

Theoretical investigations of the g factors and the hyperfine structure constants of the Cr^{4+} and Mn^{5+} centres in silicon

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The g factors and the hyperfine structure constants of the Cr^{4+} and Mn^{5+} centers in silicon are theoretically investigated using the perturbation formulas of these parameters for $3d^2$ ions in tetrahedra. In the calculations, both the contributions from the crystal-field and charge transfer mechanisms are taken into account based on the cluster approach. The calculated results show agreement with the observed values. It is found that the relative importance of the charge transfer contributions to the g -shift $\Delta g = g - g_s$ (where $g_s = 2.0023$ is the spin-only value) increases significantly with increasing the valence state of the impurity ion.

1. Introduction

Studies of chromium and manganese impurities in silicon have aroused extensive interest of researchers due to the unique photovoltaic [1], diffusion [2], thermodynamical [3], electrical [4], magnetic [5–7] and microstructure properties [8]. Normally, these properties depend strongly upon the electronic levels and structures of these impurities in the host, which can be investigated by means of the electronic paramagnetic resonance (EPR) technique [9]. Among the transition-metal ions, Cr^{4+} and Mn^{5+} belonging to the $3d^2$ configuration can be regarded as a model system with spin $S = 1$ and orbital non-degenerate 3A_2 ground state. For example, EPR experiments were carried out for Cr^{4+} and Mn^{5+} doped silicon, and the isotropic g factors and the hyperfine structure constants were also measured for the cubic Cr^{4+} and Mn^{5+} centres [10]. Up to now, however, the above EPR results have not been theoretically analyzed.

Since investigations of the g factors and the hyperfine structure constants can provide useful information about electronic states of paramagnetic impurities in crystals and would be helpful to understand the properties of this material with transition-metal dopants, theoretical studies of the EPR spectra for Cr^{4+} and Mn^{5+} in Si are of scientific and practical significance. On the other hand, the covalency effect and impurity-ligand orbital admixtures can be important of the analysis of the EPR spectra in view of the significant covalency of the host. More importantly, the contributions from the charge transfer mechanism related to the charge transfer levels may bring forward obvious influences on the g factor and the hyperfine structure constant [11,12]. Further, since the energies of the charge transfer bands decline with increasing covalency and valence state for a central ion with the same electronic configuration [13], the charge transfer contributions to the EPR spectra should be considered, especially for $3d^2$ (Cr^{4+} and Mn^{5+}) impurities of the high valence states in covalent silicon host. In this work, the g factors and the hyperfine

structure constants are quantitatively investigated using the perturbation formulas of these parameters based on the cluster approach. In the calculations, both the contributions from the conventional crystal-field mechanism and those from the charge transfer mechanism are taken into account in a uniform way.

2. Theory and calculations

When the impurity Cr^{4+} or Mn^{5+} enters the lattice of silicon, it may occupy the tetrahedral substitutional site and conserve the original cubic (T_d) symmetry. For a $3d^2$ ion situated in ideal tetrahedra, its lowest 3F state may be separated into two orbital triplets 3T_1 and 3T_2 and one orbital singlet 3A_2 . The latter is the lowest level, corresponding to the observed isotropic EPR signals of the g factor and the hyperfine structure constant [10].

The perturbation formula of the g shift $\Delta g = g - g_s$ (where $g_s = 2.0023$ is the spin-only value) for a tetrahedral $3d^2$ cluster was established by considering both the crystal-field and charge transfer contributions from the cluster approach [14]. By adopting the similar perturbation procedure in Ref. 14 and including the contributions from the ligand s -orbitals, the perturbation formulas of the g factor and the hyperfine structure constant can be expressed as follows:

$$\Delta g = g - g_s = \Delta g_{\text{CF}} + \Delta g_{\text{CT}},$$

$$\begin{aligned} \Delta g_{\text{CF}} = & -\frac{4k'_{\text{CF}}\xi_{\text{CF}}'^2}{E_1} - \frac{g_s\xi_{\text{CF}}^2 + k'_{\text{CF}}\xi'_{\text{CF}}\xi_{\text{CF}} - k_{\text{CF}}\xi_{\text{CF}}'^2/2}{E_1^2} \\ & - \frac{(g_s - k_{\text{CF}}/2)\xi_{\text{CF}}'^2}{E_2^2} - \frac{k'_{\text{CF}}\xi'_{\text{CF}}\xi_{\text{CF}}}{E_1E_2} \\ & - 6B k'_{\text{CF}}\xi_{\text{CF}}'^2 \left[\frac{2}{E_1E_2E_5} + \frac{1}{E_2^2E_5} \right], \end{aligned}$$

$$\Delta g_{\text{CT}} = 4 \left(\frac{k'_{\text{CT}}\xi'_{\text{CT}}}{E_n} + \frac{k_{\text{CT}}\xi_{\text{CT}}}{E_a} \right),$$

