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Electronic and magnetic properties of Mn-doped BeSiAs₂ and BeGeAs₂ compounds

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Abstract

The structural, electronic and magnetic properties of BeSiAs₂ and BeGeAs₂ chalcopyrite ternary compounds doped with manganese were investigated by means of *ab initio* calculations. It was found that substitution of Be atoms by Mn increases the lattice constants of both compounds that provide acceptable mismatch with conventional Si, Ge and GaAs substrates. In spite of the increase of the spin polarization upon doping, both compounds possess antiferromagnetic (AFM) ordering with the impurity in the group II position whereas ferromagnetic (FM) ordering is obtained in the case of an impurity in the group IV position.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Past interest in II–IV–V₂ materials, which are derived from III–V compounds by replacing group III elements by elements of II and IV columns, has been revived due to the possibility of their use in spintronics [1–7]. Attractive electronic, optical and magnetic properties may occur as a result of symmetry lowering by such replacement or upon doping with magnetic impurities. The Mn-doped II–IV–V₂ chalcopyrite ternary compounds merit special attention due to the possible appearance of ferromagnetism at rather high Curie temperatures [2–6] and the ease with which components can be varied by means of modern growth techniques like molecular beam epitaxy. Nonmagnetic semiconductors doped with magnetic elements may possess simultaneous charge and spin properties that make them suitable for spintronic applications. Instead of II–VI and III–V diluted magnetic semiconductors with low solubility of the magnetic element, MnGeP₂ and MnGeAs₂ chalcopyrite compounds have been synthesized and found to be FM above room temperature [4].

The aim of our work was to search for II–IV–V₂ compounds weakly lattice mismatched with conventional

semiconducting substrates, and to investigate their electronic and magnetic properties upon doping with manganese impurities [8–10]. For this purpose we have chosen stable compounds with lattice constants closely lattice-matched ($\pm 1\%$) to the substrates like silicon, germanium or gallium arsenide from 64 possible materials of the II–IV–V₂ class [7]. Among these we focused our search on arsenic compounds, since nitrogen and phosphorus based ternaries (similarly to II–V binaries) appear to be more complicated to prepare experimentally. Finally, we have chosen the two beryllium compounds BeSiAs₂ and BeGeAs₂ for which thermodynamic stability was theoretically predicted in the chalcopyrite phase [7]. According to these estimations, BeGeAs₂ has a lattice constant a of about 5.45 Å and BeSiAs₂ of about 5.34 Å, which are close to the silicon lattice.

While substitution of small beryllium atoms by larger manganese atoms may increase lattice constants of BeSiAs₂ and BeGeAs₂ and fit them to the semiconducting substrate, we considered the changes of lattice constants in the rows BeSiAs₂ → MnSiAs₂ and BeGeAs₂ → MnGeAs₂ [4], where Be atoms are replaced by different number of manganese atoms up to full substitution. We also considered the case when Mn

substitutes the atoms of group IV for a better understanding of the impact of impurities on the magnetic properties of such compounds. In this paper we will present the structural, electronic and magnetic properties of BeSiAs₂ and BeGeAs₂ doped with different concentrations of manganese.

2. Computational details

According to experiments, As-containing II–IV–V₂ ternaries are usually formed in a body centred tetragonal (chalcopyrite) structure (figure 1) [7]. Thus we have chosen this structure type for our compounds. To analyse the stability of the system we have estimated the enthalpies of formation as the difference between the total energy of the compound and the ground-state elemental phases.

In order to simulate magnetic properties we have modelled the situation when manganese atoms substitute smaller beryllium atoms. The different Mn concentrations have been modelled in a fully relaxed 64-atom supercell, which is a $2 \times 2 \times 1$ translated 16-atom simple tetragonal cell.

For structural optimization and calculation of the electronic and magnetic properties we used the density functional theory (DFT) within the generalized gradient approximation (GGA) of Perdew and Wang [11] implemented in the first-principles Vienna *ab initio* simulation package (VASP) code [12]. The electron–ion interaction is described by projector-augmented wave pseudo-potentials (PAW-PP). Relaxation of the atomic positions and lattice constants within the procedure of total energy minimization was performed by calculating the Hellmann–Feynman forces and the stress tensor. The energy cut-off for both structures was set to 330 eV and a $4 \times 4 \times 4$ grid of Monkhorst–Pack points was used. The atomic relaxation was stopped when forces on atoms were less than $1 \text{ meV } \text{Å}^{-1}$.

