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THEORETICAL STUDIES OF THE SPIN HAMILTONIAN PARAMETERS AND LOCAL STRUCTURES FOR Ag^{2+} IN AgCl AND KCl CRYSTALS**L.-J. Zhang, S.-Y. Wu, M.-Q. Kuang, X.-F. Hu, G.-L. Li***Department of Applied Physics, School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu, P. R. China*

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The spin Hamiltonian parameters (g factors, hyperfine structure constants and superhyperfine parameters) and local structures for Ag^{2+} centers in AgCl and KCl crystals are theoretically studied using the high-order perturbation formulas for a tetragonally elongated $4d^9$ cluster. The impurity centers undergo relative elongations ($\approx 0.05 \text{ \AA}$ and 0.23 \AA for Ag^{2+} in AgCl and KCl , respectively) along the C_4 axis owing to the Jahn—Teller effect. All the calculated spin Hamiltonian parameters show good agreement with the experimental data, and the ligand contributions to the spin Hamiltonian parameters are important and should be taken into account. The unpaired spin densities in the superhyperfine parameters are determined from molecular orbital coefficients based on the cluster approach, instead of being taken as the adjustable parameters in the previous treatments. Increasing tetragonal elongation from AgCl to KCl is attributed to a decrease in chemical bonding (or lower force constant) with increasing Ag^{2+} —Cl distance.

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Keywords: electron paramagnetic resonance, defect structures, Ag^{2+} , AgCl , KCl .**INTRODUCTION**

AgCl and KCl crystals containing coinage metal silver exhibit unique luminescent [1], vibrational [2], structural [3], thermodynamical [4], electrochemical [5], and photocatalytic properties [6—8]. As a second row ($4d$) transition metal ion, Ag^{2+} can be regarded as a model system due to the simple energy level structure with only one ground state and one excited state in the ideal octahedral crystal field [9, 10], and has been an important topic of electron paramagnetic resonance (EPR) research. As compared to the isoelectronic Jahn—Teller $3d^9$ (e.g., Cu^{2+} , Ni^+) ions, Ag^{2+} ($4d^9$) is only scarcely studied. Neither have the influences of the Jahn—Teller effect on defect structures been sufficiently investigated for Ag^{2+} in crystals. EPR spectra were recorded for Ag^{2+} in AgCl and KCl crystals, with the spin Hamiltonian parameters (g factors g_{\parallel} and g_{\perp} , hyperfine structure constants A_{\parallel} and A_{\perp} and the superhyperfine parameters A' and B') measured at 77 K [11, 12].

However, these experimental results have not been satisfactorily interpreted, except that the EPR signals were assigned to tetragonally elongated Ag^{2+} centers [11, 12]. Nor has the information about the local structures been obtained. Since microscopic mechanisms of the EPR spectra and information on defect structures would be significant for the understandings of the properties of materials containing Ag^{2+} impurities, further theoretical investigations on the spin Hamiltonian parameters and local structures for Ag^{2+} in AgCl and KCl are of fundamental and applied importance. In this work, the spin Hamiltonian parameters and local structures are theoretically studied for both Ag^{2+} centers from the

high order perturbation calculations of these parameters for a $4d^9$ ion under tetragonally elongated octahedra, by considering the suitable local tetragonal elongation distortions owing to the Jahn—Teller effect. The unpaired spin densities in the superhyperfine parameters are quantitatively determined from the related molecular orbital coefficients based on the cluster approach, instead of being taken as the adjustable parameters in the previous treatments.

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When Ag^{2+} is doped into the AgCl and KCl lattices, it tends to substitutionally occupy the octahedral cation sites. For a Ag^{2+} ($4d^9$) ion in an ideal octahedron, the energy system exhibits a ground orbital doublet 2E_g and an excited orbital triplet ${}^2T_{2g}$ [9, 10]. Importantly, the Jahn—Teller ion Ag^{2+} can experience the Jahn—Teller effect via vibration interactions [13, 14] by stretching the two Ag^{2+} — Cl^- bonds along [001] (or C_4) axis. As a result, the local point symmetry is reduced from original cubic (O_h) of the host cation sites to tetragonal (D_{4h}) of the impurity centers, with the twofold orbital degeneracy of original ground 2E_g removed. Conveniently, the local structures of the impurity centers can be described by a relative tetragonal elongation ΔZ .

