

Role of oxygen defects in diluted Mn:Ge

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The effects of spurious oxygen atoms on the electronic and magnetic properties of Mn-doped germanium are studied using *ab initio* calculations. Several different sites together with the formation of some defects complexes are investigated and analyzed looking at the energetics, structure, and electronic and magnetic properties of Mn and O incorporation into bulk Ge. Our study shows that the oxygen presence always lowers the heat of formation of Mn impurities in Ge thus favoring Mn incorporation; however, this result is found to be strongly dependent on the sites occupied by Mn and O and by their chemical potential. We find that oxygen binds with Ge through hybridization of their p states, while a relatively more ionic bond is found between Mn and O. As a result, Mn at low-oxygen concentrations keeps its magnetic moment and ferromagnetic alignment provided that no Mn-neighboring atoms are present. Moreover, oxygen remarkably lowers the heat of formation for Mn adsorption in interstitial sites, both tetrahedral and hexagonal, making their energy cost very similar.

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I. INTRODUCTION

Dilute magnetic semiconductors keep capturing the attention of the scientific community: exploiting several different controlled growth procedures and extremely accurate characterization techniques it has been possible to obtain several materials with rather different characteristics. However, still many problems must be solved before these materials could be massively used for technological applications. One of the main problems is related to the rather low dilution of magnetic impurities (mainly $3d$ transition elements) within the semiconductor matrix achievable before precipitation and/or phase segregation of undesired metallic phases takes place. In the most studied (Ga,Mn)As system, problems occur due to segregation of the more stable MnAs compound and to antisite Mn-As defects,¹ while in Ge other intermetallic compounds may form²⁻⁵ (mainly Mn_5Ge_3 and $\text{Mn}_{11}\text{Ge}_8$), thus hindering perfect dilution and consequently changing the transport and magnetic properties of the material. Focusing on the MnGe system, a system which has been steadily attracting interest due to its potential integrability within Si semiconducting technology, a quite broad literature has built up in the past few years including epitaxial growths (mainly molecular beam epitaxy),²⁻⁵ Mn-ion implantation^{6,7} into Ge single crystals, and furnace melting.⁸ To these *bulklike* growths, we should add the growth of nanostructured MnGe—nanowire arrays of MnGe have been recently obtained and structurally characterized,⁹ while low-temperature thin-film growth has been shown to lead to Mn-rich nanocolumns or to Mn_5Ge_3 nanoclusters embedded in the Ge matrix depending on growth conditions.¹⁰ As observed in the epitaxial growth of thin-film systems, in addition to possible undesired phases, oxygen contamination may substantially affect the surface of the sample, possibly masking the magnetic properties of the bulk layers as recently suggested.¹¹ Moreover, oxygen might play a role in the magnetic properties of the nanowire arrays since those are grown within anodized aluminum oxide membranes containing arrays of nanopores used as templates for nanowires growth.⁹ The oxygen presence has been clearly revealed by extended

x-ray-absorption fine structure (EXAFS) measurements,¹² although its effect on the nanowire magnetic properties is not yet clear at all. In this framework, we use first-principles calculations to investigate the role that oxygen might play in the electronic and magnetic properties of the compound.

The goal of the paper is to shed light on the mechanisms that may drive undesired clusters formation and on the effects that such small clusters may have on the magnetic properties of the compound. To this end, several different adsorption sites for Mn as well as oxygen are investigated also considering formation of defects such as Ge vacancies and kick-out processes. We find that oxygen lowers the formation energy of Mn incorporation such that it preferentially binds with germanium and not always lowers the total magnetic moment.

The work is organized as follows: In the Sec. II, we briefly describe the theoretical methods and provide computational details. In Sec. III, we illustrate our results for the different structures considered. In Sec. IV we discuss their electronic and magnetic properties. Finally, in Sec. V, we draw our conclusions.

II. COMPUTATIONAL DETAILS

The calculations were performed using the VASP package¹³ within generalized gradient approximations (GGA) (Ref. 14) to density-functional theory. PAW pseudopotentials¹⁵ were used for both Ge and TM atoms with semicore $3p$ and $3s$ states kept in the core shell. The kinetic energy cutoff used for the wave functions was fixed at 250 eV. In the low-doping limit ($\text{Mn}_x\text{Ge}_{1-x}$, $x=3.125\%$ and 1.6%), we considered 32- and 64-atom cells, [bcc cell with $(111)a$, $(-1, 1, 1)a$, and $(-1, -1, 1)a$ lattice vectors and $2 \times 2 \times 2$ diamond cubic cells, respectively] at the experimental Ge lattice constant ($a_{\text{expt}}=5.636 \text{ \AA}$) reproduced within about 2% by GGA calculations ($a_{\text{theo}}=5.776 \text{ \AA}$). The $(8,8,8)$ and $(4,4,4)$ k -point shells were used for the 32- and 64-atom cells, respectively, within the Monkhorst-Pack scheme. All the atomic internal positions were relaxed following the *ab initio* forces.

