



ISSN Print: 2394-7500
 ISSN Online: 2394-5869
 Impact Factor: 5.2
 IJAR 2015; 1(13): 397-403
 www.allresearchjournal.com
 Received: 20-10-2015
 Accepted: 22-11-2015

Arvinder Singh
 Vill & P.O. Daburji, Dist.
 Kapurthala, Punjab, India

Dr. Manoj S Shekhawat
 Department of Physics,
 Govt. Engineering College,
 Kapurthala, Punjab, India

To study of epr parameters for Mn^{2+} in the fluoroperovskites ABF_3

Arvinder Singh and Dr. Manoj S Shekhawat

Abstract

The electron paramagnetic resonance (EPR) parameters (g factor, the hyperfine structure constant A and the super hyperfine parameters A' and B') for Mn^{2+} in the fluoroperovskites ABF_3 ($A = K$ and Cs ; $B = Zn, Mg, Cd$ and Ca) are theoretically investigated from the perturbation formulas of these parameters for a $3d^5$ ion under ideal octahedra. In the above treatments, not only the crystal-field mechanism but also the charge transfer mechanism is considered uniformly on the basis of the cluster approach. The theoretical EPR parameters are in good agreement with the experimental data. The charge transfer contribution to the g -shift Δg ($\approx g - g_s$, where $g_s \approx 2.0023$ is the spin-only value) is opposite (positive) in sign and comparable in magnitude to the crystal-field one. Nevertheless, the charge transfer contribution to the hyperfine structure constant shows the same sign and about 10% that of the crystal-field one.

So, the conventional argument that the charge transfer contributions to the zero-field splittings are negligible for $3d^5$ ions under low symmetrically distorted fluorine octahedra is proved no longer valid for the Δ analysis of $ABF_3:Mn^{2+}$ in view of the dominant second-order charge transfer perturbation terms. The unpaired spin densities of the fluorine $2s$, $2p \sigma$ and $2p \pi$ orbitals are determined from the quantitative dependences upon the related molecular orbital coefficients, rather than obtained by fitting the observed super hyperfine parameters in the previous works.

Keywords: Electron paramagnetic resonance (EPR), Fluoroperovskites and crystal- field

1. Introduction

Fluoroperovskites ABF_3 ($A = K, Cs$ and $B = Zn, Mg, Cd, Ca$) doped with Mn^{2+} show unique photo and thermo stimulated luminescence, mechanoluminescent, dielectric, optical and structure properties. Usually, the doped Mn^{2+} impurities may play an important role in the above properties. It is known that electron paramagnetic resonance (EPR) is a useful tool to investigate the electronic states and energy levels for transition-metal ions in crystals. Mn^{2+} ($3d^5$) can be regarded as a model system with half-filled $3d$ sub-shell, corresponding to the orbital non-degenerate ${}^6A_{1g}$ ground state of high spin $S = 5/2$ [8, 9]. The EPR experiments were carried out on Mn^{2+} doped $KZnF_3$, $KMgF_3$, $KCdF_3$, $KCaF_3$ and $CsCdF_3$, and the EPR parameters (g factor, the hyperfine structure constant A and the super hyperfine parameters A' and B') were also measured for the cubic Mn^{2+} centers. Up to now, however, the above EPR results have not been satisfactorily explained, although the super hyperfine parameters were tentatively analyzed by fitting the ligand unpaired spin densities for Mn^{2+} in $KMgF_3$, $KCdF_3$ and $KCaF_3$. Nevertheless, the obtained unpaired spin densities f_s and $f_\sigma - f_\pi$ were not correlated quantitatively with the chemical bonding between the central ion and ligand orbitals but taken as adjustable parameters. In addition, the g factors and the hyperfine structure constants of these centers have not been theoretically treated yet. So, further theoretical analyses on the EPR parameters are of fundamental significance.

As regards the previous studies of the EPR parameters for $3d^5$ ions in crystals, the perturbation formulas of these parameters were established from the cluster approach, by including the ligand orbital and spin-orbit coupling contributions under the crystal-field mechanism. In fact, besides the normally considered crystal-field mechanism related to the anti-bonding orbitals, the charge transfer mechanism related to the bonding (and non-bonding) orbitals also brings forward important contributions to the EPR parameters. Despite of weak covalency, Mn^{2+} in the fluoroperovskites exhibits the delicate ($\sim 10^{-4}$) g -shift Δg ($\approx g - g_s$, where $g_s \approx 2.0023$ is the spin-only value), and thus omission of the charge transfer contribution may induce obvious relative deviation of Δg .

