Investigations on the Hyperfine and Superhyperfine Interaction Parameters for Cs_2GeF_6:Mn^{4+}

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The hyperfine structure constant A and the superhyperfine interaction parameters A' and B' of Cs_2GeF_6:Mn^{4+} are theoretically studied by the cluster approach. The orbital mixing coefficients and the unpaired spin densities in 2s, $2p_\sigma$ and $2p_\pi$ fluorine orbitals are obtained from the optical spectra and the impurity-ligand distance of the studied system. Based on a uniform scheme, the parameters A, A' and B' (as well as the g factor) are reasonably explained. The results are discussed, and the unpaired spin densities of the 2s, $2p_\sigma$ and $2p_\pi$ orbitals of the ligand F^- are compared with those in previous works.

Key words: Electron Paramagnetic Resonance (EPR); Crystal- and Ligand-field Theory; Hyperfine Interactions; Mn^{4+}; Cs_2GeF_6.

1. Introduction

Electron paramagnetic resonance (EPR) is a powerful tool to analyze the electronic states of paramagnetic impurities (e. g., transition-metal ions) in crystals. Usually the EPR results are characterized by the spin Hamiltonian parameters, such as zero-field splitting D, g factors, hyperfine (HF) structure constant A (or B) and the superhyperfine (SHF) interaction parameters A' and B'. The HF structure constant A (or B) arises from interactions of the spin of 3d electrons with that of the nucleus of the central metal ion, while the SHF parameters A' and B' originate mainly from the coupling of the spin of the 3d electrons of the central ion with that of the ligands. Particularly, the SHF parameters are important to understand the unpaired spin density in the ligands and the spin transfer from ligand to metal in clusters.

Many theoretical investigations on the HF and SHF parameters for $3d^n$ (e. g., Mn^{4+}, Mn^{2+}, Ni^{2+}) ions in octahedra were mainly based on the treatments of molecular orbit and configuration interactions [1 – 4]. Based on these studies, many EPR results were reasonably interpreted and unpaired spin densities f_s and $f_\sigma - f_\pi$ for ligand 2s, $2p_\sigma$ and $2p_\pi$ orbitals were obtained. However, for octahedral $3d^3$ ions, e.g. Cs_2GeF_6:Mn^{4+}, the HF structure constant (or the EPR g factor) was not analyzed yet. In addition, the obtained values of f_s and $f_\sigma - f_\pi$ were often acquired by fitting the experimental A' and B' data [1, 5], instead of correlating them with the chemical bonding, i. e., linear combination of atomic orbitals (LCAO-MO) in the cluster approach.

In order to improve the study of the HF and SHF parameters of Cs_2GeF_6:Mn^{4+}, in this paper uniform calculations of these parameters (as well as the g factor) are presented on the basis of their formulas for a $3d^3$ ion in cubic octahedral symmetry. In these treatments, the related LCAO-MO coefficients due to the covalency between the $3d^3$ orbitals of Mn^{4+} and the 2s (and 2p) orbitals of the ligands are calculated with the cluster approach.

2. Formulas and Calculations

An $Mn^{4+}(3d^3)$ ion in Cs_2GeF_6 may occupy the octahedral Ge^{4+} site and conserves the original cubic symmetry. For a $3d^3$ ion in an octahedron, its ^4F state may be split into two orbital doublets $^4T_{2g}$ and $^4T_{1g}$, and one singlet $^4A_{2g}$, with the latter lying lowest. Ac-

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cording to the cluster approach, the one-electron irreducible representation basis function for an octahedral $3d^3$ cluster can be expressed as [1, 6]

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

where φ_γ ($\gamma =$ e and t indicates the irreducible representations of the O_h group) are the d orbitals of the central $3d^3$ ion. $\chi_{p\gamma}$ and χ_s denote the p and s orbitals of the ligands. N_γ are the normalization factors, and λ_γ (or λ_s) are the orbital admixture coefficients that account for the mixing between corresponding orbitals.

