Ab Initio Calculations of Magnetic Properties of Wurtzite $Al_{0.9375}TM_{0.0625}N$ (TM = V, Cr, Mn, Fe, Co, Ni)

J. Kaczkowski and A. Jezierski

Institute of Molecular Physics, Polish Academy of Sciences

M. Smoluchowskiego 17, 60-179 Poznań, Poland

The electronic structure of transition metal (TM) doped aluminium nitride was presented. The calculations were made within density functional theory and supercell approximation. It was found that the ferromagnetic ground states were possible without additional dopants in V-, Cr-, Mn-doped AlN.

PACS numbers: 71.20.–b, 71.20.Nr, 71.55.–i, 71.55.Eq, 71.55.Ak

1. Introduction

In the semiconductors doped by the transition metals (TM) the half-metallic state can be observed. Such behavior leads to the interesting transport properties with carriers of the one type of spin. These materials are called diluted magnetic semiconductors (DMS) [1, 2] and are the new class of materials whose properties are important for applications in the new branch of technology called spintronics. However at this moment main barrier to commercial application of these materials is the low Curie temperature (the highest $T_C = 170$ K was observed in $Ga_{1-x}Mn_xAs$ [1]). The other problem is that doping with the TM elements not always leads to half-metallic state. From this reasons the *ab initio* calculations based on the density functional theory (DFT) give interesting information about the electronic structure of such systems. In this paper we report the results of calculations of influence of the $3d$ metals on the magnetic properties of aluminium nitride. Some theoretical [3–5] and experimental [5, 6] results published before have showed that these materials could have a high Curie temperature. In the literature we found the electronic structure calculations only for V [4], Cr [5], Mn [3]. This paper is organized as follows: the short description of method of calculations we present in Sect. 2 and the results and the discussion are given in the Sect. 3.

2. Method of calculations

The *ab initio* spin-polarized calculations were performed by using the plane-wave pseudopotential method [7] within the density functional theory [8, 9]. We have applied the Quantum-Espresso package [10, 11]. The exchange-correlations energy in the gradient approximation was based on the Perdew–Burke–Ernzerhof formula [12]. All pseudopotentials used in the present calculations were scalar-relativistic and ultrasoft type [13]. The cut off radius was equal to 50 Ry for energy and 500 Ry for the charge density. The self-consistent calculations were performed for the Brillouin zone division $4 \times 4 \times 4$ in all presented cases and for the density of states (DOS) we used $8 \times 8 \times 8$ non-shifted grid. The calculations were performed within supercell approximation for wurtzite structure. Our supercell has a size $2 \times 2 \times 2$ of the unit cell. This supercell contained the 16 atoms of aluminum and 16 atom of nitrogen in which one atom of aluminum was substituted by the one atom of the transition metal.

To estimate which state is more stable we made the calculations for the 64-atom supercell ($4 \times 2 \times 2$ of the unit cell size) with two TM atoms. The distance between TM ions was 6.2 Å. In this calculations the supercell was not optimized. In all self-consistent calculations Gaussian smearing technique was used with a smearing width of 0.005 Ry and for DOS calculations tetrahedron method was applied. The convergence of self-consistency was set at 10^{-8} Ry.

3. Results

In Fig. 1 we present the total and partial from TM ions densities of states. The transition metal dopants lead to appear d-states near Fermi level in aluminum nitride. In general, these d-states could be divided into three types of states: bonding which lies in valence band, non-bonding and anti-bonding states which are located above the valence band. The shape of DOS curves are change when we increase the number of the d-electrons on the TM impurity. For vanadium we observe that non-bonding spin up states lies below E_F and are fully occupied. The anti-bonding states are mixed with conduction band and also they mix each other. But at the Fermi level we have only one type of spin and d-electrons are fully polarized. According to [10]* we suppose that for this type of dopants we have a super-exchange mechanism of exchange.

