Electronic States of Mn$_4$ Complex Cluster in Silicon

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Abstract

Recently, Kreissl and Gehlhoff have observed an EPR spectrum which was associated with the Mn$_4$ complex cluster in Si. In order to account for the observed hyperfine lines a total spin $S = 6$ and an orbital singlet were ascribed to the complex. However, the same complex has been identified previously also by EPR in a pioneering work by Ludwig and collaborators, where a spin $S = 2$ was adopted to describe the observed hyperfine interactions. As an attempt to solve this controversy we have carried out, for the first time, SCF spin-polarized one-electron state calculations for the Mn$_4$ complex in Si. The calculations indicate that the reported interpretations of the EPR spectra ascribed to the Mn$_4$ complex in silicon must be reviewed.

Introduction

It is well known since the pioneering electron paramagnetic resonance (EPR) works of Ludwig and Woodbury that Mn leads to several deep level centers in Si [1]. Mn has been found in multiple charge states as isolated impurities in both, substitutional or interstitial sites. Pairs of Mn with shallow acceptor impurities or with other transition metal atoms have been identified. If favorable conditions for the migration of Mn atoms are created, complexes involving more than two Mn impurities are formed.

Ions of the 3d transition metal series, such as Mn, are mobile in Si even at room temperature. If samples containing only Mn are cooled slowly from elevated temperature, the impurities interact and form complexes. Ludwig, Woodbury, and Carlson (LWC) [2] were the first to show that, under the conditions described above, the dominant paramagnetic center is a complex composed of four Mn atoms. This composition was inferred from the observed EPR spectrum, which consists of 21 hyperfine (HF) lines, having a characteristic envelope of intensities, split by fine structure. Moreover, the symmetry of the spectrum shows that the four Mn atoms are equivalent and arranged in a tetrahedron.

Recently, Kreissl and Gehlhoff (KG) have also identified the Mn$_4$ complex in Si by EPR [3]. In order to interpret the spectrum ascribed to the complex, KG adopt a microscopic structure where the four Mn impurities, assumed in the neutral
charge state, are placed at nearest-neighbor tetrahedral interstitial sites. Figure 1(a) shows the HF structure or the “fingerprint” of the Mn$_4$ complex extracted from the observed EPR spectrum [2]. Figure 1(b) depicts schematically the microscopic structure of the complex used to interpret the EPR data [3].

For a complex defect in a tetrahedral symmetry, with an effective total angular momentum $\vec{J}$ and a nuclear spin $\vec{I}$, the HF interaction can be described by the spin-Hamiltonian

$$H_{\text{HF}} = A \vec{J} \cdot \vec{I}$$

where the interaction involving nuclei of the Si lattice are neglected [1]. The 21 HF lines observed from EPR, as depicted in Figure 1(a), should correspond to the $2I + 1$ values of the nuclear magnetic quantum number of the complex. Since the nuclear spin of a Mn is $I_{\text{Mn}} = 5/2$, the value of $I$ can be determined as

$$I = \sum_{i=1}^{4} I_{\text{Mn}} = 10$$

Thus, the interaction with four nuclear spins of Mn is directly inferred from the number of HF lines and their intensities.

According to KG, the consistency of the assumption concerned to the space distribution of the Mn atoms in the cluster follows from the measured value of the parameter $A$. The results 1.46 and 1.37 mT were reported by KG and LWC, respectively. These values are nearly 1/4 of the parameter $A$ of the isolated neutral Mn impurity placed at an interstitial tetrahedral site in Si, 1.47 mT [1].

The EPR spectrum associated to the Mn$_4$ complex is consistent with a ground state orbital singlet ($L = 0$). This assumption is supported by the isotropic $g$-value near 2 reported by KG (2.009) and LWC (2.0063). However, there is an essential point where these two EPR experiments are in contradiction. While LWC ascribes for the total spin of the complex the value $S = 2$, KG uses the value $S = 6$ to describe the EPR spectrum.

