Exchange interactions and $T_c$ in rhenium-doped silicon: DFT, DFT + $U$ and Monte Carlo calculations

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Abstract

Interactions between rhenium impurities in silicon are investigated by means of the density functional theory (DFT) and the DFT + $U$ scheme. All couplings between impurities are ferromagnetic except the Re–Re dimers which in the DFT method are nonmagnetic, due to the formation of the chemical bond supported by substantial relaxation of the geometry. The critical temperature is calculated by means of classical Monte Carlo (MC) simulations with the Heisenberg Hamiltonian. The uniform ferromagnetic phase is obtained with the DFT exchange interactions at room temperature for the impurities concentration of 7%. With the DFT + $U$ exchange interactions, the ferromagnetic clusters form above room temperature in MC samples containing only 3% Re.

1. Introduction

Silicon doped with rhenium belongs to the widely studied class of materials called diluted magnetic semiconductors (DMS). In this class, the host materials belong to the group III–V, II–VI and IV semiconductors or transition metal oxides (DMO). Usually the dopants are the third-row d-elements, with Mn, Fe and Cr to be most frequently published [1–6]. Interestingly, the fifth-row elements, such as Re, show different properties, especially stronger hybridization with the host, and also deserve investigation [7]. DMS attract a great deal of attention, experimental and theoretical, because of their promising application in spintronics [8–10]. To be used in the fabrication of electronic devices, materials must preserve their properties in conditions much above room temperature. To date, a very few reports on accessing room temperature has been published, and still remain controversial because Curie temperature depends a lot on the sample preparation [11–14].

Amorphous silicon doped with rhenium is ferromagnetic at room temperature, but samples lose this property after a few months [15]. Basic theoretical information about single rhenium impurities in crystalline silicon, in various crystal positions and charge states, have been recently reported [7]. However, ferromagnetism in disordered materials is a complex phenomenon, where single-site impurity characteristics are as important as interactions between the magnetic centers, and also their clustering [4, 6, 16–19]. Therefore, here, a one step closer to the experiment is done and the work focus on magnetic interactions between two Re impurities embedded in the silicon substituitional sites. The calculations are performed within the density functional theory [20]. Simultaneously, the effect of Coulomb interactions is investigated by means of the DFT + $U$ scheme [21], since it is well known that the strong interactions within the d-shell favor Hund’s rules, change the local magnetizations and the binding between impurities, and they also strongly influence the anisotropy of interactions, as well as complex observables like the critical temperature [6, 22]. In the next step, the exchange interactions, obtained within the DFT and the DFT + $U$ methods, are used in Monte Carlo simulations of the Heisenberg model and the Curie temperature is estimated.

The main findings concern the geometric, magnetic and statistical effects. In the physics of short-distance interacting pairs, the local geometry plays a very important role, since two rhenium atoms attract each other and form the chemical bonds, which in turn affect very much the magnetizations. Therefore, these cells are relaxed in the calculations. Further, the ferromagnetic (FM) and the antiferromagnetic (AF)
energy difference is examined as a function of the Re–Re distance and orientation in the crystal. In both theoretical methods, the FM interactions are lower in energy. Moreover, in the DFT + U scheme the magnetic couplings are stronger and very anisotropic. The mechanism of magnetic interactions between Re impurities in silicon is the ferromagnetic superexchange. The formation energies calculated for all pairs lead to the close pair scenario with a very few single impurities. Clusters with more than two rhenium atoms are outside the scope of this theoretical study, but in future the aggregates of the substitutional and the interstitial impurities will be investigated too. Finally, the transition from a magnetically disordered to an ordered phase has been studied by means of MC simulations. It was found that this transition was different when the magnetic interactions calculated with the DFT or the DFT + U methods were embedded in the model. Two main results are obtained: (i) the uniform growth of the total magnetization with decreasing temperature using the pair interactions calculated within the DFT method and (ii) formation of magnetic clusters when the DFT + U interactions were implanted into the MC simulations, similar to the effect of superparamagnetic blocking [6].

This paper is organized as follows: in section 2 the computational details are given, in section 3 the results for close- and medium-distance pairs are collected, in section 4 the long range effects and magnetic anisotropy are described together with the formation energies of all Re–Re pairs, in section 5 the implication of calculated exchange interactions for the Curie temperature is discussed and the summary is given in section 6.