The electronic properties of BeSiAs₂ and BeGeAs₂ compounds were also checked within the full-potential linearized augmented plane wave (FLAPW) method implemented in the WIEN2K package [13]. We also tested the correspondence between spin-polarized densities of states (DOS) obtained within the pseudo-potential and full-potential methods.

We considered the configurations Be_{1-x}Mn_xSiAs₂ and Be_{1-x}Mn_xGeAs₂, where x is varying from 0.125 to 1, i.e. up to full substitution of Be, and compared our results with those existing for MnSiAs₂ and MnGeAs₂. We also examined the case with the substitution of group IV atoms, though the case with the full substitution was not considered as we have no information about the existence of such compounds. Therefore, we have modelled the case with a small concentration of Mn ($x = 0.125$) in group IV and analysed the impurity formation energies for the cases with impurities in the group II and IV positions.

3. Results and discussion

3.1. Optimization of the crystal structure

As a result of full structural relaxation of the chalcopyrite phase, the atomic positions and lattice constants of both

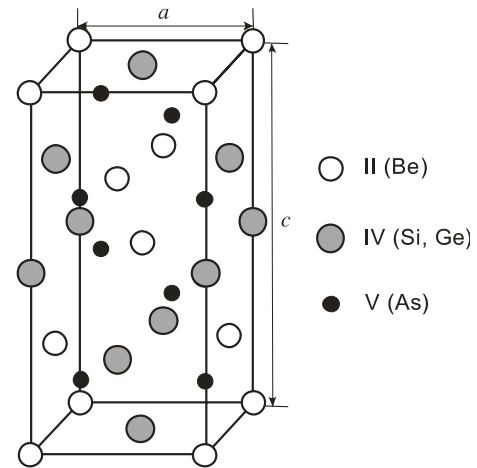


Figure 1. Crystal structure of A^{II}B^{IV}C₂^V chalcopyrite compounds.

beryllium compounds are obtained: $a = 5.369 \text{ Å}$, $c = 10.732 \text{ Å}$ (BeSiAs₂) and $a = 5.451 \text{ Å}$, $c = 10.974 \text{ Å}$ (BeGeAs₂). In table 1, the lattice constants of pure and Mn-doped materials calculated within the used approach are presented together with their mismatches to possible semiconducting substrates. Lattice constants for MnSiAs₂ and MnGeAs₂ are close to the theoretically predicted ones of $a = 5.81 \text{ Å}$, $c = 10.92 \text{ Å}$ and $a = 5.80 \text{ Å}$, $c = 11.39 \text{ Å}$, respectively [14], and experimental $a = 5.78 \text{ Å}$ and $c = 11.32 \text{ Å}$ for MnGeAs₂, obtained in [4]. According to our calculations, both beryllium compounds possess negative enthalpies of formation (-1.82 and -1.53 eV), meaning that they are thermodynamically stable. This matches well with theoretically estimated values of -1.82 and -1.55 eV for BeSiAs₂ and BeGeAs₂, respectively [7].

As far as *ab initio* estimation of the lattice constants within the approach used shows discrepancy with experimental data, we have evaluated the mismatch between both calculated and experimental values of the substrate lattices. Thus, upon our estimations: (i) BeSiAs₂ has -1.7% mismatch with the silicon substrate while Mn doping increases its a parameter up to 6.1% at full replacement of beryllium atoms by manganese; (ii) BeGeAs₂ has -0.2% mismatch only and manganese may increase the lattice up to 5.7% . The lattice changes show that it is possible to choose lattice parameters very close to the desired ones by varying the concentration. Lattice constants of Be_{1-x}Mn_xSiAs₂ and Be_{1-x}Mn_xGeAs₂ at small x fit well to a silicon substrate, whereas when x is approaching 1 they tend to a germanium one.

