

Studies of the g factors and the superhyperfine parameters for Ni^{3+} in the fluoroperovskites

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Abstract. The g factors and the ligand superhyperfine parameters A' and B' for Ni^{3+} in KMgF_3 , CsCaF_3 and RbCaF_3 are theoretically studied from the formulas of these parameters for a $3d^7$ ion under octahedral environments in the weak field scheme. The unpaired spin densities for the fluorine $2s$, $2p_\sigma$ and $2p_\pi$ orbitals are quantitatively determined from the molecular orbital and configuration interaction coefficients based on the cluster approach. The calculated results show good agreement with the experimental data, based on only one adjustable parameter (i.e., the proportionality factor ρ related to the ligand s - and p -orbitals). The superhyperfine parameters for the axial and planar ligands in $\text{RbCaF}_3:\text{Ni}^{3+}$ are satisfactorily interpreted from the different impurity–ligand distances due to the elongation of the ligand octahedron during cubic-to-tetragonal phase transition.

Keywords. Electron paramagnetic resonance; crystal- and ligand-field theory; hyperfine interactions; Ni^{3+} ; KMgF_3 ; RbCaF_3 ; CsCaF_3 .

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1. Introduction

The fluoroperovskites KMgF_3 , CsCaF_3 and RbCaF_3 have many applications due to their unique properties of tunable laser [1], crystal fields [2], electron–phonon interactions [3,4] as well as phase transition behaviours [5] when doped with some transition metal ions. In particular, local structures of these impurity ions in the fluoroperovskites have been extensively studied by means of electron paramagnetic resonance (EPR) technique [6–9], which deals mainly with the zero-field splittings, the g factors and the hyperfine structure constants of central metal ions. However, investigation on ligand superhyperfine parameters A' and B' is relatively less. Generally, these parameters originate from the interaction between the spin of the

unpaired electrons of a metal and the nuclear spin of the ligand, and play an important role in understanding spin states and electronic structures of paramagnetic ions in crystals. For example, the superhyperfine parameters (as well as the g factors) of Ni^{3+} in KMgF_3 , CsCaF_3 and RbCaF_3 were measured decades ago [10–12]. To interpret the experimental superhyperfine parameters, theoretical investigations were performed on the strong field perturbation method [10,12–14]. Nevertheless, there seems to be some shortcomings in their treatments. First, the strong field scheme may not be suitable for Ni^{3+} in the fluoroperovskites, since their crystal fields are actually not strong enough, especially when compared to those for Pt^{3+} in oxides [15]. In fact, the ground state of $3d^7$ ions under weak crystal fields is 4T_1 of high spin ($S = 3/2$), corresponding to the g factors close to 4. However, the ground state would be 2E of low spin ($S = 1/2$) for the case of strong fields, corresponding to the g values ~ 2 [16,17]. Thus, the $[\text{NiF}_6]^{3-}$ clusters in the fluoroperovskites should be treated as the case of weak fields, in view of the experimental g factors (~ 4.2 [10–12]). Second, some important parameters such as the unpaired spin densities f_s , f_σ and f_π (note: $f_\sigma \approx f_\pi$ usually assumed in the previous study) for the ligand $2s$, $2p\sigma$ and $2p\pi$ orbitals were obtained by fitting the two experimental superhyperfine parameters A' and B' . Consequently, the different (anisotropic) contributions due to the admixtures of $2p\sigma$ and $2p\pi$ orbitals were neglected in the treatments [12–14]. Third, the g factors were not theoretically explained in a uniform way.

In order to overcome the above imperfections and to study the g factors and the superhyperfine parameters of Ni^{3+} in the fluoroperovskites to a better extent, in this work, uniform calculations of the superhyperfine parameters (as well as the g factors) of these systems are carried out, by including the admixtures (configuration interactions) of the ground ${}^4T_1(F)$ and the excited ${}^4T_1(P)$ states from the weak field scheme. In addition, the related molecular orbital coefficients and the unpaired spin densities due to the admixtures between the $3d$ orbitals of Ni^{3+} and $2s$ (or $2p$) orbitals of F^- are determined quantitatively and uniformly from the cluster approach.

