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Investigations of the EPR parameters for the tetrahedral $[FeX_4]^-$ clusters in AgX (X = Cl, Br)

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The EPR parameters g factors and the superhyperfine parameters for the tetrahedral $[FeX_4]^-$ clusters in AgX (X = Cl, Br) are theoretically investigated from the perturbation formulas of these parameters for a $3d^5$ ion under tetrahedra by considering both the crystal-field and charge transfer contributions. The related model parameters are quantitatively determined from the cluster approach in a uniform way. The g-shift $\triangle g$ (= $g - g_s$, where $g_s \approx 2.0023$ is the spin only value) from the charge transfer contribution is opposite (positive) in sign and much larger in magnitude as compared with that from the crystal-field one. The importance of the charge transfer contribution increases rapidly with increasing the covalency and the spin-orbit coupling coefficient of the ligand and thus exhibits the order of AgCl < AgBr. The unpaired spin densities of the halogen ns, $np\sigma$ and $np\pi$ orbitals are quantitatively determined from the related molecular orbital coefficients based on the cluster approach.

Key words: *crystal-fields and spin Hamiltonians, electron paramagnetic resonance (EPR)*

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1. Introduction

Silver halides (AgX, with X=Cl and Br) containing iron (e.g., Fe^{3+}) have interesting electrochemical [1, 2], magnetic [3, 4], photocatalytic [5] and structural [6] properties and attract extensive attention of researchers. It is well known that these properties are closely related to the electronic states and local structures of the impurity ions in the hosts, which may be studied by means of electron paramagnetic resonance (EPR) technique. On the other hand, Fe^{3+} among the transition-metal ions belongs to the half-filled $3d^5$ configuration and exhibits $^6A_{1g}$ ground state with high spin (S=5/2) and quenched orbital angular momentum (l = 0) under weak or intermediate crystal-fields [7, 8]. Therefore, the EPR studies on Fe^{3+} in crystals are of particular importance. For example, the EPR investigations have been performed for Fe^{3+} doped AgX, and the isotropic g factors and the superhyperfine parameters were also measured decades ago [9]. Until now, however, the above experimental results have not been satisfactorily interpreted, except (i) that the centers were ascribed to the impurity Fe^{3+} on the interstitial sites in AgX with four nearest neighbour silver vacancies (V_{Ag}) as charge compensation and (ii) that the superhyperfine parameters were only qualitatively estimated by fitting the adjustable unpaired spin densities in the previous work [9].

As for the Fe^{3+} centers in AgX, the systems have strong covalency due to the high valence state of the impurity and the strong covalency of the hosts, which may bring about significant effect on the EPR parameters (e.g., the g factors and the superhyperfine parameters), as mentioned in some references for transition-metal impurities in covalent hosts [10, 11]. Thus, further systematic theoretical analysis for the EPR parameters of AgX:Fe^{3+} are of great scientific significance. According to the previous studies [12–14], the ligand orbital (or covalency) and spin-orbit coupling contributions should be considered

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for Fe^{3+} (or other transition-metal ions with high valence states) in the systems with strong covalency in view of the strong covalency and ligand spin-orbit coupling interactions (particularly for the ligand Br^-). Importantly, not only the crystal-field mechanism related to the antibonding orbitals but also the charge transfer mechanism related to the bonding (and non-bonding) orbitals can affect the g factors for these systems [15, 16]. Moreover, the energy levels of the charge transfer bands may decline with increasing atomic number of the ligand in the same group of periodic table [17]. Thus, the importance of the charge transfer contributions to the g factor is expected to increase rapidly from Cl^- to Br^- for the same central ion Fe^{3+} in the studied AgX:Fe^{3+}. In order to clarify the importance of the charge transfer contributions and to study the EPR spectra of AgX:Fe^{3+} more in detail, the perturbation formula of the g factor is adopted in this work for a $3d^5$ ion under tetrahedra containing both the crystal-field and charge transfer contributions based on the cluster approach. Meanwhile, the superhyperfine parameters of the ligands Cl^- and Br^- are also theoretically studied in a uniform way, with the related unpaired spin densities determined quantitatively from the cluster approach.