3.2. Electronic and magnetic properties

The electronic band spectra calculated by FLAPW along some high-symmetry directions of the body centred tetragonal Brillouin zone are shown in figure 2. BeSiAs₂ was found to be a direct-gap semiconductor with the gap values of 1.05 (1.07) eV, while BeGeAs₂ has an indirect gap of 0.63 (0.62) eV as obtained by PAW-PP (FLAPW). These results agree well with the theoretically predicted direct gap of about 1.05 eV for BeSiAs₂ and an indirect gap of about 0.6 eV for

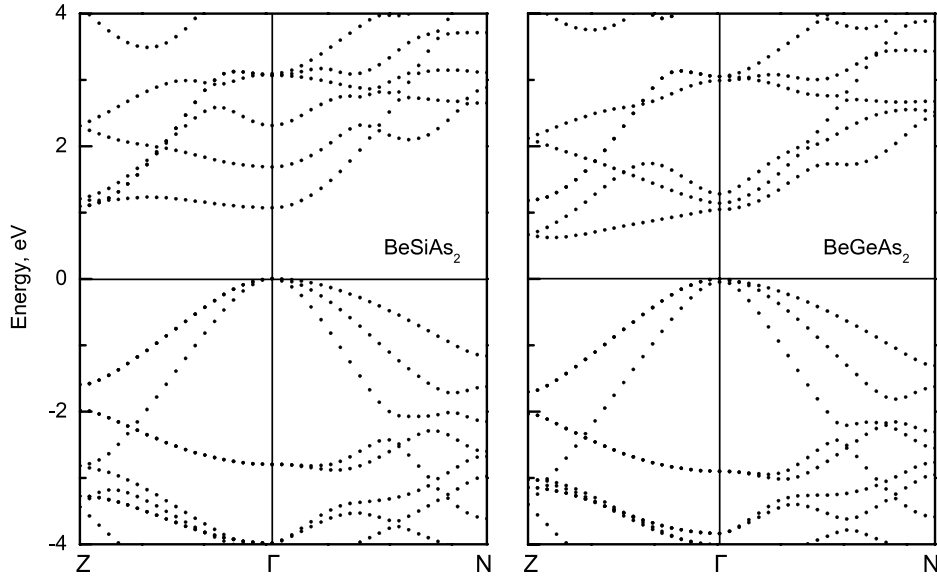


Figure 2. Band structures of BeSiAs₂ and BeGeAs₂ along some high-symmetry directions calculated by the FLAPW method. The zero level corresponds to the Fermi energy.

Table 1. Theoretical lattice constants of compounds and their mismatches with conventional substrates.

Compound	Our calculations		a (Si) (Å)		a (Ge) (Å)		a (GaAs) (Å)	
	a	c	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
	Mismatch $[a(\text{compound}) - a(\text{substrate})]/a(\text{substrate})(\%)$							
BeSiAs ₂	5.369	10.732	-1.14	-1.74	-5.11	-6.66	-5.02	-6.38
Be _{0.5} Mn _{0.5} SiAs ₂	5.551	10.954	+2.21	+1.59	-1.89	-3.49	-1.80	-3.21
MnSiAs ₂	5.796	10.869	+6.72	+6.08	+2.44	+0.76	+2.53	+1.06
BeGeAs ₂	5.451	10.974	+0.37	-0.24	-3.66	-5.23	-3.57	-4.95
Be _{0.5} Mn _{0.5} GeAs ₂	5.611	11.292	+3.31	+2.69	-0.83	-2.45	-0.74	-2.16
MnGeAs ₂	5.777	11.370	+6.37	+5.73	+2.10	+0.43	+2.19	+0.73

BeGeAs₂, calculated using ultrasoft pseudo-potentials within the GGA [7]. Meanwhile, possible significant underestimation of the band gaps within DFT should be taken into account, as we have not used the computationally expensive GW approximation for the electronic self-energy. For example, the band gaps of Si, Ge and GaAs calculated within the same GGA approach were estimated to be 0.6, 0.0 and 1.1 eV while the experimental values are 1.12, 0.66 and 1.42 eV [15]. Hence one may expect the true gaps to be ~ 0.5 eV larger than numerically computed.

