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High-resolution spectroscopy and optically detected nuclear magnetic resonance studies of Ho^{3+} ions in SrF_2 crystals containing Ba^{2+} and Ca^{2+} impurities

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Abstract. Optical–RF double-resonance techniques have been used to measure the superhyperfine transition frequencies of two Ho^{3+} centres of C_{4v} symmetry present in SrF_2:0.001%Ho^{3+} crystals containing about 0.2% of Ba^{2+} and Ca^{2+} as inadvertent impurities. One centre has a charge-compensating F^- ion located in the nearest-neighbour interstitial position along the (100) axis while the other has an additional Ba^{2+} ion also located on this axis. The superhyperfine transition frequencies are about 60% smaller than those reported for CaF_2:Ho^{3+} and these decreases are attributed principally to the decreased Ho^{3+} ground-state magnetic moment resulting from the increased energy separation between the ground and first excited state Ho^{3+} electronic energy levels. Another contribution arises from the larger host lattice dimension for SrF_2. The two sets of nearest-neighbour F^- ions have almost identical resonance frequencies for both SrF_2 centres while the interstitial F^- ion has a substantially reduced resonance frequency in the Ba^{2+} modified centre. These trends correlate with those in the relevant crystal-field parameters. Some qualitative conclusions are drawn about the positions of the Ho^{3+} and F^- ions in these centres.

1. Introduction

The ground multiplet of Ho^{3+} (in the Russell–Saunders approximation) is ${}^5I_8$. The 100% abundant isotope ${}^{165}Ho$ has nuclear spin $I = \frac{7}{2}$ and a magnetic moment of 4.17 μ_N. Well resolved hyperfine patterns have been reported for sharp electronic transitions of Ho^{3+} for several different crystal hosts, including those of Ho^{3+} ions located in S_4 symmetry sites in $LiYF_4$ [1–3], in C_{3h} symmetry sites in $LaCl_3$ [4], in C_{3v} symmetry sites in CaF_2 [5, 6] and in C_{4v} symmetry sites in CaF_2 [7–9]. For crystals with 0.01% or less of Ho^{3+} ions located in C_{3h}, C_{3v} and S_4 symmetry sites for which the electronic ground states are doubly degenerate a well resolved eight-line hyperfine structure characteristic of ${}^{165}Ho$ appears.

In CaF_2:Ho^{3+}, the Ho^{3+} substitutes for the divalent Ca^{2+} ion and charge compensation is required. The predominant centre present in crystals with less than 0.1% Ho^{3+} is one in which an F^- ion occupies the interstitial location along a (100) direction from the Ho^{3+} ion and thus provides C_{4v} symmetry. The Ho^{3+} electronic ground-level structure in this centre is unusual in having a first excited singlet state (of γ_2 symmetry under C_{4v}) just 1.9 cm^{-1} higher

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in energy than the ground state, which is a γ_1 orbital singlet under C_{4v} [10]†. Normally there is no magnetic moment associated with an electronic singlet, but the close proximity of the first excited state leads to novel effects detailed by Martin *et al* [8,9]. Essentially, mixing of the wavefunctions of the two singlet levels occurs through the parallel hyperfine interaction term $A_j I_z J_z$ of the $A_j I \cdot J$ hyperfine interaction giving the ground-state hyperfine levels an enhanced magnetic moment [11]. The resulting hyperfine resolved optical transition $Z_1(^5I_8(\gamma_1)) \rightarrow D_2(^5F_5(\gamma_5))$ is noteworthy in having just five lines, of non-uniform spacing and with an unusual intensity distribution. These spectra have been analysed in detail for the Ho^{3+} C_{4v} centre in $CaF_2:Ho^{3+}$ [9].

