Magnetic ordering in X-Y-N_2 semiconductors (X=Mg, Zn; Y=Si, Ge) doped with Cr, Mn, and Fe atoms

A.V. Krivosheeva*, V.L. Shaposhnikov

Belarusian State University of Informatics and Radioelectronics, P. Browka 6, 220013 Minsk, Belarus

**krivosheeva@bsuir.by*

Abstract

Structure and properties of ternary nitrides $MgSiN_2$, $MgGeN_2$, $ZnSiN_2$, and $ZnGeN_2$ are investigated using methods of density functional theory. Ways of its band gap modification by doping with Cr, Mn, and Fe atoms are estimated and conditions of magnetic ordering onset are determined. Data on the spin polarization and changes in the magnetic moments of ternary nitrides doped with 3*d*-elements allows to propose materials with the maximum spin polarization for application in new spintronic devices.

Keywords: ternary nitrides, magnetic ordering, spin polarization.

Introduction

Ternary semiconductors now are being intensively investigated, and particular interest is being payed to the possibility of the magnetic ordering appearance in such materials when a magnetic impurity is introduced into them [1-2]. In Mn-doped $ZnGeP_2$, $CdGeP_2$, and $CdGeAs_2$ ternary semiconductors ferromagnetism was experimentally detected at room temperature [3]. Nitride ternary compounds have been synthesized already in the 1970s [4-6] but the data on their properties is still rather scarce. Self-consistent calculations of the band structures of $ZnSiN_2$ and $ZnGeN_2$ were presented in [7]. However, a detailed study of a class of ternary nitrides doped with 3*d* elements have not been carried out.

In our work, the cases of doping II-IV-N_2 compounds with 3*d* impurities were considered in order to determine the possibility of band gap engineering and onset of magnetic ordering in such structures. The computer models of $MgSiN_2$, $MgGeN_2$, $ZnSiN_2$, and $ZnGeN_2$ compounds doped with Cr, Mn, and Fe were created in order to determine the effect of the type and location of a defect on the value of magnetic moment. The cases with vacancies on IV group element were considered as well.

Details of calculations

Calculations were performed within density functional theory using projector augmented-wave method with different approximations (PAW-LDA, PAW-GGA, PAW-PBE) as implemented in the VASP code [8]. The energy cut-off parameter was set to 520 eV. The structural relaxation was carried out on the mesh of 4×6×8 k-points. We determined a simple orthorhombic phase to be the most stable one for this class of materials. A unit cell of ternary nitrides structure is presented in Figure 1.

In order to evaluate magnetic ordering of the systems two impurity atoms of 3*d* metals were placed in positions of IV group atoms in a cell of 32 atoms (Figure 2). The distances between impurity atoms had the next values: 0.545 nm ($MgSiN_2$), 0.565 nm ($MgGeN_2$), 0.541 nm ($ZnSiN_2$), and 0.559 nm ($ZnGeN_2$).

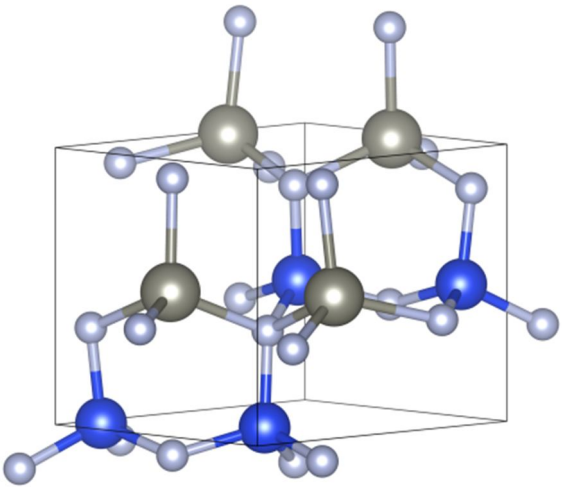

Figure 1. Crystal structure of Mg(Zn)Si(Ge)N_2 compounds. Large spheres are Mg(Zn) atoms, smaller spheres are Si(Ge) atoms, the smallest ones are N atoms

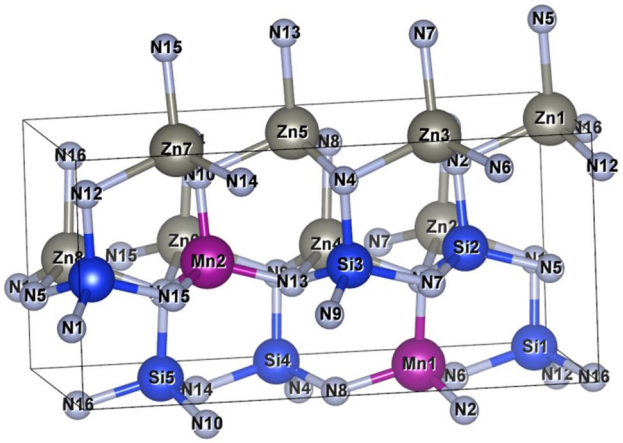

Figure 2. Crystal structure of doped $ZnSiN_2$ compound with Si atoms replaced by Mn atoms

