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# Symmetry selection rules and Hyperfine structure

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Abstract

Nuclear hyperfine interaction in crystal fields can lead to a breakdown in the usual selection rules for transitions among Stark levels in crystals containing  $Ho^{3+}$ . The existence of such a possibility was given by the author over three decades ago. Recently very high-resolution spectroscopic studies in Moscow have supplied a rich source of experimental information. The analysis of these spectra gives an interesting display of the interplay of point groups and their double groups and of crystal field and nuclear hyperfine interactions.

*What never! Well hardly ever!*

— Gilbert and Sullivan

## 1. Introduction

The lanthanides, or  $4f$ -elements, have long provided many opportunities for the effective use of symmetry considerations in the description of their spectroscopic properties<sup>1,2</sup>. Racah in his remarkable 1949 paper<sup>3</sup> showed how chains of Lie groups could be used both in the classification of the many-electron states and in simplifying the calculation of the relevant matrix elements. One of the powerful features of symmetry considerations is their exploitation in the development of selection rules, as for example, in the Laporte electric dipole selection rules. A selection rule will tell us which matrix elements are necessarily null. It does not necessarily follow that matrix elements which satisfy the

selection rules are necessarily non-zero.

In some cases situations arise where a matrix element is expected, by the stated selection rules, to be null and is found to be non-zero and the selection rule is said to be violated. This is the normal situation with so-called forbidden transitions. Thus one finds the strong angular momentum selection rule for dipole transitions  $0 \leftarrow / \Rightarrow 0$  is found to be violated in transitions observed in certain gaseous nebulae<sup>4</sup>. In these cases the violation maybe directly associated with the interaction between the nucleus and the electrons of an atom<sup>5</sup>. In deriving the original selection rule the angular momentum of the nucleus  $\mathbf{I}$  was ignored. The total angular momentum of the atom  $\mathbf{F}$  is then  $\mathbf{F} = \mathbf{I} + \mathbf{J}$  and if the nuclear angular momentum is a half-odd integer and the number of electrons is even then there is no possibility of forming a state of total angular momentum zero and the  $0 \leftarrow / \Rightarrow 0$  selection rule is weakly broken.

Forbidden transitions were observed in paramagnetic resonance studies of holmium salts<sup>6</sup> and a complicated mechanism based on the Jahn-Teller effect invoked. The alternative possibility of interaction between different crystal field levels via the nuclear magnetic moment was suggested by the author<sup>7</sup>. Hyperfine structure was observed in the optical spectra of salts containing  $Pr^{3+}$  and  $Ho^{3+}$  in the early sixties<sup>8-10</sup> but at relatively low resolution. Subsequent technological developments culminating in the Fast Fourier Transform spectrometers in the mid-eighties led to resolutions of  $0.01cm^{-1}$  permitting for the first time detailed observation of complete fully resolved patterns together with accurate intensities<sup>11-15</sup> were made for single crystals of  $LiYF_4 : Ho^{3+}$ . Similar studies have recently been made on the system  $CaF_2 : Ho^{3+}$ <sup>16,17</sup>. In this paper I outline some of the problems and objectives associated with the interpretation of hyperfine structure of  $Ho^{3+}$  doped single crystals.

## 2. Data and Type I and Type II HFS Patterns

Holmium occurs in nature as a single stable isotope with nuclear angular momentum  $I = \frac{7}{2}$  and being a deformed nucleus has both a nuclear magnetic dipole moment

and an electric quadrupole moment. The dominant hyperfine structure comes from the interaction of the nuclear magnetic moment with the electron spin and orbital magnetic moments. In the particular case of  $LiYF_4 : Ho^{3+}$  the  $Ho^{3+}$  ion substitutes into a site whose point group symmetry is  $S_4$  (not to be confused with the symmetric group which is also designated as  $S_4$ ). The ordinary irreducible representations of  $S_4$  comprise two one-dimensional  $\Gamma_1, \Gamma_2$  representations and a two-dimensional complex conjugate pair designated as  $\Gamma_{34}$ .

