Magnetic properties of substitutional 3d transition metal impurities in silicon carbide

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Using the linearized muffin-tin orbital (LMTO) method within both the atomic sphere approximation and full potential (FP) implementations and within the local spin-density-functional method and a supercell approach, we study the magnetic properties of cubic (3C) silicon carbide (SiC) doped by first-row transition metals (TM’s). The magnetic properties are found to depend strongly on the doping site. For substitution on the Si site, a nonmonotonic behavior of the magnetic moments with state filling is found. This is due to the large hybridization of the TM d states with the neighboring dangling bonds, which leads to a larger crystal field than spin splitting. This leads to low-spin states. On the other hand, for the unraveled structures, substitution on the C site leads to large-spin states, following an atomiclike Hund’s rule because of the weak hybridization with the surrounding dangling bonds. The relaxation effect, studied with FP-LMTO in selected cases, is large for the C site and small for the Si site. It leads to a suppression of the high magnetic moments for the C substitution. In any case, the calculated energies of formation indicate a strong preference for Si substitution, even when relaxation effects are included. In the case of neighboring pairs of TM dopants, there is generally a suppression of the magnetic moments, except for the Cr and Mn cases on the Si site. Ferromagnetic (FM) coupling is found to be preferred strongly for Cr. For Mn ferromagnetic coupling is found when relaxation is included. The tendencies towards ferromagnetic or antiferromagnetic (AFM) behavior are discussed in view of the Anderson-Hasegawa models of superexchange and double exchange. Thermodynamic considerations indicate that Cr and Mn doping on Si should be favorable. In fact, Si substitution would be preferred in the C-rich limit and neither Cr nor Mn is a strong carbide former. The strong energetic preference for FM over AFM ordering indicates possibly a high Curie temperature.

I. INTRODUCTION

Ferromagnetic semiconductors may pave the way towards manipulating the spin degree of freedom in electronics, or, as it is increasingly known, “spintronics.” The first generation of dilute magnetic semiconductors (DMS’s) was based primarily on Mn-doped II-VI semiconductors. Although Mn can be doped to arbitrarily high concentration in II-VI’s and exhibits useful paramagnetic effects in an external magnetic field, the fact that such materials generally do not exhibit ferromagnetic ordering limited their application. The reason is that Mn is isovalent with the group II cation and all 3d spin-up orbitals are occupied. Therefore the superexchange mechanism rather than the Zener double exchange effect is effective and an antiferromagnetic ground state is preferred. Even when separate p-type doping can lead to a hole-mediated ferromagnetism, the competition between ferromagnetism and antiferromagnetism strongly limits the achievable Curie temperatures. In order to realize ferromagnetism in DMS’s it was necessary to turn to III-V materials in which Mn can play the double role of magnetic impurity and p-type acceptor. This has only been realized recently after the low-solubility problem was overcome using non-equilibrium growth molecular-beam epitaxy methods. The outcomes are promising. Concentrations of Mn as high as 8% were obtained for (Ga,Mn)As and a corresponding Tc of 110 K was achieved after suitable annealing. It was soon used as a source of spin-polarized carriers in both light-emitting diodes and resonant tunneling diode heterostructures.

A mean-field study of hole-mediated ferromagnetism by Dietl et al.9 claimed that a higher Tc or even a room-temperature ferromagnetic DMS can be obtained in the low atomic number semiconductors. Important factors for this prediction are an increased p-d hybridization and a lower spin-orbit coupling. However, the mechanism behind the ferromagnetism in DMS is still widely under discussion. Several ab initio calculations have been performed for various semiconductors including GaAs, GaN, AlN, Ge, and CdGeP2. Here we study the other most widely used wide-band-gap semiconductor, SiC, as a potential DMS host. While SiC has a multitude of polytypes, we here consider the cubic or (3C) SiC polytype only, because we wish to focus on the fundamental questions relating only to Si or C site preference for the transition metal (TM) dopant and the occurrence of magnetic moments on these different sites, which one expects to be independent of the polytype. While most studies of magnetic semiconductors have focused on Mn as a magnetic element, we here consider the cubic or (3C) SiC polytype only, because we wish to focus on the fundamental questions relating only to Si or C site preference for the transition metal (TM) dopant and the occurrence of magnetic moments on these different sites, which one expects to be independent of the polytype. While most studies of magnetic semiconductors have focused on Mn as a magnetic element, we here consider the whole 3d TM series.

The entire family of TM’s in Si has been studied extensively by Beeler et al.19 using spin unrestricted linear muffin-tin orbital (LMTO) Green’s function calculations. It was found in that study that the early TM interstitial and late TM substitutional 3d ions prefer a low spin configuration, while substitutional Cr and Mn do exhibit spin polarization. It therefore is of interest to compare our results for the entire series of 3d impurities with those for Si. In the present study we consider only substitutional TM’s but we consider both Si and C substitutional sites. While there are similarities with the Si system, there are also striking differences.

