

ELECTRONIC AND MAGNETIC PROPERTIES OF INTERSTITIAL 3d IMPURITIES IN SILICON

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ABSTRACT

Self-consistent spin-unrestricted all-electron Green's function calculations are reported for the first time for a series of interstitial 3d impurities in silicon. The calculations, performed within the self-interaction-corrected local-spin-density formalism show: (i) not all 3d impurities follow Hund's rule: Ti^0 , Ti^- , V^0 , V^+ and Co^{2+} have a low-spin ground state, (ii) the angular momentum part g_L of g-value is quenched due to p-d hybridization effects, (iii) covalency explains also the chemical trends in the central hyperfine coupling constants, (iii) chemical trends in donor and acceptor transitions are reproduced and are consistent with a high-spin to low-spin transition at the low-Z end and high-Z end of the 3d series, (iv) A number of predictions are offered.

Introduction

A classical model for understanding the electronic structure of interstitial 3d impurities in silicon has been suggested over 20 years ago by Ludwig and Woodbury [1a]. Their phenomenological model, intended to explain the electron paramagnetic resonance (EPR) data available at their time, is an adaptation of the classical ligand field model of octahedrally coordinated impurities in oxides [2] to the problem of interstitial 3d impurities in four fold coordination. In this model, it is assumed that the tenfold degenerate atomic d orbital splits in the tetrahedral interstitial symmetry into a sixfold degenerate t_2 orbital, separated by the crystal-field energy Δ_{CF} from the four fold degenerate e orbital above it. Each of these two space orbitals is further assumed to be split by the exchange interaction Δ_x into spin-up (t_+ , e_+) and spin-down (t_- , e_-) orbitals. Ludwig and Woodbury (LW) [1a] and Ham [3] have then postulated that: (i) The level ordering for all 3d impurities is $t_+ < e_+ < t_- < e_-$ i.e. $\Delta_x > \Delta_{CF}$ always. We refer to this ordering as "high-spin-like" (HSL), to distinguish it from the alternative "low-spin-like" (LSL) ordering $t_+ < t_- < e_+ < e_-$ rejected by LW. (ii) All N valence electron of the impurity (atomic configuration $3d^m 4s^n$ with $N=m+n$) fill the levels such that a maximum spin S is achieved (Hund's rule). (iii) The fact that the angular momentum part g_L of the g-value is quenched was assumed to be a consequence of a dynamic Jahn-Teller effect [3], not due to covalent hybridization. (iv) Subsequent measurements of donor and acceptor transitions [4] were interpreted in light of assumptions (i) and (ii) above, e.g. a d^4/d^5 transition takes more energy than a d^5/d^6 transition since in a HSL level scheme the former commences from a deep e_+ orbital whereas the latter transition commences from a shallower t_- orbitals, etc.

Method

It is obvious from the data [1], [4] that much of the atomic many-electron multiplet effects are retained by such 3d impurities in the solid. In the case of 3d impurities in wider gap semiconductors (e.g. GaP), it has been possible [5] to use the observed intra-center $d \rightarrow d^*$ transitions and extract from this, through the multiplet theory of Fazzio, Caldas and Zunger [5], the relative proportion of one-electron vs many-electron contribution to various excitation processes. Using then self-consistent one-electron theory [6], it was possible to compute the mean-field one-electron part of the excitation energies, and

compare them with the experimental data from which many-electron effects have been subtracted [6]. This provided a quantitative theory of chemical trends for such impurities. This procedure is not possible for Si:3d, since no $d \rightarrow d'$ intra-center transitions have been observed so far. We have therefore adopted an alternative procedure. We neglect dynamic space correlation effects and retain only spin correlation effects by performing all-electron spin-unrestricted self-consistent Green's function calculations for Si:3d within the self-interaction corrected (SIC) LSD. This *ab initio* method of calculation has been previously described [7]. Using LSD it reproduces the earlier spin-restricted QBCF calculations of Zunger and Lindefelt [8] to within ~ 0.1 eV, when the spin-average orbital energies are compared with the spin-restricted levels. Analysis of our present results challenges all four [(i)-(iv)] assumptions of the classical LW model, yet our model produces good agreement with experiment both for ground state properties (g -values, hyperfine coupling constants), and for excited state properties (donor and acceptor transitions).

