

First-principles cluster study of electronic structures, locations and hyperfine interactions of isolated atoms and ions in silicon

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Abstract The electronic structures of the dilute transition metal (TM) impurities, V^{2+} , Cr^{+} , Mn^{2+} , and Mn^0 in silicon have been studied using the Hartree–Fock (HF) procedure combined with many-body perturbation theory (MBPT). The systems studied involved the TM impurities at the hexagonal interstitial (H_i), tetrahedral interstitial (T_i) and substitutional (S) locations. Investigations of the binding energy and local potential energy surface of the TM impurity-Si systems indicate that the TM impurities are binding at the T_i location. Hyperfine interaction constants (A) of the TM impurities at the T_i and S sites are presented and compared with available experimental results (Woodbury and Ludwig, J Phys Rev 117:102, 1960a, Phys Rev Lett 5:98, b) from Electron Paramagnetic Resonance (EPR) measurements.

Keywords Magnetic semiconductors · Transition metal impurities · Binding energies · Trapping sites · Hyperfine interactions

1 Introduction and procedure

Transition Metal (TM) impurities in silicon have been shown to produce ferromagnetism [3] at room temperature with potential applications in spintronics [4]. To

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better understand ferromagnetism in TM-silicon systems, the nature of the exchange interaction between pairs of TM impurities in the silicon should be investigated. The exchange interaction between impurities is expected to depend on their locations in the silicon lattice and their electronic wave-functions and the associated spin contributions. Examination of dilute TM impurity systems can provide a better understanding of the probable binding locations of the TM impurities in silicon. Previous band structure investigations involving the super cell approach [5] on similar dilute systems have examined binding locations and magnetic properties, but no work to date has examined the Fermi contact hyperfine interactions of dilute TM impurities in silicon. Such results are useful because there is magnetic hyperfine interaction data available [1, 2] for the very dilute TM impurities where they can be considered as isolated impurities in silicon. The present work deals with the dilute V^{2+} -Si, Cr^+ -Si, and Mn^{2+} -Si and Mn^0 -Si systems. Results shall be presented on the locations of V^{2+} , Cr^+ , Mn^{2+} , and Mn^0 in silicon. For the V^{2+} -Si, Cr^+ -Si, and Mn^{2+} -Si systems, the hyperfine interactions for $(^{51}V)^{++}$, $(^{53}Cr)^+$, $(^{55}Mn)^{++}$ respectively will be compared with experiment [1, 2].

The properties of the transition metal impurities, V^{2+} , Cr^+ , Mn^{2+} , and Mn^0 , at the H_i , T_i , and S locations in silicon have been investigated using the Hartree–Fock method combined with many body perturbation theory (MBPT). The bulk silicon lattice has been simulated using the Hartree–Fock Cluster procedure [6] implemented using Gaussian 09 [7]. Depending on the TM location, the following clusters were used: $TMSi_{18}H_{36}$ (H_i), $TMSi_{14}H_{24}$ (T_i), $TMSi_{16}H_{36}$ (S). Relaxation effects were included by energy optimization of the neighboring silicons. These relaxed TM impurity-silicon clusters were then used to investigate the binding energy, local potential surface, and magnetic hyperfine properties of the TM impurities at each location. The binding energy of the TM impurity at the interstitial locations in the silicon lattice were obtained from,

$$B.E.(Interstitial) = E_{Si\ cluster\ N} + E_{free\ impurity\ atom} - E_{cluster\ with\ impurity} \quad (1)$$

For the substitutional location, situations with (S_V), and without (S) a preexisting vacancy were considered,

$$B.E.(S_V) = E_{Si\ cluster\ N-1} + E_{free\ impurity\ atom} - E_{cluster\ with\ impurity} \quad (2)$$

$$B.E.(S) = E_{Si\ cluster\ N} + E_{free\ impurity\ atom} - E_{cluster\ with\ impurity} - E_{free\ Si} \quad (3)$$

Binding energies have been calculated at the HF and the HF+MBPT levels. To test the stability of the locations, we made small displacements of the TM impurities in the clusters along the $\langle 111 \rangle$ axis and a perpendicular axis and calculated the energy resulting change to the cluster. These calculations gave us an idea of the local potential surface and provided insight as to whether a location was stable, metastable, or unstable based on whether the location was a local minimum, local maximum, or a local saddle point. The magnetic hyperfine parameter A of the TM impurities at the T_i and S locations will be presented and compared with experimental data where available.

