MONOGRAFIAS DE FÍSICA

XVIII

PARAMAGNETIC RESONANCE OF TRANSITION METAL IONS

IN CRYSTALS

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Ions in the Free State

Before considering the effect of crystal environments on the energy levels of magnetic ions we shall first review briefly the theory of the energy levels of atoms in the free state. The energy levels of the hydrogen atom are given by the solutions of the wave equation

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$$

where $V = -\frac{e^2}{r}$. The solutions of this equation are of the form

$$\psi(r, \theta, \varphi) = R(r)\, Y_\ell^m(\theta, \varphi)$$

when the functions Y_ℓ^m are spherical harmonics and are proportional to

$$P_\ell^m(\cos\theta)\, e^{im\varphi}$$

where the $P_\ell^m(\cos\theta)$ are Legendre polynomials.

We note, for example, that

$$P_1^0 = \cos\theta$$

$$P_1^{\pm 1} = \sin\theta$$

Each wave function of hydrogen is specified by three quantum numbers n, l, m. The quantum number n determines the energy and

$$E = -\frac{2\pi^2 m e^4}{h^2 n^2}$$

where n = 1, 2, 3, ... The quantum number 1 determines

the total orbital angular momentum and $n \geqslant \ell + 1$ so that $1 = 0, 1, 2, 3, \ldots\ldots$. The quantum number m determines the z component of the orbital angular momentum and

$$m = -\ell, -\ell + 1, \ldots, +\ell$$

States of the hydrogen atom with $\ell = 0, 1, 2, 3$ etc are known as s, p, d, f states etc and a state with $n = 3$ and $\ell = 1$ is designated a 3p state.

There are three degenerate p states with $m = 1, 0, \bar{1}$ and their corresponding angular factors are

$$p_{+1} = \sin\theta \, e^{i\varphi}$$
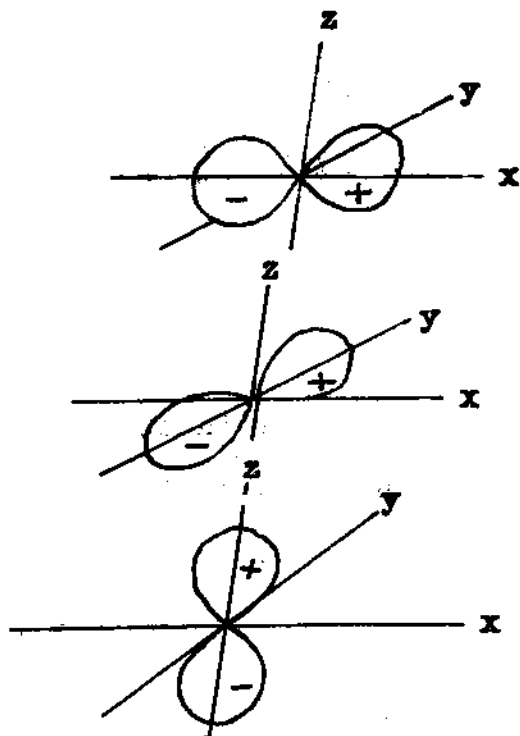$$p_0 = \cos\theta$$
$$p_{-1} = \sin\theta \, e^{-i\varphi}$$

We may generate more useful functions with their maximum amplitudes in the x, y, z directions by taking the linear combinations

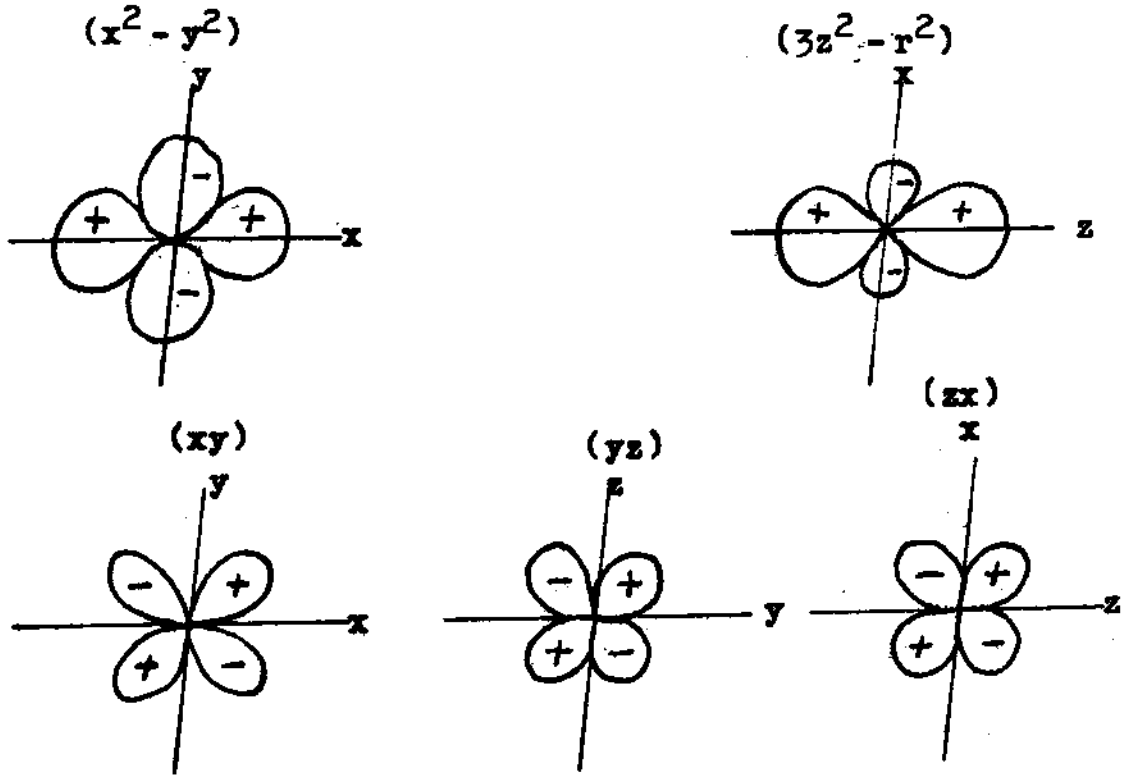$$p_x = p_{+1} + p_{-1} = \sin\theta \, \cos\varphi = x$$

$$p_y = p_{+1} - p_{-1} = \sin\theta \, \sin\varphi = y$$

$$p_z = p_0 = z$$

We have neglected numerical and phase factors in the

above expressions. In a similar fashion we may take linear combinations of d($\ell = 2$) functions giving functions with the angular dependences

$(x^2 - y^2)$ $(3z^2 - r^2)$

(xy)   (yz)   (zx)

If we neglect spin-orbit and spin-spin coupling the Hamiltonian for an atom with many electrons may be written

$$\mathcal{H} = -\frac{h^2}{8\pi^2 m} \sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{r_i} + \sum_{i>j} \frac{e^2}{r_{ij}}$$

Because of the electrostatic interaction between the electrons one cannot separate the variables as in the single electron case and the solution of the wave equation must be obtained by approximate methods.

As a starting point we get the set of one electron eigen functions which are solutions of the wave equation with the

Hamiltonian

$$\mathcal{H}_0 = - \frac{h^2}{8\pi^2 m} \sum_i \nabla_i^2 + \sum_i V(r_i)$$

where $V(r_i)$ is an effective potential for the ith electron. A more exact solution is obtained by adding the perturbation

$$\mathcal{H}' = - \sum_i \frac{Ze^2}{r_i} + \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_i V(r_i)$$

To get the best zero order solution one chooses $V(r_i)$ to make $\mathcal{H}'$ as small as possible. If we are dealing with an e-lectron whose r_i is greater than that of the other electrons, the field of the remaining electrons will approximate a charge $(-Z +1)e$ at the origin so that $V(r_i) = - \frac{e^2}{r_i}$ and the nucleus has been screened by the remaining electrons.

The eigenfunctions of $\mathcal{H}_0$ are called atomic orbitals and are similar to the hydrogen atom eigenfunctions. As before, each orbital is labelled by quantum numbers n, ℓ, m and we have 2s, 2p orbitals etc. In this case however the energy is a function of n and ℓ and 2s and 2p orbitals have different energies.

In most atoms the energies of the orbitals lie in the order

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s ... etc.

The electrons of an atom in its ground state occupy the lowest orbitals without violating the Pauli Exclusion Princi-ple. A state of an atom in which the number of electrons in each orbital is specified is called a configuration. The

normal phosphorus configuration is

$$(1s)^2 \ (2s)^2 \ (2p)^6 \ (3s)^2 \ (3p)^3$$
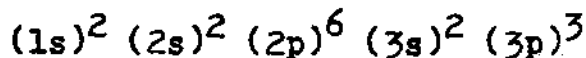
We shall not be interested in closed shells and we shall consider only valence electrons.

Let us consider the configuration p^2. If the electronic interactions are neglected the various eigenfunctions arising from the configuration are degenerate. If we assume Russel-Saunders coupling and designate the total orbital angular momentum L and the total spin angular momentum S we find that the electronic interactions split the configurations into terms denoted by their L and S values, with different energies.

In the case p^2 we have two electrons with $l_1 = 1$ and $l_2 = 1$. Combining these vectorially we get possible L values of 2, 1 and 0 and possible S values of 1, 0.

