

Studies of the g Factors and the Hyperfine Structure Constants for the Octahedral Interstitial Mn^{2+} and Cr^+ Impurities in Silicon

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The g factors and the hyperfine structure constants for the octahedral interstitial Mn^{2+} and Cr^+ impurities in silicon are theoretically studied using the perturbation formulas of these parameters for an octahedral $3d^5$ cluster. In the calculations, both the crystal-field and charge transfer contributions are taken into account in a uniform way, and the related molecular orbital coefficients are quantitatively determined from the cluster approach. The theoretical g factors and the hyperfine structure constants are in good agreement with the experimental data. The charge transfer contribution to the g -shift ($\approx g - g_s$, where $g_s \approx 2.0023$ is the spin only value) is opposite (positive) in sign and about 51%–116% in magnitude as compared with the crystal-field one for Mn^{2+} and Cr^+ , respectively. Nevertheless, the charge transfer contribution to the hyperfine structure constant has the same sign and about 12%–19% that of the crystal-field one. Importance of the charge transfer contribution shows the order $\text{Cr}^+ < \text{Mn}^{2+}$ due to increase of the impurity valence state in the same host, especially for the g factor.

Key words: Electron Paramagnetic Resonance; Defect and Impurities; Mn^{2+} ; Cr^+ ; Silicon.

1. Introduction

Silicon containing Mn^{2+} and Cr^+ shows unique ferromagnetic [1–3], magnetophotoluminescence [4], luminescence [5] and structure properties [6, 7] and arouses extensive interest of the researchers. It is well known that the doped transition-metal ions in crystals play an important role in the above properties due to the electronic structures and the energy levels of these impurities, which can be conveniently investigated by means of the electron paramagnetic resonance (EPR) technique. For example, the EPR experiments were performed for Mn^{2+} and Cr^+ doped silicon decades ago, and the spin Hamiltonian parameters (g factors and the hyperfine structure constants) were measured for the cubic Mn^{2+} and Cr^+ centers [8, 9].

These impurity centers were assigned to Mn^{2+} and Cr^+ on the octahedral interstitial site in silicon [7, 10]. Until now, however, the above EPR experimental results have not been theoretically explained. In fact, $3d^5$ ions in semiconductors can be regarded as model sys-

tems due to the half-filled $3d$ configuration and the orbital non-degenerate 6A_1 ground state [11]. Further theoretical studies on the EPR spectra of the Mn^{2+} and Cr^+ impurities in silicon would provide useful information about electronic states of transition-metal impurities and are of specific fundamental and practical significance.

In 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 based on the crystal-field mechanism [12]. For $3d^5$ ions (e. g., Mn^{2+} , Fe^{3+}) in II-VI semiconductors of strong covalency, the ligand orbital and spin-orbit coupling contributions are found to be important and cannot be neglected [13–15]. However, these treatments [12–15] include merely the crystal-field mechanism (relevant to the crystal-field levels), while the contributions from the charge transfer mechanism (relevant to the charge transfer levels) were not taken into account yet. In fact, besides the nor-

mally considered crystal-field mechanism related to the anti-bonding orbitals, the charge transfer mechanism related to the bonding (and non-bonding) orbitals also bring forward important contributions to the spin Hamiltonian parameters for the systems with strong covalency (e. g., semiconductors) [16, 17]. More importantly, the charge transfer energy levels decline with increasing the valence state of the central ion coordinated to the same ligand [18]. Consequently, importance of the charge transfer contributions is expected to increase in the order of Cr⁺ < Mn²⁺ for the 3d⁵ impurities in silicon. In order to study the EPR spectra of the 3d⁵ centers in silicon and to clarify the role of the charge transfer mechanism, the perturbation formulas of the *g* factor and the hyperfine structure constant of an octahedral (O_h) 3d⁵ cluster are established in this work for the first time and applied to these impurity centers by considering both the crystal-field and charge transfer contributions from the cluster approach.