For a $4d^9$ ion in tetragonally elongated octahedra, the lower cubic orbital doublet 2E_g can be separated into two orbital singlets ${}^2B_{1g}$ ($|x^2-y^2\rangle$) and ${}^2A_{1g}$ ($|z^2\rangle$), with the former lying lowest [9, 10]. Meanwhile, the higher cubic orbital triplet ${}^2T_{2g}$ is split into an orbital singlet ${}^2B_{2g}$ ($|xy\rangle$) and an orbital doublet 2E_g ($|xz\rangle, |yz\rangle$) [9, 10]. As a second row transition metal ion, Ag^{2+} in the chlorides may exhibit significant covalency and ligand orbital and spin-orbit coupling contributions to the spin Hamiltonian parameters. Because of this, the conventional crystal field model formulas [9, 10] including merely the central ion orbital and spin-orbit coupling contributions are no longer suitable for the EPR analysis. So, the perturbation formulas [15] of the spin Hamiltonian parameters for a tetragonally elongated octahedral $4d^9$ cluster containing the ligand contributions are adopted here [15]

$$\begin{aligned} g_{\parallel} &= g_s + 8k'\zeta'/E_1 + k\zeta'^2/E_2^2 + 4k'\zeta\zeta'/(E_1E_2) + g_s\zeta'^2[1/E_1^2 - 1/(2E_2^2)] - k\zeta\zeta'^2(4/E_1 - 1/E_2)/E_2^2 - \\ &\quad - 2k'\zeta\zeta'^2[2/(E_1E_2) - 1/E_2^2]/E_1 - g_s\zeta\zeta'^2[1/(E_1E_2^2) - 1/(2E_2^3)], \\ g_{\perp} &= g_s + 2k'\zeta'/E_2 - 4k\zeta'^2/(E_1E_2) + k'\zeta\zeta'(2/E_1 - 1/E_2)/E_2 + 2g_s\zeta'^2/E_1^2 + \zeta\zeta'(k\zeta' - k'\zeta)/(E_1E_2^2) - \\ &\quad - \zeta\zeta'(1/E_2 - 2/E_1)(2k\zeta'/E_1 + k'\zeta/E_2)/(2E_2) - g_s\zeta\zeta'^2[1/E_1^2 - 1/(E_1E_2) + 1/E_2^2]/(2E_2), \\ A_{\parallel} &= P(-\kappa - 4N/7) + P'[8k'\zeta'/E_1 + 6k'\zeta'/(7E_2) - 3k\zeta'^2/(7E_2^2) - 40k'\zeta\zeta'/(7E_1E_2) + \kappa\zeta'^2/E_2^2], \\ A_{\perp} &= P(-\kappa + 2N/7) + P'[11k'\zeta'/(7E_2) + 9k'\zeta\zeta'/(14E_2^2) - 4\zeta'^2/(7E_1^2) + \\ &\quad + 11k'\zeta\zeta'/(7E_1E_2) + \kappa\zeta'^2[2/E_1^2 + 1/(2E_2^2)]], \\ A' &= A_s + 2A_{\sigma} + 2A_D, \\ B' &= A_s - A_{\sigma} - A_D. \end{aligned} \quad (1)$$

Here g_s (≈ 2.0023) is the spin-only value. N is the covalency factor, characteristic of the covalency in bonding between the central ion and ligands; κ is the core polarization constant. The spin-orbit coupling coefficients ζ and ζ' , the orbital reduction factors k and k' , and the dipolar hyperfine structure parameters P and P' denote the anisotropic contributions (diagonal and off-diagonal elements) for the different irreducible representations γ ($= e$ and t labeling E_g and T_{2g}) of group O_h . They can be determined from the cluster approach [16]:

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), & \zeta' &= (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2), \\ k &= N_t(1 + \lambda_t^2/2), & k' &= (N_tN_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_sA/2)], \\ P &= N_tP_0, & P' &= (N_tN_e)^{1/2}P_0, \end{aligned} \quad (2)$$

where ζ_d^0 and ζ_p^0 are, respectively, the spin-orbit coupling coefficients of the free $4d^9$ and ligand ions. P_0 is the dipolar hyperfine structure parameter of the free $4d^9$ ion. N_{γ} and λ_{γ} (or λ_s) are the normaliza-

tion factors and the orbital admixture coefficients, respectively. A is the integral $R\langle n_s | \partial / \partial y | np_y \rangle$, where R is the reference impurity-ligand distance of the studied systems. The molecular orbital coefficients N_γ and λ_γ (or λ_s) can be determined from the approximate relationships [16]

$$\begin{aligned} N_t^2 &= N_t^2 [1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\ N_e^2 &= N_e^2 [1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}] \end{aligned} \quad (3)$$

and the normalization conditions [16]

$$\begin{aligned} N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1. \end{aligned} \quad (4)$$

Here S_{dpt} (and S_{ds}) are the group overlap integrals. In general, the orbital admixture coefficients increase with increasing group overlap integrals, and one can approximately adopt the proportionality relationship $\rho \lambda_e / S_{dpe} \approx \lambda_s / S_{ds}$ between the orbital admixture coefficients and the related group overlap integrals within the same irreducible representation E_g . Here the proportionality factor ρ is usually taken as an adjustable parameter.

In Eq. (1), E_1 and E_2 are the energy separations between the excited ${}^2B_{2g}$ and 2E_g and the ground ${}^2B_{1g}$ states for a $3d^9$ ion in tetragonal symmetry [15]. They can be determined from the energy matrices for a $4d^9$ ion in tetragonal symmetry in terms of the cubic field parameter Dq and the tetragonal field parameters Ds and Dt

$$\begin{aligned} E_1 &\approx 10Dq, \\ E_2 &\approx 10Dq - 3Ds + 5Dt. \end{aligned} \quad (5)$$

In the formulas of superhyperfine parameters, A_s stands for the isotropic contribution from the ligand $3s$ orbitals. A_σ and A_D denote the anisotropic contributions from the admixture between $Ag^{2+} 4d$ and $Cl^- 3p_\sigma$ orbitals and the dipole-dipole interactions between central ion electrons and ligand nucleus, respectively. $\langle r^n \rangle$ ($n = 2, 4$) are the expectation values of the square and quartic of $Ag^{2+} 4d^9$ radial wave function. The isotropic and anisotropic parts of the superhyperfine parameters can be expressed as [17]

$$A_s = f_s A_s^0, \quad A_\sigma = f_\sigma A_p^0, \quad A_D = g\beta g_n \beta_n / R^3. \quad (6)$$

Here f_s and f_σ are the unpaired spin densities; $A_s^0 = (8\pi/3)g_s \mu_B g_n \mu_n |\phi(0)|^2$ and $A_p^0 = g_s \mu_B g_n \mu_n \langle r^{-3} \rangle_{3p}$ are the related nuclear parameters of ligand ${}^{35}Cl^-$; g_n is the nuclear g value; μ_B and μ_n are the electron Bohr magneton and nuclear magneton; $\phi(0)$ is the wave function of chlorine $3s$ orbital at the nucleus. $\langle r^{-3} \rangle_{3p}$ is the expectation value of the inverse cube of $Cl^- 3p$ radial wave function. For the dipole-dipole interaction term, the g factor is conveniently taken as the average $[= (g_{||} + 2g_{\perp})/3]$ of those in Eq. (1).

The unpaired spin densities can be determined from the relevant molecular orbital coefficients based on the cluster approach

$$f_s \approx N(1 - \mu^2)/4, \quad f_\sigma \approx N\mu^2/4. \quad (7)$$

Here $\mu = S_{dpe} / (S_{dpe}^2 + \rho^2 S_{ds}^2)^{1/2}$ is characteristic of the ligand $p-s$ hybridization. It is noted that the unpaired spin densities were not quantitatively correlated to covalency of the systems but simply obtained by fitting the experimental superhyperfine parameters in the previous work [11]. However, these quantities are theoretically acquired from the uniform formulas based on the cluster approach in the present studies.

