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Site occupation and electronic structure of an interstitial Mn^{2+} impurity in GaP

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Abstract. The site occupation and electronic structure of an interstitial Mn^{2+} impurity in GaP are studied using the discrete-variational local-spin-density-functional method with cluster models. The results verify the conjecture of van Gisbergen *et al* that the Mn^{2+} impurity prefers the interstitial site surrounded by four nearest-neighbour Ga atoms and show that a small host crystal relaxation and a large formation energy of the impurity measured with respect to GaP and Mn^{2+} occur. Two deep donor levels are found in the host crystal band gap owing to the presence of the impurity. The behaviour of the impurity is analysed and compared with results of the EPR experiment.

1. Introduction

Transition-metal (TM) impurities in semiconductors have attracted a great deal of attention for many years owing to their important roles from both a technological and a theoretical point of view [1–5]. They are commonly associated with deep levels within the host crystal band gap and appear as contaminants, or deliberately introduced into the crystal for different purposes. In group-IV elementary semiconductors, single TM impurities can be on both substitutional and interstitial sites, although they favour the interstitial positions under normal diffusion conditions [6]. In compound semiconductors the situation is different. In these crystals, single TM impurities are found on substitutional sites replacing the cations. They can also form complexes with other atoms, while remaining on substitutional sites.

Recently, van Gisbergen *et al* [7] observed a new EPR spectrum of Mn in neutron-irradiated GaP. They identified that the Mn is an interstitial impurity in a $2+$ charge state with the effective spin $S = \frac{5}{2}$. On the basis of some empirical analyses, they further inferred that Mn^{2+} was on the interstitial site surrounded by four nearest-neighbour Ga atoms. Because this is the first observation of an interstitial TM impurity in a III–V compound semiconductor, it is interesting to know the behaviour of an interstitial Mn^{2+} in GaP. To our knowledge, however, there has not been a theoretical study of this.

In this paper, we study the site occupation and electronic structure of an interstitial Mn^{2+} impurity in GaP using the discrete-variational (DV) local-spin-density-functional (LSD) method with cluster models. The cluster models and computational parameters are described in section 2. Our results and discussion are presented in section 3. Finally, conclusions are given in section 4.

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2. Cluster models and computational parameters

Cluster models which have been used successfully to study impurity problems in semiconductors [8–10], are adopted in this paper. In cluster models, the perfect crystal is simulated by the cluster containing a certain number of the host atoms with an appropriate boundary condition (hereafter called the perfect cluster), and the impurity-doped crystal is simulated by the so-called defect cluster, which can be obtained by suitable modifications of the perfect cluster. For GaP, we chose two clusters $\text{Ga}_4\text{P}_6\text{Ga}_{12}\text{P}_4$ and $\text{P}_4\text{Ga}_6\text{P}_{12}\text{Ga}_4$ as our perfect clusters. They represent an interstitial centre coordinated by four first-shell atoms, six second-shell atoms, 12 third-shell atoms and four fourth-shell atoms with T_d symmetry. For an interstitial Mn^{2+} in GaP, the corresponding defect clusters $\text{MnGa}_4\text{P}_6\text{Ga}_{12}\text{P}_4$ and $\text{MnP}_4\text{Ga}_6\text{P}_{12}\text{Ga}_4$, are formed by placing Mn^{2+} at the interstitial centre of the perfect cluster.

In our calculations, two kinds of boundary condition are added to clusters for different purposes. The first is the free boundary condition, in which the problem of the saturation of the dangling bonds at the cluster surface is not considered. It is used to determine the site occupation of an interstitial Mn^{2+} and the relaxation of the host crystal. In this kind of study, we are interested only in the difference between the binding energies of clusters, which should not be changed greatly by the choice of boundary conditions [11]. We shall further examine the accuracy of such an approximate approach in section 3.1.