Two distinct types of hyperfine patterns are observed. In each case the sublevels are two-fold degenerate. In one type (*I*) eight approximately equally spaced sublevels are observed while in the second type (*II*) four irregularly spaced sublevels are observed. The widths of type *I* are usually greater than those of type *II* and normally fully resolved. The type *I* patterns are associated with  $\Gamma_{34}$  crystal field levels whereas the type *II* patterns are associated with  $\Gamma_1$  or  $\Gamma_2$  levels. In some cases a type *I* pattern may be severely distorted from the usual equal spacing pattern. This is usually indicative of mutual perturbation between the  $\Gamma_{34}$  and either a nearby (say  $< 2cm^{-1}$ )  $\Gamma_1$  or  $\Gamma_2$  level.

The groundstate of the  $Ho^{3+}$  free ion is  $4f^{10}(^5I_8)$  and in the crystal host the lowest crystal field level is a  $\Gamma_{34}$  level. The next highest crystal field level is a  $\Gamma_2$  level at  $6.85cm^{-1}$ . Very detailed experimental data is available for transitions to all the crystal field levels involving the higher members of the  $^5I$  multiplet<sup>11-15</sup>. The type *I* patterns show very regular changes in the intensity in going from one sublevel to the next whereas the type *II* patterns display highly irregular intensities.

### 3. Objectives of Pattern Analysis

An understanding of the observed HFS patterns should allow the identification of the type *I* and type *II* patterns making predictions of their widths and intensity distribution. Furthermore the distortions sometimes produced in type *I* patterns needs to be explained. The existence of 'forbidden transitions' needs to be understood.

### 4. Magnetic Dipole Hyperfine Interaction in Crystals

In the crystalline environment the electric field splittings are very much greater than the hyperfine splittings. The appropriate basis involves the quantum numbers  $JJ_zII_z$ . Let us define

$$a_\ell = \mu_B^2 (m_e/M_p) g_I \langle r^{-3} \rangle \quad (1)$$

where  $\mu_B$  is the Bohr magneton,  $g_I$  the nuclear  $g$  factor and  $\langle r^{-3} \rangle$  the average inverse-cube radius of the electron orbital  $\ell$ . Further, let

$$\begin{aligned} \mathbf{H}_m(i) &= a_\ell [\mathbf{I}_i^{(1)} - \sqrt{10}(\mathbf{s}^{(1)} \mathbf{x} \mathbf{C}^{(2)})_i^{(1)}] \\ &= a_\ell [\mathbf{I}_i^{(1)} - \sqrt{10} \mathbf{X}_i^{(1)}] \end{aligned} \quad (2)$$

with

$$\mathbf{H}_m^{(1)} = \sum_{i=1}^n H_m(i)^{(1)} \quad (3)$$

where the sum is over a group of equivalent electrons in the configuration  $\ell^n$ . The interaction of a nuclear magnetic moment with orbital and spin moments of  $n$  electrons can be written in tensor operator notation as

$$\mathcal{H}_m = a_\ell (\mathbf{H}^{(1)} \cdot \mathbf{I}^{(1)}) \quad (4)$$

Let us enlarge our state description to  $|\alpha SLJJ_zII_z\rangle$  where we allow for matrix elements non-diagonal in  $\alpha SL$  but for the moment ignore the possibility of  $J$ -mixing by the crystal field. Let us define the magnetic hyperfine structure constant as

$$A = a_\ell [\mathcal{L} + \mathcal{S}] \quad (5)$$

where

$$\mathcal{L} = \frac{\langle \alpha SLJ || L^{(1)} \alpha' S' L' J \rangle}{\sqrt{J(J+1)(2J+1)}} = \delta_{\alpha, \alpha'} \delta_{S, S'} \delta_{L, L'} (2 - g) \quad (6)$$