Correspondence

Arvinder Singh
Arvinder Singh
 Vill & P.O. Daburji, Dist.
 Kapurthala, Punjab, India

In order to study the EPR spectra of the Mn²⁺ centers in the fluoroperovskites and to clarify the role of the charge transfer mechanism, the improved perturbation formulas of the EPR parameters are established in this work for an octahedral 3d⁵ cluster. In these formulas, both the crystal-field and charge transfer contributions are considered in a uniform way using the cluster approach. In the analysis of the super hyperfine parameters, the related molecular orbital coefficients due to the covalency between the 3d orbitals of Mn²⁺ and the 2s (and 2p) orbitals of the ligands are theoretically and uniformly determined from the cluster approach.

2. Theory and calculations

When a Mn²⁺ (3d⁵) ion is doped into the fluoroperovskites, it may occupy substitutionally the divalent cation B²⁺ sites and conserve the original cubic (Oh) symmetry. For a 3d⁵ ion in regular octahedra, it exhibits the orbital non-degenerate ⁶A_{1g} ground state of high spin. From the studies of the EPR spectra for 3d⁵ ions in crystals, the combination of the spin-orbit coupling and orbital angular momentum interactions is regarded as the dominant origin of zero-field splitting and g-shift Δg. Despite of weak covalency of the studied [MnF₆]⁴⁻ clusters, the spin-orbit coupling coefficient (≈220cm⁻¹) of the ligand F⁻ is comparable with that (≈347cm⁻¹) of the impurity Mn²⁺, and thus the ligand orbital and spin-orbit coupling contributions may be significant and should be considered in view of the delicate Δg. More importantly, apart from the normally considered crystal-field mechanism related to the anti-bonding orbitals, the charge transfer mechanism related to the bonding (and non-bonding) orbitals can yield obvious contributions to the EPR parameters. Thus, the improved formulas of the g factor and the hyperfine structure constant are derived using the similar perturbation procedure in Refs. As follows:

$$\begin{aligned}
 g &= g_s + \Delta g_{CF} + \Delta g_{CT} \\
 \Delta g_{CF} &= -5\zeta_{CF}^2(1/E_1^2 + 1/E_3^2)/6 - \zeta_{CF}^2/E_2^2 - 8\zeta'_{CF}\zeta_{CF}[1/(E_1E_2) + 1/(E_2E_3)] \\
 \Delta g_{CT} &= 8\zeta'^k_{CT}/(5E_n) \\
 A &= A_{CF} + A_{CT} \\
 A_{CF} &= -P'_{CF}\{5\zeta_{CF}^2(1/E_1^2 + 1/E_3^2)/6 + \zeta_{CF}^2/E_2^2 + 8\zeta'_{CF}\zeta_{CF}[1/(E_1E_2) + 1/(E_2E_3)]\} - kP_{CF} \\
 A_{CT} &= 8P'_{CT}{}^k\zeta_{CT}/(5E_n) - kP_{CT}/4
 \end{aligned} \tag{1}$$

Where, the denominators E_i (i= 1-3) are the energy separations between the crystal-field excited ⁴T_{1g}, ⁴T_{2g} and ²T_{2g} and the ground ⁶A_{1g} states. They can be expressed in terms of the cubic field parameter Dq and the Racah parameters B and C for the 3d⁵ ion in crystals: E₁≈10B+6C-10Dq, E₂≈19B+7C and E₃≈10B+6C-10Dq. ζ_{CF}, ζ_{CT}, ζ_{CF}, ζ_{CT}, are the spin-orbit coupling coefficients, kCT', the orbital reduction factor, and P_{CF}, P_{CF}'P_{CT} and P_{CT}' are the dipolar hyperfine structure parameters of the 3d⁵ ion in crystals. Here the subscripts CF and CT denote the corresponding interactions related to the crystal field and charge transfer mechanisms, respectively. E_n is the energy difference between the charge transfer excited ⁶T₁ and the ground ⁶A_{1g} states, which can be obtained from the relationship E_n≈30,000 [χ(L) - χ(M)] cm⁻¹. Here χ(L) and χ(M) are the optical electro negativities of ligand and 3dn ions, respectively.