In order to calculate accurately the electronic structure of GaP with and without an interstitial Mn^{2+} impurity by cluster models, however, the problem left out above must be considered. To solve the problem, we add the second kind of boundary condition—the Watson sphere boundary condition [12–14]—to clusters. In this boundary condition, the rest of the crystal at the cluster boundary is simulated by first identifying V , the number of electrons in the cluster which corresponds to the valence states of the perfect crystal. In a GaP crystal, each atom is surrounded by four atoms of the opposite sort arranged at the corners of a regular tetrahedron, and Ga and P atoms have three and five valence electrons, respectively. According to the sp^3 hybridization, Ga and P atoms contribute $0.75e$ and $1.25e$ to each of Ga–P bonds between one crystal atom and its four nearest neighbours, respectively. Thus, V is the sum of the valence electrons of Ga and P atoms contributing to all the saturated Ga–P bonds in the cluster. If N is the total number of valence electrons in the cluster, there will be $N - V$ electrons filling dangling bonds at its surface. These electrons are transferred to a sphere (Watson sphere) surrounding the cluster and are kept fixed throughout calculations. Two of our clusters, namely $\text{Ga}_4\text{P}_6\text{Ga}_{12}\text{P}_4$ and $\text{MnGa}_4\text{P}_6\text{Ga}_{12}\text{P}_4$, will be treated with this boundary condition in section 3.2. The cluster $\text{Ga}_4\text{P}_6\text{Ga}_{12}\text{P}_4$, a perfect cluster, has $V = 56$ and $N = 98$; so we eliminate dangling-bond effects by transferring $N - V = 42$ electrons to the Watson sphere. For the defect cluster $\text{MnGa}_4\text{P}_6\text{Ga}_{12}\text{P}_4$, we assume that it has the same crystalline environment as the perfect cluster. That is to say, it has the same Watson sphere as the perfect cluster. The Watson sphere radius is chosen as the average distance of the outermost-shell atoms in the cluster and the first-shell atoms outside the cluster to the centre of the cluster, i.e. 11.14 au.

The binding energy and electronic structure of clusters are performed using the DV LSD method. This method is a kind of molecular orbital calculation method and its theoretical foundation is LSD theory. Since it has been described in detail elsewhere [15–17], here we do not give a further description. In our calculations, the numerical atomic basic functions are chosen as the variational basis set, which are obtained from the self-consistent atomic local-density-functional (LDF) calculations. The exchange–correlation potential is taken to be of the von Barth–Hedin [18] form, with the parameters taken from the work of Moruzzi *et al* [19].

3. Results and discussion

3.1. Site occupation

As an interstitial impurity, the Mn^{2+} ion may occupy two different sites in GaP. One is the interstitial site surrounded by four nearest-neighbour Ga atoms (hereafter, site A). Another is the interstitial site surrounded by four nearest-neighbour P atoms (hereafter, site B). We determine the site occupation of the Mn^{2+} ion by comparing the formation energies of the impurity at sites A and B. In cluster models, the formation energy of the impurity, measured with respect to the host crystal and impurity ion, can be expressed approximately as [20]

$$E^F = -[E^{\text{tot}}(\text{defect cluster}) - E^{\text{tot}}(\text{perfect cluster}) - E^{\text{tot}}(\text{impurity ion})] \quad (1)$$

that is

$$E^F = E^b(\text{defect cluster}) - E^b(\text{perfect cluster}) \quad (2)$$

where E^{tot} and E^b are the total energy and binding energy, respectively, of a cluster. Thus, for site A, we have