2. Calculations

For a $3d^7$ ion in an octahedron, the ground ${}^4T_1(F)$ orbital triplet would split into one doublet, one quartet and one sextet, and interaction with excited states via the spin-orbit coupling can separate the sextet into one doublet and one quartet [16,17]. Normally, the experimental EPR spectra are mainly related to the lowest Kramers doublet. In the following, the cluster approach is adopted to deal with the covalency (or admixtures) between the impurity and the ligand orbitals.

From the cluster approach, the one-electron basis function can be expressed as [18]:

$$\begin{aligned}\Psi_\pi &= N_\pi^{1/2}(|d_\pi\rangle - \lambda_\pi|\chi_{p\pi}\rangle), \\ \Psi_\sigma &= N_\sigma^{1/2}(|d_\sigma\rangle - \lambda_\sigma|\chi_{p\sigma}\rangle - \lambda_s|\chi_s\rangle),\end{aligned}\quad (1)$$

where γ ($= \pi$ or σ) denotes the two components of a single $3d$ electron in O_h group. $|d_\gamma\rangle$ stands for the d orbital of the central metal ion. $|\chi_{p\gamma}\rangle$ and $|\chi_s\rangle$ are the ligand

p and s orbitals, respectively. N_π and N_σ are the normalization factors, and λ_i ($i = \pi, \sigma, s$) are the orbital admixture coefficients for the corresponding orbitals. The one-electron basis functions satisfy the normalization conditions:

$$N_\pi(1 + \lambda_\pi^2 - 2\lambda_\pi S_\pi) = 1, \quad N_\sigma[1 + \lambda_\sigma^2 + \lambda_s^2 - 2\lambda_\sigma S_\sigma - 2\lambda_s S_s] = 1. \quad (2)$$

Because of the covalency effect due to the orbital admixtures between the central ion and the ligands, the interelectronic electrostatic repulsion of the 3d⁷ ion in a crystal can be weaker than that for a free state. Utilizing the Mulliken approximation [19] and neglecting the small terms of λ_γ^3 and λ_γ^4 in the electrostatic repulsion energies, one can obtain the approximate relationships [20]:

$$\begin{aligned} N^2 &= N_\pi^2(1 + \lambda_\pi^2 S_\pi^2 - 2\lambda_\pi S_\pi), \\ N^2 &= N_\sigma^2(1 + \lambda_\sigma^2 S_\sigma^2 + \lambda_s^2 S_s^2 - 2\lambda_\sigma S_\sigma - 2\lambda_s S_s), \end{aligned} \quad (3)$$

where N is the average covalency factor, characteristic of the reduction of the Racah parameters for a 3d⁷ ion in crystals. S_i ($i = \pi, \sigma, s$) are the corresponding group overlap integrals. From eqs. (2) and (3), these molecular orbital coefficients can be determined. Generally, the orbital admixture coefficients increase by increasing the group overlap integrals, and one can approximately apply the proportional relationship $\lambda_s/S_s \approx \rho(\lambda_\sigma/S_\sigma)$ within the same σ component. Here the proportionality factor ρ is usually taken as an adjustable parameter. Then, the spin-orbit coupling coefficients ζ, ζ' and the orbital reduction factors k, k' are expressed from the cluster approach [20]:

$$\begin{aligned} \zeta &= N_\pi(\zeta_d^0 + \lambda_\pi^2 \zeta_p^0/2), \quad \zeta' = (N_\pi N_\sigma)^{1/2}(\zeta_d^0 - \lambda_\pi \lambda_\sigma \zeta_p^0/2), \\ k &= N_\pi(1 + \lambda_\pi^2/2), \quad k' = (N_\pi N_\sigma)^{1/2}[1 - \lambda_\pi(\lambda_\sigma + A\lambda_s)/2], \end{aligned} \quad (4)$$

where ζ_d^0 and ζ_p^0 are, respectively, the spin-orbit coupling coefficients of the free 3d⁷ and ligand ions. The integral A denotes $R\langle\chi_s|\partial/\partial x|\chi_{px}\rangle$, with the Ni-F distance R .