The resulting S and L values cannot be combined arbitrarily since the exclusion principle must be considered and the only allowed states from the p^2 configuration are ^3P, ^1D and ^1S (the superscript gives the multiplicity, 2s + 1, of the level).

According to Hund's rule the state with maximum S is lowest and, spins being equal, the state with maximum L is lowest. A schematic energy level diagram for the p^2 configuration is given below.

We have also shown in the figure the effect of spin-orbit coupling on the energy levels. The spin-orbit coupling arises

from the interaction between the magnetic dipoles arising from the spin of the electron and its orbital motion.

This interaction, for the case of a single electron, may be written in the form

$$\xi(r)\hat{\mathbf{l}}, \hat{\mathbf{s}}$$

with

$$\xi(r) = \frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{\delta u(r)}{\partial r}$$

where $u(r)$ is the potential in which the electron moves. In an atom with more than one valence electron the spin-orbit interaction may be written

$$\sum_i \xi(r_i)\,\hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i$$

where we have neglected spin-other orbit interactions.

p²   eletrostatic intersection

3 spin-orbit interaction
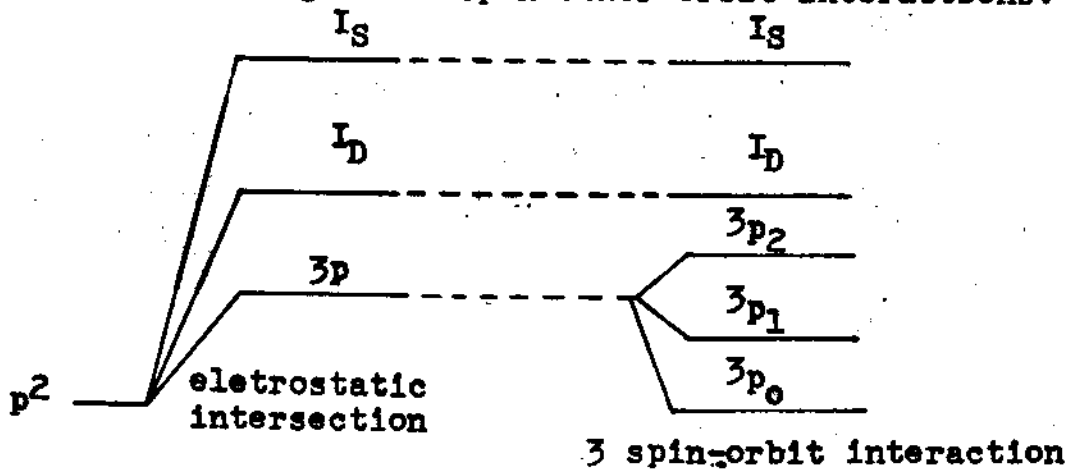
It can be shown that in a many electron system in which the energy levels are characterised by the total value of L and S that the spin-orbit interaction may be written

$$\lambda\hat{L} \cdot \hat{S}$$

where λ is a radial integral depending only on L and S. Keeping then within a system of levels specified by L and S we note that

$$\hat{J} = \hat{L} + \hat{S}$$

and

$$\hat{J}^2 = \hat{L}^2 + \hat{L}^2 + 2\hat{L}\cdot\hat{S} \qquad \text{so that}$$
$$\hat{L}\cdot\hat{S} = \tfrac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

and we find that

$$E(L,S,J) = E(L,S) + \frac{\lambda}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

The energy difference between the level J and J-1 is

$$\Delta E = E(L,S,J) - E(L,S,J-1) = \lambda J$$

and this is Lande's interval rule.

Ions in Crystals

The energy levels of a free ion are perturbed   by   a crystalline environment and an investigation of   experimental data shows that the strengths of the   crystalline   electric fields fall into three categories:

a) Strong field case in which the electrostatic   interaction between the electrons on the central ion and the   electrons on the neighbours (ligands) is greater that   the   electrostatic interactions between the electrons   on   the central ion. This situation occurs with strongly   covalent systems e.g. salts of the 4d and 5d transition groups.

b) Medium field case in which the electrostatic interaction between electrons on the central ion and the field of ligands (henceforth referred to as the crystal field) is less than the electrostatic interactions between electrons on the central ion but greater than the effects of spin-orbit coupling in the central ion. This situation is typified by iron group (3d) ions.

c) Weak field case in which the effect of the crystal field is less than the spin-orbit coupling. This situation is typified by rare earth (4f) ions.

We shall confine ourselves to cases (b) and (c) since most work has been done on these systems and we shall first discuss the crystal field method for dealing with the effects of a lattice environment on the energy levels of a transition group ion. We shall discuss an alternative method, the molecular orbital method, at a later time.

Crystal Field Theory

An outline of the crystal field approximation may be obtained by considering the configuration $3d^1$ (Ti^{3+}). The single d electron may occupy any of the 5 orbitals which have equal energy in the free ion. If negative charges are now placed at $\pm x$, $\pm y$ and $\pm z$ the five fold degeneracy is raised and we get a $d\varepsilon(t_{2g})$ triplet lower and a $d\gamma(eg)$ doublet higher

in energy. This situation occurs when iron group ions are placed in regular octahedral crystalline environments. We can give a crude qualitative explanation of the splitting of the d orbitals by noting that an electron in $d\gamma(|x^2 - y^2 \rangle, |3z^2 - r^2 \rangle)$ orbitals, which point directly at the ligands, is expected to have a greater electrostatic interaction with the ligands than an electron in $d\varepsilon$ orbitals $(|xy\rangle, |yz\rangle, |zx\rangle)$ which point between the ligands. Pursuing this viewpoint we consider the case $3d^9(Cu^{2+})$ which may be treated as a single hole in an otherwise filled shell; this will find its lowest energy in the $d\gamma$ doublet. The separation between the $d\gamma$ orbital doublet and the $d\varepsilon$ orbital triplet is called $10Dq$ and is about $10,000$ cm^{-1} for divalent iron group ions and about $18,000$ cm^{-1} for trivalent iron group ions.

The sign of the splitting of the d-orbitals produced by eight charges at the corners of a cube is opposite to that produced by six charges at the vertices of an octahedron because the $d\varepsilon$ orbitals are more closely directed towards the charges at the corners of the cube. We also see that on this model the threefold degeneracy of a p orbital is maintained in a cubic environment.

We shall make our discussion more quantitative by considering an iron group ion at the centre of a regular octahedron of six charges. Since we have already described our d wavefunctions in terms of spherical harmonics we shall expand the potential at the central ion in spherical harmonics about

the central ion as origin. We assume in making this expansion
that the d-orbitals do not overlap the ligand charges and hence
that the potential due to the ligand charges is a solution of
Laplaces equation

$$\nabla^2 V = 0$$

We may write for the potential at a point (r, θ, φ)

$$V(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} A_l^m \, r^l \, Y_l^m (\theta, \varphi)$$

where the A_l^m are constants determined by the surrounding charge
distribution and the Y_l^m are normalised spherical   harmonics
defined as

$$Y_l^m(\theta, \varphi) = (-1)^l \left[\frac{1}{4\pi} \cdot \frac{(2l+1)(l-|m|)!}{(l+|m|!)} \right] P_l^m(\cos\theta) \, e^{im\varphi}$$

The Hamiltonian corresponding to this potential is

$$\mathcal{H} = e \sum_j V(r_j, \theta_j, \varphi_j) = l \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} A_l^m \sum_j r_j \, Y_l^m (\theta_j, \varphi_j)$$

where $(r_j, \theta_j, \varphi_j)$ are the coordinates of the jth electron on
the central ion and $\sum_j$ covers the valence electrons.   Only a
limited number of terms in the expansion of V need   to   be
considered. The term with $l = 0$ is spherically symmetric   and
is responsible for the greater part of the lattice energy,   or
heat of solution of the cation. This term is of no interest to
us since, to a first approximation, it gives rise to a uniform
shift of all levels with the same number of electrons.

Consider next the integral $\int \varphi^* U \psi \, d\tau$ where φ and ψ are

d wavefunctions. The density $\varphi^* \psi$ can be expanded in spherical harmonics and does not contain harmonics with $l > 4$. If $\mathcal{U}$ is a spherical harmonic with $l > 4$ the integral vanishes by the orthogonality relationship for spherical harmonics. If φ and ψ are $f(l = 3)$ wavefunctions the integral vanishes when $l > 6$. It is also apparent that terms in the expansion of V with odd are odd and need not be considered because under inversion of the co-ordinates for these terms $\int \varphi^* U \psi \, d\tau = 0$ since φ and ψ have the same parity.

We can reduce the number of terms that need to be considered still further by realising that the potential must reflect the symmetry of the ligand configuration. Let us consider a regular octahedron with the z axis (tetragonal axis) as polar axis. The potential at (r, θ, φ) is the same as at $(r, \theta, \varphi + \frac{\pi}{2})$ and since the φ dependence is of the form $e^{im\varphi}$, m can only have the values 0 or $\pm 4 (|m| \leqslant l)$. It is now apparent that for d electrons at the centre of a regular octahedron the potential V takes the form

$$V = a \, Y_4^0 (\theta, \varphi) + b \left[Y_4^4(\theta, \varphi) + Y_4^{-4}(\theta, \varphi) \right]$$

By considering other symmetry operations of the octahedron which leave V invariant we find that

$$V = A_4^0 \, r^4 \left[Y_4^0(\theta, \varphi) + \sqrt{\frac{5}{14}} \left\{ Y_4^4(\theta, \varphi) + Y_4^{-4}(\theta, \varphi) \right\} \right]$$

or

$$V = D(x^4 + y^4 + z^4 - \frac{3}{5} r^4)$$

in Carthesion coordinates. The quantity D is readily calculated from the surrounding charge distribution and is found to be $D = \frac{35}{4} \frac{Ze}{R^5}$ for a regular octahedron, where Ze is the charge on each surrounding ion and R is the cation-anion distance.