$$E_A^F = E^b(MnGa_4P_6Ga_{12}P_4) - E^b(Ga_4P_6Ga_{12}P_4). \quad (3)$$

For site B, we have

$$E_B^F = E^b(MnP_4Ga_6P_{12}Ga_4) - E^b(P_4Ga_6P_{12}Ga_4). \quad (4)$$

According to the EPR experiment [7], the Mn^{2+} ion has a tetrahedral symmetry environment in GaP, i.e. there is only a symmetry distortion around the impurity. In order to evaluate the distortion effect, we allow the first-shell atoms to relax symmetrically outwards and inwards from the impurity ion in the defect clusters, holding the remaining atoms in the clusters fixed at their ideal lattice positions. By calculating E_A^F and E_B^F versus this relaxation, we find that the first-shell Ga atoms around the impurity at site A relax outwards, while the first-shell P atoms around the impurity at site B relax inwards (figure 1). This observation is consistent with the fact that Ga atoms have net positive charges while P atoms have net negative charges in the partially ionic semiconductor GaP. At the equilibrium configurations, we obtain $r_{Mn-Ga} = 4.49$ au and $E_A^F = 11.30$ eV for Mn^{2+} at site A, and $r_{Mn-P} = 4.32$ au and $E_B^F = 10.65$ eV for Mn^{2+} at site B. These values indicate that a small host crystal relaxation and a large formation energy of the impurity occur. Comparing the equilibrium values of E_A^F and E_B^F , we can conclude that the interstitial Mn^{2+} impurity prefers the site surrounded by four nearest-neighbour Ga atoms in GaP, which verifies the conjecture of van Gisbergen *et al.*

The accuracy of our approximate approach is examined by performing binding energy calculations to determine the equilibrium positions of the first-shell atoms of the perfect clusters $Ga_4P_6Ga_{12}P_4$ and $P_4Ga_6P_{12}Ga_4$. Just as we have done for the impurity clusters, we allow the first-shell atoms of the perfect clusters to relax symmetrically outwards from and towards the interstitial centres, holding the remaining atoms fixed at their ideal lattice positions. Figure 2 shows the curves of the binding energy versus the displacement of the first-shell atoms from the ideal lattice positions for the two clusters. One can see that the first-shell atoms of cluster $P_4Ga_6P_{12}Ga_4$ relax inwards 0.09 au, and those of cluster $Ga_4P_6Ga_{12}P_4$ outwards 0.03 au. Meanwhile, the change in the binding energy caused is less than 0.1 eV for both clusters. These results indicate that the surface dangling bonds in the free boundary condition have a very small influence on the local geometry around the interstitial centre and on the change in the cluster binding energy. Thus, it is possible for us to determine the site occupation of an interstitial Mn^{2+} impurity in GaP using the free boundary condition.

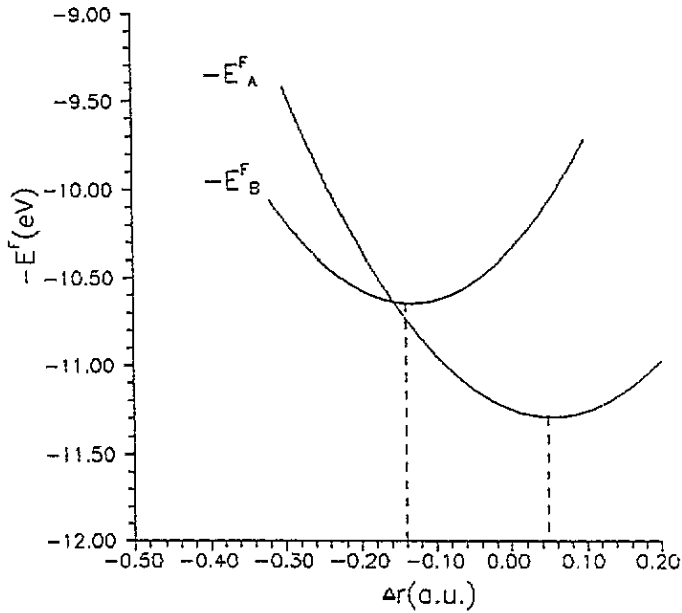


Figure 1. The formation energy of the Mn^{2+} impurity versus the displacement of the first-shell atoms of the defect clusters in T_d symmetry. The negative displacement is towards to the centre.