2. Theory and calculations

AgX has the NaCl structure. When a Fe^{3+} ion is doped into the lattice of AgX, it may occupy the octahedral interstitial site [9]. This interstital site in AgX has four nearest neighbour silver ions at the corners of a cube, and the halogen ligands form a regular tetrahedron. When impurity Fe^{3+} enters the interstitial site, the original four nearest neighbour Ag^+ may escape to infinity and leave four vacancies due to charge compensation. So, there are only four nearest neighbour halogen ligands, i.e., the tetrahedral $[FeX_4]^-$ clusters (see figure 1 of [9]).

2.1 Calculations for the g factor

A $3d^5$ ion under an ideal octahedron may exhibit the orbital non-degenerate $^6A_{1g}$ ground state of high spin $S = 5/2$ [10, 11]. According to extensive studies on $3d^5$ ions in crystals, the combination of a spin-orbit coupling and orbital angular momentum interactions may be regarded as the dominant origin of g-shift Δg and zero-field splittings [18, 19]. Applying the Macfarlane's perturbation-loop method [20], the perturbation formula of the g-shift containing both the crystal-field and charge transfer contributions for a $3d^5$ ion in tetrahedra can be expressed as:

$$\begin{aligned}
\Delta g &= g - g_s = \Delta g_{CF} + \Delta g_{CT}\,,\\
\Delta g_{CF} &= -5\zeta_{CF}'^2\left(1/E_1^2 + 1/E_3^2\right)/6 - \zeta_{CF}^2/E_2^2 + 4\zeta_{CF}'\zeta_{CF}\left(1/E_1 + 1/E_3\right)/(5E_2)\,,\\
\Delta g_{CT} &= (4/5)\left(k_{CT}\zeta_{CT}/E_n - k_{CT}'\zeta_{CT}'/E_a\right). \qquad (1)
\end{aligned}$$

Here E_1, E_2 and E_3 are respectively, the energy differences between the ground $^6A_{1g}$ and the crystal-field excited $^4T_1[t_2^4(^3T_1)e]$, $^4T_1[t_2^3(^2T_2)e^2(^3A_2)]$ and $^4T_1[t_2^2(^3T_1)e^3]$ states. They can be expressed in terms of the cubic field parameter Dq and the Racah parameters B and C for the $3d^5$ ion in crystals: $E_1 \approx 10B + 6C - 10Dq$, $E_2 \approx 19B + 7C$ and $E_3 \approx 10B + 6C + 10Dq$. E_n and E_a are those between the ground $^6A_{1g}$ and the charge transfer excited $^6T_1^n$ and $^6T_1^a$ states, which are obtained from the empirical relationships $E_n \approx 30000[\chi(L) - \chi(M)] + 56B/3 - 10Dq$ and $E_a \approx E_n - 10Dq$ [17]. Here $\chi(L)$ and $\chi(M)$ are, respectively, the optical electronegativities of the ligand and metal ions.

The subscripts CF and CT denote the related terms in the crystal-field and charge transfer mechanisms, with the corresponding spin-orbit coupling coefficients ζ_{CF}, ζ_{CF}', ζ_{CT}, ζ_{CT}' and the orbital reduction factors k_{CT}, k_{CT}'. In view of the charge transfer contribution to the g factor, one can write the many electron wave functions of the charge transfer configurations in terms of the eleven-electron wave functions out of t_2^a, t_2^b and e^n, where the superscripts a, b and n denote the anti-bonding orbitals (corresponding to the crystal-field mechanism), bonding orbitals (corresponding to the charge transfer mechanism) and non-bonding orbitals, respectively. Thus, the ground state $^6A_{1g}$ is expressed as follows [11]:

$$|^6A_1\frac{5}{2}a_1\rangle = \left[\xi^+\eta^+\zeta^+\theta^+\varepsilon^+|\xi^+\xi^-\eta^+\eta^-\zeta^+\zeta^-\right]. \qquad (2)$$