where  $g$  is the usual Landé  $g$ -factor for the electronic state and

$$\mathcal{S} = (-1)^{\ell+1} (2\ell+1) \begin{pmatrix} \ell & \ell & 2 \\ 0 & 0 & 0 \end{pmatrix} \sqrt{\frac{30(2J+1)}{J(J+1)}} \begin{Bmatrix} S & S' & 1 \\ L & L' & 2 \\ J & J & 1 \end{Bmatrix} \langle \alpha SL || V^{(12)} || \alpha' S' L' \rangle \quad (7)$$

where the last matrix element involves the double tensor  $V^{(12)}$  that acts in the spin and orbital spaces and whose one-electron reduced matrix elements satisfy

$$\langle \ell || v^{(12)} || \ell \rangle = \sqrt{\frac{3}{2}} \quad (8)$$

In the  $JJ_zII_z$  scheme the diagonal matrix elements of the magnetic hyperfine interaction are given by<sup>2,7</sup>

$$\langle \alpha SLJJ_zII_z | \mathcal{H}_m | \alpha' S' L' JJ_zII_z \rangle = J_z I_z A \quad (9)$$

whereas the off-diagonal matrix elements are given by

$$\langle \alpha SLJJ_zII_z | \mathcal{H}_m | \alpha' S' L' JJ_z \pm 1 II_z \mp 1 \rangle = \frac{1}{2} A [(J \mp J_z)(J \pm J_z + 1)(I \pm I_z)(I \mp I_z + 1)]^{\frac{1}{2}} \quad (10)$$

## 5. Intermediate Coupling Effects

The effect of spin-orbit interaction is to mix states of different  $S$  and  $L$  leading to a breakdown in the usual  $\Delta S = 0$  and  $\Delta L = 0, \pm 1$  selection rules. This breakdown may be further exacerbated by crystal field mixings. For the "free ion"  $Ho^{3+}$  we find for the ground multiplet

Table 1 Energy levels and eigenvectors for the  ${}^5I$  multiplet in  $LiYF_4 : Ho^{3+}$ .

$J$	$E_{calc}$	$E_{expt}$	Eigenvector
8	0	0	$0.9665 {}^5I_8\rangle + 0.1189 (20)^3K_8\rangle - 0.2221 (30)^3K_8\rangle$
7	5097	5152	$0.9853 {}^5I_7\rangle - 0.1462 (30)^3K_7\rangle$
6	8672	8671	$0.9772 {}^5I_6\rangle + 0.1352 (30)^3H_6\rangle$
5	11281	11242	$0.9549 {}^5I_5\rangle - 0.1377 (21)^3H_5\rangle + 0.1944 (30)^3H_5\rangle - 0.1067 (11)^3H_5\rangle$
4	13350	13188	$0.9495 {}^5I_4\rangle - 0.1620 (21)^3H_4\rangle + 0.2247 (30)^3H_4\rangle - 0.1186 (11)^3H_4\rangle$

where we have used Racah's  $G_2$  group labels to separate multiple occurring  $LS$  states.

Using the eigenvectors for  $J = 8$  and  $J = 7$  states given in Table 1 leads to the intermediate coupling results for the spin part  $\mathcal{S}$  for the lowest two members of the  ${}^5I$  multiplet as

$$\mathcal{S}({}^5I_8) = \frac{1}{60}[-0.5700], \quad \mathcal{S}({}^5I_7) = \frac{1}{420}[-3.2369] \quad (11)$$

where the first part of the result is given as a fraction and the second part is the intermediate coupling correction factor. The latter factor would be unity for pure  $LS$ -coupling. Notice that the intermediate coupling corrections for the spin part of the interaction can be quite large even for relatively small departures from  $LS$ -coupling. However, in general the spin part is very much smaller than the orbital part.