Different adsorption sites for both O and Mn were investigated together with the vacancy-oxygen complex (VO) (and, similarly, the vacancy manganese), which can occur as common defects in crystalline Ge.^{16,17} These are common in ion-irradiated Ge samples; however, vacancies are intrinsic defects in crystalline Ge and it is not unreasonable to foresee that, if there is oxygen around, it could be trapped as a VO complex having rather low formation energy. Growth of the Ge nanowires through the membrane templates, in fact, may benefit from a rather large oxygen environment that could be incorporated into the crystalline structure of the wire.

We started our investigation looking at the possible sites that the Mn atom might occupy within the Ge structure, namely, substitutional and interstitial. Then, we considered several possible nearby sites for the oxygen atom, once again substitutional and interstitial. We also considered the possibility of having several oxygens nearby occupying different sites together with configurations, in which the oxygen atoms bridge two different Mn impurities.

A. Heat of formation

The stability of defects at thermodynamic equilibrium is related to its heat of formation ΔH defined as

$$\Delta H = E^{\text{def}} - n_{\text{Ge}}\mu_{\text{Ge}} - n_{\text{O}}\mu_{\text{O}} - n_{\text{Mn}}\mu_{\text{Mn}}, \quad (1)$$

where E^{def} is the total energy of the defective cell; n_{Ge} , n_{O} , and n_{Mn} are the numbers of the atoms constituting the defective cell; and the values of the chemical potentials μ_{Ge} , μ_{O} , and μ_{Mn} are usually taken considering the system in equilibrium with the bulk form of the constituent atoms, i.e., antiferromagnetic (AFM) fcc Mn, bulk Ge zinc blende, and molecular O_2 , respectively. However, in this case, we should consider equilibrium with other possible competing phases that may as well form and segregate such as bulk MnO, GeO_2 , and Mn_5Ge_3 . This can be done considering variations of the chemical potentials in the range of values compatible with all the different equilibria, thus looking at the stability of the possible precipitates defined as¹⁸

$$E_{\text{GeO}_2} < E_{\text{Ge}}^{\text{bulk}} + 2\mu_{\text{O}} = \mu_{\text{Ge}}^0 + 2\mu_{\text{O}}; \quad (2)$$

that is, GeO_2 compound is stable if its total energy does not exceed the sum of the chemical potential of the constituents. Here and in the following, the Ge chemical potential is assumed equal to its bulk value (Ge-rich conditions). Based on the same argument, for MnO and Mn_5Ge_3 , we have

$$E_{\text{MnO}} < \mu_{\text{Mn}} + \mu_{\text{O}},$$

$$E_{\text{Mn}_5\text{Ge}_3} < 5\mu_{\text{Mn}} + 3E_{\text{Ge}}^{\text{bulk}}.$$

Now, using the total energies of the stable separate constituents and referring the chemical potentials to their respective bulk values

$$\Delta\mu_{\text{O}} = \mu_{\text{O}} - \frac{1}{2}E_{\text{O}_2} = \mu_{\text{O}} - \mu_{\text{O}}^0$$

and

$$\Delta\mu_{\text{Mn}} = \mu_{\text{Mn}} - \frac{1}{2}E_{\text{Mn}}^{\text{AFM-fcc}} = \mu_{\text{Mn}} - \mu_{\text{Mn}}^0,$$

we can rewrite Eq. (1) as

TABLE I. Summary of structural results for oxygen substitution in Ge (32 atoms/cell).