In order to derive the spin-orbit coupling coefficients, the orbital reduction factor and the dipolar hyperfine structure parameters, the nine-electron wave functions containing the anti-bonding orbitals e^a, the non-bonding orbitals tⁿ₂ and the bonding orbitals e^b are adopted here. Thus, the ground ⁶A₁ state is expressed as:

$$\left| {}^6A_1 \frac{5}{2} a_1 \geq [\xi^+ \eta^+ \zeta^+ \theta^+ \varepsilon^+ | \theta^+ \theta^- \varepsilon^+ \varepsilon^-] \right| \tag{2}$$

In the square bracket on the right side of Eq. (2), the letters ξ, η, ζ and θ, on the left column are tⁿ₂ and e^a orbitals and those (θ and ε) on the right column are e^b orbitals. There is only one excited configuration (tⁿ₂)⁴(e^a)²(e^b)³ (or ⁶Tⁿ₂) having the non-zero spin-orbit coupling interactions with the ground state ⁶A_{1g}. Therefore, the z component of ⁶Tⁿ₂ charge transfer excited state with the highest M_S = 5/2 can be given as:

$$\left| {}^6T_1 \frac{n}{2} Z \geq [\xi^+ \eta^+ \zeta^+ \zeta^- \theta^+ \varepsilon^+ | \theta^+ \theta^- \varepsilon^+] \right| \tag{3}$$

From the cluster approach, the one-electron basis functions of the octahedral 3d⁵ cluster can be expressed in terms of the LCAOMO orbitals:

$$\begin{aligned}
 \Psi_t^x &= (N_t^x)^{1/2}(\phi_t - \lambda_t^x \chi_{pt}), \\
 \psi_e^x &= (N_e^x)^{1/2}(\varphi_e - \lambda_e^x \chi_{pe} - \lambda_s^x \chi_s)
 \end{aligned} \tag{4}$$

Here the superscript x (=a or b) denotes the anti-bonding or bonding orbitals. φ_γ (γ = e) and t stands for the irreducible representations E_g and T_{2g} of the O_h group) are the pure 3d orbitals of the central ion. χ_{pγ} and χ_s are the 2p- and 2s-orbitals of

the ligands. N_γ And λ_γ (or λ_s) are, respectively, the normalization factors and the orbital admixture coefficients. From Eq. (4), one can obtain the normalization conditions

$$\begin{aligned} N_t^X [1 + (\lambda_t^X)^2 - 2\lambda_t^X S_t] &= 1, \\ N_e^X [1 + (\lambda_e^X)^2 + (\lambda_s^X)^2 - 2\lambda_e^X S_e - 2\lambda_s^X S_s] &= 1, \end{aligned} \tag{5}$$

And the orthogonality relationships

$$\begin{aligned} 1 + \lambda_t^a \lambda_t^b - (\lambda_t^a + \lambda_t^b) S_t &= 0, \\ 1 + \lambda_e^a \lambda_e^b + \lambda_s^a \lambda_s^b - (\lambda_e^a + \lambda_e^b) S_e - (\lambda_s^a + \lambda_s^b) S_s &= 0, \\ \lambda_e^a \lambda_s^b + \lambda_s^a \lambda_e^b &= 0 \end{aligned} \tag{6}$$

Here S_t , S_e and S_s are the group overlaps integrals between the 3d-orbitals of the central ion and the 2p- and 2s-orbitals of the ligands. In addition, the following approximation relationships are satisfied for the anti-bonding orbitals:

$$\begin{aligned} N^2 &\approx (N_t^a)^2 [1 + (\lambda_t^a)^2 S_t^2 - 2\lambda_t^a S_t], \\ N^2 &\approx (N_t^a)^2 [1 + (\lambda_e^a)^2 S_e^2 + (\lambda_s^a)^2 S_s^2 - 2\lambda_e^a S_e - 2\lambda_s^a S_s] \end{aligned}$$

In the above expressions, M is the average covalency factor, characteristic of the covalency (or orbital admixtures) between the impurity and ligand ions. Since the orbital admixture coefficients and the group overlap integrals have the consistent dependence upon the impurity–ligand distance R , one can approximately adopt the proportional relationship $\lambda_s/\lambda_e \approx S_s/S_e$ for the orbital admixture coefficients and the related group overlaps integrals within the same E_g irreducible representation. Applying the cluster approach, the spin–orbit coupling coefficients and the dipolar hyperfine structure parameters for the crystal-field mechanism can be expressed as follows:

$$\begin{aligned} \zeta_{CF} &= N_t^a [\zeta_d^0 + (\lambda_t^a)^2 \zeta_p^0 / 2], \zeta'_{CF} = (N_t^a N_e^a)^{1/2} [\zeta_d^0 - \lambda_t^a \lambda_e^a \zeta_p^0 / 2] \\ P_{CF} &= N_t^a P_0, P'_{CF} = (N_t^a N_e^a)^{1/2} P_0 \end{aligned} \tag{8}$$

