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LETTER TO THE EDITOR

## Superhyperfine resonances in tetragonal centres of $\text{Ho}^{3+}$ in $\text{CaF}_2$

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**Abstract.** The  $C_{4v}$  centre of  $\text{Ho}^{3+}$  in  $\text{CaF}_2$  has a ground state comprising of a pair of electronic singlet levels ( $A_1$  and  $A_2$ ) separated by  $1.7 \text{ cm}^{-1}$  and interacting via the hyperfine interaction. The interaction gives rise to anomalously large pseudoquadrupole splitting with  $P = 0.4 \text{ GHz}$ , which gives fully resolved hyperfine structure within both the  ${}^5I_8(A_2) \Rightarrow {}^5F_5(A_2)$  and  ${}^5I_8(A_1) \Rightarrow {}^5F_3(A_2)$  optical transitions. The latter transition gains its intensity from the former through the hyperfine mixing of the ground state singlets. The mixing also leads to the ground state levels having orbital angular momentum dependent on the hyperfine state and this results in the unusual situation that there are four superhyperfine resonances for each set of equivalent neighbouring  $\text{F}^-$  ions. A  $210 \text{ kHz}$  splitting of the  $\pm \frac{1}{2}$  superhyperfine resonances, which is the result of an enhanced mutual spin-flip interaction between the  $\text{Ho}^{3+}$  and  $\text{F}^-$  nuclei, is also observed. This is the first report of such a splitting.

The ground multiplet,  ${}^5I_8$ , of  $\text{Ho}^{3+}$  has a large free-ion magnetic moment of  $3.31 \mu_B$  and the naturally abundant isotope  ${}^{165}\text{Ho}$  has a nuclear spin of  $I = \frac{7}{2}$ . Not surprisingly then, the interaction between the electronic and nuclear magnetic moments leads to sizeable hyperfine splitting. When  $\text{Ho}^{3+}$  is incorporated in a crystal at a site with axial or higher symmetry there are usually low-lying degenerate levels where this large hyperfine splitting is maintained and its magnitude can be larger than the inhomogeneous linewidth of the optical transitions. Hence, optical transitions of  $\text{Ho}^{3+}$  ions at high symmetry sites in crystals cooled to low temperatures often exhibit resolved hyperfine structure (Dieke 1967) and therefore prove invaluable for the study and illustration of effects associated with hyperfine interactions. This letter reports novel effects which arise when two neighbouring electronic singlet states are strongly coupled by the axial hyperfine interaction  $AJ_zI_z$ . This interaction leads to large pseudoquadrupole splittings and hyperfine states with significant orbital angular momentum.

Normally there is no magnetic moment associated with an electronic singlet, but here, due to the hyperfine interaction, the singlets obtain an effective moment which can be thought of as arising from an electronic enhancement of the nuclear moments (Bleaney *et al* 1978). The magnitude of this magnetic moment is  $\sim \mu_B$  and the  $\text{Ho}^{3+}$  ion exerts a field of  $\sim 0.1 \text{ T}$  on the neighbouring ions in the crystal. Neighbouring nuclear spins oriented by this field will give superhyperfine levels split by several MHz.

Superhyperfine structures of this magnitude are frequently observed for degenerate electronic states but have rarely been observed in association with electronic singlets. The size of the magnetic moment depends on the nuclear spin state and, hence, a separate set of superhyperfine resonances is detected in association with each of the hyperfine levels. This situation has not been observed before. It has further been observed that the superhyperfine resonances associated with states where the axial projection of the nuclear spin  $m = +\frac{1}{2}$  hyperfine states are no longer degenerate and it will be shown that this is the result of a mutual spin-flip interaction between the holmium and fluorine nuclear spins that is only significant for the  $\pm\frac{1}{2}$  states. In other systems the equivalent interaction has been known to give rise to spin dephasing and broadening of transitions (Bai and Kachru 1991) but it has never been known to give a resolved superhyperfine splitting.