Structure	ΔH (eV/cell)	$d_{\text{Ge-O}}$ (Å)
Ge O_S	-0.76	2.19
Ge O_T	+0.34	2.16
Ge 2O_S	-2.12	2.04
Ge 3O_S	-4.21	1.95
Ge 4O_S	-5.31	1.89
Ge 4O_S^{int}	-4.41	2.06
Ge 4O_T	+1.72	1.91
Ge vacancy	1.69	$d_{\text{Ge-V}}$ 1.93
O-V	-0.93	1.89
O_S -Ge $_T$	-0.99	1.76
GeO_2 rutile	-5.76	1.87-1.90

$$\Delta H = E^{\text{def}} - n_{\text{Ge}}\mu_{\text{Ge}} - n_{\text{O}}\Delta\mu_{\text{O}} - n_{\text{Mn}}\Delta\mu_{\text{Mn}} - n_{\text{Mn}}\mu_{\text{Mn}}^0 - n_{\text{Ge}}\mu_{\text{Ge}}^0 - n_{\text{O}}\mu_{\text{O}}^0 \quad (3)$$

with the following constraints:

$$\Delta H_f^{\text{MnO}} < \Delta\mu_{\text{Mn}} + \Delta\mu_{\text{O}}, \quad (4)$$

$$\frac{1}{2}\Delta H_f^{\text{GeO}_2} < \Delta\mu_{\text{O}} \leq 0.0, \quad (5)$$

$$\frac{1}{5}\Delta H_f^{\text{Mn}_5\text{Ge}_3} < \Delta\mu_{\text{Mn}} \leq 0.0. \quad (6)$$

Stability of the defective cell is therefore achieved if the heat of formation as calculated from Eq. (3) is negative at chemical potential values satisfying the above conditions.

III. STRUCTURAL RESULTS

A. Defects in Ge

We first focus on oxygen incorporation into pure Ge, which will then be used as reference. We considered three different possibilities: (i) oxygen at substitutional sites (O_S), (ii) oxygen at the interstitial tetrahedral site (O_T), and finally (iii) the VO complex. The results obtained considering the chemical potential of molecular O_2 (that is a vanishing $\Delta\mu_{\text{O}}$ in the above equations) are reported in Table I. We observe that the heat of formation calculated for multiple oxygen substitutions (2, 3, and 4) scales linearly with the number of substitutional atoms and that the range of variation of the oxygen chemical potential that could make the defective cell stable is confined in a narrow energy region ($-1.4 \leq \Delta\mu_{\text{O}} \leq 0.0$ eV). This shows that, for equilibrium growth, the defective cell will be stable only at rather low-O concentrations when the GeO_2 compound will not form. It is interesting to observe, however, that substitutional sites are favored over interstitial sites and that stability is favored by a larger number of oxygen substitutions. Moreover, we note that the Ge-O

bondlength approaches those in stable rutile GeO_2 compound as the number of substitutions increases and that the structure in which one Ge is fully oxygen coordinated (4 O) is energetically less stable than the one in which the same number of oxygen atoms occurs on different neighboring Ge sites. Four-oxygen substitutions generate quite large local stresses since deviations from the ideal Ge-Ge bondlength (2.44 Å) are quite remarkable in all the structures considered. Finally, we observe that the defect complex made of a Ge vacancy and an interstitial oxygen nearby (VO) is far more stable than bare-oxygen substitution (for $-0.95 \leq \Delta\mu_{\text{O}} \leq 0.0$ eV). In this case, our calculation perfectly agrees with previous results^{16,17} as far as characteristic bondlength ($d_{\text{VO}} = 0.94$ Å) and energetics are concerned.

Another interesting process that could occur is a kick-out process: one oxygen impurity diffuses within the host matrix until it manages to kick a Ge out of its own lattice position and to take its place. In this scenario, the oxygen would go substitutional at a Ge site and the host atom would occupy an interstitial position ($\text{O}_S\text{-Ge}_T$). As shown in Table I, this structure is competing in energy with the VO complex and is characterized by a quite short bondlength due to the Ge-O interaction and to the fact that many more degrees of freedom are available to the Ge atom in the interstitial region to readjust local strain.

B. Mn substitutional

We now move to the analysis of possible coexistence of Mn and O defects into the Ge-host matrix. Results of our calculations regarding heats of formation calculated at vanishing values of $\Delta\mu_{\text{O}}$ and $\Delta\mu_{\text{Mn}}$ (that is, at the upper boundaries allowed) are reported on Table II. We also report, for completeness, the values of a single Mn impurity in both substitutional and interstitial sites.