2. Theory and Calculations

As mentioned before, the impurity Cr⁺ or Mn²⁺ may occupy the octahedral interstitial site in silicon [7, 10]. A 3d⁵ ion in a regular octahedron exhibits the ground ⁶A₁ non-degenerate orbital state [19, 20], and the spin-orbit coupling mechanism is regarded as the dominant origin for the *g*-shift Δ*g* (= *g* − *g*_s, with the pure spin value *g*_s ≈ 2.0023) and zero-field splittings [19, 21, 22]. Thus, the previous formulas based on the crystal-field mechanism [12] can be improved here by considering the charge transfer contributions to the *g* factor and the hyperfine structure constant. The perturbation Hamiltonian containing both the crystal-field and charge transfer contributions is expressed as follows:

$$H' = H_{\text{ele}}^{\text{b}} + H_{\text{SO}}^{\text{CF}} + H_{\text{SO}}^{\text{CT}} + H_{\text{Ze}}^{\text{CT}} + H_{\text{hf}}^{\text{CF}} + H_{\text{hf}}^{\text{CT}}. \quad (1)$$

Here H_{ele}^b, H_{SO}, H_{Ze}, and H_{hf} are, respectively, the off-diagonal part of the electrostatic Coulombic interaction, the spin-orbit coupling, the electron Zeeman, and the hyperfine interaction terms. The superscripts CF and CT denote the related terms for the crystal-field and charge transfer mechanisms with the corresponding spin-orbit coupling coefficients ζ_{CF}, ζ_{CF'} and ζ_{CT}, ζ_{CT'}, the orbital reduction factors *k*_{CT}, *k*_{CT'}, and the dipolar hyperfine structure parameters *P*_{CF}, *P*_{CF'} and *P*_{CT}, *P*_{CT'}.

In view of the charge transfer contributions, the wave functions of the ground state and the charge transfer excited states can be written in terms of the nine-electron forms out of *t*₂ⁿ, *e*^a, and *e*^b, where the superscripts a, b, and n stand for the anti-bonding, bonding, and non-bonding orbitals, respectively. Thus, the ground ⁶A₁ state is expressed as [23]

$$|{}^6\text{A}_1 \frac{5}{2} a_1\rangle = [\xi^+ \eta^+ \zeta^+ \theta^+ \varepsilon^+ | \theta^+ \theta^- \varepsilon^+ \varepsilon^-]. \quad (2)$$

In the square bracket on the right side of (2), the letters (ξ, η, ζ and θ, ε) on the left column are *t*₂^a and *e*ⁿ orbitals and those (θ and ε) on the right column are *e*^b orbitals. There is only one excited configuration (*t*₂ⁿ)⁴(*e*^a)²(*e*^b)³ (or ⁶T₁ⁿ) having the non-zero spin-orbit coupling interaction with the ground state ⁶A₁. Therefore, the *z*-component of ⁶T₁ⁿ charge transfer excited state with the highest *M*_S = 5/2 can be given as [23]

$$|{}^6\text{T}_1 \frac{5}{2} z\rangle = [\xi^+ \eta^+ \zeta^+ \zeta^- \theta^+ \varepsilon^+ | \theta^+ \theta^- \varepsilon^+]. \quad (3)$$

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

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

Here the superscript *x* (= a or b) denotes the anti-bonding or bonding orbitals. φ_γ (γ = *e* and *t* stand for the irreducible representations *E_g* and *T_{2g}* of the O_h group) are the *d* orbitals of the central ion. χ_{*pγ*} and χ_{*s*} are the *p* and *s* orbitals of the ligands. *N*_γ and λ_γ (or λ_{*s*}) are, respectively, the normalization factors and the orbital admixture coefficients. From (4), one can obtain the normalization conditions

$$\begin{aligned} N_t^x [1 + (\lambda_t^x)^2 - 2\lambda_t^x S_{dpt}] &= 1, \\ N_e^x [1 + (\lambda_e^x)^2 + (\lambda_s^x)^2 - 2\lambda_e^x S_{dpe} - 2\lambda_s^x S_{ds}] &= 1, \end{aligned} \quad (5)$$

and the orthogonality relationships

$$\begin{aligned} 1 + \lambda_t^a \lambda_t^b - (\lambda_t^a + \lambda_t^b) S_{dpt} &= 0, \\ 1 + \lambda_e^a \lambda_e^b + \lambda_s^a \lambda_s^b - (\lambda_e^a + \lambda_e^b) S_{dpe} \\ - (\lambda_s^a + \lambda_s^b) S_{ds} &= 0, \\ \lambda_e^a \lambda_s^b + \lambda_s^a \lambda_e^b &= 0. \end{aligned} \quad (6)$$

Here S_{*dpt*}, S_{*dpe*}, and S_{*ds*} are the group overlap integrals between the *d* orbitals of the 3d⁵ ion and the *p*

and *s* orbitals of the ligands. In addition, the following approximation relationships are satisfied for the anti-bonding orbitals [24]:

$$\begin{aligned} N^2 &\approx (N_t^a)^2 [1 + (\lambda_t^a)^2 S_{dpt}^2 - 2\lambda_t^a S_{dpt}], \\ N^2 &\approx (N_e^a)^2 [1 + (\lambda_e^a)^2 S_{dpe}^2 + (\lambda_s^a)^2 S_{ds}^2 \\ &\quad - 2\lambda_e^a S_{dpe} - 2\lambda_s^a S_{ds}]. \end{aligned} \quad (7)$$

In the above expressions, *N* 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 $\lambda_e^a/S_{dpe} \approx \lambda_s^a/S_{ds}$ for the orbital admixture coefficients and the related group overlap integrals within the same *E_g* irreducible representation.

