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Hyperfine coupling between crystal-field levels in the tetragonal centre of $\text{CaF}_2:\text{Ho}^{3+}$

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Abstract. This paper presents and discusses the high-resolution optical spectrum associated with ${}^5\text{I}_8(\text{A}_1) \Rightarrow {}^5\text{F}_5(\text{E})$, ${}^5\text{I}_8(\text{A}_2) \Rightarrow {}^5\text{F}_5(\text{E})$ transitions of a tetragonal Ho^{3+} centre in CaF_2 . The lowest crystal-field levels in the ground multiplet are two singlets separated by $\sim 1.7 \text{ cm}^{-1}$. With the closeness of the states, the hyperfine interaction gives rise to strongly mixed wavefunctions and anomalously large pseudoquadrupole splittings. The mixing also results in an enhanced magnetic moment associated with the hyperfine components of the singlets and the magnitude is found to depend on the hyperfine level. Consequently, there are separate superhyperfine resonances associated with each of the four non-degenerate hyperfine levels and these resonances were observed by ODNMR techniques when holeburning in the various optical hyperfine lines. More than 30 superhyperfine resonances were detected and they are assigned to interstitial and groups of near-neighbour F^- ions.

1. Introduction

The hyperfine interaction associated with the Ho^{3+} ion is large and when this ion is incorporated in crystals the strength of the hyperfine interaction can be sufficient to give optical transitions with well resolved hyperfine structure (Dieke 1967, Agladze *et al* 1986 a,b and Manson *et al* 1992). In most cases such structure is well understood by considering a single electronic state and treating the hyperfine interaction as a perturbation lifting or partially lifting the $2I + 1$ -fold degeneracy. This approach, however, is not appropriate when electronic levels are very close and the hyperfine interaction causes energy shifts and mixing of the adjacent electronic wavefunctions. The consequence can be irregular spacing of hyperfine lines, transfer of intensity between transitions (Agladze *et al* 1986) and even forbidden lines appearing in the spectrum (Boonyarith *et al* 1992). These effects cannot be explained in terms of a perturbation treatment of individual electronic levels and it is necessary to consider the two electronic states together. When this is done a good understanding of the optical features can be obtained.

An example where there are two electronic states lying adjacent to one another and interacting via the hyperfine interaction is given by a C_{4v} centre in $\text{CaF}_2:\text{Ho}^{3+}$ (defined as A centre by Seebinder and Wright 1979). The hyperfine interaction gives rise to anomalously large pseudoquadrupole splittings of the two ground-state electronic singlets and this is directly reflected in the transitions from the ground state singlets ${}^5\text{I}_8(\text{A}_1)$ and ${}^5\text{I}_8(\text{A}_2)$ to an excited state singlet ${}^5\text{F}_5(\text{A}_1)$ (Martin *et al*

1992). The interaction causes the ground-state singlets to be strongly mixed and results in a transfer of intensity between transitions. Further, the mixing leads to a significant magnetic moment being associated with the ground-state hyperfine levels and the magnitude of this moment is hyperfine-level specific causing there to be a separate set of super-hyperfine transitions with each hyperfine level. The analysis of the optical hyperfine structure and the superhyperfine resonance frequencies in this previous work was given in terms of a second-order perturbation treatment of the pair of electronic states and fair agreement with experiment was obtained.

Whereas the earlier work primarily dealt with a pair of singlet-to-singlet optical transitions ${}^5I_8(A_1) \Rightarrow {}^5F_5(A_1)$, and ${}^5I_8(A_2) \Rightarrow {}^5F_5(A_1)$ the present paper deals with two singlet-to-doublet optical transitions ${}^5I_8(A_1) \Rightarrow {}^5F_5(E)$ and ${}^5I_8(A_2) \Rightarrow {}^5F_5(E)$. The pseudoquadrupole splitting in the ground state is as large as the excited state hyperfine splitting in the excited E state and gives rise to an unusual folded hyperfine transition pattern in the optical spectrum. It is shown, then, that the previous knowledge of the strength of the interaction of the two singlets can again be used to account for the general characteristics of the optical spectrum including intensity transfer effects. However, it is found that whereas the previous perturbation approach gives a general understanding of these effects, the size of the interaction is too large to be treated simply as a perturbation and it is necessary to make a full calculation. This is particularly true for a determination of the magnetic moments associated with the ground-state hyperfine levels and reflected in the various superhyperfine resonances. Thus this paper extends the previous work on the A centre in giving a fuller treatment of the effects of the hyperfine interaction on the ground-state singlets in so far as it affects the optical and superhyperfine spectra. Excellent agreement with the experimental data is obtained.

2. Strongly coupled singlets of C_{4v} symmetry

Following the polarization data and crystal-field analysis of the A centre by Mujaji and Jones (1992), the two lowest states of the ground multiplet are assigned A_1 and A_2 symmetry. Since the dipole hyperfine interaction parameter $A({}^5I_8) \equiv A_8 \sim 0.028 \text{ cm}^{-1}$ (Margarino *et al* 1980) and the next 5I_8 state is separated by $\sim 80 \text{ cm}^{-1}$, it is reasonable to consider the two states in isolation to other states. The two singlet states will therefore experience the combined free-ion, crystal-field, hyperfine and Zeeman Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{free ion}} + \mathcal{H}_{\text{cf}} + \mathcal{H}_{\text{hyperfine}} + \mathcal{H}_{\text{Zeeman}} \quad (1)$$

where $\mathcal{H}_{\text{free ion}}$ describes the interactions amongst the electrons of the free ion, \mathcal{H}_{cf} is the C_{4v} crystal-field Hamiltonian, and the hyperfine Hamiltonian $\mathcal{H}_{\text{hyperfine}}$ is given by

$$\begin{aligned} \mathcal{H}_{\text{hyperfine}} = \mathcal{H}_M + \mathcal{H}_Q + \mathcal{H}_{Q'} = h \{ & A_{\parallel} I_z J_z + \frac{1}{2} A_{\perp} (I_+ J_- + I_- J_+) \} \\ & + P_{4f} \{ 2(\mathbf{J} \cdot \mathbf{I})^2 + \mathbf{J} \cdot \mathbf{I} - \frac{2}{3} J(J+1)I(I+1) \} \\ & + P_{3ff} \{ I_z^2 - \frac{1}{3} I(I+1) \} \end{aligned} \quad (2)$$

where A_{\parallel} , A_{\perp} and P_{4f} are the dipole and quadrupole contributions, respectively, to the hyperfine interaction between the rare-earth nucleus and its host ion (Carboni

et al 1988), and P_{latt} is the direct quadrupole interaction between the quadrupole moment of the ^{165}Ho nucleus and the electric-field gradient produced by the lattice ions. The Zeeman Hamiltonian \mathcal{H}_{Zeeman} for well separated multiplets is of the form

$$\mathcal{H}_{Zeeman} = g_J \mu_B \mathbf{J} \cdot \mathbf{H}_{app} + g_n \mu_n \mathbf{I} \cdot \mathbf{H}_{app} \quad (3)$$

with μ_B (μ_n) the Bohr (nuclear) magneton, and g_J (g_n) the electronic (nuclear) spectroscopic splitting factors within a particular multiplet. With regard to the multiplets Mujaji and Jones (1992) have calculated the intermediate coupled Ho^{3+} free-ion wavefunctions using the known energy levels for the A centre. For the 5I_8 ground multiplet the electronic wavefunctions are of the form $0.9674|^5I_8\rangle - 0.2203|^3K2_8\rangle + \dots$, where the basis states are given by the Russell-Saunders coupling scheme.

