform to this space group. The point symmetry at the lanthanide ion is C_{3h} . This ion has nine water molecules as nearest neighbours; six form a triangular prism with three above and three below the mirror plane containing the other three water oxygens and the lanthanide ion (see Fig. 5.1). In the erbium compound the Er—O distances to the prism are 0.237 nm, and the remaining three distances are 0.252 nm. If all but the nearest oxygen positions are neglected, the symmetry about the lanthanide ion is almost D_{3h} . This structure has a vertical threefold axis of symmetry; if the structure were exactly D_{3h} there would also be both a vertical and a horizontal plane of reflexion symmetry. The compounds are isomorphous throughout the group from La^{3+} to Lu^{3+} , and also with Y^{3+} . Since the ionic size of Y^{3+} is 0.093 nm, the later ions of the group (see Table 5.1) probably fit better into yttrium ethylsulphate as a diluent than into lanthanum ethylsulphate.

A second series, in which the paramagnetic resonance results are remarkably similar to those in the ethylsulphates, is formed by the anhydrous trichlorides, type LnCl_3 . LaCl_3 crystallizes in a structure whose space symmetry (see Hutchison and Wong 1958) is $C6_3/m$, the point symmetry at the La site being C_{3h} . The La^{3+} ion is surrounded by nine approximately equidistant nearest neighbours (chloride ions). Three of these are coplanar with the La^{3+} and at a distance of 0.297 nm; the other six lie, three in a parallel plane above and three in a parallel plane below, all six at a distance of 0.299 nm from the La^{3+} ion. All the lanthanide series enter LaCl_3 as a diluent with this structure, but most of the undiluted anhydrous trichlorides of the heavier ions have

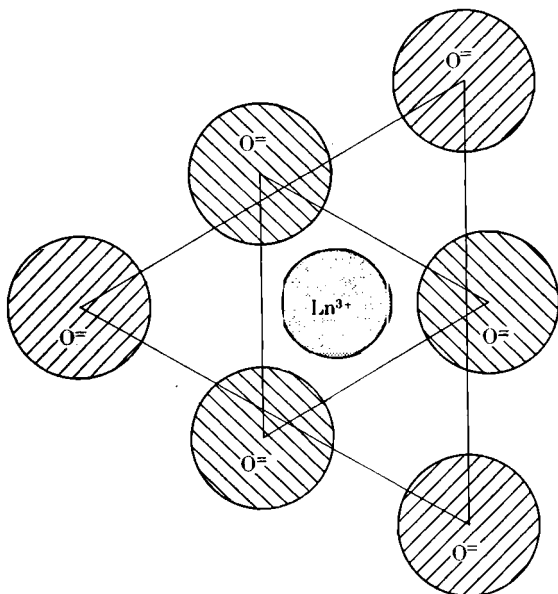


Fig. 5.1. Arrangement of the double triangular prism of water oxygen ions in the lanthanide ethylsulphates, in a plan view as seen along the crystallographic c -axis. In (R, θ, ϕ) coordinates, the Ln^{3+} ion is at the origin; there are three O^- ions in the same plane at $(0.252 \text{ nm}, \pi/2, \phi = (2n+1)\pi/3)$, and six O^- ions (above and below) at $(0.237 \text{ nm}, \theta, \phi = 2n\pi/3)$ and $(0.237 \text{ nm}, \pi-\theta, \phi = 2n\pi/3)$ with θ approximately 40° . The values of R, θ vary slightly with the lanthanide ion; the values of R given are for Er^{3+} . The radii of the circles denoting ions are drawn on about half scale relative to the inter-ionic distances.

a different structure, similar to YCl_3 . The anhydrous bromides and iodides form similar series, but less resonance work has been done on these.

A third series with somewhat different symmetry is formed by the double nitrates, formula type $\text{Ln}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$. The crystals are rhombohedral, space group $R\bar{3}$, and the hexagonal cell with $a = 1.1004(6) \text{ nm}$, $c = 2.4592(12) \text{ nm}$ (values for the cerium salt) contains three formula units. The detailed X-ray crystallographic study has been carried out by Zalkin, Forrester, and Templeton (1963). It shows that the lanthanide ion is surrounded by twelve oxygen atoms at an average distance of 0.264 nm ; these atoms, belonging to six nitrate ions, are at the corners of a somewhat irregular icosahedron. The Mg atoms are of two kinds, each surrounded by six water molecules whose oxygen atoms lie at the corners of an octahedron with an average Mg—O distance of 0.207 nm . Lanthanum is the usual diluent (yttrium does not fit into this lattice); bismuth has also been used but

its crystals are not so stable chemically. Zinc or an ion of the $3d$ group can replace magnesium.

The X-ray results confirm a number of conjectures made about the structure from paramagnetic resonance studies. In particular, Judd (1957*a*) had deduced that the crystal field resembled closely that of an icosahedron. The presence of two types of sites for $3d$ ions, with roughly 2:1 abundance, was observed by Trenam (1953), and the spectra of these ions suggested they were octahedrally coordinated. In the copper salt Bleaney, Bowers, and Trenam (1955) found that the line width was reduced in the deuterated compound, suggesting that the copper ligands are water molecules, while the rather small line width in the spectrum of the lanthanide ion suggested that its immediate neighbours are predominantly nitrate groups (Bleaney, Hayes, and Llewellyn 1957). The site symmetry at the Ce ion found by Zalkin, Forrester, and Templeton (1963) is C_3 , but the spectroscopic and resonance data have mostly been interpreted assuming the symmetry to be C_{3v} (see, however, Devine (1967)).

The arrangement of the nearest magnesium ions around a cerium ion is shown in Fig. 5.2; the nearest cerium neighbours are three at 0.856 nm and three at 0.859 nm, so that this compound is magnetically very dilute and very useful for magnetic cooling by adiabatic demagnetization. If the magnesium ions are replaced by paramagnetic ions of the $3d$ group, the compound is not particularly dilute, as can be seen from Fig. 5.2. The nearest neighbours to a Mg(1) site include six Ce at 0.698 nm and six Mg(2) at 0.715 nm, but the nearest neighbours to a Mg(2) site include another Mg(2) ion at only 0.499 nm.

In this series, and in the ethylsulphates and trichlorides, there is for magnetic purposes only one lanthanide ion per unit cell, at a site of threefold or sixfold symmetry. The ethylsulphates are also magnetically rather dilute, the nearest lanthanide neighbours being two at a distance of 0.71 nm along the c -axis. In the trichlorides the nearest lanthanide neighbours are again two along the c -axis, but at the much smaller distance of 0.43 nm.

Two other series of compounds have been examined in which threefold symmetry at the lanthanide site might be anticipated. These are LaF_3 and in contrast to this rather concentrated lanthanide compound, an unusually dilute series, lanthanum hexa-antipyrene iodide (HAPI), $\text{La}(\text{C}_{11}\text{H}_{12}\text{ON}_2)_6\text{I}_3$, (Baker and Rubins 1961, Baker and Williams 1961), doped with various lanthanide ions. The resonance results indicate a

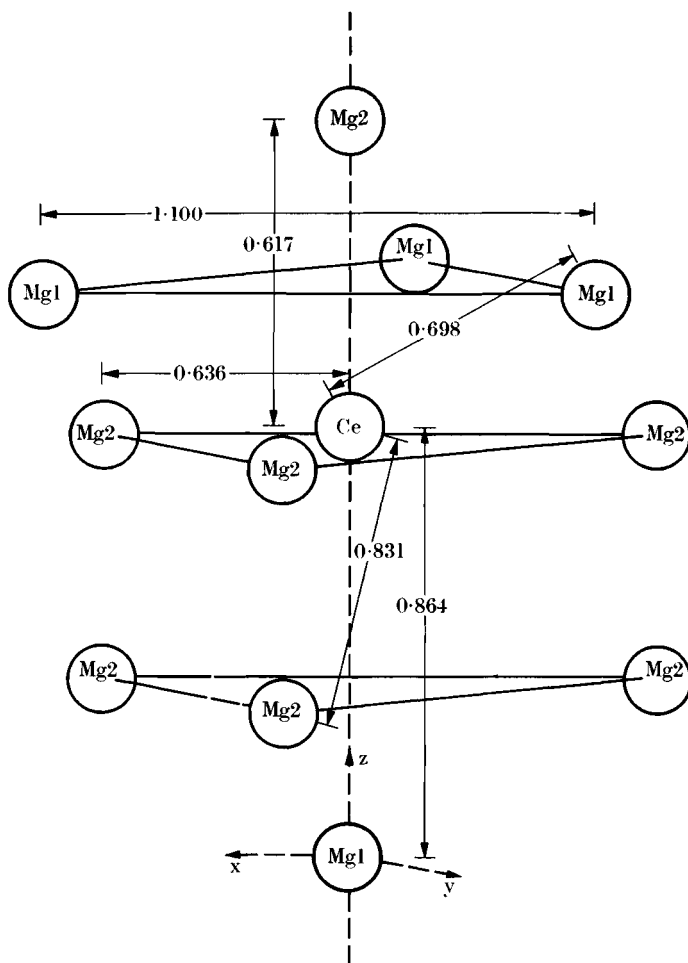


FIG. 5.2. Positions of the magnesium ions (distances in nanometres) relative to a cerium ion in cerium magnesium nitrate (Zalkin, Forrester, and Templeton 1963).

number of complexities in the crystal structure, including transitions at low temperatures, and we shall not discuss them further.

A rather different host lattice that has been used for both 4f and 3d ions is CaWO_4 , and its isomorph, SrWO_4 . These crystals (see Zalkin and Templeton 1964) are tetragonal, space group $I4_1/a$, with lattice constants $a = 0.5243$ nm, $c = 1.1376$ nm for the calcium salt. The point group at the Ca site is S_4 ; there are two calcium sites in the unit cell, but these are related by a reflection in the (001) plane, so that they are magnetically equivalent. Both trippositive and dipositive ions substitute for Ca^{2+} , and provided that charge compensation in the

former case is remote, fourfold symmetry about the c -axis is maintained for the paramagnetic ion. The calcium ion has eight oxygen neighbours at an average distance of 0.246 nm, while the tungsten has tetrahedral coordination with a tetragonal distortion.

Paramagnetic resonance studies have also been made of lanthanide ions subject to crystal fields of octahedral or cubic symmetry. The former occurs in the compounds MgO and CaO, both of which form crystals of the NaCl type (space group O_h^5), with lattice constants 0.4203 and 0.4797 nm respectively. The cation lies at the centre of a regular octahedron of six O^{2-} ions, and lanthanide ions with three positive charges can be introduced as impurities in small concentration on cation sites. Their spectrum is observed to have cubic symmetry, and charge compensation must take place at remote sites. Divalent ions such as Eu^{2+} can also be introduced, and the undiluted compounds EuO, EuS, EuSe, EuTe have the same structure.

Trivalent lanthanide ions can be introduced into CdF_2 , CaF_2 , SrF_2 , BaF_2 , and $SrCl_2$, whose crystals also belong to the O_h^5 space group, with lattice constants as given in Fig. 5.3. The structure may be

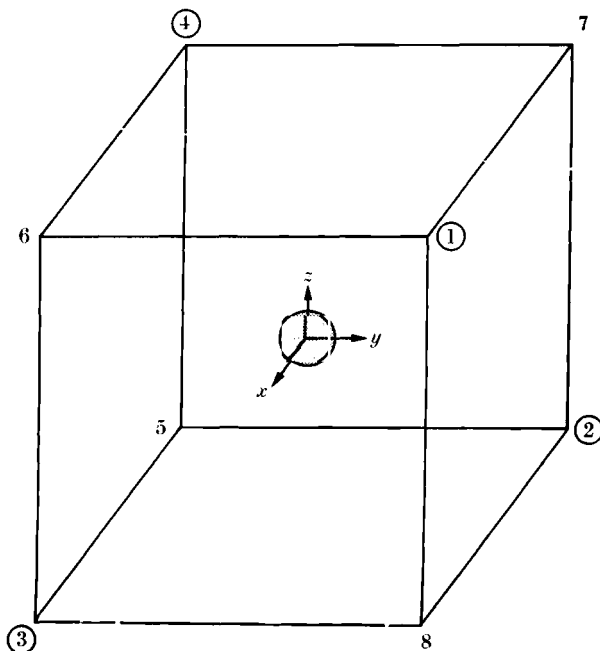


FIG. 5.3. Crystal structure of CaF_2 and isomorphous compounds. The Ca^{2+} ion is at the centre of a cube of eight F^- ions, and the (x, y, z) axes are the fourfold cubic axes. The lattice constants (twice the length of the cube edge in this diagram) are CdF_2 , 0.540 nm; SrF_2 , 0.586 nm; $SrCl_2$, 0.700 nm; CaF_2 , 0.545 nm; BaF_2 , 0.619 nm. The numbers 1 to 4, and 5 to 8, label the apices of the two tetrahedra which make up the cube.

regarded as a simple cubic array of fluorine ions with calcium ions at every other body centre. Each calcium is at the centre of a cube of eight fluorine ions (see Fig. 5.3), the Ca—F distance being 0.236 nm, and the lanthanide ions substitute for calcium. The tripositive ions are observed with cubic symmetry, or with tetragonal or trigonal symmetry. In the first case charge compensation must be remote; in the second an extra F^- ion occupies the nearest vacant interstitial site, and in the third it is presumed that an O^{2-} ion replaces an F^- ion on one apex of the immediate cube of fluorines (other possibilities may occur). A number of dipositive lanthanide ions have also been observed in CaF_2 , occurring either naturally (such as Eu^{2+} , Sm^{2+}), or produced by irradiation.

Another crystal of the same basic structure is ThO_2 or CeO_2 , where the cation is quadripositive and the anion dinegative. The lattice constants are 0.559 nm and 0.541 nm respectively, and crystals have been grown, both with four-valent lanthanide ions such as Tb^{4+} and with the more common tripositive ions, in which the paramagnetic resonance spectrum shows cubic symmetry.

5.2. The free ions

Outside the xenon core, the electrons in the lanthanide group of ions nearly all occupy either the 4f shell or the 6s shell. For the tripositive ions, the configuration is $4f^n$, where $n = Z - 57$ and Z is the atomic number of lanthanum. For the dipositive ions the configuration is $4f^{n+1}$, and for the neutral atoms the ground state is $4f^{n+1}6s^2$, except for LaI which is $5d6s^2$ and GdI which is $4f^75d6s^2$. Since $6s^2$ is a closed shell the spectroscopic ground states of the atoms and dipositive ions are the same. For the few quadripositive ions measured the configuration is $4f^{n-1}$, and hence in nearly all the cases with which we shall be concerned the magnetic properties are decided by the number of electrons in the f-shell. The coupling between these electrons is not far from perfect *LS*-coupling, the ground state being determined by Hund's rules. There are, however, some appreciable corrections that arise from the fact that the spin-orbit coupling energy is not negligible in comparison with the Coulomb energy. For example, the splittings within the ground multiplet do not obey the Landé interval rule and corrections must be applied in deriving the value of the spin-orbit coupling parameter. These are summarized in a paper by Judd and Lindgren (1961) (see also Conway and Wybourne 1963), and their magnitude can be seen from Table 5.2, which gives the energy levels

for the configuration $4f^6$. This table shows the energy levels calculated first, on pure LS -coupling, and second, after being corrected for second-order effects of the spin-orbit coupling, the spin-orbit parameter being chosen to give the best fit to the experimental values, for the

TABLE 5.2

Energy levels in the ground multiplet of $4f^6$, 7F , ($L = 3, S = 3, J = 0$ to 6), in cm^{-1} relative to $J = 0$

J	SmI (free atom)			Sm ²⁺ in SrF ₂	Sm ²⁺ (calc)	Eu ³⁺ in europium ethyl- sulphate	Eu ³⁺ (calc)
	Pure LS - coupling	Corrected	Experiment				
6	3724	4021	4021	()	3981	5000	5022
5	2660	3127	3125	(3100)	3099	3920	3921
4	1773	2275	2273	(2300)	2257	2880	2866
3	1064	1490	1490	1506	1481	1911	1888
2	532	812	812	805	808	1046	1063
1	177	291	293	263	291	376	374
0	0	0	0	0	0	0	0

The first three columns are for SmI; the first two are calculated by Conway and Wybourne (1963) using a value of $\zeta = 1064 \text{ cm}^{-1}$ chosen to fit the experimental values of Albertson (1937) in column 3. The effect of the second-order spin-orbit terms is shown by the difference between column 1 (pure LS -coupling) and column 2 (corrected for second-order terms). Column 4 gives values for Sm²⁺ (SmIII) in SrF₂, estimated from Wood and Kaiser (1962). Column 6 gives values for Eu²⁺ (EuIV) in europium ethylsulphate estimated from the analysis of Judd (1959b). Columns 5 and 7, calculated values for Sm²⁺ and Eu³⁺, are from Ofelt (1963).

SmI spectrum. The corrections are quite considerable, especially for the intermediate levels. This table shows also estimated values for Sm²⁺ (in SrF₂) and for Eu³⁺ (in europium ethylsulphate). Both these ions are isoelectronic with neutral Sm, and a comparison of Sm and Sm²⁺ shows that the removal of the $6s^2$ electrons in the latter has only a small effect, considerably less than that of the extra nuclear charge in the case of Eu³⁺.

The values of the spin-orbit coupling parameter ζ have been calculated using Hartree-Fock wave-functions by Blume, Freeman, and Watson (1964); the results are rather higher than the experimental values, as can be seen from the comparison in Table 5.3. This table gives also the ground term of the multiplet, and its value of g_J from a simple Landé formula, together with the energy of the first excited state of the multiplet. The values of g_J need a number of corrections. Besides the Schwinger electrodynamic correction for the spin g -factor

TABLE 5.3

Values of the spin orbit coupling parameter ζ for the tripositive ions of the 4f group, together with the Landé value of g_J for the ground state and the energy of the first excited state of the multiplet. The values of ζ are from Blume, Freeman, and Watson (1964). More accurate values of ζ and the energy of the first excited state, which vary slightly from salt to salt, are obtained from analyses of the optical spectra

Z		Ion	ζ (exp)	ζ (calc)	Term	g_J	Energy (cm ⁻¹)
58	4f ¹	Ce ³⁺	640	740	² F _{5/2}	⁶ / ₇	0
					² F _{7/2}		2200
59	4f ²	Pr ³⁺	750	878	³ H ₄	⁴ / ₅	0
					³ H ₅		2100
60	4f ³	Nd ³⁺	900	1024	⁴ I _{9/2}	⁸ / ₁₁	0
					⁴ I _{11/2}		1900
61	4f ⁴	Pm ³⁺			⁵ I ₄	³ / ₅	0
					⁵ I ₅		1600
62	4f ⁵	Sm ³⁺	1180	1342	⁶ H _{5/2}	⁸ / ₇	0
					⁶ H _{7/2}		1000
63	4f ⁶	Eu ³⁺	1360		⁷ F ₀	0	0
					⁷ F ₁	³ / ₂	400
64	4f ⁷	Gd ³⁺		1717	⁸ S _{7/2}	2	0
					⁶ P _{7/2}		30000
65	4f ⁸	Tb ³⁺	1620	1915	⁷ F ₆	³ / ₂	0
					⁷ F ₅	³ / ₂	2000
66	4f ⁹	Dy ³⁺	1820	2182	⁶ H _{15/2}	⁴ / ₅	0
					⁶ H _{13/2}		
67	4f ¹⁰	Ho ³⁺	2080	2360	⁵ I ₈	⁵ / ₄	0
					⁵ I ₇		
68	4f ¹¹	Er ³⁺	2470	2610	⁴ I _{15/2}	⁶ / ₅	0
					⁴ I _{13/2}		6500
69	4f ¹²	Tm ³⁺	2750	2866	³ H ₆	⁷ / ₆	0
					³ H ₅		†
70	4f ¹³	Yb ³⁺	2950	3161	² F _{7/2}	⁸ / ₇	0
					² F _{5/2}	⁶ / ₇	10000

† This level lies above ³H₄.

(which requires the use of 2.00232 for g_s instead of 2), and relativistic and diamagnetic corrections (usually of order 0.1 to 0.2 per cent), there are somewhat larger corrections due to admixtures of excited states through the spin-orbit coupling. For example, this makes the ground state of HoI (see Judd and Lindgren 1961)

$$0.9860 \left| ^4I_{15/2} \right\rangle - 0.1669 \left| ^2K_{15/2} \right\rangle + \dots,$$

(5.1)

but fortunately the admixture only effects the Zeeman splitting in the square, i.e.

$$g_J(\text{corrected}) = (0.9860)^2 g(^4I_{3/2}) + (0.1669)^2 g(^2K_{3/2}) + \dots, \quad (5.2)$$

so that the effect is fairly small (usually less than 1 per cent). The overall effect of the various corrections can be assessed from Table 5.4, which summarizes some experimental results for the neutral atoms, mostly obtained by atomic beam measurements.

5.3. Crystal field theory— C_{3h} symmetry

Early measurements of the susceptibility of rare-earth salts in the vicinity of room temperature showed that it was generally rather close to that expected from an assembly of free ions. Curie's law was fairly well obeyed, and the magnitude of the susceptibility was close to that expected from values of g_J and J appropriate to the ground term of the multiplet. Since the energy of the first excited state of the multiplet is generally a few thousand cm^{-1} , which is large compared with room temperature ($300k \equiv 200 \text{ cm}^{-1}$), contributions to the susceptibility from the excited states are negligible except for the ions $4f^5$ (Sm^{3+}) and $4f^6$ (Sm^{2+} , Eu^{3+}) where the first excited state is unusually low in energy (see, for example, Van Vleck (1932)).

The inference from these results is that the magnetic electrons are but little affected by the surroundings of the magnetic ion in a crystal, and since the $4f$ electrons form an 'inner shell' this is not surprising. (In fact $4f$ electrons have about the same radial extension as $3d$ electrons, but the diffuse outer electron shells $5s$, $5p$ keep the ligand ions away.) At temperatures well below room temperature departures from Curie's law appear, which are attributed to interactions with the ligand ions with energies of the order 10 – 100 cm^{-1} . Since bonding effects are expected to be very small or negligible for $4f$ electrons, the interaction with the ligands is treated by the approximation of a crystal potential V , set up by the electric charges on the ligands, in which the magnetic electrons move. Numerical calculation of this potential is difficult, but it must reflect the symmetry of the crystal at a rare-earth ion site. If, further, we confine ourselves to potential terms that have matrix elements within the manifold of $4f$ states, terms of odd parity can be omitted. Further it can be shown from the properties of spherical harmonics that terms of higher degree than the sixth need not be considered, since their matrix elements are zero for f -electrons.