The perturbation formula of the g factor of a 3d⁷ ion in the octahedra can be given as follows [8]:

$$g = \frac{10}{3} + \frac{2}{3}k\alpha + 5k'\zeta'\varepsilon^2/(2\Delta), \quad (5)$$

with

$$\alpha \approx \frac{3}{2}\varepsilon^2 - \tau^2. \quad (6)$$

Here Δ is the energy separation between the ground ${}^4T_1(F)$ and the excited ${}^4T_2(F)$ states, which can be obtained from the energy matrices of a 3d⁷ ion in cubic (O_h) symmetry. The configuration interaction coefficients ε and τ stand for the admixtures between the ground ${}^4T_1(F)$ and the excited ${}^4T_1(P)$ states, which obey the normalization condition

$$\varepsilon^2 + \tau^2 = 1 \quad (7)$$

and the relationship for the ratio

$$\tau/\varepsilon \approx \frac{-4Dq}{15B - 6Dq} \quad (8)$$

from the weak field energy matrices of a $3d^7$ ion in cubic symmetry. Here, Dq and B are the cubic field parameter and the Racah parameter of a $3d^7$ ion in a crystal, respectively. As stated in §1, the weak field scheme can be more suitable to explain the g factors and superhyperfine parameters of $3d^7$ ions in octahedra. So, the relationship $\tau/\varepsilon \approx 6B/(9B + 10Dq)$ in the previous works [10,12–14] based on the strong field scheme should be replaced by eq. (8) here.

The superhyperfine parameters A' and B' of the fluorine ligand can be expressed as [10,18]:

$$A' = A_s + 2A_D + A_p, \quad B' = B_s - A_D + B_p, \quad (9)$$

where A_s and B_s stand for the contributions from the contact interactions through fluorine 2s orbitals. A_p and B_p denote the contributions from the fluorine 2p orbitals. A_D is the dipole–dipole interaction term, indicating the interaction between the electron distribution of the central ion and the fluorine ligand nucleus. It can be expressed as: $A_D = g\beta g_n \beta_n / R^3$. Here g is the g factor of the central metal ion and R is the effective impurity–ligand distance. g_n , β and β_n are, respectively, the nuclear g value, the electron Bohr magneton and nuclear magneton.

Utilizing the relationships (eqs (7) and (8)) for ε and τ as well as the formulas in refs [10,18], the parameters A_s and B_s are written as follows:

$$A_s = A_s^0 N_\sigma \lambda_s^2 (5\varepsilon^2 + 2\tau^2) / 27, \quad B_s = A_s^0 N_\sigma \lambda_s^2 (20\varepsilon^2 + 11\tau^2) / 108, \quad (10)$$

with $A_s^0 = (8\pi/3)g_s\beta g_n \beta_n |\phi(0)|^2 \approx 1.503 \text{ cm}^{-1}$ [12]. Here, $g_s (=2.0023)$ is the pure spin g factor of electron and $\phi(0)$ is the wave function of the fluorine 2s orbital at the nucleus. The term $N_\sigma \lambda_s^2 / 3$ ($\approx f_s$) accounts for the unpaired spin density of the fluorine 2s orbitals.

A_p and B_p can also be expressed in terms of ε and τ and the molecular orbital coefficients as follows:

$$\begin{aligned} A_p &= A_p^0 \left[\frac{N_\sigma \lambda_\sigma^2}{3} (4 - 5\kappa') \left(\frac{\varepsilon^2}{6} + \frac{\tau^2}{45} \right) - \frac{N_\pi N_\sigma \lambda_\pi \lambda_\sigma \varepsilon \tau}{30\sqrt{3}} \right. \\ &\quad \left. + \frac{N_\pi \lambda_\pi^2}{3} \left(\frac{11 - 10\kappa'}{45} \varepsilon^2 - \frac{9 + 10\kappa'}{30} \tau^2 \right) \right], \\ B_p &= A_p^0 \left\{ -\frac{N_\sigma \lambda_\sigma^2 (2 + 5\kappa')}{3} \left(\frac{\varepsilon^2}{18} + \frac{11\tau^2}{360} \right) - \frac{11N_\pi N_\sigma \lambda_\pi \lambda_\sigma \varepsilon \tau}{60\sqrt{3}} \right. \\ &\quad \left. + \frac{N_\pi \lambda_\pi^2}{3} \left[\frac{(1 - 5\kappa')\varepsilon^2}{30} + \frac{(5 - 70\kappa')\tau^2}{180} \right] \right\}. \end{aligned} \quad (11)$$

Here $A_p^0 = 2g_s\beta_n \beta_n \langle r^{-3} \rangle_p \approx 0.2145 \text{ cm}^{-1}$ [12], with $\langle r^{-3} \rangle_p$ the expectation value of the inverse cube of the radial wave function of the p orbital. κ' stands for the core polarization constant of the fluorine ligand. The terms $N_\sigma \lambda_\sigma^2 / 3$ and $N_\pi \lambda_\pi^2 / 4$ account for the unpaired spin densities f_σ and f_π of the fluorine $2p\sigma$ and $2p\pi$

orbitals, respectively. It is noted that in the previous studies the unpaired spin densities were usually determined by fitting two experimental superhyperfine parameters [10,12,13]. In addition, the relationship $f_\sigma \approx f_\pi$ was approximately adopted by neglecting the difference between two components of the fluorine 2p orbitals [10,12,13].

Generally speaking, since the ionic radius r_i (≈ 0.74 Å [21]) of the impurity Ni³⁺ is dissimilar to the radius r_h (≈ 0.86 Å or 1.14 Å [21]) of the host cation Mg²⁺ (or Ca²⁺), the Ni–F distance R may be different from the corresponding cation–anion distance R_H (≈ 1.993 , 2.262 and 2.227 Å [3]) in pure KMgF₃, CsCaF₃ and RbCaF₃. Fortunately, studies based on experimental superhyperfine interactions and extended X-ray absorption fine structure (EXAFS) measurements have verified that the correction $\Delta R \approx (r_i - r_h)/2$ [22] may be induced relative to the host distance R_H in view of the size and charge mismatching substitution. This means that the ligand octahedron around the impurity Ni³⁺ may suffer a uniform shrinkage ΔR by about 0.06 Å or 0.2 Å for Ni³⁺ in KMgF₃ or CsCaF₃ (RbCaF₃). Second, since polyhedral compressibility increases linearly with the cube of bond length [23], the ligand octahedron in CsCaF₃ (or RbCaF₃) is easier to compress than that in KMgF₃ due to the larger metal–ligand distance of the former. Thus, the above uniform contraction ΔR of the metal–ligand bonds may be modified with a decrease (and an increase) for KMgF₃ (and CsCaF₃ or RbCaF₃), respectively. Third, RbCaF₃:Ni³⁺ yields two groups of experimental superhyperfine parameters at 30 K due to the cubic-to-tetragonal phase transition [11], which can be described as the rotation of the [NiF₆]³⁻ octahedron around C_4 axis by an angle ϕ [24,25]. Because of the centrifugal force arising from the above rotation, the distance contraction ΔR in RbCaF₃:Ni³⁺ may be reduced somewhat when compared with that in CsCaF₃:Ni³⁺. Consequently, one can tentatively estimate the effective distances as 1.983 , 2.042 and 2.040 Å (or $\Delta R \approx 0.01$, 0.22 and 0.187 Å) for KMgF₃, CsCaF₃ and RbCaF₃, respectively. Finally, the axial bond length R_a in RbCaF₃:Ni³⁺ is usually determined from the rotation angle ϕ ($\approx 5.2^\circ$ [11]) and the release factor k_{rf} (≈ 0.94 [26]) as $R_a \approx R(1+k_{rf}\phi^2)$ [27], yielding $R_a \approx 2.056$ Å. Since the axial distance R_a exhibits a slight (~ 0.016 Å) elongation as compared to the planar length R_p ($\approx R \approx 2.040$ Å), the resultant effective distance R should be polished as the average value ($\approx (R_a + 2R_p)/3 \approx 2.045$ Å) for RbCaF₃:Ni³⁺ here.

