Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Z. Hasan , Mikhail Solonenko & Levent Biyikli (1996): Spectroscopy of RE^{3+} Centers in Fluorite Host Using High Resolution Optical Hole-Burning and Double Resonance Techniques, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 291:1, 209-214

To link to this article: http://dx.doi.org/10.1080/10587259608042749

Mol. Cryst. Liq. Cryst., 1996, Vol. 291, pp. 209–214
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SPECTROSCOPY OF RE^{3+} CENTERS IN FLUORITE HOST USING HIGH RESOLUTION OPTICAL HOLE-BURNING AND DOUBLE RESONANCE TECHNIQUES

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Abstract Techniques of Optical Hole-burning, Optical-MW and Optical-RF Double Resonance have been used to study Ho^{3+} and Pr^{3+} in several trigonal and tetragonal sites in CaF_2.

INTRODUCTION

Doping CaF_2 with trivalent lanthanides (Ln^{3+}) results in many charge compensated centers. Spectra associated with these centers are complex and often overlap in energy prohibiting a clear identification by usual perturbation spectroscopy techniques. Here we present our work on three such centers and show the strength of the high resolution techniques, optical holeburning and associated double resonances, in unambiguously identifying the spectra and revealing the most intricate details of electronic and nuclear interactions.

CENTERS

Three most common charge compensated centers in CaF_2 are shown in Fig. 1. In (a) charge compensation is by a doubly negatively charged oxygen ion substituting for one of the nearest neighbor lattice fluorine, in (b) and (c) charge compensation is by F^- occupying trigonal and tetragonal interstitial sites. The symmetry at the site of the rare earth ion is C_{3v} for centers shown in (a) and (b) and C_{4v} for the center in (c).

We have studied the O^{2-} compensated center of Pr^{3+} and two Ho^{3+} centers of the types shown in Fig. 1(b) and (c), we will call these O-, B- and A- centers respectively.

HOLEBURNING

In these centers, transient holes are burnt due to the population transfer in the hyperfine and superhyperfine levels. Holes burn deep and almost 100% of the absorption line is bleached out. Holeburning spectra are shown in Fig.2 for the lowest energy zero phonon lines (ZPLs) of the three centers.

For the O-center of Pr^{3+} the lowest energy zero phonon line $^3H_4$ (E) -$^1D_2$ (E) overlaps with the spectrum associated with the F^- compensated C_{4v} center. Low resolution spectroscopy has not been able to give any information about this center. Heat treatment in the presence of water vapors was used to convert a fraction of C_{4v} centers to O-centers. This process introduces extra defects in the crystal resulting in broad inhomogeneous lines[1] and the hyperfine structure due to nuclear spin, I=5/2, of Pr is totally masked by the inhomogeneous broadening.

The holeburning spectrum for O-center is shown in Fig. 2(a). Antiholes can be seen at integral multiples of 4.12 GHz from the ZPL. This separation gives the hyperfine splitting in the ground state, $A_{g/2}$ = 4.12 GHz. Zeeman studies on the holeburning spectrum gave the excited state hyperfine splitting $A_{e/2}$ = 4.06 GHz that appeared as side holes [2]. Such large hyperfine splittings confirmed that the ground and excited electronic states are both electronic doublets. The symmetry of the O-center was confirmed by the data on superhyperfine structure discussed later.

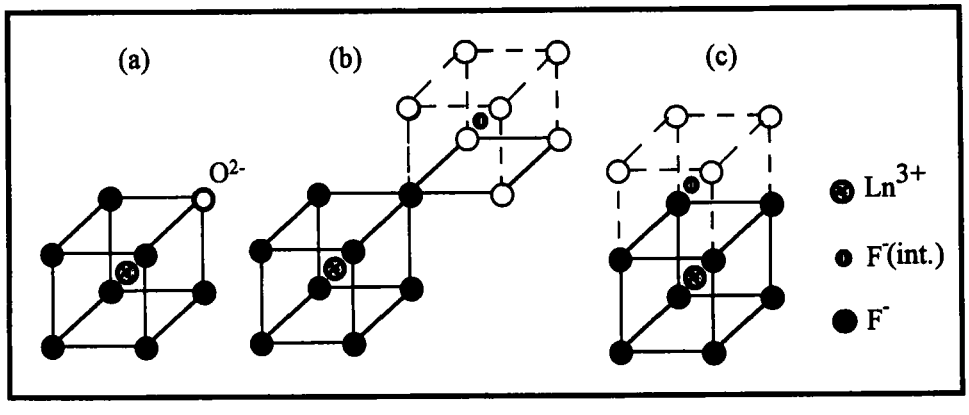

FIGURE 1 Charge compensated centers of Ln^{3+} in CaF_2. (a) Oxygen compensated C_{3v} center, (b) and (c) are fluorine compensated trigonal (C_{3v}) and tetragonal (C_{4v}) centers.

