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Optical/RF double resonances in $\text{YLiF}_4:\text{Ho}^{3+}$

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Abstract

In this paper, double resonance signals associated with CW spectral holeburning measurements of unintentional Ho^{3+} impurities in crystals of YLiF_4 are reported. The double resonance signals are detected in the microwave and radiofrequency region. The observed microwave resonances are at 4.460(1) and 4.473(1) GHz and attributed to ground state hyperfine splittings. Two radiofrequency resonances at 29.85(8) and 36.86(8) MHz are also detected and assigned to superhyperfine transitions of the two inequivalent fluorine nn sites. This assignment is supported by Zeeman measurements.

1. Introduction

The complexities of inhomogeneous optical line widths in solids have already been documented in articles by Macfarlane [1–3]. In the case of insulators containing fluorine the paramagnetic character of rare earth ions such as Ho^{3+} and Pr^{3+} create polarized shells of the surrounding fluorine nuclei. This coupling results in the individual homogeneous subgroups of ions being defined by the near neighbour fluorine nuclear spin projections as well as the crystal field and strain interactions acting on the ion. One way to quantitatively investigate this coupling in $\text{Ho}^{3+}:\text{YLiF}_4$ is with CW holeburning double resonance experiments as has been shown in $\text{Ho}^{3+}:\text{CaF}_2$ [4, 5] and $\text{Pr}^{3+}:\text{CaF}_2$ [6, 7]. However, even in deliberately low doped $\text{Ho}^{3+}:\text{YLiF}_4$ (0.1%) the concentration of Ho^{3+} causes the Ho–Ho energy transfer rate to be too high and no

CW holeburning or double resonance signals can be detected. To achieve saturated absorption with the modest laser power available requires a lower Ho^{3+} concentration. As reported in this paper a low but detectable Ho^{3+} impurity concentration can be readily found in nominally undoped YLiF_4 due to the rare earth impurity levels in the yttrium starting material. Such crystals are found to exhibit holeburning and have been used for the present study.

2. Ho^{3+} centre

Ho^{3+} ions in YLiF_4 substitute for the Y^{3+} ion and lie in a crystal field potential of S_4 symmetry. The YLiF_4 crystal is of Scheelite structure (CaWO_4) as shown in Fig. 1 with the closest 8 neighbouring fluorine ions to the Y^{3+} site arranged into two sets of 4 equivalent ions with separations of 2.41 and 2.45 Å, respectively. Because of its

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possible suitability as a laser material $\text{YLiF}_4:\text{Ho}^{3+}$ has been intensively studied by several groups. The energy levels of the Ho^{3+} ion in YLiF_4 were first established by Karayianis et al. [8], and resolved hyperfine structure has been observed in several multiplets [9, 10]. The optical transitions we have studied are between electronic states in the ground state $^5\text{I}_8$ level and the $^5\text{F}_5$ multiplet. The relevant energy levels are shown in Fig. 1. As can be seen from this figure there exists relatively small separations $\sim 7\text{ cm}^{-1}$ in both multiplets, between $\Gamma_{3,4}$ doublet states and Γ_2 singlets. The lowest state is a $\Gamma_{3,4}$ doublet and hence has a significant electronic moment. This moment interacts with the neighbouring fluorine nuclei and results in these nuclei being involved in the optical pumping cycle.

3. Experiment

A YLiF_4 crystal deliberately doped with Er^{3+} (0.02%) but containing traces of the other rare earths at levels of 1–10 ppm was cooled to temperatures between 1.6–4.2 K in a pumped helium bath. The S_4 centre of the Ho^{3+} impurity was detected in this crystal by irradiating the sample at wavelengths corresponding to the transitions shown in Fig. 1 with a tunable Coherent 699 high resolution laser. The emission from the excited $^5\text{F}_5$ multiplet to a higher level of the ground state was monitored at 657.4 nm. In practice, to obtain the optical spectra the laser would be operated in scanning mode with width 25 GHz and the signal to noise was improved by averaging many scans.