To illustrate the theory it is convenient to take a concrete example, and for this purpose we choose a crystal potential appropriate to

TABLE 5.4

Spectroscopic data for the neutral atoms with $4f^n$ configurations from atomic beam measurements. A , B are the magnetic dipole and electric quadrupole hyperfine constants. The isotopes marked \dagger are radioactive. For the nuclear moments, some data from other experimental methods are included (values marked \ddagger include the diamagnetic correction)

Atom	State	g_J	Isotope	I	A (MHz)	B (MHz)	μ_I (nuclear magnetons)	Q (barns)
$4f^3$	Pr	$^4I_{\frac{9}{2}}$	0.731044(33)	141	$\frac{5}{2}$	+926.20894(27)	-11.87375(543)	+4.25(5)
				142 \dagger	2	67.5(5)	7.0(20)	-0.0589(42)
$4f^4$	Nd	5I_4	0.6032(1)	143	$\frac{7}{2}$	-195.649(9)	+122.25(28)	$\begin{cases} \ddagger -1.063(5) \\ -1.085(60) \end{cases}$
				145	$\frac{7}{2}$	-121.627(27)	+64.60(37)	$\begin{cases} \ddagger -0.654(4) \\ -0.675(40) \end{cases}$
				147 \dagger	$\frac{7}{2}$	-95.531(19)	+60.65(70)	-0.484(20)
$4f^5$	Pm	$^6H_{\frac{5}{2}}$	0.831(5)	147 \dagger	$\frac{7}{2}$	447(9)	267(70)	+2.58(7)
		$^6H_{\frac{7}{2}}$		151 \dagger	$(\frac{7}{2})$	358(23)	777(94)	+0.74(20)
$4f^6$	Sm	7F_6	1.49840(5)	147	$\frac{7}{2}$	-33.4971(1)	-58.7543(5)	-0.8074(7)
		7F_4		149	$\frac{7}{2}$	-27.6139(1)	+16.9195(2)	-0.665
				153 \dagger	$\frac{7}{2}$	-2.100(5)	+289.042(4)	+0.021(1)
$4f^7$	Eu	$^8S_{\frac{7}{2}}$	1.99340(7)	151	$\frac{7}{2}$	-20.0523(2)	-0.7012(35)	$\ddagger +3.4630(6)$
				152 \dagger	3	9.345(6)	1.930(165)	+1.16
				153	$\frac{5}{2}$	-8.8532(2)	-1.7852(35)	$\ddagger +1.5292(8)$
				155	$\frac{5}{2}$			+2.9
	Gd							-0.2567(6)
								$\ddagger -0.2584(5)$
								+1.59(16)
								-0.3363(12)
$4f^9$	Tb	$^6H_{\frac{15}{2}}$	1.3225(30)	157	$\frac{3}{2}$	+667.9(16)	+1381(19)	+1.70(16)
				159	$\frac{3}{2}$			+2.000(12)
$4f^{10}$	Dy	5I_8	1.24166(7)	161	$\frac{5}{2}$	-115.8(10)	+1102(15)	+1.994(4)
				163	$\frac{5}{2}$	+162.9(6)	+1150(20)	-0.47(9)
				165	$\frac{7}{2}$	+800.5844(4)	-1667.957(15)	+2.36(40)
$4f^{11}$	Ho	$^4I_{\frac{15}{2}}$	1.1951540(36)	167	$\frac{7}{2}$	-120.4864(5)	-4552.959(23)	+0.66(13)
$4f^{12}$	Er	3H_6	1.16377(17)	169 \dagger	$\frac{1}{2}$	725.46(31)	—	+4.03(5)
				169	$\frac{1}{2}$	-374.137641(10)	—	+2.4
$4f^{13}$	Tm	$^2F_{\frac{7}{2}}$	1.1411891(32)	170 \dagger	1	200(3)	1010(15)	$\ddagger -0.5647(24)$
				171 \dagger	$\frac{1}{2}$	372(4)		$\ddagger 0.513(25)$
				171	$\frac{1}{2}$			$\ddagger -0.2310(15)$
				173	$\frac{5}{2}$			$\ddagger 0.2448(36)$
Yb								$\ddagger 0.2277(36)$
								$\ddagger +0.49188(2)$
								$\ddagger -0.67755(2)$
								+2.8(2)

a site of C_{3h} symmetry. In many ways this is one of the simplest, and historically it is the most important because of the experimental and theoretical work on the rare-earth ethylsulphates. Single crystals of these salts can be grown from aqueous solution for all the rare-earth ions, and were used for most of the early susceptibility measurements at low temperatures and for magnetic resonance work. The existence of experimental results for a homologous series was a vital touchstone in the development of a successful theoretical approach by Elliott and Stevens. The anhydrous chlorides, on which work was initiated later by Hutchison, have the same site symmetry, and the resonance results for this series are remarkably similar to those for the ethylsulphates. It is therefore convenient to consider them together.

For a site of C_{3h} (or D_{3h}) symmetry the crystal potential takes the form (omitting terms whose matrix elements are zero for f -electrons)

$$V = A_2^0(3z^2 - r^2) + A_4^0(35z^4 - 30z^2r^2 + 3r^4) + \\ + A_6^0(231z^6 - 315z^4r^2 + 105z^2r^4 - 5r^6) + \\ + A_6^6(x^6 - 15x^4y^2 + 15x^2y^4 - y^6). \quad (5.3)$$

This can be written in the abbreviated form

$$V = \sum V_k^q = A_2^0P_2^0 + A_4^0P_4^0 + A_6^0P_6^0 + A_6^6P_6^6 \quad (5.4)$$

by using the functions P_k^q listed in Table 15. (The terms P_4^3 and P_6^3 are proportional to odd powers of z and are missing because of reflection symmetry in the xy plane for C_{3h} ; they will be needed when dealing with the double nitrates, which have C_{3v} symmetry). The first three terms are independent of x , y and are axially symmetric about the z -axis; the fourth term has sixfold symmetry about this axis. Its form depends on a particular choice for the x -axis relative to the crystal, and there are six such choices, related by rotations of 60° about the z -axis.

The effect of this potential can be found by integrating over the wave-function of each electron and then summing over all the magnetic electrons. As, however, neither the coefficients A_k^q nor the radial parts of the atomic wave-functions are known with any accuracy, only relative values due to the different angular dependences of the wave-functions are known precisely. The calculation of the latter is greatly simplified by use of the simple relations between the matrix elements of the potential operators and the appropriate 'spin' operators, as discussed in Chapter 16. Within a manifold of states for which J is

constant the potential (5.3), for example, can be replaced by

$$A_2^0 \langle r^2 \rangle \langle J \| \alpha \| J \rangle O_2^0 + A_4^0 \langle r^4 \rangle \langle J \| \beta \| J \rangle O_4^0 + \\ + A_6^0 \langle r^6 \rangle \langle J \| \gamma \| J \rangle O_6^0 + A_6^6 \langle r^6 \rangle \langle J \| \gamma \| J \rangle O_6^6. \quad (5.5)$$

Here $\langle r^k \rangle$ is the mean value of r^k averaged over the atomic wavefunctions; some calculated values are given in Table 5.1. $\langle J \| \alpha \| J \rangle$, etc., are numerical coefficients listed for each ion in Table 20, and the O_k^q are the spin operators listed in Table 16 whose matrix elements are given in Tables 17. Thus the whole calculation is reduced to a matter of looking up numerical values in the appropriate Tables, apart from the $A_k^q \langle r^k \rangle$ which are regarded as adjustable parameters.

The theory outlined above is based on the work of Stevens and Elliott (Stevens 1952*a*, Elliott and Stevens 1952, 1953*a*, 1953*b*), who attempted a systematic treatment of the rare-earth ethylsulphates. Within a manifold of given J the results can be illustrated rather simply. Spin operators of the type O_k^0 contain only J_z and hence have only diagonal matrix elements for the $2J+1$ states characterized by different values of the magnetic quantum number J_z or M . These diagonal matrix elements are the same for the states $+J_z$ and $-J_z$ since the operators contain only even powers of J_z . Since states with different values of $|J_z|$ will in general have different energy, a crystal potential containing only such terms will produce a series of doublets characterized by states of the type $|\pm M\rangle$, with one singlet state, $|0\rangle$, if J is integral.

Spin operators O_k^q for which m is not zero have only off-diagonal elements and therefore admix states of different M to give a resultant state of the type

$$\sum_M c_M |J, M\rangle \quad (5.6)$$

with, of course, $\sum c_M^2 = 1$ to satisfy the normalization condition. In any given admixture the values of M are those with successive differences equal to q . Thus inclusion of the last spin operator O_6^6 in (5.5) produces states of the form

$$c_{M+6} |J, M+6\rangle + c_M |J, M\rangle + c_{M-6} |J, M-6\rangle,$$

where the number of states admixed is not more than three because the maximum value of J in the ground state is 8.

So far we have considered just a first-order perturbation approach in which only matrix elements within a manifold of given J are included. In a second-order approach it is necessary to include matrix elements between states of different J and these can again be obtained by the

method of operator equivalents. The most important elements are those between values of J which differ by unity, since these are adjacent in energy; they are given in eqns (16.33)–(16.36) for C_{3h} symmetry, from which it can be seen that they produce states of the form

$$\sum_M c_M |J, M\rangle + \sum_M c'_M |J', M\rangle, \quad (5.7)$$

where the values of M in J' are the same as those in J except that if $J' > J$ there may be an additional value of M which is greater than J . For the sake of simplicity admixtures of states of different J will be mostly ignored in the following general discussion; their inclusion alters the numerical values, but (with a few exceptions) does not affect the basic properties.

In this discussion it is convenient to treat first the ions with Kramers degeneracy (half-integral values of J), for which the energy levels are degenerate in pairs, with states linked by time reversal. We shall, however, leave the ions with a half-filled shell until later, since their ground state is $^8S_{\frac{7}{2}}$, which is split by the crystal field only through higher-order perturbations. Secondly we shall discuss the position for non-Kramers ions, with integral values of J .

Ions with Kramers degeneracy

For ions with an odd number of electrons (half integral values of J), the crystal field lifts the degeneracy completely except for the necessary twofold degeneracy imposed by Kramers theorem, so that the levels consist of $(J + \frac{1}{2})$ doublets. Since for such ions the maximum value of J in the ground state is $\frac{15}{2}$, the wave-functions of the Kramers doublets are linear combinations of states $|\pm M\rangle$ of the form

$$\begin{aligned} &\pm \frac{15}{2}, \pm \frac{3}{2}, \mp \frac{9}{2}, \\ &\pm \frac{13}{2}, \pm \frac{1}{2}, \mp \frac{11}{2}, \\ &\pm \frac{7}{2}, \mp \frac{5}{2}. \end{aligned} \quad (5.8)$$

The actual energy levels and relative admixtures of the states depend of course on the size of the various parameters of the crystal field. In general, the doublets are separated in energy by 10–100 cm^{-1} , so that a magnetic resonance transition is observable in the microwave region only between the two components of a doublet. At temperatures where excited doublets are populated the lifetimes of the excited states are generally so short because of relaxation to the lattice that transitions between them are too broad to be observable, so that in practice resonance is almost always restricted to the ground doublet.

To find the resonance condition we must calculate the Zeeman effect for each doublet. In a first approximation, where we consider only matrix elements within the ground manifold of a given value of \mathbf{J} , the Zeeman operator $\mathbf{L} + 2\mathbf{S}$ reduces to the simpler form $g_J\mathbf{J}$ or, in the notation of Elliott and Stevens and Chapter 16, $\langle J \| \Lambda \| J \rangle \mathbf{J}$. Thus calculation of the first-order Zeeman effect is reduced to finding the matrix elements of J_x, J_y, J_z within each doublet. Since we have axial symmetry, the matrix elements of J_x, J_y are equal, but in general different from those of J_z , so that the Zeeman effect within each doublet is described by a spin Hamiltonian with an effective spin $S = \frac{1}{2}$ and an anisotropic g -‘tensor’ with axial symmetry of the form

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) \quad (5.9)$$

where

$$\begin{aligned} g_{\parallel} &= 2 \langle J \| \Lambda \| J \rangle \langle + | J_z | + \rangle, \\ g_{\perp} &= \langle J \| \Lambda \| J \rangle \langle + | J_+ | - \rangle. \end{aligned} \quad (5.10)$$

Here $|+\rangle, |-\rangle$ are the two components of the doublet given by one of the combinations (5.8). To preserve the correct sign of g_{\parallel} , which is important for some purposes, the two states $|+\frac{1}{2}\rangle, |-\frac{1}{2}\rangle$ of the effective spin should be chosen to satisfy the correspondence

$$g_{\perp} \langle +\frac{1}{2} | S_+ | -\frac{1}{2} \rangle \equiv \langle J \| \Lambda \| J \rangle \langle + | J_+ | - \rangle.$$

Physically this correspondence is required in order that the spin Hamiltonian shall give the correct transition intensities when circularly polarized radiation is used (see Chapter 3).

It is readily seen that there are no matrix elements of the operators J_+, J_- between the two states of the first doublet listed in (5.8), so that $g_{\perp} = 0$ and no transition is allowed within the doublet (cf. §§ 1.8, 3.2). For the other two doublets g_{\perp} is finite and transitions are allowed; values of g_{\parallel} and g_{\perp} can then be measured in a resonance experiment with the external field parallel and perpendicular to the z -axis respectively. For the second doublet in (5.8) this means that all the admixture coefficients can be determined, since we have two pieces of experimental information and the normalizing relation for the coefficients means there are really only two unknowns though there are three coefficients. For the third doublet, which can be written in the form

$$\cos \theta | \pm \frac{7}{2} \rangle + \sin \theta | \mp \frac{5}{2} \rangle, \quad (5.11)$$

we have

$$\begin{aligned} g_{\parallel} &= \langle J \| \Lambda \| J \rangle (7 \cos^2 \theta - 5 \sin^2 \theta), \\ |g_{\perp}| &= \langle J \| \Lambda \| J \rangle 2 |\cos \theta \sin \theta| \{ (J + \frac{7}{2})(J - \frac{5}{2}) \}^{\frac{1}{2}}. \end{aligned} \quad (5.12)$$

This gives a relation between g_{\parallel} and g_{\perp} which is exact only in so far as we can neglect admixtures of states of different J , and experimental measurement of the two g -values gives a simple test of the validity of this approximation.

In more accurate measurements it may be necessary to take account of the corrections to $\langle J \parallel \Lambda \parallel J \rangle$ discussed in § 5.2. The most important of these are the use of 2.0023 for g_s instead of 2, and the correction for the breakdown of LS -coupling, which for most purposes can be adequately allowed for by the use of a modified value of $\langle J \parallel \Lambda \parallel J \rangle$ or g_J such as that given by eqn (5.2) for a special case. However in general the important corrections to the Zeeman energy calculation arise through the admixture of states of different J (principally $J \pm 1$, the state adjacent in energy); if these admixtures are known the corrections to the Zeeman energy can be found using §§ 16.3, 16.4 and the values of $\langle J+1 \parallel \Lambda \parallel J \rangle$ listed in Table 20.

For smaller values of J not all the values of M shown in eqns (5.6) may appear. Thus for $J < \frac{1}{2}$ the second doublet is just $|\pm \frac{1}{2}\rangle$, for which the values of both g_{\parallel} and g_{\perp} are completely defined

$$g_{\parallel} = \langle J \parallel \Lambda \parallel J \rangle; g_{\perp} = (J + \frac{1}{2}) \langle J \parallel \Lambda \parallel J \rangle \quad (5.13)$$

if admixtures of different J are negligible. Similarly in this case the first doublet will span just the values $|\pm \frac{3}{2}\rangle$ and $|\mp \frac{3}{2}\rangle$ so that it can be written in a form similar to (5.11). Obviously for every doublet whose states involve two values of J_z there is another doublet with orthogonal states given by changing θ to $\theta + \pi/2$, which has a different energy due to the crystal field. Similarly, when three values of J_z are admixed there are three orthogonal doublets, all with different energy.

At field strengths where the Zeeman energy is not small compared with the crystal field splittings it may be necessary to include Zeeman effects of higher order than the first. The second-order Zeeman effect generally results in both levels of a doublet being displaced equally by an amount proportional to H^2 ; this does not change the frequency of a transition between the two states of a doublet as far as terms of order H^2 are concerned. The third-order Zeeman effect does affect the transition frequency, since it may be of opposite sign for the two components of a doublet and displace them in opposite directions. This can be seen in another way, as a by-product of the second-order Zeeman effect. This modifies the wave-functions of a doublet in such

a way that instead of $|+\rangle, |-\rangle$ they take the form

$$\begin{aligned} (1+\alpha^2)^{-\frac{1}{2}}\{|+\rangle+\alpha|+\prime\rangle\} \\ (1+\alpha^2)^{-\frac{1}{2}}\{|-\rangle+\alpha|-\prime\rangle\} \end{aligned} \quad (5.14)$$

where α , the admixture coefficient for the other states, is proportional to H . If we now calculate the first-order Zeeman effect using the new states, its energy, which is proportional to H , will be modified by a fraction of order α^2 , so that we have a correction to the energy separation of order H^3 . This effect is most striking for a doublet for which $g_{\perp} = 0$, which is not split by a perpendicular magnetic field in first-order, but which may be split in third-order and give a weakly allowed transition at high magnetic fields. In the case of the first doublet listed in (5.8) this can be regarded as a result of admixing of states of the other two doublets by off-diagonal matrix elements of the Zeeman interaction.

Non-Kramers ions

For the rare-earth ions that have an even number of electrons in the 4f shell, the values of J are integral, with a maximum value of 8 in the ground state. Since the crystal potential for C_{3h} symmetry (eqn (5.4)) admixes states whose values of J_z differ by 6, it is readily found from the spin operators that its effect on a manifold of $2J+1$ states is to give a series of doublet and singlet energy levels. The doublets are of the form

$$\begin{aligned} \pm 8, \pm 2, \mp 4 \\ \pm 7, \pm 1, \mp 5 \end{aligned} \quad (5.15)$$

while the singlets have admixtures of the form

$$|3^s\rangle = \frac{1}{\sqrt{2}}\{|+3\rangle+|-3\rangle\}; \quad |3^a\rangle = \frac{1}{\sqrt{2}}\{|+3\rangle-|-3\rangle\} \quad (5.16)$$

or a linear combination of the form

$$+6, 0, -6. \quad (5.17)$$

The singlets (5.16) arise in the following way. The states $M = \pm 3$ are degenerate except through the action of the V_6^6 term in the crystal field, which has a matrix element between them; this splits them by an amount directly proportional to the magnitude of the V_6^6 term, with states of the simple symmetrical and antisymmetrical form given in (5.16). It can be seen that the operator J_z then has a matrix element

$$\langle 3^s | J_z | 3^a \rangle = 3\sqrt{2}$$

and it follows that an oscillatory magnetic field along the z -axis can produce transitions between them. Because of the magnitude of the V_6^6 term, this transition will usually be in the infrared.

Similarly, the states $M = \pm 6$ are degenerate except through the action of the V_6^6 term which has matrix elements

$$\langle +6 | V_6^6 | 0 \rangle = \langle 0 | V_6^6 | -6 \rangle.$$

The energy matrix will thus be a 3×3 matrix, but we can simplify it by choosing as the basic states the linear combinations

$$|6^s\rangle = \frac{1}{\sqrt{2}}\{|+6\rangle + |-6\rangle\}; \quad |6^a\rangle = \frac{1}{\sqrt{2}}\{|+6\rangle - |-6\rangle\} \quad (5.18)$$

since the second state $|6^a\rangle$ then has no matrix element with $|0\rangle$ and is thus an eigenstate. The other eigenstates are found from the energy matrix

$$\begin{vmatrix} |6^s\rangle & 0 & \sqrt{(2)c} \\ |0\rangle & \sqrt{(2)c} & d \end{vmatrix}$$

where $d = \langle 0 | \sum_k V_k^0 | 0 \rangle - \langle 6 | \sum_k V_k^0 | 6 \rangle$ and $c = \langle 0 | V_6^6 | \pm 6 \rangle$. The eigenstates are clearly of the form

$$p |6^s\rangle + q |0\rangle; \quad (p^2 + q^2 = 1). \quad (5.19)$$

When $c \ll d$ the state that lies close to $|6^a\rangle$ in energy has approximately

$$q = -\sqrt{(2)(c/d)}$$

and is depressed below $|6^a\rangle$ by an amount $\Delta = 2c^2/d$.

The basic states for the ground doublet are thus

$$\begin{aligned} |\xi'\rangle &= p |6^s\rangle + q |0\rangle \\ |\eta'\rangle &= |6^a\rangle \end{aligned}$$

where q is small and p is close to unity. In the presence of a magnetic field it is convenient to replace these states by the linear combinations

$$\begin{aligned} |\xi\rangle &= \frac{1}{\sqrt{2}}(|\xi'\rangle + |\eta'\rangle) = \frac{1}{2}(1+p)|+6\rangle - \frac{1}{2}(1-p)|-6\rangle + (q/\sqrt{2})|0\rangle \\ |\eta\rangle &= \frac{1}{\sqrt{2}}(|\xi'\rangle - |\eta'\rangle) = -\frac{1}{2}(1-p)|+6\rangle + \frac{1}{2}(1+p)|-6\rangle + (q/\sqrt{2})|0\rangle. \end{aligned} \quad (5.19a)$$

The Zeeman interaction $Z = -\boldsymbol{\mu} \cdot \mathbf{H} = \Lambda\beta\mathbf{J} \cdot \mathbf{H}$ has no matrix elements

between $|\xi\rangle$ and $|\eta\rangle$ and opposite expectation values in either state:

$$\langle\xi|Z|\xi\rangle = -\langle\eta|Z|\eta\rangle = 6\Lambda\beta p H_z \approx 6\Lambda\beta\left(1 - \frac{q^2}{2}\right)H_z.$$

Using a fictitious spin $S = \frac{1}{2}$ the spin Hamiltonian can be written as

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + \Delta_x S_x + \Delta_y S_y, \quad (5.20)$$

where approximately

$$g_{\parallel} = 12\Lambda\left(1 - \frac{q^2}{2}\right) = 12\Lambda\left(1 - \frac{c^2}{d^2}\right), \quad (5.20a)$$

$$\Delta = (\Delta_x^2 + \Delta_y^2)^{\frac{1}{2}} = 2c^2/d.$$

The individual values of Δ_x , Δ_y have no significance. Transitions occur at

$$\hbar\omega = \{(g_{\parallel}\beta H_z)^2 + \Delta^2\}^{\frac{1}{2}} \quad (5.21)$$

and are allowed when the oscillatory magnetic field is along the z -axis. The square of the magnetic dipole matrix element for the transition is

$$|\mu_z^2| = \frac{1}{4}(g_{\parallel}\beta\Delta/\hbar\omega)^2 \quad (5.22)$$

and grows progressively smaller as the frequency increases. This corresponds to a change from the states $|\xi'\rangle$, $|\eta'\rangle$ which are correct in zero magnetic field through intermediate states in a finite magnetic field to the states $|\xi\rangle$, $|\eta\rangle$ of eqn (5.19a), which are correct when the Zeeman interaction is very large compared with Δ .

