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## Superhyperfine structure of $F^-$ , $H^-$ , $D^-$ , and $T^-$ charge-compensated $Pr^{3+}$ centres in $CaF_2$ and $SrF_2$ crystals

N B Manson†, Z Hasant§, P T H Fisk†, R J Reeves‡¶, G D Jones‡ and R M Macfarlane||

† Laser Physics Centre, Research School of Physical Sciences, Australian National University, Canberra, ACT 2601, Australia

‡ Department of Physics, University of Canterbury, Christchurch, New Zealand

|| IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120, USA

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**Abstract.** Optical-RF double-resonance techniques have been used to study the superhyperfine transition frequencies in a series of  $Pr^{3+}$  centres in  $CaF_2:Pr^{3+}$  and  $SrF_2:Pr^{3+}$  crystals. In these centres  $Pr^{3+}$  substitutes for  $Ca^{2+}$  ( $Sr^{2+}$ ) and the excess positive charge is compensated by  $F^-$ ,  $H^-$ ,  $D^-$  or  $T^-$  interstitial ions along [100] directions yielding centres of  $C_{4v}$  symmetry. The superhyperfine structure is associated with RF-induced nuclear spin flips of the lattice  $^{19}F^-$  ions and of the interstitial ions that are coupled to the  $Pr^{3+}$  ion. Some qualitative conclusions are drawn about the position of the  $Pr^{3+}$  ion, the nearest-neighbour  $F^-$  ions and the interstitial ions in the lattice.

### 1. Introduction

$CaF_2:Pr^{3+}$  has been the subject of numerous laser excitation and emission studies (Kliava *et al* 1978, Lezama *et al* 1986, Tissue and Wright 1987). The  $Pr^{3+}$  ion substitutes for the divalent  $Ca^{2+}$  ion and charge compensation is achieved in various ways giving many different  $Pr^{3+}$  centres. The most extensively studied centre is one where an  $F^-$  ion occupies the interstitial location along a [100] direction from the  $Pr^{3+}$  ion and thus provides  $C_{4v}$  point group symmetry. The  $Pr^{3+}$  electronic ground state of this centre is a non-Kramers doublet (Borum *et al* 1982). This orbital degeneracy results in a large magnetic moment of  $5.44 \text{ MHz G}^{-1}$  and significant hyperfine and superhyperfine interactions associated with the ground state. The superhyperfine structure is associated with RF-induced nuclear spin flips of the surrounding lattice and interstitial ions that are coupled to  $Pr^{3+}$ . These interactions have been studied by Macfarlane *et al* (1981) and Burum *et al* (1982) using optical hole-burning and double-resonance techniques. In particular, they have measured the superhyperfine resonances using RF hole-filling techniques and in this paper equivalent techniques are used to study a series of related  $Pr^{3+}$  centres in  $CaF_2$  and  $SrF_2$  crystals. The resonant RF frequencies depend on the magnetic field of the  $Pr^{3+}$  ion as experienced by the surrounding ions. The variation in these frequencies from centre to centre can

§ Now in the Department of Physics, University of Illinois, Urbana, IL 61801, USA.

¶ Now in the Department of Physics, Oklahoma State University, Stillwater, OK 74078, USA.

be used to determine the relative positions of the nearest-neighbour ions in a similar way to what was done previously using ENDOR data (Baker *et al* 1972, Kiro and Low 1970).

When  $\text{CaF}_2:\text{Pr}^{3+}$  crystals in contact with molten aluminium are heated in an atmosphere of hydrogen gas,  $\text{H}^-$  ions diffuse into the crystal and provide charge compensation for  $\text{Pr}^{3+}$  ions. One centre formed is the hydrogenic ion analogue of the tetragonal ( $C_{4v}$ ) symmetry centre where an  $\text{H}^-$  ion is located in the interstitial position along a [100] direction from the  $\text{Pr}^{3+}$  ion. The change of the nearest-neighbour interstitial ion shifts the  $\text{Pr}^{3+}$  electronic transition energies by tens of wavenumbers to give distinct absorption line frequencies. In a similar fashion, heating in a gas with deuterium or tritium content can give centres with  $\text{D}^-$  or  $\text{T}^-$  charge compensation. The shifts in transition energies between hydrogenic ion centres are only about  $1\text{ cm}^{-1}$ . These shifts are sufficient for separate selective excitation of the different charge-compensated  $C_{4v}$  centres present in a sample that may contain hydrogen, deuterium and tritium centres simultaneously.