For a single d electron at the centre of a regular octahedron the two different groups of d-orbitals have the energies

$$E_{d\epsilon} = e \int (d_{xy})^2 \, V \, r^2 \, \sin\theta \, d\theta \, dr \, d\varphi = -4 \, Dq$$

$$E_{d\gamma} = e \int (d_{x^2-y^2})^2 \, Vr^2 \, \sin\theta \, dr \, d\theta \, d\varphi = +6 \, Dq$$

where $q = \dfrac{2\langle r^4 \rangle e}{105}$. In general, we define

$$\langle r^l \rangle = \int \left[f(r) \right]^2 \, r^l \, r^2 \, dr$$

where $\langle r^l \rangle$ is the overage value of r^l over the d orbital. The integrals over the angles are separable from the radial integrals and give the numbers -4 and +6. Calculations of Dq on a crystal field model are in very poor agreement with experiment.

It should be emphasised that the appearance of the expression for V depends on the choice of the polar axis. For example, if we choose a trigonal axis of the octahedron as our polar axis the expression for the potential will have the form

$$V = a \, Y_4^0 + b(Y_4^3 + Y_4^{-3}) \ .$$

Although this expression looks different from that already derived using a tetragonal axis as polar axis, they are, of

course identical.

If the symmetry of the octahedron is less than cubic additional terms are introduced into the expression for V. If we have a distortion of the octahedron which is axial about the tetragonal axis then terms in Y_2^0 and Y_4^0 are added to V. If the symmetry is orthorhombic then terms in Y_2^2 and Y_4^2 are introduced.

Matrix Elements of Crystal Field Operators

In general the easiest method of finding the matrix elements of crystal field operators is to use the operator equivalent method developed by Stevens and others. They have shown that, with certain symmetry restrictions, the matrix elements of a crystal field operator are proportional to the matrix elements of a similar operator in which x, y and z are replaced by L_x, L_y and L_z. It must be remembered that L_x, L_y and L_z do not commute so that

$$\sum_{\text{electrons}} x\,y \; \alpha \; (L_x\,L_y + L_y\,L_x)$$

The equivalent operator for the cubic crystal field operator

$$D_e \sum_{\text{electrons}} (x^4 + y^4 + z^4 - \frac{3}{5} r^4)$$

$$D_e\,\beta \langle r^4 \rangle \frac{1}{20} \left\{ 35\,L_z^{\,4} - 30L(L+1)\,L_z^{\,2} + 25\,L_z^{\,2} - 6\,L(L+1) \right.$$

$$\left. + 3L^2(L+1)^2 \right\} + D_e\,\beta \langle r^4 \rangle \frac{1}{8} \left\{ L_+^4 + L_-^4 \right\}$$

The proportionality factor β has been given by Stevens. Tables of matrix elements of equivalent operators have been given by various authors and are collected in a booklet available at the Clarendon Laboratory.

Matrix elements of the cubic crystal field operator for d electrons within an $L = 3$ manifold (e.g. $Ni^{2+}, {}^3F$).

Dq X	3	-1	-3	1	2	-2	0
3	3	$\sqrt{15}$					
-1	$\sqrt{15}$	1					
-3			3	$\sqrt{15}$			
1			$\sqrt{15}$	1			
2					-7	5	
-2					5	-7	
0							6

The matrix elements for the promotion and demotion operators $L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$ are

$$L_+|L, L_z\rangle = \left\{ L(L+1) - L_z(L_z+1) \right\}^{\frac{1}{2}} |L, L_z+1\rangle$$

$$L_-|L, L_z\rangle = \left\{ L(L+1) - L_z(L_z-1) \right\}^{\frac{1}{2}} |L, L_z-1\rangle$$

and it is apparent that the operators L_+^4, L_-^4 will connect the states $|L, L_z\rangle$ and $L, L_z \pm 4\rangle$.

Let us consider the effect of a cubic crystalline environment on the ${}^3F$ ground state of the Ni^{2+} ion. We neglect

spin-orbit coupling and from published tables write down the matrix elements $\langle 3, L_z|V|3, L_z'\rangle$. To determine the eigenvalues and eigenfunctions for this system is a trivial problem and they are given below with $|\rangle = |L_z\rangle$.

$$\Gamma_4 \left(^4T_{1g}\right)\begin{array}{l} \sqrt{\tfrac{3}{8}}\,|-1\rangle + \sqrt{\tfrac{5}{8}}\,|3\rangle \\[2mm] \sqrt{\tfrac{3}{8}}\,|1\rangle + \sqrt{\tfrac{5}{8}}\,|-3\rangle \\[2mm] |0\rangle \end{array} \right\} \qquad 6\ Dq$$

$$\Gamma_5 \left(^4T_{2g}\right)\begin{array}{l} \sqrt{\tfrac{5}{8}}\,|-1\rangle - \sqrt{\tfrac{3}{8}}\,|3\rangle \\[2mm] \sqrt{\tfrac{5}{8}}\,|1\rangle - \sqrt{\tfrac{3}{8}}\,|-3\rangle \\[2mm] \sqrt{\tfrac{1}{2}}\left[|2\rangle + |-2\rangle\right] \end{array} \right\} \qquad -2\ Dq$$

$$\Gamma_2 \left(^4A_{2g}\right)\sqrt{\tfrac{1}{2}}\left[|2\rangle - |-2\rangle\right] \qquad\qquad -12\ Dq \ .$$

Since Dq is positive for Ni^{2+} we are left with an orbital singlet ground state and we have here an example of "quenching" of orbital angular momentum in a crystalline environment. Since $Dq \simeq 10{,}000\ cm^{-1}$ only the ground state is populated and if we neglect spin-orbital coupling we have "spin only" magnetism.

Crystal field calculations for rare earth ions go through in the same way as for iron group ions except that we now operate on eigenstates $|J, J_z\rangle$ instead of $|L, L_z\rangle$ and the nomenclature adopted is somewhat different. The crystal field operator for a cubic environment is

$$V = B_4^0\, O_4^0 + B_4^4\, O_4^4 + B_6^0\, O_6^0 + B_4^4\, O_6^4$$

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

where B_4 and B_6 are general 4th order and 6th order parameters. The simple numerical relationships given above between B_4^0 and B_4^4 and B_6^4 hold only for a regular cubic environment. The term in B_6 is not considered for d electrons and the operator $B_4(O_4^0 + 5O_4^4)$ is identical with the cubic crystal field operator already given for d-electrons, although different in form. In terms of equivalent operators we find

$$O_4^0 = 35\, J_z^4 - \left\{30\, J(J+1) - 25\right\} J_z^2 - 6\, J(J+1) + 3\, J^2(J+1)^2$$

$$O_4^4 = \tfrac{1}{2}(J_+^4 + J_-^4)$$

$$O_6^0 = 23\, (J_z^6 - 105\left\{3J(J+1)-7\right\}J_z^4 + \left\{105\, J^2(J+1)^2\right.$$

$$- 525\, J(J+1) + 294\} J_z^2$$

$$- 5\, J^3(J+1)^3 + 40\, J^2(J+1)^2 - 60\, J(J+1)$$

$$O_6^4 = \tfrac{1}{4}\left\{(11\, J_z^2 - J(J+1) - 38)(J_+^4 + J_-^4)\right.$$

$$+ (J_+^4 + J_-^4)(11\, J_z^2 - J(J+1) - 38)\}$$

Let us consider the case Tm^{2+} ($4f^{13}$, $J = \tfrac{7}{2}$) in a cubic

Matrix elements of the cubic crystal field operator within a $J = \frac{7}{2}$ manifold (Tm^{2+})

