Calculations of rare earth hyperfine structures and application to quantum information

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Abstract

Hyperfine structures are a key element in the rare earth based schemes proposed for quantum information. Experimental determination of hyperfine level energies is often difficult, especially under a magnetic field. However, such a field is very useful to tune the hyperfine structures in order to obtain efficient quantum information systems. The calculation of these structures from crystal field wavefunctions can therefore be of great interest. In this paper, calculated hyperfine levels of Pr^{3+} in $LiYF_4$ and Tm^{3+} in YAG are compared with experimental data. An analysis of the results is also presented.
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1. Introduction

Quantum information (QI) is a recent research field in which the unique properties of quantum systems are used to manipulate data in a non-classical way [1]. The most important property used in QI is the ability for a quantum system to be in a superposition state. Such states can be observed for reasonably long times for microscopic systems well isolated from their environment. When an ensemble of such systems is available, several applications of QI can be considered like quantum cryptography, which is already commercially available, quantum computing or quantum storage. The latter aims at storing the quantum state of a photon into matter while a quantum computer would be able to perform very fast calculations. The basic information unit in QI is the quantum bit or qubit, which is simply a two-level system. A fundamental requirement for efficient QI systems is a long coherence lifetime (T_2) for the qubit transition: this coherence lifetime has to exceed by several orders of magnitude the time needed to put one qubit into an arbitrary state. Although some promising results on quantum computing and storage have been obtained in gases or liquids [2–4], a solid state system, which is intrinsically much more stable, would be very interesting. As stated above, a basic requirement for such a system is to exhibit centers with energy levels well isolated from the envi-

ronment. In this respect, rare earth ions doped crystals (REIC) are known to exhibit favorable properties: studies by coherent spectroscopy (photon echoes, spectral holeburning) have shown that optical transitions between the lowest crystal field (CF) levels of two multiplets can have long coherence lifetimes (up to 6.4 ms in $Er:Y_2SiO_5$) [5]. On the other hand, transitions between the hyperfine levels of the ground state lowest CF level can have even longer coherence lifetimes (up to 30 s in $Pr:Y_2SiO_5$) [6]. This explains that several teams have proposed QI schemes in REIC [7,8]. The levels of each qubit are chosen among the hyperfine levels of the lowest CF level of the ground multiplet. Then, an excited state is used to create and manipulate the state of the qubit by optical excitations.

Hyperfine structures are therefore central in REIC based QI experiments and applications. Since these structures are usually much smaller than the inhomogeneous linewidth of the optical transitions, hyperfine level energies are obtained by holeburning spectroscopy or double (optical-RF) resonance techniques [5]. These experiments can be difficult to perform, especially when an external magnetic field is applied because the relative orientation between the field and the sample and its magnitude in the sample have to be precisely known. Moreover, many crystals exhibit magnetically non-equivalent sites which result in very complex spectra unless special experimental conditions are used [9]. On the other hand, in many cases, rare earth doped crystals can be used for quantum information only when an strong external magnetic field is applied: it allows one to find efficient three-level Λ systems [9,10] or to increase the optical or

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hyperfine transition coherence lifetimes [11]. For this reason, the influence of a magnetic field on the hyperfine structures has to be known and theoretical calculations can be very useful before difficult experiments are tried. Hyperfine energy levels have been calculated from crystal field (CF) wavefunctions in a few REIC [12–14], including Pr^{3+}:LiYF$_4$ [15] and Tm^{3+}:Y$_3$Al$_5$O$_{12}$ [10] in which the analysis was specifically aimed at QI applications.

In this paper, we discuss in more details these results: connections between the CF levels and the hyperfine structures are analyzed as well as the comparisons between calculations and experiments.

2. Hyperfine structures of rare earth ions

The magnetic interactions which result in rare earth hyperfine structures are the electronic Zeeman, nuclear Zeeman, hyperfine and quadrupolar interactions. They are respectively given by the following expressions:

$$H_{EZ} = \beta \mathbf{B}(\mathbf{L} + g_s \mathbf{S}) \tag{1}$$

$$H_{NZ} = -g_n \beta_n \mathbf{B} \mathbf{I} \tag{2}$$

$$H_{HF} = g_s \beta \beta_n g_n \sum_{i=1}^{n} \frac{\mathbf{N}_i \mathbf{I}}{r_i^3} \tag{3}$$

$$H_Q = -e^2 \int \int \frac{\rho_e(r_e)\rho_n(r_n)}{|r_e - r_n|} \, d\tau_e \, d\tau_n \tag{4}$$

where $\mathbf{L}$ and $\mathbf{S}$ are the total angular and spin momentum and g_s is the gyro-magnetic ratio of the electron. $\mathbf{r}_i$ is the ith electron coordinate relative to the nucleus and $\mathbf{N}_i$ is given by: $\mathbf{N}_i = \mathbf{I}_i - \mathbf{s}_i + 3\mathbf{r}_i (\mathbf{s}_i\mathbf{r}_i)/r_i^2$. In the quadrupolar Hamiltonian formula, $-e\rho_e$ (r_e) and $e\rho_n$ (r_n) are the electron and nuclear charge densities with r_e and r_n taken relative to the center of the nucleus. The matrix elements of these operators can be found in Refs. [16,17]. A completely checked set of matrix elements is also given in [10].