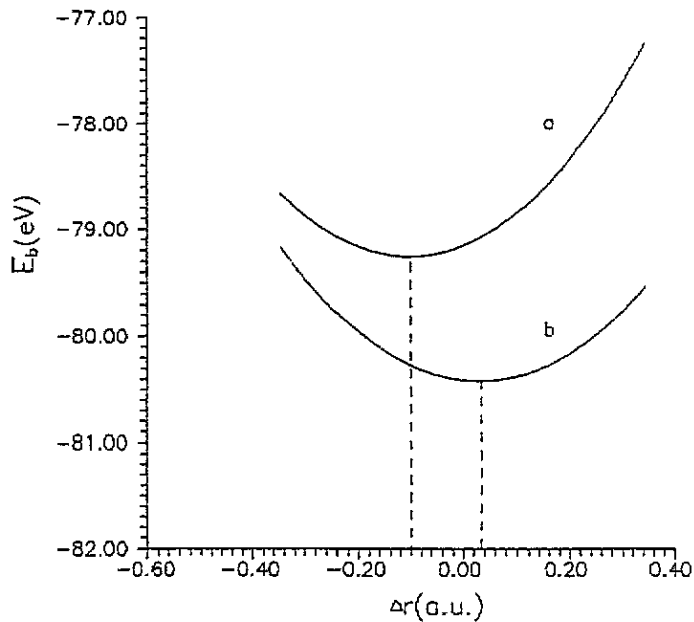


Figure 2. The cluster binding energy versus the displacement of the first-shell atoms of the perfect clusters: curve (a), $\text{P}_4\text{Ga}_6\text{P}_{12}\text{Ga}_4$; curve (b), $\text{Ga}_4\text{P}_6\text{Ga}_{12}\text{P}_4$. The negative displacement is towards the centre.

3.2. Electronic structure

With the site occupation and local relaxation obtained above, we further calculate the electronic structure of the interstitial Mn^{2+} impurity in GaP, using the defect cluster $MnGa_4P_6Ga_{12}P_4$ under the Watson sphere boundary condition.

For the perfect cluster, the lowest occupied molecular orbital (LOMO), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are $1a_1$, $2e$ and $4a_1$, respectively. The energy difference between the HOMO and the LUMO is the so-called crystal gap E_g in cluster models, which is 1.70 eV. The energy difference between the HOMO and the LOMO is defined as the valence band (VB) width E_{vb} , which is 10.7 eV. These two values are in good agreement with the bulk-crystal values ($E_g = 1.50$ eV and $E_{vb} = -12.3$ eV) obtained by Wood and Zunger [21] within the LDF approximation, and comparable with the experimental values [22] $E_g = 2.35$ eV and $E_{vb} = 12.8$ eV.

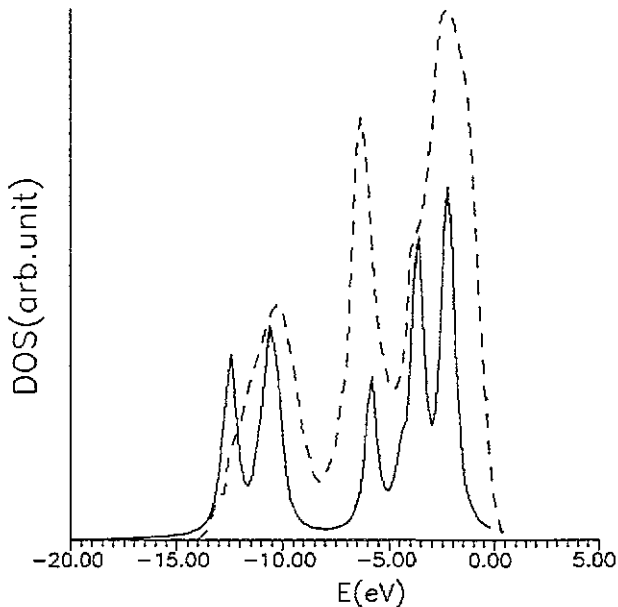


Figure 3. The calculated DOS for the perfect cluster $Ga_4P_6Ga_{12}P_4$ (—) and the photoemission spectrum of GaP crystal (---).