The tetragonal field parameters are determined from the local geometry and the superposition model [18—21]

$$\begin{aligned} Ds &\approx (4/7)\bar{A}_2(R)[(R/R_{\perp})^{t_2} - (R/R_{||})^{t_2}], \\ Dt &\approx (16/21)\bar{A}_4(R)[(R/R_{\perp})^{t_4} - (R/R_{||})^{t_4}], \end{aligned} \quad (8)$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ [18] are the power law exponents. $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parame-

Table 1

The group overlap integrals, cubic field parameters (in cm^{-1}), covalency factors, normalization factors, orbital admixture coefficients, spin-orbit coupling coefficients (in cm^{-1}), orbital reduction factors and dipolar hyperfine structure parameters (in 10^{-4}cm^{-1}) for Ag^{2+} in AgCl and KCl

Molecule	S_{dpt}	S_{dpe}	S_{ds}	A	Dq	N	N_t	N_e	λ_t	λ_e	λ_s
AgCl	0.0525	0.1215	0.0854	2.1640	2240	0.59	0.618	0.677	0.841	0.700	0.172
KCl	0.0228	0.0729	0.0433	2.3212	1560	0.60	0.611	0.646	0.820	0.714	0.197
Molecule	ζ	ζ'	k	k'	P	P'					
AgCl	1265	1078	0.836	0.355	-45.5	-47.6					
KCl	1246	1048	0.817	0.326	-45.0	-46.2					

ters. For octahedral transition metal clusters, the relationships $\bar{A}_4(R) \approx (3/4)Dq$ and $\bar{A}_2(R) \approx 10.8\bar{A}_4(R)$ [20—22] have been proved reliable in many crystals and are reasonably applied here. The impurity-ligand bond lengths parallel and perpendicular to the C_4 axis are expressed in terms of the reference distance R and the relative tetragonal elongation ΔZ due to the Jahn—Teller distortion: $R_{\parallel} \approx R + 2\Delta Z$ and $R_{\perp} \approx R - \Delta Z$. Therefore, the g factors (particularly the anisotropy $\Delta g = g_{\parallel} - g_{\perp}$) are correlated to the tetragonal field parameters and hence to the local structures of the impurity centers.

For an impurity ion doped into a crystal, the reference impurity-ligand distance R usually differs from the host cation-anion distance R_H due to the difference in ionic radius between the impurity and host ions. Conveniently, the reference distance R can be obtained from the empirical relationship $R \approx R_H + (r_i - r_h)/2$ [23]. Here, the radius of the impurity is $r_i(\text{Ag}^{2+}) \approx 0.89 \text{ \AA}$, the radii of the host ions are $r_h(\text{Ag}^+) \approx 1.26 \text{ \AA}$ and $r_h(\text{K}^+) \approx 1.33 \text{ \AA}$ [24], and the host distances R_H are 2.775 and 3.147 \AA [24] for AgCl and KCl. Thus, the distances $R \approx 2.590$ and 2.927 \AA can be determined for Ag^{2+} in AgCl and KCl, respectively. From the distances R , the group overlap integrals S_{dpt} , S_{dpe} , S_{ds} and the integral A are calculated by using the Gaussian basis sets 6-31G* [25] and LANL2DZ [26] for Cl and Ag, respectively. In the light of the optical spectral analysis for Ag^{2+} in the chlorides [9, 27], the cubic field parameters Dq and the covalency factors N are obtained for the studied systems and shown in Table 1. The normalization factors and the orbital admixture coefficients are calculated from Eqs. (3) and (4), when the proportionality factor ρ is known. The spin-orbit coupling coefficients and the orbital reduction factors can be acquired from Eq. (2) and the free-ion values ζ_d^0 ($\approx 1840 \text{ cm}^{-1}$ [10]) for Ag^{2+} and ζ_p^0 ($\approx 587 \text{ cm}^{-1}$ [28]) for Cl^- . In the formulas of hyperfine structure constants, the dipolar hyperfine structure parameter is $P_0 \approx -73.6 \times 10^{-4} \text{ cm}^{-1}$ for $^{109}\text{Ag}^{2+}$ [29]. The core polarization constant is normally determined from the relationship $\kappa = 2\xi/(3\langle r^{-3} \rangle)$ [10, 28]. Here ξ is characteristic of the unpaired spin density at the nucleus of the central ion. $\langle r^{-3} \rangle$ is the expectation value of the inverse cube of the $4d$ radial wave function. Applying the data $\langle r^{-3} \rangle \approx 8.905 \text{ a.u.}$ [10] for Ag^{2+} and $\xi \approx -5.82 \sim -9.44 \text{ a.u.}$ [29] for Ag^{2+} in various chlorides, the values $\kappa \approx 0.41$ and 0.79 are obtained for Ag^{2+} in AgCl and KCl in view of their different hyperfine structure constants [11, 12]. The nuclear parameters are $A_s^0 \approx 1570 \times 10^{-4}$ and $A_p^0 \approx 46.8 \times 10^{-4} \text{ cm}^{-1}$ for $^{35}\text{Cl}^-$ [30].