In the square bracket on the right side of equation (2), the letters (ξ, η, ζ and θ, ε) on the left column are t_2^{a} and e^{n} orbitals and those (ξ, η and ζ) on the right column are t_2^{b} orbitals. There are only two excited configurations $(t_2^{\mathrm{a}})^3(e^{\mathrm{n}})^3(t_2^{\mathrm{b}})^5$ (or ${}^6T_1^{\mathrm{n}}$) and $(t_2^{\mathrm{a}})^4(e^{\mathrm{n}})^2(t_2^{\mathrm{b}})^5$ (or ${}^6T_1^{\mathrm{n}}$) having the non-zero spin-orbit coupling interactions with the ground state ${}^6A_{1g}$. Thus, the z components of ${}^6T_1^{\mathrm{n}}$ and ${}^6T_1^{\mathrm{a}}$ states with the highest $M_S = 5/2$ can be given as [11]

$$
\begin{aligned}
&|{}^6T_1^{\mathrm{n}}\tfrac{5}{2}z\rangle = \left[\xi^+\eta^+\zeta^+\theta^+\varepsilon^+\varepsilon^-|\xi^+\xi^-\eta^+\eta^-\zeta^+\right],\\
&|{}^6T_1^{\mathrm{a}}\tfrac{5}{2}z\rangle = -\frac{1}{\sqrt{2}}\left\{\left[\xi^+\xi^-\eta^+\zeta^+\theta^+\varepsilon^+|\xi^+\xi^-\eta^+\zeta^+\zeta^-\right] + \left[\xi^+\eta^+\eta^-\zeta^+\theta^+\varepsilon^+|\xi^+\eta^+\eta^-\zeta^+\zeta^-\right]\right\}.
\end{aligned} \tag{3}
$$

From the cluster approach, the one-electron basis functions for a tetrahedral $3d^5$ cluster may be expressed as:

$$
\begin{aligned}
\Psi_t^x &= N_t^x\left(\phi_{dt} - \lambda_\sigma^x\chi_{p\sigma} - \lambda_{\mathrm{s}}^x\chi_{\mathrm{s}} - \lambda_\pi^x\chi_{p\pi t}\right),\\
\Psi_e^x &= N_e^x\left(\phi_{de} - \sqrt{3}\lambda_\pi^x\chi_{p\pi e}\right).
\end{aligned} \tag{4}
$$

Here, the superscript x (= a or b) denotes the antibonding or bonding orbitals. ϕ_{dt} and ϕ_{de} are the d orbitals of the $3d^5$ ion, and $\chi_{p\pi t}$, $\chi_{p\pi e}$, $\chi_{p\sigma}$ and χ_s are the p and s orbitals of ligands. N_t^x and N_e^x are the normalization factors, and λ_σ and λ_π (or λ_s) are the orbital admixture coefficients. From equation (4), one can obtain the normalization conditions.

$$
\begin{aligned}
&(N_t^x)^2\left[1 + (\lambda_\sigma^x)^2 + (\lambda_\pi^x)^2 - 2\lambda_\sigma^x S_\sigma - 2\lambda_s^x S_s - 2\lambda_\pi^x S_\pi\right] = 1,\\
&(N_e^x)^2\left[1 + 3(\lambda_\pi^x)^2 + 6\lambda_\pi^x S_\pi\right] = 1,
\end{aligned} \tag{5}
$$

and the orthogonality relationships

$$
\begin{aligned}
&1 + 3\lambda_\pi^{\mathrm{a}}\lambda_\pi^{\mathrm{b}} - 3(\lambda_\pi^{\mathrm{a}} + \lambda_\pi^{\mathrm{b}})S_\pi = 0,\\
&1 + \lambda_\pi^{\mathrm{a}}\lambda_\pi^{\mathrm{b}} + \lambda_\sigma^{\mathrm{a}}\lambda_\sigma^{\mathrm{b}} + \lambda_s^{\mathrm{a}}\lambda_s^{\mathrm{b}} - (\lambda_\pi^{\mathrm{a}} + \lambda_\pi^{\mathrm{b}})S_\pi - (\lambda_\sigma^{\mathrm{a}} + \lambda_\sigma^{\mathrm{b}})S_\sigma - (\lambda_s^{\mathrm{a}} + \lambda_s^{\mathrm{b}})S_s = 0,\\
&\lambda_\pi^{\mathrm{a}}\lambda_\pi^{\mathrm{b}} + \lambda_s^{\mathrm{a}}\lambda_s^{\mathrm{b}} = 0.
\end{aligned} \tag{6}
$$