From the Slater-type SCF functions [28,29] and the distances R , the group overlap integrals S_i and the integral A are calculated and listed in table 1. Since no optical spectra for Ni³⁺ in KMgF₃, CsCaF₃ and RbCaF₃ were reported, one can estimate the spectral parameters Dq and N from those ($Dq \approx 1620$ cm⁻¹ and $N \approx 0.767$, with the distance $R \approx 2$ Å [30]) for similar [NiF₆]³⁻ clusters in K₃NiF₆. According to the relationship $Dq \propto R^{-n}$ (where $n \approx 3.5$ – 4.5) [31,32] and the fact that the average covalency factor N increases slightly with the distance R [33], the spectral parameters of the studied systems are obtained and collected in table 1. Then the Racah parameter $B \approx 1195N^2$ cm⁻¹ [34] can be calculated.

Thus, in the formula of the g factor, there is only one unknown magnitude, the proportionality factor ρ , which is taken as an adjustable parameter here. Substituting the above values in eq. (5) and matching the theoretical results to the experimental data, the proportionality factor ρ can be obtained and collected in table 1. Then the molecular orbital coefficients N_γ and λ_i are acquired from eqs

Table 1. The effective impurity–ligand distance R (in Å), the group overlap and A integrals, the cubic field parameter Dq (in cm^{-1}) and the average covalency factor N , the fitted proportionality factor ρ , the molecular orbital coefficients N_γ ($\gamma = \pi$ and σ) and λ_i ($i = \pi, \sigma, s$) and the parameters in eq. (4) for Ni^{3+} in KMgF_3 , CsCaF_3 and RbCaF_3 .

Host	R	S_t	S_e	S_s	A	Dq	N	ρ	N_π
KMgF_3	1.983	0.0076	0.0279	0.0224	1.4716	-1690	0.76	0.440	0.763
CsCaF_3	2.042	0.0059	0.0227	0.0182	1.5153	-1510	0.78	0.432	0.778
RbCaF_3	2.045	0.0059	0.0224	0.0180	1.5176	-1500	0.78	0.424	0.778
	N_σ	λ_π	λ_σ	λ_s	ζ	ζ'	k	k'	
KMgF_3	0.776	0.565	0.448	0.158	598	555	0.885	0.625	
CsCaF_3	0.789	0.539	0.427	0.148	608	566	0.892	0.645	
RbCaF_3	0.788	0.539	0.427	0.145	608	567	0.892	0.646	

(2) and (3). Utilizing the free-ion values $\zeta_d^0 \approx 749 \text{ cm}^{-1}$ [34] for Ni^{3+} and $\zeta_p^0 \approx 220 \text{ cm}^{-1}$ [35] for F^- , the values of ζ , ζ' , k and k' are determined from eq. (4). These results are also given in table 1. The corresponding g factors and the unpaired spin densities f_i ($i = \pi, \sigma, s$) are shown in table 2.

In the calculations of the superhyperfine parameters, the ligand core polarization constant is taken as $\kappa' \approx 0.04$, which is widely used for F^- [10,13]. From eqs (10) and (11), the values of A_s , B_s , A_p and B_p are calculated. The dipole–dipole interaction term A_D can be determined using the above calculated g factor and the distance R . Thus, the total superhyperfine parameters A' and B' (Cal.^c) are obtained from eq. (9) and listed in table 2. In view of the difference between the bond lengths R_a and R_p due to the tetragonal elongation of the ligand octahedron via the rotation, the fitted proportionality factor ρ (≈ 0.35) for $\text{RaCaF}_3:\text{Ni}^{3+}$ in table 1 should be regarded as an effective (or average) value. More exactly, ρ can exhibit a small deviation from 0.35 for R_a and R_p , corresponding to the two groups of the experimental superhyperfine parameters. By matching the observed superhyperfine parameters of this system, we have $\rho \approx 0.32$ and 0.38 for the axial and planar ligands, respectively. The calculated results are also shown in table 2. For comparisons, the calculation results of the superhyperfine parameters (Cal.^a) by fitting the unpaired spin densities f_i to the experimental A' and B' in the previous works [10–12] and those (Cal.^b) based on eqs. (5) and (9) of this work and the configuration interaction coefficients ε and τ from the strong field scheme (as treated in the previous works [10,12–14]) are collected in table 2.