Similarly, those for the charge transfer mechanism are

$$\begin{aligned} \zeta'_{CT} &= (N_t^a N_e^b)^{1/2} [(1 + \lambda_t^a - \lambda_s^a) \zeta_d^0 - \lambda_t^a \lambda_e^a \zeta_p^0 / 2], \\ k'_{CT} &= (N_t^a N_e^b)^{1/2} [(1 - \lambda_e^a + \lambda_t^a - 2\lambda_t^a S_t S_e + \lambda_e^a \lambda_t^a S_t / 2 + A \lambda_t^b \lambda_s^a / 2], \\ P_{CT} &= N_t^b P_0, \\ P'_{CT} &= (N_t^b N_e^b)^{1/2} P_0 \end{aligned} \tag{9}$$

Here ζ_d^0 and ζ_p^0 are, respectively, the spin–orbit coupling coefficients of the free 3d⁵ and ligand ions. P_0 is the dipolar hyperfine structure parameter of the free 3d⁵ ion. The value A denotes the integral $R \langle \chi_s | \partial / \partial X | \chi_{PX} \rangle$ between the ligand 2s and 2p orbitals, with, the impurity–ligand distance R .

In the previous treatments of the super hyperfine parameters, the unpaired spin densities f_s and $f\sigma - f\pi$ of the ligand 2s and 2p σ (or $2p\pi$)

Table 1: The basic parameters for calculating the spectral parameters, the unpaired spin densities f_i (in %), the group overlap integrals and the LCAO coefficients related to both crystal-field and charge transfer mechanisms for Mn²⁺ in the fluoroperovskites.

Hosts	R	S _{dpt}	S _{dpe}	S _{ds}	A	D _q	N	λ_π^a	λ_σ^a
KZnF3	2.056	0.0123	0.0432	0.0348	1.5257	858	0.853	0.420	0.342
KMgF3	2.064	0.0119	0.0421	0.0339	1.5317	843	0.855	0.417	0.339
KCdF3	2.082	0.0111	0.0398	0.0320	1.5450	822	0.856	0.415	0.337
KCaF3	2.093	0.0106	0.0384	0.0309	1.5532	800	0.856	0.415	0.337
CsCdF3	2.147	0.0086	0.0322	0.0259	1.5933	740	0.860	0.407	0.328
Hosts	λ_s^a	λ_π^b	λ_σ^b	λ_s^b	N_t^a	N_e^a	N_t^b	N_e^b	ζ_{cf}
KZnF3	0.132	-1.201	-1.128	-0.909	0.857	0.874	0.412	0.332	0.412
KMgF3	0.126	-1.211	-1.152	-0.927	0.859	0.876	0.408	0.322	0.408
KCdF3	0.135	-1.216	-1.126	-0.906	0.860	0.875	0.406	0.332	0.406
KCaF3	0.135	-1.216	-1.126	-0.906	0.860	0.875	0.405	0.331	0.405
CsCdF3	0.143	-1.237	-1.116	-0.898	0.863	0.875	0.397	0.334	0.397
Hosts	ζ_{CF}'	ζ_{CT}'	k_{CT}'	P_{CF}	P_{CF}'	P_{CT}'	P_{CT}'	f_s (%)	$(f\sigma f\pi)$ (%)
KZnF3	287	247	0.511	160	162	69	77	0.59	-0.39
KMgF3	288	244	0.506	161	162	68	76	0.57	-0.39
KCdF3	288	245	0.508	161	162	69	76	0.53	-0.40
KCaF3	288	245	0.508	161	162	69	76	0.53	-0.40
CsCdF3	288	244	0.504	161	163	68	74	0.52	-0.44

Orbitals were usually taken as adjustable parameters, instead of being correlated quantitatively with the chemical bonding between the central ion and ligand orbitals. In order to improve the above treatments, the cluster approach is applied here to establish the uniform expressions of these parameters. Thus, the super hyperfine parameters can be written as:

$$A' = A_s + 2(A_D + A_\sigma - A_\pi), \quad (10)$$

$$B' = A_s - (A_D + A_\sigma - A_\pi)$$

Here A_s is the isotropic contribution to the super hyperfine parameters, characterizing the influence of the ligand 2s orbital. A_D and $A_\sigma - A_\pi$ denote the anisotropic contributions from the dipole-dipole interaction between the electron of the central ion and ligand nucleus and that from the ligand 2p orbital, respectively. The isotropic part can be expanded as follows.

$$A_s = \frac{f_s A_s^0}{2S} \quad (11)$$

With $A_s^0 = (8/3)g_s g_n \beta \beta_n |\Psi(0)|^2 \approx 1.5000 \text{ cm}^{-1}$ and

$$A_p^0 = g_s g_n \beta \beta_n \langle r^{-3} \rangle_{2p} \approx 1.1072 \text{ cm}^{-1}.$$

The electron spin is $S = 5/2$ for the ground ${}^6A_{1g}$ state of Mn^{2+} in the fluoroperovskites. f_s stand for the density of unpaired spin of the ligand 2s orbital. The anisotropic contribution from the fluorine 2p orbital is usually written as.

