

MAGNETIC PROPERTIES OF INTERSTITIAL 3d IMPURITIES IN SILICON

H. KATAYAMA-YOSHIDA * and Alex ZUNGER

Solar Energy Research Institute, Golden, CO 80401, USA

Using self-consistent Green's function calculations, we (i) discuss the magnetism of interstitial 3d impurities in silicon, (ii) makes a comparison of the theory with EPR data, (iii) discuss a mechanism of covalent reduction of both the hyperfine coupling constant and the orbital angular momentum part of the g -values, and (iv) propose a new type of "negative effective U ", induced by exchange-correlation.

More than twenty years ago, Ludwig and Woodbury (LW) proposed what has since become the classical model for explaining the observed electron paramagnetic resonance (EPR) spectra of 3d transition atom impurities in semiconductors [1]. This model has recently been analyzed [2] in light of new experimental observations and a recent analysis [3] of many-electron exchange-correlation effects in such systems. The studies of 3d transition atom impurities in semiconductor have received growing interest in recent years [2–8]. In this paper we apply our [6] self-consistent first principles all-electron Green's function approach within an impurity-centered dynamic basis set including the self-interaction correlation to the local *spin* density formalism. We have calculated with no empirical input the spin-polarized electronic structure of different charge states of isolated Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Cu impurities at the tetrahedral interstitial site in silicon. The result suggest a modified picture relative to the classical LW model [1]. It explains both ground state properties (e.g., the hyperfine coupling constant and the

g -value) and excited properties (e.g., donor and acceptor ionization energies) [7].

To establish the relative accuracy of our calculational scheme [6,7], we show in table 1 an example of the calculated central hyperfine coupling constant A , the g -value and the predicted ground state spin multiplet for interstitial 3d impurities in silicon. The agreement between the calculated g -values and experiment (when available) is good. We note that: (i) the simple covalency effect (i.e., opposing contributions from the p and d components of the t_2 impurity wavefunction) explains the quenching of the orbital angular momentum part of the g -values. The reason we find covalency effects throughout the series is the occurrence of strongly hybridized 3d valence band resonances which carry much of the impurity charge [6]. (ii) Our results explain the reduction of the central hyperfine coupling constant A in terms of covalent reductions in the s - d Coulomb energies. (iii) We find that A shows a near cancellation of positive ($3s$, $4s$) and negative ($1s$, $2s$) spin-densities [6]. In addition, (iv) we correctly predict the trends in the donor and acceptor ionization energies compared with the observed values [7].

Our calculation predicts a level ordering that disagrees with the LW model, yet it agrees with experi-

* Permanent address: Department of Physics, Tohoku University, Sendai 980, Japan.

Table 1
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} . Γ shows predicted multiplets

Impurity	Γ	g_{calc}	g_{exp}	A_{calc}	A_{exp}
$d^3 \left\{ \begin{array}{l} {}^{47}\text{Ti}^+ \\ {}^{51}\text{V}^{2+} \end{array} \right.$	4A_2	1.9912	1.9981	+4.7	± 5.224
	4A_2	1.9731	1.9892	-33.0	-42.10
$d^5 \left\{ \begin{array}{l} {}^{53}\text{Cr}^+ \\ {}^{55}\text{Mn}^{2+} \end{array} \right.$	6A_1	1.9986	1.9978	+11.0	+10.67
	6A_1	2.0047	2.0066	-41.0	-53.47
$d^6 \left\{ \begin{array}{l} {}^{53}\text{Cr}^0 \\ {}^{55}\text{Mn}^+ \end{array} \right.$	5T_2	3.0828	2.97	+14.0*	± 15.9
	5T_2	3.1069	3.01	-68.3*	± 73.8
$d^7 \left\{ \begin{array}{l} {}^{55}\text{Mn}^0 \\ {}^{57}\text{Fe}^+ \end{array} \right.$	4T_1	3.5265	3.362	-42.4	± 92.5
	4T_1	3.5582	3.524	-3.9	± 2.99
$d^8 \left\{ \begin{array}{l} {}^{55}\text{Mn}^- \\ {}^{57}\text{Fe}^0 \end{array} \right.$	3A_2	2.0430	2.0104	-49.1	-71.28
	3A_2	2.0210	2.0699	-5.2	± 6.98

ment; we find a low-spin-like (LSL) level arrangement (i.e., $t\downarrow$ below $e\uparrow$) for both the low-Z limit (Sc, Ti and V) and for the high-Z limit (Co and beyond) of the 3d series [7], whereas for all intermediate impurities (Cr, Mn and Fe) we find a high-spin-like (HSL) level arrangement. 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 low-spin ground states of 3T_1 , 2T_2 , 2T_2 , 3T_1 and 2E , respectively. These are not observed as yet [1], and constitute the first prediction of low-spin impurities in Si [7].