The work reported in this paper used RF-optical double resonance, also known as optically detected nuclear magnetic resonance (ODNMR), to measure how the super-hyperfine resonance frequencies vary for the four centres with different charge compensation ions in both  $\text{CaF}_2$  and  $\text{SrF}_2$  host lattices.

## 2. Experimental details

The crystals of  $\text{CaF}_2:\text{Pr}^{3+}$  and  $\text{SrF}_2:\text{Pr}^{3+}$  were grown using the Bridgman technique and contained typically 0.05% mol  $\text{Pr}^{3+}$ . Subsequently, they were heated in the appropriate hydrogenic gas and in contact with molten aluminium for several hours at  $900^\circ\text{C}$  to prepare the hydrogenic ion centres (Hall and Schumacher 1962).

Optical excitation was applied by a Coherent 699-21 ring dye laser having a nominal linewidth of 1 MHz RMS and operating with Rhodamine 590 dye. The optical signals were detected with fluorescence excitation and the emission was dispersed by a monochromator and detected by a photomultiplier tube. The RF was applied through a simple coil wrapped around the samples and driven by a Hewlett-Packard RF sweep generator amplified by an ENI 10 W power amplifier. Several 0–25 MHz sweeps were averaged on a PAR signal averager. All measurements were made with the crystals immersed in liquid helium at 1.8 K.

## 3. Results

Figure 1 shows a schematic model of the  $C_{4v}$  centres and the arrangement of the constituent ions. A  $\text{Pr}^{3+}$  ion substitutes for  $\text{Ca}^{2+}$  and is charge compensated by a negative ion occupying the neighbouring interstitial position along a [100] direction. A fourfold rotation axis exists along this [100] direction corresponding to the  $C_{4v}$  point group symmetry of the  $\text{Pr}^{3+}$  ion. Note that the eight  $\text{F}^-$  lattice ions surrounding  $\text{Pr}^{3+}$  can be divided into two equivalent sets of four, with one set being closer to the interstitial ion.

The low-temperature excitation lines observed in the spectral region under study correspond to absorption transitions from the  $^3\text{H}_4$  ground-state multiplet to the  $^1\text{D}_2$  multiplet of the  $\text{Pr}^{3+}$  ion. The transition wavelengths have been tabulated for the

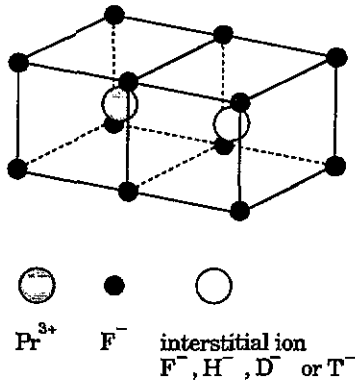


Figure 1. Schematic model of the  $C_{4v}$  symmetry centre in  $CaF_2:Pr^{3+}$  and  $SrF_2:Pr^{3+}$  crystals.

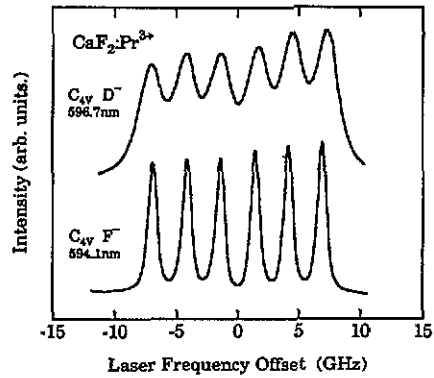


Figure 2. Fluorescence excitation spectrum at 4 K of the  $Z_1 \rightarrow D_1$  transition for the  $C_{4v} F^-$  centre, central wavelength 594.1 nm, and  $C_{4v} D^-$  centre, central wavelength 596.7 nm, in a  $CaF_2:Pr^{3+}$  crystal.