Utilizing Macfarlane's perturbation-loop method [22, 25] with the perturbation Hamiltonian in (1) and the wave functions in (2) and (3), the improved perturbation formulas of the *g*-shift and the hyperfine structure constant containing both the crystal-field and charge transfer contributions are derived for the octahedral 3*d*⁵ cluster to

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

where the denominators *E_i* (*i* = 1 ~ 3) are the energy differences between the ground ⁶A₁ and the crystal-field excited ⁴T₁[*t*₂³(³T₁)*e*], ⁴T₁[*t*₂³(²T₂)*e*²(³A₂)], and ⁴T₁[*t*₂³(³T₁)*e*³] states. They can be expressed in terms of the cubic field parameter *D_q* and the Racah parameters *B* and *C* for the 3*d*⁵ ion in crystals: *E*₁ ≈ 10*B* + 6*C* - 10*D_q*, *E*₂ ≈ 19*B* + 7*C*, and *E*₃ ≈ 10*B* + 6*C* + 10*D_q* [12]. The charge transfer energy level *E_n* for ligand to metal charge transfer can be obtained from the approximate relationship *E_n* ≈ 30 000[$\chi(L) - \chi(M)$] cm⁻¹. Here $\chi(L)$ and $\chi(M)$ are, respectively, the optical electronegativities of ligand and 3*dⁿ* ions [18].

ζ_{CF} , $\zeta_{CF'}$, ζ_{CT} , and $\zeta_{CT'}$ are the spin–orbit coupling coefficients, *k_{CT'}* is the orbital reduction factor and *P_{CF}*,

P_{CF'}, *P_{CT}*, and *P_{CT'}* are the dipolar hyperfine structure parameters of the 3*d*⁵ ion in crystals. The corresponding parameters for the crystal-field mechanism can be determined from the cluster approach [25]:

$$\begin{aligned} \zeta_{CF} &= N_t^a [\zeta_d^0 + (\lambda_t^a)^2 \zeta_p^0/2], \\ \zeta_{CF'} &= (N_t^a N_e^a)^{1/2} [\zeta_d^0 - \lambda_t^a \lambda_e^a \zeta_p^0/2], \\ P_{CF} &= N_t^a P_0, \quad P_{CF'} = (N_t^a N_e^a)^{1/2} P_0, \end{aligned} \quad (9)$$

and those for the charge transfer mechanism are

$$\begin{aligned} \zeta_{CT'} &= (N_t^a N_e^b)^{1/2} [(1 + \lambda_t^a - \lambda_s^a) \zeta_d^0 - \lambda_t^a \lambda_e^a \zeta_p^0/2], \\ k_{CT'} &= (N_t^a N_e^b)^{1/2} [1 - \lambda_e^a + \lambda_t^a - 2\lambda_t^a S_{dpt} S_{dpe} \\ &\quad + \lambda_e^a \lambda_t^a S_{dpt}/2 + w \lambda_t^b \lambda_s^a/2], \\ P_{CT} &= N_t^b P_0, \quad P_{CT'} = (N_t^b N_e^b)^{1/2} P_0. \end{aligned} \quad (10)$$

Here ζ_d^0 and ζ_p^0 are, respectively, the spin–orbit coupling coefficients of the free 3*d*⁵ and ligand ions. *P*₀ is the dipolar hyperfine structure parameter of the free 3*d*⁵ ion. The value *w* denotes the integral $R \langle \chi_s | \partial/\partial x | \chi_{px} \rangle$ with the impurity–ligand distance *R*.