The axial angular momentum operator J_Z transforms according to the A_2 irreducible representation of the C_{4v} group (Koster *et al* 1963) and, hence, the dipole hyperfine interaction will only give non-zero values for mixing between A_1 and A_2 states and between B_1 and B_2 states: i.e. $A_1 \otimes A_2 \supset A_2$, and $B_1 \otimes B_2 \supset A_2$. Thus, looking at the form of the Hamiltonian and noting that P_{4f} , $P_{latt} \ll A_{\parallel} \simeq A_{\perp} = A_8$, the two singlets will predominantly mix, in zero field, via the dipole hyperfine interaction with a matrix element of the form

$$\langle \frac{7}{2}, m | \langle \Psi_{A2} | A_8 J_z J_z | \Psi_{A1} \rangle | \frac{7}{2}, m \rangle = A_8 m \langle J_z \rangle_{1,2} \quad (3)$$

where $\langle J_z \rangle_{1,2}$ gives the effective angular momentum as a result of the interaction between the two singlet states $|\Psi_{A1}\rangle$ and $|\Psi_{A2}\rangle$. The combined Hamiltonian thus couples the two singlets in the form

$$\begin{aligned} \mathcal{H}_{TOT} |\Psi_{A1}\rangle | \frac{7}{2}, m \rangle &= (E_0 - \Delta + P_1 \{ m^2 - \frac{21}{4} \} + g_n \mu_n m H_z) |\Psi_{A1}\rangle | \frac{7}{2}, m \rangle \\ &+ (A_8 m + g_B \mu_B H_z) \langle J_z \rangle_{1,2} |\Psi_{A2}\rangle | \frac{7}{2}, m \rangle \end{aligned} \quad (3a)$$

$$\begin{aligned} \mathcal{H}_{TOT} |\Psi_{A2}\rangle | \frac{7}{2}, m \rangle &= (E_0 + \Delta + P_2 \{ m^2 - \frac{21}{4} \} + g_n \mu_n m H_z) |\Psi_{A2}\rangle | \frac{7}{2}, m \rangle \\ &+ (A_8 m + g_B \mu_B H_z) \langle J_z \rangle_{1,2} |\Psi_{A1}\rangle | \frac{7}{2}, m \rangle \end{aligned} \quad (3b)$$

where $E_0 - \Delta$ is the effect of the free-ion and crystal-field terms on Ψ_{A1} where $(E_0 + \Delta)$ is the effect of the free-ion and crystal-field terms on Ψ_{A2} , $P_1 \cong P_{latt} + P_{4f}(\langle J_z^2 \rangle_{1,1} - 24)$ and $P_2 \cong P_{latt} + P_{4f}(\langle J_z^2 \rangle_{2,2} - 24)$ (Carboni *et al* 1988), and the axial hyperfine and Zeeman interactions couple the two singlets.

The eigenvalues in zero applied field are given by

$$\begin{aligned} E_{A2,A1}(m) &= E_0 + \frac{1}{2}(P_1 + P_2)(m^2 - \frac{21}{4}) \\ &\pm \sqrt{(\Delta - \frac{1}{2}(P_1 - P_2) \{ m^2 - \frac{21}{4} \})^2 + (A_8 m \langle J_z \rangle_{1,2})^2} \end{aligned} \quad (4)$$

and their associated wavefunctions are

$$\begin{aligned} |\Psi_{A2,A1}\rangle | \frac{7}{2}, m \rangle &= [A_8 m \langle J_z \rangle_{1,2} \\ &\times ((A_8 m \langle J_z \rangle_{1,2})^2 + [E_{A2,A1} - E_0 - P_1 \{ m^2 - \frac{21}{4} \} + \Delta]^2)^{-1/2}] \\ &\times |\Psi_{A2}\rangle | \frac{7}{2}, m \rangle + [(E_{A2,A1} - E_0 - P_1 \{ m^2 - \frac{21}{4} \} + \Delta) \\ &\cdot \times ((A_8 m \langle J_z \rangle_{1,2})^2 + [E_{A2,A1} - E_0 - P_1 \{ m^2 - \frac{21}{4} \} + \Delta]^2)^{-1/2}] |\Psi_{A1}\rangle | \frac{7}{2}, m \rangle \end{aligned} \quad (5)$$

Note that, by symmetry, $\langle J_z \rangle_{1,2} = \langle J_z \rangle_{2,1}$. Such hyperfine coupling between two singlets has been discussed previously by Bleaney (1973) and Martin *et al* (1992). In both papers, however, the eigenvalues were approximated into truncated power series which is insufficient to describe the coupling between the singlets in the A centre.

3. Optical transition energies and intensities to an excited-state doublet

One of the low-lying levels of the 5F_5 multiplet is an E doublet separated from other states by 4.5 cm^{-1} and 13.5 cm^{-1} to lower and higher energy, respectively (figure 2). There is no evidence of interaction between these states and, hence, the doublet will be treated as an isolated state. Under the influence of the free-ion interactions, the C_{4v} crystal field, the hyperfine interaction, the direct quadrupole interaction, and the external magnetic field, the doublet resolves into

$$\begin{aligned} \mathcal{H}_{\text{TOT}}|\Theta_E\rangle_{\frac{7}{2}, m} &= [E_5 + (A_5 m + g_5 \mu_B H_z) \langle J_z \rangle_\theta + P_3(m^2 - \frac{21}{4})] |\Theta_E\rangle_{\frac{7}{2}, m} \\ &= E_E(m) |\Theta_E\rangle_{\frac{7}{2}, m} \end{aligned} \quad (6a)$$

$$\begin{aligned} \mathcal{H}_{\text{TOT}}|\Theta_{E'}\rangle_{\frac{7}{2}, m} &= [E_5 - (A_5 m + g_5 \mu_B H_z) \langle J_z \rangle_\theta + P_3(m^2 - \frac{21}{4})] |\Theta_{E'}\rangle_{\frac{7}{2}, m} \\ &= E_{E'}(m) |\Theta_{E'}\rangle_{\frac{7}{2}, m} \end{aligned} \quad (6b)$$

where the subscript 5 indicates that the crystal-field terms, the hyperfine interaction, and g -factor vary from one multiplet to another and, in this case, are associated with the 5F_5 multiplet; $|\Theta_E\rangle$ and $|\Theta_{E'}\rangle$ are time reversal conjugate wavefunctions, the effect of the neighbouring singlet will be a small pseudoquadrupole term which can be considered as part of the quadrupole constant P_3 (Baker and Bleaney 1958), and the magnetic moment within each of the states of the E doublets is proportional to $\langle J_z \rangle_\theta$, the effective angular momentum of the doublet state. Finally, the intermediate coupled wavefunctions of the 5F_5 multiplet are known to exhibit significant J -mixing and for the A centre Mujaji and Jones (1992) estimate the free-ion wavefunction to be $0.8946|^5F_5\rangle - 0.3158|^3G_2\rangle + \dots$