There are only two unknown quantities in the formulas of the spin Hamiltonian parameters, i.e., the relative tetragonal elongation ΔZ and the proportionality factor ρ . Substituting the related values into Eq. (1) and fitting the calculated g factors, hyperfine structure constants and superhyperfine parameters to the experimental data, one can obtain

$$\Delta Z \approx 0.05 \text{ and } 0.23 \text{ \AA}, \quad \rho \approx 0.35 \text{ and } 0.47 \quad (9)$$

for Ag^{2+} in AgCl and KCl, respectively. The corresponding molecular orbital coefficients and the relevant quantities in Eq. (2) are shown in Table 1. The calculated spin Hamiltonian parameters (Calc. c) are given in Table 2. For comparison, the results (Calc. a) of the superhyperfine parameters based on

T a b l e 2

The g factors, hyperfine structure constants and superhyperfine parameters (in 10^{-4} cm^{-1}) for Ag^{2+} in AgCl and KCl

Molecule		g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	A'	B'
AgCl	Calc. ^a	—	—	—	—	19.07	2.24
	Calc. ^b	2.240	2.056	25.4	20.5	—	—
	Calc. ^c	2.146	2.035	31.2	21.7	27.18	6.25
	Expt. [11]	2.145	2.038	28.9 (10)	22.4 (28)	26.15 (187)	—
KCl	Calc. ^a	—	—	—	—	32.8	10.7
	Calc. ^b	2.358	2.068	31.2	27.7	—	—
	Calc. ^c	2.190	2.038	37.1	28.6	30.3	5.8
	Expt. [12]	2.193 (1)	2.035 (1)	38.2 (5)	28.3 (5)	31.2 (9)	4.5 (9)

^a Calculations of the superhyperfine parameters based on the fitted unpaired spin densities (or obtained from MS-X α calculations) in the previous works [11, 31].

^b Calculations of g factors and hyperfine structure constants based on the conventional crystal-field model formulas without the ligand orbital and spin-orbit coupling contributions.

^c Calculations of the spin Hamiltonian parameters based on the uniform formulas containing the ligand contributions from the cluster approach in this work.

the fitted unpaired spin densities (or obtained from MS-X α calculations) in the previous works [11, 31] and those (Calc. ^b) of g factors and hyperfine structure constants based on the conventional crystal-field model formulas (i.e., taking $k = k' = N$, $\zeta = \zeta' = N\zeta_d^0$ and $P = P' = P_0N$) are collected in Table 2.

DISCUSSION

Table 2 demonstrates that the theoretical spin Hamiltonian parameters (Calc. ^c) based on the uniform formulas containing the ligand contributions from the cluster approach in this work show good agreement with the experimental data. However, the previous superhyperfine parameters (Calc. ^a) based on the fitted unpaired spin densities (or obtained from MS-X α calculations) [11, 31] and the g factors and hyperfine structure constants (Calc. ^b), based on the conventional crystal-field model formulas, are not so good. Thus, the EPR spectra for Ag^{2+} in AgCl and KCl are satisfactorily and consistently interpreted, and the information about the local structures of the impurity centers is also obtained.