Our results on the deep levels produced by the defects and their spin state are not only relevant to doped magnetic semi-
conductors but also to the physics of deep level traps in semiconductors and their identification by electron paramagnetic resonance. There exists a substantial literature about TM impurities in SiC as, for example, reviewed by Schneider and Maier. As the present study only includes the neutral charge states, it is not complete for the case of really dilute impurities, whose charge state may be independently varied by the position of the Fermi-level position in the gap. Since we here concentrate mainly on defects in relatively high concentration, we anticipate that the TM defect level itself determines the charge state to be the neutral one. Indeed the typical concentrations of order a few percent that are required for ferromagnetic semiconductor behavior are much larger than a typical high doping concentrations of say $10^{19}$ cm$^{-3}$. A study of the various charged states and their associated energy levels and multiplet splittings for the dilute limit is outside the scope of the present paper. Such a study would require careful consideration of the Jahn-Teller distortions in each case.

The paper is organized as follows. In Sec. II we provide the necessary information on the computational method. In Sec. III we discuss our main results on the magnetic moments and energy levels and explain the tendencies as functions of band filling. In Sec. IV we discuss the site preference. In Sec. V we present our results on the coupling between near-neighbor TM pairs to investigate the tendency towards ferromagnetic (FM) or antiferromagnetic (AFM) ordering and discuss them in the light of the Anderson-Hasegawa models of superexchange and double exchange. While most of the results of this paper were obtained using the atomic sphere approximation to the LMTO method and with unrelaxed structures, selected cases were further scrutinized using a full-potential LMTO method and including relaxation effects. These results are presented in Sec. VI. Finally, we discuss some thermodynamic aspects relating to the possibility of precipitation of competing compound phases and hence the prospects for actually realizing ferromagnetic semiconductors based on SiC as host material in Sec. VII. In Sec. VIII we summarize our conclusions.

II. COMPUTATIONAL METHODS

For most of the calculations, the LMTO method was used in the atomic sphere approximation (ASA). For selected cases a full-potential LMTO (FP-LMTO) was used to check the effects of the geometry relaxation. In the ASA calculations, equal sphere radii were used for Si, C, empty spheres (at tetrahedral interstitial sites), and the TM's. For most of the TM's, the 3p states were treated as core states but for Sc, Ti, and V, it was found necessary to treat the 3p orbitals as valence states. The FP-LMTO method used here makes use of smooth Hankel functions as the envelope function of the basis set. This leads to a larger basis set than those used in previous implementations of the FP-LMTO method without sacrificing the accuracy. It also uses a uniformly spaced mesh to describe the smooth part of the wave functions, charge density, and the potential. Thereby, it does no longer need any empty spheres. Finally, analytic calculation of the forces based on a suitable version of the force theorem is implemented in this method and automatic relaxation procedures can be used. The local spin-density approximation with the von Barth–Hedin parametrization is used as the exchange and correlation energy and potential.

To model the TM substitutional defects, a supercell of the zinc-blende structure with 64 atoms is employed. A supercell with one defect corresponds to 3% doping whereas with two defects corresponds to 6% doping. The percentage is here taken as percentage of the sublattice on which the substitution takes place. For the single defect case, the distance between the image impurities is about 8.72 A. A 4×4×4 shifted k mesh is employed, leading to four k points in the irreducible part of the Brillouin zone. While the interaction between defects is not entirely eliminated at this distance, it is sufficient to extract meaningful results.

III. MAGNETIC MOMENTS AND ENERGY LEVELS

The calculated magnetic moments for both Si and C site doping are presented in Fig. 1. It clearly reveals that the TM behaves differently at the Si and the C sites. The magnetic moments of the TM atoms change nonmonotonically when it is doped at the Si site. It shows that Ti, Fe, Co, and Zn are stable in the nonmagnetic state. Cr and Ni have the largest magnetic moments, 2 $\mu_B$, whereas Mn has only 1 $\mu_B$. In comparison with the other group IV (Refs. 16 and 19) and III-V semiconductors (also shown in Fig. 1), the magnetic moment is very small for Mn in SiC, indicating a significantly different electronic structure of the Mn impurity than in the other hosts. On the other hand, the early TM's show surprisingly high magnetic moments when doped at the C site. The magnetic moment is highest in Sc (4.5 $\mu_B$) and decreases gradually until it vanishes at Fe. The TM's later than Fe are all nonmagnetic. The spin-polarization energy is about 0.1 eV per Bohr magneton which is fairly high.