The enhanced magnetic moment [11] for the individual hyperfine levels of the electronic ground state produces a frozen core of F^- ions which allows the observation of ground-state superhyperfine optically detected nuclear magnetic resonance (ODNMR) lines. These superhyperfine resonances were first reported for the C_{4v} symmetry centre in $CaF_2:Ho^{3+}$ by Martin *et al* [8]. Those assigned to the nearest-neighbour (NN) F^- ions and to the interstitial charge-compensating F^- ion occur in the 8–24 MHz range, while resonances below 3.5 MHz are attributed to the next-nearest and next-next-nearest-neighbour F^- ions. From the analysis of the nearest neighbour and interstitial F^- resonance frequencies for the $Z_1(^5I_8) \rightarrow D_2(^5F_5)$ transition of the Ho^{3+} C_{4v} symmetry centre in CaF_2 crystals [8], the four sets of superhyperfine lines observed were assigned to corresponding I_z values of $\pm\frac{7}{2}, \pm\frac{5}{2}, \pm\frac{3}{2}$ and $\pm\frac{1}{2}$. It was found that the ratios of the sets of measured superhyperfine frequencies for each set of equivalent F^- ions closely followed the corresponding ratios of I_z values for a particular pair of spin levels. This strong correlation of superhyperfine frequency with I_z value confirms that the $A_j I_z J_z$ hyperfine interaction mixing term is the dominant contribution to the observed hyperfine structure.

In this paper, we describe similar high-resolution measurements for the analogous C_{4v} symmetry A centre and for a modified C_{4v} symmetry SB1 centre involving nearby Ba^{2+} ions in $SrF_2:0.001\%Ho^{3+}$ crystals containing BaF_2 impurity [10]. For both these centres, the two lowest energy levels are also orbital singlets with the first excited level 2.7 cm^{-1} and 2.5 cm^{-1} respectively above the ground level, while the D_1 level is doubly degenerate. We also report superhyperfine resonances, for the regular and Ba^{2+} modified C_{4v} symmetry centres in the same $SrF_2:0.001\%Ho^{3+}$ crystals with the BaF_2 impurity, which are observed to occur at lower frequencies than those for the CaF_2 A centre.

2. Experimental details

The $SrF_2:0.001\%Ho^{3+}$ crystals were grown by the Bridgman–Stockbarger method and included about 0.2% of Ba^{2+} and Ca^{2+} ions, present as inadvertent impurities in the SrF_2 starting material. Samples were cooled to 2 K by immersion in superfluid He.

The 514.5 nm Ar ion laser line from a Spectra Physics model 2030 Ar ion laser was used as the pump source for a CR 699 coherent ring dye laser. The DCM red dye used covered the $^5F_5$ multiplet region (15 550—15 800 cm^{-1}) of the Ho^{3+} ion in SrF_2 and the output from the dye laser had a linewidth of between 1 and 2 MHz. For the high-resolution experiments, the dye laser was operated in scanning mode over a 20 GHz range.

† This 1.9 cm^{-1} energy level separation has been determined more accurately by Fabry–Perot techniques as 50.43 GHz, which is the 1.7 cm^{-1} cited in [8] and [9]. However, for consistency of comparison of the SrF_2 and CaF_2 cases, the optical spectroscopy determined values for this separation of 2.7 and 1.9 cm^{-1} respectively are chosen for the analysis here.

For the ODNMR experiments, the crystal was mounted in the centre of a five-turn copper coil. With the dye laser operated in fixed-frequency mode, a variable-frequency RF voltage, as supplied to the coil by a Hewlett Packard 8443A tracking generator and ENI 10W power supply amplifier, was swept through the 21 MHz range whilst the sample was irradiated with laser light. The resulting fluorescence, from both the high-resolution and ODNMR experiments, was detected by a Spex 1400 double monochromator equipped with a thermoelectrically cooled EMI 9658R photomultiplier tube. A Princeton Applied Research 4202 signal averager was used for averaging over 50–200 scans.

3. Hyperfine splittings and ODNMR frequencies for the A and SB1 centres in $SrF_2:0.001\%Ho^{3+}$ crystals

3.1. The $A(C_{4v}$ symmetry) centre in SrF_2

The SrF_2 A centre has the C_{4v} symmetry configuration in which the charge-compensating interstitial F^- ion lies in a (100) direction from the Ho^{3+} ion [10], as shown in figure 1(a). The energy separation of the Z_1 and Z_2 levels is 2.7 cm^{-1}, compared to 1.9 cm^{-1} for the CaF_2 A centre.