2. Computational details

The ab initio calculations of total energies were performed within the density functional theory [20], using the plane-wave pseudopotential code QUANTUM ESPRESSO [23]. The scalar relativistic pseudopotential for rhenium has been generated for the valence configuration 6s2 5d5, within the ultrasoft pseudopotential (USPP) scheme [24], including the scalar relativistic pseudopotential for rhenium has been applied in order to gather all possible directions with a minimal computational cost. The first Re atom was placed at the crystal site (0, 0, 0) and the second impurity was at the site (k, l, m) in units of the silicon lattice constant divided by four. We did not account for interactions of the impurities implanted in the calculated cells with their periodic images (atoms from the neighboring cells), since for neutral cells these effects are not very pronounced [29, 30]. All calculations were performed at the lattice constant of 10.32 au, which was optimized with the applied pseudopotentials.

Monte Carlo (MC) simulations of the thermal average of magnetization \( \langle M \rangle \) were performed using the Metropolis algorithm [31] with the Heisenberg Hamiltonian:

\[
H = -\frac{1}{2} \sum_{ij} J_{ij} S_i S_j.
\]

The interaction constants \( J_{ij} \) act between two impurities at sites \( i \) and \( j \), and they are equal to the total energy difference in the antiferromagnetic and the ferromagnetic state \( (E_{AF} - E_{FM}) \). Numbers \( S_i \) and \( S_j \) are magnetic moments (+1 or −1) at the doped sites.

The cells for the simulations have been constructed from \( L \times L \times L \) replicas of the eight-atom simple cubic cell. The periodic boundary conditions were applied in MC supercells. The critical temperatures \( (T_C) \) were estimated from the crossing of the fourth-order Binder cumulant [32] curves, defined as \( U_L(T) = 1 - \langle M^4 \rangle / (3 \langle M^2 \rangle^2) \), and calculated in cells of the size \( L = 16, 20 \) and 24. The number of MC measurements was 5000 sweeps per impurity, and for the warming 500 sweeps per impurity. Some of the MC simulations were repeated with higher number of sweeps per impurity, equal to 50 000, for both the warming and the MC measurements, to check the convergence. The sites for the impurities have been chosen randomly in 3D supercells according to an algorithm of the third-order Sobolev chains [33] in order to obtain a quasiniuniform random distribution. At the end, the average over 32 random geometries was taken to find the magnetization and the \( U_L \) curves. Simulations have been performed at the concentrations of 3, 5 and 7% for the GGA pair interactions, and at lower concentrations of 2, 3 and 5% for the GGA + U interactions (in this method the rhenium ions couple much stronger than in the GGA).

3. Results for close- and medium-distance pairs

In our previous work [7], the lattice relaxation around the substitutional site was negligible, but for the impurities which interact on a short distance the geometry optimization is important. Therefore, the positions of atoms in the cells with pairs: 111, 220, 113, 331 and 333 were optimized within the Newton–Raphson optimization scheme based on the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [34]. It is found that the optimized Re–Re distances for the close pairs are shorter, and that for medium separations these distances almost do not change; the corresponding numbers
All magnetizations in the GGA+U which are nonmagnetic when one starts from the AF state. The FM and the AF state, except the pairs 111 and 111R relaxations, e.g. 111R, 220R and 11¯3 are denoted by ‘R’ and results for the cells with considerable occupations of the minority spin e¯g moment is in the relaxed cell 11¯3. The magnetization of the AF state is largely reduced. The nonrelaxed pair 220 is magnetic in both the FM and the AF states. However, the 220 pair obtained within the GGA and GGA+U methods are higher than those obtained within the GGA+ method. This is the usual behavior, due to the previous calculations [7].

Table 1. Total/absolute magnetizations (in µB) in the cells in the FM state and absolute magnetizations for the AF state, and the impurities separations Rpair in (au).