To understand all the above trends, especially the low-spin state of Mn at the Si site, we studied the projected density of states (PDOS) of the TM d states. These are not
mainly characterized as TM in Ref. 26. Although the peaks in the gap are shown here but can be found in a preliminary report of the present study in Ref. 26. The impurity energy levels are then defined by locating the relative position of these peaks to the valence band maximum (VBM). The levels for Si and C site doping are sketched in Fig. 2. The location of the VBM in the supercell was determined by inspection of the density of states, and is taken as zero reference energy in this figure. The experimental gap of 3C-SiC, 2.4 eV is used rather than the local-density approximation gap which is about 1 eV smaller. Since it is not a priori clear how the defect levels are affected by quasiparticle corrections, we do not apply any corrections to them. Also, even if some defect levels are accidentally close to the conduction band, they still are essentially localized levels in character, not shallow hydro-
genic defect levels derived from the conduction band. While we expect hybridization of the levels lying above the conduction band to from resonances and to be to some extent affected by quasiparticle shifts, we here make no attempt to estimate those effects quantitatively. We thus caution the reader that the energy-level positions should not be taken too literally. They primarily are of interest here to understand the trends with TM and the correlation of their filling with the magnetic moments. A detailed study of TM derived energy-level spectra would in any case require consideration of different charge states and many-electron multiplet configuration effects beyond the scope of this paper.

The defect levels are labeled according to the irreducible representations of the local point group \( T_d \). As is well known, in a tetrahedral environment, the \( d \) levels split into a \( t_2 \) and an \( e \) level with the \( e \) level lying below the \( t_2 \) level. Furthermore, there is a spin splitting of each of these. The dangling bonds surrounding the TM form a \( t_2 \) and an \( a_1 \) type energy level. The \( a_1 \) state occurs as a resonance in the valence band whereas the \( t_2 \) dangling bond superposition makes bonding and antibonding combinations with the crystal-field split \( t_2 \) type \( d \) level. We thus need to distinguish bonding and antibonding \( t_2 \) type levels. The bonding \( t_2 \) level is sometimes also called the crystal-field resonance (CFR) because it usually lies deep within the valence band. For Si-site doping in SiC, only Sc shows a bonding \( t_2 \) state in the gap. The bonding \( t_2 \) states of the other TM’s are buried deep into the valence bands. This bonding \( t_2 \) state is weakly spin polarized so that Sc is ferromagnetic with a very small polarization energy. The nonbonding \( e \) and the antibonding \( t_2 \) levels decrease in energy with increasing atomic number. They start out in the conduction band and enter the gap starting from V and Cr, respectively. When they are in the gap, they are spin polarized. But the spin splitting is always smaller than the crystal-field splitting (between \( e \) and \( t_2 \)). The \( e \) and the \( t_2 \) levels never cross. This is the reason why Cr, Mn, and Fe have low spin state in comparison with the other group IV semiconductors such as Si and Ge. The spin splitting disappears for Fe since the \( e \) state is fully occupied. The late TM’s such as Ni and Cu have slight spin splitting and the corresponding polarization energies are very small.

The situation at the C site is totally different. There the spin splitting is dominant for the early TM’s with a value of about 1 eV. On the other hand, the crystal-field splitting is only about 0.2–0.3 eV. Thus, the \( e \) and the \( t_2 \) states of each spin alternate and the electrons fill one spin channel for both \( e \) and \( t_2 \) states before filling the next spin channel.

To explain the obtained magnetic moments, a schematic energy-level diagram is shown in Figs. 3(a) and 3(b) for Mn at the Si site and Sc at the C site, respectively. Mn contributes five \( d \) electrons whereas Sc only one. Thus, the total number of electrons to fill the local \( d \) and dangling \( t_2 \) levels is nine and five for Mn and Sc, respectively, because there are four nearest-neighbor dangling bond electrons available. At the Si site, the TM-\( d \) level, labeled TM-\( t_2 \) in the figure and the C dangling bond C-DB-\( t_2 \) are strongly coupled because of their proximity in energy and induce a large crystal-field splitting. The states, which appear in the gap from V on, are the antibonding combinations that have therefore a

![Energy Levels at Si Site](image-url)

![Energy Levels at C Site](image-url)
slightly stronger dangling bond character than TM character, and thus low spin splitting. The bonding counterparts filled with six electrons form the CFR lying progressively deeper in the valence band. The large spin splitting in an isolated TM atom is thus heavily suppressed by the above coupling and the electrons fill both the spin-up and the spin-down channels for each level sequentially. By the filling with nine electrons, Mn obtains a net magnetic moment of 1 \( \mu_B \) in the \( e \) level. Following the same reasoning, Cr has a magnetic moment of 2 \( \mu_B \) at the Si site. The magnetic properties of the other TM’s can also be explained accordingly. The non-magnetic states of Ti and Fe are the results of the full occupation of the bonding \( t_2 \) and \( e \) states respectively. On the other hand, the zero spin polarizations for Co and Zn are caused by the delocalization of the antibonding \( t_2 \) states.