The optical transition energies between the ground-state singlets and the excited-state doublet, in zero field, are therefore of the form

$$\begin{aligned} E_E(m) - E_{A_1, A_2}(m) &= E_5 - E_0 + A_5 m \langle J_z \rangle_\theta + [P_3 - \frac{1}{2}(P_1 + P_2)](m^2 - \frac{21}{4}) \\ &\pm \sqrt{[\Delta - \frac{1}{2}(P_1 - P_2)(m^2 - \frac{21}{4})]^2 + (A_8 m \langle J_z \rangle_{1,2})^2} \end{aligned} \quad (7)$$

$$\begin{aligned} E_{E'}(m) - E_{A_1, A_2}(m) &= E_5 - E_0 - A_5 m \langle J_z \rangle_\theta + [P_3 - \frac{1}{2}(P_1 + P_2)] \\ &\times (m^2 - \frac{21}{4}) \pm \sqrt{[\Delta - \frac{1}{2}(P_1 - P_2)(m^2 - \frac{21}{4})]^2 + (A_8 m \langle J_z \rangle_{1,2})^2} \end{aligned} \quad (8)$$

As will be shown later, the parameters contained in equations (4), (6), (7) and (8) can be estimated by fitting the spectrum associated with the ${}^5I_8(A_1) \Rightarrow {}^5F_5(E)$, ${}^5I_8(A_2) \Rightarrow {}^5F_5(E)$ transitions.

In addition to fitting the energies of the hyperfine-resolved optical transitions, the intensity variation needs also to be replicated. The electric-dipole transitions observed

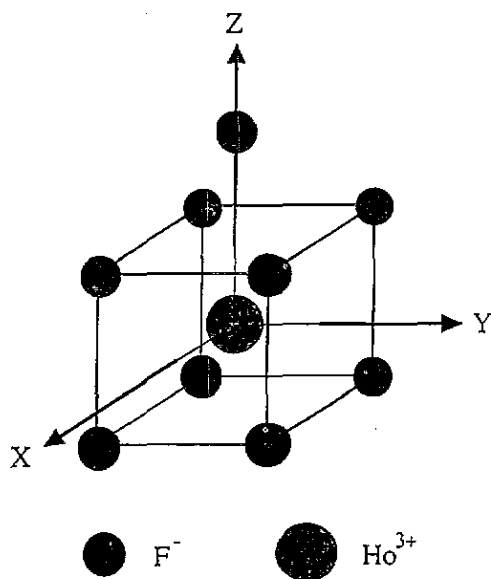


Figure 1. The structure of the C_{4v} centre $\text{CaF}_2:\text{Ho}^{3+}$

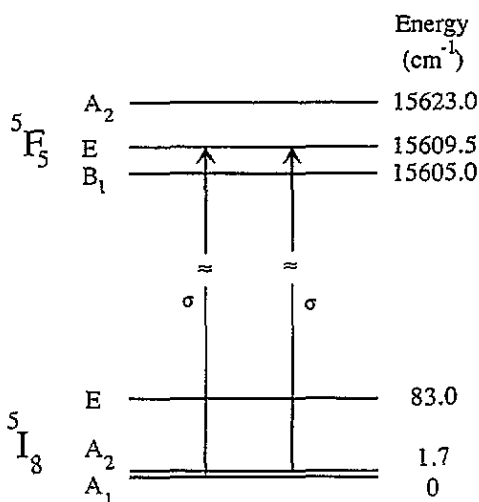


Figure 2. Energy level structure of the lower levels of the 5I_8 and 5F_5 multiplets.

within an $4f^n$ configuration are induced by the odd-parity terms in the crystal-field Hamiltonian (Judd 1962, Ofelt 1962). The transition matrix elements are therefore related by symmetry considerations. In particular, $A \Rightarrow E$ transitions are allowed by the transverse electric-dipole component and group theory gives the following relationships between the electric-dipole matrix elements (Koster *et al* 1963)

$$\langle A_1 | \mathbf{D}^+ | E \rangle = \langle A_1 | \mathbf{D}^- | E' \rangle = M \quad (9)$$

$$\langle A_2 | \mathbf{D}^+ | E \rangle = -\langle A_2 | \mathbf{D}^- | E' \rangle = N \quad (10)$$

where \mathbf{D}^+ (\mathbf{D}^-) is the right (left) circularly polarized electric-dipole operator. Thus the electric-dipole matrix elements for transitions from an A_1 state to the two components of an E state have the same magnitude and phase, whereas those for transitions from an A_2 state to the two components of an E state have the same magnitude but opposite phase.

The transition intensities are given by

$$I_{\nu} \propto |\langle f | \mathbf{D} | i \rangle|^2 (\rho_i - \rho_f) \delta(E - h\nu) \quad (11)$$

where $\langle f | \mathbf{D} | i \rangle$ is the electric-dipole matrix element linking the initial and final states, and ρ_i and ρ_f are the populations of the initial and final states. The projection number m of the nuclear spin is conserved during the electric-dipole transition but, with the mixing of the states by the hyperfine interaction, the transition matrix elements take the following form

$$\langle \frac{7}{2}, m | \langle \Theta_E | \mathbf{D} | \Psi_{A1} \rangle | \frac{7}{2}, m \rangle = a(m)M + b(m)N \quad (12a)$$

$$\langle \frac{7}{2}, m | \langle \Theta_{E'} | \mathbf{D} | \Psi_{A1} \rangle | \frac{7}{2}, m \rangle = a(m)M - b(m)N \quad (12b)$$

$$\langle \frac{7}{2}, m | \langle \Theta_E | \mathbf{D} | \Psi_{A2} \rangle | \frac{7}{2}, m \rangle = c(m)M + d(m)N \quad (12c)$$

$$\langle \frac{7}{2}, m | \langle \Theta_{E'} | \mathbf{D} | \Psi_{A2} \rangle | \frac{7}{2}, m \rangle = c(m)M - d(m)N \quad (12d)$$

where the factors $a(m)$, $b(m)$, $c(m)$ and $d(m)$ are just the wavefunction mixing coefficients of the two ground-state singlets given in expression (5).