| Pair | Rpair | MFM | GA | GGA+U | MAF | GA | GGA+U |
|------|-------|-----|----|-------|-----|----|-------|
| 111R | 4.18  | 0.00/0.00 | 1.57/1.76 | 0.00 | 0.00 |
| 111 | 4.47  | 0.00/0.00 | 1.83/2.12 | 0.00 | 2.90 |
| 220R | 5.57  | 1.29/1.45 | 1.96/2.47 | 0.00 | 0.00 |
| 220 | 7.30  | 1.86/2.06 | 1.99/2.49 | 1.14 | 2.04 |
| 113R | 8.30  | 1.10/1.20 | 1.99/2.30 | 0.85 | 1.69 |
| 113 | 8.56  | 1.70/1.84 | 1.99/2.29 | 1.42 | 1.86 |
| 400 | 10.32 | 1.86/2.04 | 2.00/2.38 | 1.44 | 2.12 |
| 331 | 11.25 | 1.76/1.89 | 1.99/2.33 | 1.40 | 2.10 |
| 333 | 13.41 | 1.81/1.98 | 1.98/2.32 | 1.82 | 2.24 |

are 6.4% for the 111 pair, 23.6% for 220, 3% for 113, 0.2% for 331 and 0.05% for 333. From now on, the relaxed cells are denoted by ‘R’ and results for the cells with considerable relaxations, e.g. 111R, 220R and 113R, will be presented in detail.

Table 1 collects the total and the absolute magnetizations per Re and impurities separations in the cells with short- and medium-distance pairs. In the GGA method, the very close medium-distance pairs. In the GGA method, the very close distances are 6.4% for the 111 pair, 23.6% for 220, 3% for 113, 0.2% for 331 and 0.05% for 333. From now on, the relaxed cells are denoted by ‘R’ and results for the cells with considerable relaxations, e.g. 111R, 220R and 113R, will be presented in detail.

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Table 2. Interactions Jint (in meV) between rhenium pairs. We assumed Jint being negligible for pairs: 755, 775, 777, 862, 866, 884 and 888 (256-atom cell). Ei is the formation energy (in meV) of the lower-energy magnetic phase for the given pair, with respect to the formation energy of the dimer 111R. The distance Rpair in (au) between Re–Re and the coordination number Npair of given distance impurities within the shell around the impurity ion at (0, 0, 0) are also given.

| Pair  | Npair | Rpair | Jint | Ei |
|-------|-------|-------|------|----|
| 111R  | 4     | 4.18  | 0.00/23.69 | —  |
| 111   | 4     | 4.47  | 0.00/65.30 | 224 |
| 220R  | 12    | 5.57  | 8.43/238.87 | 1171 |
| 220   | 12    | 7.30  | 40.41/139.80 | 1325 |
| 113R  | 12    | 8.30  | 2.18/96.31 | 1290 |
| 113   | 12    | 8.56  | 7.60/84.42 | 1340 |
| 331   | 12    | 11.25 | 9.68/46.24 | 1267 |
| 400   | 6     | 10.32 | 19.28/62.19 | 1220 |
| 333   | 4     | 13.41 | 4.22/10.66 | 1284 |
| 440   | 4     | 14.60 | 4.32/46.82 | 1237 |
| 444   | 8     | 17.88 | 2.62/4.52 | 1296 |
| 96-atom cell |
| 511   | 12    | 13.41 | 5.40/14.07 | 1233 |
| 531   | 24    | 15.26 | 7.43/21.94 | 1234 |
| 620   | 24    | 16.32 | 6.57/17.82 | 1230 |
| 533   | 12    | 16.92 | 2.96/7.72 | 1236 |
| 642   | 8     | 17.88 | 2.62/4.52 | 1240 |
| 128-atom cell |
| 711   | 12    | 18.24 | 3.56/10.25 | 1200 |
| 731   | 24    | 19.82 | 2.06/4.54 | 1203 |
| 800   | 6     | 20.64 | 1.75/11.04 | 1201 |
| 733   | 12    | 21.12 | 1.22/3.06 | 1204 |
| 822   | 24    | 21.89 | 1.67/3.69 | 1203 |
| 840   | 24    | 23.08 | 1.33/2.85 | 1200 |
| 844   | 24    | 25.28 | 0.69/0.89 | 1204 |
| 144-atom cell |
| 551   | 12    | 18.43 | 6.68/19.31 | 1182 |
| 553   | 12    | 18.78 | 1.13/3.03 | 1192 |
| 555   | 4     | 22.34 | 1.13/3.05 | 1192 |
| 660   | 12    | 21.89 | 6.74/23.31 | 1182 |
| 664   | 24    | 24.20 | 0.64/0.70 | 1191 |
| 256-atom cell |
| 751   | 24    | 22.34 | 0.43/1.07 | 1107 |
| 753   | 24    | 23.50 | 1.04/2.19 | 1105 |
| 771   | 12    | 25.67 | 1.93/4.34 | 1109 |
| 773   | 12    | 25.93 | 0.30/0.64 | 1103 |
| 880   | 12    | 29.19 | 0.65/5.60 | 1098 |