$J_z =$

	$\frac{7}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{5}{2}$	$-\frac{7}{2}$
$\frac{7}{2}$	$420B_4^0+1260B_6^0$				$12\sqrt{35}B_4^4+180\sqrt{55}B_6^4$			
$\frac{5}{2}$		$-780B_4^0-6300B_6^0$				$60\sqrt{3}B_4^4-420\sqrt{3}B_6^4$		
$\frac{3}{2}$			$-180B_4^0+1134B_6^0$				$12\sqrt{35}B_4^4+180\sqrt{55}B_6^4$	
$\frac{1}{2}$				$540B_4^0-6300B_6^0$				$60\sqrt{3}B_4^4-420\sqrt{3}B_6^4$
$-\frac{1}{2}$	$12\sqrt{35}B_4^4+180\sqrt{55}B_6^4$				$540B_4^0-6300B_6^0$			
$-\frac{3}{2}$		$60\sqrt{3}B_4^4-420\sqrt{3}B_6^4$				$-180B_4^0+1134B_6^0$		
$-\frac{5}{2}$			$12\sqrt{35}B_4^4+180\sqrt{55}B_6^4$				$-780B_4^0-6300B_6^0$	
$-\frac{7}{2}$				$60\sqrt{3}B_4^4-420\sqrt{3}B_6^4$				$420B_4^0+1260B_6^0$

lattice. From published work we can immediately write down the matrix elements of the cubic crystal field operators within the $J = \frac{7}{2}$ manifold. We shall for convenience write $b_4^0 = 60\ B_4^0$ and $b_6^0 = 1260\ B_6^0$ and we find the eigenvalues and eigenvectors to be

$$\Gamma_7 \quad \sqrt{\tfrac{3}{2}}\ |J_z = \pm \tfrac{5}{2}\rangle - \tfrac{1}{2}\ |J_z = \mp \tfrac{3}{2}\rangle \qquad -18\ b_4^0 - 12\ b_6^0$$

$$\Gamma_8 \quad \left. \begin{array}{l} \sqrt{\tfrac{7}{12}}\ |J_z = \pm \tfrac{7}{2}\rangle - \sqrt{\tfrac{5}{12}}\ |J_z = \mp \tfrac{1}{2}\rangle \\[2mm] \tfrac{1}{2}|J_z = \pm \tfrac{5}{2}\rangle + \sqrt{\tfrac{3}{2}}|\ J_z = \mp \tfrac{3}{2}\rangle \end{array} \right\} \quad 2\ b_4^0 + 16\ b_6^0$$

$$\Gamma_6 \quad \sqrt{\tfrac{5}{12}}\ |J_z = \pm \tfrac{7}{2}\rangle + \sqrt{\tfrac{7}{12}}\ |J_z = \mp \tfrac{1}{2}\rangle \qquad 14\ b_4^0 - 20\ b_6^0$$

The ground state of Tm^{2+} in the cubic field of $Ca\ F_2$ is Γ_7 and at room temperature and below this is the only level that is appreciably populated. For a general discussion of the energy levels of rare earth ions in cubic fields see Lea, Leask and Wolf, J. Phys. Chem. Solids 23, 1381, 1962.

Ligand Field Theory

The crystal field theory regards cations and anions in solids as being held together by purely ionic forces and neglects overlap of the wavefunctions of the central and ligand ions. The ligand field theory includes this overlap and now the structural unit for the wavefunction is a complex molecule rather than a single central atom. In order to construct suitable wavefunctions

we use the linear combination of atomic orbitals (LCAO) method but we shall first make a few remarks about bond types.

Let us consider two atoms P and Q separated by a distance d. We define an overlap integral

$$S = \int \psi_p^* \psi_Q \, d\tau$$

and S will depend on d. In the "principle of maximum overlapping" we assume a relationship between S and the bond strength. The value of S will increase with decreasing d but the electronic and nuclear repulsion energies also increase giving rise to an equilibrium bond distance. The bond types which can be formed between s and p orbitals on atoms P and Q are illustrated bellow. We shall call the line joining nuclei P and Q the z axis.
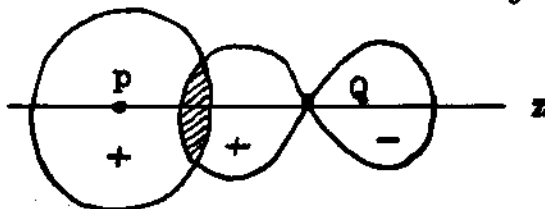
σ- bond between S orbital on P and p_z orbital on Q.
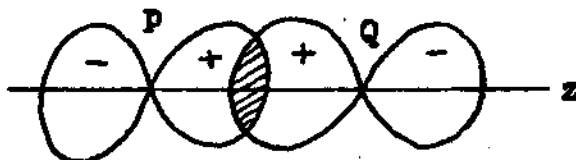
σ- bond between p_z orbital on P and p_z orbital on Q.
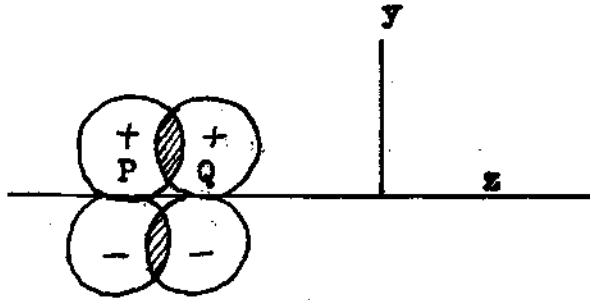
π - bond between p_y orbital on P and p_y orbital on Q.

We note that σ bonds are cylindrically symmetrical about the bond axis; π bonds are not and have a nodal (xz) plane.

If we assume that the atoms P and Q are identical and we bring them together to form a homonuclear molecule then with identical atomic orbitals ψ_P and ψ_Q we can form the linear combinations

$$\varphi_b = \psi_P + \psi_Q$$

$$\varphi_a = \psi_P - \psi_Q$$

where φ_b is a bonding molecular orbital constructed so that ψ_P and ψ_Q have the same sign in the region of overlap and φ_a is an antibonding orbital constructed so that ψ_P and ψ_Q have opposite signs in the region of overlap. The energy of an electron in the bonding orbital is given by

$$E = \frac{\alpha + \gamma}{1 + S}$$

where

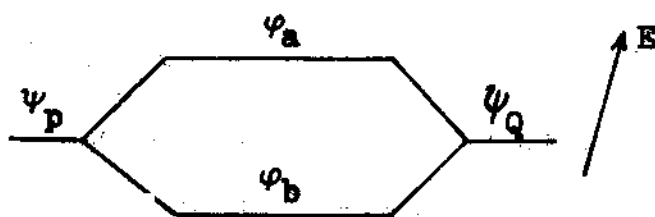$$\alpha = \int \psi_P^* \mathcal{H} \psi_P \, d\tau$$

and

$$\gamma = \int \psi_P^* \mathcal{H} \psi_Q \, d\tau$$

and S has already been defined.

The energy of an electron in the antibonding orbital is

$$E' = \frac{\alpha - \gamma}{1 - S}$$

and is, by definition, higher than E. The formation of bonding and antibonding orbitals is illustrated below.

In a molecule the most firmly bound electrons occur in the bonding levels.

Let us next consider a d-orbital in an octahedral crystal environment with e.g. F^- ions at the apices of the octahedron. The bonding orbitals on the fluorine ions will be 2s and 2p. The linear combinations of ligand orbitals which one can combine with the central ion orbitals are determined by the symmetry of the environment and the combinations of d-orbitals and 2p orbitals in a regular octahedral environment are given below. In our notation the ligands numbered 1, 2, 3 and 4, 5, 6 are on the positive and negative x, y, z axes. Linear combinations of the fluorine 2s orbitals similar to those of the $2p_z$ orbitals will also form σ bonds with the $d\gamma$ doublet.

Central atom orbitals		Ligand orbitals
$d\gamma$ σ-bonding	$\left\{ \begin{array}{l} d_{x^2-y^2} \\ \\ d_{3z^2-r^2} \end{array} \right.$	$\frac{1}{2}(p_z^1 - p_z^2 + p_z^4 - p_z^5)$ $\frac{1}{\sqrt{12}}(2p_z^3 + 2p_z^6 - p_z^1 - p_z^2 - p_z^4 - p_z^5)$
$d\varepsilon$ π-bonding	$\left\{ \begin{array}{l} d_{xy} \\ \\ d_{yz} \\ \\ d_{zx} \end{array} \right.$	$\frac{1}{2}(p_x^1 + p_y^2 - p_x^5 - p_y^4)$ $\frac{1}{2}(p_x^2 + p_y^3 - p_x^6 - p_y^5)$ $\frac{1}{2}(p_x^3 + p_y' - p_x^4 - p_y^6)$

With these sets of orbitals we can form bonding and antebonding combinations. The bonding combinations in weakly covalent systems are primarily ligand orbitals with a small admixture of central ion orbitals; the antibonding orbitals are primarily central ion d orbitals with small admixtures of ligand orbitals. With iron group ions the magnetic d^n electrons occur in the antibonding $d\gamma$ and $d\varepsilon$ levels and the separation of these levels is still called 10 Dq. To calculate 10 Dq on a molecular orbital model we must know the size of the admixtures of the ligand orbitals and we shall show later how these admixtures may be determined experimentally by magnetic resonance techniques.

The Hamiltonian for an octahedral molecular systems is a complex one but nevertheless a value of 10 Dq in good agreement with experiment has recently been calculated for Ni^{2+} in K Mg F_3 using molecular orbital wavefunctions.

The presence of bonding has two main effects. (a) it changes the $d\gamma$ - $d\varepsilon$ splitting (10 Dq) and is equivalent to a

change in the strength of the crystal field. (b) the magnetic
(d) electrons are partly delocalised.

If the bonding is very strong and Dq is very large the $d\gamma$
levels may not be occupied and Hund's rule will not apply e.g.
$(d\epsilon)^5$ with $S = \frac{1}{2}$ may be lower in energy than $d\epsilon^3 d\gamma^2$ with $S =$
$= \frac{5}{2}$; this situation occurs with $K_3 Fe (CN)_6$ and in complexes
of the 4d and 5d groups

The effect (b) is clearly evident in the resolved hyper-
fine interactions of the magnetic d electrons with the nuclei
of the ligand ions; this effect will be described in more detail
later. Effect (b) also leads to a reduction of the coulomb
interactions $\sum_{i > j} \frac{e^2}{r_{ij}}$ between the d electrons and hence to a
contraction of the spacing of the levels of the d^n configurations.
Other observable effects of (b) are a reduction of the spin-
orbit coupling constant λ and the matrix elements of the orbital
angular momentum.