![Figure 1](image-url)

Figure 1. (a) Characteristic hyperfine structure observed in the EPR spectrum of the Mn$_4$ complex in Si according to Ref. [2]; (b) Microscopic structure of the complex assumed to interpret the EPR measurements. The four Mn neutral atoms are placed at the nearest-neighbor tetrahedral interstitial sites.
There are two different interpretations for the total spin of the complex [3]. In the so-called low-spin interpretation, every isolated Mn atom in the cluster has an orbital $l_i = 0$ and a low spin $s_i = 1/2$. By assuming the coupling between the $l_i$ values and a strong exchange coupling between the four isolated spins, the values $L = 0$ and $S = 2$ are obtained for the complex. In the so-called high-spin interpretation proposed by KG, the values $l_i = 0$ and $s_i = 3/2$ are ascribed to the isolated interstitial Mn atom [1]. Follows by exchange coupling that the spin of the complex runs from 0 to 6. Assuming strong ferromagnetic coupling, the value $S = 6$ is ascribed to the ground state of the complex.

In both interpretations described above the basic assumption that the magnetic properties of the cluster can be inferred directly from the magnetic properties of the isolated impurities is made. In order to fulfill such an assumption, it is necessary that the interactions between the Mn atoms be small. The strong localization of the 3d-derived orbitals on each Mn impurity is a fundamental requirement to preserve its magnetic properties. We show in this paper, however, that the total spin of the complex does not arise from the coupling between the angular momenta of four magnetic centers but is rather related to the molecular orbitals of the complex which are spread out over the entire cluster. A similar conclusion has been reached by Assali and Leite [4–6] and Assali et al. [7] concerning the interpretation of EPR experiments performed on transition metal-related pair complexes in Si.

The discrepancies observed between the results of the EPR experiments are not the only essential point concerned with the identification of the Mn$_4$ complex in Si. The discrepancies observed in the reported positions of the energy levels induced by the complex in the gap of the Si crystal are also quite controversial. The photo-EPR results obtained by KG suggest a donor level ($0^+/+$) at $E_c - 0.5$ eV, where $E_c$ denotes the bottom of the conduction band [3]. These authors have quoted in Ref. [3] the value $E_c - 0.28$ eV obtained from combined Hall-EPR experiments and the value $E_c - 0.54$ eV yielded by combined deep level transient spectroscopy-EPR measurements.

Unfortunately, electron-nuclear double resonance (ENDOR) of Mn$_4$ clusters in Si have not been successful so far. Without any additional study of this kind, it is not possible to know with a high degree of realism if the Mn atom sits at interstitial sites or at substitutional sites. Moreover, the EPR data yields the symmetry of the complex but cannot determine the size of the cluster.

Nevertheless, a theoretical study of the microscopic model which has been proposed for the Mn$_4$ complex in Si is highly desirable. The aim of our work is to report on the results of our attempt to describe the electronic structure of the four nearest-neighbor interstitial Mn cluster. Contrary to what has been supposed, the calculations reveal that the Mn atoms in this configuration are strong interacting impurities.

**Theoretical Model**

Despite the large amount of experimental work that has been performed to characterize deep-level centers in semiconductors, only recently significative efforts have
been made to interpret the results in terms of rigorous theoretical calculations. Although considerable progress has been achieved hitherto on the understanding of the properties of the isolated 3d transition metal impurities in semiconductors [8], the theoretical study of transition metal-related complexes in these materials is at its early stage. The theoretical attempts to describe the electronic structure of complex defects in Si have been recently reviewed by Leite et al. [9].

The calculations reported here have been carried out by using the multiple-scattering (MS) Xα theory within the framework of the Watson-sphere-terminated cluster model [10,11]. The results were obtained by adopting initially a 17Si-atom cluster in order to define the band edges of the perfect Si crystal. This model has been currently used to study substitutional impurities in Si [12-15] and other semiconductors [16,17]. In order to simulate the Mn4 complex in Si, a “defect” cluster with 21 atoms has been adopted. The cluster is comprised of a central Si atom surrounded by its four nearest neighbors and 12 next-nearest neighbors in a tetrahedral configuration compatible with the Si lattice geometry and four Mn atoms placed at the interstitial sites nearest to the Si central atom. The “defect” cluster is schematically shown in Figure 1(b) and is indicated here by 17Si + 4Mn.