4. Long-distance pairs and magnetic anisotropy and formation energies

This section is focused on general trends in magnetic interactions for all pairs, and on the formation energies with respect to the most bound pair 111R; table 2 gathers all these numbers.
The formation energy of all pairs (except 111, which, however, is only given for comparison, to illustrate the relaxation effect) cost about 1 eV more than formation of the close 111R dimer. The fact that the GGA + U formation energies are lower than those from the GGA does not change the scenario of very close pairs. At this point, one could say that it is not worth dealing with the rest of the pairs because statistically there will be a very few of them in the sample. It would be reasonable to focus on clusters with more than two impurities and it will be the subject of future work. Now, the conclusions from medium- and long-distance pairs will be drawn, since in the large sample they also exist and mediate magnetic interactions for a long distance, as will be discussed in connection with the critical temperature.

The magnetic couplings $J_{\text{int}} = E_{\text{AF}} - E_{\text{FM}}$, obtained with the GGA method, decay quickly with the distance, and only the pairs in the 64-atom cell are strongly coupled, with the maximal exchange interaction found for the 220 pair. All pairs are coupled ferromagnetically (positive numbers $J_{\text{int}}$) in both methods applied here.

As for the anisotropy of magnetic interactions, the GGA numbers do not show any visible dependence on the crystal direction, while among the GGA + U values there is well-pronounced enhancement of the coupling along the 110 crystal axis. This direction is preferred for the couplings in zinc blende hosts, due to the zigzag chains, which mediate magnetic interactions via a small polarization of the host atoms neighboring the impurities. These polarizations are visible in the Löwdin population analysis [35] and amount to about 0.01–0.02 of electron charge per Si site.

The range of magnetic interactions in the GGA + U method is long. There are quite large $J_{\text{int}}$ numbers along the 110 direction for the distance over 20 au; these are, for instance, 23 meV for the 660 pair and about 6 meV for the 880 pair in the 256-atom cell. At long distances, even small couplings play a very crucial role in estimation of the Curie temperature, because they permit a percolation between impurities at small concentrations [36]. For instance, it is known that to get FM order at a concentration of 7%, the exchange interactions must extend to at least five coordination shells [6].

5. Critical temperatures

In this section, the discussion of the results of Monte Carlo simulations with the Heisenberg model is presented. The simulations were performed on a number of supercells with different sizes, and with various impurity distributions, and for a few concentrations. In the Hamiltonian, the Re–Re interactions $J_{\text{int}}$, calculated within the GGA and the GGA + U schemes (see table 2), have been used.

For the interactions $J_{\text{int}}$ obtained within the GGA method, which are rather not anisotropic in space, all samples start to magnetize at some temperature, and this magnetization saturates to high values of 0.7–0.95 per impurity, depending on the sample. The starting temperature for a visible rise of magnetization depends quite strongly on the geometry of impurities distribution. The Curie temperatures for the ferromagnetic order were estimated in two ways: (1) from the crossing of the magnetization curves and (2) from the crossing of the fourth-order cumulant curves [32]. These curves have been calculated for different supercell sizes, and each of these curves has been averaged over geometries of impurities distribution—as it is described in section 2.

The Curie temperatures, calculated with the aforementioned procedure, are presented in table 3. The temperatures obtained from the magnetization curve crossing are a bit lower than $T_{C}$ obtained from the cumulant curve crossing. The last
column shows the temperature at which the magnetization in samples starts to rise from zero \( T_{MC}^{M>0} \), and this temperature is not averaged over the impurities distributions, but it is given as a range in which fall the results from all the geometric samples used. This quantity shows how much the theoretical results for a given concentration differ just due to different distribution of impurities. It gives also an argument in the explanation why the experimental \( T_C \) published for the same material and concentration, vary a lot depending on the sample preparation.

In contrast to simulations with the GGA interactions, the GGA + \( U \) interactions implanted in the Heisenberg Hamiltonian usually do not lead to the total and uniform magnetization in the supercell. Independently of geometric parameters used in these simulations, negligible or very low magnetization is found for the samples (0.1–0.3 \( \mu_B \) per impurity) at most simulation temperatures. Interestingly, instead of homogeneous magnetization within a supercell that the ferromagnetic clusters form. In some samples there was a transition temperature at which there was found a large total magnetization, and below this temperature the magnetic clusters formed. In other samples, there is a smooth transition between a magnetically disordered phase and the phase with cluster structure. The magnetization of local clusters is also not full but grows with the decreasing temperature. One can only approximate the transition temperature by watching the pictures for different samples.