Results

1. Energy Levels: Figure 1 depicts the calculated local density of states for the e -states and the t_2 -states for a number of impurities, showing both spin-up and spin-down components. We show in the inserts the electronic charge Q_λ and local magnetic moment μ_λ (both projected on the impurity 3d orbital) for representations $\lambda = t_2$ and e . The interesting observations are: (i) Much of the impurity charge and local magnetic moments originate from the valence band resonances, and not only from the gap levels, (as is the case for 3d impurities in wide-gap oxides [2]). (ii) The level ordering for the neutral impurities is

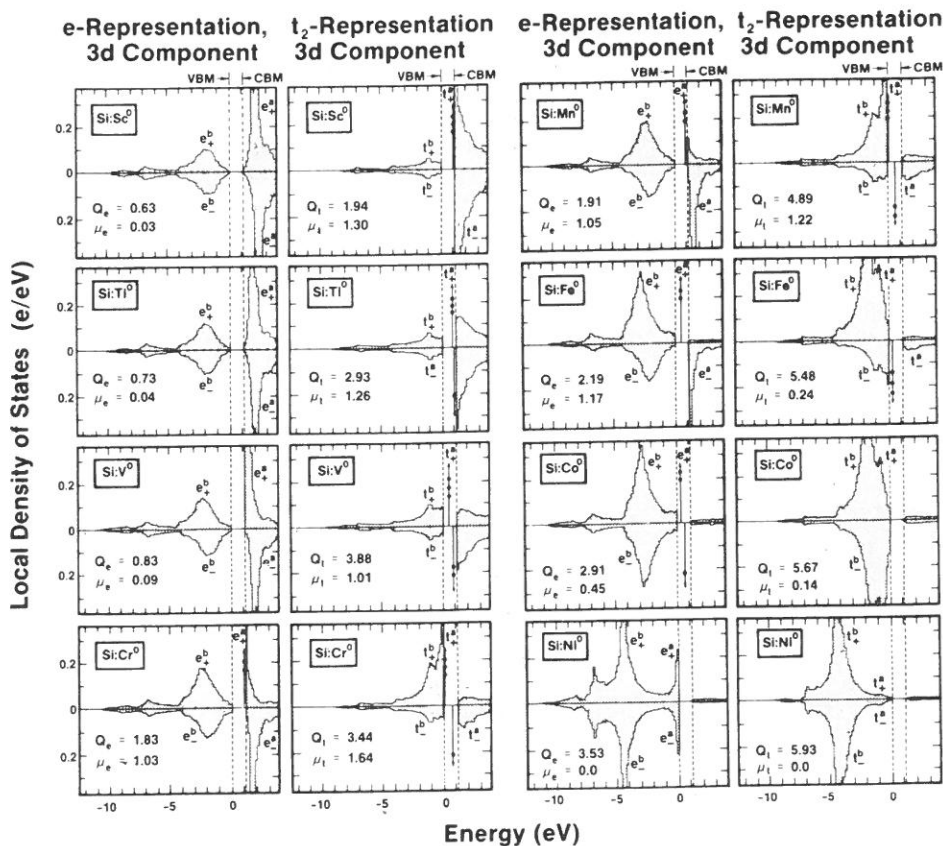


Fig. 1 Calculated local density of states for the e and t_2 -states.