$$A_\sigma - A_\pi = \frac{A_p^0 (f_\sigma - f_\pi)}{2S} \quad (12)$$

Here f_σ and f_π are the unpaired spin densities of the ligand 2p σ and 2p π orbitals, respectively. The dipole-dipole interaction between the electron distribution of the central ion and the fluorine ligand nucleus can be expressed as $A_D = g \beta g_n \beta_n / R^3$, with the g factor of the central ion. In the above expressions, the ligand unpaired spin densities can be quantitatively connected with the relevant molecular orbital coefficients based on the cluster approach.

$$f_s \approx N_e^a (\lambda_s^a)^2 / 3, f_\sigma \approx N_e^a (\lambda_\sigma^a)^2 / 3, f_\pi \approx N_t^a ((\lambda_t^a)^2 / 4) \quad (13)$$

It is noted that in the previous works the unpaired spin densities for the ligand 2s, 2p σ and 2p π orbitals were simply determined by fitting the experimental super hyperfine parameters. Instead, they are quantitatively and uniformly calculated from the cluster approach in this work.

Now the above formulas are applied to the studies of the EPR parameters for Mn^{2+} in KZnF_3 , KMgF_3 , KCdF_3 , KCaF_3 and CsCdF_3 .

The impurity-ligand distances R in the defect centers are usually different from the cation-anion distances R_H in the hosts due to the size mismatching substitution of the cations B^{2+} by the impurity Mn^{2+} . Fortunately, the empirical formula $R \approx R_H + (r_i - r_h)/2$ has been proved valid for an impurity ion in crystals by the studies of experimental super hyperfine parameters, extended X ray absorption fine structure (EXAFS) measurements. Here, r_i and r_h are the ionic radii of the impurity and host ions, respectively. According to the data $R_H \approx 2.026, 1.994, 2.167, 2.188$ and 2.232 \AA for $\text{KZnF}_3, \text{KMgF}_3, \text{KCdF}_3, \text{KCaF}_3$ and CsCdF_3 and $r_i \approx 0.80 \text{ \AA}$ for Mn^{2+} and $r_h \approx 0.74, 0.66, 0.97$ and 0.99 \AA for $\text{Mg}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}$ and Ca^{2+} , respectively, the distances R are obtained and shown in Table 1 for these systems.

From the optical spectra for Mn^{2+} in $\text{KZnF}_3, \text{KMgF}_3$ and KCaF_3 , the cubic field parameters Dq and the covalency factors N can be determined. Meanwhile, the spectral parameters for the Mn^{2+} centers in KCdF_3 and CsCdF_3 may be reasonably estimated from the relationship $Dq \propto R^{-5}$ and the tendency that the covalency factor increases slightly with increasing the distance R . These values are shown in Table 1. Thus, the Racah parameters B and C for the studied Mn^{2+} centers can be obtained from the free-ion values $B_0 \approx 960$ and $C_0 \approx 3325 \text{ cm}^{-1}$ for Mn^{2+} and the relationships $B \approx B_0 N^2$ and $C \approx C_0 N^2$. From the extrapolated values $\chi(\text{Mn}^{2+}) \approx 1.6$ and $\chi(\text{F}^-) \approx 3.2$, the charge transfer levels E_n are calculated for the studied systems. Utilizing the impurity-ligand distances R and the Slater-type self consistent field (SCF) wave functions, the group overlaps integrals S_t, S_e, S_s and the integral A are calculated and collected in Table 1.

The molecular orbital coefficients N_γ^x and λ_γ^x are acquired for the anti-bonding and bonding orbitals from Eqs. (5)-(7). Applying Eqs. (8) and (9) and the free-ion values $\zeta_d^0 \approx 347 \text{ cm}^{-1}$ and $P_0 \approx 187 \times 10^{-4} \text{ cm}^{-1}$ for Mn^{2+} and $\zeta_{\text{p}}^0 \approx 220 \text{ cm}^{-1}$ for F^- , the spin-orbit coupling coefficients, the orbital reduction factor and the dipolar hyperfine structure parameters related to the crystal-field and charge transfer mechanisms are determined and given in Table 1. The core polarization constant in the formulas of the hyperfine structure constant is usually expressed as $k \approx -2\chi / (3\langle r^{-3} \rangle)$, where χ is characteristic of the density of unpaired spins at the nucleus of the central ion and $\langle r^{-3} \rangle$ is the expectation value of the inverse cube of the Mn^{2+} 3d radial wave function. By using $\langle r^{-3} \rangle = 4.25 \text{ a.u.}$ for Mn^{2+} and $\chi \approx 3.10 - 3.18 \text{ a.u.}$ for Mn^{2+} in the fluoroperovskites, one can approximately obtain $k \approx 0.51$ for these systems here. Substituting these values into Eq. (1), the g factors and the hyperfine structure constants of the Mn^{2+} centers are calculated and shown in Table 2. The unpaired spin densities f_i ($i = \sigma, \pi, s$) as well as the isotropic contributions A_s and the anisotropic contributions $A_\sigma - A_\pi$ and A_D to the super hyperfine parameters are acquired from Eqs. (11)-(13), and thus the resultant A' and B' are obtained from Eq. (10). In order to clarify the importance of the charge transfer contributions, the theoretical g and A factors containing only the crystal-field contributions and the super