Figure 2 presents magnetization of one chosen geometric sample, calculated using the interactions from the GGA + \( U \) method, with impurity concentrations of 5%, at five temperatures: 116, 464, 696, 812 and 928 K. The sample size is \( L \times L \times L \times 8 \) with \( L = 20 \), and it is divided into a few boxes, and each of these boxes is of the size \( 4 \times 4 \times 4 \times 8 \);
thus, the whole supercell is divided into 5 × 5 × 5 pieces. Within each small box, the magnetization over impurities is averaged, and it is done over the spins obtained in the last MC measurement sweep. The 3D supercell is presented in the slices, which are cut parallel to the XY plane, and these cut slices are placed in figure 2 in columns. The averaged magnetization per impurity can take values from −1 to 1. Therefore the absolute value of box magnetization is marked by a circle with radius proportional to the magnetization and the spin direction (up or down) is depicted by the white and black colors.

One can see in figure 2 that the FM-order transition, in the presented sample, occurs between 820 and 900 K. In some other samples (not presented in figure 2), at the same concentration of 5%, the estimation of $T_{\text{FM}}$ is not so easy because one cannot find a temperature at which the total sample magnetizes; only the magnetic clusters slowly grow.

It is important to mention that this scenario with magnetic clusters does not change with a very large number of measurement sweeps, of 50 000 per impurity, and with the same number of warming sweeps in the MC simulations.

In table 4, there are listed the roughly estimated temperatures at which the cluster FM order starts to form, $T_{\text{FM}}$, for concentrations: 2, 3 and 5%. The range of these temperatures is wide, because the magnetic transition depends on the impurity distribution in the sample, as was the case with the GGA critical temperatures. At the concentrations above 4–5%, all samples form the magnetic cluster structure above room temperature.

It is known about the percolation that, if the impurity distribution is of cluster type and the clusters are large, then a superparamagnetic blocking phenomenon becomes important [6, 37]. In the simulations performed in this work, the distributions are uniform; nevertheless the superparamagnetic blocking occurs and the reason for this is the magnetic coupling of pairs which acts at a very long range. When during the MC simulations the magnetic clusters form, their internal coupling is so strong that it costs a great deal of energy to flip the whole cluster. Finally, the magnetic relaxation time is very long. Thus, the total magnetization, in some of the samples with the cluster structure, is close to zero over all temperatures, even after 50 000 MC measurements per impurity.

6. Summary

In this work, the rhenium pairs embedded in silicon in substitutional sites were calculated by means of the GGA and the GGA + $U$ methods. The formation energy of the closest pair is roughly 1 eV lower than those energies for the rest of the double combinations. This supports the cluster scenario with a very few single impurities and medium-distance pairs. It is common behavior of impurities in various DMS [16–19].

The calculated magnetic couplings $J_{\text{int}} = E_{\text{AF}} - E_{\text{FM}}$ are positive for all pairs, and very long range. The GGA couplings are not anisotropic with respect to the crystal axes. In contrast the GGA + $U$ interactions are much stronger along the 110 direction. At small distances, the Re–Re pairs become nonmagnetic for both the AF and FM phases, or only for the AF phase. At higher concentrations this effect is even stronger, but less pronounced in the GGA + $U$ method than in the GGA scheme.

The mechanism which drives this DMS magnetic is the ferromagnetic superexchange, with high critical temperatures exceeding room temperature, even for low concentrations of impurities of 7% for the GGA and 3% for the GGA + $U$. Magnetizations of Monte Carlo samples below critical temperatures are uniform for the GGA and different with the magnetic cluster structure for the GGA + $U$ scheme. Quite large and very extended magnetic couplings support percolation in this DMS and give hope to obtain still higher Curie temperature when the impurity clusters are included in the simulations.

The existence of the superparamagnetic blocking phenomenon below the Curie temperature is also plausible. But this scenario must be confirmed by further studies with clusters of the substitutionals and the interstitials together, and also employing a method for better treatment of the self-interaction effect in the host (silicon), namely the DFT with the pseudopotential self-interaction correction (pSIC) [38].

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