We return now to the doublet levels whose states are of the form (5.15). Their behaviour is considered in detail in § 18.5 (see also § 3.14) and we give here only an outline. Operating with J_z gives diagonal matrix elements of opposite sign for the two states of a doublet so that they have a linear Zeeman splitting when a magnetic field is applied along the z -axis. There are no matrix elements between the two states, so there is no Zeeman splitting with a perpendicular magnetic field, nor will transitions be allowed between them through the action of an oscillatory perpendicular magnetic field. However the fact that we are dealing with non-Kramers ions means that the doublets can be split by a crystal field of lower symmetry, such as might arise through the Jahn-Teller effect or through crystal imperfections. Any such splitting that arises from a matrix element of the distorted crystal field between the two states of the doublet will admix the two states, so that a transition is now allowed between them with an oscillatory magnetic field along the z -axis, in the same way as for the levels considered earlier in this section. An appropriate 'spin Hamiltonian' for

such a doublet ($S = \frac{1}{2}$) is again (5.20), but now Δ_x, Δ_y are allowed to have a distribution of values and Δ does not have just one value. The quantum of energy required for a transition is given by (5.21) and involves Δ , so that it will have a spread of values; the transition intensity also depends on Δ (eqn (5.22)) and vanishes for $\Delta = 0$, so that we expect a broad line, asymmetrical in shape. (This contrasts with the situation considered above, where the transition was allowed without any distortion of the crystal field, and therefore is narrow and normal in shape.)

When the point symmetry at the lanthanide site lacks a plane of inversion symmetry, a non-Kramers ion can have an electric dipole moment normal to this plane, as discussed in §§ 15.10, 18.5. In C_{3h} symmetry, there is only one plane of reflection symmetry, normal to the c -axis, so that an electric dipole moment can exist in a non-Kramers ion normal to, but not parallel to, the c -axis. If the effect of an electric field on this dipole moment is represented by an additional term (cf. eqns (3.108) or (18.67))

$$g_{\perp}^{(E)} \beta (E_x S_x + E_y S_y)$$

in the spin Hamiltonian, transitions will be allowed for an oscillatory electric field $(E_1)_{\perp}$ normal to the c -axis, whose intensity depends on $(g_{\perp}^{(E)} E_1)^2$. The transition rate is now given by eqns (3.109), (3.110).

If resonance is observed at constant frequency and variable magnetic field it will lie wholly at field strengths below the value $H_0 = (\hbar\omega/g_{\parallel}\beta)$ corresponding to $\Delta = 0$, and will be asymmetrical in shape. The exact line shape will depend on the fraction of ions with a given value of Δ^2 (see § 3.14), and will be different according to whether transitions are induced by $(H_1)_{\parallel}$ or by $(E_1)_{\perp}$. In particular, if the transition is due to $(H_1)_{\parallel}$ it will have zero intensity at $H_z = H_0$ while if it is due to $(E_1)_{\perp}$ it will have a finite intensity (in fact the maximum intensity) at $H_z = H_0$ (see Fig. 3.26).

Although we have not yet considered hyperfine structure in this chapter it is convenient to point out here that for a non-Kramers doublet the hyperfine Hamiltonian will have the simple form

$$A_{\parallel} S_z I_z + P_{\parallel} \{I_z^2 - \frac{1}{3}I(I+1)\} \quad (5.23)$$

and the only change required above is that for each hyperfine component $g_{\parallel}\beta H_z$ must be replaced by $(g_{\parallel}\beta H_z + A_{\parallel}m)$ in eqn (5.21), where $m = I_z$.

5.4. Magnetic hyperfine structure

A general expression for the hyperfine interaction is given in eqn (17.61). We shall consider first the magnetic interaction where the nuclear magnetic moment can be considered as interacting with a local magnetic field due to the surrounding electrons. This field, \mathbf{H}_e , arises partly from the orbital motion of the electrons and partly from their spin magnetization. For a free ion in LS -coupling this resultant electronic field precesses rapidly about the angular momentum vector \mathbf{J} , and to a good approximation only that component of the field that is parallel to \mathbf{J} and hence a constant of the motion need be retained. This makes it possible to reduce the magnetic hyperfine Hamiltonian

$$\begin{aligned}\mathcal{H}_n &= 2g_n\beta\beta_n\langle r^{-3}\rangle[\mathbf{L} \cdot \mathbf{I} + \xi\{L(L+1) - \kappa\}(\mathbf{S} \cdot \mathbf{I}) - \\ &\quad - \frac{3}{2}\xi\{(\mathbf{L} \cdot \mathbf{S})(\mathbf{L} \cdot \mathbf{I}) + (\mathbf{L} \cdot \mathbf{I})(\mathbf{L} \cdot \mathbf{S})\}] \\ &= 2g_n\beta\beta_n\langle r^{-3}\rangle (\mathbf{N} \cdot \mathbf{I})\end{aligned}\quad (5.24)$$

to the simple form

$$\mathcal{H}_n = A_J \mathbf{J} \cdot \mathbf{I} \quad (5.25)$$

where

$$A_J = 2g_n\beta\beta_n\langle r^{-3}\rangle\langle J \| N \| J \rangle + A'_s. \quad (5.26)$$

In these formulae g_n is the nuclear magnetogyric ratio appropriate to the nuclear magnetic moment expressed in nuclear magnetons, and $\langle J \| N \| J \rangle$ is a numerical factor given by eqns (17.51), (17.52) and listed for each ion in Table 20. A'_s is discussed below.

In the ground states of the rare-earth ions (with the exception of the half filled shell $^6S_{\frac{5}{2}}$) the magnetic hyperfine structure is due mainly to the orbital rather than the spin contribution. To illustrate this we carry out the numerical calculation of $\langle J \| N \| J \rangle$ for the ground state of the Tb^{3+} ion, 7F_6 ($L = 3$, $S = 3$, $J = 6$). From eqn (17.51) we have

$$\left. \begin{aligned}\langle J \| N \| J \rangle &= \frac{1}{J(J+1)}(\mathbf{L} \cdot \mathbf{J}) \text{ (orbital contribution)} + \\ &+ \frac{1}{J(J+1)}\xi\{L(L+1)(\mathbf{S} \cdot \mathbf{J}) - 3(\mathbf{L} \cdot \mathbf{J})(\mathbf{L} \cdot \mathbf{S})\} \text{ (spin contribution)},\end{aligned}\right\} \quad (5.27)$$

where from eqn (17.52) for this ion, $(\mathbf{L} \cdot \mathbf{J}) = (\mathbf{S} \cdot \mathbf{J}) = \frac{1}{2}J(J+1)$ and $(\mathbf{L} \cdot \mathbf{S}) = \frac{3}{14}J(J+1)$ and from eqn (17.46) $\xi = -\frac{1}{135}$. Hence

$$\langle J \| N \| J \rangle = \frac{1}{2} + \frac{1}{18} = \frac{5}{9} \text{ for } \text{Tb}^{3+}, ^7F_6,$$

where $\frac{1}{2}$ represents the orbital contribution and $\frac{1}{18}$ the spin contribution. The reason why the former dominates is that we have quite a

large orbital momentum making its full contribution, while the spin magnetization is rather uniformly distributed at any given distance so that the net field it produces at the nucleus is small (for a distribution with spherical symmetry it would vanish).

For an ion with a half-filled shell ($^8S_{\frac{7}{2}}$ ground state) the spin magnetization has spherical symmetry, and the orbital momentum is zero; we should therefore expect the magnetic hyperfine constant A to be zero. In practice a finite value is obtained (see §§ 4.7, 5.9), and this is attributed mainly to the 'core-polarization' effect (see §§ 17.5, 17.6) which produces a non-zero spin density at the nucleus. This is represented by a term similar to that in eqn (17.60).

$$A_c(\mathbf{S} \cdot \mathbf{I}) = -2g_n\beta\beta_n\langle r^{-3} \rangle \kappa(\mathbf{S} \cdot \mathbf{I}). \quad (5.28)$$

In addition we have a contribution from relativistic effects (see below) which is also of the form $(\mathbf{S} \cdot \mathbf{I})$ so that it is simplest to lump the two effects together in a term $A_s(\mathbf{S} \cdot \mathbf{I})$. As above, we must project \mathbf{S} onto \mathbf{J} using eqns (17.52), (17.53) so that we obtain for the contribution A'_s in eqn (5.26)

$$A'_s = A_s \frac{(\mathbf{S} \cdot \mathbf{J})}{J(J+1)} = A_s(\langle J \| \Lambda \| J \rangle - 1). \quad (5.29)$$

We consider now an ion subjected to a crystal field. Within the approximation where we need include only matrix elements within a given manifold J , the magnetic hyperfine calculation is simple because, like the Zeeman interaction, it requires only the matrix elements of the operator \mathbf{J} . There is therefore a linear relation between the hyperfine and the Zeeman interaction. For any sub-space of the $2J+1$ manifold which we can represent by a fictitious spin \mathbf{S} , and for which the Zeeman interaction takes the form $\beta\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}$, the hyperfine interaction will have the form $\mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$, where \mathbf{A} is a 'tensor' which obviously has the same principal axes as the g -'tensor'. The principal values of these tensors are connected by the relation

$$\frac{A_x}{g_x} = \frac{A_y}{g_y} = \frac{A_z}{g_z} = \frac{A_J}{g_J} \quad (5.30)$$

where $g_J = \langle J \| \Lambda \| J \rangle$. In measurements at constant frequency and varying field, this relation means that the hyperfine separation will be the same in field along each of the principal axes; except in the case of no anisotropy, this will not be true in other directions because of the different transformation properties of \mathbf{g} and \mathbf{A} as expressed in eqns (3.5) and (3.44). It follows also that we can find the value of A_J from

a magnetic resonance experiment by using the experimental values of g , A along the principal axes without any knowledge of the crystal field.

These simple results no longer hold when the crystal field admixes considerable amounts of states of different J . The reason for this is that, although the matrix elements of the hyperfine operator can always be related to those of the Zeeman operator (see § 17.4), the constant of proportionality does not vary in the same way for the two operators, as can be seen from eqns (17.56), (17.57). Thus in practice the extent to which the relation (5.30) is satisfied serves as a measure of the validity of the approximation in which matrix elements with states of different J are neglected.

In the absence of direct measurements of the hyperfine interaction for a free tripositive ion the value of A_J can be deduced from measurements on salts if allowance is made for the admixture of states of different J through the action of the crystal field. A list of the values obtained in this way for the ground state J of the stable isotopes is given in Table 5.5. Before any direct measurements of the nuclear

TABLE 5.5

Values of the magnetic hyperfine constant A_J for the free tripositive ions, calculated from magnetic resonance measurements on salts. The contribution from core polarization is assumed to be given by the formula $A'_c = -(63 \pm 10)(\langle J \| \Lambda \| J \rangle - 1)g_n$ (MHz), while A'_s is similar but with the parameter $-(85 \pm 10)$. The value of A_J for Tm^{3+} is estimated from measurements of Tm and Tm^{2+} (Bleaney 1964b)

Ion	Isotope	Abundance (%)	Nuclear spin (I)			
				A_J (MHz)	A'_c (MHz)	A'_s (MHz)
59 Pr ³⁺	141	100	$\frac{5}{2}$	+1093(10)	+20(3)	+27(3)
	143	12.3	$\frac{7}{2}$	-220.3(2)	-5.3(8)	-7.2(8)
60 Nd ³⁺	145	8.3	$\frac{7}{2}$	-136.9(1)	-3.3(5)	-4.5(5)
	147	radioactive	$\frac{7}{2}$	(+)599(6)	(+)20(3)	(+)27(3)
62 Sm ³⁺	147	15.0	$\frac{7}{2}$	-240(3)	-10.7(17)	-15(2)
	149	13.9	$\frac{7}{2}$	-194(3)	-8.6(14)	-11.7(14)
65 Tb ³⁺	159	100	$\frac{3}{2}$	+530(5)	-39(6)	-54(6)
66 Dy ³⁺	161	19.0	$\frac{5}{2}$	-109.5(22)	+3.4(6)	+4.6(6)
	163	24.9	$\frac{5}{2}$	+152.4(30)	-5.0(8)	-6.8(8)
67 Ho ³⁺	165	100	$\frac{7}{2}$	+812.1(10)	-17.5(27)	-24(3)
68 Er ³⁺	167	22.9	$\frac{7}{2}$	-125.3(12)	+2.0(3)	+2.7(3)
69 Tm ³⁺	169	100	$\frac{1}{2}$	(-393.5)	+4.8(8)	+6.5(8)
70 Yb ³⁺	171	14.4	$\frac{1}{2}$	+887.2(15)	-9.0(15)	-12(2)
	173	16.2	$\frac{3}{2}$	-243.3(4)	+2.5(4)	+3.4(4)

magnetic moments of the lanthanides were available, such values of A_J were used to calculate the nuclear moments by making estimates of $\langle r^{-3} \rangle$ and neglecting the core polarization effect. However, such estimates obtained in different ways showed as much as 25 per cent variation for the lighter rare earth ions. Following the introduction of Endor and atomic beam triple resonance methods, a number of the nuclear moments have been directly determined, thus affording a check on the estimates of $\langle r^{-3} \rangle$, if the contribution from core polarization is known. There is no experimental evidence about the magnitude of this contribution except from measurements on ions with the $4f^7$ configuration. If it is assumed that the magnetic field at the nucleus produced by core polarization is constant per unit of electron spin throughout the $4f$ group, as seems to be roughly true for the $3d$ group if bonding effects are small, we can estimate the contribution to the other ions from measurements on the $4f^7$ ions. On this basis one obtains (Bleaney 1964*b*)

$$A'_c = -(63 \pm 10)(\langle J \parallel \Lambda \parallel J \rangle - 1)g_n \text{ MHz} \quad (5.31)$$

for the tripositive ions, where the factor $(\langle J \parallel \Lambda \parallel J \rangle - 1)$ allows for the projection of \mathbf{S} onto \mathbf{J} (see eqn (5.29)); this corresponds to a magnetic field of $-(83 \pm 13)S$ kG at the nucleus.

It has been suggested (see Bleaney 1967) that the relativistic contribution to A_s may also be roughly constant per unit of spin in the field it produces at the nucleus, and if this is included we obtain

$$A'_s = -85(\langle J \parallel \Lambda \parallel J \rangle - 1)g_n \text{ MHz} \quad (5.32)$$

for the tripositive ions.

The values of A'_{core} and A'_s given by eqns (5.31), (5.32) are listed in Table 5.5. Obviously they may not be very accurate, but they represent a comparatively small correction in most cases, the largest being about 7 and 9 per cent respectively for Tb^{3+} . Subtraction of these from the value of A_J gives a hyperfine parameter from which $\langle r^{-3} \rangle$ can be calculated using eqn (5.26) if g_n is known. A list of such values (based on the quantity $A_J - A'_s$, with A'_s given by eqn (5.32)), is given in Table 5.6 for comparison with calculated values. Three sets of the latter are given: the Hartree-Fock values of Freeman and Watson (1962); the values of Judd (1963*a*), which are a modification of the former to allow for the effect of configuration interaction; and the values of Lindgren (1962) (see also Judd and Lindgren (1961)) obtained from the observed spin-orbit constants. The values of Judd give the best fit with the

TABLE 5.6

Values of $\langle r^{-3} \rangle$ in atomic units for the tripositive ions (after Judd 1963a). Experimental values marked † are calculated from $(A_J - A'_J)$ in Table 5.5 and the value of g_n (where known). The last column gives the experimental values after including the correction for the break-down of LS -coupling. Values in parentheses are interpolated

		Values of $\langle r^{-3} \rangle$ in atomic units				Experimental (corrected)
Ion	Lindgren	Hartree-Fock	Judd	Experimental		
58 Ce ³⁺	3.66	4.72	4.17			
59 Pr ³⁺	4.26	5.37	4.76	†5.0		
60 Nd ³⁺	4.86	6.03	5.35	5.64(6)	5.49(6)	
61 Pm ³⁺	5.46	—	(5.95)			
62 Sm ³⁺	6.07	7.36	6.56	†6.5		
63 Eu ³⁺	6.70	—	(7.22)			
64 Gd ³⁺	7.35	8.84	7.92			
65 Tb ³⁺	8.03	—	(8.60)	†8.3		
66 Dy ³⁺	8.74	10.34	9.32			
67 Ho ³⁺	9.50	—	(10.18)	†9.7		
68 Er ³⁺	10.32	12.01	10.89	10.60(12)	11.07(12)	
69 Tm ³⁺	11.20	—	(11.73)			
70 Yb ³⁺	12.18	13.83	12.63	12.50(8)		

experimental values; here it must be remembered that the values of A_J in Table 5.5 have not been corrected for deviations from LS -coupling, which may be as large as 4 per cent (see Judd 1963a) in some cases.

The magnetic hyperfine constants for the tripositive ions given in Table 5.5 may be compared with those measured for the free atoms (Table 5.4) to find how great is the difference in $\langle r^{-3} \rangle$ for the two cases. In this comparison it must be remembered that the spectroscopic state is different in the two cases, but this involves just the extraction of the factors $\langle J \| N \| J \rangle$. Allowance should also be made for a contribution from core polarization and relativistic effects in the free atom, but these appear to be rather small. If they are neglected, the value of $\langle r^{-3} \rangle_{\text{ion}} / \langle r^{-3} \rangle_{\text{atom}}$ can be easily calculated and appears to fall smoothly from about 1.17 for Pr to 1.05 for Yb; the ratio appears to be close to the ratio of the values of $\langle r^{-3} \rangle$ for ion and atom calculated by Judd and Lindgren (1961), though the values of $\langle r^{-3} \rangle$ themselves are higher.

Few experimental results are available for the hyperfine structure constants of the dipositive ions, but it seems likely that these are close to those of the free atoms which are in the same spectroscopic state. After allowing for core polarization Bleaney (1964a) has estimated

that $\langle r^{-3} \rangle$ is (1.4 ± 0.3) per cent larger for Ho^{2+} than for Ho, and (2.2 ± 0.5) per cent larger for Tm^{2+} than for Tm.

5.5. Nuclear electric quadrupole interaction

This interaction is normally so small that we need consider only matrix elements within a given manifold J . Hence we can use the form of the interaction Hamiltonian appropriate to a free ion

$$\mathcal{H}_q = -\frac{e^2 Q \langle r_q^{-3} \rangle}{I(2I-1)} \langle J \| \alpha \| J \rangle \times \\ \times \left[\frac{1}{4} \{3J_z^2 - J(J+1)\} \{3I_z^2 - I(I+1)\} + \right. \\ \left. + \frac{3}{8} \{ (J_z J_+ + J_+ J_z)(I_z I_- + I_- I_z) + (J_z J_- + J_- J_z)(I_z I_+ + I_+ I_z) \} + \right. \\ \left. + \frac{3}{8} (J_+^2 I_-^2 + J_-^2 I_+^2) \right]. \quad (5.33)$$

Furthermore, the nuclear electric quadrupole interaction is normally so small that, except in rather precise Endor experiments, we need consider only matrix elements that are diagonal within the electronic states left as groups of sub-states by the crystal field. If the latter has threefold or higher symmetry about the z -axis, a given electronic state will consist of admixtures of $J_z = M$ differing by 3 or more. In eqn (5.33) only the operator $\{3J_z^2 - J(J+1)\}$ will have non-zero matrix elements, so that the nuclear electric quadrupole operator will have axial symmetry and be of the form

$$P_{\parallel} \{I_z^2 - \frac{1}{3}I(I+1)\}, \quad (5.34)$$

where

$$P_{\parallel} = -\frac{3e^2 Q \langle r_q^{-3} \rangle}{4I(2I-1)} \langle J \| \alpha \| J \rangle \langle \quad | 3J_z^2 - J(J+1) | \quad \rangle \quad (5.35)$$

and $\langle \quad | 3J_z^2 - J(J+1) | \quad \rangle$ is the matrix element of this operator computed for the given electronic state. Clearly P_{\parallel} has the same value for any pair of states differing only in the sign of J_z , and which form a degenerate doublet (Kramers or non-Kramers) in such a crystal field. If the crystal field has only rhombic symmetry, so that the z -axis is only a twofold axis, then the crystal field states will contain values of J_z differing by 2, so that the terms J_+^2, J_-^2 in eqn (5.33) will also have diagonal matrix elements, and the quadrupole interaction will be of the more general form (cf. eqn (3.40c))

$$P_{\parallel} [\{I_z^2 - \frac{1}{3}I(I+1)\} + \frac{1}{3}\eta(I_x^2 - I_y^2)] \quad (5.36)$$

where, since $(I_x^2 - I_y^2) = \frac{1}{2}(I_+^2 + I_-^2)$, the value of η is given by

$$\eta = \frac{3 \langle |J_z^2| \rangle}{\langle |3J_z^2 - J(J+1)| \rangle}. \quad (5.37)$$

The matrix elements of the operator $3J_z^2 - J(J+1)$ are given in Table 17. Thus for the states $\cos \theta |\pm \frac{7}{2}\rangle + \sin \theta |\mp \frac{5}{2}\rangle$ of eqn (5.11) belonging to a manifold with $J = \frac{9}{2}$ we have

$$\langle |3J_z^2 - J(J+1)| \rangle = 12 \cos^2 \theta - 6 \sin^2 \theta.$$

This result is sharply dependent on the value of θ (it changes sign at $\tan \theta = \sqrt{2}$), and is always small compared with the maximum value of $3J_z^2 - J(J+1)$ which is obtained for a pure state $|\pm J_z\rangle = |J\rangle$ and equals 36 for $J = \frac{9}{2}$. It follows that the quadrupole term may often be rather small for the ground doublet of a rare-earth ion, and also that to evaluate the quantity $Q\langle r_q^{-3} \rangle$ from an experimental result we are dependent in first order on a knowledge of the crystal field.

To proceed further, and estimate Q , we need to know what value to use for $\langle r_q^{-3} \rangle$. The simplest assumption is that it has the same value as the $\langle r^{-3} \rangle$ that appears in the magnetic hyperfine structure, and hence can be determined from the latter if the value of the nuclear magnetic moment is known. However distortion of the charge cloud of the inner closed shells of electrons produces an appreciable change in the electric field gradient at the nucleus (Sternheimer shielding), which may be represented by writing $\langle r_q^{-3} \rangle = (1-R)\langle r^{-3} \rangle$. The contributions to R are both positive (shielding) and negative (anti-shielding), but it seems probable that the net effect is a small amount of shielding.