hyperfine parameters based on fitting the unpaired spin densities for Mn^{2+} in $KMgF_3$, $KCdF_3$ and $KCaF_3$ in the previous works are also collected in Table 1.

Table 2: The g-shift Δg , the hyperfine structure constant A (in 10^{-4} cm^{-1}) and the super hyperfine parameters (in 10^{-4} cm^{-1}) for Mn^{2+} in the fluoroperovskites.

	KZnF ₃	KMgF ₃	KCdF ₃	KCaF ₃	CsCdF ₃
Δg					
Cal. ^a	-0.0032	-0.0032	-0.0030	-0.0032	-0.0030
Cal. ^b	-0.0002	-0.0003	-0.0001	-0.0002	~0
Expt. [10–12]	-0.0002 (5)	-0.0002 (5)	-0.0008 (5)	-0.0003(20)	0.0007(5)
Cal.	-81.49	-81.66	-82.52	-83.16	-83.11
Cal.	-91.00	-91.10	-91.98	-92.70	-92.41
Expt. [10–12]	-90.86	-91.0 (5)	-92.6 (9)	-93.1 (9)	-91.37
A					
Cal. ^a		24.0	23.5	23.0	
Cal. ^b	23.26	22.8	20.4	20.2	19.5
Expt. [10–12]	24.19(2)	23.9(5)	21.6	21.1	20.1
B					
Cal.		12.8	11.7	11.5	
Cal.	15.46	14.3	14.1	13.8	13.9
Expt. [10–12]	15.05(7)	13.8(5)	12.9	12.7	13.5

^a Calculations of the g and A factors based on only the crystal-field contributions and those for the super hyperfine parameters by fitting the ligand unpaired spin densities in the previous studies for Mn^{2+} in $KMgF_3$, $KCdF_3$ and $KCaF_3$.

^b Calculations based on inclusion of both the crystal-field and charge transfer contributions

3. Discussions

From Table 2, one can find that the EPR parameters (Cal. ^b) for Mn^{2+} in the fluoroperovskites are in reasonable agreement with the experimental data, while those (Cal. ^a) for the g-shifts and the hyperfine structure constants are not. This means that the improved formulas of the g and A factors including both the crystal field and charge transfer contributions adopted in this work can be regarded as suitable. Meanwhile, the super hyperfine parameters are reasonably and uniformly interpreted for all the systems.