The first adsorption site we investigated for Mn is the substitutional site (Mn_S) which has been shown to be the most favorable for Mn incorporation into a Ge matrix.¹⁹ In this case, several different positions for oxygen on sites close to Mn have been considered, namely: (i) oxygen at a substitutional nearest-neighbor site (O_S^m), (ii) oxygen at a nearest-neighbor interstitial site (O_T^m), and finally (iii) oxygen at half a way the edge of the cubic diamond cell (O_T^{edge}). Some of the most representative structures together with the notation used in the paper are depicted in Fig. 1. Table II shows that addition of oxygen in the neighboring of the magnetic impurity atom lowers considerably the formation energy of a single Mn impurity, making it negative and indicating that the oxygen presence favors Mn incorporation. The largest negative value of heat of formation is found for both Mn and O substituting as nearest neighbors of Ge sites. These are exothermic reactions which would not compromise the magnetic properties (the magnetic moment would be rather large in all cases). The fact that there are quite large negative heats of formation despite the rather large local stresses associated (bondlengths sensibly deviate from the ideal Ge-Ge bondlength) indicates that conspicuous energy gains are involved into the chemical Mn-O and Ge-O bonds. In this respect, the Mn-O pair is rather stable. If in fact we compare

TABLE II. Summary of structural results for Mn-O in Ge (32 atoms/cell).

Structure	ΔH (eV/cell)	μ_T (μ_B)	$d_{\text{Mn-Ge}}$ (Å)	$d_{\text{Ge-O}}$ (Å)	$d_{\text{Mn-O}}$ (Å)
Mn_S	1.54	3.00	2.38		
Mn_SO_S^m	-0.40	3.80	2.49	2.17	2.04
Mn_SO_S^n	0.61	3.00	2.38	2.09	
Mn_SO_T^m	-0.14	1.92	2.39	3.05	1.68
Mn_SO_T	2.11	0.0	2.28	2.03	3.44
$\text{Mn}_S\text{O}_T^{\text{edge}}$	-0.22	3.00	2.37	2.12	1.76
Mn_T	+2.62	3.24	2.52		
$\text{Mn}_T 1 \text{O}_S^m$	+0.21	2.99	2.44	1.85	2.9
$\text{Mn}_T 2 \text{O}_S^m$	-1.66	2.57	2.42	1.88	2.9
$\text{Mn}_T 4 \text{O}_S^m$	-6.30	2.72	2.44	1.87	2.9
Mn_TO_T^m	+1.55	4.94	2.6	2.20	2.17
Mn_TO_T	+1.53	4.70	2.50	1.90	3.80
$\text{Mn}_T 4\text{O}_T$	+0.66	0.00	2.81	2.36	1.73
Mn_H	2.96	3.08	2.41		
$\text{Mn}_H 1 \text{O}_S$	0.22	3.00	2.34	1.87	1.94
$\text{Mn}_H 3 \text{O}_S$	-4.69	0.00	2.23	1.88	3.11
$\text{Mn}_H 6 \text{O}_S$	-7.33	0.32	3.18	1.90	2.28

the heat of formation for the Mn_SO_S^m pair with that corresponding to Mn and O on substitutional next-neighbor sites (Mn_SO_S^n), we find that the former structure has a total energy of about 1 eV lower than the latter, thus confirming that the Mn-O bond is energetically favored. Moreover, we can see how the energetics of this system are consistent and additive. If we start from one Mn substituting in Ge (energy cost $\Delta H_f = +1.54$ eV) and now consider an additional substitutional oxygen (energy cost $\Delta H_f = -0.76$ eV in pure Ge) far away from Mn, we should end up with a heat of formation $\Delta H_f = +0.78$ eV for the two noninteracting substitutions. Actually, this is the limit value of the heat of formation for the Mn_SO_S complex with Mn and O at infinite distance (at $d = a_0\sqrt{2}$, we find $\Delta H_f = +0.69$ eV).

C. Mn interstitial

Very interesting are also the possible cases studied with Mn occupying an interstitial site [the most stable tetrahedral site (Mn_T)] and oxygen atom(s) substitutional on nearby sites as EXAFS results¹² on Mn:Ge nanowire arrays seem to suggest. Of course, the experimental situation is rather different from the simulation. In the former case, Ge's are anchored to the oxygens of the porous membrane, while in the latter the O atoms are introduced within the Ge matrix and occupy one of the four nearest diamond sites surrounding the interstitial site. The results reported on Table II once again indicate that the oxygen presence makes the structure stable over a quite wide range of chemical potentials variations ($\Delta\mu_{\text{O}} < 1.0$ eV and $\Delta\mu_{\text{Mn}} < 2.5$ eV) in the case of four substitutional oxygens. We find that the Ge-O distance is much lower than the Ge bondlength ($d^{\text{ideal}} = 2.44$ Å), while the Mn-O distance keeps the overall Ge-O-Mn bondlength constant