Using equivalent operators and first and second-order perturbation theory, these interactions can be expressed as a spin Hamiltonian [18]. Moreover, in the case of electronic singlets and for point symmetries high enough (at least orthorhombic), the hyperfine and quadrupolar tensors have the same principal directions, which also coincide with the (x, y, z) crystal field axes. The spin Hamiltonian is then greatly simplified and reads:

$$H_{SH} = \sum_{i=x,y,z} \gamma_{ii} \mathbf{B} \mathbf{I} + D\left(I_z^2 - \frac{1}{3}I(I+1)\right) + E(I_x^2 - I_y^2) \tag{5}$$

where $\mathbf{B}$ is the magnetic field and $\mathbf{I}$ the nuclear spin operator. The parameters in H_{SH} involve the crystal-field levels of the considered J multiplet:

$$D = D_a + P, \qquad E = E_a + \eta\frac{P}{3} \tag{6}$$

$$D_a = A_J\left(\frac{\Lambda_{xx} + \Lambda_{yy}}{2} - \Lambda_{zz}\right), \quad E_a = A_J\frac{\Lambda_{yy} - \Lambda_{xx}}{2} \tag{7}$$

where P is the quadrupole-coupling constant, η an asymmetry parameter and A_J is the hyperfine interaction constant. The

Table 1
Calculated and experimental energy levels (in cm^{-1}) for Pr:LiYF$_4$ (selected multiplets)

$^3H_4$		$^1D_2$	
Exp.	Calc.	Exp.	Calc.
0	7	16,740	16,817
79	84	16,810	16,868
220	217	17,083	17,080
–	218	17,406	17,404
496	497		
–	512		
–	514		

second-order parameters read:

$$\gamma_{ii} = -g_N \beta_N - 2g_J \beta \Lambda_{ii} \tag{8}$$

and

$$\Lambda_{ii} = \sum_{n \neq 0} A_J \frac{|\langle 0|J_i|n\rangle|^2}{E_n - E_0} = \sum_{n \neq 0} \Lambda_{ii}^n \tag{9}$$

where g_N (g_J) is the nuclear (electronic) g-factor and β_N (β) is the nuclear (electronic) Bohr magneton. The index 0 denotes the first crystal-field level of a given multiplet, n the other CF levels and E_i is the energy of the CF level i. Λ_{ii}^n is defined as the term corresponding to level n in the sum of Eq. (9). Each CF level of a J multiplet is characterized by a set of D, E and γ_{ii} values.

3. Hyperfine structures in Pr:LiYF$_4$ and Tm:YAG

The validity of the spin Hamiltonian model was first checked by comparing hyperfine energies computed directly from the complete Hamiltonian (free ion, CF and magnetic interactions) with the values found by first computing the spin Hamiltonian parameters from the CF wavefunction and then computing the hyperfine energies from this spin Hamiltonian. A very good agreement was found for both Pr:LiYF$_4$ and Tm:Y$_3$Al$_5$O$_{12}$, consistent with the lack of large J mixing in the considered levels.

3.1. Pr^{3+}:LiYF$_4$

Pr^{3+} substitutes Y^{3+} in LiYF$_4$ in a site of S$_4$ point symmetry. The nuclear spin of the 100% abundant isotope ^{141}Pr is 5/2. Since the site symmetry is axial, the spin Hamiltonian describing Pr^{3+} hyperfine structure is given, for singlets, by Eq. (5) with equivalent x and y axes and $E = 0$. The CF analysis of Ref. [19] was used for spin Hamiltonian parameter computations. The optical transition usually studied in coherent spectroscopy is $^3H_4(0)$–$^1D_2(0)$ which lies in the orange region ($\approx$600 nm) and can be excited by ultra-stable dye lasers. The experimental and calculated energy levels for the $^3H_4$ and $^1D_2$ multiplets are given in Table 1. Both $^3H_4(0)$ and $^1D_2(0)$ levels are singlets. The ground state energies are well reproduced but large discrepancies are found for the excited state. This has been observed in several Pr^{3+}doped compounds and more advanced CF models could improve the calculated energies [20,21]. The experimental [18,22] and calculated spin Hamiltonian parameters are shown