Meanwhile, the following approximation relationships are satisfied for the antibonding orbitals [19]:

$$
\begin{aligned}
N^2 &\approx \left[1 + 6\lambda_\pi^{\mathrm{a}}S_\pi + 9(\lambda_\pi^{\mathrm{a}})^2S_\pi^2\right]\left[1 + 3(\lambda_\pi^{\mathrm{a}})^2 + 6\lambda_\pi^{\mathrm{a}}S_\pi\right]^{-2},\\
N^2 &\approx \left[1 + 2\lambda_\pi^{\mathrm{a}}S_\pi + 2\lambda_\sigma^{\mathrm{a}}S_\sigma + 2\lambda_s^{\mathrm{a}}S_s + 2\lambda_\pi^{\mathrm{a}}S_\pi\lambda_\sigma^{\mathrm{a}}S_\sigma + 2\lambda_\pi^{\mathrm{a}}S_\pi\lambda_s^{\mathrm{a}}S_s + (\lambda_\pi^{\mathrm{a}})^2S_\pi^2 + (\lambda_\sigma^{\mathrm{a}})^2S_\sigma^2 + (\lambda_s^{\mathrm{a}})^2S_s^2\right]\\
&\times \left[1 + (\lambda_\pi^{\mathrm{a}})^2 + (\lambda_\sigma^{\mathrm{a}})^2 + (\lambda_s^{\mathrm{a}})^2 + 2\lambda_\pi^{\mathrm{a}}S_\pi + 2\lambda_\sigma^{\mathrm{a}}S_\sigma + 2\lambda_s^{\mathrm{a}}S_s\right]^{-2}.
\end{aligned} \tag{7}
$$

Here S_π, S_σ and S_s are the group overlap integrals between the d orbitals of the $3d^5$ ion and p or s orbitals of the ligands. N is the average covalency factor characteristic of the covalency (or orbital admixtures) between the impurity and ligand ions. In general, the orbital admixture coefficients increase with an increase of the group overlap integrals, and one can approximately adopt the proportional relationship $\lambda_\sigma^{\mathrm{a}}/S_\sigma \approx \lambda_s^{\mathrm{a}}/S_s$ for the orbital admixture coefficients and the related group overlap integrals within the same σ component.

From the cluster approach, the corresponding spin-orbit coupling coefficients for the crystal-field mechanism in equation (1) are expressed as [21]:

$$
\begin{aligned}
\zeta_{\mathrm{CF}} &= (N_t^{\mathrm{a}})^2\left\{\zeta_d^0 + \left[\sqrt{2}\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{a}} - (\lambda_\pi^{\mathrm{a}})^2/2 - \sqrt{2}A\lambda_\pi^{\mathrm{a}}\lambda_s^{\mathrm{a}}\right]\zeta_P^0\right\},\\
\zeta'_{\mathrm{CF}} &= N_t^{\mathrm{a}}N_e^{\mathrm{a}}\left\{\zeta_d^0 + \left[\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{a}}/\sqrt{2} + (\lambda_\pi^{\mathrm{a}})^2/2 - A\lambda_\pi^{\mathrm{a}}\lambda_s^{\mathrm{a}}/\sqrt{2}\right]\zeta_p^0\right\}.
\end{aligned} \tag{8}
$$

Here, ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients for a free $3d^5$ and ligand ions, respectively. A denotes the integral $R\langle ns|\frac{\partial}{\partial y}|np_y\rangle$, where R stands for the impurity-ligand distance. Similarly, the spin-orbit coupling coefficients and the orbital reduction factors for the charge transfer mechanism are written as:

$$
\begin{aligned}
\zeta_{\mathrm{CT}} &= N_t^{\mathrm{b}} N_t^{\mathrm{a}} \left[\zeta_d^0 + \left(\frac{\lambda_\pi^{\mathrm{a}} \lambda_\sigma^{\mathrm{b}} + \lambda_\pi^{\mathrm{b}} \lambda_\sigma^{\mathrm{a}}}{\sqrt{2}} - \frac{\lambda_\pi^{\mathrm{a}} \lambda_\pi^{\mathrm{b}}}{2} - \sqrt{2} A \lambda_s^{\mathrm{a}} \lambda_\pi^{\mathrm{b}} \right) \zeta_p^0 \right], \\
\zeta'_{\mathrm{CT}} &= N_e^{\mathrm{a}} N_t^{\mathrm{b}} \left[\zeta_d^0 + \left(\frac{\lambda_\pi^{\mathrm{a}} \lambda_\sigma^{\mathrm{b}}}{\sqrt{2}} + \frac{\lambda_\pi^{\mathrm{a}} \lambda_\pi^{\mathrm{b}}}{2} - \frac{A \lambda_s^{\mathrm{a}} \lambda_\pi^{\mathrm{b}}}{\sqrt{2}} \right) \zeta_p^0 \right], \\
k_{\mathrm{CT}} &= N_t^{\mathrm{a}} N_t^{\mathrm{b}} \left[-\frac{\lambda_\pi^{\mathrm{a}} \lambda_\pi^{\mathrm{b}}}{2} + \frac{\lambda_\pi^{\mathrm{a}} \lambda_\sigma^{\mathrm{b}} + \lambda_\pi^{\mathrm{b}} \lambda_\sigma^{\mathrm{a}}}{\sqrt{2}} + (\lambda_\sigma^{\mathrm{a}} + \lambda_\sigma^{\mathrm{b}}) S_\sigma + (\lambda_\sigma^{\mathrm{a}} + \lambda_\sigma^{\mathrm{b}}) S_\sigma + (\lambda_\pi^{\mathrm{a}} + \lambda_\pi^{\mathrm{b}}) S_\pi - \sqrt{2} A \lambda_s^{\mathrm{a}} \lambda_\pi^{\mathrm{b}} \right], \\
k'_{\mathrm{CT}} &= N_t^{\mathrm{b}} N_e^{\mathrm{a}} \left[1 + \left(\frac{\lambda_\pi^{\mathrm{a}} \lambda_\pi^{\mathrm{b}}}{2} + \frac{\lambda_\pi^{\mathrm{a}} \lambda_\sigma^{\mathrm{b}}}{\sqrt{2}} \right) + 3\lambda_\pi^{\mathrm{a}} S_\pi + \lambda_\pi^{\mathrm{b}} S_\pi + \lambda_\sigma^{\mathrm{b}} S_\sigma + \lambda_s^{\mathrm{b}} S_s - \frac{A \lambda_s^{\mathrm{a}} \lambda_\pi^{\mathrm{b}}}{\sqrt{2}} \right].
\end{aligned}
\tag{9}
$$

For the studied $[FeX_4]^-$ clusters, the impurity-ligand distances are $R \approx 2.403$ and 2.500 Å [22] for the interstitial sites in AgCl and AgBr, respectively. Thus, the group overlap integrals and the integral A can be calculated using the distances R and the Slater-type self-consistent field (SCF) functions [23, 24]. From the optical spectra for Fe^{3+} in AgX (or similar tetrahedral environments) [25, 26], the cubic field parameters Dq and the covalency factors N are obtained and shown in table 1. The related molecular orbital coefficients N_γ^x and λ_γ^x are determined from equations (5)–(7). According to the free-ion values $\zeta_d^0 \approx 588$ cm^{-1} [27] for Fe^{3+} and $\zeta_p^0 \approx 587$ and 2460 cm^{-1} [28] for Cl^- and Br^-, the spin-orbit coupling coefficients and the orbital reduction factors can be obtained for the crystal-field and charge transfer mechanisms from equations (8) and (9). These values are also listed in table 1. The Racah parameters in the energy denominators of equation (1) are determined from the relationships $B \approx N^2 B_0$ and $C \approx N^2 C_0$ [29] and the free-ion values $B_0 \approx 1322$ cm^{-1} and $C_0 \approx 4944$ cm^{-1} [27] for Fe^{3+}. From $\chi(Fe^{3+}) \approx 2.4$, $\chi(Cl^-) \approx 2.8$ and $\chi(Br^-) \approx 2.6$ [11], the charge transfer levels E_{n} and E_{a} are calculated. Substituting the above values into equation (1), the g-shifts (Cal.[b]) for the Fe^{3+} centers in AgX are obtained and presented in table 2. In order to clarify the importance of the charge transfer contribution, the results (Cal.[a]) containing merely the crystal-field contribution are also presented in table 2.