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$$A = A_{CF} + A_{CT},$$

$$A_{CF} = P'_{CF} \Delta g_{CF} - P_{CF} \kappa,$$

$$A_{CT} = \frac{8P'_{CT} k'_{CT} \xi'_{CT}}{3E_n} - \kappa P_{CT}. \quad (1)$$

Here E_i ($i = 1, 2, 5$) are the zero-order energy separations between the crystal-field excited ${}^3T_2(t_2e)$, ${}^1T_{2a}(t_2^2)$, ${}^1T_{2b}(t_2e)$ and the ground ${}^3A_2(e^2)$ states, which can be written in terms of the cubic field parameter D_q and the Racah parameters B and C for a $3d^2$ ion in crystals: $E_1 \approx 10D_q$, $E_2 \approx 8B + 2C + 10D_q$ and $E_5 \approx 9B + 2C + 20D_q$ [14]. E_n and E_a are the energy differences between the two lowest charge transfer excited ${}^3T_2^n[(e^n)^3(t_2^b)^5]$, ${}^3T_{2a}[(t_2^a)(e^n)^2(t_2^b)^5]$ and the ground 3A_2 states. They are obtained from the empirical relationship $E_n \approx 30000[\chi(L) - \chi(M)] - 28B/3$ and $E_a \approx E_n - 28B/3 + 10D_q$ [13]. Here $\chi(L)$ and $\chi(M)$ are, respectively, the optical electronegativities of the ligand and metal ions. ξ , k and P are, respectively, the spin-orbit coupling coefficients, orbital reduction factors and the dipolar hyperfine structure parameters for the $3d^2$ ion in crystals, with the superscripts CF and CT denoting the crystal-field and charge transfer mechanisms; κ is the core polarization constant.

In the cluster approach [14,15] containing both the crystal-field and charge transfer contributions, the single electronic wave function for a tetrahedral $3d^2$ cluster can be expressed as the linear combination of the $3d$ orbitals of the central ion and the $3s$ and $3p$ orbitals of the ligands:

$$\begin{aligned} \psi_t^x &= N_t^x (\phi_{dt} - \lambda_\sigma^x \chi_{p\sigma} - \lambda_x^x \chi_s - \lambda_\pi^x \chi_{p\pi}), \\ \psi_e^x &= N_e^x (\phi_{de} - \sqrt{3} \lambda_\pi^x \chi_{p\pi e}). \end{aligned} \quad (2)$$

Here the subscript e or t denotes the irreducible representation E or T_2 of T_d group. The superscript $x = a$ or b stands for the anti-bonding or the bonding orbitals. ϕ_{dt} and ϕ_{de} are the d orbitals of the $3d^2$ 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 , λ_π (or λ_s) are the orbital admixture coefficients. From Eq. (2), one can obtain the normalization conditions

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

and the orthogonality relationships

$$\begin{aligned} 1 + 3\lambda_\pi^a \lambda_\pi^b - 3(\lambda_\pi^a + \lambda_\pi^b) S_\pi &= 0, \\ 1 + \lambda_\pi^a \lambda_\pi^b + \lambda_\sigma^a \lambda_\sigma^b + \lambda_s^a \lambda_s^b - (\lambda_\pi^a + \lambda_\pi^b) S_\pi \\ - (\lambda_\sigma^a + \lambda_\sigma^b) S_\sigma - (\lambda_s^a + \lambda_s^b) S_s &= 0, \\ \lambda_\pi^a \lambda_\pi^b + \lambda_s^a \lambda_s^b &= 0. \end{aligned} \quad (4)$$