Now the above formulas are applied to the studies of the EPR spectra for Mn²⁺ and Cr⁺ in silicon. From the impurity–ligand distance (≈ 2.715 Å [26]) of the octahedral interstitial site in silicon and the Slater-type self consistent field (SCF) wave functions [27, 28], the group overlap integrals are calculated: *S_{dpt}* ≈ 0.0215, *S_{dpe}* ≈ 0.0488, *S_{ds}* ≈ 0.0348, and *w* ≈ 0.9468 for Si:Mn²⁺ as well as *S_{dpt}* ≈ 0.0281, *S_{dpe}* ≈ 0.0622, *S_{ds}* ≈ 0.0459 and *w* ≈ 0.9468 for Si:Cr⁺, respectively. Since the optical spectra are not reported for Cr⁺ and Mn²⁺ in silicon, the cubic field parameters and the covalency factors may be estimated from those for some 3*d*⁵ ions in various crystals [29, 30], i. e., *D_q* ≈ 1340 and 1310 cm⁻¹ and *N* ≈ 0.72 and 0.73 for Mn²⁺ and Cr⁺ in silicon, respectively. Thus, the Racah parameters are determined from the relationships *B* ≈ *N*²*B*₀ and *C* ≈ *N*²*C*₀ [31] with the corresponding free-ion values *B*₀ ≈ 960 and 830 cm⁻¹ and *C*₀ ≈ 3325 and 3430 cm⁻¹ for Mn²⁺ and Cr⁺, respectively [32]. From the extrapolated values $\chi(\text{Mn}^{2+}) \approx 1.6$, $\chi(\text{Cr}^+) \approx 0.4$, and $\chi(\text{Si}) \approx 2.5$ [18], the charge transfer levels *E_n* are calculated for the studied systems. The molecular orbital coefficients *N_γ^x* and λ_γ^x are acquired from (5)–(7). According to (9) and (10) and the free-ion values $\zeta_d^0 \approx 347$ and 230 cm⁻¹ [32] and *P*₀ ≈ 187 and -29.5 · 10⁻⁴ cm⁻¹ [33] for Mn²⁺ and Cr⁺ as well as

$\zeta_p^0 \approx 215 \text{ cm}^{-1}$ [34] for silicon, 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 shown in Table 1. In the calculations of the hyperfine structure constants, the core polarization constant is expressed as $\kappa \approx -2\xi N / (3\langle r^{-3} \rangle)$, where ξ 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 radial wave function of the $3d$ orbital [33]. Applying $\langle r^{-3} \rangle \approx 4.25$ and 2.968 a. u. [11] and $\xi \approx -2.6$ and -2.30 a. u. [30] for Mn^{2+} and Cr^+ in various crystals, one can obtain $\kappa \approx 0.3$ and 0.41 for $\text{Si}:\text{Mn}^{2+}$ and $\text{Si}:\text{Cr}^+$, respectively. Substituting the above values into the formulas of the spin Hamiltonian parameters, the corresponding theoretical results (Calc. ^b) are calculated and shown in Table 2. To clarify importance and tendency of the charge transfer contributions for Mn^{2+} and Cr^+ in silicon, the results (Calc. ^a) based on only the crystal-field contributions are also collected in Table 2 for comparison.

3. Discussion

Table 2 reveals that the theoretical g factors and the hyperfine structure constants based on both the crystal-field and charge transfer contributions show good agreement with the observed values, whereas those based on only the crystal-field ones do not. This means that the improved perturbation formulas estab-

lished in this work can be regarded as suitable for covalent $3d^5$ clusters.

The charge transfer contribution to the g -shift has the opposite (positive) sign to the crystal-field one, and importance (characterized by the ratio $|\Delta g_{\text{CT}}/\Delta g_{\text{CF}}|$) increases rapidly with increasing valence state of the impurity, i. e., Cr^+ (51%) < Mn^{2+} (116%). In fact, $3d^5$ ions in such semiconductors as silicon with strong covalency may suffer significant impurity–ligand orbital admixtures and charge transfer contributions due to the low charge transfer level E_n . Although the spin–orbit coupling coefficient ($\approx 215 \text{ cm}^{-1}$ [34]) of the ligand silicon is not large as compared with that (≈ 347 or 230 cm^{-1} [32]) of the central ion Mn^{2+} or Cr^+ , the related parameters for the charge transfer mechanism are large enough due to the obvious impurity–ligand orbital admixtures and cannot be neglected. Importantly, the Δg are delicate ($\sim 10^{-3}$) for $3d^5$ ions in silicon (see Tab. 2 and (8)), and omission of the charge transfer contributions would bring forward significant relative deviations (i. e., much larger in magnitude than the observed values) of the theoretical results (Calc. ^a). Therefore, the charge transfer contribution to the g -shift should be taken into account for $3d^5$ ions in silicon.

The ligand contributions to Δg_{CF} of the crystal-field term for Mn^{2+} and Cr^+ in silicon are also important. This can be illustrated by the influences of the relative difference (or anisotropy) between ζ_{CF} and $\zeta_{\text{CF}'}$ (i. e., $\zeta_{\text{CF}}/\zeta_{\text{CF}'} - 1 \approx 20\% - 30\%$) in the formula of Δg_{CF} , which are relevant to the low covalency factor N

Table 1. Molecular orbital coefficients, spin-orbit coupling coefficients (in cm^{-1}), orbital reduction factor, and dipolar hyperfine structure parameters (in 10^{-4} cm^{-1}) related to the crystal-field and charge transfer mechanisms for Mn^{2+} and Cr^+ in silicon.