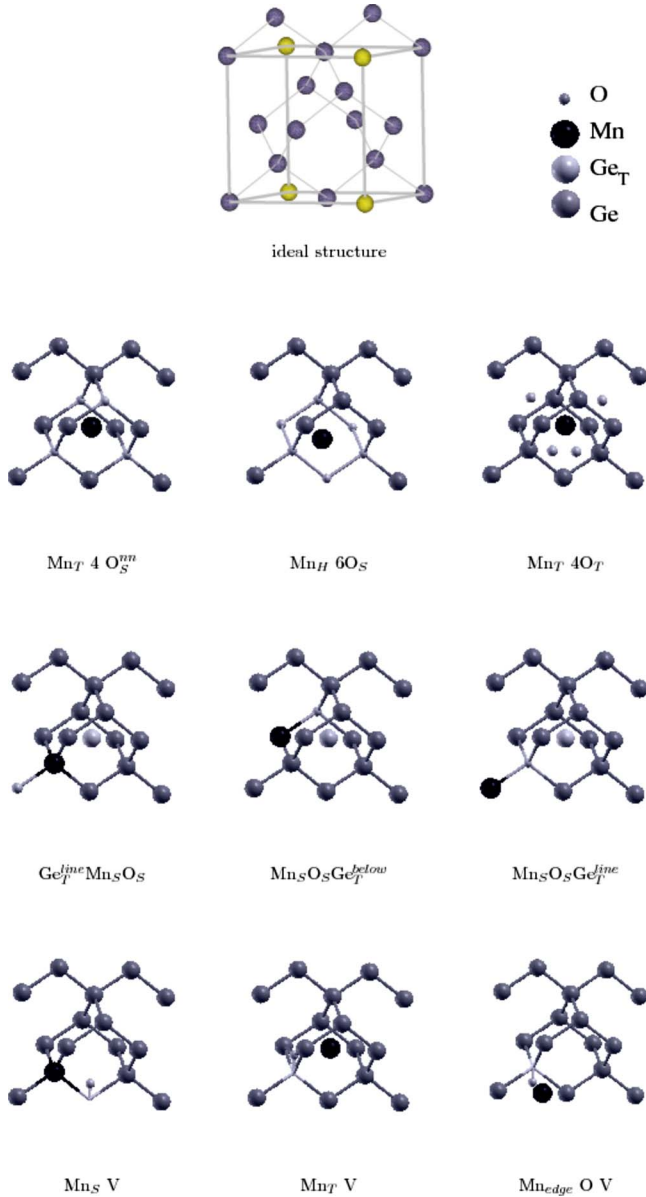


FIG. 1. (Color online) Atomic structures of some of the configurations considered. The central topmost panel shows the ideal zinc blende structure. The dark spheres label the ideal positions of the host matrix slice considered in all the lower panels. In the following panels, large dark (light) gray balls represent substitutional (interstitial) Ge, while small and black balls indicate oxygen and Mn atoms, respectively. Missing balls denote the Ge vacancy.

(4.75–4.78 Å against the ideal 4.88 Å). At the same time, Mn stays on the interstitial site (deviations from the ideal position are very small) while the distortions brought about by the Ge-O bonds affect the Ge's occupying the face centers of the diamond cell, bringing them closer to the Mn at the cell center ($d_{\text{Mn-Ge}}^{\text{ideal}} = a_0/2 = 2.82$ Å against $d_{\text{Mn-Ge}} = 2.44$ Å). Thus, it is clear that a strong bond is formed between O and Ge (see discussion on the electronic properties later on).

Interestingly, we find that the energy gained into the Ge-O chemical bond is present when the oxygen atom goes interstitial as well. In fact, in all cases considered, the presence of O lowers the heat of formation with respect to the situation

where only interstitial Mn is present although the heat of formation is always less favorable than in the substitutional Mn case. The cases considered here are the following (see Fig. 1): (i) Mn and O occupy two nearest interstitial tetrahedral sites (Mn_TO_T^m), (ii) Mn and O at two next neighboring interstitial tetrahedral sites (Mn_TO_T), and (iii) Mn on the interstitial tetrahedral site and 4 O on the nearby interstitial sites. Once again, we find the shortest bondlength for the Ge-O bond and the tendency to form nonmagnetic Mn-O bonds only when interstitial Mn is surrounded by four interstitial oxygens.