In contrast, for the C site doping, the coupling between the TM \( d \) states and the Si dangling bond states (Si-DB-\( t_2 \)) is very weak because they are far from each other in energy. As the TM \( d \) levels are lower than the dangling bond level \( sp^3 \) hybridized states of Si), the bonding \( t_2 \) states mainly consist of the TM-\( t_2 \) orbitals whereas the antibonding \( t_2 \) states mainly consist of the dangling bond Si-DB-\( t_2 \) states which lie high up in the conduction band. As a result, the TM impurity at the C site behaves rather like an isolated atom and satisfies the Hund’s rule. The large spin splitting remains, although it is still slightly smaller than in the free atom. The electrons now fill the majority spin channel of both \( e \) and \( t_2 \) states first before starting to fill the minority spin channel. Consequently, the magnetic moment is 5 \( \mu_B \) for Sc and decreases gradually to 0 for Fe since both the \( e \) and bonding \( t_2 \) states are fully occupied. The actual magnetic moment is found to be somewhat lower for Sc because of the delocalization. The antibonding \( t_2 \) states are not spin polarized because they are composed mainly of the dangling bond states. Thus, the late TM impurities show no magnetism at the C site.

The observed strong interaction for TM on the Si site and weak interaction for the C site is perhaps a little surprising from the point of view that the C-dangling bond orbitals may be expected to be less extended than the Si dangling bonds. Clearly, this difference is primarily due to a match or mismatch in energy. For a TM on a C site, the surrounding positively charged Si atoms provide an attractive potential, lowering the TM \( d \) states to be well below the high-lying Si dangling bond states. For a TM on a Si site, on the other hand, the surrounding negatively charged C atoms push the TM \( d \) level up to being close to the C dangling bonds with which a strong hybridization takes place.

The general competition between covalency (strong \( e-t_2 \) coupling) and spin polarization was also noted in Ref. 19 in the case of TM in Si. The situation in SiC is rather different though because of the relative energy positions of the TM \( d \) states with respect to the mostly C-like valence-band maximum. Whereas in Si, the TM-\( t_2 \)-like states are always well inside the valence band forming a resonance, they here lie within the band gap for the early TM’s. This is simply a result of the relative position of the C-like valence band with respect to the TM \( d \) levels on an absolute energy scale. Hence there is a very strong tendency towards high-spin states for the C site for the early TM’s. Unfortunately, the Si site appears to be the favored site for substitution on the basis of the energy of formation, as will be discussed in Sec. IV and thereafter the high-spin state for the C site will be shown to be suppressed when atomic relaxations are included in Sec. VI.

IV. SITE PREFERENCE

To study the site preference for substitution, we calculate the formation energy for all the TM’s at both Si and C sites. The energy of formation is defined as

\[
\Delta H_f(TM_a) = E[SiC:TM_a] - E[SiC] - \mu_{TM} + \mu_a, \tag{1}
\]

where \( E[SiC:TM_a] \) is the total energy of the supercell with the TM impurity substituting at site \( a \), \( E[SiC] \) is the total energy of supercell of pure SiC without the impurity, \( \mu_{TM} \) is the chemical potential of the TM, and \( \mu_a \) is the chemical potential of the atom substituted, \( a \) being Si or C. The chemical potentials depend on the growth conditions but their range of variation is restricted by thermodynamic considerations of chemical equilibrium. It is convenient to define excess chemical potentials as the difference between their absolute values \( \mu^e \) and their values in a chosen bulk reference state, \( \mu^0 \), i.e., \( \mu^e = \mu^0 + \mu^e \). For simplicity, we will from here on drop the superscript \( e \) and assume that all chemical potentials represent excess quantities. For each element, a positive excess chemical potential means that the element will precipitate out in its bulk elemental form and thus one condition is that \( \mu_{Si} = 0 \) for each component in the system. The condition for the chemical equilibrium with SiC is

\[
\mu_{Si} + \mu_C = \Delta H_f(SiC), \tag{2}
\]

and the allowed ranges of Si and C excess chemical potentials are

\[
\Delta H_f(SiC) \leq \mu_{Si} \leq 0, \tag{3}
\]

\[
\Delta H_f(SiC) \leq \mu_C \leq 0.
\]

For the TM’s we arbitrarily pick \( \mu_{TM} = 0 \) corresponding to equilibrium with bulk TM. In fact, this ignores the possibility
of carbide and silicide formation, which we will examine in Sec. VII. In this section, we are primarily interested in the energy difference between Si and C substitution, for which the value of \( \mu_{\text{TM}} \) is irrelevant as long as we choose it the same for C substitution as for Si substitution.