In addition to the electric field gradient at the nucleus due to the 4f electrons, there will be a contribution in the solid state from the lattice, associated with the term $A_2^0(3z^2 - r^2)$ and other second-degree terms in the crystal field. Here again a shielding (anti-shielding) factor must be introduced, which is generally written as a multiplicative factor $(1-\gamma_\infty)$. In the case of axial symmetry the contribution to P_\parallel from the lattice or crystal field is then

$$P_\parallel (\text{lattice}) = -\frac{3QA_2^0}{I(2I-1)}(1-\gamma_\infty), \quad (5.38)$$

which must be added to (5.35). The size of the lattice contribution has been measured directly by Edmonds (1963), using nuclear magnetic resonance for three lanthanum salts, where the La^{3+} ion has no 4f electrons. Using calculated values of A_2^0 , and $Q = 0.27$ barns for ^{139}La ,

an estimate of around 20 was obtained for $(1-\gamma_\infty)$, the sign being probably positive. A number of theoretical calculations give even larger negative values; for example, Ghatikar, Raychaudhuri, and Ray (1965) find $(1-\gamma_\infty)$ to be +81 for Pr^{3+} and +75 for Tm^{3+} . On the other hand, their values of R are quite small (+0.20 and +0.15 for these two ions respectively). The large anti-shielding factors for the lattice contribution mean that this may predominate over the gradient from the 4f electrons in cases when the latter is exceptionally small (see § 4.8 for Nd^{3+} and below for Eu^{3+}). The relative importance of the two contributions has been measured directly in Mössbauer experiments on two salts of thulium by Barnes, Mössbauer, Kankeleit, and Poindexter (1964). A more general analysis is given by Blok and Shirley (1966).

In cases of cubic symmetry there is no lattice contribution but the appropriate form of the nuclear electric quadrupole interaction due to the 4f electrons is more complicated; it is discussed in §§ 4.7, 5.9, 5.10 and Chapter 18.

5.6. Experimental results for ethylsulphates and anhydrous chlorides

These two salts have C_{3h} point symmetry at the rare-earth site and it is convenient to consider them together; in fact the electron spin results in the two salts are remarkably similar. The ethylsulphates were the first rare-earth salts to be measured by resonance, and the theoretical interpretation by Elliott and Stevens was based mainly on the resonance results; with this limited range of experimental data they succeeded in making remarkably good estimates of the crystal field parameters. The application of high resolution optical and infrared spectroscopy has greatly changed the situation, giving directly and accurately many of the crystal field splittings in the ground state and in some of the excited states. From these the crystal field parameters have been derived for almost all the ethylsulphates and anhydrous chlorides, and these are quoted in Tables 5.7 and 5.8. In each case the V_6^0 term is much the largest; the general trends are that V_6^0 and V_6^6 fall as we proceed along the series to the heavy end, V_4^0 varies little (with perhaps a slight drop in the middle of the series), while V_2^0 increases noticeably in the ethylsulphates (less so in the chlorides). If the crystal field potential were the same throughout a series, the changes in V_k^q would be entirely due to changes in $\langle r^k \rangle$, which we should expect to diminish steadily towards the heavy end because the

TABLE 5.7

Crystal field parameters in cm^{-1} for the rare-earth ethylsulphates; the crystals are undiluted except where the symbol (La) occurs, meaning diluted in the lanthanum salt

	$A_2^0 \langle r^2 \rangle$ (cm^{-1})	$A_4^0 \langle r^4 \rangle$ (cm^{-1})	$A_6^0 \langle r^6 \rangle$ (cm^{-1})	$ A_6^0 \langle r^6 \rangle$ (cm^{-1})	Reference
Ce	+9	-42	-45	680	see Birgeneau (1967a)
Pr(La)	+15	-88	-49	548	Gruber (1963)
Pr	+23	-80	-44	695	Hüfner (1962)
Nd	+58	-68	-43	595	Gruber and Satten (1963)
Pm					
Sm	+60	-64	-40	575	Hill and Wheeler (1966)
	+78	-53			Hüfner (1962)
Sm(La)	+45	-25	-30	450	Larson and Jeffries (1966a)†
Eu	+80	-63	-39	510	Judd (1959b)
Gd					
Tb	+110	-75	-34	465	Hüfner (1962)
Dy	+124	-79‡	-31	492	Powell and Orbach (1961)
	+144	-85	-33	535	Hill and Wheeler (1966)
Ho	+125	-79	-30	391	Hüfner (1962)
Er	+126	-81	-31	387	Erath (1961)
	+119	-74	-30	376	Hill and Wheeler (1966)
Tm(La)	+130	-71	-29	433	Wong and Richman (1961)
Yb					

† Estimated values, which with $A_4^0 \langle r^4 \rangle \approx 360 \text{ cm}^{-1}$, fit the g -values and splittings for the $J = \frac{5}{2}$ manifold.

‡ Corrected value, Hüfner (1962).

increasing nuclear charge pulls the electron orbits into smaller radii. As can be seen from Table 5.1, Hartree-Fock calculations suggest that as we go from Ce^{3+} to Yb^{3+} the values of $\langle r^2 \rangle$, $\langle r^4 \rangle$, and $\langle r^6 \rangle$ fall by factors of (roughly) 2, 4, and 7 respectively. The experimental results show that the crystal potential cannot be assumed to remain constant, presumably because the positions of the ligand ions change as the size of the central ion is reduced (small angular displacements may well be more important than small changes in distance). It is also possible that there are important shielding or anti-shielding effects due to distortion of the outer closed shells of electrons by the crystal field, which will vary throughout the series. The importance of shielding effects is a vexed question; Burns (1962) has argued that shielding effects are quite small, while Freeman and Watson (1964) take the opposite view. They also suggest that non-linear shielding may occur, i.e. that shielding effects are different for wave-functions with different angular distributions of the electronic charge (if this were appreciable,

TABLE 5.8

Crystal field parameters in cm^{-1} for the anhydrous rare earth chlorides (LaCl_3 structure, hexagonal). The symbol (La) indicates that the measurements were made in a sample diluted with LaCl_3 . The energy levels in the ground manifold and the corresponding wave-functions are listed for most of the ions by Mikkelsen and Stapleton (1965)

	$A_2^0 \langle r^2 \rangle$ (cm^{-1})	$A_4^0 \langle r^4 \rangle$ (cm^{-1})	$A_6^0 \langle r^6 \rangle$ (cm^{-1})	$ A_6^8 \langle r^6 \rangle$ (cm^{-1})	Reference
Ce	+65	-41	-64	399	Hellwege, Orlich and Schaaek (1965), Bagguley and Vella-Colleiro (1969)
Pr(La)	+50	-40	-39	397	Judd (1957b)
	+47	-41	-40	405	Margolis (1961) (see also Hutchings and Ray 1963)
Nd(La)	+104	-36	-45	426	Judd (1959a)
	+98	-39	-44	443	Eisenstein (1963b)
Pm					
Sm	+81	-23	-44	426	Axe and Dieke (1962)
Eu(La)	+89	-38	-51	495	de Shazer and Dieke (1963)
Gd(La)	+97	-42	-30	290	Piksis, Dieke, and Crosswhite (1967)
Tb(La)	+92	-40	-30	290	Thomas, Singh, and Dieke (1963)
Dy(La)	+90	-40	-23	253	Crosswhite and Dieke (1961)
Ho(La)	+122	-45	-28	280	Dieke and Pandey (1964)
Er(La)	+114	-34	-28	277	Rajnak and Krupke (1967, 1968)
	+94	-37	-27	265	Eisenstein (1963a)

it would not be possible to fit the crystal field levels observed experimentally with a single set of parameters V_k^q). Further calculations have been made by Sternheimer (1966) and Sternheimer, Blume, and Peierls (1968), which suggest that shielding may be much more important for V_2 than for V_4 or V_6 . Finally, we note that some attempts have been made to compute the crystal potential and hence to find effective values of $\langle r^k \rangle$ by comparison with the spectroscopic crystal field parameters. A detailed calculation of this kind has been carried out for PrCl_3 and PrBr_3 by Hutchings and Ray (1963), with the surprising results that the effective values of $\langle r^2 \rangle$ are a good deal smaller (a factor of 10 to 30) than the Hartree-Fock values; on the other hand the effective value of $\langle r^4 \rangle$ is somewhat larger, and that of $\langle r^6 \rangle$ is about 10 times larger than the Hartree-Fock value. A similar result has been obtained for $\langle r^4 \rangle$, $\langle r^6 \rangle$ by Bleaney (1964a) for Tm^{2+} in CaF_2 ; Axe and Burns (1966) suggest this may be partly due to covalency and overlap effects (see also Ellis and Newman (1966), Watson and Freeman (1967b)).

The paramagnetic resonance data for the ethylsulphates are summarized in Table 5.9, and for the anhydrous chlorides in Table 5.10.

TABLE 5.9
Paramagnetic resonance data for the diluted ethylsulphates $\text{Ln}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$

Ion	Diluent	T (°K)	g_{\parallel}	$ g_{\perp} $	Isotope	A_{\parallel} (cm^{-1})	$ A_{\perp} $ (cm^{-1})	P_{\parallel} (cm^{-1})
Ce	La	4.2	(+)0.955(5)	2.185(10)		ground state		
			(-)3.72(1)	0.20(5)		excited doublet at 3(1) cm^{-1}		
Pr	Y	20	1.525(20)		141	0.0755(20)		
Nd	La	20	(+)3.535(1)	2.072(1)	143	(-)0.03803(1)	0.01989(5)	$<10^{-4}$
					145	(-)0.02364(1)	0.01237(5)	$<10^{-4}$
Pm	La		0.432(4)		147	0.01655(13)		
Sm	La	4.2	(+)0.596(2)	0.604(2)	147	(-)0.0060(1)	0.0251(1)	$<4 \times 10^{-4}$
					149	(-)0.0049(1)	0.0205(1)	
Tb	Y	12	17.72(2)		159	0.209(2)		
Dy	Y	14.4	(10.8)	(0)		ground state—no resonance		
			(+)5.86(10)	8.4(5)		excited doublet at 15(4) cm^{-1}		
Ho	Y	13	15.41(1)		165	0.3354(4)		
						excited singlet at 5.5(1) cm^{-1}		
Er	La	4	(+)1.47(3)	8.85(20)	167	(-)0.0052(1)	0.0314(1)	0.0030(3)
Tm	Y	13	no resonance					
Yb			no resonance					

TABLE 5.10

Paramagnetic resonance data for the diluted trichlorides LnCl_3 (Hutchison and Wong 1958)

Ion	Diluent	T (°K)	g_{\parallel}	$ g_{\perp} $	Isotope	A_{\parallel} (cm^{-1})	$ A_{\perp} $ (cm^{-1})	P_{\parallel} (cm^{-1})
Ce	La	4.2	(-)4.0366(15)	0.17(8)				
Pr	La	4.2	1.035(5)		141	0.0502(3)		
Nd	La	4.2	(+)3.996(1)	1.763(1)	143	(-)0.0425(2)	0.0167(1)	$<10^{-4}$
					145	(-)0.0264(2)	0.0104(1)	$<10^{-4}$
Sm	La	4.2	(+)0.5841(3)	0.6127(6)	147	(-)0.00607(2)	0.0245(1)	
					149	(-)0.00499(2)	0.0202(1)	
Tb	La	4.2	17.78(1)		159	0.212(3)		
Dy	La	4.2	no resonance					
Ho	La	4.2	16.01(2)		165	0.351(7)		
Er	La	4.2	(+)1.989(1)	8.757	167	(-)0.00664(3)	0.0304(2)	(+)0.00086
Tm	La	4.2	no resonance					
Yb	La	4.2	no resonance					

These tables include both the non-Kramers and the Kramers ions, with the exception of the half-filled shell, Gd^{3+} , $4f^7$, ${}^8S_{\frac{7}{2}}$, which will be considered separately. In most cases resonance data are available only for the ground state, and we shall discuss briefly the interpretation for each ion on the lines adopted in the original theoretical papers, since this illustrates the way in which the problem would be tackled in the absence of detailed knowledge about the crystal field, apart from its symmetry.

Ce^{3+} , $4f^1$, 2F ($S = \frac{1}{2}$, $L = 3$; *ground state* $J = \frac{5}{2}$, $\langle J \parallel \Lambda \parallel J \rangle = \frac{6}{7}$)

In the free ion the first excited state ${}^2F_{\frac{7}{2}}$ lies some 2200 cm^{-1} above the ground state ${}^2F_{\frac{5}{2}}$, which is very much greater than the splittings produced by the crystal field, so that in first approximation we take J as a good quantum number. Inside the manifold $J = \frac{5}{2}$ the sixth-degree terms in the crystal potential have no matrix elements, so that effectively we have just the simple operator

$$V = A_2^0 \langle r^2 \rangle \langle J \parallel \alpha \parallel J \rangle O_2^0 + A_4^0 \langle r^4 \rangle \langle J \parallel \beta \parallel J \rangle O_4^0, \quad (5.39)$$

where the matrix elements of O_2^0 , O_4^0 are given in Table 17 and the values of $\langle J \parallel \alpha \parallel J \rangle$, $\langle J \parallel \beta \parallel J \rangle$ in Table 20. The matrix elements are all diagonal in J_z , so that the crystal field would give three Kramers doublets whose wave-functions are just

$$|J_z = \pm \frac{1}{2}\rangle, |J_z = \pm \frac{3}{2}\rangle, |J_z = \pm \frac{5}{2}\rangle,$$

for which the principal g -values are, since $\langle J \parallel \Lambda \parallel J \rangle = \frac{6}{7}$ for the ground state $J = \frac{5}{2}$, (cf. eqns 1.80)

$$\left. \begin{aligned} |\pm \frac{1}{2}\rangle \quad g_{\parallel} &= \frac{6}{7} = 0.86; \quad g_{\perp} = \frac{1}{7} = 2.57; \\ |\pm \frac{3}{2}\rangle \quad g_{\parallel} &= \frac{1}{7} = 2.57; \quad g_{\perp} = 0; \\ |\pm \frac{5}{2}\rangle \quad g_{\parallel} &= \frac{3}{7} = 4.29; \quad g_{\perp} = 0. \end{aligned} \right\} \quad (5.40)$$

Comparison with the experimental results in Tables 5.9 and 5.10 shows that there is no exact fit, but that the first-order theory is qualitatively correct if we assume that the ground doublet in the chloride and the low-lying excited doublet in the ethylsulphate are approximately $|\pm \frac{5}{2}\rangle$, and the ground doublet in the latter salt is approximately $|\pm \frac{1}{2}\rangle$. We therefore look to see whether quantitative agreement with experiment can be obtained if contributions from the state $J = \frac{7}{2}$ are taken into account.

At this point we must use the more general potential operator (5.4) or (5.5) rather than the truncated operator (5.39) which suffices within

the $J = \frac{5}{2}$ manifold. For the case of $J_z = \pm\frac{1}{2}$, the terms V_k^0 have matrix elements between $|J, J_z\rangle = |\frac{5}{2}, \pm\frac{1}{2}\rangle$ and $|\frac{7}{2}, \pm\frac{1}{2}\rangle$ but V_6^0 has no matrix elements so that the most general form of the states is

$$\begin{aligned} |\xi\rangle &= \cos \varphi |\frac{5}{2}, +\frac{1}{2}\rangle - \sin \varphi |\frac{7}{2}, +\frac{1}{2}\rangle, \\ |\bar{\xi}\rangle &= \cos \varphi |\frac{5}{2}, -\frac{1}{2}\rangle + \sin \varphi |\frac{7}{2}, -\frac{1}{2}\rangle. \end{aligned} \quad (5.41)$$

However, since we are dealing with a one-electron system, this doublet is spanned in the $|l_z, s_z\rangle$ representation by the wave-functions

$$\begin{aligned} |\xi\rangle &= \cos \theta | +1, -\rangle - \sin \theta | 0, +\rangle, \\ |\bar{\xi}\rangle &= -\cos \theta | -1, +\rangle + \sin \theta | 0, -\rangle, \end{aligned} \quad (5.42)$$

which is simpler to handle. We can use real admixture coefficients, $\cos \theta$ and $\sin \theta$, because, in the expansion (equ (16.1)) of the crystal potential, all the B_k^a and therefore all the matrix elements of the crystalline field can be chosen real for symmetry C_{3h} as explained in § 16.1 (which incidentally justifies the use of the expansion (16.10) with the P_k^a , rather than the more general expansion (16.1)). The admixture coefficients $\cos \varphi$ and $\sin \varphi$ in (5.41) are also real because the Clebsch-Gordan coefficients relating the representations $|l_z, s_z\rangle$ and $|J, J_z\rangle$ are all real.

From (5.42) we find

$$\begin{aligned} g_{\parallel} &= 2\langle \xi | l_z + 2s_z | \xi \rangle = 2 \sin^2 \theta, \\ |g_{\perp}| &= 2\langle \xi | l_x + 2s_x | \bar{\xi} \rangle = 2 |\sqrt{3} \sin 2\theta - \sin^2 \theta|, \end{aligned} \quad (5.43)$$

from which we can check that the first-order approximation in which $\varphi = 0$ in (5.41) and $\sin \theta = (\frac{3}{7})^{\frac{1}{2}}$ in (5.42) gives the same g -values as in (5.40). If we eliminate θ between the two eqns (5.43) we find that g_{\parallel} and g_{\perp} should satisfy the relation

$$(g_{\parallel} + g_{\perp})^2 / 12g_{\parallel}(2 - g_{\parallel}) = 1. \quad (5.44)$$

The experimental values give 0.82 for this ratio, showing that no value of θ in (5.43) will give exact agreement with experiment.

For a pure $J_z = \pm\frac{5}{2}$ doublet, g_{\perp} is zero and no resonance is observable. The finite value of g_{\perp} here arises solely because of the admixture of the $J = \frac{7}{2}$ states, which gives the wave-functions

$$\begin{aligned} |+\rangle &= p_1 |\frac{5}{2}, -\frac{5}{2}\rangle + q_1 |\frac{7}{2}, -\frac{5}{2}\rangle + r_1 |\frac{7}{2}, +\frac{7}{2}\rangle, \\ |-\rangle &= -p_1 |\frac{5}{2}, +\frac{5}{2}\rangle + q_1 |\frac{7}{2}, +\frac{5}{2}\rangle + r_1 |\frac{7}{2}, -\frac{7}{2}\rangle, \end{aligned} \quad (5.45)$$

or, in the $|l_z, s_z\rangle$ representation,

$$\begin{aligned} |+\rangle &= p_2 | -2, -\rangle + q_2 | -3, +\rangle + r_2 | +3, +\rangle, \\ |-\rangle &= p_2 | +2, +\rangle + q_2 | +3, -\rangle + r_2 | -3, -\rangle, \end{aligned} \quad (5.46)$$

with, of course, $p^2 + q^2 + r^2 = 1$ in each case. (Note that p_1, q_1, r_1 can be related directly to p_2, q_2, r_2 by using the expansions for $|J, J_z\rangle$ in terms of $|l_z, s_z\rangle$, which give $r_1 = r_2$ and

$$\begin{aligned} -p_1 + \sqrt{6}q_1 &= \sqrt{7}p_2, \\ \sqrt{6}p_1 + q_1 &= \sqrt{7}q_2; \end{aligned} \quad (5.47)$$

these formulae can be used to check those for the g -values given below.) In both (5.45) and (5.46) we have chosen as the $|+\rangle$ state that which requires operation by $l_- + s_-$ to generate the $|-\rangle$ state, so as to preserve the correct handedness in the effective spin Hamiltonian if circularly polarized radiation is used; the correct signs in the $|-\rangle$ state are related to those in the $|+\rangle$ state by the time reversal formula (15.29).

The formulae for g_{\parallel} and g_{\perp} are found, using $\langle \frac{7}{2} \parallel \Lambda \parallel \frac{7}{2} \rangle = \frac{8}{7}$, eqns (16.39), (16.40), and Table 20 applied to (5.45), to be

$$\begin{aligned} g_{\parallel} &= \frac{2}{7}(-15p_1^2 + 2\sqrt{6}p_1q_1 - 20q_1^2 + 28r_1^2), \\ g_{\perp} &= \left| \frac{2}{\sqrt{7}}r_1(\sqrt{6}p_1 + 8q_1) \right|, \end{aligned} \quad (5.48)$$

while from (5.46) we have

$$\begin{aligned} g_{\parallel} &= 2(-3p_2^2 - 2q_2^2 + 4r_2^2), \\ g_{\perp} &= |2r_2(\sqrt{6}p_2 + 2q_2)|. \end{aligned} \quad (5.49)$$

It is clear that when r is small compared with the other coefficients, g_{\parallel} will be negative, because the $|+\rangle$ state will have a negative Zeeman energy; we have therefore inserted a negative sign in parentheses before the corresponding entries in Tables 5.9 and 5.10, although these signs have not been verified experimentally.

For (La, Ce)Cl₃ all the 4f levels have been observed by optical spectroscopy, and are shown in Fig. 5.4. The calculated best fit to these levels with a single set of crystal field parameters (those given in Table 5.8) is also shown, a value of $\zeta = 626.5 \pm 1.6 \text{ cm}^{-1}$ being used for the spin-orbit coupling parameter. This value is smaller by a factor 0.9745 than that for the free Ce³⁺ ion, and Hellwege, Orlich, and Schaak (1965) find that a slightly better fit to the resonance value of g_{\parallel} for the ground doublet is obtained by using an orbital reduction factor k assumed equal to 0.9745. The calculated value of $|g_{\parallel}|$ is thereby reduced from 4.222 to 4.078, the measured value being 4.0366 (but see below).

We return now to the question of the g -values of the ground doublets in cerium ethylsulphate. Elliott and Stevens (1962) pointed out that,

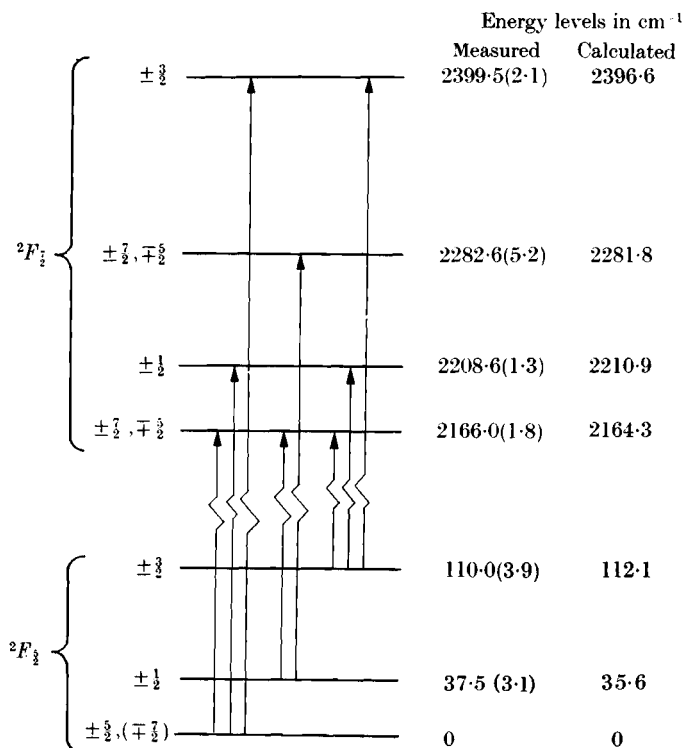


FIG. 5.4. Levels and allowed optical transitions for (Ce, La)Cl₃. The states are characterized by their values of $\pm J_z$, the lowest having an admixture of $(\mp \frac{7}{2})$ from the $J = \frac{7}{2}$ manifold. The measured energy values are compared with those calculated from the crystal field parameters given in Table 5.8 together with a spin-orbit coupling parameter $\zeta = 626.5 \pm 1.6$ cm⁻¹. (After Hellwege, Orlich, and Schaack 1965.)

because of the proximity of the two low-lying doublets, the theory is very sensitive to any small departure from reflection symmetry in the xy -plane. This would introduce terms $V_4^{\pm 3}$, $V_6^{\pm 3}$ into the crystal potential which couple into the ground doublet $|J_z = \pm \frac{1}{2}\rangle$ admixtures (which may have complex amplitudes) of $|J_z = \mp \frac{5}{2}\rangle$. It is then possible to fit simultaneously the g -values for both the low-lying doublets, and the temperature variation of the susceptibility. The latter is for the undiluted salt, where the two low-lying doublets are inverted in energy, the $|J_z = \pm \frac{5}{2}\rangle$ doublet being in this case the lower of the two. This change requires, however, only a small alteration in the crystal field coefficients, since the two doublets lie so close together only through the accidental cancellation of large terms.

