Journal of Luminescence 53 (1992) 251–254
North-Holland

JOURNAL OF
LUMINESCENCE

# Spectral hole burning in the hyperfine lines of $LaCl_3:Ho^{3+}$

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Two laser spectral hole burning in the hyperfine split 649.9 nm ($^5I_8$–$^5F_5$) line of a 0.1% $Ho^{3+}$ doped $LaCl_3$ crystal at 2 K is presented and discussed. The process of hole burning in this centre is thought to arise from optically induced spin flips which under CW conditions compete with the relaxation processes causing electron–electron and nuclear–nuclear spin flips. In support of this mechanism, we also discuss a simple rate equation model which describes the interaction between the optical pumping and relaxation processes.

## 1. Introduction

There have only been a few hole burning studies of systems with electronic degeneracy split by hyperfine interactions and of these the hole burning spectrum and associated double resonance measurements have not been straightforward to explain. This is partly because inhomogeneous broadening can mask the hyperfine structure in the optical spectra and hence the mechanism whereby sideholes and/or antiholes occur at separations of the hyperfine splittings has been hard to establish. For example in $CaF_2:Pr^{3+}:O^2$ antiholes occur at separations of ~4 GHz in the absence of a magnetic field whereas there are sideholes at 4 GHz in the presence of a magnetic field [1]. To assist with understanding such phenomena it is helpful to investigate systems exhibiting resolved hyperfine structure. These systems permit observation of the hole burning spectra for each discrete hyperfine line and its associated holes and/or antiholes. The only previous report of such a hyperfine resolved system has been for a tetragonal $Pr^{3+}$ centre in cubic $CaF_2$ [2].

In this paper we report the optical hole burning spectra in $LaCl_3:Ho^{3+}$ which in some ways is simpler than the $CaF_2:Pr^{3+}$ system. This is because hole burning in $CaF_2:Pr^{3+}$ occurs via both electron and nuclear spin flips [2,3]. More importantly, there is only one orientation of the $Ho^{3+}$ centre in $LaCl_3$ and this enables observation of the splitting of the hyperfine lines for very weak external magnetic fields. The use of low fields proved to be of great benefit in understanding the hole burning spectra by resolving all the hyperfine lines of the ground state.

## 2. Previous work

The optical spectrum of $LaCl_3:Ho^{3+}$ has been investigated by Dieke [4]. Many of the absorption lines have well resolved nuclear hyperfine structure with eight near equidistant components. The particular line of interest in the present investigation is at 694.9 nm and is associated with a transition between the lowest energy component of the $^5I_8$ ground state and the lowest energy component of the $^5F_5$ multiplet. The $Ho^{3+}$ substitutes for $La^{3+}$ at a site of $D_{3h}$ symmetry with the ground state an E doublet and the excited state an $A_1$ singlet. The transition E → A is allowed as a forced electric dipole transition with

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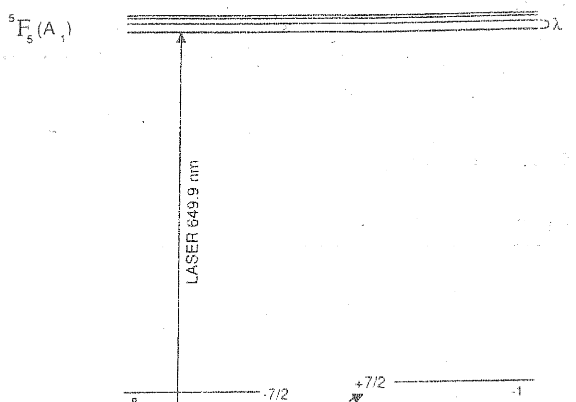

Fig. 1. Energy levels for $LaCl_3:Ho^{3+}$.

the electric vector polarized perpendicular to the trigonal axes of the centre. Holmium has only one naturally occurring isotope with a spin $I = 7/2$. In the nondegenerate excited state the nuclear spin may give rise to a small quadrupole splitting but it is not significant for this investigation. On the other hand in zero applied field the ground state is split by the hyperfine interaction into eight lines, see fig. 1.