The system studied is the A centre in  $\text{CaF}_2:\text{Ho}^{3+}$  (Seelbinder and Wright 1979). The trivalent rare earth ion replaces a  $\text{Ca}^{2+}$  ion and charge compensation is achieved by the incorporation of an extra  $\text{F}^-$  ion in an interstitial position along one of the tetragonal axes giving the centre  $C_{4v}$  site group symmetry. The lowest levels of the ground  $^5I_8$  multiplet are an  $A_1$  and an  $A_2$  singlet and are separated by only  $\Delta \sim 1.7 \text{ cm}^{-1}$  (51.31 GHz). The angular momentum operator  $J_z$  of the electronic states transforms as a component of the  $A_2$  irreducible representation and, therefore, from symmetry considerations it is seen that the hyperfine interaction  $AJ_zI_z$  couples the  $A_1$  and  $A_2$  singlet levels. Using second-order perturbation theory it can be seen that the hyperfine levels of the  $A_1$  and  $A_2$  electronic states associated with the same nuclear projection  $m$  repel one another by an amount

$$E_m = \frac{m^2 A^2 \langle A_1 | J_z | A_2 \rangle^2}{\Delta} = \frac{m^2 \epsilon^2}{\Delta} \quad (1)$$

where  $\epsilon \equiv |A \langle A_1 | J_z | A_2 \rangle|$ . This pseudoquadrupole splitting results in four doubly degenerate levels with separations in the ratio 3:2:1. These splittings give the dominant contribution to the structure in the  $^5I_8(A_2) \Rightarrow ^5F_5(A_2)$  and  $^5I_8(A_1) \Rightarrow ^5F_5(A_2)$  transitions shown in figure 1(a). The small quadrupole splitting in the excited state singlet adds to the splittings in one transition and subtracts in the other such that comparison of the two transitions readily establishes the ground state pseudoquadrupole splittings to be 2.37, 1.58 and 0.79 GHz. Given  $\Delta = 51.31$  GHz, the value of  $\epsilon$  is then equal to 4.50 GHz.

The unequal intensities of the four hyperfine nuclear transitions (figure 1) arise as a consequence of the mixing of the wavefunctions and hence the transfer of intensity being dependent on the nuclear state. The wavefunctions are of the form

$$|A_1, m\rangle' = \left[ 1 / \sqrt{1 + (m^2 \epsilon^2 / \Delta^2)} \right] \{ |A_1, m\rangle - (m\epsilon / \Delta) |A_2, m\rangle \} \quad (2a)$$

$$|A_2, m\rangle' = \left[ 1 / \sqrt{1 + (m^2 \epsilon^2 / \Delta^2)} \right] \{ |A_2, m\rangle + (m\epsilon / \Delta) |A_1, m\rangle \}. \quad (2b)$$

The  $A_1 \Rightarrow A_2$  optical transition is forbidden by  $C_{4v}$  symmetry and, hence, the intensities of transitions from the nominally  $A_1$  and  $A_2$  ground state levels to an  $A_2$  excited state arise solely from the  $|A_2, m\rangle$  component of the ground state wavefunctions. Thus, the loss of intensity for the  $^5I_8(A_2) \Rightarrow ^5F_5(A_2)$  transition is greater for the hyperfine levels with the larger  $m$ -values. This is consistent with the observation

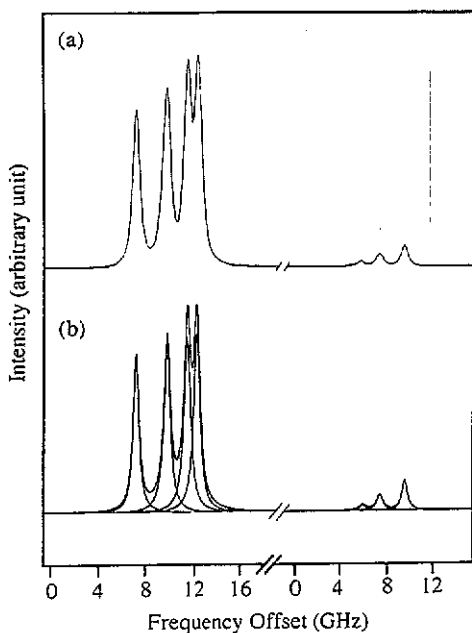


Figure 1. (a) The low-temperature (4.2 K) optical excitation spectrum of the  ${}^5I_8(A_2) \rightarrow {}^5F_3(A_2)$  transition at  $15\,621.3\text{ cm}^{-1}$  and the  ${}^5I_8(A_1) \rightarrow {}^5F_5(A_2)$  transition at  $15\,623\text{ cm}^{-1}$ . (b) Predicted intensities for the above transitions using  $\epsilon = 4.50\text{ GHz}$ .

in figure 1(a) where there is the greatest transfer of intensity from the  $A_2$  to  $A_1$  initial states for the outside lines, i.e. those displaced by the largest amounts, and hence associated with the  $m = \pm\frac{7}{2}$  hyperfine levels. The transfer of intensity is then progressively less for the  $m = \pm\frac{5}{2}$ ,  $\pm\frac{3}{2}$  and  $\pm\frac{1}{2}$  hyperfine components. The intensities predicted using the hyperfine interaction parameter  $\epsilon = 4.50\text{ GHz}$  give excellent agreement with the observed intensities, see figures 1(a) and (b).