(a)

(b)
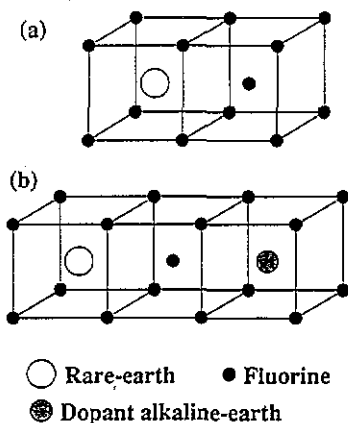
○ Rare-earth   ● Fluorine

◉ Dopant alkaline-earth

Figure 1. Model configurations of (a) the C_{4v} symmetry centre proposed for the A centre; (b) the modified C_{4v} symmetry centre proposed for the SB1 centre.

The high-resolution spectra for the A centre, as shown in figure 2(a), were obtained with excitation of the $Z_2(\gamma_2) \to D_1(\gamma_5)$ and $Z_1(\gamma_1) \to D_1(\gamma_5)$ transitions at 15 590.3 and 15 593.0 cm^{-1} respectively, while monitoring the $D_1 \to Z_{10}$ transition at 15 200.0 cm^{-1}. The hyperfine structure (figure 2(a)) consists of two sets of four lines with similar profile as observed for the CaF_2 A centre [9]. The hyperfine lines observed for the SrF_2 case here are broader because of the small amounts (about 0.2%) of Ca^{2+} and Ba^{2+} ions present in the crystals as an impurity [10].

By burning a hole in each of the hyperfine lines of the $Z_1 \to D_1$ transition at 15 593.0 cm^{-1} shown in figure 2(a), the corresponding superhyperfine resonances were measured (figure 3). Because of overlap between the somewhat broad hyperfine lines, burning a hole in any single hyperfine line gave weaker resonances from other lines as well. Nevertheless, the resonances for the particular transition being burnt were much stronger than any from other overlapping hyperfine lines enabling an unambiguous assignment of the lines according to their I_z (nuclear spin) levels. As shown in table 1, the resonances are
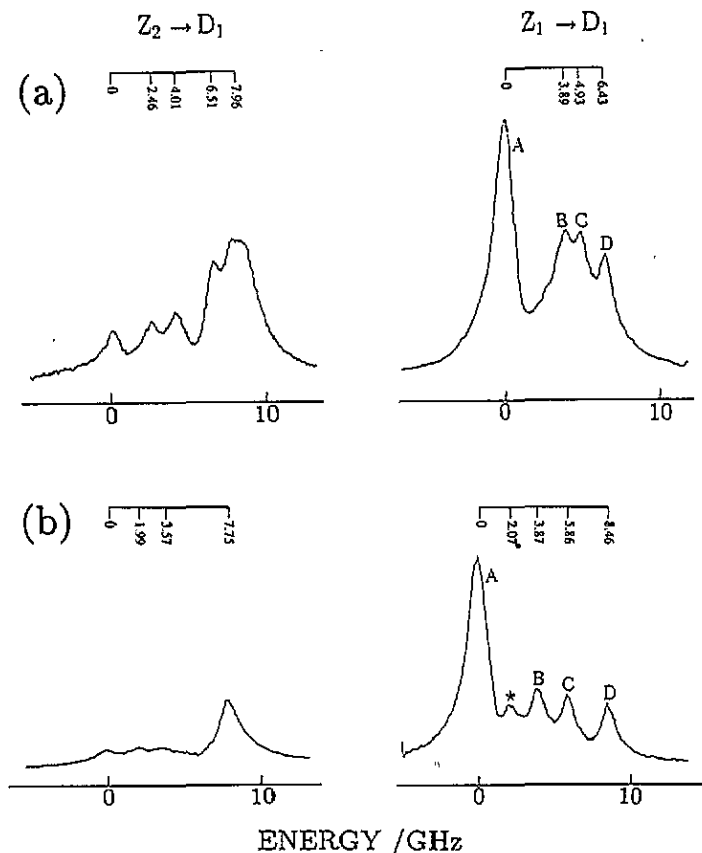
Figure 2. 2 K excitation spectra for (a) the C_{4v} symmetry A centre and (b) the modified C_{4v} symmetry SB1 centre in $SrF_2:0.001\%Ho^{3+}$ crystals. Relative positions (in GHz) of the hyperfine lines are indicated.