$C_{4v} F^-$  and hydrogenic ion centres in both  $CaF_2:Pr^{3+}$  and  $SrF_2:Pr^{3+}$  crystals (Reeves *et al* 1992). The wavelength of the transition between the lowest energy level ( $Z_1$ ) of  $^3H_4$  and the lowest energy level ( $D_1$ ) of  $^1D_2$  is given in table 1 for the centres studied. For the  $F^- C_{4v}$  centre in  $CaF_2:Pr^{3+}$  this line lies at 594.1 nm and exhibits hyperfine structure as shown by Macfarlane *et al* (1981). The only other absorption line found to exhibit hyperfine structure was the corresponding transition associated with the  $D^-$  compensated centre in  $CaF_2$ , and the line profiles for both centres are shown in figure 2.

Table 1. Summary of experimental data and established parameters for  $CaF_2:Pr^{3+}$  and  $SrF_2:Pr^{3+} C_{4v}$  centres.

System	Interstitial ion and nuclear spin	Absorption wavelength, $Z_1 \rightarrow D_1$ (nm)	Fluorescence lifetime ( $\mu s$ ) <sup>a</sup>	Nuclear $g$ -value, $g_N$ , of the interstitial ion	ODNMR frequency of the NN $^{19}F^-$ ions (MHz)	ODNMR frequency of the interstitial ion (MHz)
$CaF_2:Pr^{3+}$	$F^- \frac{1}{2}$	594.1	420	5.255	9.20, 9.75	20.6
	$T^- \frac{1}{2}$	596.7	—	5.958	9.35, 9.60	18.2
	$D^- 1$	596.7	95	0.857	9.35, 9.55	2.11
$SrF_2:Pr^{3+}$	$H^- \frac{1}{2}$	596.7	0.38	5.585	9.30, 9.55	17.5
	$F^- \frac{1}{2}$	593.2	2030	5.255	7.9, 8.8	16.8
	$T^- \frac{1}{2}$	594.6	—	5.958	8.2, 8.9	15.7
	$D^- 1$	594.6	405	0.857	8.1, 8.8	—
	$H^- \frac{1}{2}$	594.5	2.69	5.585	7.6, 8.6	15.3

<sup>a</sup> Fluorescence lifetime data from Reeves *et al* (1987).

The crystal-field wavefunction of the  $\text{Pr}^{3+}$  ion ground state in these  $C_{4v}$  centres is the  $|^3H_4, \Gamma_5, \gamma_5\rangle$  orbital doublet whose  $JJ_z$  composition is little altered by the particular interstitial ion present. Thus, as expected, the hyperfine structure for the  $C_{4v}$   $D^-$  centre is found to correspond to that of the  $C_{4v}$   $F^-$  centre (figure 2). However, the hyperfine splitting is larger in the  $D^-$  centre and this can be attributed to the larger magnetic moment of the  $\text{Pr}^{3+}$  ion ground state here. Electronic Zeeman experiments have determined the  $\text{Pr}^{3+}$  ion ground-state splittings to be  $5.44 \text{ MHz G}^{-1}$  and  $5.78 \text{ MHz G}^{-1}$  for the  $C_{4v}$   $F^-$  and  $D^-$  centres respectively in  $\text{CaF}_2:\text{Pr}^{3+}$  (Reeves *et al* 1992).

For the ODNMR measurements the laser was tuned in frequency to coincide with the  $Z_1 \rightarrow D_1$  transition. The laser then causes hole-burning through a redistribution of population in the hyperfine and superhyperfine levels. Here we are concerned with the hole-burning associated with the superhyperfine levels, and when an RF field resonant with a superhyperfine transition is applied there is filling of the hole. Sweeping the RF while monitoring the intensity of the optical emission then gives the ODNMR spectrum. The ODNMR spectra for the four  $C_{4v}$  centres in  $\text{CaF}_2:\text{Pr}^{3+}$  are shown in figure 3. Although the spectrum for the  $C_{4v}$  centre has already been reported by Burum *et al* (1982), it is shown here for comparison.