Here S_π , S_σ and S_s are the group overlap integrals between the d -orbitals of the $3d^2$ ion and the p - and s -orbitals of the ligands. In addition, the following approximation relationships are satisfied for the anti-bonding orbitals [15]:

$$\begin{aligned} N^2 &\approx [1 + 6\lambda_\pi^a S_\pi + 9(\lambda_\pi^a)^2 S_\pi^2] [1 + 3(\lambda_\pi^a)^2 + 6\lambda_\pi^a S_\pi]^{-2}, \\ N^2 &\approx [1 + 2\lambda_\pi^a S_\pi + 2\lambda_\sigma^a S_\sigma + 2\lambda_s^a S_s + 2\lambda_\pi^a S_\pi \lambda_\sigma^a S_\sigma \\ &\quad + 2\lambda_\pi^a S_\pi \lambda_s^a S_s + (\lambda_\pi^a)^2 S_\pi^2 + (\lambda_\sigma^a)^2 S_\sigma^2 + (\lambda_s^a)^2 S_s^2] \\ &\quad \times [1 + (\lambda_\pi^a)^2 + (\lambda_\sigma^a)^2 + (\lambda_s^a)^2 + 2\lambda_\pi^a S_\pi \\ &\quad + 2\lambda_\sigma^a S_\sigma + 2\lambda_s^a S_s]^{-2}. \end{aligned} \quad (5)$$

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 $\lambda_\sigma^a/S_\sigma \approx \lambda_s^a/S_s$ 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, orbital reduction factors and dipolar hyperfine structure parameters for the crystal-field mechanism in Eq.(1) are expressed as follows [15]:

$$\begin{aligned} \xi_{CF} &= (N_t^a)^2 \left\{ \xi_d^0 + \left[\sqrt{2} \lambda_\pi^a \lambda_\sigma^a - \frac{(\lambda_\pi^a)^2}{2} - \sqrt{2} A \lambda_\pi^a \lambda_s^a \right] \xi_p^0 \right\}, \\ \xi'_{CF} &= N_t^a N_e^a \left\{ \xi_d^0 + \left[\frac{\lambda_\pi^a \lambda_\sigma^a}{\sqrt{2}} + \frac{(\lambda_\pi^a)^2}{2} - \frac{A \lambda_\pi^a \lambda_s^a}{\sqrt{2}} \right] \xi_p^0 \right\}, \\ k_{CF} &= (N_t^a)^2 \left\{ 1 - \frac{(\lambda_\pi^a)^2}{2} + \sqrt{2} \lambda_\pi^a \lambda_\sigma^a - 2\lambda_\sigma^a S_\sigma \right. \\ &\quad \left. - 2\lambda_s^a S_s - 2\lambda_\pi^a S_\pi - \sqrt{2} A \lambda_\pi^a \lambda_s^a \right\}, \\ k'_{CF} &= N_t^a N_e^a \left\{ 1 + \frac{(\lambda_\pi^a)^2}{2} + \frac{\lambda_\pi^a \lambda_\sigma^a}{\sqrt{2}} - 4\lambda_\pi^a S_\pi - \lambda_\sigma^a S_\sigma \right. \\ &\quad \left. - \lambda_s^a S_s - \frac{A \lambda_\pi^a \lambda_s^a}{\sqrt{2}} \right\}, \\ P_{CF} &= (N_t^a)^2 P_0, \\ P'_{CF} &= (N_t^a N_e^a) P_0. \end{aligned}$$

In the above expressions, ξ_d^0 and ξ_p^0 stand for the spin-orbit coupling coefficients of a free $3d^2$ and ligand ions, respectively. P_0 is the dipolar hyperfine structure parameter of the free $3d^2$ ion. A denotes the integral $R \langle ns | \frac{\partial}{\partial y} | np_y \rangle$, with the impurity-ligand or reference distance R . The related parameters for the charge transfer mechanism can

Table 1. The group overlap integrals, the cubic field parameter D_q (in cm^{-1}) and the covalency factor, the normalization factors and the orbital admixture coefficients, the spin-orbit coupling coefficients (in cm^{-1}), the orbital reduction factors and the dipolar hyperfine structure parameters (in 10^{-4}cm^{-1}) related to the crystal-field and charge transfer mechanisms for Cr^{4+} and Mn^{5+} in silicon

	S_t	S_e	S_s	A	D_q	N	N_t^a	N_e^a	λ_t^a	λ_e^a
Cu^{4+}	0.0215	-0.0448	0.0348	0.9468	2600	0.62	0.518	0.665	0.901	-0.402
Mn^{5+}	0.0215	-0.0488	0.0348	0.9468	2800	0.57	0.449	0.616	1.041	-0.508
	λ_s^a	N_t^b	N_e^b	λ_t^b	λ_e^b	λ_s^b	ξ_{CF}	ξ'_{CF}	ξ_{CT}	ξ'_{CT}
Cr^{4+}	1.459	0.494	0.704	-0.353	0.974	0.218	192	263	153	202
Mn^{5+}	1.685	0.510	0.761	-0.302	0.964	0.187	229	321	214	279
	k_{CF}	k'_{CF}	k_{CT}	k'_{CT}	P_{CF}	P'_{CF}	P_{CT}	P'_{CT}		
Cr^{4+}	0.119	0.691	0.497	0.710	-23	-26	-23	-26		
Mn^{5+}	0.106	0.707	0.517	0.758	117	137	124	146		