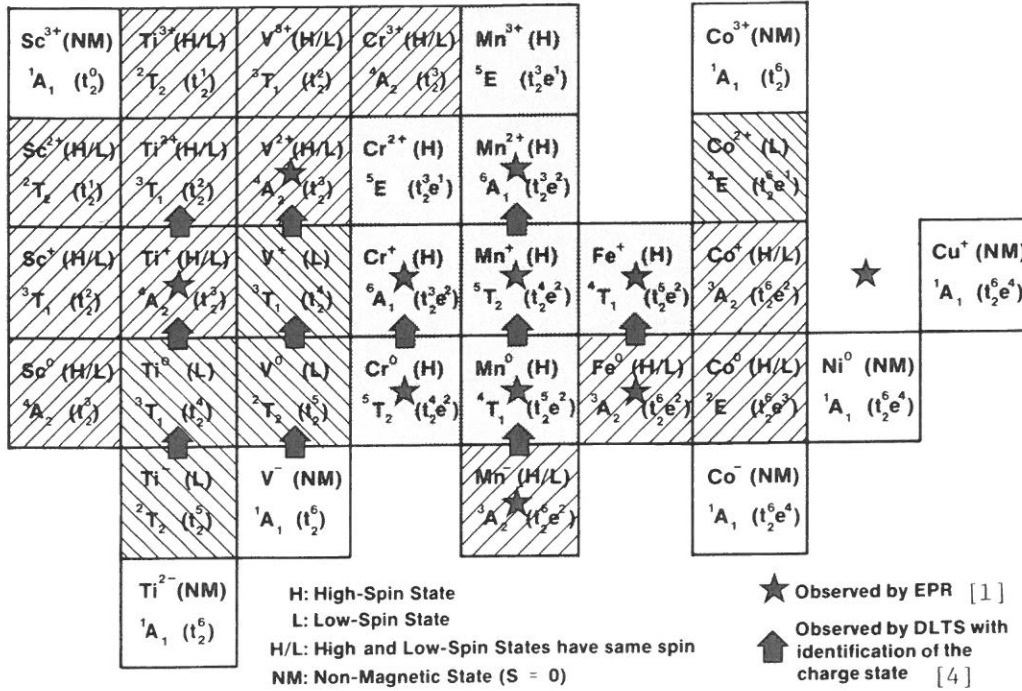


Fig. 2 Calculated and observed [1] spin states.

LSL, not HSL. Nevertheless, the calculated ground state has maximum-spin, since for Cr^0 and Mn^0 we find the $t_+^3 t_-^1 e_+^2$ and $t_+^3 t_-^2 e_+^2$ configurations to be the lowest energy ones. In these configurations the t_- orbital has 2 or 1 (Cr^0 and Mn^0 , respectively) holes below the occupied e_+ orbital. This is identical to what has been previously found in LSD calculations [9] for the free atoms Fe and Co. Figure 2 shows the calculated and observed [1] spin states for Si:3d. Our calculation agrees with the data of LW for all impurities which they measured. However, for Ti^0 , Ti^- , V^0 , V^+ and Co^{2+} we predict a low-spin ground state of ${}^2T_2(t_+ t_-)$, ${}^2T_2(t_+ t_-)$, ${}^3T_1(t_+ t_-)$ and ${}^2E(t_+ t_- e_+)$ respectively. These were not observed as yet. Our conclusion is that there is no universal HSL level ordering and Hund's rule spin. Instead, Hund's rule is satisfied at the center of the 3d series, where $\Delta_x > \Delta_{CF}$, however, both at the low-Z end (Sc, Ti, V) and at the high-Z end (Co, Ni, Cu) we find $\Delta_{CF} > \Delta_x$, and a low-spin ground state. This has been predicted to be the case also for substitutional GaP:3d [6] and Cu, Ag, and Au in Si [10]. In contrast, cluster calculations [11] which assume spherical muffin-tin potential lead consequently to an artificial reduction in covalency effects (hence Δ_{CF}) and predict a universal high-spin ($\Delta_x \gg \Delta_{CF}$) ground state. Experiments on Ti^0 , Ti^- , V^0 , V^+ and Co^{2+} in silicon are needed to establish the validity of our model.