4. Experimental results and discussion

The sample was a 5 mm × 4 mm × 2 mm single crystal of Ho³⁺ doped (0.0005%) CaF₂ grown by the Bridgeman technique. It was cooled to temperatures of 1.6–4.2 K in a helium bath cryostat and irradiated with a Coherent 699-21 ring dye laser (linewidth ~ 2 MHz) in the wavelength region of the ⁵I₈ ⇒ ⁵F₅ transition. The excitation spectrum was subsequently detected by observation of the emission at 644.6 nm corresponding to transitions from the excited-state doublet to a high level of the ground multiplet. The light emitted was dispersed by a double-pass Spex spectrometer with a resolution of 0.3 nm and detected by an EMI 9958 thermoelectrically cooled photomultiplier. The laser was scanned in frequency by up to 20 GHz and the signal-to-noise of the observed optical spectrum was improved by averaging many scans in a Princeton Applied Research 4202 signal averager.

For the ODNMR experiments, the Coherent 699-21 laser was operated at a fixed frequency and caused bleaching of the absorption corresponding to a subgroup of Ho³⁺ ions within the sample. The single crystal was placed inside a five-turn coil within the cryostat and, while the laser was continuously burning a spectral hole, was subjected to swept radiofrequency radiation. The radiofrequency signal (0–30 MHz) was produced by a Hewlett Packard 8443A tracking generator and amplified by an ENI power amplifier (50 dB, 0.25–110 MHz). The magnitude of the emission signal was recorded by the signal averager and averaged for repeated sweeps of the radiofrequency radiation.

For the ⁵I₈(A₁) ⇒ ⁵F₅(E) and ⁵I₈(A₂) ⇒ ⁵F₅(E) optical transitions (figure 3(a)), 10 hyperfine lines can be observed along with a shoulder on one component. This data are in agreement with those reported by Hasan (1990). The interesting aspect of this spectrum is the apparent discrepancy with the 16 hyperfine lines predicted in equations (7) and (8). There is, however, a superposition of some of the transitions as can be noted from the fact that the inner lines have markedly higher intensity. The extreme lines of the spectrum though, A and K, are clearly single transitions and, therefore, can be readily assigned. For example, from equations (7) and (8), it can be observed that the highest-energy transition A is unambiguously given by the degenerate pair of transitions $|\Psi_{A1}\rangle_{\frac{7}{2}, \frac{7}{2}} \Rightarrow |\Theta_E\rangle_{\frac{7}{2}, \frac{7}{2}}$ and $|\Psi_{A1}\rangle_{\frac{7}{2}, -\frac{7}{2}} \Rightarrow |\Theta_{E'}\rangle_{\frac{7}{2}, -\frac{7}{2}}$. Similarly, the lowest-energy transition K is given by the pair $|\Psi_{A2}\rangle_{\frac{7}{2}, -\frac{7}{2}} \Rightarrow |\Theta_{E'}\rangle_{\frac{7}{2}, -\frac{7}{2}}$ and $|\Psi_{A2}\rangle_{\frac{7}{2}, \frac{7}{2}} \Rightarrow |\Theta_E\rangle_{\frac{7}{2}, \frac{7}{2}}$.

The next symmetrical pair of transitions, B and J, even if accepted as single hyperfine transitions, can no longer be unambiguously assigned to a given nuclear spin state. These transitions could be associated with the nuclear spin $\pm\frac{5}{2}$ projections or, alternatively, they could be associated with the second set of transitions involving the $\pm\frac{7}{2}$ projections. The correct choice depends particularly on the values of the three parameters $A_5\langle J_Z \rangle_\theta$, Δ and $A_8\langle J_Z \rangle_{1,2}$ for this centre. Note that the almost mirror symmetry of the spectrum (figure 3(a)) implies that all the quadrupole interactions are small.

The ODNMR spectra shown in figures 5 and 6, however, can be used to identify the nuclear spin state associated with the various spectral lines. As has been discussed in the previous paper (Martin *et al* 1992) and will also be discussed more fully in the

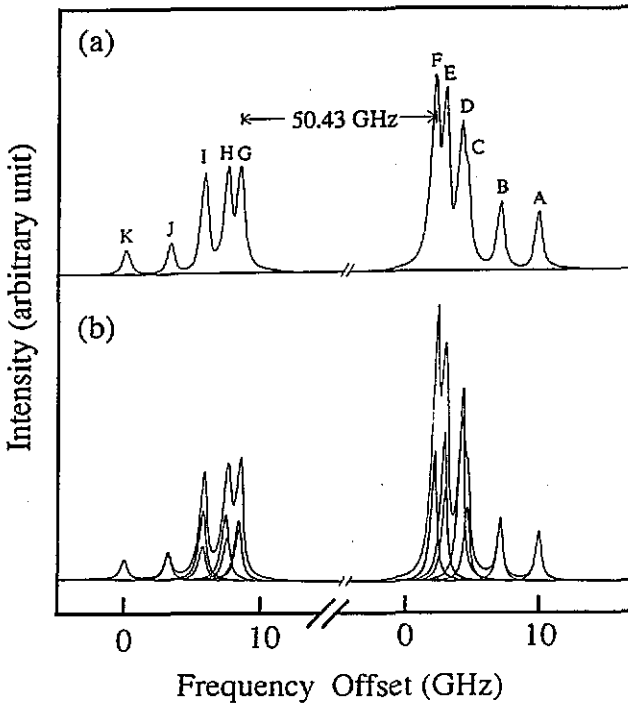


Figure 3. (a) The low-temperature excitation spectrum of the ${}^5\text{I}_8(\text{A}_1) \Rightarrow {}^5\text{F}_5(\text{E})$, ${}^5\text{I}_8(\text{A}_2) \Rightarrow {}^5\text{F}_5(\text{E})$ optical transitions. (b) Theoretical spectrum of the above transitions using the parameters given in the text.

next section, a particular property of the superhyperfine resonances for the A centre is that they are very sensitive to the hyperfine state of the holmium ion. Figures 5 and 6 can, therefore, be used to assign hyperfine state labels to all the optical lines in the ${}^5\text{I}_8(\text{A}_1) \Rightarrow {}^4\text{F}_5(\text{E})$ and ${}^5\text{I}_8(\text{A}_2) \Rightarrow {}^5\text{F}_5(\text{E})$ transitions, respectively. For example, by using figure 5, the hyperfine line B is shown to be associated with nuclear $\pm\frac{5}{2}$ states. Other lines can be assigned in this way.