be similarly determined using the cluster approach:

$$\xi_{\text{CT}} = N_t^b N_t^a \left\{ \xi_d^0 + \left[\frac{\lambda_\pi^a \lambda_\sigma^b + \lambda_\pi^b \lambda_\sigma^a}{\sqrt{2}} - \frac{\lambda_\pi^a \lambda_\pi^b}{2} - \sqrt{2} A \lambda_s^a \lambda_\pi^b \right] \xi_p^0 \right\},$$

$$\xi'_{\text{CT}} = N_e^a N_t^b \left[\xi_d^0 + \left(\frac{\lambda_\pi^a \lambda_\sigma^b}{\sqrt{2}} + \frac{\lambda_\pi^a \lambda_\pi^b}{2} - \frac{A \lambda_s^a \lambda_\pi^b}{\sqrt{2}} \right) \xi_p^0 \right],$$

$$k_{\text{CT}} = N_t^a N_t^b \left[-\frac{\lambda_\pi^a \lambda_\pi^b}{2} + \frac{\lambda_\pi^a \lambda_\sigma^b + \lambda_\pi^b \lambda_\sigma^a}{\sqrt{2}} + (\lambda_\sigma^a + \lambda_\sigma^b) S_\sigma + (\lambda_\sigma^a + \lambda_\sigma^b) S_\sigma + (\lambda_\pi^a + \lambda_\pi^b) S_\pi - \sqrt{2} A \lambda_s^a \lambda_\pi^b \right],$$

$$k'_{\text{CT}} = N_t^b N_e^a \left[1 + \left(\frac{\lambda_\pi^a \lambda_\pi^b}{2} + \frac{\lambda_\pi^a \lambda_\sigma^b}{\sqrt{2}} \right) + 3 \lambda_\pi^a S_\pi + \lambda_\pi^b S_\pi + \lambda_\sigma^b S_\sigma + \lambda_s^b S_s - \frac{A \lambda_s^a \lambda_\pi^b}{\sqrt{2}} \right],$$

$$P_{\text{CT}} = N_t^b N_t^a P_0,$$

$$P'_{\text{CT}} = N_e^a N_t^b P_0. \quad (7)$$

Then the above formulas are applied to the studies of the g factors and the hyperfine structure constants for the Cr^{4+} and Mn^{5+} centers in Si. The cubic field parameters D_q and the covalency factors N can be obtained from the optical spectra [16] for Cr^{4+} or Mn^{5+} in similar tetrahedral environments and are shown in the Table. Applying the impurity-ligand distance $R \approx 2.351$ [17] of the substitutional site in silicon and the Slater-type self-consistent field (SCF) functions [18,19], the group overlap integrals (as well as the integral A) are calculated. The related molecular orbital coefficients N_y^x and λ_y^x are determined from Eqs (3)–(5). Using the free-ion values $\xi_d^0 \approx 328$ and 452cm^{-1} [20] for Cr^{4+} and Mn^{5+} and $\xi_p^0 \approx 215 \text{cm}^{-1}$ [21] for Si, the spin-orbit coupling coefficients, the orbital reduction factors and the dipolar hyperfine structure parameters for the crystal-field and charge transfer mechanisms can be obtained from Eqs (6) and (7). These values are also listed in

Table 1. The Racah parameters in the energy denominators of Eq. (1) are determined from the relationships $B \approx N^2 B_0$ and $C \approx N^2 C_0$ [22] and the free-ion values $B_0 \approx 1039$ and 1092cm^{-1} and $C_0 \approx 4238$ and 5160cm^{-1} [20] for Cr^{4+} and Mn^{5+} , respectively. According to Ref. 13, the extrapolated values $\chi(\text{Cr}^{4+}) \approx 1.9$, $\chi(\text{Mn}^{5+}) \approx 2.4$ and $\chi(\text{Si}) \approx 3.2$ can be obtained, and the charge transfer levels E_n and E_a are determined for Cr^{4+} and Mn^{5+} in silicon. In the formula of the hyperfine structure constant, $P_0 \approx -45$ and $250 \cdot 10^{-4} \text{cm}^{-1}$ for Cr^{4+} and Mn^{5+} , respectively. As regards the core polarization constant, the expectation value $\kappa \approx 0.3$ [20] of $3d^n$ ions in crystals is adopted for both the systems here.

