



Intensities of hyperfine transitions of Pr^{3+} and Ho^{3+} in CaF_2

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Abstract

Computational techniques for the calculation of transition intensities between crystal field levels of f^N systems are extended to the calculation of intensities between hyperfine levels. Good agreement between theory and experiment is obtained for selected optical transitions in $\text{CaF}_2:\text{Pr}^{3+}$ and $\text{CaF}_2:\text{Ho}^{3+}$.

Keywords: Hyperfine intensities; Calcium fluoride; Praseodymium; Holmium

1. Introduction

The calculation of crystal field energy levels of the f^N configuration of rare earth ions in crystals is well known [1]. Methods for parameterising the transition intensities between the crystal field states have been developed over the last few decades (e.g. see Ref. [2]). Hyperfine splittings of the crystal field levels are also quite well understood [1]. In contrast, the intensity patterns arising from transitions between hyperfine splitting levels has received relatively little theoretical attention. The most usual ad hoc approach is to assume some value for the intensity of the non-hyperfine splitting level and distribute the intensity over the hyperfine splitting levels (with attention to Boltzmann populations, etc.). While this is an adequate approach in many cases, it is likely to be inadequate in the more interesting cases, where hyperfine coupling between nearby crystal field levels leads to spectacular patterns.

In this paper we extend our techniques for the calculation of transition intensities [3] to hyperfine transitions. Since the transitions of most interest to us involve close crystal field levels, the hyperfine mixing, and therefore the intensity calculations, are highly dependent on the splitting. In some cases we have to augment the one-electron crystal field model with two-electron effects to obtain the needed accuracy. We illustrate our methods with selected transitions in C_{4v} symmetry sites in $\text{Pr}^{3+}:\text{CaF}_2$ and $\text{Ho}^{3+}:\text{CaF}_2$.

2. Theory

The anisotropic one-electron crystal field components are conventionally expressed as

$$H_{\text{CF}} = \sum_{kq} B_q^k C_q^{(k)} \quad (1)$$

where $C_q^{(k)}$ are spherical tensor operators acting within the 4f electronic configuration. It is conventional when working with sites of C_{4v} symmetry to use new operators which are defined as combinations of the C_q^k operators. These are defined by the Hamiltonian

$$\begin{aligned} H_{\text{CF}} = & B_A^2 C_0^{(2)} + B_A^4 \left[C_0^{(4)} - \sqrt{\frac{7}{10}} (C_4^{(4)} + C_{-4}^{(4)}) \right] \\ & + B_C^4 \left[C_0^{(4)} + \sqrt{\frac{5}{14}} (C_4^{(4)} + C_{-4}^{(4)}) \right] + B_A^6 \left[C_0^{(6)} \right. \\ & + \sqrt{\frac{1}{14}} (C_4^{(6)} + C_{-4}^{(6)}) \left. \right] + B_C^6 \left[C_0^{(6)} - \sqrt{\frac{7}{2}} (C_4^{(6)} \right. \\ & \left. + C_{-4}^{(6)}) \right] \end{aligned} \quad (2)$$

which is now parameterised by new B parameters. Although such a single electron parameterisation works well, the effects of electron correlation on the crystal field interactions are required for a full treatment (see, for example, Judd [4] and Reid [5]). Parameters fitted to the states of maximum spin multiplicity often yield poor results for other multiplets (Wybourne [1]). Thus the single electron crystal field parameters are absorbing some of the correlation effects, which reduces the precision of the fits.

Reid and coworkers [2] have added other crystal field

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operators to account for the two-electron effects. These are based on theoretical models of the ‘mechanics’ of the interactions. However, a full treatment of this sort can lead to a proliferation of parameters that in our case, where we are considering only two or three multiplets, are unnecessary and somewhat redundant.

We therefore take a simpler approach. The two-body effects may be taken into account by defining additional parameters for each multiplet:

$$H_{\text{cef}} = \sum_{KQ} B_Q^K(SLJ) C_Q^{(K)}(SLJ) \quad (3)$$

where $C_Q^{(K)}(SLJ)$ is understood to have non-zero matrix elements only within a particular multiplet (see Newman [6]). This parameterisation allows us to adjust individual energy levels within multiplets much more effectively than using the conventional one-electron parameters only. Hence we can obtain better estimates of the eigenvectors without sacrificing too much of the simplicity of the conventional method. An alternative to this procedure would be to arbitrarily adjust the energy levels. This would have the disadvantage of not allowing for a change in the eigenvectors.