essentially determined by the dominant $A_j I_z J_z$ term of the ground-state hyperfine interaction, which gives a strong correlation of the measured frequencies with the I_z values, just as found for the CaF_2 case. The observed hyperfine lines were assigned to the specific I_z values of $\pm\frac{7}{2}, \pm\frac{5}{2}$ and $\pm\frac{3}{2}$ (figure 3) while no resonance was observed for I_z of $\pm\frac{1}{2}$. There is a general trend towards weaker and less well defined superhyperfine resonances for the central hyperfine lines and the absence of the expected I_z of $\pm\frac{1}{2}$ resonances is attributed to additional dephasing processes such as the spin flip-flop process $\pm\frac{1}{2} \rightleftharpoons \mp\frac{1}{2}$, which does not occur for the other I_z projections as it requires ΔI_z values of unity.

By comparison with the CaF_2 case, the superhyperfine ODNMR lines observed are assigned as arising from resonances of the two sets of four nearest-neighbour lattice F^- ions and of the single interstitial charge-compensating F^- ion. For the CaF_2 A centre [8], the resonances of the nearest-neighbour and interstitial F^- ions were found to occur in the 8–24 MHz range while corresponding resonances for the SrF_2 case here are found to occur in the 4–12 MHz range (figure 3). Overall, the resonance frequencies for the SrF_2 A centre are about 50–60% of the corresponding frequencies for the CaF_2 A centre, with the spacing between the two resonances from the two sets of four nearest-neighbour F^- ions being three times larger for the SrF_2 case (table 1). These decreases can be compared to those found for the corresponding Pr^{3+} centres in CaF_2 and SrF_2 [12]. The interstitial F^- resonance for the Pr^{3+} C_{4v} centre in $SrF_2:Pr^{3+}$ decreased to 81% of the CaF_2 value, while the two nearest-neighbour F^- resonances in SrF_2 decreased somewhat less to 86% and 90%. These decreases scale well with the cubic power dependence of the dipolar interaction term on
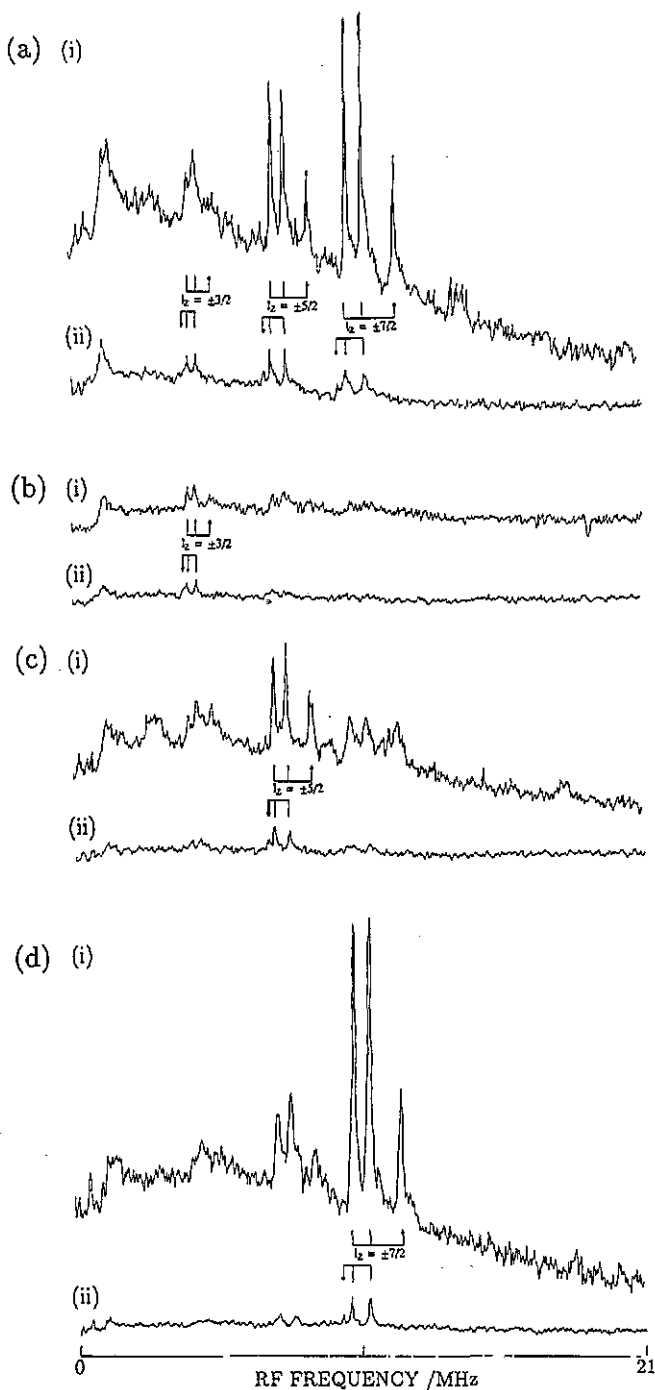
Figure 3. 2 K syperhyperfine ODNMR spectra of (i) the A centre and (ii) the SB1 centre in SrF_2:0.001%Ho^{3+} crystals measured with hole-burning of the four hyperfine lines (A–D) of the respective $Z_1 \rightarrow D_1$ transitions. The I_z assignments are indicated, with the F^- interstitial ion resonance in each case arrowed and the two sets of nearest-neighbour F^- ion resonances indicated by unarrowed lines. The hyperfine line indicated by ★ in figure 2(*b*) does not yield any superhyperfine resonance.