Again, using the eigenvectors for the  $J = 8$  and  $J = 7$  states given in Table 1 leads to the intermediate coupling results for the orbital part  $\mathcal{L}$  for the two lowest members of the  ${}^5I$  multiplet as

$$\mathcal{L}({}^5I_8) = \frac{3}{4}[1.0082], \quad \mathcal{L}({}^5I_7) = \frac{23}{28}[0.9964] \quad (12)$$

The corrections for small departures from  $LS$ -coupling make for quite small corrections compared with those for the spin part of the magnetic hyperfine interaction.

The total intermediate coupling correction for the magnetic-dipole hyperfine structure comes from combining Eqs. (6) and (7) to form total magnetic hyperfine interaction matrices and then transforming them to diagonal form with the appropriate intermediate coupling eigenvectors to yield

$$[\mathcal{L} + \mathcal{S}]({}^5I_8) = \frac{23}{30}[0.9735], \quad [\mathcal{L} + \mathcal{S}]({}^5I_7) = \frac{173}{210}[0.9591] \quad (13)$$

Here we see again that the total effect is quite small and comes primarily from the factor  $(2-g)$ . The dominance of that term means that in most cases the spin part of the hyperfine interaction can be ignored if results to within 10% are desired. Intermediate coupling correction for the orbital part is accomplished by simply replacing  $g$  by its intermediate coupling value.

## 5. Crystal Field States

In a crystal field of finite symmetry neither  $J$  nor  $J_z$  survive as "good" quantum numbers. In many cases  $J_z$  is strongly broken while  $J$  survives to a "good" quantum number to a good approximation and  $J$ -mixing may be ignored. In that case a given crystal field level may be characterised by

$$|\alpha J \Gamma_i\rangle = \sum_M a_{JM} |JM\rangle \quad (14)$$

In the case of  $S_4$  point group symmetry the expansions involve the states

$$|\alpha J \Gamma_1\rangle \quad |J0\rangle, |J \pm 4\rangle, |J \mp 8\rangle, \dots \quad (15a)$$

$$|\alpha J \Gamma_2\rangle \quad |J2\rangle, |J-2\rangle, |J6\rangle, |J-6\rangle, \dots \quad (15b)$$

$$|\alpha J \Gamma_{34}\rangle \quad |J \pm 1\rangle, |J \mp 3\rangle, |J \pm 5\rangle, |J \mp 7\rangle, \dots \quad (15c)$$

The crystal field potential for  $S_4$  point symmetry acting on  $f$ -electrons can be written as

$$S_4 : V = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_{\pm 4}^4 C_{\pm 4}^{(4)} + B_{\pm 4}^6 C_{\pm 4}^{(6)} \quad (16)$$

where

$$B_{\pm q}^k = B_q^k \pm i A_q^k \quad (17)$$

and both  $B_q^k$  and  $A_q^k$  are real. In practice we can perform a rotation of the  $x$  and  $y$  axes about the  $z$ -axis to eliminate the imaginary part of either  $B_{\pm 4}^4$  or  $B_{\pm 4}^6$ . Most workers choose  $B_{\pm 4}^4$  to be real.

It is useful to introduce, for the  $\Gamma_1$  and  $\Gamma_2$  states, the symmetric and antisymmetric linear combinations

$$|JM\rangle_{\pm} = \frac{1}{\sqrt{2}}(|JM\rangle \pm |J-M\rangle) \quad (18)$$

We then have that

$$\langle JM|V|JM'\rangle_{++} = \langle JM|V|JM'\rangle_{--}, \text{ real} \quad (19a)$$

$$\langle JM|V|JM'\rangle_{+-} = \langle JM|V|JM'\rangle_{-+}^*, \text{ imaginary} \quad (19b)$$

Explicit calculation involves construction of the crystal field energy matrices followed by their diagonalisation to yield energy eigenvalues and their associated eigenvectors to give

the relevant  $a_J M$  expansion coefficients. Thus we find, for example, for the lowest  ${}^5I_8$  level of the groundstate of  $LiYF_4 : Ho^{3+}$