The formation energies, \( \Delta H_f(\text{TM}_C) \) and \( \Delta H_f(\text{TM}_\text{Si}) \) are shown in Fig. 4 for both the Si-rich and C-rich cases. It clearly reveals a large formation energy difference for the two sites, in fact of order of several eV and a strong preference to substitute at the Si site. This tendency is stronger for earlier TM and has a minimum for Co and Ni. It should be noted that even in the unfavorable case of the Si-rich limit, substitution on the Si site is strongly preferred over substitution on the C site. This is not a surprising result since the ionicity is totally different for C and the TM and there is a large mismatch between their ion sizes. Only the neutral charged states are considered here, so there is no dependence on the electron chemical potential. The chemical potentials of the substituted atoms do play a role. However, it is too small to change the substitution preference. Relaxation effects also do not change this conclusion as will be discussed in Sec. VI.

The energies of formation for the Si site are of the order of a few eV per TM atom, which indicates that a reasonable solubility is expected. On the other hand, for the C substitution of the early elements we find a very high energy of formation. In fact, this is largely due to the neglect of relaxations. The fairly large early TM atoms do not fit at all in the C site, because their bond lengths with Si are strongly compressed. Relaxation effects will be discussed in Sec. VI but we already indicate here in Fig. 4 that these strongly reduce

The energy of formation for the C site to a more reasonable value. Nevertheless, the C site always stays at higher energy than the Si site. One may notice that the effect decreases as we go towards the middle TM’s since these become smaller and do fit in better in the C site. On the Si site, on the other hand, the relaxation effects are small

**V. MAGNETIC ORDERING**

The doping rate for (Ga,Mn)As can be as high as 8%. As shown by a theoretical study, the Mn impurities have a tendency to cluster. The neighboring magnetic coupling in the case of GaAs was found to be ferromagnetic for Mn and Cr but antiferromagnetic for Fe and was explained by van Schilfgaarde and Mryasov in terms of the d-level filling following the Anderson-Hasegawa model of ferromagnetic double exchange being favored versus antiferromagnetic superexchange.

To study this neighboring coupling in SiC, we place two TM impurities as nearest neighbors in one 64 atom supercell. By nearest neighbors we here mean fcc-sublattice nearest neighbors because we assume that the doping will either be on Si site or C site but not mixed. The magnetic moments and the energy differences between the FM or AFM and the nonmagnetic state are listed in Table I. In the FM case, the total magnetic moment per unit cell is given divided by 2 because there are two magnetic impurities per cell. In the AFM case, the total magnetic moment per cell is zero. Thus, the moments are estimated from the local PDOS in each TM atomic sphere. We find in all cases that the magnetic moment is almost completely confined to the Mn site, so that this is an excellent approximation. The main result of these calculations is that the magnetism is strongly suppressed by the interactions between near-neighbor TM’s both for substitution on Si and C sites. The only exceptions are Cr and Mn at the Si site, which are therefore highlighted in the table. Furthermore, we can see that Cr appears to favor ferromagnetic and Mn antiferromagnetic coupling. The magnetic moments per atom for Cr and Mn in the FM case are the same as for single doping. The moments in the AFM case differ substan-
and considers only the singly occupied levels of the dimer. The bonding and antibonding states are mainly resulting from indirect interactions via the intervening ligands (here C atoms if the TM substitutes on a Si site). Thus, the interactions are called double exchange in the FM case and superexchange in the AFM case. If the neighbors have parallel spins (FM case) the resulting levels of the dimer are

\[ \pm V \] for the spin-up derived levels

\[ J \pm V \] for the spin-down derived levels, \( J \geq 2V \) \( J < 2V \), assuming that the spin-up levels have the lower energy in the atoms. If the neighbors have antiparallel spin, then the levels of the dimer are

\[ (J/2) \pm \sqrt{(J/2)^2 + V^2} = \begin{cases} \frac{-V^2}{J} & \text{for } -\text{sign} \\ \frac{V^2}{J} & \text{for } +\text{sign} \end{cases} \] (5)

FIG. 5. Energy levels and filling in the Anderson-Hasegawa model for Mn and Cr pairs of FM or antiferromagnetically aligned spins.
generally favors antiferromagnetic alignment because of their nonzero overlap and the fact that the TM here are rather close to each other.

In summary of this section, the AH model applied to the levels of $e$ symmetry predicts Cr to have AFM coupling and Mn FM coupling. The latter is in agreement with our full potential and relaxed calculations to be discussed below, but in disagreement with our unrelaxed ASA result. The discrepancy can possibly be explained by incorporating a mixing of $e$ and $t_2$ states. For Cr, the calculations show that FM is preferred, which we again interpret as an indication that the $e$ states cannot be exactly half filled by admixture of the $t_2$ states.

VI. RELAXATION EFFECTS

The main results were so far obtained from the ASA calculations without relaxation. Although we have not yet completed a full study of the relaxation effects in all cases, we have investigated the most important cases, or rather addressed specific questions that arose from the ASA results.