The positiveness of the Mott–Hubbard effective Coulomb energy U for impurities is manifested by the usual occurrence of donor transitions lower in the gap than acceptor transitions, if both commence from the same orbital. In general, the donor–acceptor separation U can be thought of as consisting of three contributions [2,3]: (i) U_{ver} , the vertical Hubbard U , corresponding to the Coulomb repulsion in Franck–Condon transitions, when many-electron effects (e.g., spin and space correlations) are negligible, (ii) a correction $\Delta U_{R,JT}$ due to lattice relaxation (R) and Jahn–Teller (JT) distortions, and (iii) a correction ΔU_{MC} due to multiplet corrections (MC), [8] i.e., spin and orbital correlation effects. “Anderson’s negative U ” [9] corresponds to the case where the negative $\Delta U_{R,JT}$ overwhelms U_{ver} . Caldas et al. [8] have suggested that the negative correlation correction ΔU_{MC} might also overwhelm U_{ver} due to the stability of d^5 (Hund’s rule), yielding $U < 0$ even in optical transitions (where $\Delta U_{R,JT} = 0$). To quantitatively examine this idea, we have carried out a self-consistent spin-polarized calculation for the d^3 , d^4 , d^5 system of Si:Cr $^{3+}$, Si:Cr $^{2+}$ and Si:Cr $^{1+}$, respectively. The key point in our model is that when the atom is placed into a polarizable host system, its Coulomb and exchange-correlation interactions each respond in a fundamentally different way to screening by the host: the former, responding to long wavelength (monopole) screening is reduced far more than the latter (multipole screening). As host crystals, semiconductors provide a special mechanism to reduce U_{ver} without affecting the exchange energy J : what is special about deep impurities in semiconductors is that they often show [2,6,7] both localized gap levels and hybridized valence band resonances. Under these conditions, Haldane and Anderson [10] have shown in a model calculation that the effective charge $Q^*(q)$ on the impurity can depend very weakly on its formal charge q , resulting in a strong reduction in the vertical repulsion energy $U_{ver} \propto (\partial Q^*/\partial q)^2 U_0$, relative to the atomic value U_0 . To illustrate this self-regulating response mechanism [11,12], we decompose the electronic charge Q^* and the local magnetic moment μ in the impurity subspace into contributions Q_{gap} and μ_{gap} from the gap orbitals and the contribution Q_{VB} and μ_{VB} from the valence band resonances (fig. 1). For Si:Cr $^{3+}$ with empty gap levels, we have $Q_{gap} = \mu_{gap} = 0$. All of the impurity charge ($Q_{VB} = 5.33$ e) and mag-

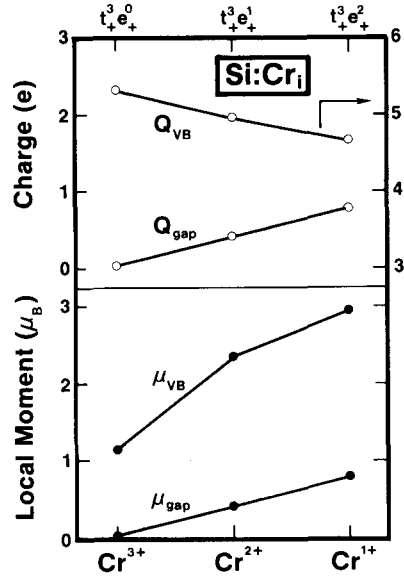


Fig. 1. Decomposition of the local charge Q^* and the local magnetic moment μ into gap and valence band contributions for interstitial Cr $^{3+}$, Cr $^{2+}$ and Cr $^{+}$ in Si.