Eigenvalues and eigenvectors for  $J = 8$  for  $\Gamma_1$  states

$$\begin{array}{l}
 \text{Eigenvalue} \\
 |80\rangle \\
 |84\rangle_+ \\
 |88\rangle_+ \\
 |84\rangle_- \\
 |88\rangle_-
 \end{array}
 \begin{pmatrix}
 45.9 & 218.6 & 290.1 & 51.6 & 274.6 \\
 .17575 & .87070 & -.45932 & 0 & 0 \\
 .73385 & .19446 & .64932 & -.032543 & .030424 \\
 .65532 & -.45164 & -.60543 & -.00140 & -.00151 \\
 -.03273i & -.00868i & -.02897i & -.72989i & .68215i \\
 -.001356i & .00093i & .00125i & -.68280i & -.73056i
 \end{pmatrix}$$

Eigenvalues and eigenvectors for  $J = 8$  for  $\Gamma_2$  states.

$$\begin{array}{l}
 \text{Eigenvalue} \\
 |82\rangle_+ \\
 |86\rangle_+ \\
 |82\rangle_- \\
 |86\rangle_-
 \end{array}
 \begin{pmatrix}
 320.7 & 280.7 & 26.3 & 7.0 \\
 .84454 & -.062284 & .52961 & -.048188 \\
 -.52791 & .06899 & .84164 & -.08921 \\
 .06672i & .78857i & .04192i & .61000i \\
 -.05992i & -.60792i & .09559i & .78589i
 \end{pmatrix}$$

Eigenvalues and eigenvectors for  $J = 8$  for  $\Gamma_{34}$  states

$$\begin{array}{l}
 \text{Eigenvalue} \\
 |81\rangle \\
 |8-3\rangle \\
 |85\rangle \\
 |8-7\rangle
 \end{array}
 \begin{pmatrix}
 271.5 & 303.4 & 76.5 & 0 \\
 .81810 + .00046i & .26792 - .00011i & .50101 + .07371i & -.05078 - .00008i \\
 -.20867 + .06104i & .72162 - .21129i & .015696 - .00222i & .59736 - .17382i \\
 -.49134 - .01021i & -.13187 - .00262i & .84838 + .14242i & -.034439 - .00076i \\
 .19423 - .065253i & -.55716 + .18742i & .057251 - .010321i & .74017 - .24759i
 \end{pmatrix}$$

Notice that the components of the eigenvectors are complex.

## 6. Quenching of Angular Momentum and Hyperfine Patterns

The advantage of choosing the symmetric and antisymmetric linear combinations is apparent - the angular momentum for the  $\Gamma_1$  and  $\Gamma_2$  states is completely quenched. Meaning, of course, that the matrix elements of  $J_z$  vanish within and between the  $\Gamma_1$  and  $\Gamma_2$  states. This leads us immediately to the conclusion that there can be no first-

order magnetic hyperfine splittings for those states. Thus only the  $\Gamma_{34}$  states can show a first-order splitting which readily explains why  $\Gamma_{34}$  levels are associated with type *I* hyperfine patterns and  $\Gamma_1$  and  $\Gamma_2$  states with type *II* hyperfine patterns. A distorted type *I* pattern implies magnetic hyperfine coupling of a  $\Gamma_{34}$  state with nearby  $\Gamma_1$  and  $\Gamma_2$  states. Conversely, the appearance of a type *II* pattern implies interaction of a  $\Gamma_1$  (or  $\Gamma_2$ ) state with a nearby  $\Gamma_{34}$ . These perturbations are usually greater than the normal electric quadrupole contributions and indeed act as a pseudo-electric quadrupole interaction. The appearance of a type *II* pattern signals a breakdown of the usual crystal field selection rules since the states no longer correspond to pure representations of the ordinary point group but rather involve spin representations of the so-called double group.