Hyperfine interactions are typically developed as multipole expansions of the interactions between the nucleus and electronic environment. The two most significant effects are the magnetic dipole and electric quadrupole interactions. The magnetic dipole interaction arises from unpaired nucleon spins that give the nucleus a magnetic dipole moment that interacts with the dipole moments of the electronic spin and orbital momenta. It can be expressed as a function of angular momentum operators:

$$H_{\text{md}} = \hbar \left[A_{\parallel} I_z J_z + \frac{1}{2} A_{\perp} (I_+ J_- + I_- J_+) \right] \quad (4)$$

parameterised by A_{\parallel} and A_{\perp} . These are typically defined within single multiplets so that, for instance, in holmium we would have $A_{\parallel}(^5I_8)$ and $A_{\perp}(^5I_8)$ parameters for the ground multiplet. In our work the multiplet dependent parts of these parameters are calculated within the programs, and we use a single parameter A to describe the magnetic dipole interaction. For use in our calculations we prefer Hamiltonians based on tensorial expressions. To derive such a Hamiltonian we start with an expression equivalent to Eq. (4) (see Weissbluth [7]):

$$H_{\text{md}} = 2\beta \left[\frac{\boldsymbol{\mu} \cdot (\mathbf{l} - \mathbf{s})}{r^3} + \frac{(\boldsymbol{\mu} \cdot \mathbf{r})(\mathbf{s} \cdot \mathbf{r})}{r^5} + \frac{8\pi}{3} \delta(\mathbf{r}) \boldsymbol{\mu} \cdot \mathbf{s} \right] \quad (5)$$

where $\boldsymbol{\mu} = \gamma \hbar \mathbf{i}$, \mathbf{l} and \mathbf{s} are the electronic orbital spin angular momentum operators and $\boldsymbol{\mu}$ is the nuclear angular momentum operator. \mathbf{r} is the position vector of the electron. Using standard angular momentum techniques (e.g. Judd [8]) the matrix element between any two states labelled by the electronic quantum numbers $sljm$ and the nuclear quantum numbers im_i is

$$\begin{aligned} \langle sljmim_i | H_{\text{md}} | s'l'm'i'm'_i \rangle &= A \sqrt{[j][j'][i](i+1)} \delta_{ss'} \delta_{ii'} \\ &\times \left[(-1)^{l'+s+m+i+m_i+1} \sqrt{[l](l+1)} \delta_{ll'} \begin{Bmatrix} l & l & 1 \\ j' & j & s \end{Bmatrix} \right. \\ &\quad \left. - (-1)^{j+m+l+i+m_i} \sqrt{30[l][l'][s](s+1)} \right. \\ &\quad \left. \times \begin{pmatrix} l' & 2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} s & s' & 1 \\ l & l' & 2 \\ j & j' & 1 \end{Bmatrix} \right] \\ &\times \sum_{q=-1}^1 (-1)^q \begin{pmatrix} j & 1 & j' \\ -m & q & m' \end{pmatrix} \begin{pmatrix} i & 1 & i' \\ -m & q & m'_i \end{pmatrix} \quad (6) \end{aligned}$$

where the magnetic dipole hyperfine parameter is defined as

$$A = 2\beta\gamma\hbar \langle r^{-3} \rangle \quad (7)$$

The electric quadrupole interaction arises as a result of a non-spherical nuclear charge distribution. This gives the nucleus an electric quadrupole moment which interacts with the electric field gradient generated by the surrounding electrons. However, for the transitions discussed in this work the effects of the quadrupole interaction on the energy levels and intensity patterns are negligible in comparison with the magnetic dipole interaction.

It is assumed that observed transition strengths are entirely due to electric and magnetic dipole moment coupling to the electronic states. The line strengths, or intensities, of these transitions are evaluated using the general formula

$$S_{12} = |\langle \psi_1 | \hat{V}_{\text{eff}} | \psi_2 \rangle|^2 + |\langle \psi_1 | \hat{m} | \psi_2 \rangle|^2 \quad (8)$$

The transition is between two electronic levels with wave functions ψ_1 and ψ_2 . \hat{V}_{eff} is an effective electric dipole operator and \hat{m} is the magnetic dipole operator.

Magnetic dipole transitions are well understood and effectively characterised by a single parameter. Hence in this work the magnetic dipole transition strengths are given an arbitrary value and the electric dipole transition strengths are scaled appropriately. The electric dipole transitions are much more complex than the magnetic dipole case. We use here a general parameterisation that is based on the work of Newman and Balasubramanian [9], which was extended by Reid and coworkers [3]. The electric dipole strength is defined as

$$P = e^2 \sum_{q=-1}^1 |\langle \psi_1 | V_q^{(1)} | \psi_2 \rangle|^2 \quad (9)$$

where $V^{(1)}$ is an even parity operator, expressed as a combination of unit tensors:

$$V_q^{(1)} = \sum_{\lambda \neq 0} A_{\lambda p}^{\lambda} \sum_l U_l^{(\lambda)} (-1)^{t+p+q} \sqrt{2t+1} \begin{pmatrix} 1 & \lambda & t \\ q & -1 & p \end{pmatrix} \quad (10)$$

Complete sets of intensity parameters for rare earth ions in CaF_2 are not available. The parameters can be estimated by point-charge and point-polarisability calculations, as has been done by Reid et al. [10]. However, in the cases in which we are interested such estimates prove unnecessary.