If this hypothesis were correct, it would lead to g -values that are

very sensitive to the splitting between the two doublets, as pointed out by Birgeneau (1967*a*), since this splitting appears as an energy denominator in the perturbation theory for the admixtures. In fact, experiments with different host lattices (La, Ce, Sm, and Y ethylsulphates) in which the energy splitting $W_{\pm\frac{1}{2}} - W_{\pm\frac{3}{2}}$ varies from -3.9 to $+17.4 \text{ cm}^{-1}$ show only very small changes in the g -values for the $|\pm\frac{5}{2}\rangle$ doublet. The value of g_{\perp} is constant within the experimental error; g_{\parallel} increases only from 3.70 to 3.81, whereas the theoretical values for g_{\parallel} are all close to 4.14.

Since the correction to g_{\parallel} for the $|\pm\frac{5}{2}\rangle$ doublet is proportional to the square of the admixture of the $|\pm\frac{1}{2}\rangle$ states, it should vary as $(W_{\pm\frac{1}{2}} - W_{\pm\frac{3}{2}})^{-2}$ on a static crystal field theory. If the admixture is due to a dynamic crystal field in which lattice vibrations introduce crystal field terms of the necessary lower symmetry, the energy denominator in the admixture contains a phonon energy as well as the static crystal field splitting. The admixtures and the corrections to the g -values will thus be much less dependent on $(W_{\pm\frac{1}{2}} - W_{\pm\frac{3}{2}})$ if the main phonon energies involved are large compared with this splitting. In this way Birgeneau (1967*a*) has succeeded in explaining quantitatively the low values of g_{\parallel} for the $|\pm\frac{5}{2}\rangle$ doublet in the ethylsulphate. Bagguley and Vella-Colleiro (1969) have applied a simple correction of the same kind to the value of g_{\parallel} for the analogous doublet in $(\text{Ce, La})\text{Cl}_3$, as well as to the $|\pm\frac{1}{2}\rangle$ doublet of the $J = \frac{7}{2}$ level (see Fig. 5.4).

As pointed out by Birgeneau, corrections of this type (which may be positive or negative), originally proposed by Inoue (1963), give a clear-cut explanation of the rather large corrections to the g -values, whereas a covalent orbital reduction would here require overlap and covalent contributions to the static crystal field far larger than the actual crystal field.

Pr^{3+} , $4f^2$, 3H_4 ($S = 1$, $L = 5$; ground state $J = 4$, $\langle J \parallel \Lambda \parallel J \rangle = \frac{4}{5}$)

With two electrons in the 4f shell we have a non-Kramers ion whose ground state is $J = 4$. In C_{3h} symmetry we see from eqns (5.15)–(5.17) that the crystal field splits the ninefold $J = 4$ manifold into three singlet states and three doublets, the latter being of the form $|4, \pm 1\rangle$,

$$\begin{aligned} |\xi\rangle &= \sin \theta |4, +2\rangle + \cos \theta |4, -4\rangle, \\ |\bar{\xi}\rangle &= \sin \theta |4, -2\rangle + \cos \theta |4, +4\rangle, \end{aligned} \quad (5.50)$$

and

$$\begin{aligned} |\xi'\rangle &= \cos \theta |4, +2\rangle - \sin \theta |4, -4\rangle, \\ |\bar{\xi}'\rangle &= \cos \theta |4, -2\rangle - \sin \theta |4, +4\rangle, \end{aligned} \quad (5.51)$$

the two states in each case being conjugated by time reversal. The two sets of states are mutually orthogonal, and (5.51) can be derived from (5.50) by replacing θ by $\theta + \pi/2$. In each case the Zeeman Hamiltonian has opposite expectation values in the two conjugate states, separating them by an amount $g_{\parallel} \beta H_z$ which for (5.51) has the value

$$g_{\parallel} \beta H_z = 2\beta \langle J \parallel \Lambda \parallel J \rangle H_z (2 \cos^2 \theta - 4 \sin^2 \theta) \quad (5.52)$$

with $\langle J \parallel \Lambda \parallel J \rangle = \frac{4}{5}$ for this ion. In the ethylsulphate the value of $g_{\parallel} = 1.52_5$ observed for the ground state can be fitted using $\theta = 24^\circ$ in (5.51), with an appreciable correction from admixture of the next excited state $J = 5$; the rather smaller value of $g_{\parallel} = 1.03_5$ in the anhydrous chloride requires a somewhat larger value of θ .

From the resonance results alone we have no means of telling whether the state $|\xi'\rangle$ or $|\bar{\xi}'\rangle$ has the positive Zeeman energy, and clearly the experimental results could be fitted by a different value of θ if g_{\parallel} were taken as negative in (5.52); it is easily seen that this alternative does not correspond to using (5.50) instead of (5.51). In any given case the choice between the two alternatives must be made on other evidence; usually thermal, magnetic, or spectroscopic experiments will give some information that makes one choice plausible, if not decisive.

Since we are dealing with a non-Kramers doublet for which $g_{\perp} = 0$, resonance is observed only through distortions of the crystal field which admix the two conjugated states, giving an asymmetrical line whose intensity is greatest when the oscillatory magnetic field is also along the crystal axis. The theory of this is given in detail in § 18.5 and summarized in §§ 3.14, 5.3. The value of Δ_0 or \hbar_0 (eqns (3.103), (3.105)) deduced from the experimental results on the assumption of magnetic dipole transitions varies considerably. For Pr^{3+} in yttrium ethylsulphate Baker and Bleaney (1958) found $\Delta_0 = 0.11 \pm 0.04 \text{ cm}^{-1}$, with a larger value (0.19 cm^{-1}) in the lanthanum ethylsulphate; in the undiluted praseodymium ethylsulphate it is much larger still. For Pr^{3+} in LaCl_3 Hutchison and Wong (1958) find the much smaller value $\Delta_0 \approx 0.02 \text{ cm}^{-1}$, or $\hbar_0 \approx 37 \text{ G}$. A detailed comparison of the experimental and theoretical line shapes has been made by Williams (1967), and shows (see Fig. 3.27), that a much better fit is obtained for (Pr, Y) ethylsulphate using (3.111) assuming $\Delta_0 = 0.15 \pm 0.04 \text{ cm}^{-1}$ and that the transitions are primarily due to the perpendicular component of the oscillatory *electric* field.

Nd^{3+} , $4f^3$, $4I_{\frac{3}{2}}$ ($S = \frac{3}{2}$, $L = 6$; ground state $J = \frac{9}{2}$, $\langle J \parallel \Lambda \parallel J \rangle = \frac{8}{11}$)

Inside the ground manifold $J = \frac{9}{2}$, for C_{3h} symmetry, the possible wave-functions for the Kramers doublets have the forms

- (a) $|\pm\frac{1}{2}\rangle$, for which $g_{\perp} = 5g_{\parallel} = 5\langle J \| \Lambda \| J \rangle$;
- (b) two doublets with admixtures $|\pm\frac{3}{2}, \mp\frac{3}{2}\rangle$, for which $g_{\perp} = 0$;
- (c) two doublets of the form of eqn (5.11), whose g -values are given by (5.12).

Only the latter can fit the observed values for the ground state, and we can test the accuracy of the fit by calculating the value of the quantity

$$9g_{\perp}^2/4(g_{\parallel} + 5\Lambda)(7\Lambda - g_{\parallel}),$$

which is obtained by eliminating θ from eqns (5.12) and which should equal unity if the first-order theory is correct. Inserting

$$\Lambda = \langle J \| \Lambda \| J \rangle = \frac{8}{11}$$

and the experimental g -values we obtain 0.86 for the ethylsulphate and 0.84 for the trichloride, showing that the first-order theory is not a bad approximation. The best value for the ethylsulphate is $\theta = 24^\circ$, which gives (cf. Table 5.9)

$$g_{\parallel} = 3.65, g_{\perp} = 2.16.$$

Neodymium has two odd isotopes of mass 143 and 145, both with nuclear spin $I = \frac{7}{2}$ (incidentally these were the first nuclear spins in the 4f group to be determined by electron paramagnetic resonance). From eqn (5.30) we should expect, on first-order theory, that

$$(g_{\parallel}/g_{\perp})/(A_{\parallel}/A_{\perp}) = 1;$$

the experimental values for both ethylsulphate and trichloride are both 0.89, showing again that the first-order theory is approximately correct.

In a second approximation the crystal field terms will introduce into the ground doublet admixtures from the next excited level $J = \frac{11}{2}$ with the same values of J_z . By varying the amplitudes of these admixtures it is possible to improve the agreement between the calculated and experimental values of g_{\parallel} , g_{\perp} , and A_{\parallel}/A_{\perp} . The most extensive calculations of this kind have been carried out by Halford (1962) in order to interpret Endor measurements on the Nd^{3+} isotopes in LaCl_3 . The complete crystal field and spin-orbit coupling energy matrix for the $^4I_{\frac{3}{2}}$, $^4I_{\frac{5}{2}}$, and $^4I_{\frac{7}{2}}$ manifolds was computed and diagonalized numerically, using the crystal field parameters obtained by Judd (1959a) with corrections for intermediate coupling. These parameters were obtained by fitting the levels observed in the optical fluorescence

spectrum, and they lead to g -values for the ground doublet of

$$g_{\parallel} = +4.1016, |g_{\perp}| = 1.7925,$$

which are in good agreement with Halford's measurements of

$$g_{\parallel} = 3.9903(5), |g_{\perp}| = 1.7635(12),$$

which are more accurate than those of Hutchison and Wong (1958) given in Table 5.10.

Details of the Endor spectrum, including discussion of a number of important corrections, are given in § 4.8.

Pm^{3+} , $4f^4$, 5I_4 ($S = 2$, $L = 6$; *ground state* $J = 4$, $\langle J_{\parallel} \Lambda_{\parallel} J \rangle = \frac{3}{5}$)

This ion has no radioactively-stable isotopes, but resonance has been observed for the isotope ${}^{147}\text{Pm}$, which has a half-life of 2.64 years and is a beta-emitter. The magnetic ground state of Pm^{3+} incorporated in lanthanum ethylsulphate is a non-Kramers doublet which is fitted by a spin Hamiltonian of the type given in eqn (5.20) with the addition of a hyperfine term $A_{\parallel} S_z I_z$. Stapleton, Jeffries, and Shirley (1961) observed eight hyperfine lines, corresponding to $I = \frac{7}{2}$, with an asymmetric shape, but the line width appeared to increase rapidly with time after crystal growth, presumably owing to radiation damage of the crystal. Their results for g_{\parallel} and A_{\parallel} are listed in Table 5.9, and are fitted by wave-functions of the form (5.51) with $\theta \sim 38^\circ$ (and admixtures of order 0.03 from the $J = 5$ functions) which correspond to a negative value of g_{\parallel} in eqn (5.52), though this of course has no physical significance.

Sm^{3+} , $4f^5$, ${}^6H_{\frac{5}{2}}$ ($S = \frac{5}{2}$, $L = 5$; *ground state* $J = \frac{5}{2}$, $\langle J_{\parallel} \Lambda_{\parallel} J \rangle = \frac{2}{7}$)

In the ground state the small value of $J = \frac{5}{2}$ means that, as in the case of cerium, the first-order theory is very simple, and only the doublet $|\pm\frac{1}{2}\rangle$ has g_{\perp} different from zero. However it would have $g_{\parallel} = \frac{2}{7}$, $g_{\perp} = \frac{6}{7}$, which are very different from the observed values (see Tables 5.9, 5.10) that lie close to 0.6 with remarkably little anisotropy. Samarium has two odd isotopes, each with $I = \frac{7}{2}$, whose magnetic hyperfine constants have been measured, and these give for the ratio $(g_{\parallel}/g_{\perp})/(A_{\parallel}/A_{\perp})$ the values 0.24 for the ethylsulphate and 0.26 for the chloride. This shows that the first-order theory is completely inadequate for Sm^{3+} , and in view of the fact that the first excited state $J = \frac{7}{2}$ lies at about 1000 cm^{-1} this is not too surprising.

In the next order of perturbation theory the doublet becomes

$$\cos \theta \left| \frac{5}{2}, \pm \frac{1}{2} \right\rangle \pm \sin \theta \left| \frac{7}{2}, \pm \frac{1}{2} \right\rangle \quad (5.53)$$

for which

$$\begin{aligned} g_{\parallel} &= \frac{2}{7}(\cos^2\theta + \frac{2}{9}\sin^2\theta + 3\sqrt{(10)\sin 2\theta}), \\ g_{\perp} &= |\frac{2}{7}(3\cos^2\theta - \frac{10}{9}\sin^2\theta - \frac{3}{2}\sqrt{(10)\sin 2\theta})|, \end{aligned} \quad (5.54)$$

and

$$\begin{aligned} A_{\parallel} &= 2g_n\beta\beta_n\langle r^{-3} \rangle \left(\frac{488}{315}\cos^2\theta + \frac{5056}{4725}\sin^2\theta - \frac{437\sqrt{(10)}}{525}\sin 2\theta \right), \\ A_{\perp} &= \left| 2g_n\beta\beta_n\langle r^{-3} \rangle \left(\frac{488}{105}\cos^2\theta - \frac{20224}{4725}\sin^2\theta + \frac{437\sqrt{(10)}}{1050}\sin 2\theta \right) \right|, \end{aligned} \quad (5.55)$$

where the factors used are given in Table 20 except $\langle \frac{7}{2} \| \Lambda \| \frac{7}{2} \rangle = \frac{5}{6}$ and $\langle \frac{7}{2} \| N \| \frac{7}{2} \rangle = \frac{5}{4}\frac{9}{2}\frac{6}{5}$. With the relatively small admixture of the $J = \frac{7}{2}$ state given by $\theta = 0.07$ rad the correct value of $(g_{\parallel}/g_{\perp})/(A_{\parallel}/A_{\perp})$ can be obtained for the ethylsulphate, and the theoretical g -values are then $g_{\parallel} = 0.66$, $g_{\perp} = 0.65$, which is as good as can be expected from a second-order theory that makes such drastic changes. It can readily be seen that these are due to the terms in $\sin 2\theta$ that arise from the off-diagonal elements between $J = \frac{5}{2}$ and $J = \frac{7}{2}$; their coefficients are relatively large, particularly for the g -values, and, classically, this corresponds to a situation where there are large components of \mathbf{L} precessing about \mathbf{J} as can be seen in a vector diagram.

Eu^{3+} , $4f^6$, 7F_0 ($S = 3$, $L = 3$; ground state $J = 0$)

Obviously, no electron paramagnetic resonance can be expected for an ion with $J = 0$. Elliott (1957) has considered the possibility of a nuclear magnetic resonance experiment in the ground state, and has shown that this is considerably affected by off-diagonal effects from the low-lying $J = 1$ level at about 300 cm^{-1} . The magnetic hyperfine structure produces a pseudo-nuclear quadrupole splitting, and heavy magnetic 'shielding' (i.e. a pseudo-nuclear Zeeman effect of opposite sign to the true nuclear Zeeman interaction) in the $J = 0$ state. Judd, Lovejoy, and Shirley (1962) have observed the quadrupole splitting in the ethylsulphate using nuclear alignment techniques for ${}^{152}\text{Eu}$ and ${}^{154}\text{Eu}$, and find it to be considerably larger and of opposite sign to that predicted by Elliott. Edmonds (1963) has shown that this can be ascribed to the electric field gradient at the nucleus due to the crystal field V_2^0 , assuming it to be enhanced by the same large negative anti-shielding effects as observed for ${}^{139}\text{La}$.

Gd³⁺, 4f⁷, ⁸S_{7/2} ($S = \frac{7}{2}$, $L = 0$); see § 5.9

Tb³⁺, 4f⁸, ⁷F₆ ($S = 3$, $L = 3$; *ground state* $J = 6$, $\langle J \| \Lambda \| J \rangle = \frac{3}{2}$)

This is a non-Kramers ion where resonance is observed in the ground state when the oscillatory magnetic field is parallel to the crystal axis. The lines are however narrow and of normal shape; measurements at different frequencies show that the behaviour is that of a doublet with a small initial splitting of 0.2 to 0.3 cm⁻¹, and a value of g_{\parallel} close to 18. These results identify the ground doublet as consisting principally of the states $J_z = |\pm 6\rangle$, split by a small amount and slightly admixed with the $J_z = |0\rangle$ state through the term V_6^e in the crystal potential. It is fitted with a spin Hamiltonian of the type given by eqn (5.20) with a single value of $\Delta = (\Delta_x^2 + \Delta_y^2)^{\frac{1}{2}}$, with the addition of hyperfine terms, so that the transitions occur at

$$\hbar\omega = \{(g_{\parallel}\beta H_z + A_{\parallel}m)^2 + \Delta^2\}^{\frac{1}{2}}. \quad (5.56)$$

Baker and Bleaney (1958) attempted to deduce values of the crystal field parameters from the experimental results for Δ and $(18 - g_{\parallel})$, but even with corrections for intermediate coupling (which affects g_{\parallel}) and for an admixture of the state $J = 5$, $J_z = 0$ through the V_6^e term (which affects Δ) they arrived at values considerably different from the optical values in Table 5.7 found later by H \ddot{u} fn \ddot{u} r (1962) for Tb³⁺ in the ethylsulphate. In fact the difference between g_{\parallel} and 18 is predominantly due to intermediate coupling, and the correction to Δ is of the same order as the experimental values, so that such a discrepancy in the crystal field parameters is hardly surprising. H \ddot{u} fn \ddot{u} r's crystal field parameters give $c = 5.7$ cm⁻¹, $d = 111$ cm⁻¹, and (from eqns (5.20a) with the corrections mentioned above) $\Delta = 0.2$ cm⁻¹, $g_{\parallel} = 17.8$, in reasonable agreement with the resonance results $\Delta = 0.387$ cm⁻¹, $g_{\parallel} = 17.72$.

Dy³⁺, 4f⁹, ⁶H_{15/2} ($S = \frac{5}{2}$, $L = 5$; *ground state* $J = \frac{15}{2}$, $\langle J \| \Lambda \| J \rangle = \frac{4}{3}$)

No resonance has been observed in the ground state of either ethylsulphate or trichloride, indicating that $g_{\perp} = 0$. This is confirmed by susceptibility measurements (Cooke, Edmonds, McKim, and Wolf 1959) in the ethylsulphate, which give $g_{\parallel} = 10.8$, $g_{\perp} = 0$. Magnetic resonance has been observed in the first excited doublet by Baker and Bleaney (1958), who estimated it to lie at 15 ± 3 cm⁻¹ from relative intensity measurements, with $g_{\parallel} = 5.86$, $g_{\perp} = 8.4$. Optical measurements of Gramberg (1960) give 16.0 cm⁻¹ for this splitting, with

another doublet at 21 cm^{-1} . These results made it possible for Powell and Orbach (1961) to determine the four constants of the crystal potential (see Table 5.7), and hence the energies and wave-functions of the $J + \frac{1}{2} =$ eight doublets into which the crystal field splits the multiplet $J = \frac{1}{2}^5$. The ground doublet is a $\pm\frac{1}{2}^5, \pm\frac{3}{2}, \mp\frac{3}{2}$ combination, which has $g_{\perp} = 0$, and the first excited doublet is a $\pm\frac{7}{2}, \mp\frac{5}{2}$ combination of the type (5.11).

A weak resonance, corresponding to $g_{\perp} \approx 10^{-2}$ in the ground doublet of the ethylsulphate, has been reported by Gill (1963), while Brower and Stapleton (1967) have similarly observed resonance in the ground doublet of $(\text{Dy, La})\text{Cl}_3$. These results are attributed to small distortions of the crystal field. In the latter salt resonance was also observed from a slightly split quartet of states at about 9.9 cm^{-1} above the ground doublet, essentially consisting of two doublets that accidentally lie very close together (only 0.135 cm^{-1} apart in zero magnetic field).