Table 1. The group overlap integrals, the cubic field parameter (in cm^{-1}) and the covalency factor, the normalization factors and the orbital admixture coefficients as well as the spin-orbit coupling coefficients (in cm^{-1}) and the orbital reduction factors in the crystal-field and charge transfer mechanisms for Fe^{3+} in AgX (X=Cl and Br).

Hosts	S_π	S_σ	S_S	A	Dq	N	N_t^{a}	N_e^{a}	λ_t^{a}	λ_e^{a}	λ_s^{a}
AgCl	0.0069	−0.0298	0.0210	1.489	−430	0.74	0.729	0.745	0.456	−0.345	−0.321
AgBr	0.0072	−0.0314	0.0264	1.467	−380	0.70	0.683	0.706	0.516	−0.380	−0.312
Hosts	N_t^{b}	N_e^{b}	λ_t^{b}	λ_e^{b}	λ_s^{b}	ζ_{CF}	ζ'_{CF}	ζ_{CT}	ζ'_{CT}	k_{CT}	k'_{CT}
AgCl	0.273	0.403	−0.733	1.027	−1.040	208	380	482	375	0.813	0.646
AgBr	0.272	0.463	−0.654	1.040	−1.081	−599	188	1112	713	0.768	0.630

2.2 Calculations for the superhyperfine parameters

In the previous treatments of the superhyperfine parameters [30], the unpaired spin densities f_s and $f_\sigma - f_\pi$ of the ligand $2s$ and $2p\sigma$ (or $2p\pi$) orbitals were usually taken as adjustable parameters, instead of being quantitatively correlated with the chemical bonding between the impurity and ligands. In order to improve the above treatments, the cluster approach [21] is applied to establish the uniform expressions of these quantities. Thus, the superhyperfine parameters can be written as:

$$
\begin{aligned}
A' &= A_s + 2(A_{\mathrm{D}} + A_\sigma - A_\pi), \\
B' &= A_s - (A_{\mathrm{D}} + A_\sigma - A_\pi).
\end{aligned}
\tag{10}
$$

Table 2. The g-shift Δg and the superhyperfine parameters (in 10^{-4} cm^{-1}) for Fe^{3+} in AgX.

		Δg	A'	B'
AgCl	Cal.[a]	−0.0006	3.9	1.7
	Cal.[b]	0.0128	3.6	2.8
	Expt. [9]	0.0133(4)	3.3(5)	2.0(5)
AgBr	Cal.[a]	−0.0013	21.1	6.8
	Cal.[b]	0.0420	16.0	8.5
	Expt. [9]	0.0427(50)	16.2(15)	7.8(15)

[a] Calculations of the g factor based only on the crystal-field contribution and those for the superhyperfine parameters of the previous studies [9] by fitting the unpaired spin densities.
[b] Calculations based on the inclusion of both the crystal-field and charge transfer contributions.

Here A_s is the isotropic contribution to the superhyperfine parameters, charactering the effect of the ligand ns 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 np orbital, respectively. The isotropic part can be expanded as [30]:

$$A_s = f_s A_s^0/(2S), \tag{11}$$

with $A_s^0 = (8/3) g_s g_{\mathrm{n}} \beta \beta_{\mathrm{n}} |\Psi(0)|^2 \approx 555.7 \times 10^{-4}$ and 7815.0 cm^{-1}, and $A_p^0 = g_s g_{\mathrm{n}} \beta \beta_{\mathrm{n}} \langle r^{-3} \rangle \approx 46.7 \times 10^{-4}$ and 232.2×10^{-4} for Cl^- and Br^-, respectively [31]. f_s denotes the unpaired spin-density of the ligand ns orbital. The electron spin is S =5/2 for the ground state $^6A_{1g}$. The anisotropic contribution from the ligand np orbital is usually expressed as [30]:

$$A_\sigma - A_\pi = A_p^0 (f_\sigma - f_\pi)/(2S). \tag{12}$$

Here, f_σ and f_π are the unpaired spin densities of the ligand $np\sigma$ and $np\pi$ orbitals, respectively. The dipole-dipole interaction between the electron distribution of the central ion and the halogen ligand nucleus can be expressed as $A_{\mathrm{D}} = g\beta g_{\mathrm{n}} \beta_{\mathrm{n}}/R^3$, 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:

$$f_s \approx N_e^{\mathrm{a}} (\lambda_s^{\mathrm{a}})^2/3, \qquad f_\sigma \approx N_e^{\mathrm{a}} (\lambda_e^{\mathrm{a}})^2/3, \qquad f_\pi \approx N_t^{\mathrm{a}} (\lambda_t^{\mathrm{a}})^2/4. \tag{13}$$

It is noted that in the previous works [9, 30] the unpaired spin densities were simply treated as the adjustable parameters by fitting the experimental superhyperfine parameters. Instead, they are quantitatively and uniformly calculated from the cluster approach in this work.

The unpaired spin densities f_i $(i = \sigma, \pi, s)$ as well as the isotropic contribution A_s and the anisotropic contribution $A_\sigma - A_\pi$ and A_{D} to the superhyperfine parameters are acquired from equations (11)–(13), and thus the resultant A' and B' are obtained from equation (10). In addition, by fitting the unpaired spin densities, the theoretical results of the previous work [9] are also collected in table 2.

3. Discussion

Table 2 reveals that the theoretical g factors (Cal.[b]) for AgX:Fe^{3+} based on the inclusion of both the crystal-field and charge transfer contributions show reasonable agreement with the experimental data, whereas those (Cal.[a]) based only on the conventional crystal-field contribution are merely 3% – 5% of the observed values. Meanwhile, the superhyperfine parameters are also suitably analyzed from the uniform quantitative relationships between the unpaired spin densities and the relevant molecular orbital coefficients based on the cluster approach.

1) The charge transfer contribution to the g-shift has opposite (positive) sign and much larger magnitude as compared to the crystal-field one. With an increase of the ligand spin-orbit coupling coefficient ζ_p^0 and a decease of the covalency factor N, the importance of the charge transfer contribution (characterized by the relative ratio $\Delta g_{\mathrm{CT}}/\Delta g_{\mathrm{CF}}$) increases rapidly from 13 for Cl^- to 34 for Br^-. So, for $3d^5$ ions (especially Fe^{3+} with high valence state) in covalent hosts, the charge transfer contribution to the g-shift is significant due to the low charge transfer levels E_{n} and E_{a}.

2) Apart from the increase of the charge transfer contribution from Cl^- to Br^-, the Δg_{CF} from the crystal-field contribution also shows a similar but less significant tendency (see table 2). This can be ascribed to the relative difference (or anisotropy) between ζ_{CF} and ζ'_{CF} in the formula of Δg_{CF}, which is relevant to the low covalency factors N ($\approx 0.7 \ll 1$, which are much smaller than the values 0.90 and 0.87 for Fe^{3+} in fluorides and oxides [32]) and the obvious orbital admixture coefficients ($\approx 0.3-0.5$) as well as the large ζ_p^0. Especially, the ratios $\zeta_{\mathrm{CF}}/\zeta'_{\mathrm{CF}}$ are 83% and 165% for AgCl and AgBr, increasing rapidly with the increase of ζ_p^0. Therefore, the impurity-ligand orbital admixtures and the anisotropic contribution from the ligand spin-orbit coupling coefficient should be taken into account in the analysis of the g factors for AgX:Fe^{3+}. Further, the relatively weaker dependence of Δg_{CF} on the covalency or the ligand contributions than Δg_{CT} is attributable to the dominant third-order perturbation terms (inversely proportional to the square of the energy separation E_1, E_2 or E_3) in the former and the second-order perturbation terms (inversely proportional to the charge transfer levels E_{n} or E_{a}) in the latter.