- 1) The charge transfer contributions to the g-shifts are opposite (positive) in sign and comparable in magnitude as compared with the crystal-field ones and should be taken into account for the sake of more exact analysis of the EPR spectra for Mn^{2+} in the fluoroperovskites. Although the systems show weak covalency, the parameters K_{CT} and ζ_{CT}' of the charge transfer mechanism are comparable with but slightly smaller than those of the crystal-field one, since the ligand spin-orbit coupling coefficient ($\approx 220 \text{ cm}^{-1}$) is close to that ($\approx 347 \text{ cm}^{-1}$) of the central ion. More importantly, the Δg is delicate ($\sim 10^{-4}$) for $3d^5$ ions in octahedral (see Table 2 and Eq. (1)), and so omission of the charge transfer contribution would lead to some deviation (i.e., one order in magnitude larger than the observed value). From Eq. (1), the correlation of Δg_{CT} with the covalency or the ligand contributions is relatively stronger than Δg_{CF} because of the dominant second order perturbation terms (inversely proportional to the charge transfer level E_n) in the former and the third-order perturbation terms (inversely proportional to the square of the energy separation E_1 , E_2 or E_3) in the latter. Interestingly, the charge transfer contributions to the g-shifts are largely canceled by the crystal field ones, and thus almost the same g-shifts for all the systems can be understood. In the previous studies on the zero-field splitting D and E for $3d^5$ ions in fluorides of low symmetry, the conventional crystal-field formulas are actually suitable approximations and the charge transfer contributions to the zero-field splitting are normally regarded as negligible. This is attributed to the dominant ionicity of the ligand and the higher (third or fourth) order charge transfer perturbation terms arising from the combination of the low symmetrical distortion and the spin-orbit coupling interactions. As regards the rarely treated Δg , however, the above argument is no longer conclusive due to the relatively more important (i.e., second-order perturbation terms) charge transfer contributions. Thus, the present calculations reveal that the charge transfer contributions to the g (and A) factors should be taken into account for Mn^{2+} in some fluorides.
- 2) The charge transfer contributions A_{CT} to the hyperfine structure constant are the same in sign and about 10% in magnitude compared to ACF from the crystal-field contributions. From Eqs. (1) and (9), A_{CT} is sensitively related to the dipolar hyperfine structure parameters (P_{CT} and P_{CT}'), the orbital reduction factor k_{CT} and the spin-orbit coupling coefficient ζ_{CT}' (which depends upon the ratio ζ_p^0/ζ_d^0) of the charge transfer mechanism. Dissimilar to the g factor, the hyperfine structure constant is less sensitive to the charge transfer effect because of the dominant isotropic term proportional to the core polarization constant k . Even though, inclusion of the charge transfer contributions still brings forward some improvements in the calculated A factors. On the whole, the magnitudes of the hyperfine structure constant for Mn^{2+} in the fluoroperovskites obey tiny increasing tendency with the increase of the distance R (or the decrease of the covalency), which is consistent with the studies on the relationship between covalency and the magnitude of the A factor.
- 3) The unpaired spin densities f_s and $f_\sigma - f_\pi$ are about 0.5% and -0.4% based on the present calculations, which are not faraway from those ($\approx 0.5\text{--}0.6\%$ and $0.3\text{--}0.6\%$) for $KMF_3:Mn^{2+}$ ($M=Mg, Ca$ and Cd) obtained by directly fitting the experimental super hyperfine parameters in the previous works and can be regarded as suitable. The small super hyperfine parameters for Mn^{2+} in the fluoroperovskites can be uniformly described as the weak impurity-ligand orbital admixtures (i.e., the low orbital admixture coefficients) and the ligand spin transfers (i.e., the low unpaired spin densities). Moreover,

the general tendency of slight decrease of the super hyperfine parameters from $\text{KZnF}_3:\text{Mn}^{2+}$ to $\text{CsCdF}_3:\text{Mn}^{2+}$ is also attributable to the declines of the orbital admixtures and the spin transfers with the increase of R . By establishing the quantitative relationships between the unpaired spin densities and the molecular orbital coefficients, the present calculations seem more suitable than the previous studies and are applicable to the investigations of the super hyperfine parameters for $3d^5$ ions in other fluorides.

- 4) It is noted that there are some errors in the above calculations. The approximations of the theoretical model and the formulas may lead to some errors. Importantly, the perturbation calculations are based on the cluster approach where only the six nearest neighbour ligands (i.e., $[\text{MnF}_6]^{4-}$ clusters) are taken into account, while the influence of the rest of the lattice is neglected. This would be valid when the clusters are roughly uncoupled with lattice and the electrostatic potential generated by the rest of the lattice is approximately flat. However, recent density function theory (DFT) investigations on transition-metal ions in the fluoroperovskites reveal that LiBaF_3 of the inverted perovskite structure may exhibit different shapes of the electrostatic potential due to all ions lying outside of the $[\text{MF}_6]^{4-}$ clusters (M denotes divalent impurity ions) and hence different optical and magnetic behaviors'. Therefore, the theoretical study of this work is actually an approach to this problem. In order to evaluate the accuracy of the present results and to make more exact investigations of the EPR spectra and the electronic states for the Mn^{2+} centers, one should utilize the more powerful and reliable DFT calculations.

4. Conclusion

The EPR parameters for Mn^{2+} in the fluoroperovskites are theoretically investigated from the perturbation formulas containing both the crystal-field and charge transfer contributions established here for the first time. The charge transfer contribution to the g shift Δg is positive and comparable to the crystal-field one, while the charge transfer contribution to the hyperfine structure constant has the same sign and about 10% that of the crystal-field one. Importantly, the conventional argument that the charge transfer contributions to the zero-field splitting are negligible for $3d^5$ ions under low symmetrically distorted fluorine octahedra is proved no longer valid for the Δg analysis of $\text{ABF}_3:\text{Mn}^{2+}$ in view of the dominant second-order charge transfer perturbation terms. The unpaired spin densities of the fluorine $2s$, $2p\sigma$ and $2p\pi$ orbitals are determined from their quantitative relationships with the related molecular orbital coefficients, rather than obtained by fitting the observed super hyperfine parameters in the previous works.