When considering the intensities of transitions between hyperfine-split crystal field levels, we are particularly interested in whether the hyperfine intensities are a simple extension of the crystal field intensities. That is, can we ‘share’ the total crystal field transition intensity over the hyperfine subtransitions that appear with the addition of the I and M_I quantum numbers? The observed transitions obey the selection rule $\Delta M_I = 0$, i.e. there are no transitions between nuclear states of differing $|M_I\rangle$.

Energy levels that are isolated by a significant amount (e.g. 20 cm^{-1} or more) would experience little admixture by the hyperfine interaction of nearby levels. Transitions between such isolated levels would be expected to obey the intensity sharing proposition well. However, if we get two or three close lying levels, separated by only a few wavenumbers, that do become significantly mixed by the hyperfine interactions, such a sharing hypothesis could be expected to fail.

3. Results

To test our calculations we investigated the tetragonal symmetry (C_{4v}) sites of $\text{CaF}_2:\text{Pr}^{3+}$ and $\text{CaF}_2:\text{Ho}^{3+}$.

3.1. The $\text{CaF}_2:\text{Pr}^{3+}$ system

The crystal field transition investigated here is that between the lowest energy levels of the $^3\text{H}_4$ and $^1\text{D}_2$ multiplets. The electronic ground state is doubly degenerate and the excited state is a singlet. The extra correlation crystal field parameters were not required, since the energy levels are sufficiently isolated to make such corrections unnecessary. Initial values of the crystal field parameters were taken from Wells [11], which we modified by fitting to experimental data. The fitted crystal field parameters are listed in Table 1. Having calculated the crystal field energy scheme we then apply the hyperfine calculations. A magnetic dipole parameter of $A = 0.01\text{ cm}^{-1}$ was found to be optimal. The magnetic dipole interaction is sufficient to describe the splittings, the electric quadrupole interaction

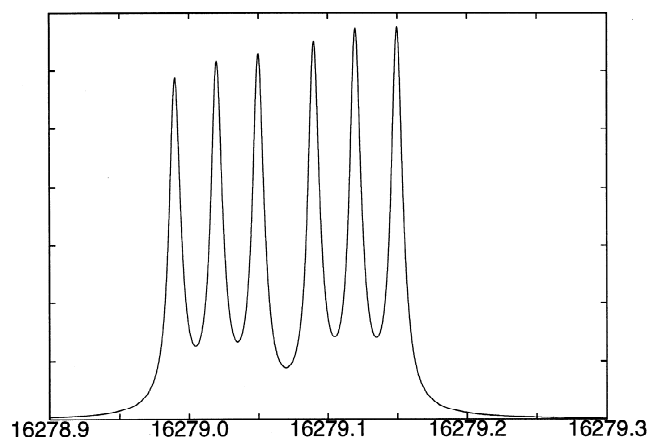


Fig. 1. Calculated hyperfine intensity pattern for the transitions between the lowest crystal field levels of the $^3\text{H}_4$ and $^1\text{D}_2$ multiplets of $\text{CaF}_2:\text{Pr}^{3+}:\text{C}_{4v}$. Energy scale is in cm^{-1} . Arbitrary intensity scale. Temperature 2 K.

was too small to make any difference to the splittings or the intensity patterns.

The praseodymium doped system was special in that the magnetic dipole transitions are very weak, owing to the free ion selection rule $\Delta J = 0$, forbidding transitions between the $^3\text{H}_4$ ground multiplet and the $^1\text{D}_2$ excited levels. Thus it is practically a pure electric dipole transition. It was found that the intensity pattern is insensitive to the A_{fp} parameters. Any electric dipole intensity parameters were able to reproduce the intensity pattern (within a scale factor). The pattern we calculated is shown in Fig. 1, and compares favourably with that measured experimentally by Martin et al. [12]. The Boltzmann populations of the energy levels are calculated at a temperature of 2 K, as in the experiment, but varying this temperature over a few kelvin has little effect on the intensity pattern.