One may expect a stronger relaxation for the C- than for the Si-site substitution on the basis of the atomic sizes. Figure 6 shows the covalent radius and the $2+\text{ ion radius}$ for TM’s and the covalent radii of some group III, IV, and V elements. While doped at the Si site, the TM is neither covalent nor 2+ ionic. So its radius should be in between the two extreme states but probably closer to the covalent radius. As shown, the Si covalent radius is right in this region. One can expect a small relaxation while doping the Si site with TM’s. On the other hand, the C covalent radius is much smaller, so a larger relaxation is expected for TM doping. This may enhance the coupling between the TM $d$ states and the neighboring dangling bonds and thus may affect the preference for a high-spin state.

Thus two question arise: (1) can this change the site preference, and (2) how will this affect the unusually high magnetic moments for the C-substitution case? Full-potential calculations for Sc, Ti, and V show that the relaxation energy is substantial but not large enough to interchange the site preference. For instance, for C-rich chemical potentials, the relaxed (unrelaxed) energies of formation for Sc, Ti, and V are, respectively, 0.66 Ry (1.68 Ry), 0.82 Ry (1.54 Ry), and 1.00 Ry (1.58 Ry). These correspond to relaxation energies of $-14 \text{ eV}$, $-9 \text{ eV}$, and $-8 \text{ eV}$ as already indicated in Fig. 4. This trend can be easily understood: as the TM decreases in size it fits better in the C site and has less compressed TM-Si bonds. The Si-TM bond lengths change by 26%, 20%, and 15%, respectively. This relaxation is obviously outward, because the typical Si-TM bond length is larger than the Si-C bond length.

On the other hand for Mn and Cr on the Si site, we obtain bond length relaxations of only 5% and 3% and relaxation energies of only $-0.35$ and $-0.02 \text{ eV}$. We did not perform the corresponding calculations for Sc, Ti, and V at the Si site because these calculations are time consuming and our main interest here was to check the unusual result of the high magnetic moments for the C site and the results for the most important cases for magnetism, namely, Mn and Cr. However, it is clear that our conclusion on the Si-site preference will not change because relaxation of the Si site can only lower its energy, not increase it.

On the other hand, the effect of the relaxations for the C-site magnetic moment is indeed important. The magnetic moments for Sc, Ti, and V reduce to $1\mu_B$, $0\mu_B$, and $1\mu_B$ instead of $4.5\mu_B$, $4\mu_B$, and $3\mu_B$ without relaxation. Clearly, the strong relaxation leads to a stronger hybridization with the Si dangling bonds and hence a suppression of the magnetism.

Next, we further investigate the most important case for magnetic coupling: Mn and Cr on the Si site. As already mentioned, the relaxation effects for the single substitution are small in this case. What about the neighboring pair substitution? Figure 7 shows the relaxation of the tetrahedron containing the two Mn and the nearest-neighbor C atom.
CrC have a rocksalt structure, which is common for all the transition metal carbides. Thus, the bond angle of Mn-C-Mn has a slight tendency to approach 90°. But as shown in Fig. 7, this angle is 106.8° for a relaxed tetrahedron, indicating that the relaxation is small.

As for the magnetic ordering, the conclusion of FM ordering for Cr remains confirmed by the FP-LMTO calculations including relaxation. On the other hand, the conclusions on the magnetic ordering for Mn change dramatically from our ASA calculations. First of all, we find that even without relaxation the FP-LMTO method indicated a preference for ferromagnetic ordering as opposed to AFM ordering. We have already mentioned that the appearance of an antiferromagnetic ordering is unexpected on the basis of the Anderson-Hasegawa model and required a rather subtle explanation involving the proximity of the \( t_2 \) levels leading to an increased magnetic moment for the AFM case. The full-potential calculation, in principle, is more reliable, so we must conclude that the actual coupling is ferromagnetic. Furthermore, if we recalculate the energy difference between FM and AFM states of the relaxed structure (found with FP-LMTO) with ASA, we find also ferromagnetism to be preferred. In conclusion, while the preference for AFM in ASA is in disagreement with the FP-LMTO results for the unrelaxed structure, ASA and FP agree that FM is preferred for the relaxed structure. Clearly, the competition between FM and AFM tendencies is rather subtle in this case and sensitive to the computational method. However, the final conclusion is that independent of the method the relaxed geometry for the Mn neighboring pairs prefers a ferromagnetic alignment and this is also in agreement with the prediction of the AH model because the bands are not half filled.

VII. THERMODYNAMIC CONSIDERATIONS

An important consideration for the feasibility of obtaining a dilute ferromagnetic semiconductor is the solubility limit and the competition with TM-compound formation. While strictly speaking nonequilibrium growth techniques may overcome some of these limitations, it is important to be aware of the thermodynamic equilibrium conditions to provide guidance for tuning the growth conditions appropriately.