Results and discussion

Previously [9] we have reported that $ZnGeN_2$ and $MgGeN_2$ are direct-gap semiconductors with a transition at the point Γ, while the $ZnSiN_2$ and $MgSiN_2$ compounds are indirect-gap semiconductors. It is found that presence of Cr, Mn, and Fe impurity atoms leads to the appearance of additional energy levels in the band gap and a corresponding decrease of the gap. Moreover, three of compounds (except $ZnSiN_2$) obtain half-metallic properties as they demonstrate 100% spin polarization. However, this is true only for Mn and Fe impurities, whereas upon doping with Cr atoms all the compounds stay semiconductors in both channels. Spin-polarized band structures and densities of states (DOS) in FM state for all compounds considered are presented in Figure 2 and Figure 3, respectively. Spin-up and spin-down states in the DOS are shown as positive and negative components.

Magnetic moments on impurity atoms are different for every compound and maximal for the case of doping with Fe atoms (Table 1), the highest value of 3.06 μ_B/atom has $MgGeN_2$:Fe system. When there is a vacancy on the position of IV group atom (not shown) in the $MgGeN_2$ compound the total magnetic moment decreased up to zero, while in $MgSiN_2$, $ZnGeN_2$, and $ZnSiN_2$ compounds the magnetic moment just significantly decreased.

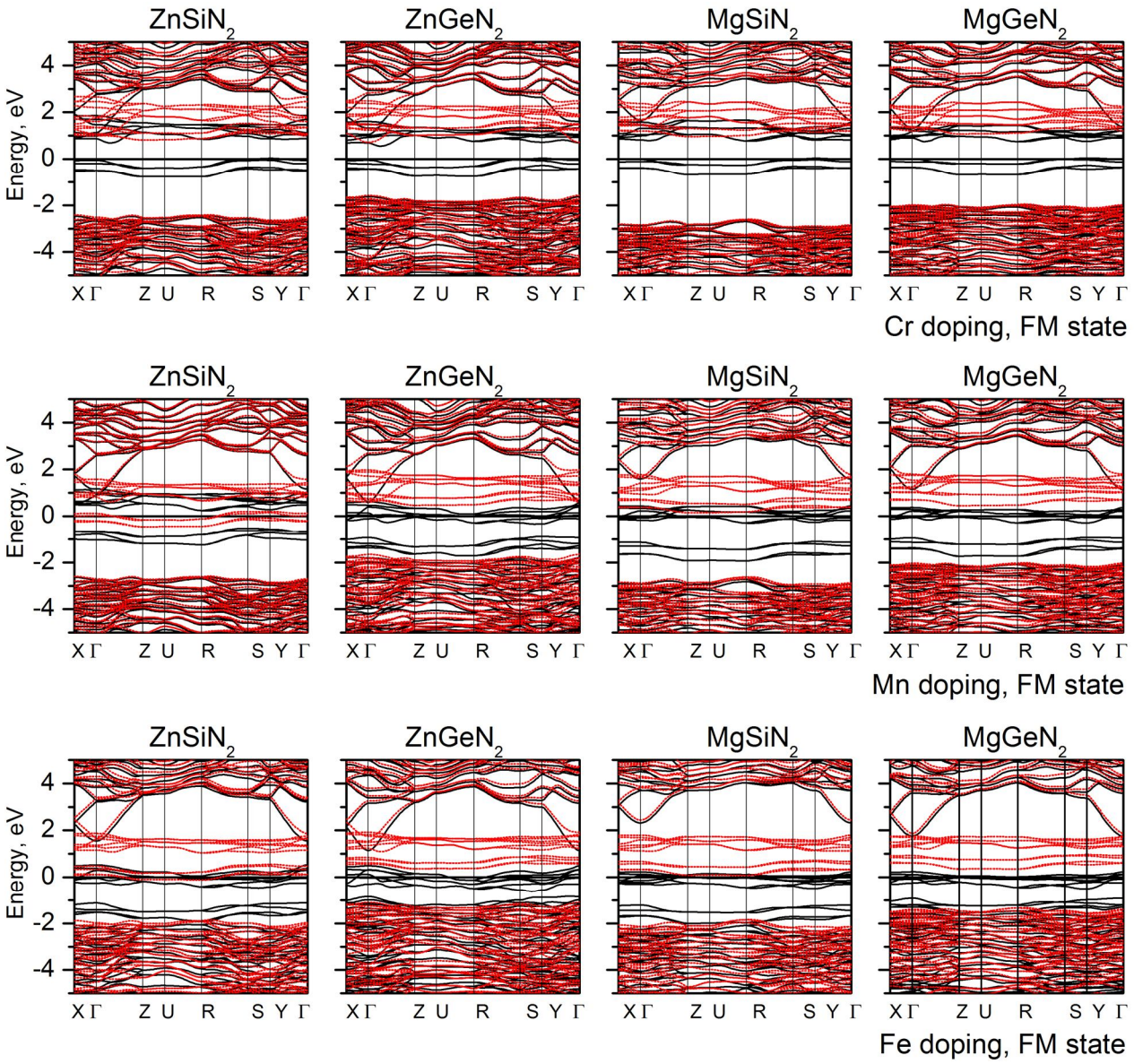

Figure 2. Spin-polarized band structures of doped Mg(Zn)Si(Ge)N_2 compounds in FM states. Solid lines – spin-up states, dotted line – spin-down states