5. References

- Springis M, Sharakovsky A, Tale I, Rogulis U. *Phys. Status Solidi C*, 2005; 2:511-514.
- Makarova NY, Tatmyshevsky KV. *Instrum. Exp. Technol.* 2006; 49:135-140.
- Lal B, Khosa SK, Tickoo R, Bamzai KK, Kotru PN. *Chem. Phys.* 2004; 83:158-168.
- Mazurak Z, Ratuszna A, Daniel P. *Spectrochim. Acta A*, 1999; 55:375-380.
- Jiang LQ, Guo JK, Liu HB, Zhu M, Zhou X, Wu P *et al.* *J. Phys. Chem. Solids*, 2006; 67:1531-1536.
- Huang B, Hong JM, Chen XT, Yu Z, You XZ. *Mater. Lett.* 2005; 59:430-433.
- Tyagi N, Ghanti E, Gupta N, Lalla NP, Nagarajan R. *Bull. Mater. Sci.* 2009; 32:583-587.
- Abragam A, Bleaney B. *Electron Paramagnetic Resonance of Transition Ions*, Oxford University Press, London, 1970.
- Chakravarty AS. *Introduction to the Magnetic Properties of Solids*, Wiley Inter-Science, New York, 1980.
- Ogawa S. *J. Phys. Soc. Jpn.* 1960; 15:1475-1481.
- Jeck RK, Krebs JJ. *Phys. Rev.* 1972; B5:1677-1687.
- Ziaei ME. *Can. J. Phys.* 1981; 59:298-304.
- Owen J, Thornley JHN. *Rep. Prog. Phys.* 1966; 29:676-728.
- Wu SY, Yan WZ, Gao XY. *Spectrochim. Acta A*. 2004; 60:701-707.
- Lever ABP. *Inorganic Electronic Spectroscopy*, Elsevier Science Publishers, Amsterdam, 1984.
- Sharma RR, Thosar BV. In: P.K Lyenga (Ed.), *Advances in Mössbauer Spectroscopy*, Elsevier Science, Amsterdam, 1983, 707.
- Yu WL, Zhao MG. *Phys. Rev. B*, 1988; 37:9254-9267.
- McPerson GL, Kach RC, Stucky GD. *J. Chem. Phys.* 1974; 60:1424-1431.
- Griffith JS. *The Theory of Transition-Metal Ions*, Cambridge Press, London, 1964.
- Wu SY, Gao XY, Dong HN. *J. Magn. Magn. Mater.* 2006; 301:67-73.
- Hall TPP, Hayes W, Stevenson RWH. J. Wilkens, *J. Chem. Phys.* 1963; 39:35-39.
- Moreno M, Barriuso MT, Aramburu JA. *Appl. Magn. Reson.* 1992; 3:283-304.
- Weast RC. *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, 1989, 187.
- Trueba A, García-Lastra M, Barriuso MT, Aramburu JA, Moreno M. *Phys. Rev. B*. 2008; 78:075108-1–075108-11.
- Yu WL. *Phys. Rev. B*, 1989; 39:622-632.
- Moreno M. *J. Phys. Chem. Solids*. 1990; 51:835-859.
- Moreno M, Barriuso MT, Aramburu JA. *Int. J. Quantum Chem.* 1994; 52:829-835.
- Drickamer HG. in: F. Seitz, D. Turnbull (Eds.), *Solid State Physics*, Academic Press, New York, 1965; 17:1.
- Zhao MG, Xu JA, Bai GR, Xie HS. *Phys. Rev. B*, 1983; 27:1516-1522.
- Clementi E, Raimondi DL. *J. Chem. Phys.* 1963; 38:2686-2689.
- Clementi E, Raimondi DL, Reinhardt WP. *J. Chem. Phys.* 1967; 47:1300-1307.
- McGarvey BR. *J. Phys. Chem.* 1967; 71:51-66.
- Yu WL, Zhao MG. *J. Phys. C*. 1985; 18:L1087-L1096.
- Vanhaelst M, Matthys P, Boesman E. *Solid State Commun.* 1977; 23:535-537.
- García-Lastra JM, Buzare JY, Barriuso MT, Aramburu JA, Moreno M. *Phys. Rev. B*, 2007; 75:155101-1-155101-6.

36. Fernández PG, Barriuso MT, Aramburu JA, Moreno M. Chem. Phys. Lett. 2003; 374:151-156.
37. Garcia-Lastra JM, Aramburu JA, Barriuso MT, Moreno M. Chem. Phys. Lett. 2004; 93:226402-1-226402-4.
38. Moreno M, Aramburu JA, Garcia-Lastra JM, Barriuso MT. J. Mol. Struct. –THEOCHEM. 2006; 759:195-199.