The Calculation of g-factors in Electron Spin Resonance Spectra

The Hamiltonian for the Zeeman interaction is

$$\mathcal{H} = \beta \hat{H} \cdot \sum_i (\hat{l}_i + 2\hat{s}_i) = \beta \hat{H} \cdot (\hat{L} + 2\hat{s})$$

Here β is the Bohr magneton and the factor 2 appears within the
bracket because of the anomalous magnetic moment of the e-

lectronic spin. In a cubic crystalline environment the separation between neighbouring components of a Zeeman multiplet may be expressed in the form

$$h\nu = g\beta H$$

where g is called the spectroscopic splitting factor. For free ions g becomes the Landé g-factor and may be written

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

when Russel-Saunders coupling holds. The g-value for an ion in a crystalline environment is generally considerably different from g_J. Let us consider the Ni^{2+} ion in a regular octahedral environment. We have already shown that the orbital contribution to the ground state, neglecting spin-orbit coupling, is

$$|L_z\rangle = \frac{1}{\sqrt{2}}\left[|2\rangle - |-2\rangle\right]$$

We now include the spin S = 1 and writing the ground state in the form $|L_z\rangle |S_z\rangle$ we obtain the threefold degenerate state

$$\psi_1 = |L_z\rangle|1\rangle$$
$$\psi_2 = |L_z\rangle|0\rangle$$
$$\psi_3 = |L_z\rangle|-1\rangle$$

By evaluating $L_z + 2S_z$ we get

$$\langle\psi_1|\hat{L}_z + 2\hat{S}_z|\psi_1\rangle = 2$$
$$\langle\psi_2|\hat{L}_z + 2\hat{S}_z|\psi_2\rangle = 0$$
$$\langle\psi_3|\hat{L}_z + 2\hat{S}_z|\psi_3\rangle = -2.$$

The only good quantum number here is

$$m = L_z + S_z$$

and the magnetic dipole transitions which we observe in paramagnetic resonance have the selection rule $\Delta m = \pm 1$. In the case of Ni^{2+} we therefore observe magnetic dipole transitions between $\psi_1 \longleftrightarrow \psi_2$ and $\psi_2 \longleftrightarrow \psi_3$ and the g factor is 2 in this approximation. The energy level diagram is shown below and it is apparent
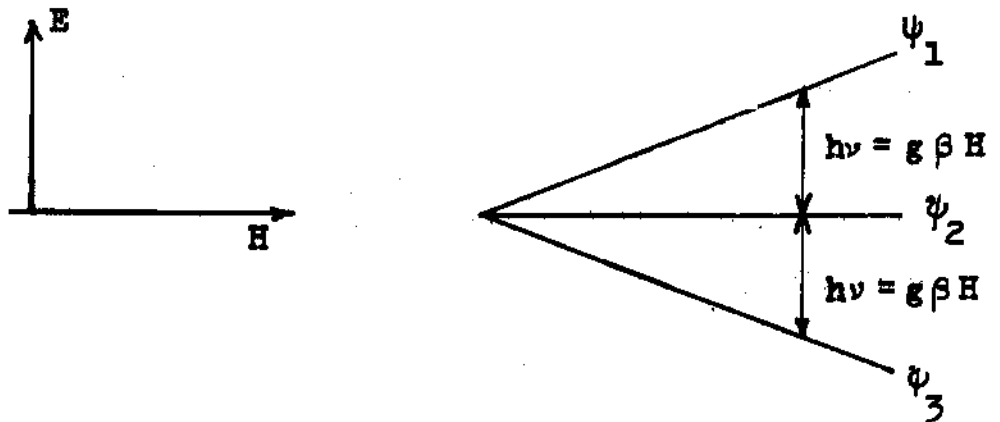
that the two allowed transitions $\psi_1 \longleftrightarrow \psi_2$ and $\psi_2 \longleftrightarrow \psi_3$ are coincident.

When we include the spin-orbit coupling in our calculations we find that the first excited orbital triplet Γ_5 is mixed into the ground state Γ_2. To calculate this admixture we require the matrix elements of the operator $\lambda \hat{L} \cdot \hat{S} = \lambda \left[\hat{L}_z \hat{S}_z + \frac{1}{2} (\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+) \right]$ between the two states. When we include this admixture we find that the g-value now becomes

$$g = 2 - \frac{8\lambda}{10Dq}$$

where 10 Dq is the separation of Γ_5 and Γ_2. From the paramagnetic resonance spectrum of $Ni(H_2O)_6^{2+}$ we get $g = 2.25$. If we take the value of $\lambda = 324\ cm^{-1}$ obtained from the free ion

spectrum of Ni^{2+} and the value 10 Dq = 8500 cm^{-1} measured optically for Ni $(H_2O)_6^{2+}$ we calculate g = 2.29. This discrepancy may be surmounted for if we remember that the magnetic electrons are not completely localised in d orbitals but spend part of the time in ligand orbitals. The $3d^8$ Ni^{2+} electrons are spread over the crystal field states in the form $d\varepsilon^6$ $d\gamma^2$ and in magnetic resonance experiments we observe the two unpaired $d\gamma$ electrons. If we write the antibonding $d\gamma$ molecular orbitals in the form

$$\alpha\, d\gamma - \sqrt{1-\alpha^2} \text{ (ligand combinations)}$$

we can show that the expression for the g value of Ni^{2+} becomes approximately

$$g = 2 - \frac{8\alpha^2\lambda}{10Dq}$$

and we get agreement with our measured g-value by making $\alpha \approx 0.9$. Our measured g-value therefore indicates that the antibonding $d\gamma$ orbitals are composed mainly of metal ion 3d wavefunctions.

The g factors of other iron group ions may differ considerably from two. The ground state of $Fe^{2+}(d^6, {}^5D)$ in a regular octahedral environment is a degenerate triplet and the wavefunctions in terms of $|L_z, S_z\rangle$ are, to zero order in $\frac{\lambda}{10Dq}$,

$$\sqrt{\tfrac{3}{20}}\left[|2,1\rangle + |-2,1\rangle + 2|1,2\rangle\right] + \sqrt{\tfrac{1}{10}}\,|-1,0\rangle$$

$$\sqrt{\tfrac{3}{10}}\left[|-1,1\rangle + |1,1\rangle\right] + \sqrt{\tfrac{1}{5}}\left[|-2,0\rangle + |2,0\rangle\right]$$

$$\sqrt{\tfrac{3}{20}}\left[|-2,-1\rangle + |2,-1\rangle + 2|-1,-2\rangle\right] + \sqrt{\tfrac{1}{10}}\,|1,0\rangle$$

Operating within this triplet, as in the case of Ni^{2+},

with the operator $\hat{L}_z + 2\hat{S}_z$ we find

$$g = g_L + g_S = \frac{1}{2} + 3 = 3.5$$

The measured g-value of Fe^{2+} in the octahedral cubic environment of MgO is 3.428 and in NaF is 3.420. To get exact agreement between the measured and calculated g-values we must include admixtures of excited states into the ground state through the spin-orbit coupling, as in the case of Ni^{2+}, and make allowance for the fact that the orbital angular momentum does not make its full contribution to the g-value. This latter effect again arises from the delocalisation of the 3d magnetic electrons and we define an orbital reduction factor k by the relationship

$$\langle \varphi | L | \varphi \rangle = k \langle d | L | d \rangle$$

where the wavefunctions φ are antibonding molecular orbitals constructed from the d wavefunctions and ligand orbitals. We find that $k \simeq 0.9$ for iron group ions in crystals. The value of k decreases with increasing covalency.

As a further example of a considerable deviation of a g-value from 2 we consider the case of $Co^{2+}(d^7, {}^4F)$ in a regular octahedral environment. The ground state wavefunctions in terms of $|L_z, S_z\rangle$ are, to zero order in $\frac{\lambda}{10Dq}$

$$\sqrt{\tfrac{3}{16}} \left| -1, \tfrac{3}{2} \right\rangle + \sqrt{\tfrac{5}{16}} \left| 3, \tfrac{3}{2} \right\rangle + \sqrt{\tfrac{1}{16}} \left| 1, -\tfrac{1}{2} \right\rangle + \sqrt{\tfrac{5}{48}} \left| -3, -\tfrac{1}{2} \right\rangle - \sqrt{\tfrac{1}{3}} \left| 0, \tfrac{1}{2} \right\rangle$$

$$\sqrt{\tfrac{3}{16}} \left| +1, -\tfrac{3}{2} \right\rangle + \sqrt{\tfrac{5}{16}} \left| -3, -\tfrac{3}{2} \right\rangle + \sqrt{\tfrac{1}{16}} \left| -1, \tfrac{1}{2} \right\rangle + \sqrt{\tfrac{5}{48}} \left| 3, \tfrac{1}{2} \right\rangle - \sqrt{\tfrac{1}{3}} \left| 0, -\tfrac{1}{2} \right\rangle$$

The calculated g-value is

$$g = g_L + g_S = 1 + \frac{10}{3} = 4.33$$

The measured g-value of Co^{2+} in the cubic octahedral environment of MgO is 4.278 and in NaF is 4.391. Again, the differences between the measured and calculated g-values is due to neglect of orbital reduction and spin orbit coupling.