The hyperfine states of the form of equation (2) have an associated electronic contribution to their angular momentum and, hence, the significant magnetic moment

$$\mu_z(m) = \beta h' \langle A_1, m | J_z | A_1, m \rangle = 2m\beta h / [(1 + m^2\epsilon^2/\Delta^2)A\Delta]. \quad (3)$$

The nuclei in the neighbourhood of the  $\text{Ho}^{3+}$  ion therefore experience a large field from the rare earth ion. The novel feature of this system is, as can be seen from equation (3), that the magnitude of the magnetic moment and the effective field experienced by the neighbouring ions is dependent on which of the hyperfine levels is occupied. The neighbouring  $\text{F}^-$  ions have the nuclear spin  $F = \frac{1}{2}$  and, hence, each can have two orientations in the field of the  $\text{Ho}^{3+}$  ion with the observed superhyperfine resonance corresponding to the transition energy required to cause a spin flip,  $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ . There are, however, within the singlet states four possible field strengths and so for each set of equivalent  $\text{F}^-$  ion sites there will be four resonances. The ratio of the frequencies of these resonances will be proportional to the magnetic moments and hence the ratio in first order would be 7:5:3:1. For larger mixing as occurs here the normalization parameter is significant and this gives a ratio of 6.29:4.70:2.90:1.

The superhyperfine resonances were detected using optically detected NMR techniques. This involved spectral holeburning using a high resolution dye laser with a linewidth of  $\sim 1\text{ MHz}$  tuned to one of the hyperfine lines. RF from a sweep generator

was then amplified by an ENI power amplifier and applied to a six-turn 5 mm diameter coil wrapped round the sample. The depth of the hole is recorded as a function of the frequency of the RF by monitoring the intensity of the emission at  $15\,513.5\text{ cm}^{-1}$ , corresponding to a transition from the lowest level of the  ${}^5F_5$  multiplet. In principle, the superhyperfine spectrum can be obtained with holeburning in any of the transitions to  ${}^5F_5$  multiplet levels such as the above  ${}^5I_8(A_2) \Rightarrow {}^5F_5(A_2)$  transition. However, in practice the best signal to noise was obtained with holeburning in the lower energy transition  ${}^5I_8(A_1) \Rightarrow {}^5F_5(E)$  (see figure 2).

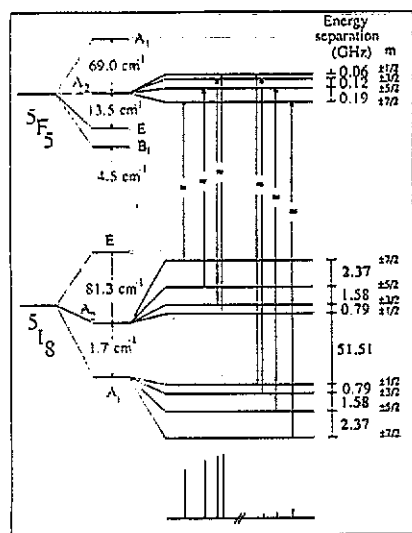
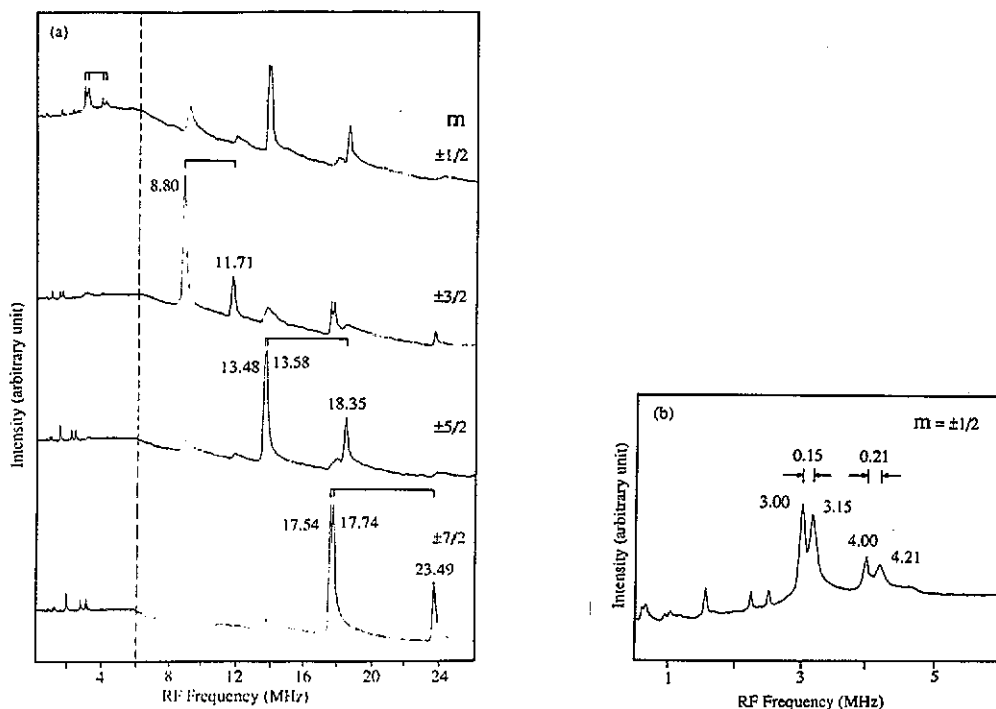