## 3. Experimental results

The $LaCl_3:Ho^{3+}$ crystals were grown by the Bridgeman technique in quartz ampules and had a nominal concentration of 0.1% $Ho^{3+}$. To observe spectral hole burning two Coherent 699-21 dye lasers were employed. The frequency of one high resolution dye laser was tuned to match the maximum absorption in one hyperfine line while the excitation spectrum of all eight hyperfine lines was concurrently measured by sweeping the frequency of the second high resolution laser. The experiments were performed at 1.8 K by immersing the sample in a pumped helium bath.

In fig. 2(a), the spectrum obtained by hole-burning one of the extreme lines is displayed. It can be immediately observed that all hyperfine lines are affected by simply hole-burning one line. To better understand some of the complex hole/antihole structures observed hole-burning spectrums in the presence of small magnetic fields were also obtained. Figure 2(b) corresponds to an applied field of 0.01 T along the trigonal axes, while fig. 2(c) was obtained in a field of 0.02 T. It is clearer to first discuss the spectrum in fig. 2(c). In this figure it can be seen that the applied field is sufficient to split the eight individual hyperfine lines into two components. One of the components can be associated with the positive electron spin multiplet of the ground state and the other component with the negative electron spin multiplet of the ground state (see fig. 1).

The hole-burning spectrum shown in fig. 2(c) arises through competition between several processes. Firstly, the fixed frequency laser is resonant with one subgroup of ions and for this group the laser excites ions from the lowest level in the $^5I_8$ ground state to the lowest level in the $^5F_5$ multiplet. Next, while the ions are in this excited state, thermal fluctuations can further excite the ions to one of the other nuclear sublevels in the

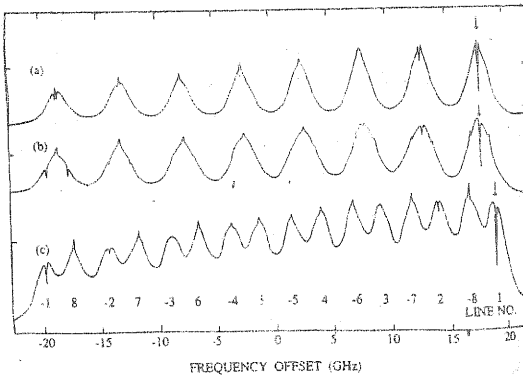

Fig. 2. Hole-burning spectrum in different applied fields.

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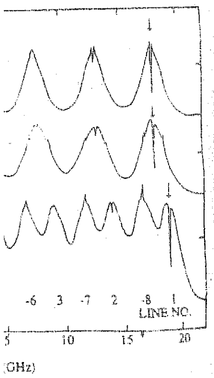

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$^5F_5$ multiplet. On optical decay therefore, since the new nuclear order is maintained, the ions will return to one of the other 15 hyperfine lines shown in fig. 2(c). If only these two processes were present then the spectrum would have one hole and fifteen antiholes, this is clearly not the case.

What introduces further complexity to the spectrum are the relaxation processes within the ground state. For $LaCl_3:Ho^{3+}$ there are two significant relaxation mechanisms within the $^5I_8$ ground state. Firstly, because the ground state has electronic degeneracy (only partially lifted in weak magnetic fields), mutual electron spin flips will occur in order to maintain equilibrium between the two electron states present. These electron spin flips also retain nuclear order, hence this process has the effect of establishing a hole in the line complementary to that line resonant with the laser (see fig. 1). A slower but still significant process is that of nuclear spin flips which will attempt to re-establish a Boltzman distribution within the active subgroup of ions. With $\Delta I_Z = \pm 1$ transitions being preferred, depopulated levels will be filled from adjacent levels and consequently holes may appear in lines of the same electron spin state immediately adjacent to any deep holes.