Figure 3 presents the densities of states (DOS) for the perfect cluster, which is obtained by a Lorentzian extension of the occupied levels and a summation over them. As a comparison, the photoemission spectrum [22] of a GaP crystal is also included in figure 3. From figure 3, one can see that the peaks in our DOS are almost in one-to-one correspondence to those in the experimental spectrum. All the above results obviously suggest that the electronic environment in this cluster is already reasonably bulk like, and the Watson sphere boundary condition can be used to study the impurity problems in GaP.

In the defect cluster, the Mn 3d levels are split into states of e and t_2 symmetry by the tetrahedral field of the neighbouring host atoms. The e and t_2 components hybridize with ligand states of e and t_2 symmetry, respectively, leading to $2e$, $3e$, $5t_2$ and $6t_2$ levels with substantial d-like character. Table 1 gives the orbital populations of these levels. From this table, one can see that the levels $2e\uparrow$, $3e\downarrow$, $5t_2\uparrow$ and $6t_2\downarrow$ have strong contributions from

Table 1. The orbital populations of the impurity-related levels.

Level	Centre	First shell	Second shell	Third shell	Fourth shell
	Mn	Ga	P	Ga	P
2e↑	67	1	26	6	0
2e↓	16	4	61	19	0
3e↑	29	7	45	19	0
3e↓	77	4	9	10	0
5t ₂ ↑	62	5	23	7	3
5t ₂ ↓	1	8	66	23	2
6t ₂ ↑	4	11	64	17	4
6t ₂ ↓	66	20	3	3	8

the Mn 3d states (62–77%), while the levels 2e↓, 3e↑, 5t₂ ↓ and 6t₂ ↑ have small Mn 3d character (less than 30%).

Among the impurity-related levels mentioned above, two levels 3e↑ and 5t₂ ↓ appear in the vicinity of the host band gap (now the 2t₁ ↓ is taken as the VB edge instead of the 2e in the perfect cluster). They are both donor levels. The 3e↑ is below the conduction band (CB) edge, at $E_c - 0.25$ eV, while the 5t₂ ↓ is just above the VB edge, at $E_c - 1.69$ eV. If we bring our underestimated band gap result of GaP into close agreement with experiment by shifting the VB levels down with respect to the CB, the same correction procedure would probably lower positions of the donor levels relative to the CB by an amount comparable with the shift in the VB levels [23]. As a result, the corrected donor levels are expected at $E_c - 0.90$ eV and $E_c - 2.34$ eV, respectively.

Although the calculated energies indicate that the 3e↑ and 5t₂ ↓ levels are both deep donor levels, their wavefunctions are nonetheless long ranged. This point can be seen in table 1, where the 3e↑ and 5t₂ ↓ levels have strong contributions from the second- and third-shell atoms in their formation.

Table 2. The Mulliken populations for the atomic orbitals.

Atom	Charge	Net spin	Atom	Charge	Net spin
Mn 3d	5.28	4.33	P(2) 3s	1.83	0.00
4s	0.53	0.08	3p	3.54	0.03
4p	0.49	0.07	Total	5.37	0.03
Total	6.10	4.48	Ga(3) 4s	0.34	0.00
Ga(1) 4s	1.25	0.00	4p	0.12	0.00
4p	1.18	0.03	Total	0.46	0.00
Total	2.43	0.03			
P(4) 3s	1.38	0.02			
3p	0.42	0.00			
Total	1.80	0.02			