1) The positive relative elongations ΔZ in Eq. (9) are in accordance with the expectation based on the positive anisotropies Δg [11, 12] for an octahedral d^9 cluster suffering the Jahn—Teller tetragonal elongation. The larger tetragonal elongation for $\text{KCl}:\text{Ag}^{2+}$ than $\text{AgCl}:\text{Ag}^{2+}$ is ascribed to the longer reference distance R and hence weaker bonding (or lower force constant) in the former, which is easier to undergo elongation distortion via vibration interactions. So, Ag^{2+} prefers to experience tetragonal elongation distortion of the Jahn—Teller nature under octahedral environments, although the original cation sites in AgCl and KCl belong to cubic (O_h) symmetry. Similar tetragonally elongated Ag^{2+} centers of the Jahn—Teller nature were reported for silver doped MgO , CaO , and SrO based on *ab initio* studies [32]. Interestingly, the tetragonal elongation ($\approx 0.23 \text{ \AA}$) obtained for $\text{KCl}:\text{Ag}^{2+}$ in this work agrees well with that ($\approx 0.22 \text{ \AA}$) based on the MS-X α calculations [31] and can be regarded as suitable. Charge mismatch substitution of the host Ag^+ or K^+ by Ag^{2+} would induce some means of charge compensation (e.g., cation vacancies). In fact, the probability of production of a cationic vacancy can be very small at low temperature (77 K). Meanwhile, the Jahn—Teller effect may depress production of local cationic vacancies. Thus, possible charge compensation can be regarded as far from the impurity centers, and its influence on the defect structures may be negligible. On the other hand, a non-axial

compensator would induce lower symmetrical (e.g., rhombic, orthorhombic and monoclinic) components of the crystal-fields, and hence anisotropic EPR signals along X and Y axes, which contradicts the measured axial g factors and hyperfine structure constants [11, 12]. Therefore, the local structures of the tetragonally elongated Ag^{2+} centers in AgCl and KCl can be understood here.

2) The g factors (and the hyperfine structure constants) (Calc. ^c) containing the ligand orbital and spin-orbit coupling contributions are in better agreement with the experimental data than those (Calc. ^b) in the absence of the above contributions. Because of the significant covalency and obvious ligand orbital and spin-orbit coupling interactions, the average g [$= (g_{\parallel} + 2g_{\perp})/3$] and the anisotropy Δg (Calc. ^b) without the ligand contributions are much higher than the observed values. Importance of the ligand contributions can be further illustrated by the small covalency factors N ($\sim 0.6 \ll 1$), the obvious orbital admixture coefficients (≈ 0.2 — 0.8) as well as the relative deviations (anisotropies) $(k - k')/k' \approx 135$ — 151 % and $(\zeta - \zeta')/\zeta' \approx 17$ — 19 % for the orbital reduction factors and the spin-orbit coupling coefficients from the cluster approach calculations. Therefore, the ligand contributions should be taken into account in the analysis of the EPR spectra for such covalent systems as $4d^9$ impurities in chlorides. In addition, the average of g factors is larger for $\text{KCl}:\text{Ag}^{2+}$ than $\text{AgCl}:\text{Ag}^{2+}$, which is attributable to the slightly weaker crystal fields (lower Dq) and covalency (higher N) due to the relatively longer distance R in the former.

3) In the light of Eq. (1), hyperfine structure constants originate mainly from the isotropic contribution proportional to κ , characteristic of the Fermi contact interactions between the ground $4s^2 4d^9$ configuration and the excited ones (e.g., $4s^1 4d^9 5s^1$) containing s -orbitals for Ag^{2+} in crystals. The higher κ value for $\text{KCl}:\text{Ag}^{2+}$ than for $\text{AgCl}:\text{Ag}^{2+}$ can be illustrated by stronger configuration interactions ($\text{Ag}^{2+} 4d$ — $4s/5s$ orbital admixtures) for the lowest ${}^2B_{1g}$ ($4d_{x^2-y^2}$) state due to the larger tetragonal elongation in the former. On the other hand, the anisotropic parts of the hyperfine structure constants are related to N and g shifts, which are insensitive to the local structures (tetragonal distortions) of the impurity centers. The smaller A factors for $\text{AgCl}:\text{Ag}^{2+}$ can be attributed to the more significant exchange polarization of the Ag^{2+} bonding orbitals (i.e., stronger covalency or lower N) and hence more intense covalent reduction of the hyperfine structure constants [33].