Table 1. 2 K superhyperfine ODNMR frequencies (in MHz) for the nearest-neighbour and interstitial ^{19}F nuclei for the A and SB1 centres in SrF_2:0.001%Ho^{3+} crystals.

I_z assignment	^{19}F ODNMR frequencies				
	Nearest-neighbour F^- ion resonances		Interstitial F^- ion resonance		Ratio of frequencies[a]
	A	SB1	A	SB1	
$\pm\frac{7}{2}$	10.7	10.7			
			11.94	9.84	1
	10.1	10.1			
$\pm\frac{5}{2}$	7.89	7.89			
			8.81	7.26	0.737 (0.714)
	7.45	7.45			
$\pm\frac{3}{2}$	4.79	4.83			
			5.35	4.40	0.447 (0.429)
	4.52	4.52			

[a] Ratios of corresponding I_z values are given in brackets.

distance, which predicts a decrease to $(2.73/2.89)^3$ or 84% of the CaF_2 value in going to SrF_2. While the B_0^2 crystal-field parameter values for the respective Pr^{3+} centres in SrF_2 and CaF_2 are not well established because of difficulties of fitting the levels of the $^1D_2$ multiplet for this ion, an estimated ratio for these parameter values is 70%.

The decrease of 50–60% in resonance frequencies (from 23.49 to 11.94 MHz and from 17.74, 17.54 to 10.7, 10.1 MHz for the interstitial and the nearest-neighbour F^- ions respectively) and in the B_A^2 crystal-field parameter value (from 685 cm^{-1} to 338 cm^{-1}) for Ho^{3+} in going from CaF_2 to SrF_2 is evidently more than can be attributed simply to a change in host lattice dimension, which accounts for a decrease to just 84% of the CaF_2 values. Most of the decrease is attributed to the change in the magnetic moment of the Ho^{3+} ion in the ground state, which is strongly dependent on the energy separation Δ of the $Z_1(\gamma_1)$ and $Z_2(\gamma_2)$ levels. Assuming the same $A_J\langle I_z \rangle$ value for Ho^{3+} in CaF_2 and in SrF_2, the hyperfine splittings and magnetic moments are inversely proportional to Δ, and the superhyperfine resonance frequencies in SrF_2 are, therefore, expected to decrease by the ratio $\Delta_{CaF_2}/\Delta_{SrF_2}$ or 1.9/2.7 to 70% of the CaF_2 values.