———

* We used the pseudopotentials from the http://www.quantum-espresso.org distribution excluding ultrasoft pseudopotential for nitrogen which was generated in scalar-relativistic approximation with Andrea Dal Corso code which is part of QE distribution.

In case of Cr and Mn d-electrons behave in the different way than in V. The non-bonding states are fully occupied and are located below the Fermi level but closer to the valence band than in the case of V. The anti-bonding states are split and we obtain localized and non-overlapping spin up and spin down states. The spin up states are partially occupied. The spin down states are above E_F and are slightly mixed with conduction band. This is similar to behavior of the same impurities in gallium nitride and is a result of Zener double exchange mechanism.

The next dopant was iron. In this situation non-bonding and anti-bonding spin down states are mixed. The non-bonding state is localized in the middle of the gap and is partially occupied and spin down anti-bonding state lies above Fermi level and does not overlap conduction band. The spin up state lies close to the valence band. The similar situation have place in case of Co but in this case the non-bonding and anti-bonding spin up states are slightly mixed. In case of Ni we see that non-bonding and anti-bonding spin up states lie in the same positions as before and anti-bonding spin down states are split into two parts of which one is partially occupied. For Fe, Co and Ni the anti-bonding spin down states lie closer to valence band than in other impurities. We suggest that in this case we have competition between double and super-exchange mechanism. From comparison of total energy differences between FM and AFM we see that in the last case the superexchange mechanism wins and leads to the antiferromangetic state (see Table II).

In Table I we present the values of magnetic moments for transition elements TM = V, Cr, Mn, Fe, Co, Ni in $Al_{0.9375}TM_{0.0625}N$, and the total magnetic moment per cell. For V, Cr and Mn most of magnetic moments are localized on TM metal ions. In other cases situations are changed and some magnetic moments appear also on atoms in neighbors of TM. From Table II we see that ferromagnetic state is a ground state for V, Cr, and Mn, for other cases the antiferromagnetic couple is energetically more favorable. In case of V the mentioned difference is very small in comparison to other ferromagnetic states. This could be a result of the different exchange mechanism. As we mentioned above the ferromagnetic state in AlN:V could be caused by the superexchange mechanism rather than double exchange like in case of Mn and Cr.

TABLE I

Magnetic moments on TM and total per cell.

Transition metal	Magnetic moment on TM [μ_B]	Total magnetic moment per cell [μ_B]
V	1.87	2.00
Cr	2.77	3.00
Mn	3.62	4.00
Fe	3.64	5.00
Co	2.48	4.00
Ni	1.69	3.00

TABLE II

The calculated total energies for non-magnetic (NM), ferromagnetic (FM) and antiferromagnetic (AFM) states and the total energies differences between FM and AFM states.