Table 2
Experimental and computed spin Hamiltonian parameters for Pr^{3+} in $LiYF_4$. x and y axes are equivalent

Parameter	$^3H_4$		$^1D_2$	
	Exp.	Calc.	Exp.	Calc.
$-g_N\beta_N$ (MHz/T)	−12.21		−12.21	
γ_{xx} (MHz/T)	−80	−87.5	−14.5	−21.0
γ_{zz} (MHz/T)	−20	−18.5	−16.5	−12.2
D (MHz)	4.75	4.75	−2.56	−2.89
E (MHz)	0	0	0.017	0
D_a (MHz)		3.4		0.25
A_J (MHz)		1094.2		815.0
g_J		0.81		1.03
Λ_{xx}		3.3×10^{-3}		3.4×10^{-4}
Λ_{xx}^i, (i)		3.2×10^{-3}, (1)		3.0×10^{-4}, (3)
Λ_{zz}		2.8×10^{-4}		0.0
Λ_{zz}^i, (i)		2.8×10^{-4}, (8)		

in Table 2. It can be seen that a good agreement is found for the gyromagnetic tensor and the pseudo-quadrupolar parameter D in the ground state. The corresponding D_a value shows that the zero field splitting is mainly due to the second order hyperfine interaction. This confirms that the gyromagnetic tensor is well reproduced by the calculations. It can also be noted that γ_{xx} is much larger than γ_{zz}. This is explained by the contribution from Λ_{xx}^1 to Λ_{xx}. Since $E_n - E_0$ increases rapidly with n (see Table 1), Λ_{xx}^1 tends to be larger than Λ_{xx}^i with $i > 1$. Indeed, Λ_{zz} is much smaller compared to Λ_{xx} because it depends only on Λ_{zz}^8. The magnitude of the $|\langle 0|J_i|n\rangle|$ matrix elements can be qualitatively deduced from the m_J dependence of CF wavefunctions or equivalently from their irreducible representations (see next paragraph).

The agreement between theoretical and experimental gyromagnetic tensors of the excited state is not as good as in the ground state case (Table 2). The pseudo-quadrupolar parameter D is however well reproduced but is entirely due to the quadrupolar interaction ($D_a \approx 0$). Note that the CF calculations indicate that D is negative. This cannot be deduced from the usual holeburning experiments which are only sensitive to the energy differences between hyperfine levels so that the ordering of these levels remain unknown. The gyromagnetic tensor γ_{ii} is quite small and close to the nuclear Zeeman component $-g_N\beta_N$. Following the discussion of the ground state results, this is explained by the zero Λ_{xx}^1 and Λ_{zz}^1 parameters. This is due to the $^1D_2(0)$ wavefunction which is a pure $m_J = 0$ one (and the only one in this case in the $^1D_2$ multiplet). This gives zero matrix elements for J_z and therefore zero Λ_{zz}. Concerning J_x, the first CF level with a strong $m_J = \pm 1$ component is $^1D_2(3)$. This level lies at 263 cm^{-1} from $^1D_2(0)$ which results in a rather small Λ_{xx}. The discrepancies between experimental and calculated values of the gyromagnetic tensor seem to be linked to the energies computed from the CF analysis which give too small energy differences. This artificially increases the calculated γ_{xx}. For γ_{zz}, the problem rather lies in the wavefunctions themselves and could be linked to a deviation from the ideal S_4 symmetry. Such a deviation is suggested by the small experimental value of E which cannot be accounted for by the calculations since it should be zero in a perfectly axial symmetry.

3.2. $Tm^{3+}:Y_3Al_5O_{12}$

Tm^{3+} has a single natural isotope ^{169}Tm with a $I = 1/2$ nuclear spin. In YAG, Tm^{3+} occupy sites with a D_2 point symmetry. In this case, all electronic levels are singlets and no hyperfine structure appears without an external magnetic field: due to the 1/2 value of the nuclear spin, magnetic quadrupolar and second-order magnetic hyperfine interactions (i.e. D and E parameters in Eq. (5)) vanish. The spin Hamiltonian is simply given by:

$$H_{SH} = \sum_{i=x,y,z} \gamma_{ii}\mathbf{BI} \qquad (10)$$

The transition excited in QI experiments is $^3H_6(0) \rightarrow ^3H_4(0)$ which is in resonance with a ultra-stable diode laser [23]. The computed and experimental spin Hamiltonian parameters for Tm:YAG are reported in Table 3. Some discrepancies can be noticed between experiment and theory and could be due to inaccuracies in CF wavefunctions, although the energy levels for the $^3H_6$ and $^3H_4$ multiplets are rather well reproduced by the CF calculations [10]. However, it should also be noted that the holeburning experiments used to determine the gyromagnetic tensor are quite difficult in Tm:YAG. First of all, a precise measurement of the magnetic field intensity and direction is required. Moreover, the six magnetically non-equivalent sites for Tm ions lead to complicated spectra which explains that some components of the gyromagnetic tensor cannot be determined precisely (only upper bounds can be estimated) [9]. For these reasons, it is possible that the experimental errors are in fact larger than those originally estimated and quoted in Table 3. Further experiments on double optical-RF resonances may clarify this point.

The gyromagnetic tensor exhibit two other interesting features: a strong anisotropy along the y axis in the ground and excited state and a very large y component (560 MHz/T) in the ground state. These properties are fundamental to build a three-level Λ system [10]. The anisotropy can be linked to the symmetry or the m_J components of the wavefunctions, as in the case of Pr^{3+}. For example, $^3H_6(0)$ is mainly proportional to $|m_J = -1\rangle - |m_J = 1\rangle$ and $^3H_6(1)$ to $|m_J = 0\rangle$. There is no J_x or J_z matrix elements between these levels. Λ_{xx} and Λ_{zz} have there-

Table 3
Spin Hamiltonian parameters for Tm^{3+} in YAG

Parameter	$^3H_6$		$^3H_4$	
	Exp.	Calc.	Exp.	Calc.
$-g_N\beta_N$ (MHz/T)	3.56		3.56	
γ_{xx} (MHz/T)	<52	19.0	20 ± 11	22.3
γ_{yy} (MHz/T)	403 ± 2	559.6	82 ± 2.5	75.2
γ_{zz} (MHz/T)	<40	11.24	14 ± 8	6.3
A_J (MHz)		-470.3		-678.3
g_J		1.17		0.95
Λ_{xx}		-4.7×10^{-4}		-7.1×10^{-4}
Λ_{xx}^i, (i)		-4.1×10^{-4}, (3)		-7×10^{-4}, (3)
Λ_{yy}		-1.7×10^{-2}		-2.7×10^{-3}, (3)
Λ_{yy}^i, (i)		-1.7×10^{-2}, (1)		-2.0×10^{-3}, (1)
Λ_{zz}		-2.4×10^{-4}		-1.0×10^{-4}
Λ_{zz}^i, (i)		-2.2×10^{-4}, (2)		-0.55×10^{-4}, (4)

fore low values because they can involve only Λ^i with $i > 1$. On the opposite, J_y has a non zero matrix element between levels $^3H_6(0)$ and $^3H_6(1)$ and this lead to a large Λ_{yy} value. The same behavior is found in the excited state: only J_y has a matrix element between the two first CF levels of the $^3H_4(0)$ multiplet. The very large value of γ_{yy} in the ground state comes in part from the small value of the energy separation between $^3H_6(0)$ and $^3H_6(1)$: $27\,cm^{-1}$. This is smaller than in the $^3H_4$ multiplet ($37\,cm^{-1}$) or in the $^3H_4$ or $^1D_2$ multiplets of Pr^{3+}. This also shows the importance of the electronic contribution to the gyromagnetic tensor: even if the nuclear Zeeman interaction is larger in Pr^{3+} than in Tm^{3+}, the total gyromagnetic tensor of Tm^{3+}:YAG can be about five times stronger than in Pr^{3+}:LiYF$_4$.

4. Conclusion

Rare earth doped crystals are promising candidates for solid state quantum information (QI) systems. Because of their long coherence lifetimes, hyperfine transitions are usually used in QI schemes. Moreover, an external magnetic field is often used to tune the hyperfine structures in order to build Λ systems or to increase the transition coherence lifetimes. Experimental determination of these hyperfine structures can be difficult, especially under a magnetic field. It requires holeburning spectroscopy, precise knowledge of field orientation and magnitude and may be complicated by magnetically non-equivalent sites. Calculation of hyperfine structures from the crystal field wavefunctions is therefore an attractive tool to predict properties before starting experiments.

The hyperfine structures of Pr^{3+}:LiYF$_4$ and Tm^{3+}:YAG have been computed in this way and compared to experimental values. A reasonable agreement is found in both cases although a better crystal field modeling of Pr^{3+} could improve the results for the $^1D_2(0)$ level. Several properties of the gyromagnetic tensors (anisotropy, magnitude) are explained by selection rules and energy differences between crystal field levels.

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