The one-electron basis functions satisfy the normalization conditions [6]

$$\begin{aligned}&N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) = 1,\\ &N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) = 1,\end{aligned} \tag{2}$$

and the approximate relationships [6]

$$\begin{aligned}f_t &= N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}],\\ f_e &= N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2\\ &\qquad - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}],\end{aligned} \tag{3}$$

where $f_t[= f_e \approx (B/B_0 + C/C_0)/2]$ is the ratio of the Racah parameters for a $3d^3$ ion in a crystal to those in the free state. $S_{dp\gamma}$ (and S_{ds}) are the corresponding group overlap integrals arising from the admixture of the d orbitals of the central ion with the $2p_\sigma$, $2p_\pi$ and 2s orbitals of the ligand. From (2) and (3), these LCAO-MO coefficients can be determined. Generally, the admixture coefficients increase with increasing the group overlap integrals, and one can approximately adopt the proportional relationship between λ_i and S_i ($i = \sigma$, s), i. e., $\lambda_e/S_{dpe} \approx 6\lambda_s/S_{ds}$ within the same irreducible representation e_g. Thus, the spin-orbit coupling coefficients ζ, ζ', the orbital reduction factors k, k' and the dipole hyperfine structure parameters P and P' can be written as [6]

$$\begin{aligned}&\zeta = N_t(\zeta_d^0 + \lambda_\pi^2\zeta_p^0/2),\\ &\zeta' = (N_t N_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2),\\ &k = N_t(1 + \lambda_t^2/2),\\ &k' = (N_t N_e)^{1/2}[1 - \lambda_t(\lambda_e + A\lambda_s)/2],\\ &P = N_t P_0, \quad P' = (N_t N_e)^{1/2} P_0,\end{aligned} \tag{4}$$

where ζ_d^0 and ζ_p^0 are, respectively, the spin-orbit coupling coefficient of the d electron of the $3d^3$ ion and that of the p electron of the ligand in free ions. P_0 is the dipolar hyperfine structure parameter of the free $3d^3$ ion. The parameter A denotes the integral $A = R\langle\chi_s|\partial/\partial x|\chi_{px}\rangle$, with the impurity-ligand distance R.

2.1. Formulas of the HF Structure Constant

The perturbation formulas of the HF structure constant and the g factor for a $3d^3$ ion in octahedral crystals are [6, 7]:

$$\begin{aligned}g &= g_s - 8\zeta'k'/(3E_1) - 2\zeta(2k'\zeta - k\zeta' + 2g_s\zeta')/(9E_1^2) + 4\zeta'^2(k - 2g_s)/9E_3^2 - \zeta^2(k + g_s)/(3E_2^2)\\ &\quad - 4\zeta\zeta'k'[1/(3E_1E_2) + 1/(9E_1E_3) + 1/(3E_2E_3)],\\ A &= P'\{-8\zeta'k'/(3E_1) - 2\zeta(2k'\zeta - k\zeta' + 2g_s\zeta')/(9E_1^2) + 4\zeta'^2(k - 2g_s)/9E_3^2 - \zeta^2(k + g_s)/(3E_2^2)\\ &\qquad - 4\zeta\zeta'k'[1/(3E_1E_2) + 1/(9E_1E_3) + 1/(3E_2E_3)]\} - \kappa P,\end{aligned} \tag{5}$$

where $g_s(= 2.0023)$ is the spin-only value. The denominators E_i ($i = 1 \sim 3$) are the energy separations between the excited states $^4T_2$, $^2T_{2a}$ and $^2T_{2b}$ and the ground state $^4A_2$. κ is the core polarization constant of the $3d^3$ ion.

2.2. Formulas of the SHF Parameters

The SHF parameters A' and B' of fluorine ligand can be written as [1, 8]

$$\begin{aligned}A' &= A_s + A_\kappa + 2(A_d + A_\sigma - A_\pi),\\ B' &= A_s + A_\kappa - (A_d + A_\sigma - A_\pi),\end{aligned} \tag{6}$$

where A_s and A_κ are the isotropic contributions to the SHF parameters. They can be expressed as follows [1, 8]:

$$A_s = f_s A_s^0/(2S), \quad A_\kappa = -\kappa' A_p^0(f_\sigma + 2f_\pi)/(2S), \tag{7}$$

with $A_s^0 = (8\pi/3)g_s\beta g_n\beta_n|\phi(0)|^2 \approx 1.5981\ \text{cm}^{-1}$ and $A_p^0 = g_s\beta g_n\beta_n\langle r^{-3}\rangle_{2p} \approx 0.0505\ \text{cm}^{-1}$ [9]. κ' stands for the core polarization constant of the fluorine ligand. $S(= 3/2)$ is the spin of the Mn^{4+}. The anisotropic term $A_\sigma - A_\pi$ due to the fluorine 2p orbitals is usually written as [1, 8]

$$A_\sigma - A_\pi = A_p^0(f_\sigma - f_\pi)/(5S). \tag{8}$$

Table 1. The HF and SHF parameters (in 10^{-4} cm^{-1}), g factors and the calculated unpaired spin densities f_i ($i = \pi$, σ, s, in %) for Cs_2GeF_6:Mn^{4+}.