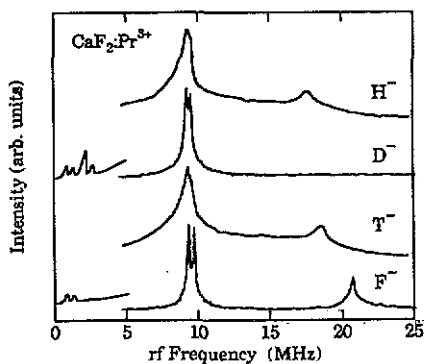


Figure 3. ODNMR spectrum at 1.8 K of  $\text{CaF}_2:\text{Pr}^{3+}$  with  $H^-$ ,  $D^-$ ,  $T^-$  and  $F^-$  interstitial ions. The  $D^-$  and  $F^-$  spectra were measured with improved RF field homogeneity at IBM. The low-frequency range was measured separately with higher sensitivity.

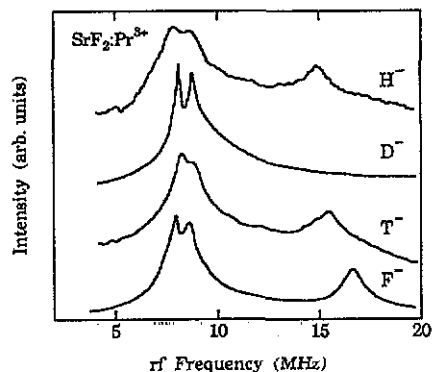


Figure 4. ODNMR spectrum at 1.8 K of  $\text{SrF}_2:\text{Pr}^{3+}$  with  $H^-$ ,  $D^-$ ,  $T^-$  and  $F^-$  interstitial ions.

The results of applied magnetic field experiments on the  $C_{4v}$   $F^-$  centre assigned the principal resonance lines at 9.20 MHz and 9.75 MHz to the two sets of four nearest-neighbour fluorine ions located on either side of the  $\text{Pr}^{3+}$  ion along the tetragonal axis (Borum *et al* 1982). The high-frequency resonance line at 20.6 MHz was associated with the interstitial  $F^-$  ion. There are also additional low-frequency resonance lines at 0.89 MHz and 1.35 MHz which are attributed to next-nearest-neighbour  $F^-$  ions (Borum *et al* 1982).

In the  $H^-$ ,  $D^-$  and  $T^-$  charge-compensated  $C_{4v}$  centres the  $Z_1 \rightarrow D_1$  transitions

all lie close to 596.7 nm. To confirm that the appropriate centre had been located, an acoustic-optic modulator was used to gate the laser and the lifetime of the emission was checked against established values (Reeves *et al* 1987). The fluorescence emitted by the hydrogenic ion centres is much weaker than that from the centres with F<sup>-</sup> compensation because of quenching by hydrogenic ion local mode phonons as reflected in the change in fluorescence lifetime (table 1). The ODNMR spectra for the corresponding centres in SrF<sub>2</sub>:Pr<sup>3+</sup> are shown in figure 4 and the resonant frequencies for all centres are listed in table 1.

### 3.1. Nearest-neighbour resonances

The measured resonant frequencies for the eight nearest-neighbour (NN) F<sup>-</sup> ions in the C<sub>4v</sub> F<sup>-</sup> centre in CaF<sub>2</sub>:Pr<sup>3+</sup> agree with those measured previously (Borum *et al* 1982). They have frequencies of 9.20 MHz and 9.75 MHz with the lower-frequency line corresponding to the set of four equivalent F<sup>-</sup> ions *nearest* to the interstitial ion (Macfarlane and Shelby 1987). The present assignment corrects the earlier assignment in Burum *et al* (1982) of this line to the set furthest from the interstitial ion.