The separation between the unperturbed singlets, 2Δ , is approximately known, and it is established by the symmetry of the optical lines that quadrupole effects are small. This means that the optical transition energies are, therefore, mainly determined by just two parameters, $A_5\langle J_Z \rangle_\theta$ and $A_8\langle J_Z \rangle_{1,2}$, and an estimate of these can be obtained when just a few lines are assigned. Employing equations (7) and (8) therefore, the following values for the parameters were established: $\Delta = 25.61(35)$ GHz, $A_8\langle J_Z \rangle_{1,2} = 4.72(15)$ GHz, $A_5\langle J_Z \rangle_\theta = 0.826(11)$ GHz, $P_3 - (P_1 + P_2)/2 = -0.024(5)$ GHz and $P_1 - P_2 \approx 0$. The energy level and line spectrum pattern are given in figures 4(a) and 4(b), respectively.

Note the value for $A_8\langle J_Z \rangle_{1,2}$ compares reasonably with the (rescaled) value 4.90(5) GHz obtained by Kornienko and Rybaltovskii (1972) using EPR. Given the current value for $A_8\langle J_Z \rangle_{1,2}$ and the value for A_8 obtained by Margarino *et al* (1980) in $\text{LiYF}_4:\text{Ho}^{3+}$, the value for the matrix element $\langle J_Z \rangle_{1,2}$ is estimated to be 5.62. This calculation is supported by the measured g_{\parallel} value of Kornienko and Rybaltovskii (1972). Since g_{\parallel} is equivalent to $g_8\langle J_Z \rangle_{1,2}$ where $g_8 = 1.2427$ for the intermediate coupled ${}^5\text{I}_8$ multiplet (Mujaji and Jones 1992), using the g_{\parallel} obtained by

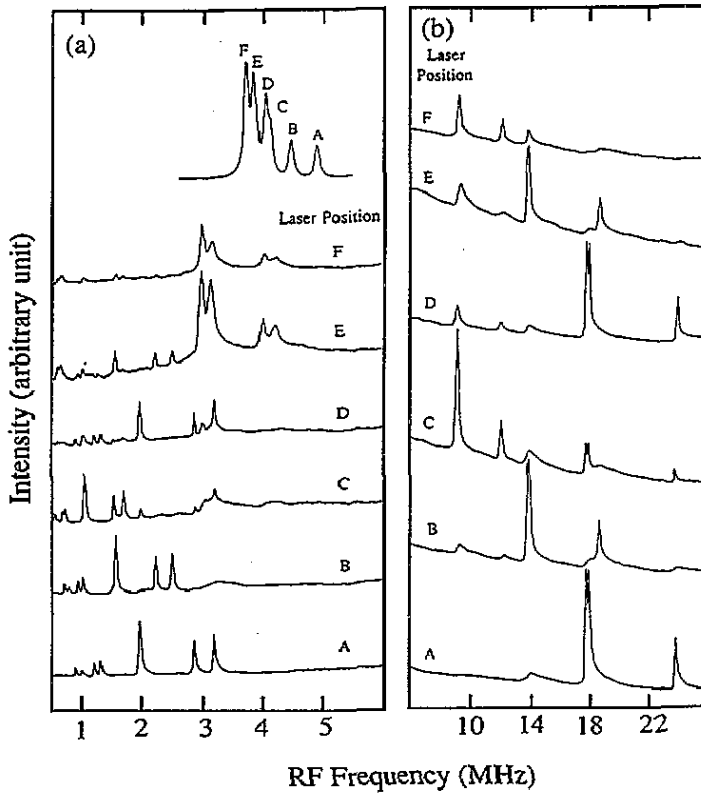


Figure 5. Superhyperfine resonances detected via ODNMR. (a) 0.5–6 MHz and (b) 6–26 MHz. Spectra shown correspond to holeburning at six different wavelengths, A–F (as indicated), within the ${}^5I_8(A_1) \Rightarrow {}^5F_5(E)$ transition.

hyperfine transition of the two singlets is assigned a linewidth of Lorentzian shape with $\sigma = 0.3$ and 0.25 GHz, respectively and the mixing coefficients $a(m)$, $b(m)$, $c(m)$ and $d(m)$ (equations (5) and (12)) were calculated using the fitted parameters. As can be seen this predicted spectrum is in good agreement with the experimental spectrum in figure 3(a). The remaining differences between experiment and theory can be attributed to the assumption about populations of the states, variation in laser intensity with frequency and, the error in estimating the base line or zero-intensity level. The fitted ratio of $M/N = 1$ shows that in the absence of hyperfine interactions the two transitions from the A_1 and A_2 states to the E doublet in the 5F_5 multiplet would have equal intensity. This presumably arises because the singlet states $|\Psi_{A1}\rangle$ and $|\Psi_{A2}\rangle$, have essentially the same magnitude in their coefficients for each $|J, J_Z\rangle$ component of their wavefunctions (Mujaji and Jones 1992). By symmetry, therefore, the odd-parity components of $|\Psi_{A1}\rangle$ and $|\Psi_{A2}\rangle$ should also have the same magnitude and this would result in equal transition intensities to a doublet state.

The unusual hyperfine structure is, therefore, explained primarily in terms of one hyperfine splitting parameter of the excited state, one off-diagonal hyperfine parameter between the ground-state levels and one intensity parameter. Although the correspondence can be improved by including some quadrupole interaction in the

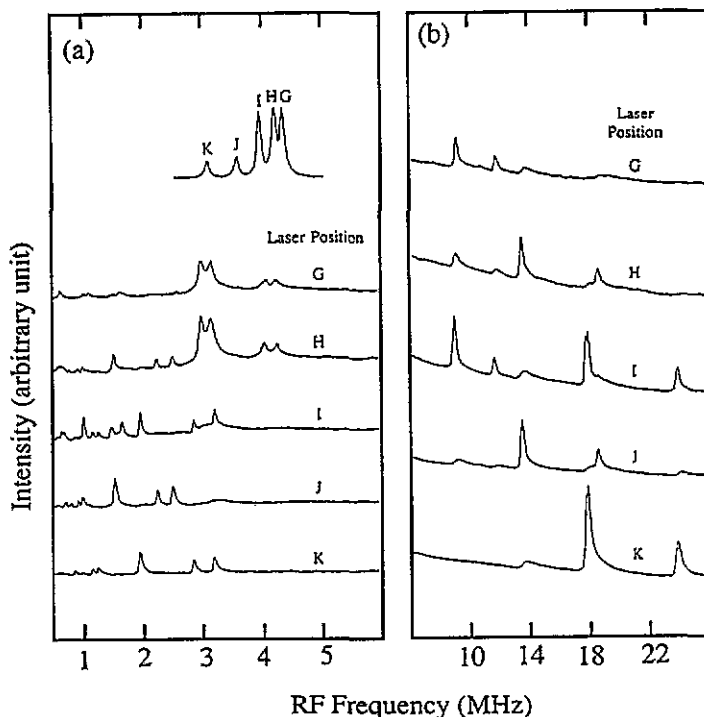


Figure 6. Superhyperfine resonances associated with the ${}^5I_8(A_2) \Rightarrow {}^5F_5(E)$ transition.

excited multiplet, the essence of the agreement between the predicted line shape and experiment is achieved by a model with only three adjustable parameters.