The spectra in fig. 2 have been measured during continuous irradiation of the hole-burning laser and hence they arise as a competition between the optical pumping, optical decay, nuclear spin flips in the excited state, electron spin flips and nuclear spin flips in the ground state. This competition can be described by a set of coupled rate equations between the 24 levels involved. Of the 16 nuclear levels in the doublet ground state the rate equations are of the form

$$\frac{dn_i}{dt} = \beta(n_{i+1} - xn_i) - \beta(n_i - xn_{i-1}) + \gamma(n_{-i} - yn_i) + \omega m_{|i|}, \quad (1)$$

for levels 2 to 7 and −2 to −7. While for levels 1, −1, 8 and −8 the rate equations are given by

$$\frac{dn_1}{dt} = \beta(n_2 - xn_1) + \gamma(n_{-1} - yn_1) + \omega m_1, \quad (2)$$

$$\frac{dn_8}{dt} = -\beta(n_8 - xn_7) + \gamma(n_{-8} - yn_8) + \omega m_8, \quad (3)$$

$$\frac{dn_{-1}}{dt} = -\beta(n_{-1} - xn_{-2}) - \gamma(n_{-1} - yn_1) + \omega m_1, \quad (4)$$

$$\frac{dn_{-8}}{dt} = \beta(n_{-7} - xn_{-8}) - \gamma(n_{-8} - yn_8) + \omega m_8. \quad (5)$$

Similarly, for the 8 nuclear levels in the singlet excited state, the rate equations for levels 2 to 7 can be written

$$\frac{dm_i}{dt} = \lambda(m_{i+1} - zm_i) - \lambda(m_i - zm_{i-1}) - 2\omega m_i \quad (6)$$

and

$$\frac{dm_1}{dt} = \lambda(m_2 - zm_1) - 2\omega m_1, \quad (7)$$

$$\frac{dm_8}{dt} = -\lambda(m_8 - zm_7) - 2\omega m_8, \quad (8)$$

for levels 1 and 8 respectively. In the above equations, $n_i(m_i)$ are the populations in the ground state (excited state) levels shown in figure 1, $\beta$ and $\gamma$ are the nuclear and electron spin flip rates in the ground state, $\lambda$ is the nuclear spin flip rate in the excited state, $1/2\omega$ is the optical lifetime of the excited state, and $x$, $y$ and $z$ describe the respective thermal barriers for upward transitions of the three types of spin flip. In addition to the above terms, for the two levels resonant with the laser a term $\alpha(m_i - n_i)$ is also included, where $\alpha$ is the optical pumping rate. For the sake of simplicity we have assumed in this model that i) the nuclear and electron spin flip rates do not depend on the nuclear sublevels involved [5], ii) the doublet ground state only has magnetic hyperfine splitting ~ 5.4 GHz, and iii) the splitting in the excited state is negligible (i.e. $z \approx 1$).

The agreement that can be obtained with the experimental spectrum using, $\alpha = 231\ s^{-1}$, $1/\beta = 29$ ms, $1/\gamma = 3.6$ ms, $1/\lambda = 39$ µs and the measured optical lifetime $1/2\omega = 27$ µs, is shown in

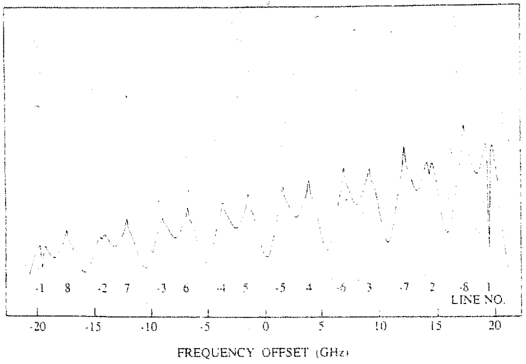

Fig. 3. Calculated hole-burning spectrum.

fig. 3. We note that while the calculated spectrum is in reasonable agreement with the experimental spectrum it was not possible to fully test the model due to uncertainties in the experimental data. However it does appear that the model can adequately describe what is causing the observed spectrum.

Finally, the complex hole/antihole shapes in fig. 2 can now be simply understood as an overlap of spectra from simultaneously burning two subgroups of ions, one in each electron state of the ground state.

## 4. Conclusions

The complex hole-burning structure observed in $LaCl_3:Ho^{3+}$ and other systems with electronic degeneracy in the ground state can now be understood in terms of a dynamic interaction between the optical pumping rate and the electron and nuclear relaxation processes. In addition, the sensitivity of hole-burning spectra under the above circumstances can also be further exploited in double resonance experiments to extract hyperfine and superhyperfine information.

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