It should be pointed out that if the Co^{2+} ion is placed at the centre of a regular tetrahedron of charges or a regular cube of eight charges the order of the splitting of the F state is opposite to that found with an octahedron. We now have a situation analogous to that of Ni^{2+} in an octahedron with the Γ_2 orbital singlet lowest. To zero order in $\frac{\lambda}{10Dq}$ the orbital angular momentum will not contribute to the g-value and we expect a g-value of 2. Inclusion of the spin orbit coupling will change the g-value to $g = 2 - \frac{8\lambda}{10Dq} \simeq 2.3$.

When dealing with rare earth ions we are operating within $|L,S,J,J_z\rangle$ states. When calculating the g-values of rare earth ions we again require the matrix elements of $\hat{L}_z + 2\hat{S}_z$. Now

$$\hat{J}_z = \hat{L}_z + \hat{S}_z$$

so that

$$\hat{L}_z + 2\hat{S}_z = \hat{J}_z + \hat{S}_z$$

Now

$$\langle L,S,J,J_z|\hat{J}_z|L,S,J,J_z\rangle = J_z$$

and

$$\langle L,S,J,J_z|\hat{S}_z|L,S,J,J_z\rangle$$

$$= \frac{J_z}{J(J+1)}\langle L,S,J,J_z|\hat{S}\cdot\hat{J}|L,S,J,J_z\rangle$$

$$= \frac{J_z}{J(J+1)} \cdot \frac{1}{2} \left[J(J+1) - L(L+1) + S(S+1) \right]$$

so that

$$\langle L,S,J,J_z | \hat{J}_z + \hat{S}_z | L,S,J,J_z \rangle$$

$$= g_J J_z \; .$$

where g_J is the Lande g-factor.

We have already mentioned that the ground state of Im^{2+} in CaF_2 in terms of $|J_z\rangle$ is

$$\sqrt{\frac{3}{2}} \left| \pm \frac{5}{2} \right\rangle - \frac{1}{2} \left| \mp \frac{3}{2} \right\rangle$$

The g_J value for Im^{2+} is $\frac{8}{7}$ and the g-value is therefore $3 \times \frac{8}{7} = 3.42$. The measured g-value for Im^{2+} in CaF_2 is 3.45. The small discrepancy is due to admixture of an excited state into the ground state by the crystal field and a small orbital reduction factor (k = 0.99). The 4f orbit is screened by the filled 5S and 5p shells and the 4f electrons do not bond strongly so that k is very close to unity.

Observation of Excited Crystal Field States

We can observe paramagnetic resonance only in the crystal field ground state or in states within at most a few hundred wavenumbers of the ground state. To give a detailed interpretation of ESR spectra in these states it is usually necessary to know the positions of more excited crystal field states. We have seen, for example, in the case of Ni^{2+} that the g-value is

affected by the position of the excited Γ_5 triplet which occurs at 8500 cm^{-1} above the ground state. It is possible to observe these excited crystal field states by carrying out absorption measurements in the infra red and visible spectral regions.

An electric dipole transition occurs between the states a and b if the integral $\int \psi_a^* \, \hat{r} \, \psi_b \, d\tau$ is not zero. If ψ_a and ψ_b are both even or both odd then $\int \psi_a^* \, \hat{r} \, \psi_b \, d\tau$ is odd since $\hat{r}$ is odd and the integral must vanish. Electric dipole transitions can only occur between even and odd states. An atomic wavefunction is even or odd as $\sum_i \ell_i$ is even or odd and all states which arise from the same configuration have the same parity. The selection rule for a one electron transition is

$$\Delta \ell = \pm 1$$

and for a two electron transition is

$$\Delta \ell_1 = \pm 1, \quad \Delta \ell_2 = 0, \pm 2.$$

To the extent that we neglect spin in the Hamiltonian operator the spin and co-ordinate wavefunctions are separable and the dipole integral will vanish because of the orthogonality of the spin functions unless the spin is the same in the initial and final states; we therefore have the selection rule

$$\Delta S = 0$$

Electric dipole transitions within the levels of a configuration d^n are forbidden by parity and there may be spin restrictions.

Allowed electric dipole transitions have an oscillator strenght (f-value) of the order of unity. The transition observed between the crystal field states of 3d ions are "forbidden"

electric dipole transitions with f-values of the order of 10^{-4}.
These transitions occur by the mixing in of orbitals of op-
posite parity into the levels of the $3 d^n$ configurations by

(a)   absence of a centre of symmetry in the crystal field
and

(b)   destruction of a centre of symmetry by vibrations.

A regular tetrahedron of charges does not have a centre of
symmetry and a term with the angular dependence x y z occurs in
the expansion of the crystal field; this can admix states with
the angular dependence xy (e.g. dϵ orbitals) and z (e.g. p_z
orbitals) and the perturbed d wavefunctions become

$$\psi'(d) = \psi^o(d) + \sum_r \frac{\langle \psi^o(d)|v|\psi^o(r)\rangle}{E^o_r - E^o_d} \psi^o(r)$$

where $\psi^o(r)$ are excited p states on the central ion having odd
parity.

If an electric dipole transition between d^n crystal field
states is allowed by vibrations the intensity will fall with
temperature until a temperature is reached at which only the
ground vibrational states are populated. In the case of
$K Cr(SO_4)_2 \cdot 12 H_2O$ the f value was found to vary as

$$f = f_o(1 - \exp^{\theta/T})$$

where $\theta = 277$ cm^{-1}. Variations of 50% in f may be observed in
some systems in going from 300° K to 80° K. Values of 10 Dq
have been directly measured for iron group ions in a large
number of crystalline environments.

Magnetic dipole transitions may occur between crystal field states and these depend on non vanishing matrix elements of the form

$$\langle \psi_a | \hat{r} \times \hat{p} | \psi_b \rangle$$

Since $\hat{r} \times \hat{p}$ is on even operator, magnetic dipole transitions may occur within the levels of a given d^n configuration. However, for magnetic dipole transitions $f \simeq 10^{-8}$ and transitions of this type are only of interest in rare earth complexes where the interaction of the 4f electrons with the lattice is small.

Hyperfine Structure in Paramagnetic Resonance

Hyperfine structure of iron group ions

We have a paramagnetic ion in a cubic environment the hyperfine interaction of the unpaired electron with the nucleus may be written

$$\mathcal{H} = A \, \hat{I} \cdot \hat{S}$$

where $\hat{I}$ is the nuclear spin and $\hat{S}$ the electronic spin. To calculate A we require the matrix elements of the operator

$$\mathcal{H} = 2g_n \beta \beta_n \sum_i \left[\frac{\hat{l}_i \cdot \hat{I}}{r_i^3} - \frac{\hat{s}_i \cdot \hat{I}}{r_i^3} + 3 \frac{(\hat{r}_i \cdot \hat{s}_i)(\hat{r}_i \cdot \hat{I})}{r_i^5} + \frac{8\pi}{3} \delta(\hat{r}_0)(\hat{s}_i \cdot \hat{I}) \right]$$

where the summation covers the magnetic electrons. If we neglect the Fermi contact term in $\mathcal{H}$ we may write

$$\mathcal{H} = 2g_n \beta \beta_n \langle r^{-3} \rangle | \hat{L} \cdot \hat{I} + \xi \{ L(L+1) \, \hat{S} \cdot \hat{I}$$

$$-\frac{3}{2}(\hat{L}\cdot\hat{S})(\hat{L}\cdot\hat{I}) - \frac{3}{2}(\hat{L}\cdot\hat{I})(\hat{L}\cdot\hat{S})\}\Big]$$

where

$$= \frac{(2l+1) - 4S}{S(2l-1)(2l+3)(2L-1)}$$

and $l = 2$ for a d electron and $l = 3$ for an f electron.

The Fermi contact term is due to the finite amplitude of unpaired S electrons at the nucleus and is a potent source of h.f.s.; if we are dealing with a pure d^n configuration this term does not occur. However, the unpaired electrons of a $3d^n$ configuration polarize the filled 1s, 2s and 3s shells and we have a resultant unpaired spin density at the nucleus from these shells which makes a large contribution to the hyperfine structure of iron group ions. This effect is accounted for by adding to $\mathcal{H}$ a term

$$\frac{4}{3} g_n \beta \beta_n \; x \; \hat{S}\cdot\hat{I}$$

The introduction of the term in x is essential to describe the h.f.s. of Mn^{2+} in solids. The ground state of Mn^{2+} is $d^5 \, {}^6S_{\frac{5}{2}}$ and it should have no hyperfine structure if we neglect core polarization. However exchange polarization of the $1s^2$, $2s^2$ and $3s^2$ shells by the d electrons produces a resultant field He at the nucleus opposite in direction to the field applied in an ESR experiment. An analysis of the measured values of the h.f.s. of iron group ions in solids gives

	$V^{2+}(3d^3)$	$Mn^{2+}(3d^5)$	$Co^{2+}(3d^7)$	$Cu^{2+}(3d^9)$
$x =$	-2.8	-3.1	-2.5	-2.9
$H_e(K.G.) =$	-354	-650	-315	-122

It should be remembered that χ is a measure of the effective magnetic field (He) at the nucleus per unpaired spin and it is remarkably constant through the iron group. Attempts have been made by Freeman and Watson to calculate χ and He for iron group ions and we give their results below for Mn^{2+}. We see that the resultant field is a sum of large partly cancelling contributions. We expect that χ and He will be sensitive

direction of d electrons

				$H\uparrow + H\downarrow$ K.G.
1s	↑	2,502,480	K.G.	
1s	↓	-2,502,870	" "	-30
2s	↑	226,670	" "	
2s	↓	-228,080	" "	-1400
3s	↑	31,210	" "	
3s	↓	-30,470	" "	+ 740

He = - 640 K.G.

to environment because of the distortions of the 3d orbitals by bonding effects. The effects of bonding on the h.f.s. of Mn^{2+} may be seen from the following measurements:

ligand	H_2O	F^-	CO_3^{2-}	O^{2-}	S^{2-}	Te^{2-}
H_e(K.G.)	-695	-695	-665	-600	-490	-420

it is apparent that increasing covalency reduces H_e. It is also

interesting to note that the free manganese atom ($3d^5 4S^2$) has a value of H_e (+ 170 K.G.) of opposite sign to that of the ion and this is due to the contribution to H_e of the polarized 4S shell.