3. Discussion

It can be seen from table 2 that the theoretical g factors and the superhyperfine parameters (Cal.^c) of Ni^{3+} in the fluoroperovskites in this work based on the weak field scheme are in better agreement with the experimental data than those (Cal.^a) based on fitting of the unpaired spin densities to the observed superhyperfine

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Table 2. The g factors and the superhyperfine parameters (in 10^{-4} cm^{-1}) as well as the unpaired spin densities f_i for Ni^{3+} in the fluoroperovskites.

Host		g	A'	B'	f_σ (%)	f_π (%)	f_s (%)
KMgF ₃	Cal. ^a	–	151	36	8.5	8.5	0.72
	Cal. ^b	4.233	162	18	5.2	6.1	0.65
	Cal. ^c	4.160	150	22	5.2	6.1	0.65
	Exp. [10]	4.163(1)	147(1)	24(1)			
CsCaF ₃	Cal. ^a	–	145	31	8.5	8.5	0.65
	Cal. ^b	4.237	148	14	4.8	5.7	0.58
	Cal. ^c	4.186	141	17	4.8	5.7	0.58
	Exp. [11]	4.183	141	18			
RbCaF ₃ (planar)	Cal. ^a	–	153	32	9.2	9.2	0.67
	Cal. ^b	4.242	151	16	4.8	5.7	0.61
	Cal. ^c	4.191	144	19	4.8	5.7	0.60
	Exp. [12]	4.191(3)	149(2)	18(2)			
RbCaF ₃ (axial)	Cal. ^a	–	136	28	7.9	7.9	0.61
	Cal. ^b	4.242	142	12	4.8	5.7	0.51
	Cal. ^c	4.191	135	15	4.8	5.7	0.51
	Exp. [12]	4.191(3)	132(2)	17(2)			

^aCalculations based on fitting of the unpaired spin densities f_i to the experimental A' and B' in the previous works [10,12–14].

^bCalculations based on eqs (5) and (9) in this work and the configuration interaction coefficients ε and τ determined from the strong field scheme.

^cCalculations based on eqs (5) and (9) and the configuration interaction coefficients ε and τ determined from the weak field scheme (i.e., eq. (8)).

parameters and those (Cal.^b) based on the present formulas and the strong field scheme [10,12–14]. More importantly, the related molecular orbital and configuration interaction coefficients are quantitatively and uniformly determined from the cluster approach in the present calculations, with only one adjustable parameter (the proportionality factor ρ). Therefore, the theoretical model and formulas established from the cluster approach and the weak field scheme in this work can be regarded as more reasonable.

(1) The magnitudes of the superhyperfine parameters of Ni^{3+} in the fluoroperovskites can be illustrated from the Ni–F distance R in these systems. The larger the distance R , the smaller the covalency, the cubic field parameter Dq and the configuration interaction coefficient τ (or the orbital admixture coefficients λ_i) and hence the larger the k' and ζ' , the larger is the resulting g factor (i.e., the order $\text{KMgF}_3:\text{Ni}^{3+} < \text{CsCaF}_3:\text{Ni}^{3+} < \text{RbCaF}_3:\text{Ni}^{3+}$). This point is also supported by the experimental g factors of isoelectronic Co^{2+} in some fluoroperovskites (i.e., $\text{LiBaF}_3:\text{Co}^{2+} < \text{KMgF}_3:\text{Co}^{2+} < \text{KZnF}_3:\text{Co}^{2+} < \text{CsCdF}_3:\text{Co}^{2+}$ [10,35–37]). On the other hand, the magnitudes of the unpaired spin densities f_i decrease quadratically with the decrease of the orbital admixture coefficients λ_i , which decrease with increase in the distance R (see tables 1 and 2). Consequently, the total superhyperfine parameters also obey the same (decreasing) tendency. The above decrease in