As shown in figure 3, the calculated DOS for BeSiAs₂ and BeGeAs₂ confirm the semiconducting nature of the compounds. As can be seen from the partial DOS, the valence band near the Fermi level is composed primarily of p and d states of As, while s electrons of Si or Ge play the dominant role in the formation of the conduction band near the gap. The contribution of Be atoms (not shown here) as well as p electrons of Si or Ge does not have much influence on states near the Fermi level. The DOS calculated using the FLAPW method show qualitative similarity with the ones obtained with the pseudo-potential method.

To determine the magnetic properties of Mn-doped compounds, we have performed spin-polarized calculations and obtained magnetic moments for Mn atoms of approximately $3.7\text{--}3.8 \mu_B$ in Be_{1-x}Mn_xGeAs₂ which is close to the experimental $3.42 \mu_B$ per Mn atom in MnGeAs₂ [4] and about $3.9\text{--}4.0 \mu_B$ in Be_{1-x}Mn_xSiAs₂ ($0.125 < x < 1$) (see table 2).

The magnetic moment per Mn atom practically does not depend on the Mn concentration. The difference between magnetic moments in FM and AFM states is rather small, about $0.16\text{--}0.17 \mu_B$ in MnSiAs₂ and $0.04\text{--}0.05 \mu_B$ in MnGeAs₂, indicating that spin moments are weakly coupled. They are primarily localized at the impurity position, thus manganese atoms are responsible for the main contribution to the total magnetic moment of the system. The spin-polarized densities of states of Be_{1-x}Mn_xSiAs₂ and Be_{1-x}Mn_xGeAs₂ as well as BeMn_xSi_{1-x}As₂ and BeMn_xGe_{1-x}As₂ in the FM state when $x = 0.125$ are presented in figure 4. Spin-up and spin-down states in the DOS are shown as positive and negative components, respectively.

It is evident that the addition of manganese leads to the appearance of new states in the band gap and

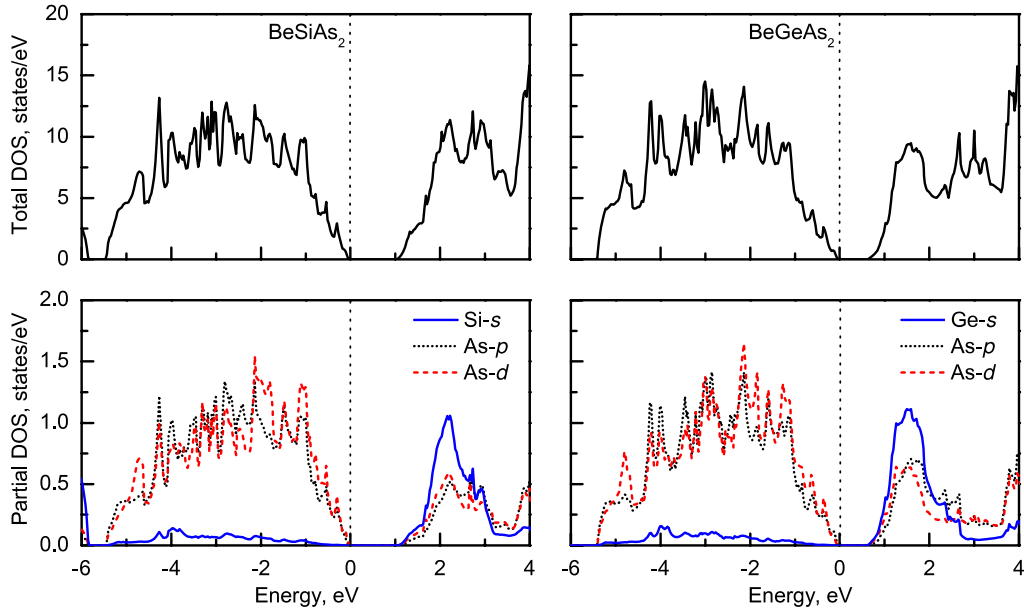


Figure 3. Total and partial DOS of BeSiAs₂ and BeGeAs₂ calculated with PAW-PP.