## 7. Calculations of Magnetic Hyperfine Structure

The magnetic hyperfine structure constant  $A$  was defined in Eq. (5) as

$$A = a_\ell[\mathcal{L} + \mathcal{S}] \quad (5)$$

In a crystal the average spacing, in first-order, between successive hyperfine levels,  $E_{hfs}$ , will be

$$E_{hfs} = \langle J_z \rangle A \sim \langle J_z \rangle (2 - g_{IC}) \quad (20)$$

The total width,  $W_{hfs}$ , of a hyperfine pattern of type *I* will be

$$W_{hfs} = (2I + 1)E_{hfs} \quad (21)$$

The first part of a practical calculation is to diagonalise the crystal field matrices to produce eigenvalues and eigenvectors of the form (in the absence of  $J$ -mixing)

$$|\alpha\Gamma_\rho I_z\rangle = \sum_{J_z} a_{J\Gamma_\rho J_z} |\alpha J J_z I_z\rangle \quad (22)$$

where the  $a_{J\Gamma_\rho J_z}$  are *complex* eigenvector components which are independent of the nuclear spin projection  $I_z$  and the nuclear spin  $I$  is assumed to be fixed. The first-order magnetic hyperfine matrix elements are then

$$\langle \alpha J \Gamma_\rho I_z | \mathcal{H}_{mag} | \alpha J \Gamma_\rho I_z \rangle = \delta_{\Gamma_\rho, \Gamma_{34}} A \langle J_z \rangle I_z \quad (23)$$

The magnetic hyperfine constant  $A$  for the groundstate is  $\sim 2.79 \times 10^{-2} cm^{-1}$  which is a typical value for  $Ho$  and thus the splittings are  $\sim 0.15 cm^{-1}$ . When the crystal field levels are very close we can anticipate that the second-order magnetic hyperfine interaction will couple the  $\Gamma_{34}$  states to those of  $\Gamma_1, \Gamma_1$ . To calculate these effects we need to compute matrix elements that are non-diagonal in  $J_z$  and  $I_z$  such that  $J_z + I_z = J'_z + I'_z$  to give

$$\langle \alpha J \Gamma_{\rho} I_z | \mathcal{H}_{mag} | \alpha J \Gamma_{\rho'} I_z \mp 1 \rangle = \sum_{J_z} a_{\Gamma_{\rho} J_z I_z}^* a_{\Gamma_{\rho'} J_z \pm 1 I_z \mp 1} \langle \alpha J J_z I I_z | \mathcal{H}_{mag} | \alpha' J J_z \pm 1 I I_z \mp 1 \rangle \quad (24)$$

As an example we consider five  $\Gamma_{34}$  type  $I$  patterns studied by the Moscow group and listed in Table 2 below

$J$	$E_{\epsilon}$	$E_c$	$E_{hfs_{\epsilon}}$	$E_{hfs_c}$	$\langle J_z \rangle_{\epsilon}$	$\langle J_z \rangle_c$	$\langle g_{z_{\epsilon}} \rangle_{\epsilon}$	$\langle g_{z_c} \rangle_{\epsilon}$
8	0	0	-0.147	-	-5.2	-5.09	13.0	12.6
7	3.4	6.0	0.082	0.071	2.75	2.47	6.49	5.8
	32.4	32	-0.131	-0.140	-4.39	-4.87	10.36	11.5
	75.5	82	-0.08	-0.081	-2.74	-2.81	6.48	6.6
	140.6	145	-	0.035	-	1.22	-	2.9

**Table 2.** Comparison of Experimental and Calculated  $\Gamma_{34}$  Levels

The experimental quantities are subscripted by an  $\epsilon$  and calculated quantities by a  $c$ .  $E_{hfs}$  is the mean spacing of the hyperfine levels in  $cm^{-1}$ .  $\langle g_z \rangle$  is the magnetic splitting factor. The energy levels for the  $J = 7$  states are relative to that of the lowest  ${}^5I_7$  state.