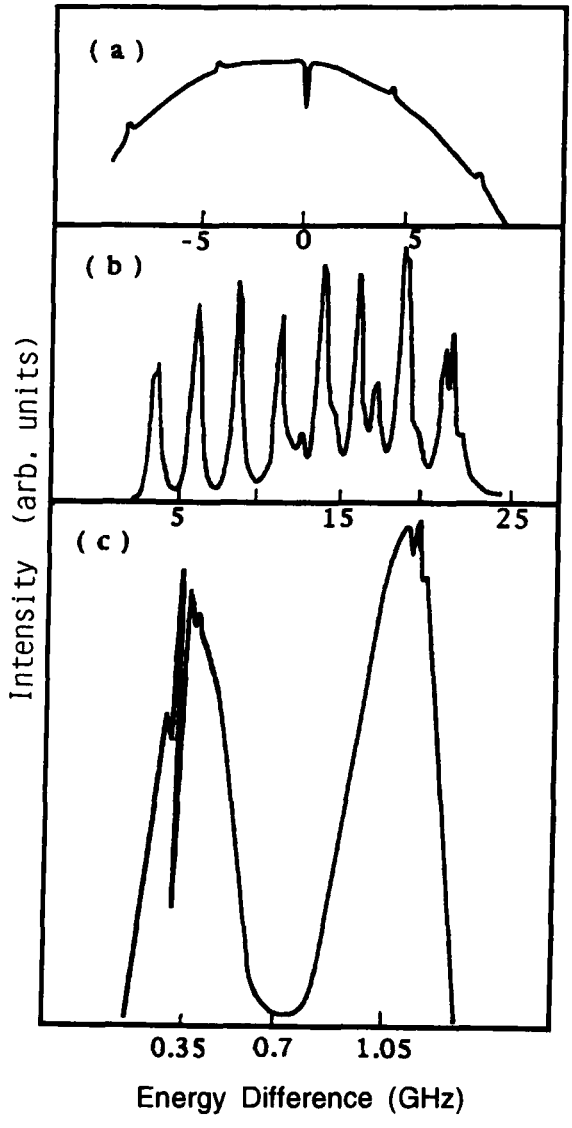

FIGURE 2 Holeburning spectra of (a): O-center of Pr^{3+}, (b): B-center of $Ho^{3+}$and (c): A- center of Ho^{3+}.

Holburning spectra of A- and B-centers of Ho^{3+} are shown in figures 2c, and 2b respectively. For lightly doped crystals the inhomogeneous broadening is small.The hyperfine splitting due to the I=7/2 nuclear spin and a large free ion magnetic moment ($3.31\mu_B$) of ^{165}Ho is considerably large in comparison. For the A-center the zero phonon transition is $^5I_8$ (A_1)-$^5F_5$ (E) and for the B-center it is $^5I_8$ (E)-$^5F_5$ (E). High resolution

excitation spectra of these centers show a very complicated hyperfine pattern. Burning holes in any hyperfine line shows clear antihole/side hole structure in other lines. The holeburning spectrum was used to confirm the symmetry of the electronic states and it showed that the complicated pattern of hyperfine splittings is due to higher order hyperfine interactions between close by crystal field states. Such states exist for both A- and B-centers and higher order interactions are observable due to the large magnetic moment of $^{165}Ho^{3+}$[5]. The transient holes in these centers last for only a fraction of a second at 2K. Double resonance studies are convenient and also more informative as discussed below.

MICROWAVE-OPTICAL DOUBLE RESONANCE

A completely resolved hyperfine interaction in case of Ho^{3+} B-center allowed microwave-optical double resonance experiments to be performed on individual hyperfine lines in this system. The sample was placed in a parallel plate cavity with the laser burning hole in one specific hyperfine line I_Z. A change in emission intensity was observed whenever the microwave frequencies were in resonance with the adjacent hyperfine levels of the ground state, $I_Z = I_Z \pm 1$. Fig. 3. shows the spectrum thus obtained.

The spin hamiltonian for an electron doublet can be written as ,[6]

$$H = g_{\parallel}\beta H_Z S_Z + A I_Z S_Z + D[I_Z^2 - I(I+1)/3] + \gamma_{\parallel} H_Z I_Z + \gamma_{\perp}(H_X I_X + H_y I_y),$$