2. g-factors and Hyperfine Coupling Constants: We have calculated the g-values from $g = g_S + g_L + \Delta g_{LS}$, where g_S and g_L are the electron spin and orbital angular momentum parts, respectively. The contribution of the spin-orbit interaction Δg_{LS} is calculated from the effective crystal-field splitting Δ_{eff} (obtained from a transition state calculation) and the spin-orbit coupling constant λ , i.e., $\Delta g_{LS} = n\lambda k / (m\Delta_{eff})$. The hyperfine coupling constants A is obtained as a sum of the contact interaction A_C and the contribution A_L from the orbital magnetic moment. A_C is given by $A_C = 8\pi/3 g_S \mu_B g_N \beta_N \delta\rho(0)/2S$, where g_S and g_N are the electron and nuclear g-values, μ_B and β_N are the electron and nuclear bohr magneton, S is the electron spin, and $\delta\rho(0)$ is the calculated net spin density at the impurity nucleus. For $L=0$, A_L is given by $A_L = 2 \mu_B g_N \beta_N \Delta g \langle r^{-3} \rangle$, where the g-shift is $\Delta g = g - 2.0023$ and $\langle r^{-3} \rangle$ is the average of r^{-3} over the impurity orbital at the Fermi energy. In the case of $L=1$, $S=3/2$, and

$J=1/2$, A_L is given by $A_L = 2\mu_B g_N \beta_N \langle r^{-3} \rangle [g_L - \frac{k}{2} g_S]$, where $g_S = 2.002: (\mathbf{S} \cdot \mathbf{J}) / (\mathbf{J} \cdot \mathbf{J})$, $g_L = \gamma (\mathbf{L} \cdot \mathbf{J}) / (\mathbf{J} \cdot \mathbf{J})$, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, and the covalency factor is $\gamma = \langle \phi_t(r) | \mathbf{L} | \phi_t(r) \rangle$. Here, $\phi_t(r)$ denotes the impurity wavefunction of the t_2 level, and k denotes the spin orbit reduction factors in the solid (calculated from the ratio $k = \langle r^{-3} \rangle_{\text{solid}} / \langle r^{-3} \rangle_{\text{atom}}$). We find the covalency factor γ to be very small ($\gamma \approx 0$) because of an effective cancellation between the contributions of d and p orbitals to the matrix elements of \mathbf{L} . Table I shows our results. We conclude that: (i) The simple covalency effect (i.e. opposing contribution of p and d orbitals to g_L) explains the quenching of g_L . In contrast with Ham's model [3], we find no compelling reason to invoke other effects (e.g. dynamic Jahn-Teller coupling) to explain this quenching. The reason that we find covalency effects throughout the series, despite the occurrence of LSL-HSI variations in level ordering is that common to all impurities is the occurrence of strongly hybridized VB resonances (Fig. 1) which carry much of the impurity

Table I: Calculated and observed [1] g -values and hyperfine coupling constants A of interstitial 3d impurities in Si. Asterisks denote calculated values of contact interaction alone. A is in units of 10^{-4}cm^{-1} . Error bars are given only in the case of Si:Ti^+ [$g=1.99806 \pm 0.00004$, $A=(\pm 5.224 \pm 0.010) \times 10^{-4} \text{cm}^{-1}$] [1b].