The combined contributions from the change in Ho^{3+} ground-state magnetic moment and from the altered host lattice dimension collectively predict the superhyperfine resonance frequencies in SrF_2 to be about 59% of those in CaF_2, in good agreement with observation.

Previous ENDOR [13] and hole-burning [14] results have shown that the cubic lattice of F^- ions is distorted by the presence of the trivalent rare-earth and interstitial F^- ions. The threefold-increased spacing of the resonances from the two sets of four nearest-neighbour F^- ions in SrF_2 indicates larger differences in the displacements for the two sets of F^- ions in SrF_2, while all F^- ions are displaced outwards in accordance with the larger SrF_2 lattice.

3.2. The SB1(Ba^{2+} modified C_{4v} symmetry) centre

The SB1 centre has the modified C_{4v} symmetry configuration in which the Ho^{3+} and Ba^{2+} ions are on opposite sides of the interstitial F^- ion [10], as shown in figure 1(b). The energy separation of the Z_1 and Z_2 levels is 2.5 cm^{-1}, compared to the 2.7 cm^{-1} for the SrF_2 A centre.

The high-resolution spectra for the SB1 centre, as shown in figure 2(b), were obtained with excitation of the $Z_2(\gamma_2) \rightarrow D_1(\gamma_5)$ and $Z_1(\gamma_1) \rightarrow D_1(\gamma_5)$ transitions at 15 585.5 and

15 588.0 cm^{-1} respectively, while monitoring the $D_1 \rightarrow Z_{10}$ transition at 15 205.5 cm^{-1}. Both transitions show a similar line pattern as found for the SrF$_2$ A centre, but with different separations between some of the lines, as can be seen from comparison of figures 2(a) and (b). As for the SrF$_2$ A centre, the superhyperfine lines could be assigned to the specific I_z values of $\pm\frac{7}{2}$, $\pm\frac{5}{2}$ and $\pm\frac{3}{2}$ (figure 3) while no resonance was observed for I_z of $\pm\frac{1}{2}$. The hyperfine line marked by ★ in figure 2(b) does not give any superhyperfine resonances, but may under more favourable excitation and detection conditions reveal the expected weaker I_z of $\pm\frac{1}{2}$ resonances. Again, as found for both the CaF$_2$ [8] and SrF$_2$ A centres, the correlation of the observed resonance frequencies with their assigned I_z values is pronounced (table 1).

As the nearest-neighbour F$^-$ ion resonances for the SB1 centre have identical frequencies to those for the SrF$_2$ A centre (table 1 and figure 2), the nearest-neighbour F$^-$ ions retain essentially the same positions in going from the parent C$_{4v}$ symmetry A centre in SrF$_2$ to the modified C$_{4v}$ symmetry SB1 centre. Thus, the cubic arrangement of the F$^-$ ions around the Ho^{3+} ion is not measurably altered by the presence of the Ba^{3+} ion located two lattice spacings away. This observation is in agreement with crystal-field analyses [10] which gives closely similar cubic crystal-field parameters for both centres.

In contrast, the resonance frequency for the charge-compensating interstitial F$^-$ ion in the SB1 centre is vastly displaced relative to that for the SrF$_2$ A centre, with this resonance frequency for the SB1 centre being displaced below those for both sets of nearest-neighbour F$^-$ ions. Introduction of the Ba^{2+} ion next to the interstitial F$^-$ ion therefore has a profound effect on the positioning to the interstitial F$^-$ ion. It is believed that the Ba^{2+} ion, being larger than the Sr^{2+} ion, causes an outward shift of the four lattice F$^-$ ions between the Ba^{2+} and the interstitial F$^-$ ions to accommodate the Ba^{2+} ion. The interstitial F$^-$ ion then *repositions itself closer to the Ba^{2+} ion and further away from the Ho^{3+} ion*. Such repositioning reduces the dipolar field experienced by the interstitial F$^-$ ion and hence its resonance frequency. Alternatively, were the interstitial F$^-$ ion shifted towards the Ho^{3+} ion by the Ba^{2+} ion, the dipolar field contribution from the Ho^{3+} ion would be increased, but then the covalency contribution would need to alter proportionally more in compensation to give a net lower resonance frequency.