	g	A	A'	B'	A_s	A_κ	$A_\sigma - A_\pi$	A_D	f_s	$f_\sigma - f_\pi$
Cal.[a]	–	–	–	–	–	–	–	–	0.10	−9.2
Cal.[b]	1.98	−62.70	−13.71	15.83	17.94	3.41	−40.11	10.59	0.091	−9.92
Expt. [5]	∼ 2	−72.0	−13.5	15.0						

[a] Calculations in [1, 5]. [b] Calculations in present work.

The dipole-dipole interaction between the electron distribution of the central ion and the fluorine ligand nucleus can be written as $A_D = g\beta g_n\beta_n/R^3$, with the g factor of the central metal ion and the metal-ligand distance R. In the above formulas, the spin densities f_s, f_σ and f_π for unpaired spin in the 2s, $2p_\sigma$ and $2p_\pi$ orbitals of a fluorine ligand are naturally included [1], i. e.,

$$f_s \approx (N_e\lambda_s)^2/3,\ f_\sigma \approx (N_e\lambda_e)^2/3,\ f_\pi \approx (N_t\lambda_t)^2/4. \quad (9)$$

In the previous works, the spin densities for 2s, $2p_\sigma$ and $2p_\pi$ orbitals of the ligands were usually determined by fitting the experimental SHF parameters. Based on the studies of [1, 8], the sign of f_σ should be considered as negative since only the spin down may transfer from the ligand $2p_\sigma$ orbitals to the corresponding 3d orbitals of the central ion.

2.3. Calculations for Mn^{4+} in Cs_2GeF_6

Now the above formulas are applied to study the HF and SHF parameters of Cs_2GeF_6:Mn^{4+}. In general, since the ionic radius r_i of the impurity differs from the radius r_h of the host ion, the impurity-ligand distance R may be unlike the corresponding cation-anion distance R_H in the pure crystal. However, one can reasonably estimate R from the approximate formula: $R \approx R_H + (r_i - r_h)/2$ [10, 11]. For Mn^{4+} on the Ge^{4+} site in Cs_2GeF_6, $R_H \approx 1.74$ Å [1, 6], $r_i \approx 0.60$ Å and $r_h \approx 0.53$ Å [12], we have $R \approx 1.775$ Å. From the Slater-type SCF functions [13, 14] and the distances R, the group overlap integrals $S_{dpt} \approx 0.0358$, $S_{dpe} \approx 0.0998$, $S_{ds} \approx 0.0807$ and the integral $A \approx 1.3172$ are calculated. According to the optical spectra of the studied system [15], $Dq \approx 2185$ cm^{-1}, $B \approx 500$ cm^{-1} and $C \approx 4042$ cm^{-1} can be obtained. Thus, the LCAO-MO coefficients N_γ and λ_i are acquired from (2) and (3), as well as the free-ion parameters $B_0 \approx 1160$ cm^{-1} and $C_0 \approx 4303$ cm^{-1} [15] for Mn^{4+}. Thus the parameters $\zeta \approx 368$ cm^{-1}, $\zeta' \approx 327$ cm^{-1}, $k \approx 0.906$, $k' \approx 0.677$, $P \approx 183 \cdot 10^{-4}$ cm^{-1} and $P' \approx 189 \cdot 10^{-4}$ cm^{-1} are calculated from (4) and the free-ion values $\zeta_d{}^0 \approx 405$ cm^{-1} [15] and $P_0 \approx 235 \cdot 10^{-4}$ cm^{-1} [16] for Mn^{4+} and $\zeta_p{}^0 \approx 220$ cm^{-1} [17] for F^-.