Table 2. Calculated magnetic moments and total energy difference between FM and AFM states of Be_{1-x}Mn_xSiAs₂ and Be_{1-x}Mn_xGeAs₂ compounds, 0.125 < x < 1.

Compound	Total magnetic moment (μ_B /atom)		Partial magnetic moment (μ_B)		$\Delta E_{\text{tot}} = (E_{\text{AFM}} - E_{\text{FM}})/\text{cell}$ (eV)	Type
	FM		FM	AFM		
Be _{0.875} Mn _{0.125} SiAs ₂	4.99		3.9	± 3.8	-0.049	Semiconductor
Be _{0.75} Mn _{0.25} SiAs ₂	5.00		4.0	± 3.9	-0.009	Semiconductor
Be _{0.5} Mn _{0.5} SiAs ₂	5.00		4.0	± 3.9	-0.035	Semiconductor
Be _{0.25} Mn _{0.75} SiAs ₂	4.93		4.0	± 3.9	-0.464	Metal
Be _{0.125} Mn _{0.875} SiAs ₂	4.89		4.0	± 3.9	-0.645	Metal
MnSiAs ₂	4.86		4.0	± 3.9	-0.840	Metal
Be _{0.875} Mn _{0.125} GeAs ₂	4.99		3.8	± 3.8	-0.046	Metal
Be _{0.75} Mn _{0.25} GeAs ₂	4.84		3.8	± 3.8	-0.026	Metal
Be _{0.5} Mn _{0.5} GeAs ₂	4.88		3.9	± 3.9	-0.062	Metal
Be _{0.25} Mn _{0.75} GeAs ₂	4.47		3.8	± 3.7	-0.374	Metal
Be _{0.125} Mn _{0.875} GeAs ₂	4.29		3.8	± 3.7	-0.461	Metal
MnGeAs ₂	3.99		3.7	± 3.7	-0.527	Metal

changes the semiconducting nature of the compounds. Be_{1-x}Mn_xSiAs₂ and Be_{1-x}Mn_xGeAs₂ in the FM state, in contrast to semiconducting BeSiAs₂ and BeGeAs₂, demonstrate preferably metallic behaviour, with the exception of Be_{1-x}Mn_xSiAs₂, which remains a semiconductor in both spin channels at small x. An impurity in the group IV position transforms compounds to half-metals with the 100% value of spin polarization. When x = 1, Be_{1-x}Mn_xSiAs₂ and Be_{1-x}Mn_xGeAs₂ become MnSiAs₂ and MnGeAs₂ and the DOS calculated for these materials are in good agreement with those presented in [14] and show the metallic behaviour of these materials, while in some experimental works MnGeAs₂ was suggested to be a FM semiconductor [4].

Analysis of partial DOS (figure 5) has shown that the spin-up states near the Fermi level mainly comprise As 4p and 3d electrons, whereas Si 3s electrons in Be_{1-x}Mn_xSiAs₂ and Ge 4s electrons in Be_{1-x}Mn_xGeAs₂ hybridized with As 4p and 3d

electrons are responsible for the main peaks in the spin-down DOS at the Fermi level. Mn 3d electrons fill the majority spin and have practically no influence on the minority spin states; thus hybridized with As 4p they comprise mainly the spin-up states in the region from -2 to 2 eV.

The applicability of materials for spintronic devices may be estimated by means of spin polarization, i.e. the relation between DOS at the Fermi level in spin-up and spin-down states. Comparison of the spin-polarized DOS in figure 6 for compounds with a high concentration of Mn atoms (x = 0.875 and 1) with the DOS presented in figure 4 for the case of small Mn concentration (x = 0.125) show that the value of spin polarization increases with increasing manganese concentration.