Ho^{3+} , $4f^{10}$, 5I_8 ($S = 2$, $L = 6$; ground state $J = 8$, $\langle J \parallel \Lambda \parallel J \rangle = \frac{5}{4}$)

The ground state in both the ethylsulphate and the chloride is a non-Kramers doublet in which the transitions can be described by eqn (5.56) with g_{\parallel} about 16 and A_{\parallel} about 0.35 cm^{-1} for the single stable isotope ^{165}Ho , $I = \frac{7}{2}$. The lines are asymmetric in shape and fairly narrow, so that the hyperfine components, which are over 450 G apart, are well resolved. Other sets of lines (see Fig. 5.5) can be observed at high fields, as well as some intermediate lines, in the ethylsulphate. It turns out that in this case the ground doublet, which is of the type

$$\left| \begin{smallmatrix} \xi \\ \eta \end{smallmatrix} \right\rangle = \pm \{ \alpha |\pm 7\rangle + \beta |\pm 1\rangle + \gamma |\mp 5\rangle \} \quad (5.57)$$

for either salt, lies a little below the singlet

$$\zeta = \cos \delta |6^s\rangle + \sin \delta |0\rangle \quad (5.58)$$

and it is possible to observe transitions between ξ and η with the oscillatory magnetic field parallel to the crystal axis, and also transitions between ζ and ξ or η with the oscillatory magnetic field perpendicular to the crystal axis. The resonance data can be described by means of a fictitious spin $S = 1$, where ξ and η are eigenstates $S_z = \pm 1$, and ζ is the eigenstate $S_z = 0$. The spin Hamiltonian is then

$$\begin{aligned} \mathcal{H} = D\{S_z^2 - \frac{1}{3}S(S+1)\} &+ g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + \\ &+ A_{\parallel}S_z I_z + A_{\perp}(S_x I_x + S_y I_y) + \\ &+ \{(P_1 - P_0)S_z^2 + P_0\}\{I_z^2 - \frac{1}{3}I(I+1)\}, \end{aligned} \quad (5.59)$$

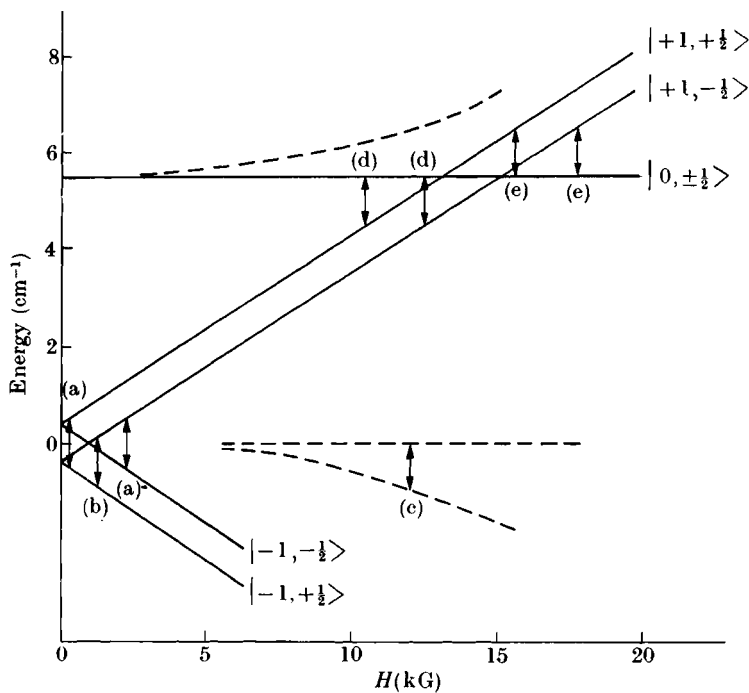


Fig. 5.5. Schematic representation of the three lowest energy levels of diluted holmium ethylsulphate. Continuous lines: behaviour of the energy levels when \mathbf{H} is parallel to the crystal axis (for clarity only two hyperfine components are shown); Broken lines: behaviour when \mathbf{H} is normal to the crystal axis (hyperfine components omitted). The various transitions observed are (in terms of $S = 1$): (a) $|+1, m\rangle \leftrightarrow |-1, m\rangle$ (\mathbf{H} parallel), (b) $|+1, m\rangle \leftrightarrow |-1, m+1\rangle$ (\mathbf{H} parallel), (c) $|+1, m\rangle \leftrightarrow |-1, m\rangle$ (\mathbf{H} perpendicular), (d), (e) $|+1, m\rangle \leftrightarrow |0, m\rangle$ (\mathbf{H} parallel). (After Baker and Bleaney 1958.)

where $D = -5.5 \text{ cm}^{-1}$ is the energy by which the doublet states lie above into singlet (in this case the negative sign means that the doublets lie below the singlet). The other constants are (Baker and Bleaney 1958)

$$\begin{aligned}
 g_{\parallel}/\Lambda &= 7\alpha^2 + \beta^2 - 5\gamma^2, \\
 g_{\perp}/\Lambda &= \{\sqrt{(\frac{1}{2})}\alpha + \sqrt{(\frac{2}{2})}\gamma\}\cos\delta + 6\beta\sin\delta, \\
 \frac{A_{\parallel}}{g_{\parallel}} &= \frac{A_{\perp}}{g_{\perp}} = 2g_n\beta\beta_n\langle r^{-3} \rangle \frac{\langle J_{\parallel} N_{\parallel} J \rangle}{\langle J_{\parallel} \Lambda_{\parallel} J \rangle},
 \end{aligned} \tag{5.60}$$

where $\langle J_{\parallel} N_{\parallel} J \rangle = \frac{23}{60}$, $\langle J_{\parallel} \Lambda_{\parallel} J \rangle = \Lambda = \frac{5}{4}$. P_1 and P_0 are the strengths of the quadrupole coupling in the doublet and singlet respectively.

It should be noticed that in using the $S = 1$ formalism the experimental values of g_{\parallel} and A_{\parallel} are just half what they would be in the

spin $S = \frac{1}{2}$ formalism, apart from a correction to A_{\parallel} of order A_{\perp}^2/D . In Tables 5.9 and 5.10 the $S = \frac{1}{2}$ formalism is used for the doublet; for the ethylsulphate the constants in the spin Hamiltonian (5.59) are

$$g_{\parallel} = 7.71, |g_{\perp}| \sim 4, \\ A_{\parallel} = 0.167 \text{ cm}^{-1}, |A_{\perp}| \sim 0.09 \text{ cm}^{-1}.$$

Er^{3+} , $4f^{11}$, ${}^4I_{\frac{15}{2}}$ ($S = \frac{3}{2}$, $L = 6$; *ground state* $J = \frac{15}{2}$, $\langle J \parallel \Lambda \parallel J \rangle = \frac{9}{5}$)

The first excited state $J = \frac{13}{2}$ is some 8000 cm^{-1} away and first-order theory should be quite accurate. This is confirmed by observation of the hyperfine structure due to the odd isotope ${}^{167}\text{Er}$, which yields a ratio $(g_{\parallel}/g_{\perp})/(A_{\parallel}/A_{\perp}) = 1.00$ in the ethylsulphate and 1.04 in the chloride. The ground doublet is of the form (5.11); its g -values could be fitted also by the combination $\pm \frac{1}{2}$, $\pm \frac{1}{2}$, $\mp \frac{1}{2}$ but for this to be the ground doublet would require rather unreasonable values for the crystal field parameters. The theoretical g -values given by eqn (5.12) with $J = \frac{15}{2}$ yield the relation

$$\left(\frac{g_{\parallel} - \Lambda}{6\Lambda}\right)^2 + \frac{1}{55} \left(\frac{g_{\perp}}{\Lambda}\right)^2 = 1 \quad (5.61)$$

and this relation is well obeyed both by the ethylsulphate and by the chloride.

Tm^{3+} , $4f^{12}$, 3H_6 ($S = 1$, $L = 5$; *ground state* $J = 6$, $\langle J \parallel \Lambda \parallel J \rangle = \frac{7}{6}$)

No resonance has been observed for this ion in either the ethylsulphate or the chloride, and the crystal field parameters predict that the ground state should be a singlet.

Yb^{3+} , $4f^{13}$, ${}^2F_{\frac{7}{2}}$ ($S = \frac{1}{2}$, $L = 3$; *ground state* $J = \frac{7}{2}$, $\langle J \parallel \Lambda \parallel J \rangle = \frac{8}{7}$)

Here again no resonance has been observed. The crystal field theory predicts a ground doublet $|J_z = \pm \frac{3}{2}\rangle$ (in keeping with susceptibility measurements) for which obviously $g_{\perp} = 0$.

5.7. Experimental results for the double nitrates,

$\text{Ln}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$

Magnetic resonance results for the rare-earth double nitrates were interpreted by Judd (1955), with the aid of some data from optical spectroscopy, on the basis of a crystal field of C_{3v} symmetry, a result that has been confirmed by X-ray crystallography (see § 5.1). The crystal potential then has the form (5.3) with the additional terms

$$A_4^3 z(x^3 - 3xy^2) + A_6^3(11z^3 - 3zr^2)(x^3 - 3xy^2), \quad (5.62)$$

which have operator equivalents

$$A_4^3 \langle r^4 \rangle \langle J \| \beta \| J \rangle O_4^3 + A_6^3 \langle r^6 \rangle \langle J \| \gamma \| J \rangle O_6^3, \quad (5.63)$$

where the O_k^q are given in Table 16 and their matrix elements in Table 17. The extra terms correspond to the site having threefold instead of sixfold symmetry about the crystal axis. It appears that they are rather large, as can be seen from Table 5.11, which gives the parameters

TABLE 5.11

Crystal field parameters for the rare-earth double nitrates,
 $\text{Ln}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$

	$A_2^0 \langle r^2 \rangle$ (cm ⁻¹)	$A_4^0 \langle r^4 \rangle$ (cm ⁻¹)	$A_4^3 \langle r^4 \rangle$ (cm ⁻¹)	$A_6^0 \langle r^6 \rangle$ (cm ⁻¹)	$A_6^3 \langle r^6 \rangle$ (cm ⁻¹)	$ A_6^6 \langle r^6 \rangle$ (cm ⁻¹)	Reference
Ce	-70 -155	-30 +6	±900 ±1780	-60 -43	±2800 ±4960	850 2390	Judd (1955) Leask, Orbach, Powell, and Wolf (1963)
Pr	-70	-20	±420	-50	±2300	700	Judd (1955)
Nd	-50 -73	-30 -18	±400 ±790	-40 -70	±1950 ±1760	700 1330	Judd (1955) Tinsley (1963)
Pm							
Sm	-30 -14	-30 -15	±400 ±1440	-40	±1800	700	Judd (1955) Friederich, Hellwege, and Lämmerman (1960)

assumed by Judd (1955). Here only the relative signs and not the absolute signs of A_4^3 and A_6^3 are given, since they change sign on rotation by 180° about the crystal axis, unlike the remaining terms. The actual signs thus depend on the orientation chosen for the x -axis. It was pointed out by Judd (1957a) that these values lie fairly close to those appropriate to a crystal field of icosahedral symmetry, for which

$$|A_6^3/A_6^0| = 14\sqrt{5}, \quad |A_6^6/A_6^0| = 14, \quad (5.64)$$

all the other A_k^q being zero. This point has also been confirmed by the X-ray analysis, which shows that the lanthanide ion is surrounded by twelve oxygens at the corners of a somewhat irregular icosahedron. An important result is that for pure icosahedral symmetry, levels with J less than 3 are not split, while remarkable degeneracies occur for higher values of J . For example, $J = 3$ splits into a triplet and a quartet, whereas even in a pure cubic field it splits into three levels (two triplets and a singlet). The splittings for all manifolds with integral or half-integral values of J up to 8 are given by Judd (1957a) and

TABLE 5.12

Paramagnetic resonance data for the double nitrates $\text{Ln}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$. Taken from the tables of Bowers and Owen (1955) and Orton (1959), except for (a) Stapleton, see Ruby, Benoit, and Jeffries (1962); (b) Judd and Wong (1958)

Ion	Diluent	T (°K)	g_{\parallel}	$ g_{\perp} $	Isotope	A_{\parallel} (cm^{-1})	$ A_{\perp} $ (cm^{-1})	P_{\parallel} (cm^{-1})
Ce	La	4.2	(\pm)0.25(5)	1.84(2)				
			(a) (\pm)0.032(68)	1.8264(13)				
Pr	La	4.2	1.55(2)		141	0.077(2)		
Nd	La	4.2	(-)0.45(5)	2.72(2)	143	(+)0.0052(5)	0.0312(1)	
					145	(+)0.0032(3)	0.0194(1)	
Pm								
Sm	Sm	4.2	(-)0.76(1)	0.40(5)	147	(+)0.0346(5)	<0.010	
					149	(+)0.0287(5)	<0.010	
Dy	La		(+)4.281(6)	8.923(160)	161	(-)0.01161(7)	0.02463(15)	-0.00142(10)
					163	(+)0.01622(7)	0.03415(15)	-0.00168(15)
Er	La		(b) (+)4.21(1)	7.990(10)	167	(-)0.0142(1)	0.0274(1)	+0.0013

Wybourne (1965), with their group-theoretical representations. Further details can be found in McLellan (1961).

The main effect of the extra terms (5.63) is to admix states whose values of J_z differ by 3, so that the states are more complicated than in the case of C_{3h} symmetry where only states whose values of J_z differ by 6 are admixed. The experimental magnetic resonance results are listed in Table 5.12, and we give here only a brief discussion.

Ce^{3+} , $4f^1$, $^2F_{\frac{5}{2}}$

First-order theory gives wave-functions for the ground doublet of the type

$$\cos \theta \left| \frac{5}{2}, \pm \frac{1}{2} \right\rangle \pm \sin \theta \left| \frac{5}{2}, \mp \frac{5}{2} \right\rangle \quad (5.65)$$

for which

$$\begin{aligned} g_{\parallel} &= \frac{6}{7}(\cos^2 \theta - 5 \sin^2 \theta), \\ g_{\perp} &= \frac{6}{7}(3 \cos^2 \theta). \end{aligned} \quad (5.66)$$

These are connected by the relation $2g_{\perp} - g_{\parallel} = \frac{30}{7} = 4.29$, but the experimental values (taking g_{\parallel} as zero) give 3.68 showing that the first-order theory is inadequate.

In second order no less than three admixtures from the $J = \frac{7}{2}$ state have to be included, with $J_z = \pm \frac{7}{2}$, $\pm \frac{1}{2}$, and $\mp \frac{5}{2}$; formulae for the g -values in this case are given by Judd (1955). The resonance results can then be fitted within experimental error, using the crystal field parameters given in Table 5.11.

Cerium magnesium nitrate is very useful in adiabatic demagnetization and as a magnetic thermometer; all its magnetic ions are equivalent, the g -tensor is highly anisotropic, and interactions between the ions are very small. It is also one of the first substances in which an Orbach relaxation process was observed, from which an excited doublet is found to lie at 34°K (Finn, Orbach, and Wolf (1961)). This splitting has been verified by magnetic susceptibility and calorimetric measurements, and has been observed directly by far infrared spectroscopy by Thornley (1963) who finds it to be $36.25 \pm 0.4^\circ\text{K}$ in cerium magnesium nitrate and $30.2 \pm 0.4^\circ\text{K}$ in the corresponding zinc salt. Leask, Powell, Orbach, and Wolf (1963) have attempted to compute the crystal field parameters from susceptibility measurements, obtaining the values given in Table 5.11. They worked in the L_z, S_z representation, and quote the eigenstates in this form; they show also that if a small orbital reduction ($k = 0.95$) is assumed, crystal field parameters some 10 to 20 per cent different are required to fit the experimental results.

$\text{Pr}^{3+}, 4f^2, {}^3H_4$

Optical spectroscopic results of Hellwege and Hellwege (1953) and Brochard and Hellwege (1953) were used by Judd (1955) in the analysis for this ion. The results predict a ground doublet of the non-Kramers type

$$\alpha |\pm 4\rangle \pm \beta |\pm 1\rangle + \gamma |\mp 2\rangle \quad (5.67)$$

for which $g_{\parallel} = \frac{8}{5}(4\alpha^2 + \beta^2 - 2\gamma^2)$ and $g_{\perp} = 0$. Values of $\alpha = 0.458$, $\beta = -0.756$, $\gamma = 0.467$ give $g_{\parallel} = 1.56$ in good agreement with the resonance result. Note that the reversed signs (which follow from time reversal, eqn (15.29)) of the coefficient of $|\pm 1\rangle$ in the two substates lead to $g_{\perp} = 0$, as expected for a non-Kramers doublet.

$\text{Nd}^{3+}, 4f^3, {}^4I_{\frac{3}{2}}$

First-order theory gives for the ground doublet

$$\pm \cos \theta \cos \varphi |\frac{3}{2}, \pm \frac{7}{2}\rangle + \sin \theta \cos \varphi |\frac{3}{2}, \mp \frac{5}{2}\rangle + \sin \varphi |\frac{3}{2}, \pm \frac{1}{2}\rangle,$$

which with the parameters given by Judd (see Table 5.11) leads to

$$g_{\parallel} = -0.52, |g_{\perp}| = 2.91$$

but with rather too low a value of A_{\perp} . Second-order theory gives four extra admixed states from $J = \frac{1}{2}$, with $J_z = \pm \frac{7}{2}, \pm \frac{1}{2}, \mp \frac{5}{2}$, and $\mp \frac{1}{2}$, for which the detailed formulae are given by Judd (1955), who obtains the calculated values

$$g_{\parallel} = -0.32, |g_{\perp}| = 2.72 \text{ and } |A_{\perp}| = 0.0184 \text{ cm}^{-1}$$

in good agreement with experiment. The rather different crystal field parameters of Tinsley (1963) are based on an analysis of the optical spectrum observed by Dieke and Heroux (1956).

$\text{Sm}^{3+}, 4f^5, {}^6H_{\frac{5}{2}}$

Since the ground state has $J = \frac{5}{2}$ and the first excited state is $J = \frac{7}{2}$, the theory is similar to that for Ce^{3+} except that the second-order terms are more important (see Judd (1955)). Excited doublets of the $J = \frac{5}{2}$ manifold have been observed at 46.5 cm^{-1} and 68.9 cm^{-1} by means of optical spectroscopy (Friederich, Hellwege, and Lämmermann 1960), and the crystal field parameters attributed to them in Table 5.11 represent a fit to these splittings using first-order theory only (i.e. neglecting admixtures of the $J = \frac{7}{2}$ state); see Scott and Jeffries (1962).

Dy^{3+} , $4f^9$, ${}^6H_{15/2}$ and Er^{3+} , $4f^{11}$, ${}^4I_{15/2}$

It is convenient to take these two ions together because each has ground state $J = \frac{1}{2}^5$, and the theoretical interpretation uses the icosahedral crystal field as a starting point. In such a field the $J = \frac{1}{2}^5$ manifold breaks up into two sextet states and one quartet (Γ_8); for both ions the latter is expected to lie lowest. When a perturbation of lower (C_{3v}) symmetry is included, the quartet breaks up into two doublets, one of which would be

$$\begin{aligned} \mp |\pm\rangle = & \sqrt{(\frac{8}{12} \frac{1}{15})} |\pm \frac{1}{2}^3\rangle \mp \sqrt{(\frac{1}{2} \frac{2}{3})} |\pm \frac{7}{2}\rangle - \sqrt{(\frac{7}{40} \frac{7}{5})} |\pm \frac{1}{2}\rangle \pm \\ & \pm \sqrt{(\frac{5}{2} \frac{5}{3})} |\mp \frac{5}{2}\rangle + \sqrt{(\frac{1}{2} \frac{1}{15})} |\mp \frac{1}{2}\rangle, \quad (5.68) \end{aligned}$$

where the coefficients are those appropriate to a pure icosahedral field, and are uniquely defined in a group-theoretical treatment since the quartet (Γ_8) occurs only once in the reduction of $J = \frac{1}{2}^5$. For this doublet

$$g_{\parallel} = g_{\perp}/2 = (\frac{1}{5}^7) \langle J_{\parallel} \Lambda \parallel J \rangle,$$

which gives the values

$$g_{\parallel} = 4.53, |g_{\perp}| = 9.07 \text{ for } \text{Dy}^{3+} \quad (\text{Judd 1957a})$$

and

$$g_{\parallel} = 4.08, |g_{\perp}| = 8.16 \text{ for } \text{Er}^{3+} \quad (\text{Judd and Wong 1958})$$

in remarkably good approximation to the observed values (Table 5.12).

Relaxation measurements (Larson and Jeffries 1966a) indicate the presence of another doublet at 15 cm^{-1} in the case of Dy^{3+} .

5.8. Lanthanide ions in cubic symmetry

As mentioned in Chapter 18 and in § 5.1, the resonance spectra of a number of lanthanide ions, both di- and tri-positive, have been observed on sites of cubic symmetry in crystals such as MgO , CaO (octahedral symmetry) and CaF_2 , SrF_2 , BaF_2 , ThO_2 (cubic, eightfold coordination). In cubic symmetry the way in which a manifold of given J is split is readily found from group theory, and the results are summarized in Table 5.13. Manifolds with J less than 2 are not split; half-integral values of J give rise to doublets (Γ_6 , Γ_7) and quartets (Γ_8); integral values of J give singlets (Γ_1 , Γ_2), doublets (Γ_3) and triplets (Γ_4 , Γ_5). When a given representation occurs only once, its wave-functions are uniquely determined from symmetry alone and a number are listed in Tables 4 and 9. When a given representation occurs more than once, the wave-functions depend on the value of x (see eqns (5.72) or (18.14)). The doublets Γ_6 , Γ_7 can be described by spin

TABLE 5.13

Group theoretical representation of the decomposition of manifolds of various J in a cubic field, showing how often the various representations occur

J	Γ_6 (doublet)	Γ_7 (doublet)	Γ_8 (quartet)
$\frac{1}{2}$	1		
$\frac{3}{2}$			1
$\frac{5}{2}$		1	1
$\frac{7}{2}$	1	1	1
$\frac{9}{2}$	1		2
$\frac{11}{2}$	1	1	2
$\frac{13}{2}$	1	2	2
$\frac{15}{2}$	1	1	3

J	$\Gamma_1(A_1)$ (singlet)	$\Gamma_2(A_2)$ (singlet)	$\Gamma_3(E)$ (doublet)	$\Gamma_4(T_1)$ (triplet)	$\Gamma_5(T_2)$ (triplet)
1				1	
2			1		1
3		1		1	1
4	1		1	1	1
5			1	2	1
6	1	1		1	2
7		1	1	2	2
8	1		2	2	2

Hamiltonians with $S = \frac{1}{2}$ and have isotropic g -values; where they occur in the ground manifolds $J = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$, or $\frac{15}{2}$ of the lanthanide ions, the wave-functions are uniquely determined and so are the g -factors, a list of which (in first-order theory) is given in Table 22. Apart from small effects induced by the external magnetic field (see § 5.10), the magnetic hyperfine interaction is isotropic, and the nuclear electric quadrupole interaction is zero. The Γ_8 quartets can be described by a spin Hamiltonian with $S = \frac{3}{2}$, but they have rather peculiar properties which are discussed in Chapter 18; in particular, the Zeeman interaction and magnetic hyperfine interaction are not isotropic; there may be a nuclear electric quadrupole coupling whose form is somewhat similar to that of a free ion with $J = \frac{3}{2}$ (but needing two constants instead of one), and a complicated 'pseudo-nuclear' Zeeman coupling.

In the non-Kramers cases (integral J), the singlet states are of course of no interest in electron paramagnetic resonance, though in nuclear magnetic resonance they may show an isotropic 'pseudo-Zeeman' interaction as well as a true nuclear Zeeman interaction, with

no nuclear electric quadrupole splitting. The Γ_3 doublets have no first-order Zeeman interaction (though a second-order splitting has been observed in an electron magnetic resonance experiment for Dy^{2+} in CaF_2 ; see below), and similarly no magnetic hyperfine coupling, though they may have a nuclear electric quadrupole coupling (see Chapter 18). The Γ_4 , Γ_5 triplets can be represented by a spin Hamiltonian with $S = 1$, with isotropic Zeeman interaction and magnetic hyperfine interaction, but the nuclear electric quadrupole coupling can be represented by a formula similar to that for Γ_8 quartets (with $S = 1$ instead of $S = \frac{3}{2}$) in which again two constants are needed.

A crystal field interaction of cubic symmetry is conveniently expressed in the operator equivalent form

$$\mathcal{H} = B_4 O_4 + B_6 O_6, \quad (5.69)$$

where

$$O_4 = O_4^0 + 5O_4^4; \quad O_6 = O_6^0 - 21O_6^4; \quad (5.70)$$

and

$$B_4 = A_4 \langle r^4 \rangle \langle J \| \beta \| J \rangle; \quad B_6 = A_6 \langle r^6 \rangle \langle J \| \gamma \| J \rangle. \quad (5.71)$$

Since we have only two parameters in (5.69) the energy levels and eigen functions can be computed numerically, on a reduced energy scale, for various values of the ratio of the two parameters. This has been carried out by Lea, Leask, and Wolf (1962); for numerical convenience they write (see eqns (18.14), (18.15))

$$B_4 F_4 = Wx; \quad B_6 F_6 = W(1 - |x|) \quad (5.72)$$

so that the Hamiltonian becomes

$$\mathcal{H} = W\{x(O_4/F_4) + (1 - |x|)(O_6/F_6)\}, \quad (5.73)$$

where F_4 , F_6 are numbers listed by them, and which are mostly (though not invariably) the same as those in the columns headed F in Tables 17. With these definitions $B_4/B_6 = 0$ for $x = 0$ and $\pm \infty$ for $x = \pm 1$, so that the whole range is contained between $x = -1$ and $+1$.