We can estimate  $A[{}^5I_8]$  from the experimentally determined values of  $E_{hfs}$  and  $\langle J_z \rangle$  to give

$$A[{}^5I_8]_{\epsilon} = 0.0271 \times 10^{-2} cm^{-1} \quad (25)$$

Then using Eq.(13) we can deduce a value of

$$A[{}^5I_7]_c = 0.0287 \times 10^{-2} cm^{-1} \quad (26)$$

The entries in the fifth column of Table 2. then follow by multiplication of  $A[{}^5I_7]_c$  by the appropriate value of  $\langle J_z \rangle_c$ . The results are in relatively close agreement with the experimental values, probably to within experimental accuracy. We note that the calculated mean spacing for the last level is quite small ( $0.035 \times 10^{-2} cm^{-1}$ ) which is at the limit of resolution and explains the paucity of experimental data for this level.

## 8. Selection Rules and 'Forbidden Transitions'

Electric dipole transitions involve the matrix elements of  $z$  for polarisation parallel to the  $z$ -axis ( $\pi$ -polarisation) and for polarisation perpendicular to the  $z$ -axis ( $\sigma$ -polarisation) matrix elements of  $x \pm iy$ . For  $S_4$   $z$  transforms as the  $\Gamma_2$  representation and  $x \pm iy$  as  $\Gamma_{34}$  leading to the electric dipole selection rules

$$\begin{array}{c}
 E.d \\
 \Gamma_1 \\
 \Gamma_2 \\
 \Gamma_3 \\
 \Gamma_4
 \end{array}
 \begin{array}{cccc}
 \Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 \\
 \left( \begin{array}{cccc}
 - & \pi & \sigma & \sigma \\
 \pi & - & \sigma & \sigma \\
 \sigma & \sigma & - & \pi \\
 \sigma & \sigma & \pi & -
 \end{array} \right)
 \end{array}
 \quad (20)$$

For magnetic dipole transitions we need the matrix elements of  $J_z$  for  $\sigma$ -polarisation and  $J_x \pm iJ_y$  for  $\pi$ -polarisation. For  $S_4$   $J_z$  transforms as  $\Gamma_1$  and  $J_x \pm iJ_y$  as  $\Gamma_3, \Gamma_4$  leading to the magnetic dipole selection rules

$$\begin{array}{c}
 M.d \\
 \Gamma_1 \\
 \Gamma_2 \\
 \Gamma_3 \\
 \Gamma_4
 \end{array}
 \begin{array}{cccc}
 \Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 \\
 \left( \begin{array}{cccc}
 \sigma & - & \pi & \pi \\
 - & \sigma & \pi & \pi \\
 \pi & \pi & \sigma & - \\
 \pi & \pi & - & \sigma
 \end{array} \right)
 \end{array}
 \quad (21)$$

The experimental study of the polarisation of transitions gives a further tool for determining the symmetry of the observed levels. Note that the electric dipole transitions are *forced* electric dipole transitions as they nominally occur between states of the same parity. The crystal field potential expansion possesses *odd rank* terms that can mix states of opposite parity. Furthermore, the crystal field can mix states of different  $J$  and  $L$  lifting the  $\Delta J$ ,  $\Delta L = 0, \pm 1$  of the free ion while spin-orbit interaction can lead to a breakdown of the spin selection rule  $\Delta S = 0$ . Magnetic dipole transitions are allowed between states of the same parity. In the free ion in pure  $LS$ -coupling we have the magnetic dipole selection rules

$$\Delta S, \Delta L = 0, \quad \Delta J = 0, \pm 1 \quad (22)$$

Again these selection rules can be broken by spin-orbit interaction and crystal field selection rules. Nevertheless, the selection rules of Eq. (20) and (21) are, in the absence of other interactions, rigorous. An interaction which can break those selection rules is the nuclear hyperfine interaction that can weakly mix close-by crystal field levels.