Table 1. Magnetic moments per impurity atoms of doped Mg(Zn)Si(Ge)N_2 compounds

Compound	Partial magnetic moment, μ_B/atom		
	Cr	Mn	Fe
$MgSiN_2$	1.72	2.38	2.85
$MgGeN_2$	1.87	2.64	3.06
$ZnSiN_2$	1.72	0.83	2.56
$ZnGeN_2$	1.89	2.68	3.14

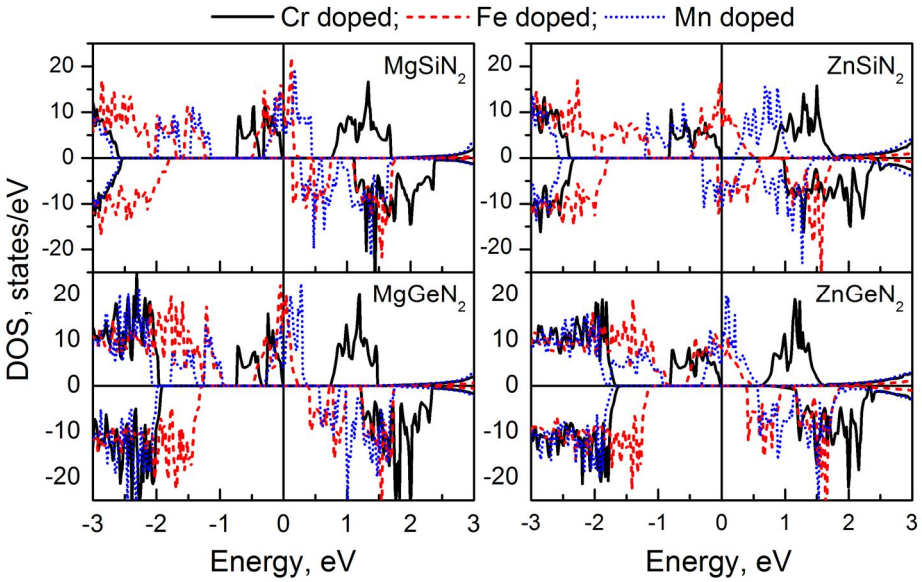

Figure 3. Spin-polarized density of states of $MgSiN_2$, $MgGeN_2$, $ZnSiN_2$ and $ZnGeN_2$ doped with Cr, Mn, and Fe atoms in FM states

Conclusion

Structure and electronic properties of ternary nitride semiconductors $MgSiN_2$, $MgGeN_2$, $ZnSiN_2$ and $ZnGeN_2$ are investigated by means of theoretical modeling and the ways of their modification by doping with Cr, Mn, and Fe atoms are discussed. Conditions of appearance of magnetic ordering in such structures are determined. It is revealed that the presence of Cr, Mn, Fe impurities in group IV site leads to the appearance of magnetic ordering and spin polarization in the considered materials. It is determined that the maximum magnetic moment appears when the compounds are doped with Fe atoms, and the highest value of 3.06 μ_B/atom is found for $MgGeN_2$:Fe system. Doped with Mn and Fe atoms $MgSiN_2$, $MgGeN_2$, and $ZnGeN_2$ compounds demonstrates appearance of half-metallic properties and thus can be considered as candidates for new spintronic devices. The presence of a vacancy in the IV group atoms site in the $MgGeN_2$ compound decreases the total magnetic moment up to zero, while in $MgSiN_2$, $ZnGeN_2$, and $ZnSiN_2$ compounds the magnetic moment is still persists, although its value decreases significantly.

Acknowledgment

This work was supported by the State Program of Scientific Research of the Republic of Belarus “Materials science, novel materials and technologies” (2021-2025).

References:

[1] S. C. Erwin, I. Žutić, Nat. Mat. 3(2004) 410–414.
[2] S. Picozzi, Nat. Mat. 3 (2004) 349–350.
[3] S. Cho [et al.], Phys. Rev. Lett. 88 (2002) 257203.
[4] M. Maunaye, J. Lang, Mater. Res. Bull 5 (1970) 793–796.
[5] T. Endo, Y. Sato, H. Takizawa, M. Shimada, J. Mater.Sci. Lett. 11 (1992) 424–426.
[6] J. David, Y. Laurent, and J. Lang, Bull. Soc. Fr. Mineral. Cristallogr. 93 (1970) 153–159.
[7] A. Punya, W. R. L. Lambrecht, M. van Schilfgaarde, Phys. Rev. B. 84 (2011) 165204.
[8] G. Kresse, J.Furthmüller, Phys. Rev. B 54 (1996) 11169–11186.
[9] A. V. Krivosheeva, V. L. Shaposhnikov, Proc. Nat. Acad. Sci. Belarus 58(4) (2022) 424–430 (in Russian).