netism ($\mu_{VB} = 1.15\mu_B$) is hence contributed by the impurity induced valence band resonances. As we raise the Fermi level E_F , the gap orbital $e\uparrow$ can capture one or two electrons, changing the formal charge state from Cr $^{3+}$ to Cr $^{2+}$ and Cr $^{+}$, respectively. Fig. 1 shows that in this sequence both μ_{gap} and μ_{VB} are increased, whereas the valence band and gap contributions to the charge act in opposite directions (Q_{gap} increases, Q_{VB} decreases) partially cancelling one another. This implies that Coulomb interactions (underlying the charge Q^*) are effectively screened by the semiconductor, whereas spin interactions (underlying μ) are not. As a result of this feedback self-regulating response to the charge [10,11], the total electronic charge $Q^* = Q_{gap} + Q_{VB}$ on the impurity changes extremely slowly with the formal charge q (i.e., $\partial Q^*/\partial q \approx 0.12$), leading to a strong renormalization $U_{ver} \propto (\partial Q^*/\partial q)^2 U_0$ of the bare U_0 . This leads to the possibility that $U_{ver} < |\Delta U_{MC}|$, where ΔU_{MC} is the change in exchange energy $J^{(N-1)} + J^{(N+1)} - 2J^{(N)}$ associated with the transition. We find in our calculations [10] for the Franck–Condon transitions in Si:Cr that the triple donor transition Cr $^{2+}$ /Cr $^{3+} = E_c - 0.36$ eV is lower in the gap than the double donor Cr $^{1+}$ /Cr $^{2+} = E_c - 0.55$ eV transition energy. We hence predict for the Franck–Condon transitions that Cr $^{2+}$ is an exchange-correlation induced negative effective U center, with $U = 0.36 - 0.55 = -0.19$ eV. No experimental test of this idea is available as yet.

We believe our exchange-correlation induced mechanism for reduction of U can be operative in diverse systems in which a localized state, capable of sustaining occupation-dependent local magnetic moments, interacts with a continuum of states with which it can

exchange charge. Possible examples include f-electron impurities, mixed-valence compounds and surface magnetism. Our work offers a new way to examine computationally such effects: comparing the variations of $\mu(N)$ and $Q^*(N)$ with occupation N and the spin-restricted Hubbard energy $U_{\text{ver}} = E^{(N-1)} + E^{(N+1)} - 2E^{(N)}$ (where E is the total energy) with its exchange correction $\Delta U_{\text{MC}} = J^{(N-1)} + J^{(N+1)} - 2J^{(N)}$. A situation in which $U_{\text{ver}} < |\Delta U_{\text{MC}}|$ can lead to many interesting physical effects, since in such a case $A^q(n)$ is never the ground state, but instead disproportionates into $A^{q-1}(N+1) + A^{q+1}(N-1)$. "Missing oxidation states" (e.g., often Mn^{4+} and Mn^{2+} exist, but Mn^{3+} does not; In^{1+} and In^{3+} exist, but in In^{2+} does not) could be such a case.

We acknowledge support by the Office of Energy Research, Materials Science Division, US Department of Energy, Grant no. DE-ACO2-77-CH00178.

[1] G.W. Ludwig and H.H. Woodbury, in: Solid State Phys., Vol. 13, eds. F. Seitz and D. Turnbull (Academic Press, New York, 1962) p. 263.

- [2] A. Zunger, in: Solid State Physics, eds. H. Ehrenreich, F. Seitz and D. Turnbull (Academic Press, New York, in press).
- [3] A. Fazzio, M. Caldas and A. Zunger, Phys. Rev. B 24 (1984) 5999, 30 (1984) 3430.
- [4] P. Vogl and J.M. Baranowski, Proc. 17th Intern. Conf. on the Physics of Semiconductors (1985) p. 623.
- [5] F. Beeler, O.K. Andersen and M. Scheffler, Proc. MRS Symp., San Francisco (15-18 April 1985) in press.
- [6] H. Katayama-Yoshida and A. Zunger, Phys. Rev. Lett. 53 (1984) 1256; Phys. Rev. B 31 (1985) 7877.
- [7] H. Katayama-Yoshida and A. Zunger, Phys. Rev. B 31 (1985) 8317; Proc. MRS Symp., San Francisco (15-18 April 1985) in press.
- [8] M. Caldas, A. Fazzio and A. Zunger, Proc. 13 Intern. Conf. on Defects in Semiconductors (1985) p. 1035.
- [9] P.W. Anderson, Phys. Rev. Lett. 34 (1975) 953.
- [10] F.D.M. Haldane and P.W. Anderson, Phys. Rev. B 13 (1976) 2553.
- [11] A. Zunger and U. Lindelfelt, Solid State Commun. 45 (1983) 343.
- [12] H. Katayama-Yoshida and A. Zunger, Phys. Rev. Lett. (September 1985) in press.