4) The superhyperfine parameters (Calc. ^c) based on the present uniform formulas from the cluster approach show some improvement from those (Calc. ^a) based on the fitted unpaired spin densities (or obtained from MS-X α calculations) [11, 31]. The proportionality factors ρ (≈ 0.35 and 0.47) reveal 53—65 % reduction of the ratio λ_s/S_{ds} with respect to λ_e/S_{dpe} . Normally, the admixture of $\text{Ag}^{2+} 4d$ orbital with $\text{Cl}^- 3s$ orbital can be less than that with $\text{Cl}^- 3p$ orbital, because the $3s$ orbital is usually more compact than the $3p$ one for the same ligand. The unpaired spin densities ($f_s \approx 0.84$ % and 1.06 % and $f_{\sigma} \approx 13.9$ % and 13.4 % for Ag^{2+} in AgCl and KCl , respectively) obtained from the present cluster approach calculations are not far from those ($f_s \approx 0.5$ % and 1.14 % and $f_{\sigma} \approx 12$ % and 15.45 % [11, 31]) obtained in the previous treatments and can be regarded as reasonable.

5) The errors of the present studies can be analyzed as follows. First, the cluster approach for the calculations of the spin-orbit coupling coefficients and the orbital reduction factors are based on some approximate relationships from the semi-empirical LCAO-MO method [16]. This may lead to some errors as compared with the results based on the more powerful *ab initio* calculations.

Second, the superposition model [18—21] is applied to determine the tetragonal field parameters, which are expressed as a sum of six independent contributions arising from the six nearest neighbor ligands by neglecting the contributions from the rest of the lattice. Moreover, the approximation for the ratio $\bar{A}_2(R)/\bar{A}_4(R) \approx 10.8$ may also induce some errors in the tetragonal field parameters and the resultant spin Hamiltonian parameters. As the ratio varies within the widely accepted range of 9—12, the errors for the final spin Hamiltonian parameters and the tetragonal elongations ΔZ are estimated to be no more than 1.4 %. Noteworthy, our treatment is valid when the clusters are roughly uncoupled with the lattice, the electrostatic potential generated by the rest of the lattice is approximately flat and the cluster volume is large enough to contain some nearest neighbor ions. Thus, our theoretical investigation is an approach to this problem, and the calculated tetragonal elongations ΔZ in Eq. (9) should be regarded as merely tentative results. Therefore, in order to make more exact inves-

tigations of the defect structures and the EPR spectra for Ag^{2+} in AgCl and KCl, one may further employ the more powerful and reliable density functional theory (DFT) calculations [34–36].

Third, the impurity-ligand distances R determined from the empirical relationship [23] can bring forward some errors. However, variation of R would affect only the related group overlap integrals slightly, e.g., adoption of the host distances R_{H} may induce the errors of not more than 1.0 % for the spin Hamiltonian parameters. Finally, the errors of the group overlap integrals based on distinct basis sets can also influence the relevant quantities and bring forward the errors of about 1.5 % for the calculation results.

CONCLUSIONS

The spin Hamiltonian parameters and local structures are theoretically studied for Ag^{2+} in AgCl and KCl. The impurity centers undergo relative elongations of about 0.05 Å and 0.23 Å, respectively, along the C_4 axis due to the Jahn–Teller effect. The ligand orbital and spin-orbit coupling contributions are important and cannot be neglected because of significant covalency and ligand spin-orbit coupling interactions. The unpaired spin densities in the superhyperfine parameters are quantitatively determined from the related molecular orbital coefficients using the cluster approach, dissimilar to the previous treatments of being taken as adjustable parameters. The increase of tetragonal elongation from AgCl to KCl is attributed to the weaker bonding (or lower force constant) due to the longer reference distance R in the latter.

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