The muffin-tin atomic spheres were chosen so as to touch each other having the same radii, consistent with the Si lattice parameter, 5.431 Å [18]. The sphere which surrounds the whole cluster touches the cluster surface atomic spheres and is coincident with the Watson sphere [19]. The exchange parameters α utilized were 0.72751 and 0.72700 for Si and Mn atoms, respectively [20]. We have used the values α = 0.72741 for the interatomic region and α = 0.72751 for the outer region. The inner atomic shells up to 2p in Si were kept frozen as in the free atom. All the electrons of Mn atoms were included in the self-consistent calculations. The basis set for the expansion of the wave functions included l = 0, 1, 2 for the outer region and for Mn and central Si atoms. For the remaining spheres the values l = 0, 1 have been used.

Successful applications of the Watson-sphere-terminated MS-Xα molecular cluster model to the study of complex defects in Si have been recently reported by Assali et al. [7], Assali and Leite [4,5,21], and Gomes and Leite [22,23]. It is worth mentioning that, in the present calculations and in the previous one as well, the relativistic effects and lattice relaxations and distortions were not taken into account. These effects have been found to be small for the 3d transition metal impurities in Si [8].

**Results**

An interstitial neutral Mn impurity in Si gives rise to deep donor levels in the band gap [8] and corresponds to a high spin state, S = 3/2, according to EPR experiments [1]. Following the Ludwig and Woodbury rule [1], which has been confirmed by the calculations for the case of Mn in Si, the 3d-atomic states of the impurity at interstitial sites split due to the crystal field in a threefold degenerate level, t̃2, and a twofold degenerate level, e, with t̃2 below e in the crystal band gap. The electrons which are occupying the atomic states 3d^54s^2 of Mn are then dis-
tributed in the $t_2$ and $e$ states in order to maximize the total spin of the center. Accordingly, the gap states induced by Mn in silicon have the configuration $t_2^3e^2$ which corresponds to the value $S = 3/2$ for the total spin. It is also found from the calculations that the interstitial Mn impurity induces an $e$ and a $t_2$ resonances within the valence band of the Si crystal. They are bonding states fully occupied by 10 electrons [8,24].

We now bring together four interstitial Mn atoms and allow them to interact. According to the group theory, the Mn 3d-atomic orbitals centered at the first "shell" of interstitial sites induce the $1a_1 + 2e + 2t_1 + 3t_2$ states in the crystal energy bands. If the interaction between the 3d states of different Mn atoms is very small, all these states will degenerate into the $t_2$ and $e$ states of the isolated interstitial Mn impurity. In this case we should be able to identify the states which are localized in every Mn atom and quite easily identify the four equivalent and independent individual spins. This fact must be true in order to support the hypothesis which has been adopted to interpret the EPR experiments.

Table I summarizes the main features of our calculations. The entries refer to the Mn 3d-derived gap levels and resonances identified in the $17\text{Si} + 4\text{Mn}$ cluster spectrum. They are classified according to the irreducible representations of the tetrahedral point group. All the levels, except for an $a_1$, were not present in the

<table>
<thead>
<tr>
<th>Level (occupancy)</th>
<th>Spin (occupancy)</th>
<th>$S = 0$ $E$ (eV)</th>
<th>Q (%)</th>
<th>$S = 6$ $E$ (eV)</th>
<th>Q (%)</th>
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<tr>
<td>$1t_2$ (6)</td>
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<td>$-0.91$</td>
<td>65</td>
<td>$-2.83$</td>
<td>84</td>
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<td></td>
<td>$\downarrow$ (3)</td>
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<td>$1e$ (4)</td>
<td>$\uparrow$ (2)</td>
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<td>$-3.01$</td>
<td>87</td>
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<tr>
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<td>$\uparrow$ (3)</td>
<td>$-0.39$</td>
<td>77</td>
<td>$-2.26$</td>
<td>39</td>
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<tr>
<td></td>
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</tr>
<tr>
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<td>85</td>
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* $E$ is the level position relative to the top of the valence band. $Q$ is the percentage of charge, normalized to one electron, within the Mn shell. $S$ is the total spin of the complex. The arrows indicate up ($\uparrow$) and down ($\downarrow$) spins.
"perfect" cluster spectrum; thus we interpret them as impurity states induced by the Mn₄ complex. The occupancy of these levels, as indicated in Table I, adds to 28 electrons as expected from the 3d⁵4s² electronic configuration of each Mn atom. The parameter Q in Table I indicates the percentage of charge, normalized to one electron, within the Mn shell. Except for the 4t₂ state, the charge concentration on the four Mn atoms is very high, indicating a strong localization of the 3d-derived states on the Mn shell. The comparison between the spectra of the "defect" and "perfect" clusters shows that one of the two a₁ states originates from the bulk. It mixes with the other a₁ state induced by the complex. Taking this fact into consideration and noticing that the 4t₂ state has only 25% of charge on the Mn shell, we conclude that the impurity bonding states induced by the Mn 3d atomic orbitals are exactly those predicted by group theory.