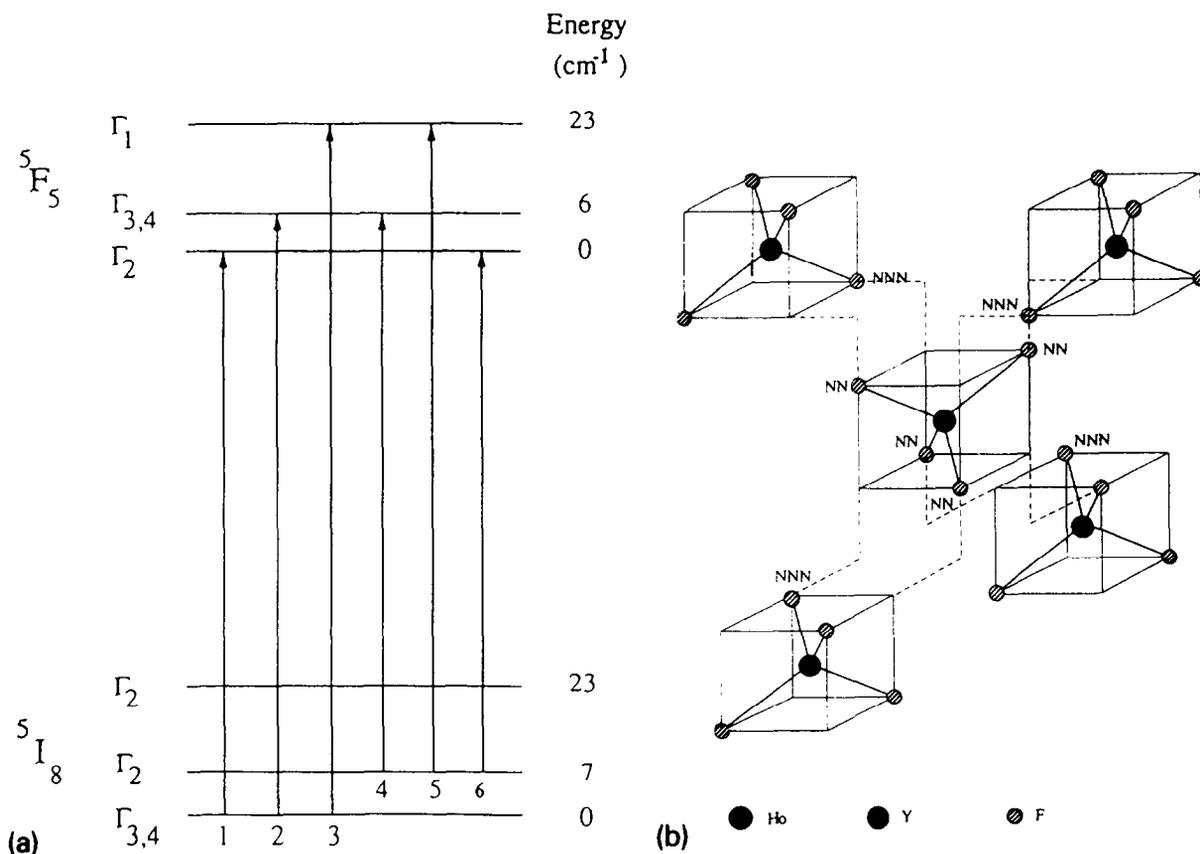


Fig. 1. (a) Energy level diagram for $\text{Ho}^{3+}:\text{LiYF}_4$; (b) crystal structure.

Fig. 2 displays the low temperature optical spectra associated with transitions from the ground $\Gamma_{3,4}$ state to the three lowest levels of the 5F_5 multiplet. The hyperfine structure is very clearly resolved for these three transitions. Interesting points to note about the spectra are that firstly

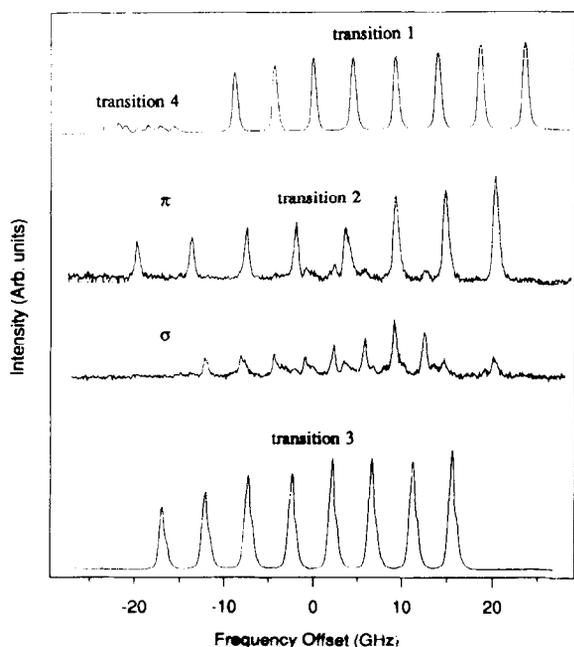


Fig. 2. High resolution optical spectra for transition 1 (15485 cm^{-1}), transition 2 (15491 cm^{-1}), transition 3 (15508 cm^{-1}) and transition 4 (15484 cm^{-1}) as labelled in Fig. 1.

with the low dopant level the observed spectra are narrow $\sim 1\text{ GHz}$. Narrower spectral features $\sim 240\text{ MHz}$ however, have been observed for this centre in the $^5I_8 \rightarrow ^5I_7$ transitions by Agladze et al. [10]. Secondly, because of the narrow line width the individual σ and π transitions between the two $\Gamma_{3,4}$ states in the two multiplets are well resolved (transition 2) as the polarization of the incident laser is rotated. Finally, an anomalous asymmetry is apparent on all the hyperfine lines of transition 3. Following the work of Agladze et al. [10], this asymmetry may be due to isotope shifts of the transition caused by neighbouring Li^+ ions.