Impurity	S	J	g_S	g_L	Δg_{LS}	g_{calc}	g_{exp}	A_{calc}	A_{exp}		
d^3	$^{45}\text{Sc}^0$	3/2	0	3/2	2.0023	0.	-0.0138	1.9885	-	-13.6	-
	$^{47}\text{Ti}^+$	3/2	0	3/2	2.0023	0.	-0.0111	1.9912	1.9981	+4.7	± 5.224
	$^{51}\text{V}^{2+}$	3/2	0	3/2	2.0023	0.	-0.0292	1.9731	1.9892	-33.0	-42.10
d^5	$^{53}\text{Cr}^+$	5/2	0	5/2	2.0023	0.	-0.0037	1.9986	1.9978	+11.0	+10.67
	$^{55}\text{Mn}^{2+}$	5/2	0	5/2	2.0023	0.	0.0024	2.0047	2.0066	-41.0	-53.47
d^6	$^{53}\text{Cr}^0$	2	1	1	3.0035	0.0878	-0.0085	3.0828	2.97	+14.0*	± 15.9
	$^{53}\text{Cr}^0$	2	1	2	1.6686	-0.0293	-	1.6393	1.72	+8.3*	-
	$^{53}\text{Cr}^0$	2	1	3	1.3349	-0.0585	-	1.2764	-	+6.4*	-
	$^{55}\text{Mn}^+$	2	1	1	3.0035	0.0887	0.0147	3.1069	3.01	-68.3*	± 73.8
	$^{55}\text{Mn}^+$	2	1	2	1.6686	-0.0296	-	1.6390	1.68	-38.1*	± 46.1
	$^{55}\text{Mn}^+$	2	1	3	1.3349	-0.0591	-	1.2758	1.34	-30.4*	-
d^7	$^{55}\text{Mn}^0$	3/2	1	1/2	3.3372	0.1583	0.0310	3.5265	3.362	-42.4	± 92.5
	$^{55}\text{Mn}^0$	3/2	1	3/2	1.4684	-0.0633	-	1.4051	1.46	-35.6*	-
	$^{57}\text{Fe}^+$	3/2	1	1/2	3.3372	0.1531	0.0671	3.5582	3.524	-3.9	± 2.99
	$^{57}\text{Fe}^+$	3/2	1	3/2	1.4684	-0.0612	-	1.4072	-	-3.8*	-
d^8	$^{55}\text{Mn}^-$	1	0	1	2.0023	0.	0.0187	2.0430	2.0104	-49.1	-71.28
	$^{57}\text{Fe}^0$	1	0	1	2.0023	0.	0.0187	2.0210	2.0699	-5.2	± 6.98
	$^{59}\text{Co}^+$	1	0	1	2.0023	0.	0.0577	2.0600	-	-13.8	-

charge. (ii) Our model explains the reduction of the central hyperfine constant A (Table I) in terms of covalency effects: covalency reduces the s - d intraatomic Coulomb repulsion (relative to the free-ions), hence it reduces the negative core-polarizations. (iii) We find that A is a result of a near-cancellation of positive and negative spin-densities in the core and valence orbitals [7], e.g., for Si:Fe^0 the different orbital contributions (in kG) are $1s$ (-24.5), $2s$ (-278.52), $3s$ (+179.70) and $4s$ (+8.18).

3. Electrical Levels: Figure 3 shows our calculated electrical levels for the first donor and acceptors in Si:3d . Our results follow the experimental trends [4], although since they were calculated for static Frank-Condon transitions (and hence, should in principle be compared with optical excitation energies which are, however, unavailable) they tend to be at higher energies than the observed equilibrium transition (DLTS and Hall effect data). Note that we find the expected minimum for $E(0/+)$ in $\text{V}(d^4/d^5)$ relative to $\text{Cr}(d^5/d^6)$, due to high-spin effects. However, the classical model would argue that the same effect should exist in the acceptor spectra: $E(-/0)$ for $\text{Ti}(d^4/d^5)$ should be lower in the gap than $\text{V}(d^5/d^6)$. The data shows that the opposite is true, in agreement with our calculation. The reason for this is that we find Ti^0 and V^0 to be in low-spin ground state. Our calculation does not show the anomalies observed in cluster calculations [11] (e.g., V acceptor higher in gap than the Cr acceptor, Fe acceptor stable, Mn acceptor higher in gap than Fe acceptor, V donor inside the conduction band, and higher than the Cr donor).