Finally, we investigated the hexagonal interstitial (Mn_H) site and possible coabsorption of substitutional oxygen in this case. The situation is not so different from what is found for the interstitial tetrahedral site. Since Mn incorporation on interstitial site is energetically more expensive on the hexagonal rather than on the tetrahedral site, we would expect that the energetics would all be less favorable in the former than in the latter case. However, this is not the case. The oxygen presence makes the heat of formation of the Mn-O pair very similar in both cases, which could therefore make occupation of the hexagonal interstitial site competitive with the tetrahedral interstitial site. This is in line with the results obtained in the case of group-V dopants in Ge.²⁰ The dopant presence in this case makes absorption of Mn_H energetically favored with respect to Mn_T .

As the number of substitutional oxygens is increased, the heat of formation lowers linearly as in the Mn_T case. Once again, we find larger deviations from the ideal zinc blende nearest-neighbor bondlength for the Ge-O bond than for the Mn-O bond. As a result the Mn-Ge bondlength is also remarkably changed (about 3.2 Å to be compared with 2.41 Å of Mn without oxygen). The bondlength values found in this case are very close to those found experimentally on MnGe nanowires grown in alumina templates¹² ($d_{\text{Ge-O}} = 1.74$ Å, $d_{\text{Mn-O}} = 2.11$ Å, and $d_{\text{Ge-Mn}} = 3.03$ Å), and this may substantiate the hypothesis that this kind of clusters may form at the interface between the Ge nanowire and the alumina membrane. Being made of planes on the [111] direction, the Ge-nanowire surface's hexagonal interstitial site is certainly exposed to the interface and then could trap oxygen atoms from the membrane.

In order to give an estimate of the possible stability of the substitutional Mn-O pair (Mn_5O_5), which appear to be the most stable structure, it is useful to evaluate the energy difference between the defective solid containing this kind of defect (E_{pair}) with the energy of the cell containing one oxygen atom in the substitutional position and one Mn in an interstitial site nearby (Mn_5O_T), E_{int} , (in order to correctly take into account the number of Ge atoms, we will have to add the chemical potential of one extra Ge):

$$\Delta E_{\text{pair}} = (E_{\text{pair}} + \mu_{\text{Ge}}^0) - E_{\text{int}}. \quad (7)$$

We find $\Delta E_{\text{pair}} = -0.56$ eV which is still a negative value and would indicate stability of the pair; however, this value has to be compared with the energy difference for single Mn impurities in substitutional and interstitial site which results to be, at the experimental Ge lattice constant, $\Delta E = -1.00$. We therefore infer that the oxygen presence is not stabilizing Mn

TABLE III. Summary of structural results for Mn-O-Mn and other structures considered in Ge (32 atoms/cell).

Structure	ΔH (eV/cell)	μ_T (μ_B)	$d_{\text{Mn-Ge}}$ (\AA)	$d_{\text{Ge-O}}$ (\AA)	$d_{\text{Mn-O}}$ (\AA)
Mn ₅ -O _{edge} -Mn ₅ FM	+0.23	5.98	2.40	1.94	1.84
Mn ₅ -O _{edge} -Mn ₅ AFM	+0.15	0.0(2.7)	2.37	1.96	1.81
Mn ₅ -O _S ⁱⁿ -Mn ₅ FM	-0.08	7.22	2.47	2.13	2.03
Mn ₅ -O _S ⁱⁿ -Mn ₅ AFM	-0.26	0.0(3.34)	2.48	2.11	2.02
Mn ₅ V	+1.75	3.12	2.64		
Mn _T V	+2.45	3.32	2.47		
Mn ₅ VO	-0.43	2.82	2.44	1.84	1.78
Mn _T VO	0.86	3.66	2.35	1.87	1.89
Mn _{edge} VO	0.40	3.00	2.41	1.86	
kick-out					
Mn ₅ Ge _T	3.66				
Ge _T ^{line} Mn ₅ O _S	+2.03	0.02	2.36	2.21	1.92
Mn ₅ O _S Ge _T ^{below}	+1.20	3.98	2.37	1.95	1.98
Mn ₅ O _S Ge _T ^{line}	-0.02	3.00	2.36	1.81	1.70

adsorption on the substitutional site at variance with the case of group-V dopants (P, As, and Sb) as recently reported.²⁰

D. Other structures

In order to complete our study we also investigated several other structures involving more Mn atoms as well as different arrangements of Mn and oxygen atoms. We report on Table III the most interesting structure considered. First of all, we examined formation of possible Mn-O-Mn complexes. While the single Mn-O pair has always negative heat of formation, the presence of an additional Mn nearby makes the heat of formation positive, in the case of substitutional Mn and oxygen at the cubic cell edge, and less negative in the case of O and Mn substituting on nearby sites (Mn₅O_SⁱⁿMn₅). In both cases, the preferred magnetic alignment would be AFM and the tendency is confirmed by calculations on larger cells (256 atoms). Also, we find that two Mn_T-O_S pairs belonging to nearby Ge cubic cells show a very weak magnetic interaction. The energy difference between the AFM and the ferromagnetic (FM) state is only 3 meV in a cell of 256 atoms, i.e., within the limit of our numerical accuracy.