The Mulliken populations for atomic orbitals are listed in table 2. From this table, one can obtain that the charges and net spins on the Mn 3d shell are 5.28 and 4.33, and those on the Mn 4s shell are only 0.53 and 0.08, respectively. We use these values to estimate the hyperfine parameter A of the interstitial Mn²⁺ impurity in GaP. According to Low's [24] analysis, the hyperfine parameter A can be considered as having three parts: a contribution due to unpaired s electrons (Fermi contact interaction), a contribution due to spin-orbit coupling, and an orbital contribution. Since the orbital part is zero in T_d symmetry and the spin-orbit part is very small, the main contribution to A comes from the contact

interaction. The Fermi contact interaction means that the electron density is not zero on the Mn nucleus. It results from the residual spin density in the 4s shell, and polarization of the inner s shells by the spin density in the 3d shell. The contribution of the inner s shells to the hyperfine parameter is negative and that of the 4s shell is positive. A free Mn^{3+} ion with configuration Ar $3d^5$ has a hyperfine splitting due to the polarization of the 1s, 2s and 3s electron shells by the half-filled 3d shell. This gives a hyperfine interaction parameter $A = -304$ MHz [25]. Compared with 5.0 net spins on the 3d shell of a free Mn^{2+} ion, 4.33 net spins on the Mn^{2+} 3d shell in the defect cluster lead to a localization of 86% of the $3d^5$ electrons on the Mn core. From this, if the small admixture of spin density in the 4s shell is not considered, we can estimate that $A = -263$ MHz, which is close to the experimental value, $A = -266.8$ MHz [6].

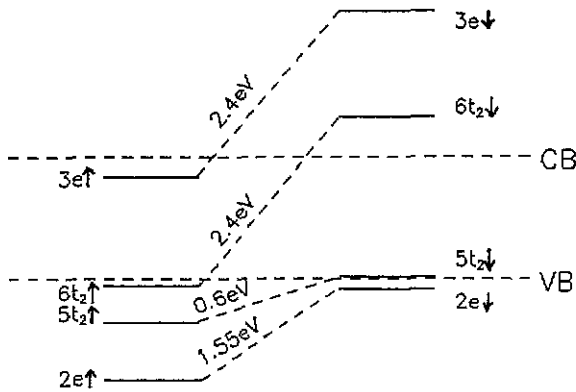


Figure 4. Crystal-field splittings and exchange splittings of the impurity-related levels.

Owing to the strong interaction between the d states and the tetrahedral crystal field, the crystal-field splitting of the Mn^{2+} 3d levels in GaP is of the order of 1.5 eV (figure 4). The impurity-related levels also have a significant exchange splitting, in a range from 0.6 to 2.4 eV. The large exchange splitting results from the facts that the Mn^{2+} impurity is in a high-spin state with the effective spin $S = \frac{5}{2}$ and that there is a large difference between the Mn 3d contributions in the spin-up and spin-down levels.

4. Conclusions

In summary, we have investigated the site occupation and electronic structure of an interstitial Mn^{2+} impurity in GaP using the DV LSD method and cluster models. The results verify the conjecture of van Gisbergen *et al* that the Mn^{2+} impurity prefers the interstitial site surrounded by four nearest-neighbour Ga atoms and show that a small host crystal relaxation and a large formation energy of the impurity measured with respect to GaP and Mn^{2+} occur. Two deep donor levels $3e\uparrow$ and $5t_2\downarrow$ are found in the host crystal band gap owing to the presence of the impurity. Their energy positions are predicted to be at $E_c - 0.90$ eV and $E_c - 2.34$ eV, respectively. Their wavefunctions are found to be of a rather long-range nature. A large localization of the $3d^5$ electrons on the Mn core and a small Mn 4s spin-density admixture are obtained. The hyperfine parameter A is estimated to be -263 MHz, in good agreement with the EPR experimental value (-266.8 MHz). In addition, the crystal-field splitting and exchange splitting of the impurity-related levels are analysed and discussed.

Acknowledgments

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