Table 1 Binding energy (Hartrees) of transition metal ions and atoms in silicon clusters

Cluster	HF	HF+MP2
H_i		
$Cr^+Si_{18}H_{36}$	-0.0642	0.0263
$V^{2+}Si_{18}H_{36}$	0.0989	0.2203
$Mn^{2+}Si_{18}H_{36}$	0.1283	0.2513
$Mn^0Si_{18}H_{36}$	-0.1288	-0.1005
T_i		
$Cr^+Si_{14}H_{24}$	-0.0433	0.0441
$V^{2+}Si_{14}H_{24}$	0.1375	0.2665
$Mn^{2+}Si_{14}H_{24}$	0.1392	0.2699
$Mn^0Si_{14}H_{24}$	-0.1449	-0.1581
S		
$Cr^+Si_{16}H_{36}$	-0.3428	-0.3882
$V^{2+}Si_{16}H_{36}$	-0.1492	-0.444
$Mn^{2+}Si_{16}H_{36}$	-0.1613	-0.0634
$Mn^0Si_{16}H_{36}$	-0.2993	-0.2401
S_V		
$Cr^+Si_{16}H_{36}$	0.0241	-0.0043
$V^{2+}Si_{16}H_{36}$	0.2360	0.3395
$Mn^{2+}Si_{16}H_{36}$	0.2056	0.3204
$Mn^0Si_{16}H_{36}$	0.0676	0.1438

2 Results and discussions

The results of the binding energy calculations of the TM impurities at the silicon lattice locations H_i , T_i , S are given in Table 1. For the substitutional location, both binding scenarios, S and S_V discussed earlier, are presented. The Mn^{2+} and V^{2+} ions have the strongest binding energy in each location. This is likely due to the ion inducing dipoles in the surrounding silicon atoms that in turn are producing an attractive potential at the ion. This would explain the ion Cr^+ having stronger binding in the interstitial locations than the Mn^0 yet having weaker binding than the stronger Mn^{2+} and V^{2+} ions. The binding at the substitutional site is stronger for the Mn^0 than the Cr^+ ion, probably due to the Mn^0 being better able to form bonds with the surrounding silicon atoms. The binding energies for the Mn^{2+} , V^{2+} , and Mn^0 TM impurities are strongest in the case of a preexisting vacancy at the substitutional sites. However, the likelihood of such a formation is low because it has to be produced by a direct hit by either the same TM ion that is getting trapped at the S site or has to be produced by a previous hit by another TM ion or it could be generated by a thermal activation process. In either case the formation of the trapped Mn^{2+} ion at S_V is less likely than the formation of a trapped Mn^{2+} ion at the T_i site because the T_i site is always empty and can trap the Mn^{2+} ion when it approaches it. Among the positive binding energy sites then, from among the probable binding sites, the T_i site is more stable and the H_i location the next most stable. We investigated the local potential energy surface of the H_i and T_i locations to determine if the locations were stable or metastable for TM impurities. Displacements along the $\langle 111 \rangle$ axis and perpendicular to the $\langle 111 \rangle$ axis for both the H_i and T_i locations provide very clear local minimums for the T_i site while for the H_i location, displacements perpendicular to the $\langle 111 \rangle$ axis resulted in larger energies whereas displacements along the $\langle 111 \rangle$ axis resulted in lower energies. This means that the H_i position is