The first interesting feature which emerges from the calculations is that the ground state of the complex has total spin \( S = 0 \). The highest occupied level, 2e, is filled with four electrons; thus no EPR signal is expected from this closed shell system. However, the complex induces a sequence of unoccupied states in the gap. The entries in Table I show that these levels are close enough to favor excited states with different values for the total spin. This finding may solve the controversy related to the fact that the complex have been observed in two different configurations. In order to exploit this idea one step further, we have simulated various spin configurations for the complex, by populating the lowest unoccupied levels and by carrying out the calculations to the spin polarized limit.

We have chosen to discuss here the results obtained for the total spin \( S = 6 \). Table I displays the exchange splittings of the impurity levels and the charge redistribution which follows the spin alignments. The 28 electrons are now distributed between up and down spins as indicated in Table I, leading to the value \( S = 6 \) for the complex.

We emphasize now the fact that the four interstitial Mn atoms are strong interacting impurities. In order to do that, we depict in Figure 2 the Mn 3d-derived energy levels for an isolated interstitial impurity and for the Mn₄ complex in both spin configurations, \( S = 0 \) and \( S = 6 \). The levels ascribed to the complex are those listed in Table I. Figure 2(a) shows the positions of the energy levels t₂ and e, relative to the top of the valence band, \( E_v \), induced by the isolated interstitial Mn impurity in Si, according to a non-spin-polarized cluster model calculation performed by DeLeo et al. [24]. We observe that the crystal field splittings of the Mn 3d states, or the energy differences between the e and t₂ levels, are about 0.35 eV for the resonances and 0.25 eV for the gap levels. Figure 2(b) shows, for the case \( S = 0 \), the spread of the Mn 3d states which occurs when the Mn₄ complex is formed. The bonding states, which run from 1t₂ to 3t₂ in Figure 2(b), span a region of 1.43 eV. This spread, which is mostly due to the Coulomb interaction between the d states of different Mn impurities, is about five times larger than the crystal field effect on the d states of the isolated impurity.

If we simulate now the spin \( S = 6 \) for the complex, the spread of the Mn 3d states, which runs from 1e↑ to 3t₂↓ states in Figure 2(b), increases to 4.1 eV. If the fact that the 4t₂↓ state has now 45% of charge inside the Mn shell is taken into
account, we conclude that this spread is even larger, say, 4.7 eV. In other words, about 16 times larger than the crystal field effect on the d states of the isolated impurity.

Table I shows that for the $S = 6$ spin configuration of the complex, the highest occupied level is $2t_2\downarrow$, with two electrons, placed at $E_v + 0.31$ eV. Although this may be taken as an indication that the complex can give rise to a donor level close to midgap, total energy calculations are required in order to obtain a more reliable value.

Conclusions

The crystal field effect on the 3d states of an isolated interstitial Mn impurity in Si is about 0.3 eV. We have shown that this effect combined with the Coulomb interactions between the 3d states of the four Mn atoms in the Mn$_4$ complex produce a spread of about 1.4 eV. If the spin polarization effects are included by simulating the total spin of the complex from $S = 0$ to $S = 6$, we have demonstrated that the spread of the 3d states increases from 1.4 to 4.7 eV, respectively. These results indicate a rather large Coulomb and exchange interactions between the d states as compared to the same effects observed for the isolated Mn impurity. We conclude that the four Mn atoms in the cluster are strong interacting impurities, which determines the failure of the assumptions previously made to interpret the experimental results.
Therefore, the different spin configurations of the complex do not arise from the coupling between the equivalent four independent centers but originates from the different electronic populations of the molecular orbitals of the complex.

We have also shown that the Mn$_4$ complex in Si leads to occupied and unoccupied levels in the band gap, each close to the other. This finding opens the possibility for several spin states, which could provide explanation for the controversy related to the fact that two different spins have been ascribed to the complex.

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