5. Superhyperfine resonance frequencies in strongly coupled singlets

As the fluorine nuclei in the neighbourhood of the Ho^{3+} ion also experience a magnetic field from the rare-earth ion, and vice versa, the full spin Hamiltonian for the system is then

$$\mathcal{H}_{\text{system}} = \mathcal{H}_{\text{TOT}} + \sum_i g_n \mu_n \mathbf{H}_{\text{app}} \cdot \mathbf{F}_i + \sum_{i,j} \mathbf{F}_i \cdot \mathbf{D} \cdot \mathbf{F}_j + \sum_i \mathbf{J} \cdot \mathbf{A} \cdot \mathbf{F}_i + \sum_i \mathbf{I} \cdot \mathbf{d} \cdot \mathbf{F}_i \quad (15)$$

where \mathcal{H}_{TOT} is given by equation (1), the additional terms describe the interaction of the neighbouring fluorine ions with the external field (\mathbf{H}_{app}), other fluorine nuclei, the electronic state of the rare-earth ion, and the holmium nucleus (Baker 1974), respectively. Note that the superhyperfine interaction term \mathbf{A} , particularly for nearest neighbours, can obtain both dipole and exchange contributions (Baker 1974).

A great simplification of equation (15) can be afforded by using the observation that the rare-earth ion in the two electronic singlet states exerts an enormous field

~ 0.1 T on the neighbouring ions. Under these circumstances, the Hamiltonian for an individual fluorine ion can be approximated by

$$\mathcal{H}_i \approx \mathbf{J} \cdot \mathbf{A} \cdot \mathbf{F}_i \approx A_{\parallel} J_z F_{i,z} \quad (16)$$

This is similar to the Zeeman approximation in ordinary NMR analysis where the interaction amongst the fluorine nuclei is treated as a perturbation. It will be shown that equation (16) explains the major hyperfine dependence of the superhyperfine resonances.

Another way of understanding the interaction of the fluorine nuclei with the rare-earth ion via equation (16) is that the fluorine nuclei sees the magnetic field generated by the effective magnetic moment of the rare-earth ion (possibly enhanced by exchange effects). The strength of the field scales as the magnetic moment of the ion which, for the present system, varies from one hyperfine level to another. For well separated A_1 and A_2 states, by using second-order perturbation theory, the magnitude of the effective magnetic moment for the ^{165}Ho hyperfine levels are

$$\langle \frac{7}{2}, \pm m | \langle \Psi_{A1} | \mu_m | \Psi_{A1} \rangle | \frac{7}{2}, \pm m \rangle = \pm m [g_n \mu_n + A_8 g_8 \mu_B \langle J_z \rangle_{2,1}^2 / \Delta] = \pm m \mu_{\text{eff}, A1} \quad (17)$$

$$\langle \frac{7}{2}, \pm m | \langle \Psi_{A2} | \mu_m | \Psi_{A2} \rangle | \frac{7}{2}, \pm m \rangle = \pm m [g_n \mu_n - A_8 g_8 \mu_B \langle J_z \rangle_{2,1}^2 / \Delta] = \pm m \mu_{\text{eff}, A2} \quad (18)$$

where $\mu_m = \mu_B(L + g_s S) + \mu_n g_n I \approx \mu_B g_J J + \mu_n g_n I$, and m is the nuclear-spin projection number of the holmium nucleus. Thus, the neighbouring nuclei will experience a different magnetic field depending on the hyperfine state of the Ho^{3+} ion. From equation (17) and (18), it can be seen that the size of the ion's effective magnetic moment for the hyperfine levels $\pm \frac{7}{2}$, $\pm \frac{5}{2}$, $\pm \frac{3}{2}$, and $\pm \frac{1}{2}$ varies in the ratio 7:5:3:1. Note that if $g_n \mu_n \sim A_J g_J \mu_B (\langle J_z \rangle_{2,1})^2 / \Delta$ then the hyperfine levels of the two singlets will exhibit different effective magnetic moments. It should also be mentioned that while the individual hyperfine levels of the singlet have non-zero magnetic moments the sum of the moments is zero (as must be the case).

In the present system, however, the coupling between the singlets is significant, and the first-order and second-order approximations are not sufficient. (Bleaney (1973), Martin *et al* 1992). For the two coupled singlets of the C_{4v} centre in $\text{CaF}_2:\text{Ho}^{3+}$, the moments are given by

$$\begin{aligned} \langle \frac{7}{2}, m | \langle \Psi_{A1} | \mu_m | \Psi_{A1} \rangle | \frac{7}{2}, m \rangle &= a(m)b(m)[g_8 \mu_B \langle J_z \rangle_{1,2} + g_8 \mu_B \langle J_z \rangle_{2,1}] + g_n \mu_n m \\ &= 2a(m)b(m)g_8 \mu_B \langle J_z \rangle_{1,2} + g_n \mu_n m \end{aligned} \quad (19a)$$

$$\begin{aligned} \langle \frac{7}{2}, m | \langle \Psi_{A2} | \mu_m | \Psi_{A2} \rangle | \frac{7}{2}, m \rangle &= c(m)d(m)[g_8 \mu_B \langle J_z \rangle_{1,2} + g_8 \mu_B \langle J_z \rangle_{2,1}] + g_n \mu_n m \\ &= 2c(m)d(m)g_8 \mu_B \langle J_z \rangle_{1,2} + g_n \mu_n m \end{aligned} \quad (19b)$$

where μ_m , $\langle J_z \rangle_{1,2}$ and m are as defined earlier and $a(m)$, $b(m)$, $c(m)$ and $d(m)$ are the mixing coefficients of $|\Psi_{A1}\rangle$ and $|\Psi_{A2}\rangle$ given in equation (5). Since $m \mu_n \ll a(m)b(m)\mu_B \langle J_z \rangle_{1,2}$ for the coupled singlets, the field experienced by the fluorine nucleus, therefore, scales with the Bohr magneton and the effective magnetic moment of the rare-earth ion which depends on the nuclear state. Using equation (19)

and the parameters obtained earlier, in zero magnetic field, it is predicted that the effective magnetic moments of the hyperfine levels will be in the ratio 5.79:4.47:2.85:1. The reduction of the relative size of the magnetic moment for the $\frac{7}{2}$ hyperfine level in particular is too large to be adequately handled by the second-order perturbation approaches of Bleaney (1973) and Martin *et al* (1992).