However, comparison of the total energies in FM and AFM states (table 2) when Mn atoms are in group II positions indicates a negative value for the energy difference $E_{\text{AFM}} - E_{\text{FM}}$,

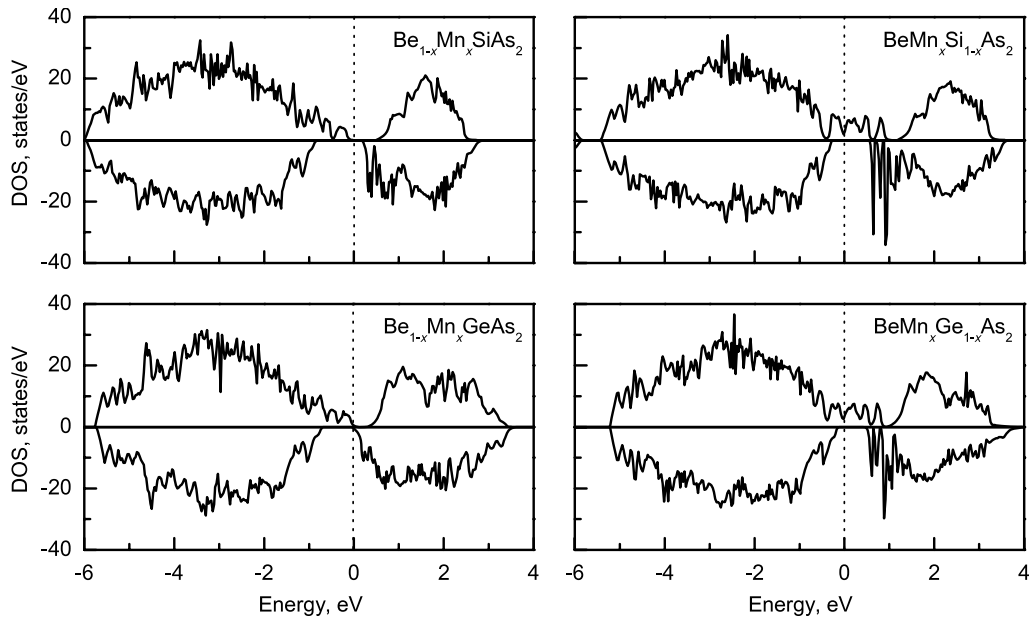


Figure 4. Spin-polarized total DOS of $\text{Be}_{1-x}\text{Mn}_x\text{SiAs}_2$, $\text{Be}_{1-x}\text{Mn}_x\text{GeAs}_2$, $\text{BeMn}_x\text{Si}_{1-x}\text{As}_2$ and $\text{BeMn}_x\text{Ge}_{1-x}\text{As}_2$ in the FM state, $x = 0.125$.

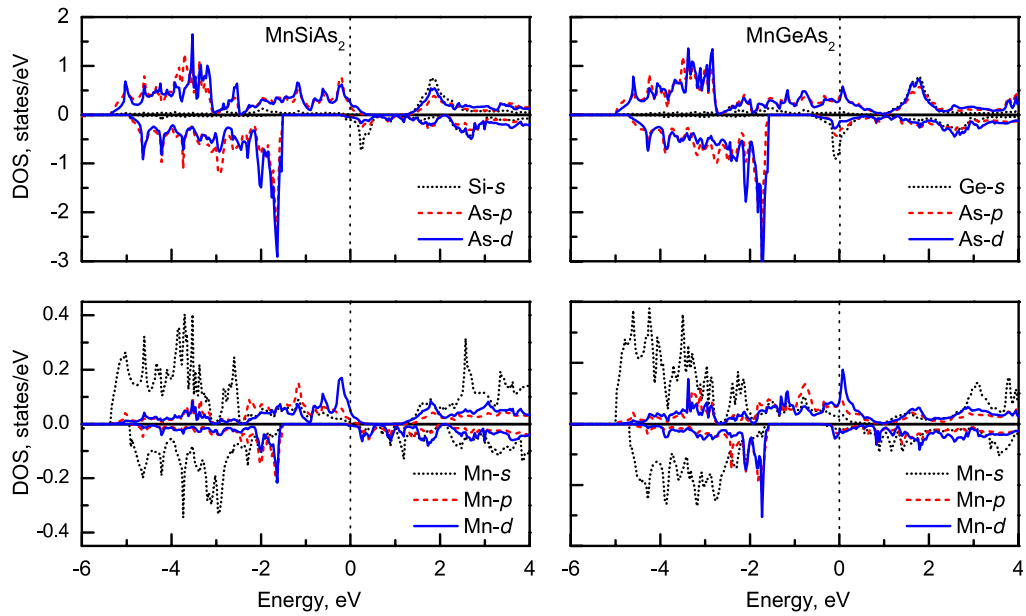


Figure 5. Partial spin-polarized DOS of MnSiAs_2 and MnGeAs_2 .