3.2. The $\text{CaF}_2:\text{Ho}^{3+}$ system

In the $\text{Ho}^{3+}\text{C}_{4v}$ site the two lowest crystal field levels of the $^5\text{I}_8$ ground state are split by 1.9 cm^{-1} . The transitions from these two levels to the lowest level of the $^5\text{I}_7$ multiplet give an interesting optical spectrum. Unlike the praseodymium system, the holmium doped system did require the extra crystal field parameters because it is important to get the ground state splitting accurate to produce a good intensity pattern. Crystal field parameters

Table 1
Crystal field parameters fitted to experimental energy levels. The usual one-electron parameters are labelled as ‘conventional’, while the correlation crystal field correction parameters are labelled as ‘single multiplet’. All values are in cm^{-1}

Crystal field parameter	Pr^{3+} conventional	Ho^{3+} conventional	Ho^{3+} $^5\text{I}_8$ single multiplet	Ho^{3+} $^5\text{I}_7$ single multiplet
B_{C}^4	−1831	−1186	57	196
B_{C}^6	908	504	48	−114
B_{A}^2	859	609	−1	143
B_{A}^4	609	290	159	−339
B_{A}^6	369	664	−250	−143

from Mujaji et al. [13] were used as a starting point for our parameter fits. Using only the conventional crystal field parameters we cannot accurately reproduce the splitting. The single multiplet parameters are also necessary for the 5I_7 excited multiplet to place the levels in their correct relative positions. The fitted crystal field parameters are given in Table 1. The ‘conventional’ parameters are the conventional single electron parameters. The holmium ‘single multiplet’ parameters are the effective two-electron parameters as defined in Eq. (3), and represent corrections to the single electron parameters to account for correlation crystal field effects. These two-electron parameters are quite small for the 5I_8 ground multiplet, where they are used to get the required ground state crystal field splitting, but are more significant in the 5I_7 multiplet where it is necessary to place many levels in the correct relative positions. This may indicate a problem with the assignments. The magnetic dipole hyperfine parameter was found to be $A = 0.027 \text{ cm}^{-1}$.

The holmium doped system differs from the praseodymium system in that the magnetic dipole transitions are now allowed by the selection rules. However, using only the magnetic dipole interaction the intensity pattern does not agree with the experimental spectrum, so electric dipole intensity parameters are required. The magnetic dipole contribution, supplemented only by the A_{54}^6 electric dipole parameter, is sufficient to reproduce the experimental pattern. Unlike the praseodymium system then, the intensity pattern is sensitive to the A_{ip}^{λ} parameters.

Our calculated spectrum is shown in Fig. 2 and agrees well with spectra measured by Wells [11]. The temperature is taken to be 10 K, as in the experiment, and variation of this over a few kelvin has an insignificant effect on the intensities.

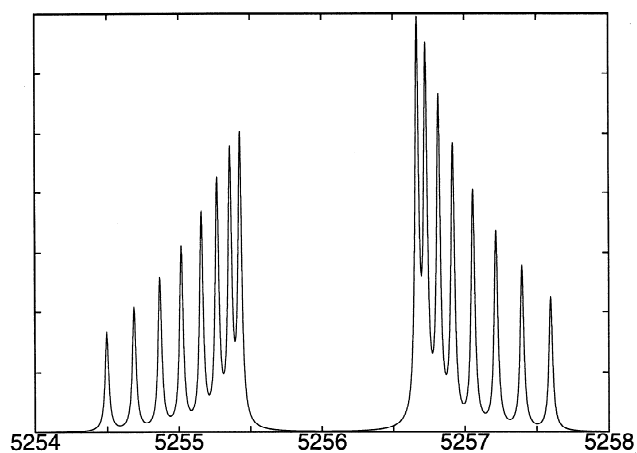


Fig. 2. Calculated hyperfine intensity pattern for the transitions between the lowest crystal field levels of the 5I_8 and 5I_7 multiplets of $\text{CaF}_2:\text{Ho}^{3+}:\text{C}_{4v}$. Energy scale is in cm^{-1} . Arbitrary intensity scale. Temperature 10 K.

4. Conclusions

We find that using the existing electric dipole intensity parameterisation techniques we can successfully reproduce intensity patterns of holmium and praseodymium doped calcium fluoride systems. The Pr^{3+} spectrum was found to be insensitive to the electric dipole intensity parameters. Hence it is not possible with such limited data to get limits on these parameters. The Ho^{3+} spectrum, however, was sensitive to the intensity parameters and this can put limits on the parameters. We find that hyperfine intensities can be calculated using ‘sharing’ of crystal field intensities, where the total intensity of a crystal field transition is shared over the hyperfine ‘subtransitions’. However, when considering transitions to multiple crystal field levels regard must be paid to ensuring that the correct relative intensities are assigned and maintained in moving to the hyperfine transitions.

It was necessary in the holmium doped system to add correction terms to account for correlation crystal field effects, to enable us to get the ground state splitting and placement of the excited crystal field levels correct. This involves the addition of extra crystal field parameters acting within individual multiplets to simulate the two-electron crystal field effects. This was not necessary for the praseodymium system as the levels are sufficiently isolated.

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