The core polarization constant for the central ion in the HF structure constant may be expressed as $\kappa \approx -2\chi/(3\langle r^{-3}\rangle)$, where χ is characteristic of the density of unpaired spins at the nucleus of the central metal ion and $\langle r^{-3}\rangle$ the expectation value of the inverse cube of the radial wavefunction of the 3d orbital [18]. By using the value $\langle r^{-3}\rangle \approx 5.361$ a.u. [16] for Mn^{4+} and $\chi \approx -2.45$ a.u. [16] for the studied system, we have $\kappa \approx 0.3$. The core polarization constant for the ligand in (7) is taken as $\kappa' \approx -0.14$, which is close to that (≈ -0.1) reported for the free F atom [19]. These values are shown in Table 1. From the above parameters, the unpaired spin densities $f_i (i = \pi, \sigma, s)$ are obtained. By using (7) and (8), the contributions A_s, A_κ and $A_\sigma - A_\pi$ to the SHF parameters are calculated and collected in Table 1.

Substituting these parameters into (5), the HF structure constant and the g factor are obtained. By using the calculated g factor and the distance R, the dipole-dipole interaction term A_D can be calculated. The total SHF parameters A' and B' are therefore obtained from (6). These results are also shown in Table 1.

3. Discussion

From the above studies one can find that by using the cluster approach, the SHF interaction parameters (as well as the HF structure constant A and the g factor) for Cs_2GeF_6:Mn^{4+} can be reasonably interpreted in an uniform way. Furthermore, the unpaired spin densities f_s and $f_\sigma - f_\pi$ for the ligand 2s, $2p_\sigma$ and $2p_\pi$ orbitals obtained in the present work are also comparable with those reported in the previous works [1, 5]. This means that the theoretical formulas and the related parameters adopted here can be regarded as suitable.

1.) The significant anisotropy between the SHF parameters A' and B' arises from mainly the large value of the term $A_\sigma - A_\pi$ [see (6)], which depends upon the magnitude of $f_\sigma - f_\pi$ due to the difference between the orbital admixture coefficients λ_e and λ_t [see (9)]. On the other hand, the smaller isotropic contributions A_s and A_κ may be attributed to the very small value of the unpaired spin density f_s (despite of the large $A_s{}^0$)

of the 2s orbital and the core polarization constant κ' of the ligand, respectively. For the studied system, the small f_s compared with f_π (or f_σ) may be due to the much lower 2s energy level of the F^- ligand and hence less admixture with those of the metal orbitals (or small spin transfer from ligand to metal).

2.) Apart from the SHF parameters, the HF structure constant A and the g factor are explained in a uniform way, yielding reasonable theoretical values with respect to experimental ones. The calculated g factor (≈ 1.98) is slightly lower than the observed one (~ 2.0 [5]), suggesting that some charge-transfer (CT) may contribute. Based on our recent studies on $3d^3$ ions (V^{2+}, Cr^{3+} and Mn^{4+}) in octahedral crystals [20], the above contribution to the g factor from the CT levels is estimated to be about 0.02. This value accounts approximately for the discrepancy in the g factor between theory and experiment in Table 1. Meanwhile, the small calculated A seems also due to neglecting the CT contribution, which may be roughly $-6 \cdot 10^{-4}$ cm^{-1}. Thus the estimated A value ($\approx -68.7 \cdot 10^{-4}$ cm^{-1}), including the CT mechanism, is closer to but still smaller than the experimental result. This value, however, is also comparable with that ($\approx -63.2 \cdot 10^{-4}$ cm^{-1} [21]) for Mn^{4+} in similar octahedral fluoride LiF and can be regarded as reasonable. Therefore, the Mn^{4+},F^- bond in $Cs_2GeF_6:Mn^{4+}$ has some covalency character due to the small impurity-ligand distance (≈ 1.775 Å).

3.) There are some errors in the above calculations. First, the theoretical results (A' and B' as well as the spin densities) are sensitive to the admixture coefficients λ_i ($i =$ s, e and t). These coefficients depend largely upon the optical spectra of the system and lead to the main errors. Second, the factor 6 in the ratio λ_e and λ_s may be only taken as a tentative value, which is introduced in consideration of the much smaller admixture between the 2s orbital of the ligand and the 3d one of the metal, so as to diminish the value of λ_s (and hence f_s and the final SHF parameters). The above empirical relationship seems to be variable from system to system. Finally, approximation of the core polarization constants κ and κ' would also result in some errors in the theoretical results.

4. Summary

In this work, the SHF interaction parameters (and also HF structure constant and the g factor) for $Cs_2GeF_6:Mn^{4+}$ are reasonably interpreted within the scheme based on the cluster approach. The above studies may be applied to the analyses of these parameters for other $3d^3$ ions (e.g., V^{2+}, Cr^{3+}) in octahedral environments.

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