3) Reasonable agreement between theory (Cal.$^{\mathrm{b}}$) and experiment is achieved for A', but slightly worse for B'. This may be ascribed to the errors arising from the theoretical model (e.g., the ligand field model and the cluster approach) and formulas. Importantly, the present calculations are based on the uniform model and formulas by establishing the quantitative relationships between the unpaired spin densities and the relevant molecular orbital coefficients from the cluster approach. Thus, the quantities f_s and $f_\sigma - f_\pi$ in equations (11) and (12) are determined theoretically from the cluster approach in a uniform way. These quantities were normally taken as the adjustable parameters by fitting two experimental superhyperfine parameters in the previous works [9, 30]. The calculated values of f_s ($\approx 0.6\%$ and 0.7%) and $f_\sigma - f_\pi$ ($\approx 1.95\%$ and 1.6%) for AgCl:Fe^{3+} and AgBr:Fe^{3+} in this work are comparable with the estimated values ($f_s \approx 0.86\%$ and 0.74%, and $f_\sigma - f_\pi \approx 3.4\%$ and 6.5%, respectively) by directly fitting two experimental superhyperfine parameters in the previous study [9], while the lower unpaired spin densities yield slightly better results. Apparently, the theoretical model and formulas in this work can also be applied to the EPR analysis for $3d^5$ ions in other fluorides.

4) There are some errors in the present calculations, e.g., the theoretical B' is slightly larger than the observed value in view of the experimental uncertainty. The errors may be ascribed to the approximations of the theoretical model (e.g., the ligand field theory and the cluster approach) and formulas, i.e., only the central ion $3d$ orbitals and the valence (ns and np, with $n = 3$ or 4 for Cl^- or Br^-) orbitals of the nearest neighbour ligands are included in the cluster approach calculations. All the intermediate parameters (ζ_{CF}, ζ'_{CF}, ζ_{CT}, ζ'_{CT}, k_{CT}, k'_{CT}) are quantitatively determined from the related cluster approach formulas. Except the spectral parameters Dq and N obtained from the optical spectral measurements, no adjustable parameters are induced in the calculations. Of course, the theoretical calculations and results in this work should be regarded as tentative ones. In order to make further investigations on the EPR spectra (especially the superhyperfine parameters) for AgX:Fe^{3+}, one may adopt more powerful and reliable density function theory (DFT) treatments [33–35].

4. Summary

The EPR parameters of AgX:Fe^{3+} are theoretically studied from the perturbation formulas containing both the crystal-field and charge transfer contributions. The g-shift Δg from the charge transfer contribution is opposite (positive) in sign and much larger in magnitude as compared to that from the crystal-field one. Moreover, the importance of the charge transfer contribution increases rapidly with an increase of the covalency and the spin-orbit coupling coefficient of the ligand, i.e., $Cl^- < Br^-$. The unpaired spin densities are quantitatively obtained from the relevant molecular orbital coefficients using the cluster approach instead of being treated as adjustable parameters by fitting the experimental superhyperfine parameters in the previous works.

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Дослідження параметрів EPR для тетраедральних кластерів $[FeX_4]^-$ у AgX (X = Cl, Br)

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Параметри g факторів електронного парамагнітного резонансу і супертонкі параметри для тетраедральних кластерів $[FeX_4]^-$ у AgX (X = Cl, Br) досліджуються теоретично, використовуючи теорію збурень для цих параметрів для $3d^5$ іона в тетраедрі з врахуванням вкладів від кристалічного поля і перенесення заряду. Параметри моделі кількісно визначаються з кластерного підходу в єдиний спосіб. Вклад у g-зсув $\triangle g$ ($= g - g_s$, де $g_s \approx 2.0023$ — значення спіну), отриманий із врахування зарядового перенесення є протилежний (позитивний) за знаком і набагато більший за величиною в порівнянні з вкладом, отриманим від врахування кристалічного поля. Важливість врахування зарядового перенесення зростає з ростом ковалентності і коефіцієнту спін-орбітальної взаємодії ліганди і отже демонструє, що AgCl < AgBr. Густини неспарених спінів галогенів, $np\sigma$ і $np\pi$ орбіталей кількісно визначаються з молекулярних орбітальних коефіцієнтів, що базуються на кластерному підході.

Ключові слова: *гамільтоніани кристалічних полів і спінів, електронний парамагнетний резонанс (EPR)*