the superhyperfine parameters with increasing bond lengths was widely supported by the studies of various transition metal ions (e.g., Co^{2+} , Mn^{2+} and Fe^{3+}) in fluorides [18].

(2) Although the order is $\text{KMgF}_3 < \text{RbCaF}_3 < \text{CsCaF}_3$ for the host cation–anion distance R_{H} [3], the effective local impurity–ligand distance R satisfies $\text{KMgF}_3 < \text{CsCaF}_3 < \text{RbCaF}_3$ due to the size mismatching substitution and the tetragonal elongation of the ligand octahedron during the phase transition in $\text{RbCaF}_3:\text{Ni}^{3+}$. As a result, the effective distance R approximately exhibits a reduction of 0.01, 0.22 and 0.192 Å for Ni^{3+} in KMgF_3 , CsCaF_3 and RbCaF_3 , respectively. This point is qualitatively in agreement with the previous estimations of R (≈ 1.99 , 2.01 and 2.013 Å) of these systems based on the analysis of the superhyperfine parameters [11] and can be regarded as reasonable. Further, for the tetragonally elongated octahedral $[\text{NiF}_6]^{3-}$ cluster in $\text{RbCaF}_3:\text{Ni}^{3+}$, the relative relaxation of the axial bond length R_{a} (≈ 2.056 Å) as compared with the planar R_{p} (≈ 2.04 Å) can also account for the slightly lower values of the experimental superhyperfine parameters for the axial fluorine ligands [12]. Interestingly, the relative elongation ($\approx 0.8\%$) of the axial impurity–ligand distance obtained in this work from the phase transition analysis is also comparable with that ($\approx 1\%$) in the previous work [11] by fitting the experimental superhyperfine parameters. Therefore, the information about the local structures for Ni^{3+} in the fluoroperovskites acquired in this work can be regarded as suitable.

(3) The adjusted proportionality factors ρ obtained in this work are lower than unit, suggesting that the ratio $\lambda_{\text{s}}/S_{\text{s}}$ is no more than half of $\lambda_{\sigma}/S_{\sigma}$. This point can be attributed to the less admixture of the 3d orbital of Ni^{3+} with the 2s orbital of F^- than that with the 2p one of F^- , since the 2s orbital is more compact than the 2p one for the same ligand. Further, the order $\text{KMgF}_3:\text{Ni}^{3+} > \text{CsCaF}_3:\text{Ni}^{3+} > \text{RbCaF}_3:\text{Ni}^{3+}$ for the proportionality factor ρ is also consistent with that for the group overlap integrals (see table 1) with increase in the effective Ni–F distance R . This tentatively indicates more rapid decrease of the Ni^{3+} 3d orbital admixture with the F^- 2s orbital than that with the F^- 2p one as R increases.

(4) The results (Cal.^a and Cal.^b) based on the strong field scheme are not as good as those (Cal.^c) based on the weak field scheme. In particular, the g factors are larger than the experimental data due to the smaller configuration interaction coefficients τ (~ 0.17) based on the strong field scheme, when compared with those (~ 0.3) based on the weak field scheme. Meanwhile, the calculated A' and B' for all the systems in this work are also slightly better than those in the previous works by fitting the experimental superhyperfine parameters based on the strong field scheme [10,12–14]. This means that the crystal fields around Ni^{3+} in the fluoroperovskites can be reasonably treated as weak field case, and then some improvement is achieved for the g factors and the superhyperfine parameters from the cluster approach in this work. In addition, the present calculations can also be applicable to other $3d^7$ ions (e.g., Co^{2+} , Fe^+) in fluoroperovskites.

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