There is no orbital contribution to the hyperfine structure in the case if Mn^{2+} but the effect of orbital contribution may be observed in the case of Co^{2+}. In a cubic octahedral environment the orbital angular momentum contributes a value of ~1 to the g-value and the $|A|$ value is ~100×10^{-4} cm^{-1}. In an environment of eight charges (cubic) the orbital contribution to the g-value is ~0.3 and the $|A|$ value is ~20×10^{-4} cm^{-1}.

Hyperfine Structure of Rare Earth Ions

If we neglect the contact term our hyperfine operator may be written in the form

$$\mathcal{H} = 2\, g_n \beta \beta_n \langle r^{-3} \rangle\, \hat{N} \cdot \hat{I}$$

where

$$\hat{N} = \sum_i \left[\hat{\ell}_i - \hat{S}_i + \frac{3\, \hat{r}_i (\hat{r}_i\, \hat{S}_i)}{r_i^2} \right]$$

The problem of finding the matrix elements of N has been considered by Elliott and Stevens who show that

$$\langle J | \hat{N} | J \rangle = \langle J \| N \| J \rangle \langle J | \hat{J} | J \rangle$$

and they give tables of the multiplicative factors $\langle J \| N \| J \rangle$ (Proc. Roy. Soc. A218, 553, 1953).

Their theory assumes Russel-Saunders coupling but they

show that departures from R-S coupling in the rare earths do not affect the theory appreciably.

If we write the hyperfine interaction within a ground doublet in the form

$$A \; \hat{I} \cdot \hat{S}'$$

with a fictitious spin $S' = \frac{1}{2}$ we then define the spectroscopic splitting factor by the relationship

$$\hat{L} + 2\hat{S} = g \; \hat{S}'$$

Consider the interaction

$$2g_u \beta \beta_n \langle r^{-3} \rangle \hat{N} \cdot \hat{I} = P \hat{N} \cdot \hat{I}$$

Now

$$\langle J | \hat{N} | J \rangle = \langle J \| N \| J \rangle \langle | \hat{J} | \rangle$$

and

$$\langle | \hat{L} + 2\hat{S} | \rangle = g_J \langle | \hat{J} | \rangle = g \langle | \hat{S}' | \rangle$$

$$\therefore \; \langle | \hat{J} | \rangle = g \frac{\langle | \hat{S}' | \rangle}{g_J}$$

and

$$\langle | \hat{N} | \rangle = g \frac{\langle \| N \| \rangle \langle | \hat{S}' | \rangle}{g_J}$$

$$\therefore \; A = \frac{P \; g \langle \| N \| \rangle}{g_J}$$

This relationship holds accurately if the spin orbit interaction is bigger than the crystal field splittings so that admixture of other J levels by the crystal field can be neglected. The relationship could be used to determine nuclear g_n values from measured A-values if the value of $\langle r^{-3} \rangle$ were known. However, values of $\langle r^{-3} \rangle$ can only be calculated

with an accuracy of 10-20%. Values of g_n are now being directly measured by atomic beam and ENDOR methods and from known values of g_n we may calculate values of $\langle r^{-3} \rangle$.

Let us consider an ion in the free state. We may write the hyperfine interaction in the form

$$P \, \hat{N} \cdot \hat{I} = a \, \hat{J} \cdot \hat{I}$$

where

$$P = 2g_n \beta \beta_n \langle r^{-3} \rangle$$

Now

$$P \langle |\hat{N}| \rangle = P \langle \| N \| \rangle \langle |\hat{J}| \rangle$$

$$\therefore \quad a = P \langle \| N \| \rangle$$

and hence

$$\frac{A}{g} = \frac{a}{g_J}$$

Our discussion has so far neglected core polarization but this effect has been observed in the case of Eu^{2+} in CaF_2. Both the Eu^{2+} ion and the atom have a half filled f shell with an $^8S_{\frac{7}{2}}$ ground state. There are two stable isotopes, 151 and 153, each with I = 5/2. Measurements on the Eu atom have been made by atomic beam methods and the contact interactions of the atom and ion are compared below:

$$^{151}Eu^{2+} \qquad A_{core} = -83 \text{ Mcs}$$

$$^{151}Eu^{0} \qquad A_{core} = -2 \text{ Mcs}$$

it is apparent that the core polarization in the atom is negligible. For $^{151}Eu^{2+}$ we find $A_{core}/g_n = -61$ Mcs and for other divalent rare earth ions we may write

$$A_{core} \simeq -61(g_J - 1)g_n \text{ Mcs}$$

if we assume that the core polarization for spin is the same for all rare earth ions. The factor $(g_J - 1)$ gives the projection of S on J since we are interested only in the spin. It should be remembered that the hyperfine interaction for rare earth ions will vary with covalency (up to 10%) although the effect is not as pronounced as in the iron group.

We may apply the relationship

$$\frac{A}{g} = \frac{a}{g_J}$$

to the Im^{2+} ion in a solid and the free Im atom since they differ only by the filled 6S shell and they have the same ground state ($^2F_{\frac{7}{2}}$). The measured value of a for the Im atom is -374.14 Mcs. For the Im^{2+} ion in CaF_2 we find g = 3.454 and A = ⁻1101.4 Mcs and making allowance for orbital reduction and core polarization we find a value of a for the Tm^{2+} ion of -382.4 Mcs. This difference in a values may be assigned to a 2% increase in $\langle r^{-3} \rangle$ in going from the atom to the ion and this small change is due to the fact that removal of the $6S^2$ electrons does not effect the inner 4f orbitals appreciably.

Hyperfine Interactions with Distant Nuclei

The interactions of magnetic electrons with the nuclei of distant ions is due to the presence of covalent bonding. In our discussion of this problem we shall first consider a two atom three electron system. Let us assume we are dealing only

with a $3d_{3z^2-r^2}$ orbital and a $p\sigma$ ligand orbital.

$$3z^2-r^2 \qquad\qquad p\sigma$$
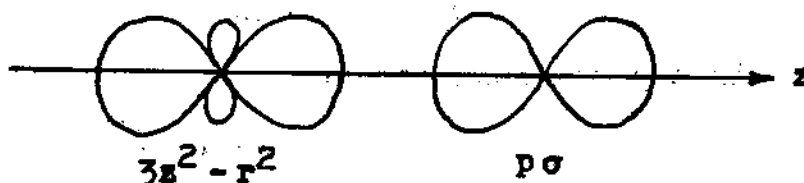
The Heitler-London state will be obtained by placing two electrons in the p-orbital, one in p_α and the other in p_β and the third electron in d_α or d_β. This represents a ligand with a partly filled 3d shell. The wave function is

$$\psi_{HL} = N \sum_{p} (-1)^p \, P \, d_\alpha(1) \, p_\alpha(2) \, p_\beta(2)$$

The only other state we can form from this system is

$$\psi_{T} = N \sum_{P} (-1)^P \, P_\alpha(1) \, d_\beta(2) \, p_\alpha(3)$$

where the subscript T indicates transfer of one electron from the ligand to the d-orbital. The ground state will be a linear combination

$$\psi_b = \left[1 + 2B\langle d|p\rangle + B^2\right]^{-\frac{1}{2}} \left[\psi_{HL} + B \, \psi_T\right]$$

We get on alternative description of the system by constructing bonding and antibonding orbitals. The bonding orbital is

$$\varphi_b = M(p + Bd)$$

where B is a small quantity which is in fact identical with the B in ψ_b and is therefore a measure of charge transfer or covalency and

$$M = \left[1 + 2B\langle p|d\rangle + B^2\right]^{-\frac{1}{2}}$$

The antibonding orbital is

$$\varphi_a = N(d - Ap)$$

where A is a samll quantity and

$$N = \left[1 - 2A\langle p|d\rangle + A^2\right]^{-\frac{1}{2}}$$

The condition that φ_a and φ_b be orthogonal gives the relationship

$$\varphi_a \cdot \varphi_b = NM\left[\langle p|d\rangle + B - A - AB\langle p|d\rangle\right] = 0$$

$$A = \frac{B + \langle p|d\rangle}{1 + B\langle p|d\rangle}$$

$$\simeq B + \langle p|d\rangle = B + S$$

In situations which concern us the unpaired electrons are in antibonding orbitals and the unpaired spin density in the ligand orbital is

$$f = N^2(B + S)^2$$

The quantity S takes care of the ligand orbital polarization due to overlap and describes a purely ionic situation. The quantity B takes care of transfer of charge from the ligand to the d orbital leaving an unpaired spin density on the ligand.