In addition to observing the optical spectra we also performed two double resonance experiments

exploiting the property that the centre exhibited weak (20%) hole burning at this low concentration. The first double resonance experiment was the observation of two hyperfine transitions of the Ho nucleus at $4.446(1)$ and $4.473(1)\text{ GHz}$ (Fig. 3) which we assign to the ground $\Gamma_{3,4}$ state. The second experiment measured resonances in the MHz region which are attributed to superhyperfine transitions. In both experiments the laser was fixed in frequency while the microwave (radiofrequency) frequency was swept. The presence of these CW double resonance signals indicates that the hyperfine and superhyperfine states are involved in the optical pumping cycle, at least on long time scales. This behaviour is consistent with other rare earth impurity centres surrounded by fluorine lattices where spontaneous electron–electron and nuclear–nuclear spin flips cause significant energy transfer from resonant to nonresonant homogeneous packets [1–7].

Following previous work on analysing hyperfine double resonance signals in rare earth impurity centres [5, 7, 11] the observation of only two Ho^{3+} microwave transitions is insufficient to obtain unique values for the magnitudes of the magnetic hyperfine interaction parameter A , and the total nuclear quadrupole interaction parameter P in the ground $\Gamma_{3,4}$ state. The two possible assignments of hyperfine splittings to the two observed microwave transitions are (i) the transitions are between the

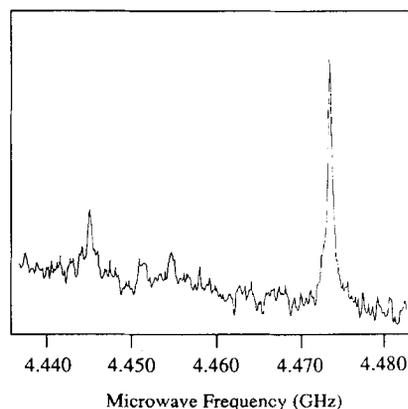


Fig. 3. Observed hyperfine spectra in zero applied field.

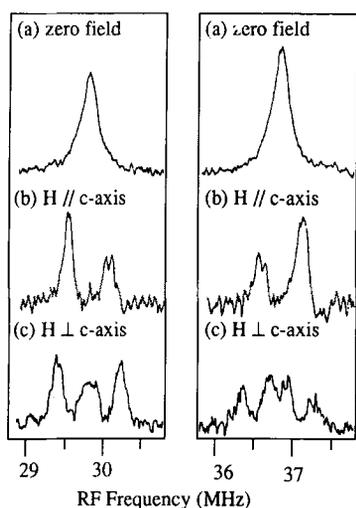


Fig. 4. Observed superhyperfine spectra in (a) zero applied field, (b) an applied field 65 G \parallel C_4 axis, and (c) an applied field 65 G \perp C_4 axis.

$|7/2 \rightarrow |5/2\rangle$ hyperfine states at each higher and lower energy extreme of the $\Gamma_{3,4}$ state or (ii) the transitions are between the $|7/2 \rightarrow |5/2\rangle$ and $|5/2 \rightarrow |3/2\rangle$ states at the lower energy end of the $\Gamma_{3,4}$ state. The first assignment gives the relationships $|A_{\parallel}| + 6|P| = 4.473$ GHz and $|A_{\parallel}| - 6|P| = 4.446$ GHz and hence that $|A_{\parallel}| = 4.460(2)$ GHz and $|P| = 2.3(2)$ MHz. Alternatively, the second assignment gives the relationships $|A_{\parallel}| + 6|P| = 4.473$ GHz and $|A_{\parallel}| + 4|P| = 4.446$ GHz and hence that $|A_{\parallel}| = 4.439(2)$ GHz and $|P| = 13.5(10)$ MHz. Since other Ho^{3+} systems with doublet ground states exhibit nuclear quadrupole interactions of 6.8(5) MHz [5] and $-32(1)$ MHz [11] neither hyperfine splitting estimates given above can be regarded as unphysical.

The superhyperfine resonances were observed at 29.85(8) and 36.86(8) MHz (Fig. 4(a)) due to the two inequivalent sets of near neighbour F^- ions. Confirmation of the identification of the superhyperfine resonances can be found in the low field Zeeman measurements of Figs. 4(b) and (c). The changes from doublet to multiple splittings depending

on magnetic field orientation is consistent with the nearest two sets of fluorine neighbours and their lattice positions. It is interesting however that the two transitions are $\sim 15\%$ different in frequency yet only 2% different in distance to the Ho^{3+} ion. It could be argued that one set of fluorine ions must form more direct chemical bonds with the Ho^{3+} ion and hence have a higher exchange interaction.

4. Conclusion

The incorporation of rare earth ions as a chemical impurity of other materials proves to be a very useful source of low doped materials for optical hole burning studies. In $\text{YLiF}_4:\text{Ho}^{3+}$ our double resonance experiments have again illustrated the dominant role that neighbouring fluorine nuclei have in the optical absorption of paramagnetic rare earth impurity optical centres.

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