Table 2 Fermi contact of transition metal ions and atoms in silicon at HF level

Cluster	HF	Experiment
	MagHyp(10^{-4})cm $^{-1}$	MagHyp(10^{-4})cm $^{-1}$
T_i		
Cr $^{+}$ Si $_{14}$ H $_{24}$	19.67	10.67
V $^{2+}$ Si $_{14}$ H $_{24}$	-81.81	-42.10
Mn $^{2+}$ Si $_{14}$ H $_{24}$	-84.29	-53.47
Mn 0 Si $_{14}$ H $_{24}$	-74.71	Not available
S		
Cr $^{+}$ Si $_{16}$ H $_{36}$	14.73	10.67
V $^{2+}$ Si $_{16}$ H $_{36}$	-48.45	-42.10
Mn $^{2+}$ Si $_{16}$ H $_{36}$	-55.34	-53.47
Mn 0 Si $_{16}$ H $_{36}$	-51.75	Not available

a metastable saddle-point in the local potential energy surface. Similar examination of the T_i location indicated a stable local minimum there. Thus, even though the H_i location has positive binding energy for the TM ions, it can be eliminated as a possible binding location due to local potential energy considerations.

The magnetic hyperfine properties of the TM impurities at the T_i and S locations (H_i being metastable is not shown) were investigated. Since these locations have tetrahedral symmetry, where magnetic dipolar contributions vanish [6], only the Fermi contact results are presented. The results, calculated at the HF level in Table 2, show closer agreement between the substitutional results for all cases where experimental results were available. Please note that unlike the binding energies presented in Table 1, the calculated Fermi contacts at the substitutional site are independent of the preconditions of the binding (vacancy or no vacancy), thus no distinction between S and S_V is necessary in Table 2. It is important to remember that Fermi contact involves the difference of calculated wave-functions at a single point and is particularly sensitive to MBPT effects [8]. Unfortunately, we were unable to calculate the Fermi Contact for these clusters at the HF combined with MBPT level due to computational constraints in carrying out such calculations. However, an approximation can be made in the case of Mn $^{2+}$ by determining a scaling factor using the MBPT and relativistic contributions found in available atomic manganese investigations [8]. Such an estimation is reasonable for low order MBPT contributions because the 4s electrons in atomic manganese are similar to the distortions introduced by the silicons surrounding the Mn $^{2+}$. Inclusion of such a scaling factor yields magnetic hyperfine constants of $-59.26 \cdot 10^{-4} \text{ cm}^{-1}$ (Mn $^{2+}$ at the T_i site) and $-38.90 \cdot 10^{-4} \text{ cm}^{-1}$ (Mn $^{2+}$ at the S site). Comparison with the experimental result of $-53.47 \cdot 10^{-4} \text{ cm}^{-1}$ shows that the T_i location is in better agreement with experiment than the S location.

We have examined the possible binding locations of TM impurities in silicon using binding energies and magnetic hyperfine constants. The H_i is found to be a metastable saddle point on the potential surface and is eliminated as a possible binding location for all TM impurities examined. Channeling data [9] from experimental measurements in our group favor the T_i location for Mn $^{2+}$ impurities, even though the S_V site is found to have a higher binding energy than the T_i . The lower probability of formation of the S_V site leads us to conclude that the T_i site is the preferred binding location for the TM impurities. It is worth noting that if the silicon were prepared in advance of implantation with a significant number of vacancies, our results indicate

the S_V would then clearly be the preferred binding location. Such a method of implantation may be a useful way to reducing the likelihood of TM impurities forming clusters in the silicon during annealing. We have compared the calculated magnetic hyperfine constants of Mn^{2+} ion at the S and T_i sites and found that the T_i site agrees more closely with experiment. It would also be valuable to have Electron Nuclear Double Resonance (ENDOR) data in the future for hyperfine interactions of ^{29}Si atom neighbors of Mn^{2+} at T_i site to compare with predictions that could be made from our calculated positions for these neighbors and our electronic wave-functions for this system. Future investigations will include TM pair interactions in silicon clusters to determine whether the systems are ferromagnetic.

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