The antibonding single electron d-orbitals for a regular octahedral environment may be written

$$d\gamma \quad \sigma\text{-bonding} \begin{cases} \varphi_{x^2-y^2} = N\left[d_{x^2-y^2} - \frac{\lambda}{2}(\psi_1 + \psi_4 - \psi_2 - \psi_5)\right] \\ \varphi_{3z^2-r^2} = N\left[d_{3z^2-r^2} - \frac{\lambda}{\sqrt{12}}(2\psi_3 + 2\psi_6 - \psi_1 - \psi_4 - \psi_2 - \psi_5)\right] \end{cases}$$

$$d\varepsilon \quad \pi\text{-bonding} \quad \begin{cases} \varphi_{xy} = N' \left[d_{xy} - \frac{\lambda_\pi}{2} (\pi_1 + \pi_2 - \pi_4 - \pi_5) \right] \\[2ex] \varphi_{yz} = N' \left[d_{yz} - \frac{\lambda_\pi}{2} (\pi_2 + \pi_3 - \pi_5 - \pi_6) \right] \\[2ex] \varphi_{zx} = N' \left[d_{zx} - \frac{\lambda_\pi}{2} (\pi_3 + \pi_1 - \pi_4 - \pi_6) \right] \end{cases}$$

In the case of the $d\gamma$ orbitals the ligand functions $\psi_1 \ldots \psi_6$ are composed of S and $p\sigma$ functions (e.g. 2S and 2pσ in the case of F^- ligands) and may be written $\psi = \alpha S + \beta\, p\sigma$; it follows if we write $\lambda\psi = \lambda_s s + \lambda_\sigma\, p\sigma$ that $\lambda = \lambda s/\alpha = \lambda\sigma/\beta$.

If we are dealing with a regular octahedron of F^- ions the point symmetry at the ligand site is tetragonal and the hyperfine interaction with the ligand nucleus may be written

$$A\, I_z^F S_z + B\, (I_x^F S_x + I_y^F S_y)$$

where the z direction is the bond axis and, in general,

$$A = A_s + 2(A_D + A_\sigma - A_\pi)$$
$$B = A_s - (A_D + A_\sigma - A_\pi)$$

Here A_S is the hyperfine interaction through the fluorine 2S orbital, $A_D = g\beta\, g_n \beta_n / R^3$ is the dipole-dipole interaction between the magnetic electrons and the ligand nucleus and A_σ and A_π are the interactions through fluorine 2pσ and 2pπ orbitals.

When the two $d\gamma$ orbitals are singly occupied as in the case of $Mn^{2+}(d\varepsilon^3\, d\gamma^2)$ and $Ni^{2+}(d\varepsilon^6\, d\gamma^2)$ the unpaires spin

densities in the fluorine 2S and 2pσ orbitals are

$$f_s = \frac{N^2\lambda^2_s}{3} = 2\,A_s\,S/A_{2s}$$

$$f_\sigma = \frac{N^2\lambda^2_\sigma}{3} = 2\,A_\sigma\,S/A_{2p}$$

where S is the true spin of the magnetic ion (5/2 in the case of Mn^{2+} and 1 in the case of Ni^{2+}) and

$$A_{2S} = \frac{8\pi}{3}\,g\beta\,g_n\,\beta_n\,|\psi(o)|^2_{2S}$$

$$A_{2p} = \frac{2}{5}\,g\beta\,g_n\,\beta_n\,\langle r^{-3}\rangle_{2p}$$

are the hyperfine interactions of a single unpaired 2S and 2p electron on an F^- ion.

When the three $d\epsilon$ orbitals are singly occupied as in the case of $Cr^{3+}(d\epsilon^3)$ the spin density in the fluorine 2pπ orbitals is

$$f_\pi = \frac{N'^2\lambda^2_\pi}{4} = 2\,A_\pi\,S/A_{2p}$$

In our analysis of bonding interactions we can estimate A_D assuming point dipoles and known lattice parameters and from our measurements we can determine A_s and $(A_\sigma - A_\pi)$.

The relative sizes of A_σ and A_π for iron group ions may be estimated from a comparison of measurements on Cr^{3+} where we have three π-bonding electrons, Mn^{2+} where there are 3π-bonding and two σ-bonding electrons and in the case of Ni^{2+} where there are two σ-bonding magnetic electrons. It should be emphasised that in ESR measurements we measure only the bonding of unpaired

spins. The measurements given below on impurities in K Mg F_3 show that $f_\sigma \simeq f_\pi$ for iron group ions

	f_s %	$f_\sigma - f_\pi$ %
Cr^{3+}	$- 0.03$	$- 4.76$
Mn^{2+}	0.55	0.3
Ni^{2+}	0.49	4.51

We expect overlap (S) to make the more important contribution to f_s because the 2S electrons are firmly bound leading to little charge transfer. However in the case of the less firmly bound 2p electrons we expect charge transfer (B) to be the dominant contributor to $f_\sigma \simeq f_\pi$.

The theory out lined above neglects all orbital contribution to the hyperfine structure and this is a good approximation in the case of Cr^{3+}, Mn^{2+} and Ni^{2+}. However, we have seen that the orbital angular momentum of Fe^{2+} and Co^{2+} is not quenched in a cubic octahedral environment and more extensive calculations are required for these systems.

Very Weak Hyperfine Interactions

The hyperfine interaction of iron group ions with fluorine ligands is easily resolved in ESR measurements but the interactions of the weakly bonding 4f electrons of rare earth ions are not. Hyperfine structure which is unresolved in the ESR spectrum may be resolved by the ENDOR method.

The ENDOR technique has two advantages over the ESR method:

(1) nuclear moments may be measured directly

(2) electron-nuclear interactions are measured to higher precision because of narrower line widths.

If we have paramagnetic ions in a crystal the ESR lines are in homogeneously broadened by ramdomly oriented fluorine nuclear magnets, other magnetic ions and random distortions of the crystal field. The random static fields contribute to the ENDOR line width by (1) direct interaction with the nuclear moment and by (II) interaction through the electronic spin. However, because these interactions are with a nuclear rather than an electronic magnet we get lines about 10^3 narrower and therefore we can get precise hyperfine measurements and resolve hyperfine structure unresolved in the ESR spectrum. In effect we combine the precision and resolution of an N.M.R. experiment with the sensitivity of an ESR experiment.

Let us consider the simplest possible system, that of an electron coupled to a nucleus with $I = \frac{1}{2}$.
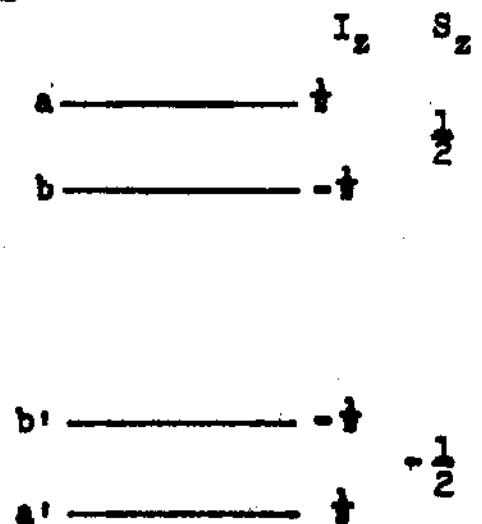
The energy levels are given by the spin Hamiltonian

$$\mathcal{H} = g\beta \hat{H}\cdot\hat{S} + A\,\hat{I}\cdot\hat{S} - g_n\,\beta_n\,\hat{H}\cdot\hat{I}$$

If we assume $g\beta H \gg A$, $g_n\beta_n H$ we find that the energy levels are given to a good approximation by

$$a,b = \tfrac{1}{2}\,g\beta H \pm \tfrac{1}{4}\,A \mp \tfrac{1}{2}\,g_n\,\beta_n\,H$$

$$b',a' = -\tfrac{1}{2}\,g\beta H \pm \tfrac{1}{4}\,A \pm \tfrac{1}{2}\,g_n\,\beta_n\,H$$

The electron spin transition a$\longleftrightarrow$a' is now partly
saturated with microwave power by maintaining the condition

$$hV_e = g \beta H + A/2 .$$

A varying nuclear frequency of order $h\nu_n = A/2$ is now
applied and when

$$h\nu_n = A/2 - g_n \beta_n H$$

nuclear transitions a$\longleftrightarrow$b occur and when

$$h \nu_n' = A/2 + g_n \beta_n H$$

nuclear transitions a'$\longleftrightarrow$b' occur and change the intensity of
the EPR signal. From the above relationships we find

$$\nu_n + \nu_n' = A/h$$

$$\nu_n - \nu_n' = 2g_n \beta_n H/h .$$

When we apply this technique to Tm^{2+} in CaF_2 we obtain

$$|A_s| = 2.36 \text{ Mcs}, \quad |A_\sigma - A_\pi| = 2.2 \text{ Mcs}$$

for the fluorine bonding parameters and these values are about
an order of magnitude smaller than the bonding parameters of
iron group ions in fluoride crystals. The small orbital reduc-
tion observed in the case of Tm^{2+} is consistent with these meas-
urements.

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