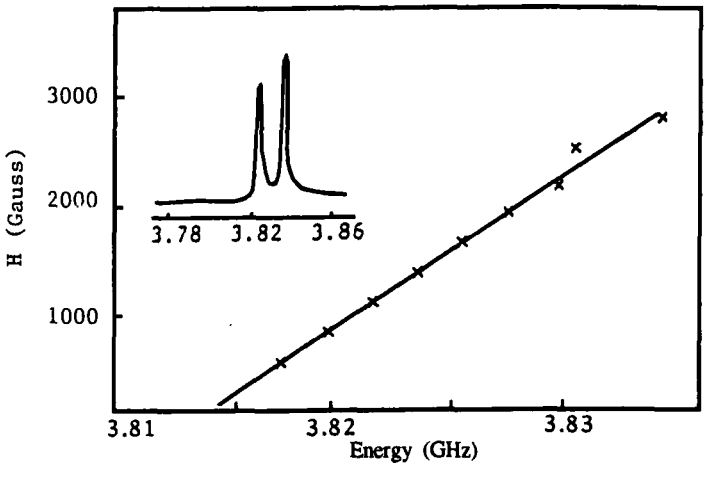

FIGURE 3 Hyperfine resonances of the Ho^{3+} B-center and their variation with the magnetic field. The laser was tuned to Iz=5/2 state, two peaks correspond to the population transfer from Iz=3/2 and Iz=7/2 to Iz=5/2 spin state. The separation between the two lines is 2 D.

Using this hamiltonian the position of microwave signal gives the hyperfine interaction parameter A, splitting and the displacements of MW resonances with the magnetic field along different symmetry directions give the quadrupole interaction parameter, D, and the nuclear gyromagnetic ratios, γ's, respectively. The following set of parameters was obtained for the ground $^5I_8$ (E) state of the C_{3v} center of Ho^{3+}: $g_{\|} = 10$ along<111>, hyperfine interaction parameter (Ag/2 = 3.85 GHz), quadrupole interaction parameter, D= -6.01 MHz, nuclear gyromagnetic ratio $\gamma_{\|} = 7.3$kHz/G and $\gamma_{\perp} = 5.62$kHz/G.

RF-OPTICAL DOUBLE RESONANCE

In a similar way as for the microwave-optical double resonance the sample for these experiments was placed in a RF coil and the RF-field was scanned across the superhyperfine levels. These levels are due to the coupling of fluorine nuclear spins (I=1/2) to the

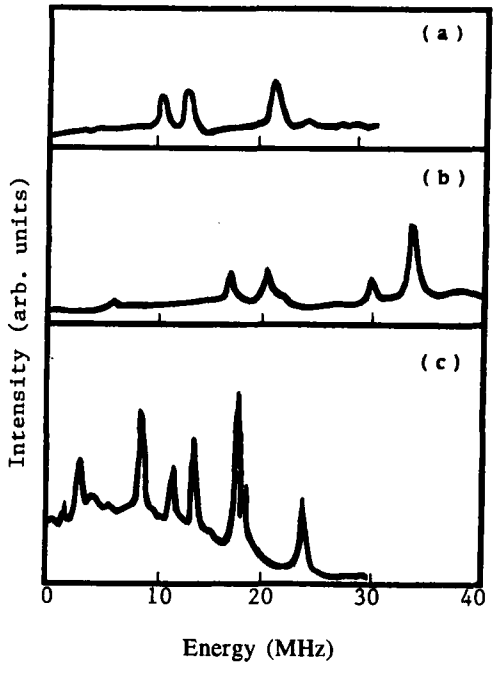

FIGURE 4 RF-optical double resonance spectra. (a) Pr: O-center, three major peaks are due to n.n fluorines resonances, (b) Ho: B-center the four major peaks are due to the n.n fluorines, and (c) Ho: A- center hyperfine resonances.

electronic spin of the rare earth ion. Superhyperfine spectrum would generally give the information about the symmetry of fluorine spins surrounding the rare earth ion and hence the symmetry of the center. Superhyperfine spectra for the three centers under consideration are given in Fig. 4.

For the O-center there are three signals corresponding to two sets of three F^- ions in (111) planes and one along the C_3 axis, Fig. 1. The highest energy line is due to the F^- along the C_3 axis. For the B-center of Ho^{3+} (Fig. 1b) an additional signal is due to an extra fluorine on the corner of the cube containing the rare earth ion at its center. RF-Optical double resonance confirms the site symmetry of the centers in these two cases to be C_{3v}.

Although for A-center there are only three distinct sets of nearest neighbor F^- ions (two sets of four in (100) planes and one interstitial), the superhyperfine spectrum of A-center is much richer than that for the other two centers. A detailed study of the spectrum reveals up to four sets of three signals from the nearest neighbor fluorines. The reason for it is that the ground $^5I_8(A_1)$ state interacts with another singlet, $^5I_8(A_2)$, ~ 55 GHz apart and these two states together behave like a pseudo doublet.[3,7] This second order hyperfine interaction gives four unequally spaced hyperfine lines for each A_1 and A_2 states, all having distinct superhyperfine structure associated with them. A detailed analysis of the superhyperfine spectra in this center has revealed a wealth of information about the higher order hyperfine interactions that are observable due to large nuclear moment of ^{165}Ho and very narrow inhomogeneous line widths.[1,7]

ACKNOWLEDGMENT

This work was partially supported by a grant from the Air Force Office of Scientific Research (Grant no. F49620-96-1-0347).

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