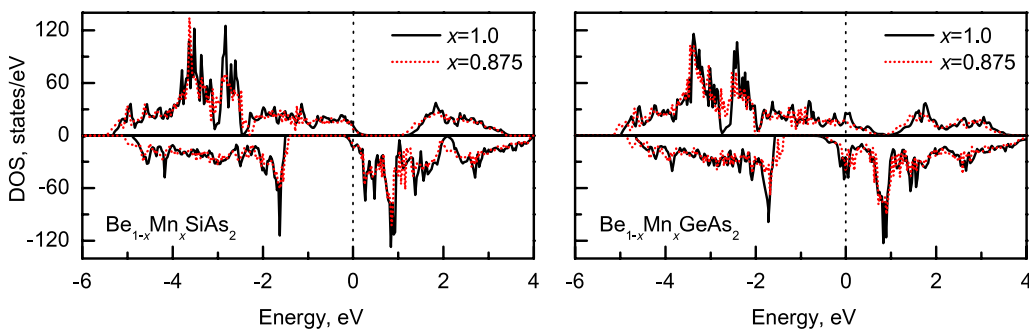


Figure 6. Partial spin-polarized DOS of $\text{Be}_{1-x}\text{Mn}_x\text{SiAs}_2$ and $\text{Be}_{1-x}\text{Mn}_x\text{GeAs}_2$ ($x = 0.875; 1.0$) in the FM state.

i.e. irrespective of manganese concentration AFM ordering is energetically favourable for both structures. Materials stay AFM even at full replacement of Be atoms by manganese [14]. However, the calculations were performed at 0 K, while AFM to FM transition may take place at higher temperatures (for example, AFM to FM transition for the $\text{ZnGeP}_2\text{:Mn}$ system occurs at 47 K [2]).

For impurities in group IV positions we have obtained a positive energy difference, i.e. materials are in the FM state. Our analysis of impurity formation energies shows that an energetically preferable configuration occurs when manganese occupies positions of group II atoms in BeSiAs_2 and group IV atoms in BeGeAs_2 . Thus, upon substitution of group II atoms with manganese materials show either metallic or semiconducting behaviour in both spin channels, and this fact does not support the idea of using such materials as half-metals, though limited use for spintronic applications is still possible. On the contrary, substitution of group IV atoms in BeGeAs_2 may be useful from the practical point of view, as material shows itself to be a stable half-metal in the FM state.

4. Conclusions

Changes in structural, electronic and magnetic properties of $\text{Be}_{1-x}\text{Mn}_x\text{SiAs}_2$ and $\text{Be}_{1-x}\text{Mn}_x\text{GeAs}_2$ when x is varying from 0 to 1 have been predicted by first-principles calculations. For $x = 0$ both compounds were found to be semiconductors with the lattice constants $a = 5.369 \text{ \AA}$, $c = 10.732 \text{ \AA}$ (BeSiAs_2) and $a = 5.451 \text{ \AA}$, $c = 10.974 \text{ \AA}$ (BeGeAs_2). BeSiAs_2 has a direct gap of about 1.05 eV, while BeGeAs_2 has an indirect gap of 0.63 eV. It was found that the addition of Mn atoms changes the semiconducting behaviour of materials and leads to the appearance of a spin moment. The increase in Mn concentration leads to the growth of the spin polarization; however, the preferable state remains AFM with the exception of BeGeAs_2 , when Mn occupies the group IV position. It is revealed that replacement of Be atoms by Mn increases the lattice parameters of the compounds, which may fit them into the silicon or other semiconducting lattice.

Acknowledgments

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