The values of A_4 and A_6 based on a point charge model and including only the nearest neighbours are given for a regular octahedron and cube by eqns (16.15) and (16.16). The lattice sums converge rapidly and for the CaF_2 lattice the inclusion of more distant neighbours gives values of A_4 and A_6 that differ by -8.7 and $+8.8$ per cent respectively from those in (16.16). If Ca^{2+} is replaced by a dipositive ion, calculation of the crystal potential should be rather accurate if no distortion takes place of the crystal lattice. On this supposition Bleaney (1964a) has shown from the optical spectrum of Tm^{2+} in CaF_2 that the effective

values of $\langle r^4 \rangle$ and $\langle r^6 \rangle$ are some 4 and 10 times larger respectively than the values calculated by Freeman and Watson (Table 5.1, and interpolation). If Ca^{2+} is replaced by a tripositive ion without local charge compensation, so that cubic symmetry is retained, the induced dipoles on nearby lattice sites give roughly a 20 per cent increase in the crystal potential, and on applying this to the crystal field parameters estimated by Bierig and Weber (1963) for Dy^{3+} in CaF_2 one again finds that the effective values of $\langle r^4 \rangle$, $\langle r^6 \rangle$ are some 3 and 8 times larger respectively than those of Freeman and Watson. The results of Kiss (1965) show that the crystal field parameters of Dy^{2+} in CaF_2 are very similar to those for Dy^{3+} . From a comparison of Dy^{2+} in CaF_2 , SrF_2 , and BaF_2 Kiss finds that B_4 varies approximately as R^{-2} rather than R^{-5} , where R is the lattice spacing, showing that the crystal field model is inadequate unless considerable local distortion of the lattice is assumed.

Also, the effect of uniaxial stress on optical transitions in $\text{Tm}^{2+}:\text{CaF}_2$ and $\text{Tm}^{2+}:\text{SrF}_2$ is found by Axe and Burns (1966) to be larger than that predicted by a point charge model, and their calculations (see also Watson and Freeman 1967b) suggest a sizable covalent contribution to the ligand field splitting.

The possibility that CaF_2 with suitable lanthanide doping would provide a good laser material has led to intensive investigation of its spectra. The following examples illustrate some points associated with the electron magnetic resonance spectra.

$4f^3$, $^4I_{\frac{3}{2}}$. Pr^{2+} (cubic)

The paramagnetic resonance spectrum of this ion in CaF_2 with cubic symmetry has been observed by Merritt, Guggenheim, and Garrett (1966). They find the ground state to be a Γ_8 quartet, with a large hyperfine structure. The Zeeman splittings are fitted with a value of -0.55 for the parameter x of Lea, Leask, and Wolf (1962), which is close to the value of $|x|$ needed to fit the spectra of a number of lanthanide ions in CaF_2 .

$4f^9$, $^6H_{\frac{1}{2}}$. Dy^{3+} (cubic)

In CaF_2 Bierig and Weber (1963) find the ground state to be a Γ_8 quartet, with a Γ_7 doublet as the first excited state at $8.5 \pm 1 \text{ cm}^{-1}$ higher in energy. The doublet has an isotropic $g = 7.52(5)$, which agrees well with the predicted value of $(\frac{1}{3})\langle J \parallel \Lambda \parallel J \rangle = 7.55$. When the magnetic field is parallel to a $\langle 100 \rangle$ axis, three resonance lines are observed within the Γ_8 quartet at $2.63(5)$, $5.48(15)$, and $14(1) \times (\beta H)$,

which can be fitted with calculated values of 2.57, 5.36, and 13.3 using $x = +0.6$ (eqn (5.72)). This is also the value of x at which Γ_7 and Γ_8 states lie lowest and very close together in the calculations of Lea, Leask, and Wolf (1962). Bierig and Weber find that the results can be fitted with the approximate crystal field parameters of

$$A_4\langle r^4 \rangle \sim -200 \text{ cm}^{-1}, A_6\langle r^6 \rangle \sim +30 \text{ cm}^{-1}.$$

They have verified that the Zeeman effect in the Γ_8 quartet has the correct angular dependence for $x = 0.6$ when \mathbf{H} is rotated in a $\{100\}$ plane, and that it is independent of orientation when \mathbf{H} is in a $\{111\}$ plane, as expected from eqn (18.28), since the quantity

$$\{1 - 5(n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2)\}$$

is invariant in this plane.

Low and Rubins (1963*b*) have observed an isotropic line at $g = 6.60(5)$ for Dy^{3+} in CaO , which they identify as the Γ_6 doublet that lies lowest in an octahedral field when x lies between -1 and -0.48 . Its theoretical g -value is 6.67, and they suggest that there may be an orbital reduction factor $k = 0.98$.

$4f^{10}, {}^5I_8, \text{Dy}^{2+}$ (cubic)

The spectrum of Dy^{2+} in CaF_2 has been extensively investigated. The ground state is a Γ_3 doublet, with a Γ_4 triplet at 4.863 cm^{-1} (determined by a direct measurement; Mergerian, Stomblor, and Harrop 1965), and a Γ_5 triplet at 28.6 cm^{-1} (Kiss, Anderson, and Orbach 1965). The remaining levels, two triplets, a doublet and a singlet lie above 312 cm^{-1} . Such a grouping of levels occurs near $x = -0.46$ for $J = 8$ (see Lea, Leask, and Wolf 1962). The calculated g -value for the Γ_4 triplet is 6.84, but because of the cluster of low-lying states the levels are strongly perturbed when a magnetic field is applied (cf. Fig. 5.6). Their behaviour has been studied by Sabisky (1964), who finds $g = 6.76(2)$ after allowing for a quadratic Zeeman effect. The Γ_3 doublet is also split by the quadratic Zeeman effect, and transitions become allowed between the two components of the doublet when \mathbf{H} is not along an $\langle 001 \rangle$ axis. This occurs then because the magnetic field admixes some of the Γ_4 states characterized by J_z values $(\pm 5, \pm 1, \mp 3, \mp 7)$ into the Γ_3 states which are characterized by $(\pm 6, \pm 2)$ and $(\pm 8, \pm 4, 0)$, so that transitions of the type $\Delta J_z = 0, \pm 1$ become allowed. Obviously transitions between the Γ_3 doublet and Γ_4 triplet are allowed in zero field for the same reason, and from

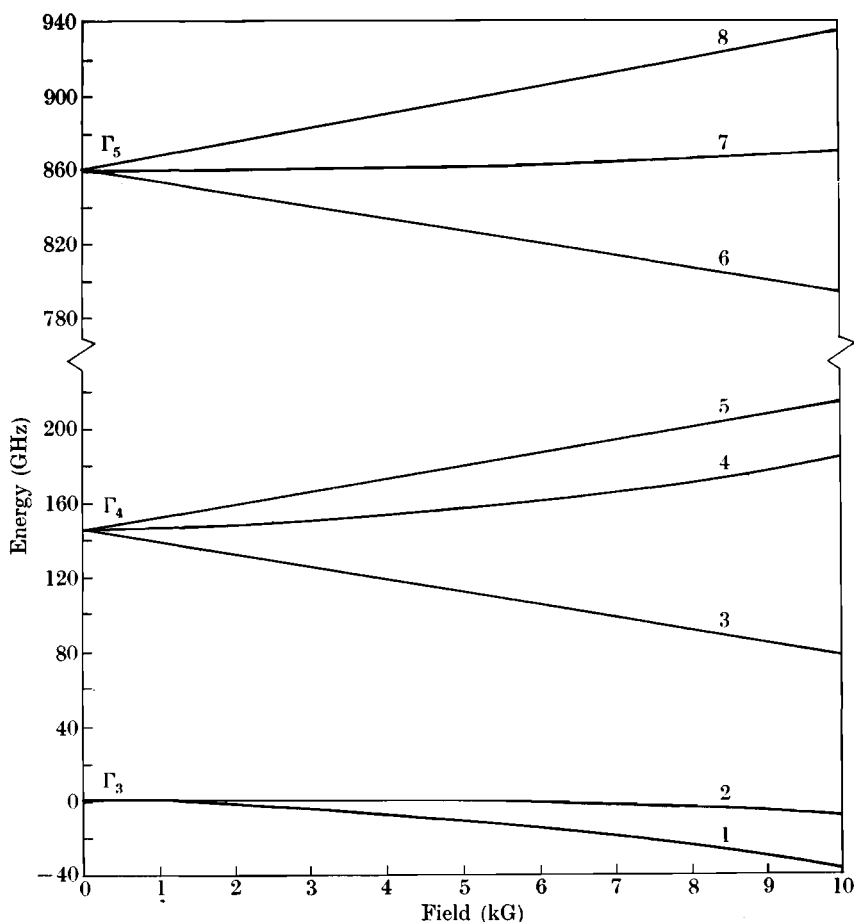


FIG. 5.6. Theoretical calculations of the Zeeman splitting of the lowest eight levels of Dy^{2+} ($4f^{10}$, 5I_8) in CaF_2 with \mathbf{H} parallel to a $\langle 100 \rangle$ axis. (After Mergerian, Harrop, Stombler, and Krikorian 1967.)

a study of such transitions Mergerian, Harrop, Stombler, and Krikorian (1967) have determined the $\Gamma_4 - \Gamma_3$ splitting to be 145.89 GHz.

$4f^{11}$, $^4I_{1\frac{5}{2}}$, Er^{3+} , Ho^{2+} (*cubic*)

The resonance results for these ions are summarized in Table 5.14.

The theoretical g -value for the Γ_7 doublet is (+)6.8 (or 6.77 allowing for intermediate coupling) while that for Γ_6 is (−)6; the rather low value for Ho^{2+} suggests that a small amount of orbital reduction is present (see Bleaney 1964a), which may be partly due to spin-phonon interactions (Inoue 1963). The fact that the ground states are different

TABLE 5.14

Resonance data for ground states of Ho^{2+} , Er^{3+} ($4f^{11}$, $^4I_{15/2}$) in a cubic field. The hyperfine constants are for ^{165}Ho and ^{167}Er ($I = \frac{7}{2}$ in both cases).

			g	A (MHz)	Reference			
<i>Eightfold coordination</i>								
Ho ²⁺ in CaF ₂	doublet	Γ ₆	(-)	5·912(3)	(-)	3921(1)	Lewis and Sabisky (1963)	
Er ³⁺ in CaF ₂	doublet	Γ ₇	(+)	6·785(2)	(-)	677(10)	Ranon and Low (1963)	
	CdF ₂	doublet	Γ ₇	(+)	6·758(10)	(-)	693(10)	Zverev, Kornienko, Prokhorov, and Smirnov (1962)
	ThO ₂	doublet	Γ ₇	(+)	6·752(5)	(-)	697·8(9)	Abraham, Weeks, Clark, and Finch (1965)
	CeO ₂	doublet	Γ ₇	(+)	6·747(6)	(-)	696·3(9)	Abraham, Weeks, Clark, and Finch (1966)
<i>Fourfold coordination</i>								
Er ³⁺ in ZnSe(I)	doublet†	Γ ₇	(-)	5·950(5)			Kingsley and Aven (1967)	
	quartet	Γ ₈		at 6·5±1 cm ⁻¹	above doublet			
	(II) quartet	Γ ₈		ground state				
<i>Sixfold coordination</i>								
Er ³⁺ in MgO	quartet	Γ ₈		ground state			Descamps and Merle D'Aubigné (1964) Belorizky, Ayant, Descamps, and Merle D'Aubigné (1966)	

† Note that the conventional nomenclatures for doublets Γ_6 , Γ_7 in a tetrahedral field are interchanged from those for cubic (eightfold) field (see Kingsley and Aven (1967)).

for Er^{3+} and Ho^{2+} in CaF_2 indicates that we are near the point $x = -0.45$, where these two states cross, the value of $|x|$ being slightly greater in the latter case. The calculations of Lea, Leask, and Wolf (1962) show that there should also be a low-lying Γ_8 quartet. Lewis and Sabisky (1963) have observed 'forbidden' transitions in the hyperfine structure of Ho^{2+} in the Γ_6 doublet which show a very large 'pseudo-nuclear' Zeeman effect, from whose magnitude they deduce that the Γ_8 quartet lies at $32 \pm 4 \text{ cm}^{-1}$, in good agreement with optical results of Weakliem and Kiss (1967) who find a Γ_8 quartet at 30.1 cm^{-1} and a Γ_7 doublet at 33.5 cm^{-1} .

The results for Er^{3+} in MgO are discussed in detail in Chapter 18 in connection with the general treatment of the Γ_8 quartet. Ayant and Belorizky (1964) find that the results are fitted best with a value of $\langle J \| \Lambda \| J \rangle$ which is 1.8 per cent lower than the simple free ion value of $\frac{6}{5} = 1.2$. Of this, 0.4 per cent is due to the admixture of states with different values of J , and if the remainder is ascribed to a reduction of the orbital k -value one obtains $k = 0.979$. Allowing for these effects, the results correspond to $x = 0.714$; the results of Low and Rubins for the same ion in CaO can be interpreted similarly with $x = 0.73$ (Descamps and Merle D'Aubigné 1964). A detailed study of the hyperfine structure of Er^{3+} in MgO by Belorizky, Ayant, Descamps, and Merle D'Aubigné (1966) confirms the expected form of the interactions, and gives a quadrupole coupling in good agreement with that calculated from atomic beam measurements on the free atom, the lattice contribution being of course zero in cubic symmetry.

The spectrum of Er^{3+} in cubic symmetry has also been observed for $(\text{Er}, \text{Zn})\text{Se}$ by Kingsley and Aven (1967). Two sets of spectra are found, believed to be associated with

- (I) Er^{3+} substituting for Zn^{2+} (surrounded by a tetrahedron of Se^{2-} ions);
- (II) Er^{3+} at an interstitial site (normally surrounded by a tetrahedron of 4 Zn^{2+} sites and an octahedron of 6 Se^{2-} ions).

In spectrum I, the ground state is a Γ_7 doublet, with a Γ_8 quartet $6.5 \pm 1 \text{ cm}^{-1}$ higher in energy. In spectrum II the ground state is a Γ_8 quartet.

$4f^{13}, {}^2F_{\frac{7}{2}}, \text{Yb}^{3+}, \text{Tm}^{2+}$ (*cubic*)

A number of experimental resonance results are summarized in Table 5.15.

TABLE 5.15
Experimental results for Yb³⁺ and Tm²⁺ (4f¹³) in cubic symmetry

			g	$^{171}\text{A} \ (I = \frac{1}{2})$ (MHz)	$^{173}\text{A} \ (I = \frac{5}{2})$ (MHz)	Reference
Yb ³⁺	CaO	Γ_6	(-)2·585(3)	(-)2094(18)		Low and Rubins (1963b)
	CaF ₂	Γ_7	(+)3·438(2)	(+)2638·70(5)	(-)727·094(60)	Baker, Blake, and Copland (1969)
	CdF ₂	Γ_7	(+)3·4359(8)	(+)2649(5)	(-)726(1)	Konyukhov, Pashinin, and Prokhorov (1962)
	ThO ₂	Γ_7	(+)3·423(1)	(+)2631(3)	(-)725(1)	Abraham, Weeks, Clark, and Finch (1965)
	CeO ₂	Γ_7	(+)3·424(1)	(+)2631(3)	(-)726(1)	Abraham, Weeks, Clark, and Finch (1966)
			g	$^{169}\text{A} \ (I = \frac{1}{2})$ (MHz)		
Tm ²⁺	CaF ₂	Γ_7	(+)3·443(2)	(-)1101·376(4)	$J = \frac{7}{2}$	Bessent and Hayes (1965)
		Γ'_7	(-)1·453(2)	(+)1160(5)	$J = \frac{5}{2}$	Sabisky and Anderson (1966)

In eightfold coordination the Γ_7 doublet should be the ground state except for values of x less than about $+0.2$; in sixfold coordination (x negative) the Γ_6 doublet always lies lowest. The spectrum of Tm^{2+} in CaF_2 has been studied in considerable detail. From the optical spectrum of Kiss (1962), values of the crystal field were deduced by Bleaney (1964a), who interpreted the g -factor in the ground doublet as giving evidence for an orbital factor $k = 0.991$. Later, paramagnetic resonance measurements on the $J = \frac{5}{2}$, Γ_7 doublet were made by Sabisky and Anderson (1966) using an optical pumping technique to populate this doublet indirectly. In this case the deviation of the g -factor requires $k = 0.986$, so that $(1-k)$ is here significantly larger than in the ground doublet. One explanation of the deviation in the g -factors is that it is due to electron-phonon interactions, for which Inoue (1963) has estimated $\Delta g = -0.01$, a result that is rather smaller than the observed deviation of -0.025 . However, measurements of the fluorine hyperfine structure (Bessent and Hayes 1965) show that the interaction, which is point dipole for more distant shells of fluorines, is larger than point dipole for the first shell, suggesting that there may also be a contribution from covalent bonding. For the isoelectronic ion $\text{Yb}^{3+}:\text{CaF}_2$ (cubic), a value of $k = 0.984$ is found for the Γ_7 ground doublet (Baker, Blake, and Copland 1969); this is a larger value of $(1-k)$ than for the ground doublet of $\text{Tm}^{2+}:\text{CaF}_2$, and it may be significant that in the fluorine ligand hyperfine structure (see Table 4.4) the value of A_p is appreciably larger for Yb^{3+} than for Tm^{2+} . On the other hand, Axe and Burns (1966) estimate that for Tm^{2+} covalency gives a value for $(1-k)$ of order 10^{-3} rather than 10^{-2} .

For the Γ_6 doublet of Yb^{3+} in CaO (where the analysis is simpler because it is not admixed with any $J = \frac{5}{2}$ state), Low and Rubins (1963b) find that the rather low value of g , which on simple theory ($k = 1$) should be $-\frac{7}{3}\langle J \parallel \Lambda \parallel J \rangle = -2.667$, corresponds to a value of $k = 0.959(1)$.

A comparison of magnetic hyperfine measurements on two doublets, such as given in Table 5.15 for Tm^{2+} in CaF_2 , makes it possible to extract the $A_s(\mathbf{S} \cdot \mathbf{I})$ contribution to the hyperfine structure. If no corrections are applied for electron-phonon or covalent effects in the hyperfine structure, a value is found (Sabisky and Anderson 1966) of $(+87(13) \text{ MHz})$, which is equivalent to a coefficient of $-190(30) \text{ MHz}$ in eqn (5.31) or (5.32), between 2 and 3 times the numerical values assumed in these equations. However this result depends on, and is rather sensitive to, the assumption that $\langle r_l^{-3} \rangle = \langle r_{\text{sc}}^{-3} \rangle$ (see § 17.7), and

that these quantities are the same for doublets belonging to the $J = \frac{7}{2}$ and $J = \frac{5}{2}$ manifolds.

The hyperfine structure of Yb^{3+} in CaF_2 is discussed in § 5.10.

5.9. Ions with a half-filled 4f-shell, $4f^7$, ${}^8S_{\frac{7}{2}}$. Eu^{2+} , Gd^{3+} , Tb^{4+}

If the ground state of the $4f^7$ ions were a pure ${}^8S_{\frac{7}{2}}$ state, the only non-zero interaction in a magnetic resonance experiment would be the Zeeman interaction

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S}, \quad (5.74)$$

where g would be isotropic and very close to the free spin value of 2.00232 (corrections for diamagnetic and relativistic effects, estimated by Judd and Lindgren (1961), reduce this to 2.0005 for the Eu atom, whose configuration is $4f^7 6s^2, {}^8S_{\frac{7}{2}}$). However, even for a free atom or ion, there is a significant amount of intermediate coupling, which on including a first-order correction makes the ground state

$$(1 - \alpha^2)^{\frac{1}{2}} {}^8S_{\frac{7}{2}} + \alpha {}^6P_{\frac{7}{2}} (+\text{etc.}) \quad (5.75)$$

whose g -value is

$$g = (1 - \alpha^2)g({}^8S_{\frac{7}{2}}) + \alpha^2g({}^6P_{\frac{7}{2}}). \quad (5.76)$$

For the Eu atom the best estimates of α give a result in good agreement with the experimental value of 1.9935(3). Less information is available for the ions in the solid state on which to base an estimate of α , but the measured g -values of Eu^{2+} and Gd^{3+} given in Table 5.16 (which

TABLE 5.16

Values of g and the cubic splitting parameters b_4 , b_6 for a number of $4f^7$ ions in cubic fields. A number of the original sign determinations have been corrected. (See Shuskus 1962, and Low and Rubins 1963a)

	g	$b_4 = 60B_4$ (MHz)	$b_6 = 1260B_6$ (MHz)	Reference
Eu^{2+} in CaO	1.9914(10)	-77.1(15)	+4.5(15)	Shuskus (1962)
Eu^{2+} in CaF_2	1.9926(3)	-176.12(2)	+0.78(2)	Baker and Williams (1962)
Eu^{2+} in SrCl_2	1.995(1)	39		Low and Rosenburger (1959)
Gd^{3+} in CaO	1.9925(10)	-36.6(3)	+3.6(3)	Shuskus (1962)
Gd^{3+} in CaF_2	1.991(2)	(-)138(4)	(+)3(2)	Low (1958)
Gd^{3+} in ThO_2	1.991(1)	-168.75(60)	-1.28(60)	Low and Shaltiel (1958)
				Hurrell (1965)
Gd^{3+} in SrCl_2	1.9906(10)	(±)29.7(1)	(∓)0.2(1)	Low and Rosenburger (1959)
Th^{4+} in ThO_2	2.0146(4)	-2527.53(10)	-24.84(4)	Baker, Chadwick, Garton, and Hurrell (1965)

are typical of many experimental results) seem to be explicable on this basis, while the value of 2.0146(4) for Tb^{4+} in ThO_2 is not.

In the solid state where an ion is subjected to a ligand field the Zeeman interaction may be expected to be more complicated, with terms linear in H but involving higher powers of the components of S . The form of these terms (which are experimentally very small) will be considered in § 5.10, together with comparable terms in the magnetic hyperfine structure. The latter have been determined with much greater certainty, because of the higher accuracy possible in Endor measurements (see Chapter 4).