TM's typically can form both carbides and silicides. The equilibrium conditions for these phases provide more stringent restrictions on the chemical potential of the TM, than the one already discussed, namely, we must have \( \mu_{\text{TM}} \leq 0 \) to prevent precipitation of bulk TM. For instance, if a compound \( \text{TM}_n\text{Si}_m \) exists, then we must have

\[
n \mu_{\text{TM}} + m \mu_{\text{Si}} \leq \Delta H_f (\text{TM}_n\text{Si}_m) \tag{6}
\]

in order to prevent precipitation of \( \text{TM}_n\text{Si}_m \). It is instructive to plot the equilibrium lines for various phases in a graph of \( \mu_{\text{TM}} \) as a function of \( \mu_{\text{Si}} \). We assume throughout that the equilibrium with SiC is satisfied such that \( \mu_{\text{C}} = \Delta H_f (\text{SiC}) \). In Figs. 8, 9, and 10 we show such plots for Ti, Mn, and Cr, respectively.

We here use experimental data from Ref. 28 where available and complement them with calculated values in some cases. Specifically, since no experimental data were available for MnC, MnSi, and CrC, we calculated them by performing FP-LMTO calculations of their cohesive energies and subtracting from them the corresponding calculated cohesive energies of the TM’s in bulk and those of diamond Si and C. For Cr we used the experimental bcc structure and for Mn fcc. While the actual structure of Mn at low temperature is rather complex, fcc is a high-temperature phase. We found fcc to have lower energy than bcc by 0.09 eV per atom and
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not to have a magnetic moment. It is important in these calculations to use the same approximations for the different cases. For MnC and CrC, we used the rocksalt (B1) structure while for MnSi, we used the B20 structure, of which FeSi is the prototype. As an example for SiC, this gives $\Delta H_f$/SiC $\approx 0.65$ eV while the experimental value is 0.68 eV. For the TM compounds somewhat larger errors are expected. For C and Si we used the diamond structure, thus neglecting the small energy difference between graphite and diamond for C. For consistency, we used the experimental value 0.68 eV for the energy of formation of SiC in the figures where the other energies of formation were also obtained from experimental values, i.e., in Figs. 8 and 10, but the calculated value in Fig. 9. In any case, this choice makes little difference because theory and experiment are in excellent agreement with each other.

In these figures, the more we go to the right, the closer we approach the Si-rich limit. Beyond $\mu_{Si}>0$, bulk Si would precipitate. On the left the Si-poor limit is restricted by $\mu_{Si} > \Delta H_f$/SiC, beyond which bulk C (presumably graphite) will precipitate. In order to prevent either TM-carbide or silicide or metallic TM from precipitating, $\mu_{TM}$ must stay below each of the lines and below zero. The carbide lines correspond to positive slope, the silicide lines to negative slope. For instance for Ti, we see that for most of the range the upper limit of $\mu_{Ti}$ is determined by the very strong tendency to form TiC. Only in the very Si-rich limit, TiSi$_2$ places a stronger restriction on $\mu_{Ti}$.

For Mn, we see that the opposite is the case. In fact, we found that MnC has a positive energy of formation of 0.61 eV per MnC formula unit and thus does not come into play. MnC in B1 structure was found to have a high density of states at the Fermi level and to develop a magnetic moment of about 1.3$\mu_B$. Without the magnetization stabilization energy the energy of formation would have been 0.71 eV. In any case, because of its positive energy of formation, it comes not into consideration as a possible equilibrium phase. This also agrees qualitatively with the results of Ref. 29 which provides experimental estimates of the cohesive energy of B1 MnC and ASA calculations. The experimentally known compound Mn$_5$C$_3$ only becomes stable for very C rich and sufficiently high Mn chemical potential above the range where already MnSi is also stable. For MnSi in the B20 structure, however, we found a negative energy of formation of $-0.99$ eV/formula unit which makes it the limiting phase for all values of chemical potential. We used the calculated value of $\Delta H_f$/SiC in Fig. 9 to be consistent with the calculated values for MnSi on which we could not find experimental data. Nevertheless, it should be noted that the chemical potential of Mn can be allowed to be much higher than that of Ti without producing MnSi. If we want to prevent silicide formation, we need to keep $\mu_{Mn}$ roughly below $-0.5$ eV and work near the Si-poor, C-rich limit. This means that $\Delta H_f$/SiC:MnSi reported in Fig. 4 must be increased by $0.5$ eV compared to its value using $\mu_{Mn}=0$. This will limit the concentration of Mn that is allowed but not nearly as much as in the Ti case.

For Cr, we also found CrC in the B1 structure to have a positive energy of formation of 0.75 eV (nonmagnetic) simi-
lar to MnC. For CrSi, our FP non-spin-polarized calculations give $\Delta H_f$/CrSi = $-0.55$ eV compared to $-0.61$ eV experimentally. Including spin polarization, we find a small magnetic moment of 0.6$\mu_B$ and a magnetic stabilization energy of only 2.4 meV/CrSi unit. We see that Cr is a less strong silicide former and for Si-poor conditions, the $\mu_{Cr}$ becomes limited by the formation of Cr$_x$C$_2$. Similar to Mn, the restrictions on the $\mu_{Cr}$ are not too strong. In Fig. 10 we used only experimental data.