Figure 2. Energy levels and transitions associated with the  $C_{4v}$   $\text{CaF}_2:\text{Ho}^{3+}$  system. The  ${}^5I_8(A_2) \Rightarrow {}^5F_5(A_2)$  transition is allowed whereas the  ${}^5I_8(A_1) \Rightarrow {}^5F_5(A_2)$  transition gains all of its intensity as a consequence of the hyperfine mixing of the  ${}^5I_8(A_2)$  and  ${}^5I_8(A_1)$  levels.

The ODNMR spectrum is dependent on the ground state hyperfine level involved as selected by the optical frequency. If, for example, the optical frequency selects transitions originating in the ground state  $\pm\frac{7}{2}$  nuclear hyperfine level then three prominent resonances are detected at 23.49 MHz and a doublet of 17.74 and 17.54 MHz (figure 3(a)). By drawing an analogy with the superhyperfine structure of the  $C_{4v}$  centre of  $\text{Pr}^{3+}$  in  $\text{CaF}_2$  (Burum *et al* 1982), the higher frequency signal can be assigned as due to the interstitial  $\text{F}^-$  ion and the two lower closely separated frequency signals as due to the two sets of four nearest neighbours  $\text{F}^-$ . The equivalent resonances associated with the  $\pm\frac{5}{2}$  hyperfine level are at 18.35, 13.58 and 13.48 MHz. For the  $\pm\frac{3}{2}$  hyperfine level the interstitial resonance is at 11.71 MHz and those for the nearest-neighbour shell lie at 8.8 MHz (i.e. not resolved). Finally, there are equivalent resonances when the optical transition selects the  $\pm\frac{1}{2}$  hyperfine level and they lie in the region of 4 MHz and 3 MHz. Note however from figures 3(a) and 3(b) the resonances for  $\pm\frac{1}{2}$  hyperfine levels have split. Ignoring this extra effect in the  $\pm\frac{1}{2}$  hyperfine levels for the present and assigning average values of 4.11 and 3.08 MHz for the interstitial and nearest-neighbour resonances, respectively, the change in the frequency of the hyperfine resonances associated with the different hyperfine levels is due to their differing magnetic moments. The interstitial resonances occur, for example, in the ratio 5.72:4.47:2.85:1 which roughly agrees with the perturbation re-

sults. The frequencies of the nearest-neighbour  $F^-$  ions are all lower than that of the interstitial and display the same ratio for the resonances of the various hyperfine levels. A complete calculation of the relative values of the magnetic moments but still just considering the two ground state levels and the single excited state gives agreement with experiment to within 1% (Martin *et al* 1992).