The main result of the ligand field is to produce a splitting of the electronic states in zero magnetic field, with a consequent 'fine structure' in the resonance spectrum. This is possible only through perturbations of high order, so that the splitting is usually rather small, whereas for the lanthanide ions which are not in S -states the comparable splitting is of order 10^3 cm^{-1} . Fortunately the experimentalist can include such effects in his spin Hamiltonian by the simple device of introducing spin operators which reflect the symmetry of the site on which the ion is placed in the solid. Thus for cases of cubic symmetry we add to eqn (5.74) the general cubic terms

$$B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4), \quad (5.77)$$

whose effects on the spectrum are discussed in § 3.4. B_4 , B_6 are regarded as parameters to be determined experimentally, and a representative list of results is given in Table 5.16. For numerical convenience the modified parameters $b_4 = 60B_4$, $b_6 = 1260B_6$ are used, where the numerical multipliers are those listed in the column F for $J = \frac{7}{2}$ in Tables 17. For comparison with the nomenclature of Low (1960) we give the equivalence $c = 4b_4$, $d = 4b_6$ (see also Table 3.8).

The experimental results do not give any very firm guide to the theoretical interpretation. The values of b_4 appear to be negative both in octahedral and cubic (eightfold coordinated) sites, suggesting that perturbation mechanisms linear in the crystal field can be ruled out, but the magnitude of b_4 does not seem to be correlated in any obvious way with the strength of the crystal field estimated on a point charge model. The unusually large value of b_4 for Tb^{4+} in ThO_2 (all transitions observed come at intermediate fields—see Fig. 5.7), together with other abnormalities (see Baker, Chadwick, Garton, and Hurrell 1965) suggests that bonding effects are important in this case, but b_4 is not particularly large for Eu^{2+} in CaO (Shuskus 1962) though the magnetic

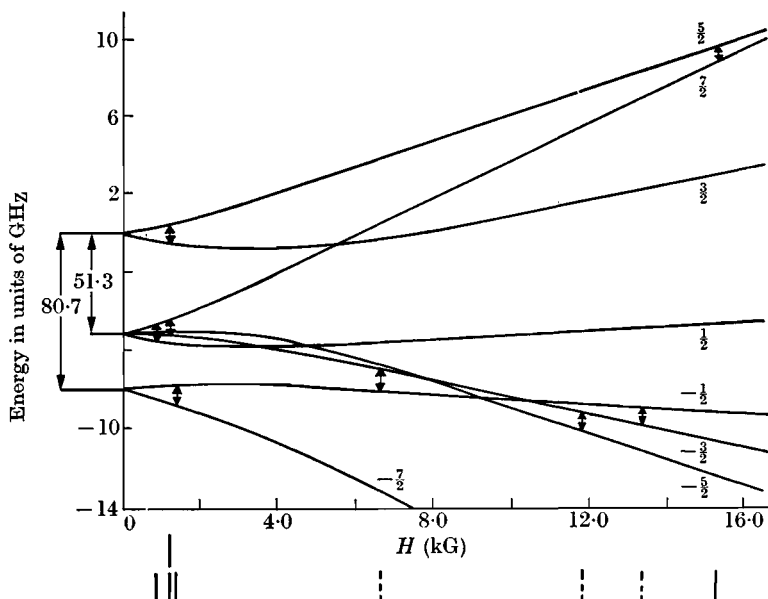


FIG. 5.7. Energy levels of Tb^{4+} in ThO_2 plotted as a function of a magnetic field applied in a $\langle 100 \rangle$ direction, showing the transitions observed at a frequency of ~ 9 GHz. The position of the lines is shown below, the broken lines being those on which Endor was observed. (After Baker and Hurrell 1965.)

hyperfine structure is distinctly smaller than for Eu^{2+} in CaF_2 , a result that in $3d^5$ ions usually indicates a greater degree of covalent bonding. Furthermore, the value of b_4 for Eu^{2+} changes sign in the series of host lattices CaO , SrO , BaO (see Overmeyer and Gambino 1964, Miyata and Argyle 1967).

The value of b_6 always seems to be small compared with b_4 , but because of the numerical multipliers perhaps the most direct comparison can be made by considering the crystal field splittings in zero magnetic field. The 6S state then divides into two doublets (Γ_6 , Γ_7) and a quartet (Γ_8), the ratio of the separations being

$$\frac{W(\Gamma_6) - W(\Gamma_8)}{W(\Gamma_8) - W(\Gamma_7)} = \frac{12b_4 - 36b_6}{20b_4 + 28b_6},$$

so that if $b_6 = 0$ the ratio is just 0.6. The deviation from this value is only a few per cent for the eightfold coordinated ions in Table 5.16, which are all in CaF_2 type lattices. On the other hand, for Tm^{2+} in CaF_2 , whose ground state is $J = \frac{7}{2}$, the comparable ratio is 0.06. This seems to be in line with the suggestion (Lacroix 1957) that for $4f^7$, 8S

states the crystal field produces the b_6 term only through higher-order perturbation mechanisms than are required for b_4 .

In compounds where the symmetry is less than cubic a larger number of spin operators will be required, but these must still reflect the symmetry of the site. Thus for C_{3h} symmetry (LaCl_3 , the ethylsulphates) we need to add to (5.74) the terms

$$B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^8 O_6^8. \quad (5.78)$$

In experiments where these terms are small compared with the Zeeman interaction (as is often the case), the first three terms, which are diagonal, can be determined at once from the positions of the transitions when the external magnetic field is applied along the axis. The last term then enters only in second order, and can be found more accurately by measurements with the magnetic field in the plane normal to the symmetry axis. If the direction of the magnetic field is then taken as the z -axis of the spin operators, the Hamiltonian can be transformed, using the formulae in Table 5 of Jones, Baker, and Pope (1959), to (\mathbf{H} at angle $\theta = \pi/2$, ϕ to z -axis)

$$\mathcal{H} = g\beta HS_z - \frac{1}{2}B_2^0 O_2^0 + \frac{3}{8}B_4^0 O_4^0 + \frac{1}{16}O_6^0(B_6^8 \cos 6\phi - 5B_6^0), \quad (5.79)$$

where only the diagonal terms have been retained. These are similar to those in (5.78) except for numerical changes, but the presence of $\cos 6\phi$ in the last term means that the line spacings will vary as $\cos 6\phi$ as the magnetic field is rotated in the plane normal to the crystal axis. The value of B_6^8 can be obtained directly from this variation.

When the symmetry is only C_3 , or C_{3v} , we must add to (5.78) the terms

$$B_4^3 O_4^3 + B_6^3 O_6^3, \quad (5.80)$$

which affect the transition frequencies only in second order when the magnetic field is along the threefold axis. When the magnetic field is normal to this axis, the expectation values of O_4^3 and O_6^3 are zero, so that as \mathbf{H} is rotated in this plane the variation in the spectrum reflects only the O_6^8 term. Thus to first order the behaviour of the spectrum under these conditions is the same as for C_{3h} symmetry, and measurements must be made at intermediate directions to determine the terms in (5.80), as is discussed for Gd^{3+} in Al_2O_3 by Geschwind and Remeika (1961), and in the hexa-antipyrene iodide by Baker and Williams (1961).

The results for Gd^{3+} measured in four compounds of three or sixfold symmetry are given in Table 5.17. The main feature of the results is

TABLE 5.17

'Fine structure' splitting parameters for Gd^{3+} in four compounds. They are somewhat temperature sensitive; in the first three cases the temperature for which values are given is $90^\circ K$, in the last it is $4.2^\circ K$. For Gd^{3+} in Al_2O_3 the additional parameters $b_4^3 = 3B_4^3 = 18.3(10)$, $b_6^3 = 36B_6^3 \approx 1.0$ (in units of 10^{-4} cm^{-1}) have been determined

		g	$b_2^0 = 3B_2^0$	$b_4^0 = 60B_4^0$	$b_6^0 = 1260B_6^0$	$ b_6^6 = 1260B_6^6 $	Reference
			in units of 10^{-4} cm^{-1} (2.998 MHz)				
$LaCl_3$	C_{3h}	1.991(1)	+16.0(2)	+2.13(5)	+0.25(5)	1.4(3)	Hutchison, Judd, and Pope (1957)
Lanthanum ethylsulphate	C_{3h}	1.990(2)	+204.7(20)	-3.96(30)	+0.63(60)	3.5(5)	Bleaney, Scovil, and Trenam (1954)
Bismuth magnesium nitrate	C_{3v}	1.992(2)	+124(1)	+0.9(1)	+0.6(1)	12(1)	Trenam (1953)
Al_2O_3	C_3	1.9912(5)	+1032.9(20)	+26.0(10)	+1.0(5)	5.0(5)	Geschwind and Remeika (1961)

TABLE 5.18

Principal hyperfine constants of some ions with $4f^7$, $^8S_{7/2}$ ground states, as measured by Endor. The column $-AS/g_I\beta$ gives the magnetic field at the nucleus in the fully polarized state $S_z = S$. The following columns give the estimated contributions from f -electrons (A_I/g_n) including relativistic effects, and from core polarization (A_c/g_n). A , B are the magnetic dipole and electric quadrupole parameters (see eqn (4.42)); g_I , g_n are the nuclear g -factors referred to Bohr magnetons and nuclear magnetons respectively

	I		(A) (MHz)	μ_I (nuclear magnetons)	$-AS/g_I\beta$ (kG)	A_I/g_n (MHz)	A_c/g_n (MHz)	B (MHz)	Q (barns)	B/Q (MHz/barn)
CaF ₂	Eu ²⁺ 151	$\frac{5}{2}$	-102.907(1)	+3.4413(9)				-0.7855(52)	+1.16(8)	
	Eu ²⁺ 153	$\frac{5}{2}$	-45.673(2)	+1.5196(13)				-2.0294(68)	+2.92(20)	
	Eu ²⁺				340	-15	-60			-0.68(5)
CeO ₂	Gd ³⁺ 155	$\frac{7}{2}$	(+)12.048(3)	(-)0.2567(6)						
	Gd ³⁺ 157	$\frac{7}{2}$	+15.809(5)	-0.3357(6)						
ThO ₂	Gd ³⁺ 157	$\frac{7}{2}$	+15.768(3)	-0.3371(6)				-0.687(18)	+1.70(16)	
	Gd ³⁺				320	-18	-52			-0.40(4)
ThO ₂	Tb ⁴⁺ 159	$\frac{3}{2}$	-73.891(23)	+1.994(4)	250	-22	-33	+6.194(38)	1.23(10)	+5.0(4)

References: Eu²⁺, Baker and Williams (1962).

Gd³⁺, Hurrell (1965), Baker, Copland, and Wanklyn (1969).

Tb⁴⁺, Baker, Chadwick, Garton, and Hurrell (1965).

that, except for Gd^{3+} in LaCl_3 , the 'fine structure' is dominated by the 'quadrupole' term B_2^0 . This suggests that such a term is produced by lower order perturbation mechanisms than the other terms, since the B_2^0 term is far from dominant in the splittings of other lanthanide ions that are not in S -states. Wybourne (1966) has shown that when relativistic effects are included, a term of the right order of magnitude (but of the wrong sign) can be produced by a second-order process involving the first power of the spin-orbit coupling and of the crystal field.

We consider now the principal hyperfine interactions, listed in Table 5.18 for some $4f^7$ ions in cases of cubic symmetry. We can isolate the electronic effects by dividing through by g_I (or g_n) and by Q . The column headed $-AS/g_I\beta$ gives the electronic magnetic field at the nucleus in the state $S_z = S$, and is of interest in a comparison with the corresponding field in a substance (such as the metals) which enter a magnetically co-operative state. This field shows a small but significant decrease as the valency of the ion increases. The following two columns give the contributions (A_f/g_n) from f -electrons including relativistic effects, and (A_c/g_n), from core polarization, as estimated by Baker, Chadwick, Garton, and Hurrell (1965), and show that the latter decreases markedly for Tb^{4+} , a result again consistent with increased covalent bonding. The column (B/Q) shows a more dramatic difference in that this quantity is much larger and of opposite sign for Tb^{4+} than for the two other ions.

In these and a number of other cases small higher-order terms in the spin Hamiltonian have been determined experimentally. Some of these are outlined in the following section.

5.10. Higher-order terms in the spin Hamiltonian

In the spin Hamiltonian the allowed terms have the dimensions $H^r S^s I^t$, where $r+s+t$ must be even to satisfy time reversal invariance, and where $s \leq 2S$, $t \leq 2I$ because operators containing higher powers have zero matrix elements. The chief terms in the spin Hamiltonian are those for which $r+s+t = 2$, except in the case $r = t = 0$, when powers of S up to 4 are encountered for d -electrons and 6 for f -electrons. These are the 'fine structure' terms that occur for d^5 (see § 7.12) and for f^7 (see §§ 5.9, 6.2, 6.3), and whose effect on the spectrum has been discussed for the case of cubic symmetry in § 3.4. Fine structure terms with $r = t = 0$, $s = 2$ occur for other configurations, and are similarly discussed in §§ 3.5, 3.6.

The case $r = s = 0$ arises only for the nuclear electric quadrupole interaction, which under non-cubic symmetry may be expressed in a form with $t = 2$ for a Kramers doublet and sometimes also for non-Kramers doublets (an exception to the latter is discussed in § 18.6). Occasionally such a form suffices for manifolds of higher degeneracy, but then we may need terms for which $s = t = 2$. We have already met such terms in § 4.7, where a nuclear electric quadrupole interaction of the same form as for a free atom was assumed for Eu^{2+} , $4f^7$ in CaF_2 . This is not strictly correct, since even in cubic symmetry two parameters rather than one are needed in this interaction (see §§ 18.4 and 18.6), but the error is not likely to be serious for Eu^{2+} where the size of the interaction is close to that for the free Eu atom.

Fine structure terms are often comparable with or larger in energy than the electronic Zeeman interaction. In contrast, the nuclear electric quadrupole interaction, although one of the two principal hyperfine interactions, is usually rather small. The remaining terms with which we shall be concerned in this section are also rather small, with one exception. For an ion with appreciable 'unquenched' orbital momentum, such as Co^{2+} in a tetrahedral field or a rare-earth ion in a cubic field (cf. § 5.8), groups of states with degeneracies up to four may occur, as in the Γ_8 quartet. The spin Hamiltonian for this is discussed in some detail in Chapter 18, using an effective spin $S = \frac{3}{2}$. Terms of the form HS^3 may then be as important as the simple Zeeman term HS , but the reason for this is that in using $S = \frac{3}{2}$ to describe the quartet we are labelling the states by quite fictitious quantum numbers that have no simple relation to the actual angular momenta. It would be incorrect to ascribe terms of dimensions HS^3 to an electronic magnetic octupole moment, since this would interact only with a non-uniform magnetic field which has an octupole-like distribution over the region of the electronic magnetic moment, whereas H is a uniform field. Terms in IS^3 arise in a similar way from the magnetic field of the nucleus, but the fact that this field is non-uniform over the electronic distribution does not play a significant role.

In considering other terms, we confine ourselves to cases of cubic symmetry. Nevertheless, we can perhaps further emphasize our point about the effective spin by referring to § 18.6, where it is shown that terms of degree SI^2 are allowed for a Γ_3 doublet in a cubic field. This is possible because for a non-Kramers doublet (see § 18.5) the components of the effective spin S may not be time-odd operators, whereas the condition that $r+s+t$ must be even rests on the assumption that

the components of S are time-odd operators. General discussions of the allowed terms are given by Koster and Statz (1959) and Tuhina Ray (1963), and below we illustrate the situation by outlining two sets of experimental results.

For an ion with configuration $4f^7$, whose ground state $S = \frac{7}{2}$ has an eightfold multiplicity, we may anticipate a number of higher-order terms. In the electronic Zeeman interaction, additional terms that have been explored are

$$\mathcal{H}'_{\text{Zeeman}} = g_1 \beta H_z \{1/\sqrt{(10)}\} \{5S_z^3 - 3S_z S(S+1) + S_z\} + g_2 \beta H_z \{1/3\sqrt{(56)}\} \times \\ \times \{63S_z^5 - 70S_z^3 S(S+1) + 105S_z^3 + 15S_z S^2(S+1)^2 - 50S_z S(S+1) + 12S_z\} + \\ + g_3 \beta H_z \{5/8\sqrt{(10)}\} \{S_z(S_+^4 + S_-^4) + (S_+^4 + S_-^4)S_z\}, \quad (5.81)$$

where the last term applies when H_z is along a cube axis of fourfold symmetry. (The parameter g_1 in (5.81) is of course quite different from that in eqn (3.9).) Similarly, in addition to the principal hyperfine terms in eqn (4.42), we have

$$\mathcal{H}'_{\text{hfs}} = A'(S_x^3 I_x + S_y^3 I_y + S_z^3 I_z) + \\ + A''(S_x^5 I_x + S_y^5 I_y + S_z^5 I_z) + B' \beta H_z S_z I_z^2. \quad (5.82)$$

Here we have retained the nomenclature of Baker and Williams (1962); more symmetrical forms of the terms in S^3 (which have the advantage that they vanish for $S < \frac{3}{2}$) are given in eqn (18.21)).

Some experimental results are listed in Table 5.19. As we would expect for ions where the orbital angular momentum is very small, the terms of higher degree become rapidly smaller. They arise from the

TABLE 5.19

Electron paramagnetic resonance and Endor data for some $4f^7$ ions. A , g are the usual parameters; the others are defined by eqns (5.77), (5.81), and (5.82). For references, see Table 5.18

	Eu ³⁺ in CaF ₂	Gd ³⁺ in ThO ₂	Tb ⁴⁺ in ThO ₂
$60B_4$ (MHz)	-176.12(2)	-168.75(60)	-2527.53(10)
$1260B_6$ (MHz)	+0.78(2)	-1.28(60)	-24.84(4)
g	1.9926(3)	1.991(1)	2.0146(4)
g_1	$0(1) \times 10^{-5}$	—	$0(2) \times 10^{-5}$
g_2	$0(1) \times 10^{-6}$	—	$2.1(4) \times 10^{-6}$
g_3	—	—	$1.1(5) \times 10^{-6}$
	Isotope 151	Isotope 157	Isotope 159
A (MHz)	-102.907(1)	+15.7679(33)	-73.891(23)
A' (kHz)	+13.77(46)	-3.05(30)	+103.3(23)
A'' (kHz)	+0.084(31)	—	—
B'	—	—	+1.02(14) $\times 10^{-6}$

small admixture of excited states through the spin-orbit coupling and the ligand field. This means that we might expect the ratio A'/A to be of the same order as $g_1/\Delta g$ rather than g_1/g , where $\Delta g = g_s - g$ is a measure of the orbital admixture. The measurements of g_1 are not sufficiently accurate to check this expectation, and the fact that (in contrast) fairly accurate values of A'/A are listed reflects the fact that Endor measurements are often higher in precision than electron paramagnetic resonance measurements (cf. § 1.13 or § 4.1).

An interesting contrast is provided by Endor measurements on Yb^{3+} (cubic) in CaF_2 , where the ground state is an electronic Kramers doublet Γ_7 (see Table 5.15). The Endor spectrum is fitted to the spin Hamiltonian (with $S = \frac{1}{2}$)

$$\begin{aligned} \mathcal{H} = & g\beta\mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S} - g^{(I)}\beta\mathbf{H} \cdot \mathbf{I} + \\ & + \beta h \{ S_x I_x^2 H_x + S_y I_y^2 H_y + S_z I_z^2 H_z - \frac{1}{3} I(I+1)(\mathbf{S} \cdot \mathbf{H}) \} + \\ & + \beta q \{ (S_x H_y + S_y H_x)(I_x I_y + I_y I_x) + (S_y H_z + S_z H_y)(I_y I_z + I_z I_y) + \\ & + (S_z H_x + S_x H_z)(I_z I_x + I_x I_z) \} + \\ & + C [I_x^3 S_x + I_y^3 S_y + I_z^3 S_z - \frac{1}{5} \{ 3I(I+1) - 1 \} (\mathbf{S} \cdot \mathbf{I})] + \\ & + D \{ 35I_x^4 - 30I_x^2 I(I+1) + 25I_z^2 - 6I(I+1) + 3I^2(I+1)^2 + \\ & + \frac{5}{2}(I_+^4 + I_-^4) \}, \end{aligned} \quad (5.83)$$

where the nomenclature (apart from the pseudo-nuclear Zeeman term) is that of Baker, Blake, and Copland (1969). For the isotope ^{171}Yb , $I = \frac{1}{2}$, and terms in higher powers of I than the first are allowed only

TABLE 5.20

Nuclear and hyperfine parameters for Yb^{3+} (cubic) in CaF_2 , for the Γ_7 Kramers doublet ground state, with $g = +3.4380(5)$. The Endor spectrum is fitted to the spin Hamiltonian of eqn (5.83), and the data are from Baker, Blake, and Copland (1969), except for the values of g_I which are those of Olschewski and Otten (1967)

	$^{171}\text{Yb}(I = \frac{1}{2})$ <100> axis	$^{173}\text{Yb}(I = \frac{3}{2})$ mean of <100> and <110> axes
A (MHz)	+2638.70(5)	-727.094(60)
$g^{(I)}$	+8.702(50) $\times 10^{-4}$	-2.396(12) $\times 10^{-4}$
g_I	+5.35816 $\times 10^{-4}$	-1.4761 $\times 10^{-4}$
βh (HzG $^{-1}$)		+49.6(7)
βq (HzG $^{-1}$)		+65.2(10)
C (kHz)		+12(5)
D (kHz)		+133(33)
$g^{(I)}/g_I$	+1.6240	+1.6231

for the other stable isotope ^{173}Yb , for which $I = \frac{5}{2}$. The measured parameters are given in Table 5.20, those for ^{173}Yb being a weighted mean of measurements in $\langle 100 \rangle$ and $\langle 110 \rangle$ directions. The external magnetic field admixes the excited Γ_8 quartet states into the ground Γ_7 doublet, and this accounts for the difference between the effective value $g^{(I)}$ and the true nuclear g -factor g_I measured by optical pumping experiments (Olschewski and Otten 1967) in the free atom. From the difference, the energy of the Γ_8 level is found to be $604 \pm 10 \text{ cm}^{-1}$.

This same admixture is responsible for the terms in βh and βq ; physically they correspond to interactions between the nuclear electric quadrupole moment and an electric field gradient arising from a distortion of the electronic charge cloud whose magnitude is proportional to the applied magnetic field. The same admixture contributes to the terms in C and D , which are essentially second-order effects of the nuclear electric quadrupole interaction, together with (in C) cross terms between the nuclear magnetic dipole and electric quadrupole interactions. In addition, such second-order effects admix the excited Γ_6 states, giving further contributions to C , D ; finally, there is a small contribution to A from such terms which similarly involves admixtures from both the Γ_8 and Γ_6 levels. When allowance is made for this, the following corrected values of A were obtained.

$$^{171}A = +2638.84(5) \text{ MHz}, \quad ^{173}A = -726.91(5) \text{ MHz}.$$

The size of the correction can be seen by comparing these values with those in Table 5.20.

Although the various nuclear parameters in eqn (5.83) were determined from the Endor spectrum as six independent constants, the results were also successfully analyzed by Baker, Blake, and Copland in terms of just the two principal free ion hyperfine parameters (magnetic dipole and electric quadrupole), together with two energy differences, those of the Γ_8 , Γ_6 levels relative to the ground Γ_7 doublet.