Substituting all these values into Eq. (1), the g and A factors (Cal.^b) for the Cu^{4+} and Mn^{5+} centers in silicon are obtained and given in Table 2. In order to clarify the importance of the charge transfer contributions, the results (Cal.^a) based on only the crystal-field contributions are also collected in Table 2.

3. Discussion

It can be found from Table 2 that the theoretical results (Cal.^b) including both the crystal-field and charge transfer contributions for the Cr^{4+} and Mn^{5+} centers in silicon are

Table 2. The g -shifts and the hyperfine structure constants for Cr^{4+} and Mn^{5+} in silicon

	Δg			$A (10^{-4} \text{cm}^{-1})$		
	Cal. ^a	Cal. ^b	Expt. ^c	Cal. ^a	Cal. ^b	Expt. ^c
Cr^{4+}	-0.0342	-0.0081	-0.0061	7.08	12.83	12.54
Mn^{5+}	-0.0377	0.0233	0.0236	-34.22	-66.13	-63.09

Note: ^a Calculations based on only the crystal-field contributions.

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

^c Ref. 10.

in better agreement with the experimental data than those (Cal.^a) including only the crystal-field ones. Therefore, the observed EPR spectra for the $3d^2$ impurity ions in Si are reasonably explained in this work.

The charge transfer contributions to the g -shifts are opposite (positive) in sign and much larger in magnitude as compared with the crystal-field contributions. As the increase of the valence state (and decrease of the covalency factor N) of the central ion, the importance of the charge transfer contributions (characterized by the relative ratio $|\Delta g_{CT}/\Delta g_{CF}|$ shows significant increase from 76% for Cr^{4+} to 162% for Mn^{5+} . As a result, the total g -shift changes sign from negative in $\text{Si}:\text{Cr}^{4+}$ to positive $\text{Si}:\text{Mn}^{5+}$. This means that $3d^2$ ions of high valence states in strong covalent environments (e.g., silicon) exhibit significant covalency and the charge transfer contributions due to the low charge transfer levels E_n and E_a [13], although the spin-orbit coupling coefficient ($\sim 215 \text{ cm}^{-1}$) of the ligand Si is smaller than that (~ 328 or 452 cm^{-1}) of the impurity Cr^{4+} or Mn^{5+} . On the other hand, increase of the covalency (or decline of the covalency factor N) also leads to the increase of the ligand contributions to the g -shift in the crystal-field mechanism, i.e., $|\Delta g_{CF}(\text{Cr}^{4+})| < |\Delta g_{CF}(\text{Mn}^{5+})|$. This may be described as the relative differences (or anisotropies) $k'_{CF}/k_{CF}-1$ and $\xi'_{CF}/\xi_{CF}-1$ for the orbital reduction factors and the spin-orbit coupling coefficients, which amount to 500 and 40% based on the present cluster approach calculations. In fact, such kind of $3d$ orbital delocalization and anisotropic expansion was also reported in the studies for some transition-metal (e.g., V^{3+} , Cu^{2+}) ions in semiconductors [23,24]. So, the theoretical calculations based on the cluster approach in this work can be regarded as suitable for the Cr^{4+} and Mn^{5+} centers in silicon.

As for the hyperfine structure constant, A_{CT} from the charge transfer mechanism is the same in sign and about 80–90% larger in magnitude than A_{CF} from the crystal-field mechanism. Therefore, the charge transfer contributions to the hyperfine interactions for the $3d^2$ ions of high valence states in silicon should be taken into account. The larger magnitude of the A factor for Cr^{4+} than that for Mn^{5+} can be attributed to the larger dipolar hyperfine structure parameter P_0 and the higher covalency factor N in the former. In addition, the opposite signs of the hyperfine structure constants for Cr^{4+} and Mn^{5+} in silicon originate from the opposite signs of the P_0 (see Eqs (1) and (6)).

4. Conclusion

The f factors and the hyperfine structure constants for the Cr^{4+} and Mn^{5+} centers in silicon are theoretically studied using the perturbation formulas of these parameters containing both the crystal-field and charge transfer contributions based on the cluster approach. The relative importance of the charge transfer contributions to the g -shift Δg increases rapidly with increasing the valence state of the impurity ion, i.e., $\text{Cr}^{4+} < \text{Mn}^{5+}$. The charge transfer

contributions should be taken into account due to the significant covalency and the low charge transfer levels for the $3d^2$ impurities of the high valence states in the covalent Si host.

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