4. Broken Symmetries: Nominally closed-shell species like Ti^{2-} , V^- , Co^{3+} with $t_+^3 t_-^3$ configurations have a total spin of zero and a total magnetic moment of zero. It is normally expected that their local magnetic moment is also zero. In contrast, we find small nonvanishing moments, for these impurities. These are broken symmetry solutions, similar to what has recently discovered for diatomic molecules of d elements [12a] and atomic tungsten [12b]. This simply suggests that within the impurity subspace there is no exact cancellation of spin-up and spin-down densities. This corresponds to a single-site-like spin density wave.

5. Exchange-Correlation Negative U : The positiveness of effective interelectronic Coulomb repulsions for impurities is manifested by the fact

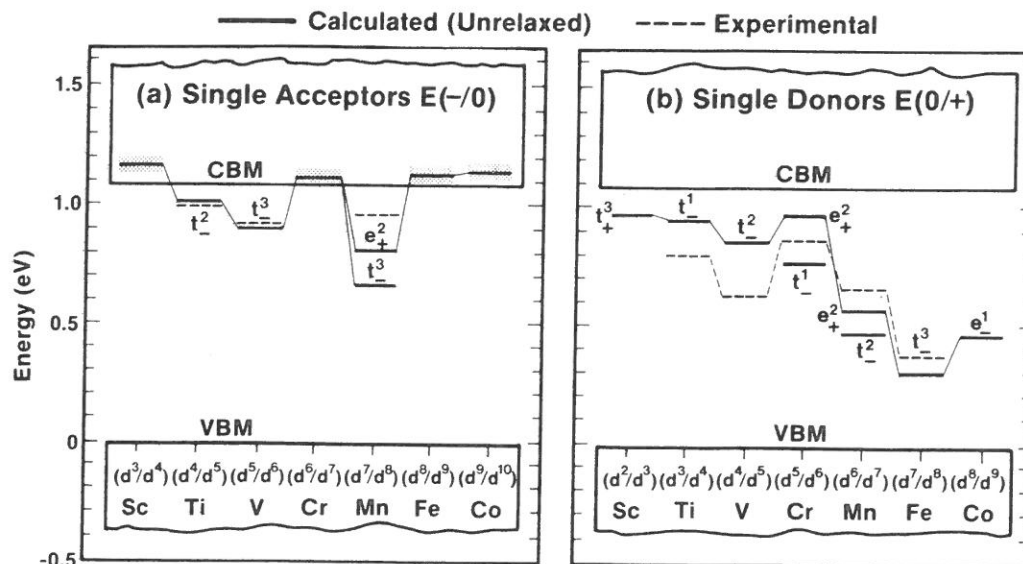


Fig. 3 Calculated and observed chemical trends in ionization energies of Si:3d . Shaded areas denote unstable transitions within the host bands.

that usually the donor transitions are lower in the gap than acceptor transitions, if both commence from the same orbital. In general, their separation U can be thought of as consisting of 3 contributions: (i) U_{ver} , or the vertical Hubbard U , corresponding to repulsions in Frank-Condon transitions, when many-electron effects (e.g. spin and space correlations) are negligible, (ii) a correction $\Delta U_{R, JT}$ due to relaxation (R) and Jahn-Teller (JT) distortions, (iii) a correction ΔU_{MC} due to multiplet corrections (MC), e.g. spin exchange and space correlations. "Anderson's negative U " corresponds to the case where the negative $\Delta U_{R, JT}$ overwhelms U_{ver} . Following an earlier suggestion [5], we have found [13] a new type of negative U mechanism, i.e. when the negative ΔU_{MC} outweighs U_{ver} . This can occur when the gain in exchange energy upon excitation (e.g. $t_{+e_1}^5 \rightarrow t_{+e_1}^3 e_1^2$ and $t_{+e_1}^3 \rightarrow t_{+e_1}^1 e_1^2$) can outweigh the Coulomb repulsion. We find in our calculation that this is the case in Frank-Condon transitions in Si:Cr; the triple donor $\text{Cr}^{2+}/\text{Cr}^{3+}$ is lower in the gap than the double donor $\text{Cr}^{1+}/\text{Cr}^{2+}$ transition. This interesting result awaits experimental testing.

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