We now consider the possibility of a Ge vacancy (V). We find that the heat of formation for Mn₅ in the presence of a vacancy ($\Delta H=1.75$ eV) does not differ sensibly from the isolated Mn₅ case (only 0.03-eV difference) and, remarkably, it is also very close to the energy cost of a vacancy in pure Ge ($\Delta H=1.69$ eV, cf. Table I). Finally, the vacancy lowers the energy cost of a Mn_T (about 0.2 eV); therefore, this kind of defects present in the Ge lattice may generally favor Mn incorporation. The same does not hold true in the presence of O. While the formation heats for Mn_T-O-V complexes are generally lower than isolated Mn_T, they are generally larger than the corresponding defects without V (≈ 0.62 eV in both cases).

Finally, we examine the structures suggested by a recent study²⁰ regarding possible Mn-adsorption mechanism assisted by the presence of a dopant. These structures are obtained examining possible paths that would involve a kick-out process of a Ge-host atom toward an interstitial site and the consequent adsorption of Mn₅ in proximity of a substitutional dopant atom. This kind of process could be actually favored since we found that the complex O_S-Ge_T, that is the kick-out process, in pure Ge is very stable ($\Delta H=-0.93$ eV as shown in Table I). To this end we consider three possible configurations (see Fig. 1, lower panels): (i) in-line nearest neighbors Ge_T, Mn₅, and O_S (Ge_T^{line}Mn₅O_S), (ii) a similar sequence, Mn₅, O_S, and Ge_T, still in-line (Mn₅O_SGe_T^{line}) with O bridging Mn and Ge, and finally (iii) Mn₅, O_S, and Ge_T where Ge_T is at the interstitial tetrahedral site underneath O_S. The results reported in Table III show that the heats of formation of these structures including O are all energetically favored with respect to the bare Mn-Ge kick-out process without O and that the energy cost is strongly dependent on the relative position of O and Ge. In fact, the first structure in which Ge_T is not bonding with O_S results to be the less stable while the last one in which Ge_T is exclusively bonding with O_S is found to have much lower formation energy of the Mn_T-O_S complex and to be even slightly exothermic ($\Delta H=-0.02$ eV), thus indicating that this could be a possible mechanism for Mn incorporation on substitutional sites.

IV. ELECTRONIC AND MAGNETIC PROPERTIES

In order to describe the bond between oxygen and Ge we plot in Fig. 2 the projected density of states on each atomic site resolved in angular momentum contributions for those components mainly involved in the chemical bond. We can easily see that oxygen bonds essentially with germanium and very little with Mn. In fact, most of the oxygen *p* states are at rather high-binding energy (around -5 eV below the Fermi

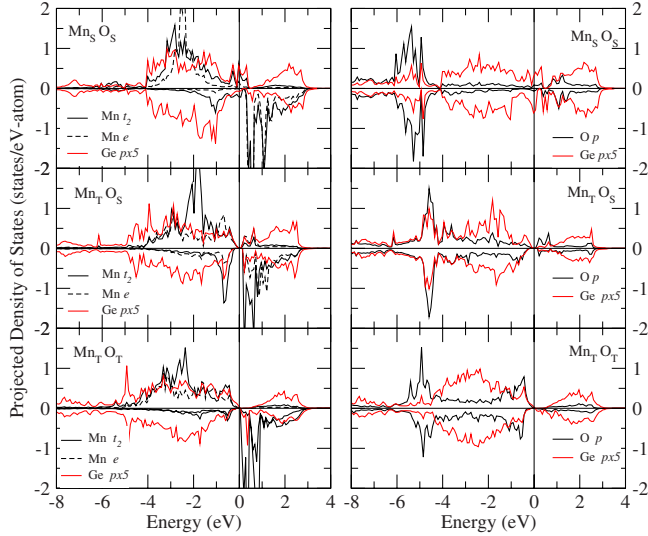


FIG. 2. (Color online) Projected density of states per atomic site and orbital momentum component for three of the cases considered: nearest-neighbor substitutional manganese and oxygen, Mn_5O_5 (upper panels); nearest-neighbor interstitial manganese and substitutional oxygen, Mn_7O_5 (middle panels); and nearest-neighbor interstitial manganese and oxygen, Mn_7O_7 . Panels on the left show contributions from Mn- d resolved in t_2 (solid line) and e -like (dashed line) character and germanium- p (multiplied by a factor of 5, gray line) while panels on the right show contributions from oxygen- p and nearby germanium- p (multiplied by a factor of 5, gray line).