The magnetic field at the ligand sites results from the orbital angular momentum of the Pr<sup>3+</sup> valence electrons. In a dipole field the resonant frequency of a nearest-neighbour F<sup>-</sup> nucleus at a [111] position is

$$\nu = g_N \mu_N \mu_0 g_{\parallel} / 4\sqrt{2} \pi r^3 \quad (1)$$

where  $g_{\parallel}$  is the electronic Zeeman splitting for Pr<sup>3+</sup>,  $g_N$  the <sup>19</sup>F<sup>-</sup> nuclear  $g$ -value and  $r$  the separation between the Pr<sup>3+</sup> and F<sup>-</sup> nuclei. In the CaF<sub>2</sub> lattice the distance from the Pr<sup>3+</sup> ion to a [111] F<sup>-</sup> ion is 2.36 Å. In this centre  $g_{\parallel} = 5.44$  MHz G<sup>-1</sup> and from equation (1) the dipolar contribution to the NN F<sup>-</sup> frequency is 7.8 MHz. The difference between this value and the observed frequencies of 9.20 and 9.75 MHz arises from covalent bonding effects.

In the C<sub>4v</sub> D<sup>-</sup> centre in CaF<sub>2</sub>:Pr<sup>3+</sup>, the resonant frequencies of the two sets of NN F<sup>-</sup> ions are 9.35 MHz and 9.55 MHz (table 1). In this centre the Pr<sup>3+</sup> magnetic moment is 6% larger than in the F<sup>-</sup> centre which will cause an equivalent increase in the dipole contribution to the resonant frequency. However, the increase in the resonant frequency of the F<sup>-</sup> ions closest to the interstitial is only 2% (9.20 → 9.35 MHz) and, moreover, the resonant frequency from the other set of F<sup>-</sup> ions has actually decreased (9.75 → 9.55 MHz). Thus, these data suggest that there are significant changes in the positions of the nearest-neighbour F<sup>-</sup> ions when a D<sup>-</sup> ion replaces an F<sup>-</sup> ion at the interstitial site. Of course both the dipole field and covalent bonding interactions contribute to the measured frequencies, but the results suggest that, overall, all the NN F<sup>-</sup> ions are displaced further away from the Pr<sup>3+</sup> ion when there is a D<sup>-</sup> interstitial ion.

The variation in the NN F<sup>-</sup> resonant frequencies between H<sup>-</sup>, D<sup>-</sup> and T<sup>-</sup> C<sub>4v</sub> centres is not large but a qualitative trend can be identified. The perturbation of NN F<sup>-</sup> ion positions relative to the C<sub>4v</sub> F<sup>-</sup> centre is greatest for the centre with the lightest ion, H<sup>-</sup>, and least for the centre with the heaviest ion, T<sup>-</sup> (table 1).

In the SrF<sub>2</sub> crystal all the corresponding superhyperfine resonances are lower in frequency than those in CaF<sub>2</sub>, consistent with the larger lattice constant of SrF<sub>2</sub> and the greater inter-ionic separations. The qualitative trends in the variation of the NN F<sup>-</sup> resonant frequencies with C<sub>4v</sub> centres discussed above for CaF<sub>2</sub> are also apparent

in the SrF<sub>2</sub> results (table 1). Experimental difficulties associated with weak emission, especially from the H<sup>-</sup> centre, and large linewidths preclude a more quantitative discussion in this case.

### 3.2. Interstitial resonances

The interstitial ions all have nuclear spin and the associated resonances were detected in all cases except for that of the D<sup>-</sup> centre in SrF<sub>2</sub> (figures 3 and 4). In CaF<sub>2</sub>:Pr<sup>3+</sup>:F<sup>-</sup> the resonance at 20.6 MHz was associated with the interstitial F<sup>-</sup> ion (Borum *et al* 1982). H<sup>-</sup> and T<sup>-</sup>, having the same nuclear spin  $I = \frac{1}{2}$  and similar nuclear  $g$ -values as F<sup>-</sup> (5.585, 5.958 and 5.255 for H<sup>-</sup>, T<sup>-</sup> and F<sup>-</sup> respectively), are expected to give resonances in the same frequency region. Therefore, in CaF<sub>2</sub> the resonances at 17.5 MHz and 18.2 MHz are assigned to the H<sup>-</sup> and T<sup>-</sup> interstitial ions respectively.