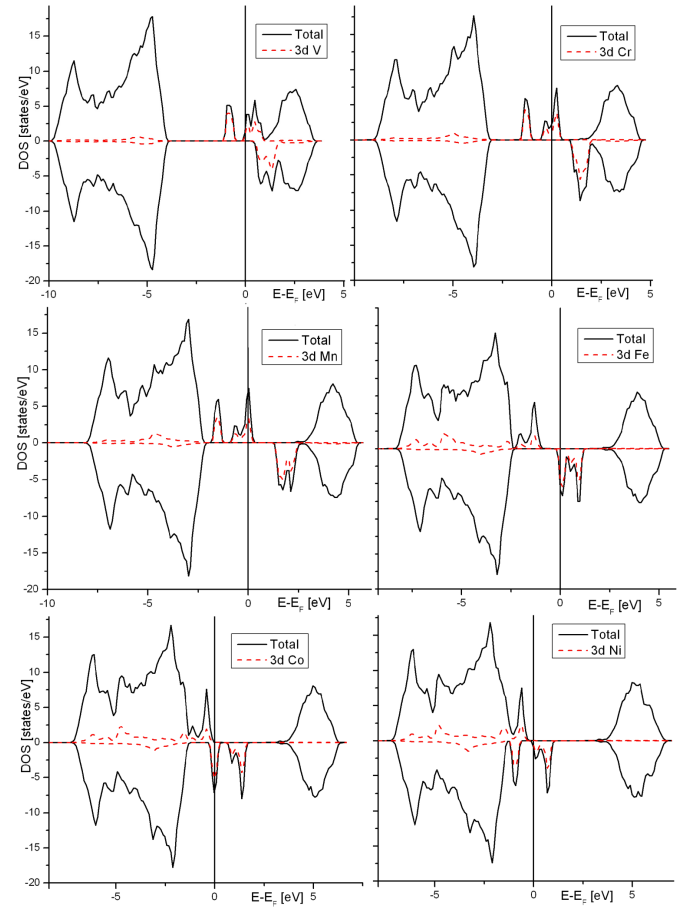| TM	NM [Ry]	FM [Ry]	AFM [Ry]	δ_{FM-AFM} [mRy]
V	−1303.40828796	−1303.51697704	−1303.51687402	−0.10
Cr	−1363.94401590	−1364.10213140	−1364.08793400	−14.20
Mn	−1434.28608730	−1434.46416318	−1434.45857982	−5.58
Fe	−1127.25048835	−1127.46672121	−1127.47294979	6.23
Co	−1164.45510247	−1164.54237547	−1164.54776992	5.39
Ni	−1187.37443496	−1187.45511238	−1187.46627258	11.16

Fig. 1. The total and partial density of states of TM d-states for AlN in the ferromagnetic state.

4. Conclusions

In this paper we present our preliminary results for AlN doped with TM. From the calculations we have observed that for V-, Cr-, Mn-doped AlN we should obtain ferromagnetic phase without additional dopants. In case of Co-, Ni- and Fe-doped AlN we obtain antiferromagnetic phase. Investigated situation is very similar to other III-nitrides semiconductors.

References

[1] T. Jungwirth, J. Sinova, J. Masek, J. Kucera, A.H. MacDonald, *Rev. Mod. Phys.* **78**, 809 (2006).

[2] F. Matsukara, H. Ohno, T. Dietl, *Handbook of Magnetic Materials*, Ed. K. Bushow, Elsevier, Amsterdam 2002, Vol. 14, p. 1.

[3] R. de Paiva, R.A. Nogueira, J.L.A. Alves, *J. Appl. Phys.* **96**, 6565 (2004).

[4] V.A. Dinh, H. Katayama-Yoshida, *J. Elec. Micro.* **54**, i61 (2005).

[5] S.Y. Wu, H.X. Liu, Lin Gu, R.K. Singh, L. Budd, M. van Schilfgaarde, M.R. McCartney, David J. Smith, N. Newman, arXiv:cond-mat/0212459v1.

[6] H.X. Liu, Stephen Y. Wu, R.K. Singh, L. Gu, D.J. Smith, N. Newman, N.R. Dilley, L. Montes, M.B. Simmonds, *Appl. Phys. Lett.* **85**, 4076 (2004).

[7] J. Kohanoff, *Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods*, Cambridge University Press 2006.

[8] P. Hohenberg, W. Kohn, *Phys. Rev. Lett.* **136**, B864 (1964).

[9] W. Kohn, L. Sham, *Phys. Rev. Lett.* **14**, A1133 (1965).

[10] QUANTUM-ESPRESSO is a community project for high-quality quantum-simulation software, based on density-functional theory, and coordinated by Paolo Giannozzi. See http://www.quantum-espresso.org and http://www.pwscf.org.

[11] B. Belhadji, L. Bergqvist, R. Zeller, P.H. Dederichs, K. Sato, H. Katayama-Yoshida, *J. Phys.: Condens. Matter* **19**, 436227 (2007).

[12] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

[13] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).