From the crystal-field analyses for both the SrF$_2$ A and SB1 centres [10], the second-degree axial crystal-field parameter B_A^2 for the SB1 centre is about half the value of that for the SrF$_2$ A centre while the changes in the cubic crystal-field parameters are minimal. These trends support the repositioning of the interstitial F$^-$ ion towards the Ba^{2+} ion and away from the Ho^{3+} ion.

A modified C$_{4v}$ symmetry SC1 centre is also present in the SrF$_2$:0.001%Ho^{3+} crystals [10] which has a Ca^{2+} ion as the dopant alkaline earth ion (figure 1(b)). However, measurements could not be made as the relevant optical transitions were too weak for the particular crystals examined. Optimally doped CaF$_2$ in SrF$_2$:Ho^{3+} crystals are needed. One would expect that, as Ca^{2+} is smaller than Sr^{2+}, the resonances for the interstitial F$^-$ ion would be at slightly lower frequencies than those found for the SrF$_2$ A centre. Any change is not expected to be as large as observed here for the SB1 centre because there is only a relatively small decrease in the value of the second-degree axial crystal-field parameter B_A^2 [10] of the SC1 centre from that for the SrF$_2$ A centre.

Other modified C$_{4v}$ symmetry centres are the CS1 and CB1 centres found in the CaF$_2$ crystals [10], and these have Sr^{2+} and Ba^{2+} ions as the dopant alkaline earth ions respectively (figure 1(b)). Studies of these centres would be helpful for establishing trends in the shift in resonance frequency of the interstitial F$^-$ ion and of detailed model configurations for these centres. As Sr^{2+} and Ba^{2+} are both larger ions than Ca^{2+}, the CS1 and CB1 centres would be expected to show decreases of the interstitial F$^-$ resonance frequency. The CB1

centre would be expected to show the greater decrease following the respective decreases of 25% and 40% in the B_A^2 crystal-field parameter value in going from the parent A centre to the CS1 and CB1 centres. Given the relative placement of the nearest-neighbour F^- and interstitial F^- resonances of the CaF_2 A centre, it is unlikely that the interstitial F^- resonance would shift below those for the nearest-neighbour F^- ions. For the so-called A2 C_{4v} symmetry centre in $CaF_2:1.0\%SrF_2:Pr^{3+}$ crystals [15] a shift in the interstitial F^- resonance frequency from 20.6 MHz to 18.2 MHz was observed.

4. Conclusion

The larger Z_1–Z_2 energy level separations for the SrF_2 A and SB1 centres, compared to that for the CaF_2 A centre, result in weaker hyperfine interaction mixing effects in these cases, but essentially the same hyperfine patterns are observed. Both the larger lattice dimension of SrF_2 and the decreased Ho^{3+} ground-state magnetic moment (resulting from the greater first-excited-state-to-ground-state energy separation) account for the observed lower-frequency superhyperfine ODNMR resonances. Observation of identical ODNMR frequencies for the two sets of four nearest-neighbour F^- ions for both the A and SB1 centres in $SrF_2:Ho^{3+}$ shows that the dopant cation does not have any appreciable effect on the position of the nearest-neighbour lattice F^- ions, but greatly affects the position of the interstitial F^- ion. The proposed repositioning of this interstitial F^- ion further away from the Ho^{3+} ion for the SB1 centre is consistent with the decrease found for the B_A^2 axial crystal-field parameter. Other mixed-crystal C_{4v} symmetry centres (SC1, CS1 and CB1) need to be studied to obtain a consistent picture of the effect of dopant cations on the positioning of the interstitial F^- ion in C_{4v} symmetry centres.

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