The situation for the D<sup>-</sup> interstitial is different as deuterium has nuclear spin  $I = 1$  and a smaller nuclear  $g$ -value (0.857) than the other three nuclei. The ODNMR spectrum from the C<sub>4v</sub> D<sup>-</sup> centre shows two lines with frequencies of 2.11 MHz and 2.69 MHz. These are assigned to the interstitial D<sup>-</sup> ion and correspond to the two transitions between  $I_z = 0 \rightarrow I_z = +1$  and  $I_z = 0 \rightarrow I_z = -1$  nuclear spin levels. Thus, the nuclear spin levels are split by the combination of a nuclear quadrupole splitting  $2.69 - 2.11 = 0.58$  MHz and a magnetic Zeeman splitting of  $2.69 + 2.11 = 4.80$  MHz.

At the interstitial site the dipole field will give a resonant frequency of

$$\nu = g_N \mu_N \mu_0 g_{\parallel} / 4\pi r^3 \quad (2)$$

for the interstitial ion, where the symbols have the definitions discussed earlier. In an undistorted CaF<sub>2</sub> lattice the separation between the Pr<sup>3+</sup> and interstitial ions is the lattice constant of 2.73 Å. However, in the C<sub>4v</sub> F<sup>-</sup> centre in CaF<sub>2</sub>:Ce<sup>3+</sup>, Kiro and Low (1970) used ENDOR to estimate the Ce<sup>3+</sup>-F<sup>-</sup> separation as 2.55 Å. This results from the close-packed fluorite lattice distorting under the attraction between the trivalent rare-earth ion and its charge compensator. Since there is little size difference between Pr<sup>3+</sup> and Ce<sup>3+</sup> ions it is expected that the Pr<sup>3+</sup>-F<sup>-</sup> separation is close to 2.55 Å. Using this value and  $g_{\parallel} = 5.44$  MHz G<sup>-1</sup>, the above expression gives a dipole contribution of 8.7 MHz to the measured frequency of 20.6 MHz. This is a contribution of 42% which is similar to the 38% component determined for the same centre in a CaF<sub>2</sub>:Nd<sup>3+</sup> crystal (Kiro and Low 1970). Note that Pr<sup>3+</sup> and Nd<sup>3+</sup> ions have both  $\sigma$ - and  $\pi$ -bonding with the interstitial F<sup>-</sup> ion. This contrasts with the Ce<sup>3+</sup> ion as its single 4f electron configuration has no  $\sigma$ -bonding with the F<sup>-</sup> ion. In the C<sub>4v</sub> F<sup>-</sup> centre in CaF<sub>2</sub>:Ce<sup>3+</sup>, Kiro and Low (1970) showed that 70% of the interaction energy arose from the dipole field.

The nuclear  $g$ -value of H<sup>-</sup> is larger than that of F<sup>-</sup> but a lower-frequency ODNMR line is observed (table 1). This could lead to the conclusion that the H<sup>-</sup> ion experiences a weaker interaction and is thus further from the Pr<sup>3+</sup> ion than is F<sup>-</sup>. However, this conclusion assumes that a similar covalent interaction is experienced by both interstitial ions. This is not the case as the 1s<sup>2</sup> configuration of H<sup>-</sup> has no first-order  $\sigma$ - or  $\pi$ -bonding with Pr<sup>3+</sup> and the observed ODNMR frequency should correspond to a pure dipole interaction, i.e. the dipole contribution is larger for the H<sup>-</sup> ion. Therefore, the H<sup>-</sup> ion experiences a larger field than F<sup>-</sup> and these data corroborate the conclusion of Kiro and Low (1970) that the interstitial H<sup>-</sup> ion is closer to the Pr<sup>3+</sup> ion than is the F<sup>-</sup> ion. However, the measured interaction energy does contain

a covalent bond contribution as, for example, odd crystal-field components mix higher electron configurations into the ground state. The extent of the covalent contribution can be seen by calculating an approximate dipole component. Assuming the same ion separation (2.55 Å) and using  $g_{\parallel} = 5.78 \text{ MHz G}^{-1}$  gives a dipole contribution of 9.8 MHz, i.e. 56% of the observed H<sup>-</sup> resonant frequency of 17.5 MHz. This agrees well with the 50% dipole contribution measured in the Nd<sup>3+</sup>-H<sup>-</sup> (i) centre (Kiro *et al* 1969).