In conclusion, it turns out that the two cases of interest for magnetic semiconductors, Cr and Mn are not strong carbide formers and thus in the Si-poor limit, where one wants to operate to optimize substitution on Si site, carbide formation does not impose too strong a restriction on how rich one can make the system in the TM. Nevertheless, silicide formation slightly restricts how rich one is allowed to make the system in the TM.

Finally, it is also important to consider the magnetic properties of the expected precipitates. CrSi was reported to be either weakly paramagnetic or diamagnetic while MnSi has a helical spin structure below its Néel temperature of 29 K. This is qualitatively consistent with the small values of the energy difference between spin-polarized and non-spin-polarized calculations we obtained. Thus, it appears unlikely that ferromagnetic precipitates would give the misleading impression of dilute ferromagnetism.

VIII. CONCLUSIONS

In conclusion, we found that the magnetic properties of the 3d TM are totally different for its Si-site and C-site substitutions. For Si-site doping, the strong coupling with the surrounding C dangling bonds causes a large crystal-field $e$-$t_2$ splitting that overtakes the spin polarization. As a result, the TM is in a low-spin state, especially Cr has a magnetic moment of 2$\mu_B$ whereas Mn has only 1$\mu_B$. As for the C site, the crystal-field splitting is weak and the TM behaves more like an isolated atom. So the large spin splitting remains for the early TM’s. Including the four electrons from dangling bonds, the TM develops very high spin states for early TM’s such as Sc, Ti, and V. Unfortunately, the energy-of-formation calculations indicate that the C site is not really accessible since the Si site is strongly preferred as substitution site over the C site, even in the unfavorable Si-rich case. Relaxation calculations using the FP-LMTO method indicate that this conclusion holds even when the relatively strong relaxation for C sites is included. They also indicate that the strong magnetic moments for early TM’s on the C site are quenched by increased hybridization with the Si-dangling bonds after relaxation. An important conclusion one can draw from our calculations is the following. While the theory of Dietl et al. predicts that low Z element semiconductor hosts are favorable for a higher $T_c$ because of an increased $p$-$d$ exchange coupling, we see that smaller interatomic distances also lead to stronger hybridization and covalency effects, which are in competition with the magnetism and lead to lower magnetic moments.

The interactions between near-neighbor dopants strongly suppresses the magnetism except for Cr and Mn doped at the Si site. The preferred coupling was found to be definitely...
ferromagnetic for Cr whereas for Mn the results depend sensitively on relaxation and computational method. For unrelaxed structure and using the atomic sphere approximation adopted throughout most of the paper, Mn-Mn coupling was found to be antiferromagnetic. For relaxed structures, however, the coupling was found to be ferromagnetic whether full-potential or atomic sphere approximation was used. The ASA unrelaxed results are unexpected from the point of view of the Anderson-Hasegawa model, which predicts exactly the opposite: Mn FM and Cr AFM because Cr corresponds to exactly half filling of the e-derived levels. A possible explanation for the occurrence of an AFM ground state for Mn is that some admixture of the nonbonding TM e states with nearby antibonding TM-t2 dangling bond C-DB-t2 states could take place, which would increase the magnetic moments in the AFM alignment case and thereby lower its energy. However, the FP-LMTO calculations in both relaxed and unrelaxed case actually provide a ferromagnetic ground state for Mn in agreement with the AH model. The FM ground state of the Cr case also indicates that some deviation from exact half filling of the e states occurs through admixture of the t2 states. In that case, the magnetic moments are found to be larger for the FM alignment and thereby favor it. In any case, even though the geometry relaxation of the pair substitutions is found to be small, it seems to favor ferromagnetic alignment. Finally, we pointed out that both Mn and Cr are favorable cases from the point of view of thermodynamics. In fact, even for C-rich, Si-poor conditions, which is the desirable regime for Si-substitution, these TM’s do not have a strong tendency to form TM carbidies. The Mn chemical potential is in fact restricted by the condition of not forming MnSi even in the most C-rich situation. Neither the silicides nor carbidies of Mn and Cr have very negative formation energies, however, thus allowing for a situation fairly rich in the TM before precipitation is expected. Even if precipitates occur, the MnSi and CrSi compounds are not expected to be ferromagnetic and would thus not obscure the dilute magnetic semiconductor ferromagnetism. Overall, then both Mn and Cr seem fairly good candidates for designing ferromagnetic semiconductors based on a SiC host. The fairly large energy stabilization of the FM versus the AFM state indicate that possibly a high Curie temperature may be achievable with these systems.

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