level taken as zero reference energy in Fig. 2) and are mainly hybridized with Ge- p states. In this energy region, in fact, Mn has an almost vanishing contribution. On the other hand, the main Mn- d Ge- p hybridization at lower-binding energy is left almost unchanged by the oxygen presence. Due to symmetry rules, only Mn- t_2 -like states can hybridize (at the zone center) with Ge- p states. Moreover, only in the case of nearest-neighbor Mn_5O_5 , the germanium bonding oxygen along the (110) zinc blende bond chain shows states at the Fermi level and a spin polarization induced by Mn. In all the other cases, the Ge-O bond is rather ionic with a partial charge transfer toward O and a completely unpolarized and semiconductorlike Ge density of states.

The local Ge-O hybridization and the consequent bond is responsible for the energy gain and the stability of the defective structure containing substitutional oxygen ($\text{Mn}_{5,7}\text{O}_5$) (cf. the Ge- p states at low-binding energies ≈ -5 eV). In fact, in the Mn_7O_7 case (see Fig. 2 bottom-right panel) where we find a rather low O_p - Ge_p hybridization (close to the -5 eV energy region in particular), the formation energy is positive and rather large. Therefore, we can state that oxygen is able to stabilize the defective structure as long as it occupies substitutional sites in the Ge-host matrix, where Ge-O hybridization is allowed.

As for the magnetic properties, we find that FM alignment is hindered when oxygen bridges two Mn's (cf. $\text{Mn}_5\text{-O}_{\text{edge}}\text{-Mn}_5$ and $\text{Mn}_5\text{-O}_S^{\text{nn}}\text{-Mn}_5$, Table III), while it is kept in the case of isolated Mn-O complexes where we generally find a magnetic moment very close to $3 \mu_B$ as in the case of an isolated Mn impurity. This kind of behavior was also

found in the case of several Mn impurities nearby²¹ where once again interactions among neighboring Mn's would hinder FM alignment. Ferromagnetism suppression is also found when several oxygens bind a single Mn atom (cf. Mn at the interstitial hexagonal site). It is interesting to observe, however, that magnetic interactions decay pretty fast with distances. Calculations performed on a 256-atom cell found very small [less than 5 meV/(256-atom cell)] energy differences between FM and AFM alignments in the case of $\text{Mn}_7\text{-O}_5$ and $\text{Mn}_5\text{-O}_5$ while the same energy difference for the two magnetic alignments was found in the case of $\text{Mn}_5\text{-O}_5\text{-Mn}_5$ complexes showing that the 32-atom cell is large enough to obtain reliable results.

V. CONCLUSIONS

Several different defective structures of Mn and O coadsorbed in Ge have been investigated. As well known, oxygen contamination constitutes a rather important problem overall in those growth techniques that involve incorporation of oxygen within the bulk material rather than just on the surface, where post-growth chemical treatments could easily remove it.¹¹ Our study pointed out several interesting results that we here summarize. The oxygen presence lowers in general the energy cost of Mn incorporation into the Ge-host matrix forming a Mn-O cluster complex. Mn, however, keeps its magnetic moment ($\approx 3 \mu_B$) and FM alignment as long as there are no other Mn impurities nearby. In this case AFM alignment would be more stable. In addition, O makes the hexagonal interstitial site competitive with the tetrahedral one lowering the energy cost of more than 2.5 eV. In fact, we find that the Mn-O structures experimentally observed¹² could be ascribed to oxygen atoms trapped from the template membrane by Mn occupying hexagonal interstitial sites. This defect complex well reproduces the bondlength distances measured by EXAFS analysis. Finally, from our study we are able to answer the question: Is oxygen adsorption weakening the electronic and magnetic properties of dilute MnGe? Our calculations show that as long as no large complexes, involving several Mn and O atoms, are formed the oxygen presence may even stabilize adsorption of Mn in substitutional sites without hindering its magnetic nor electronic properties through formation of stable isolated Mn-O pairs. However, if the oxygen content increases, then adsorption of Mn into interstitial sites (both tetrahedral and hexagonal) might become energetically favored together with the formation of Mn-O-Mn complexes. In these cases, the magnetic properties of the compound will be greatly reduced or even suppressed.

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