The trends among hydrogenic ion centres can be followed by calculating the dipolar magnetic fields experienced by each interstitial ion from their measured frequencies. For example the 9.8 MHz frequency determined above as the dipolar energy for the H<sup>-</sup> centre corresponds to a magnetic field of 0.23 T. Using the same 56% dipole contribution, the D<sup>-</sup> and T<sup>-</sup> centres have fields of 0.21 and 0.22 T respectively. Although the differences between these fields are small they are expected to be different as H<sup>-</sup>, D<sup>-</sup> and T<sup>-</sup> ions occupy slightly different positions within the potential well formed by the lattice. In a treatment of these ions as anharmonic oscillators, the H<sup>-</sup> ion has the largest displacement from the centre of the interstitial position. Jacobs *et al* (1971) calculate these displacements to be 0.006, 0.004 and 0.003 Å for hydrogen, deuterium and tritium respectively in the hydrogenic C<sub>4v</sub> centres in CaF<sub>2</sub>:Ce<sup>3+</sup> crystals. Similar displacements are expected here for the hydrogenic Pr<sup>3+</sup> c<sub>4v</sub> centres. Thus, qualitatively it is expected that the H<sup>-</sup> centre would correspond to the largest field as its equilibrium position is closer to the Pr<sup>3+</sup> ion than the positions of the other two isotopes.

The interstitial resonant frequencies in the SrF<sub>2</sub> lattice are all smaller than those in the CaF<sub>2</sub> lattice, consistent with the larger inter-ionic separations in SrF<sub>2</sub>. The same trends in interstitial ion frequencies as discussed above for the centres in CaF<sub>2</sub> crystals are also apparent in the SrF<sub>2</sub> centres.

#### 4. Summary

Optical hole-burning of C<sub>4v</sub> centres in CaF<sub>2</sub>:Pr<sup>3+</sup> occurs through population storage in superhyperfine levels (Macfarlane *et al* 1981). Radiofrequency fields resonant with the superhyperfine transitions can reduce this hole depth and this response has been used here to obtain the frequencies of various superhyperfine transitions for a series of four Pr<sup>3+</sup> centres in CaF<sub>2</sub> and four similar centres in SrF<sub>2</sub>. In all eight centres studied two resonances associated with the nearest-neighbour shell of F<sup>-</sup> ions are detected and in seven out of the eight cases the resonances associated with a charge-compensated interstitial ion along the [100] direction are also detected.

The location of the substitutional and neighbouring ions determines the resonant frequencies, which can therefore be used to follow ion position trends for the various centres. Previous ENDOR and hole-burning results have shown the cubic lattice of fluorine ions is distorted by the interstitial F<sup>-</sup> ion. The results presented here indicate additional change in the ligand positions when a hydrogenic ion replaces an F<sup>-</sup> ion at the interstitial position. Both sets of nearest-neighbour F<sup>-</sup> ions experience a lower field when the centre contains a hydrogenic interstitial ion and are thus determined to be further away from the Pr<sup>3+</sup> ion.

The results also show that the hydrogenic interstitial ions are closer to the Pr<sup>3+</sup> than an F<sup>-</sup> interstitial ion. These results are consistent with a model where both the Pr<sup>3+</sup> and H<sup>-</sup> ions are displaced towards each other from their respective cube-centre



positions while the surrounding lattice of  $F^-$  ions distorts to compensate. The four NN  $F^-$  ions between the  $Pr^{3+}$  and interstitial  $H^-$  are pushed further outwards thus reducing the field they experience. Similarly, the additional displacement of  $Pr^{3+}$  towards  $H^-$  increases the distance to the other set of four NN  $F^-$  ions.

There are also smaller changes in the NN  $F^-$  positions when the interstitial ion is changed through the series  $H^-$ ,  $D^-$  and  $T^-$ . The results show that the greatest perturbation occurs for the  $H^-$  ion and the smallest for the  $T^-$  ion. The  $H^-$ ,  $D^-$  and  $T^-$  ions themselves have slightly different lattice site positions because of the anharmonicity of the potential well in which they vibrate. These shifts, estimated to be  $0.002 \text{ \AA}$  between  $H^-$  and  $D^-$  ions, account at least partially for the observed trends in the ODNMR resonances.

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