**Figure 3.** (a) ODNMR spectrum with the optical frequency selecting transitions originating from the various hyperfine levels as indicated on the right. The frequencies associated with the interstitial  $F^-$  ions and nearest-neighbour  $F^-$  ions are indicated. The data corresponds to that for the  $^5I_8(A_1) \Rightarrow ^5F_5(E)$  optical transition where there is overlap of hyperfine lines and, hence, the superhyperfine resonances associated with the different ground state hyperfine levels are not totally separated. (b) ODNMR spectrum for the  $\pm\frac{1}{2}$  hyperfine level indicating the splitting of the interstitial and nearest-neighbour superhyperfine resonances. Signals below 3 MHz are associated with more distant  $F^-$  neighbours.

In contrast to the other interstitial resonances, the interstitial resonances at  $\sim 4$  MHz associated with the  $\pm\frac{1}{2}$  hyperfine levels rather than being degenerate are separated by 210 kHz (figure 3(b)). The resonances at  $\sim 3$  MHz associated with the nearest-neighbour  $F^-$  ions similarly exhibit a doublet structure with an observed splitting of 150 kHz which is much larger than that expected for the two inequivalent sets of nearest-neighbour ions (3.5 kHz). The cause of these splittings is anomalous, originating from a mutual spin-flip interaction of the holmium and fluorine nuclei. The superhyperfine resonances are determined by the interaction  $J \cdot A_F \cdot F$  between the magnetic moments of the  $Ho^{3+}$  ion and that of the neighbouring  $F^-$  ions and includes dipole-dipole and exchange contributions. It must be remembered that the  $Ho^{3+}$  magnetic moment arises from the mixing of the electronic states as given in equation (3). However, as only the singlet levels are involved the interaction can

initially be restricted to the axial interaction  $A_F J_z F_z$ . This term dominates the superhyperfine splittings. There can also be a contribution from the axial term of the direct dipole-dipole interaction  $d I_z F_z$  between the holmium nuclei and the  $F^-$  nucleus which will add to the former interaction.

However, for the  $m = \pm \frac{1}{2}$  hyperfine levels the interactions  $J \cdot A_F \cdot F$  and  $I \cdot d \cdot F$  also give transverse terms which can lift, in principle, the degeneracy of the direct product states  $|A_i, \frac{1}{2}, -\frac{1}{2}\rangle$  and  $|A_i, -\frac{1}{2}, \frac{1}{2}\rangle$  where the last quantum label refers to the spin state of the fluorine nucleus and accounts for the observed anomalous splitting. The mutual spin-flip interaction between the  $\text{Ho}^{3+}$   $m = \pm \frac{1}{2}$  hyperfine states and the nuclear spins of neighbouring  $F^-$  ions can cause a splitting of the associated superhyperfine levels. If, however, this splitting was to come solely from the nuclear dipole-dipole coupling, the magnitude would be 4.1 kHz, which is much smaller than that observed. The above treatment, however, has only considered the interaction of the two singlets. If allowance is made for hyperfine coupling between these singlet levels and neighbouring E states then there are further contributions from the transverse hyperfine interaction  $A(J^+ I^- + J^- I^+)/2$  which can also effect the observed splittings. By deriving the enhanced non-axial nuclear moment in the singlet states due to an E state located  $81.3 \text{ cm}^{-1}$  higher in energy with known wavefunctions (Mujaji and Jones 1992) and comparing to the observed splitting of 210 kHz the values of  $A_F = 7.27 \text{ MHz}$  and  $d = 5.85 \text{ kHz}$  were obtained. The latter value is in reasonable agreement with the point dipole estimate of 4.1 kHz given earlier. The electronic enhancement of the transverse nuclear moment is, therefore, responsible for the observed spin-flip splitting of the  $\pm \frac{1}{2}$  superhyperfine resonances.

The data presented in this paper, therefore, gives very dramatic illustrations of the effect that the hyperfine interaction has for an electronic non-degenerate A state. Interaction with a nearby singlet level is shown to give significant pseudoquadrupole splittings and hence a large enhancement of the nuclear magnetic moments which is strongly dependent on the hyperfine level involved. The consequence of the latter effect is that for this ground state there are four times the number of superhyperfine resonances that are normally observed: four associated with an interstitial  $F^-$  ion and four for each group of  $F^-$  nearest-neighbour ions. Interaction of a singlet with a degenerate E state also gives rise to pseudoquadrupole splittings but enhancement now occurs for the transverse component of the nuclear magnetic moment. In this centre large enhancements of both the axial and transverse components of the nuclear magnetic moment have been observed and in particular the coupling of the ground state singlets to an E state  $81.3 \text{ cm}^{-1}$  higher in energy gives rise to a novel splitting of the superhyperfine resonances.

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