6. ODNMR measurements and discussion

The superhyperfine ODNMR signals are shown in figures 5 and 6. These signals arise as a consequence of the optical pumping cycle causing a depopulation of one of the superhyperfine levels and, hence, a loss of absorption at the laser wavelength. When RF is applied at the superhyperfine frequency some of the population is restored and, with its subsequent laser absorption, the emission increases. It can be seen, as discussed earlier and as predicted in the above analysis, that various resonances appear depending on the wavelength of the holeburning laser. This variation is a consequence of the changes in the effective magnetic moment in the ground-state hyperfine levels. A separate set of lines is, therefore, obtained for holeburning associated with each of the four hyperfine levels. For example, holeburning in one of the extreme spectral lines, such as line A, depopulates the $\pm\frac{7}{2}$ nuclear hyperfine levels and gives resonances at 23.9, 17.74, 17.54, 3.20, 2.85, 1.94, 1.28, 1.19, 1.02, and 0.90 MHz. Such a set of lines comprises resonances arising from the interstitial F^- ion and various groups of neighbouring F^- ions. It is noted that the sequence of frequencies is analogous to that obtained for the superhyperfine resonances of the C_{4v} centre in $CaF_2:Pr^{3+}$ reported by Burum *et al* (1982) and, guided by this work, most of the above resonances can be assigned. The resonance at 23.9 MHz is associated with the interstitial F^- ion along the C_{4v} axis as shown in figure 1. The resonances at 17.74 and 17.54 MHz are associated with the nearest-neighbour (NN) F^- ions in figure 1. The four NN F^- ions between the Ho^{3+} ion and interstitial F^- ion are crystallographically equivalent, and, therefore, give one resonance. The other four NN F^- ions furthest from the interstitial F^- ion are, likewise, crystallographically equivalent to each other and give the other resonance. It is worth noting that the observed larger intensity ($\sim 2x$) of the NN superhyperfine resonances compared to the interstitial superhyperfine resonance is to be expected given the presence of four equivalent NN ions compared to only one interstitial ion.

Beyond the NN and interstitial F^- ions, it is expected, in the paramagnetic material, that the dipolar field from the magnetic moment of the Ho^{3+} ion becomes the dominant term compared to any exchange contribution. This assumption is supported by a comparison of the observed superhyperfine resonances at 3.20, 2.85, 1.94 MHz with the three next-nearest-neighbour (NNN) resonances reported by Burum *et al* (1982). There is a scaling factor of 2.21(6) between the NNN resonances of the two centres which correlates with the larger moment present in the A centre of $CaF_2:Ho^{3+}$. Thus, again, using Burum *et al*, (1982), the 3.20 MHz resonance can be assigned to the four NNN F^- ions furthest from the interstitial, the 2.85 MHz resonance to the four NNN F^- ions closest to the interstitial while the 1.94 MHz belongs to the other sixteen NNN F^- ions. The latter assignment, in particular, is strengthened by the observed larger intensity ($\sim 2x$) of the 1.94 MHz resonance compared to the 3.20 and 2.85 MHz resonances. Such a relative change in intensities is consistent with the assignment of sixteen, four and four NNN ions, respectively,

to the above resonances and with the observed relative intensities of the NN and interstitial resonances mentioned earlier.

When the selected optical transition involves the ground-state $\pm\frac{5}{2}$ nuclear levels, there is a consistent reduction in the frequencies of the observed superhyperfine resonances. They now occur at 18.35, 13.58, 13.48, 2.49, 2.22, 1.53, 1.02, 0.95, 0.82, and 0.70 MHz. As indicated in the previous section, the change in frequencies is a consequence of the change in the Ho^{3+} magnetic moment. It was also observed that there is a different set of superhyperfine frequencies for the $\pm\frac{3}{2}$ nuclear levels and, likewise, for the $\pm\frac{1}{2}$ nuclear levels (see figures 5 and 6). The superhyperfine resonances are all summarized in table 1 where it is further shown that the relative change in observed frequencies involving the different hyperfine levels is very close to that predicted using equations (19).

Table 1. Observed superhyperfine frequencies and comparison with scaled values.

Frequency (MHz)		
Experimental interstitial	Theoretical	Hyperfine level
23.49	23.49 ^a	$\pm\frac{7}{2}$
18.35	18.14	$\pm\frac{5}{2}$
11.71	11.57	$\pm\frac{3}{2}$
4.21, 4.00	4.06	$\pm\frac{1}{2}$
Nearest neighbours		
17.74, 17.54	17.74 ^a , 17.54 ^a	$\pm\frac{7}{2}$
13.58, 13.48	13.70, 13.54	$\pm\frac{5}{2}$
8.80	8.74, 8.64	$\pm\frac{3}{2}$
3.15, 3.00	3.07, 3.03	$\pm\frac{1}{2}$
Second-shell neighbours		
3.20, 2.85, 1.94	3.20 ^a , 2.85 ^a , 1.94 ^a	$\pm\frac{7}{2}$
2.49, 2.22, 1.53	2.47, 2.20, 1.50	$\pm\frac{5}{2}$
1.53, 1.45, 1.02	1.58, 1.40, 0.96	$\pm\frac{3}{2}$
	0.55, 0.49, 0.34	$\pm\frac{1}{2}$
Third-shell neighbours		
1.28, 1.19, 1.02, 0.90	1.28 ^a , 1.19 ^a , 1.02 ^a , 0.90 ^a	$\pm\frac{7}{2}$
1.02, 0.95, 0.82, 0.70	0.99, 0.92, 0.79, 0.69	$\pm\frac{5}{2}$
0.70, 0.65, 0.52	0.63, 0.59, 0.50, 0.44	$\pm\frac{3}{2}$
	0.22, 0.21, 0.18, 0.16	$\pm\frac{1}{2}$

^a Values chosen to match experimental values. Following values are then scaled according to the ratio of the predicted effective magnetic moment of the Ho^{3+} ion within each hyperfine level of the ground-state singlets.

One important anomaly in the observed ODNMR spectrum, however, is the presence of resolved 206 kHz (150 kHz) splittings in the interstitial (NN) superhyperfine resonances for the spin $\pm\frac{1}{2}$ state of the holmium nucleus. In the previous paper (Martin *et al* 1992), these splittings were discussed and briefly explained in terms of the more general Hamiltonian of equation (15). A closer examination of the effect of the Hamiltonian (15) on the basis states $|A_i\rangle|I, +\frac{1}{2}\rangle|F, -\frac{1}{2}\rangle$ and $|A_i\rangle|I, -\frac{1}{2}\rangle|F, +\frac{1}{2}\rangle$ reveals that the diagonal flip-flop interaction between the holmium and fluorine nuclei, $-(d/4)\{I^+F^- + I^-F^+\}$, lifts

the degeneracy of the superhyperfine states of the spin $\pm\frac{1}{2}$ hyperfine states of a singlet. Such an interaction has been previously known to occur for AX spin systems (Abragam and Bleaney 1970). An estimation of the magnitude of d can easily be obtained since the two nuclei behave as point dipoles over interatomic distances. Thus, the bare field exerted by the holmium nucleus on the nucleus of the interstitial F^- ion is given by