	λ_π^a	λ_σ^a	λ_s^a	λ_π^b	λ_σ^b	λ_s^b	N_t^a	N_e^a	N_t^b
Mn^{2+}	0.630	0.523	0.336	-0.796	-0.590	-0.420	0.730	0.796	0.618
Cr^+	0.617	0.513	0.371	-0.815	-0.573	-0.415	0.743	0.767	0.609
	N_e^b	ζ_{CF}	$\zeta_{\text{CF}'}$	$\zeta_{\text{CT}'}$	$k_{\text{CT}'}$	P_{CF}	$P_{\text{CF}'}$	P_{CT}	$P_{\text{CT}'}$
Mn^{2+}	0.675	284	230	275	0.690	136	138	116	121
Cr^+	0.692	201	148	179	0.691	-22	-22	-18	-19

Table 2. g -shifts Δg ($= g - g_s$) and hyperfine structure constants (in 10^{-4} cm^{-1}) for Mn^{2+} and Cr^+ in silicon.

	Calc. ^a	Δg Calc. ^b	Expt. [8, 9]	Calc. ^a	A Calc. ^b	Expt. [8, 9]
Mn^{2+}	-0.0258	0.0041	0.0043	-47.65	-53.48	-53.47
Cr^+	-0.0089	-0.0044	-0.0045	8.96	10.68	10.67

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

($\approx 0.7 \ll 1$) and the significant orbital admixture coefficients ($\approx 0.3-0.6$). Thus, the impurity–ligand orbital admixtures and the anisotropic contributions from the ligand spin–orbit coupling coefficient should be included in the analysis of the g factors for Mn^{2+} and Cr^+ in silicon. In essence, similar delocalization and anisotropic expansion of the $3d$ orbitals are found for some transition-metal (e. g., Mn^{2+} , Cu^{2+}) ions in semiconductors [35, 36]. Besides, the relatively weaker correlation of Δg_{CF} with the covalency or the ligand contributions than Δg_{CT} can be ascribed 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 term (inversely proportional to the charge transfer level E_n) in the latter.

For the hyperfine structure constant, the charge transfer contribution A_{CT} is the same in sign and about 12%–19% in magnitude as compared with the crystal-field one. From (8) and (10), A_{CT} depends strongly upon the dipolar hyperfine structure parameters (P_{CT} and $P_{\text{CT}'}$), the orbital reduction factor $k_{\text{CT}'}$, and the spin–orbit coupling coefficient $\zeta_{\text{CT}'}$ for the charge transfer mechanism, which are related to the covalency factor N and the ratio ζ_p^0/ζ_d^0 . In addition, the opposite signs of the hyperfine structure constants for Mn^{2+} and Cr^+ in silicon may result from their opposite signs of P_0 . On the other hand, the larger magnitude of the A factor for Mn^{2+} than Cr^+ can be roughly attributed to the larger P_0 of the former.

The studied $3d^5$ centers are ascribed to the impurities Mn^{2+} and Cr^+ occupying the octahedral interstitial sites in silicon. This point can be supported

by the studies of structure [7], paramagnetic resonance [10], and diffusion, solubility, and electrical properties [37] for $3d^n$ (e. g., Mn^{2+}) ions in silicon which reveal that manganese and chromium can enter the octahedral interstitial sites with high stability. Although transition-metal ions are possible to occupy both the tetrahedral substitutional and octahedral interstitial sites in silicon, the studied Mn^{2+} and Cr^+ centers are reasonably assigned to the octahedral interstitial impurities.

4. Conclusion

The g factors and the hyperfine structure constants for the octahedral interstitial Mn^{2+} and Cr^+ impurities in silicon are theoretically studied from the perturbation formulas containing both the crystal-field and charge transfer contributions based on the cluster approach. The calculation results show good agreement with the experimental data. The charge transfer contribution to the g -shift is opposite (positive) in sign and about 51%–116% in magnitude as compared with the crystal-field one for Mn^{2+} and Cr^+ , respectively. And the charge transfer contribution to the hyperfine structure constant has the same sign and about 12%–19% that of the crystal-field one. Importance of the charge transfer contribution exhibits the order $\text{Cr}^+ < \text{Mn}^{2+}$ with increasing the impurity valence state in the same host.

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