The nuclear spin of  $Ho$  is half-integer while the electronic angular momentum is integer leading to a net angular momentum in the free ion that is necessarily half-integer. As a result the crystal field levels, in the presence of the hyperfine interaction, will involve states belonging to the double group of  $S_4$ . The additional irreducible representations  $\Gamma_i$   $i = 5, \dots, 8$  are one-dimensional but occur as complex pairs. For electric-dipole transitions the  $\sigma$ -polarisation transitions involve the matrix elements of  $z$  which transforms as the  $\Gamma_2$  irreducible representation while for  $\pi$ -polarisation transitions  $x \pm iy$  transform as the  $\Gamma_3, \Gamma_4$  irreducible representations of  $S_4$  leading to the electric-dipole selection rules for the relevant irreducible representations as

$$\begin{array}{c}
 E.d \\
 \Gamma_5 \\
 \Gamma_6 \\
 \Gamma_7 \\
 \Gamma_8
 \end{array}
 \begin{array}{cccc}
 \Gamma_5 & \Gamma_6 & \Gamma_7 & \Gamma_8 \\
 \left( \begin{array}{cccc}
 - & \sigma & \pi & \sigma \\
 \sigma & - & \sigma & \pi \\
 \pi & \sigma & - & \sigma \\
 \sigma & \pi & \sigma & -
 \end{array} \right)
 \end{array}
 \quad (23)$$

Likewise, for magnetic-dipole transitions we have

$$\begin{array}{c}
 M.d \\
 \Gamma_5 \\
 \Gamma_6 \\
 \Gamma_7 \\
 \Gamma_8
 \end{array}
 \begin{array}{cccc}
 \Gamma_5 & \Gamma_6 & \Gamma_7 & \Gamma_8 \\
 \left( \begin{array}{cccc}
 \sigma & \pi & - & \pi \\
 \pi & \sigma & \pi & - \\
 - & \pi & \sigma & \pi \\
 \pi & - & \pi & \sigma
 \end{array} \right)
 \end{array}
 \quad (24)$$

Taking into account the degeneracy of the pairs  $\Gamma_{56}, \Gamma_{78}$  we see that some of the transitions

will occur in pure  $\pi$ - or  $\sigma$ - polarisation with the rest as  $\sigma\pi$ -polarisation as shown below

$$\begin{array}{l} E.d \quad \Gamma_{56} \quad \Gamma_{78} \\ \Gamma_{56} \begin{pmatrix} \sigma & \sigma\pi \\ \sigma\pi & \sigma \end{pmatrix} \\ \Gamma_{78} \end{array} \quad (25)$$

and

$$\begin{array}{l} M.d \quad \Gamma_{56} \quad \Gamma_{78} \\ \Gamma_{56} \begin{pmatrix} \sigma\pi & \pi \\ \pi & \sigma\pi \end{pmatrix} \\ \Gamma_{78} \end{array} \quad (26)$$

which gives a way of sometimes distinguishing the different symmetries by polarisation measurements. Within the ground  $^5I$  multiplet we expect the transitions within and between the sublevels for  $J = 7, 8$  to exhibit both magnetic dipole and forced electric dipole transitions whereas for transitions from sublevels of  $J = 8$  to levels with  $\Delta J \geq 2$  should exhibit only electric dipole transitions.

## 9. Concluding Remarks

We have attempted to give a simple explanation of the origin of 'forbidden transitions' in crystals containing ions possessing nuclear magnetic moments and show how quite simple calculations can lead to an understanding of the broad features of the hyperfine patterns in crystals. Calculations showing the effects of  $J$ -mixing and hyperfine mixing have been done but not presented in this paper<sup>18</sup>. It is hoped that these notes will be of assistance to those undertaking the task of analysing much of the new data, taken at very high resolution, that is becoming available. The Moscow group has presented interesting data on the effect of different isotopes of  $Li$  on the hyperfine structure<sup>13</sup>. It would be very interesting, and possibly allow simpler interpretation, to substitute for some of the  $F^-$  ions  $H^-$ ,  $D^-$  and  $T^-$  isotopes of hydrogen. Extensive studies of such substitutions have been made by the University of Canterbury group under Dr. G. D. Jones but as yet not applied to magnetic hyperfine studies. There would seem to be a rich future for such studies.

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