$$d \approx \mu_0 \mu_{163\text{Ho}} / 4\pi r^3 = 4.1 \text{ kHz} \quad (20)$$

where $r = 2.73 \text{ \AA}$ and $\mu_{163\text{Ho}} = 4.125 \mu_n$. Therefore, the direct dipole-dipole interaction between the fluorine and holmium nuclei is insufficient to explain the observed anomalous splitting. This discrepancy can, however, be accounted for by including the effect of doublet electronic states mixed via the hyperfine interaction into the two singlet states. It can be noted that, while the effect of coupling a singlet to another singlet produces an enhanced axial magnetic moment for the hyperfine levels, the effect of coupling to a doublet state is to produce an enhanced transverse magnetic moment for the hyperfine levels of the singlet (Bleaney 1973). This enhanced transverse magnetic moment then produces the observed anomalous splitting of the superhyperfine resonances for the $\pm\frac{1}{2}$ hyperfine levels. To put the above idea on a more quantitative basis, more terms of equation (15) need to be considered in addition to equation (16)

$$\begin{aligned} \mathcal{H}_{\text{flip-flop}} = & \mathcal{H}_{\text{TOT}} + A_{\parallel} J_Z F_Z + A_{\perp} (J_+ F_- + J_- F_+) \\ & + 2d \{ I_Z F_Z - \frac{1}{4} (I_+ F_- + I_- F_+) \} \end{aligned} \quad (21)$$

where it is assumed that the interaction between non-equivalent F^- ions is negligible since the different superhyperfine resonances are well separated, and the interaction between equivalent F^- ions is much smaller than the observed frequencies and anomalous splittings $\sim 1\text{--}10 \text{ kHz}$, (see equation (20)) and, hence, should only contribute to broadening of the resonances. Thus, using second-order perturbation theory, which is valid for the hyperfine $\pm\frac{1}{2}$ levels due to the smaller mixing, and including the coupling to the doublet state at 83 cm^{-1} (see figure 2), we find

$$A_8 A_{\parallel} (\langle J_Z \rangle_{1,2})^2 / 2\Delta + d = 4.12 \text{ MHz} \quad (22)$$

$$8A_8 A_{\perp} (\langle E_+ | J_+ | A_1 \rangle)^2 / (E_0 - \Delta - E_E) + \sqrt{15}d = 0.206 \text{ MHz} \quad (23)$$

where equations (22) and (23) describe the effect of the axial and transverse enhanced moments, respectively, of the Ho^{3+} ion in the $\pm\frac{1}{2}$ hyperfine level of the ground electronic state on the interstitial F^- ion, A_8 , Δ and $\langle J_Z \rangle_{1,2}$ are as given earlier, $E_0 - \Delta - E_E = 83 \text{ cm}^{-1}$ is the separation between the A_1 and E states, and $\langle E_+ | J_+ | A_1 \rangle = -3.49$ is the estimated matrix element of the hyperfine interaction between the singlet and doublet states (Mujaji and Jones 1992).

In Martin *et al* (1992), it was assumed that the magnetic interaction between the rare-earth ion and the interstitial ion was dipolar in nature (i.e., $A_{\perp} = -A_{\parallel}/4$) and hence the values $A_{\parallel} = 7.27 \text{ MHz}$ and $d = 5.85 \text{ kHz}$ were obtained. This value for d is consistent with the calculation of equation (20). In contrast to that approach, the dipolar and exchange contributions to the interaction between the Ho^{3+} ion and the interstitial F^- nucleus may be estimated by assuming the value of d given in

equation (20). Then, it is found that $A_{\parallel} = 7.25$ MHz and $A_{\perp} = 5.79$ MHz. The relative sizes of A_{\parallel} and A_{\perp} do not agree with the interaction between the ions being purely dipolar but rather estimate that $A_{\text{dip}} = -2.88$ MHz and $A_{\text{ex}} = 10.13$ MHz or $A_{\text{dip}} = 2.88$ MHz and $A_{\text{ex}} = 4.37$ MHz for the dipole and exchange contributions to the interaction between the rare-earth ion and the interstitial. In both sets of values it can be seen that the exchange interaction between the interstitial F^- ion and the rare-earth ion is indeed the major coupling mechanism.

Note that this effect will only occur in the case where the electronic ground state is a singlet as the above flip-flop interaction only couples the spin $\pm\frac{1}{2}$ hyperfine states and requires that at least part of the electronic wavefunction must be the same for the two projections. The interaction, of course, will be present for all singlet levels, and it is observed here only because of the anomalously large axial and transverse magnetic moments. The axial component is associated with the hyperfine interaction between the two singlet states, whereas the transverse component arises from the interaction between the singlet level and the doublet E state at 83 cm^{-1} (Martin *et al* 1992). These enhanced moments cause the superhyperfine resonances and flip-flop interaction to be in the 0.1–25 MHz range and, hence, the anomalous splitting can be resolved.

7. Conclusions

This paper has given an account of two optical transitions between the $^5\text{I}_8$ and $^5\text{F}_5$ multiplets of Ho^{3+} in CaF_2 which exhibited very unusual hyperfine structure. The origin for the unexpected structure is the presence of a large hyperfine interaction between two adjacent singlet levels in the ground state. The significant factors were that the two levels are particularly close, 1.7 cm^{-1} ; and the hyperfine interaction, because it is associated with a high-angular-momentum multiplet, is large. Normally, in considering optical spectra, the effect of the hyperfine interaction mixing states can be neglected, but this is certainly not the case here. The large dipole-hyperfine interaction leads to nuclear pseudoquadrupole splittings within the interacting singlets which, in this case, are as large as the observed hyperfine splittings for doublet levels. The position of the normal eight hyperfine lines for an $A \Rightarrow E$ transition rather than being at regular intervals are folded back such that several of the lines overlap one another. The other change from the regular $A \Rightarrow E$ pattern is that, because of the mixing between the two singlets, there is a transfer of intensity among the hyperfine transitions, and this coincidentally enhances the lines that are overlapping and diminishes those which were isolated. It has also been shown that a full treatment of the coupling between the singlets gives a very good account of the details of the observed hyperfine spectrum.

There are also unusual features about the superhyperfine resonances in this system which has origins in the interacting singlet levels. Normally, there is no magnetic moment associated with the singlet state and, hence, no superhyperfine resonances. This is changed by the mixing between the two singlets giving a magnetic moment $\sim \mu_B$ within each hyperfine level. Superhyperfine resonances in the MHz region can then be observed through holeburning optical/RF double resonance techniques. The unusual feature is, however, that the degree of mixing and, hence, the size of the magnetic moment depends on the hyperfine level involved. This means that there is a different set of superhyperfine resonances for each ground-state hyperfine level and,

experimentally, different groups of superhyperfine signals are detected for holeburning in the different optical lines. Further the relative magnitudes of the different sets of hyperfine resonances could only be accurately accounted for by proper consideration of the strong mixing between the singlets. This is the first system for which such an effect has been reported.

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