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Electronic and magnetic properties of IIA–V nitrides

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Electronic and magnetic properties of several IIA–V compounds have been analyzed using *ab initio* calculations. Two crystal structures have been considered, zinc blende (zb) and rock salt (rs), as well as the observed monoclinic phase for SrN. The results indicate that IIA–V nitrides in the rs phase are ferromagnetic half-metals. Ferromagnetism of cubic IIA–V compounds originates in the spin polarization of the p-shell of anions, as given by Hund's rule, which persists in solids after formation of bonds. Magnetism of the monoclinic SrN is due to its mixed valence character.

Key words: *magnetically ordered materials; permanent magnet; magnetic film; multilayer*s

1. Introduction

Magnetism in solids is due to the presence of transition metal cations with partially occupied d or f shells. However, it was recently proposed that spin polarization may exist in systems that do not contain transition metals. Intensive studies were devoted to magnetism in organic materials [1–3]. Next, Kukasabe et al. [4] analyzed CaP, CaAs, and CaSb in the zinc-blende (zb) structure finding that they are half-metals. (Half-metals are metals with a total spin polarization of free carriers, such as several Heusler alloys). II–V compounds were also investigated by Sieberer et al. [5] and by the present authors [6] who showed that a number of II–V crystals are half-metals. These results confirmed the presence and stability of FM in this family of materials. (For the sake of brevity, we refer to the spin-polarized and spin-unpolarized phases as ferro- and paramagnetic, and denote them by FM and PM, respectively). Kukasabe et al. [4] have attributed FM to a large contribution of d(Ca) orbitals to the bonds, while Seiberer et al. [5] explain the effect by the "flat band magnetism" of holes.

However, the zb structure analyzed in Refs. [4–6] is not a stable crystalline structure of these compounds [7]. Moreover, N atoms exhibit a tendency to form N_2 dimers in the nitrides [8]. The question therefore arises what are the stable phases, and

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*Corresponding author, e-mail: bogus@ifpan.edu.pl whether the spin polarization persists in these structures. In fact, in contrast to III–V or II–VI compounds that typically crystallize in the zb structure, II–V compounds crystallize in variety of structures, the most common being Zn_3P_2. Here, we extend our previous work to the rs phase. Since SrN has been observed both in the rock salt (rs) [9] and in the monoclinic [10] structure, we analyze both phases in some detail.

2. Method of calculations

The calculations have been performed within the framework of density functional theory. The exchange and correlation effects have been treated using the generalized gradient approximation, which typically is more accurate than the local spin density approximation for magnetic systems [11]. We have used ESPRESSO code [12], ultrasoft atomic pseudopotentials [13], and the plane wave basis with the kinetic energy cutoff of 35 Ry. Brillouin zone integrations were performed using a regular mesh of (12×12×12) k-points for the zb and rs structures, and equivalent grids for the monoclinic m-SrN. Lattice constants of the zb phase were given in [6], and that of the rs-SrN is 4.34 Å [7]. The monoclinic m-SrN has the space group C2/m (12). The calculations were performed for the experimental lattice parameters $a = 13.472$ Å, $b = 3.8121$ Å, $c = 6.7284$ Å, and $\beta = 94.72°$ [10]. The unit cell of m-SrN, shown in Fig. 1, contains 16 atoms. There are two types of N ions that differ by their local coordination. First, two neighbouring N_{pair} atoms form an N–N dimer, and there are two such molecules in the unit cell. The remaining 4 nitrogen atoms N_{iso} do not form pairs, and have 6 Sr neighbours. Both isolated N_{iso} ions and N_{pair} ions forming dimers occupy octahedra formed by Sr atoms.

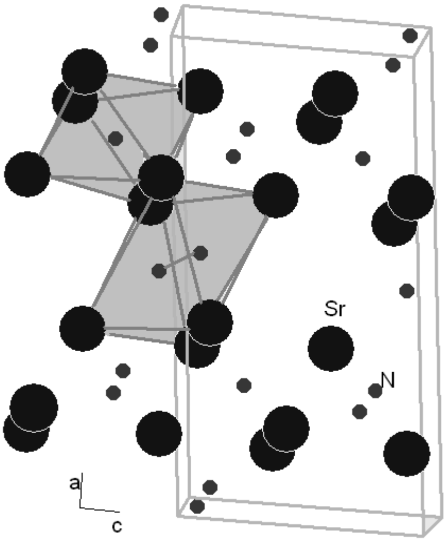

Fig. 1. Unit cell of m-SrN; N and Sr atoms are denoted by small and big dots, respectively

3. Magnetic properties and electronic structure of IIA–V compounds

The calculated magnetic parameters of the considered compounds at equilibrium are summarized in Table 1, which gives the difference in energies of the spin -polarized and spin-unpolarized phases, $\Delta E^{\mathrm{FM-PM}}$, for all investigated crystals, as well as the difference in energies of FM and antiferromagnetic (AFM) phases, $\Delta E^{\mathrm{FM-AFM}}$. First, we see that the spin polarization of the considered compounds in the zb structure is non-vanishing. Next, in both the rs and the zb structure only the II-nitrides are FM. Finally, independent of the crystal structure, the calculated magnetic moment μ per two atoms is always equal to 1 μ_B in the FM phase. A borderline case is rs-CaP, for which the very small $\Delta E^{\mathrm{FM-PM}} = -3$ meV is practically vanishing within our numerical accuracy, consistently with its small magnetic moment, 0.2 μ_B.

Table 1. Energies of spin polarization $\Delta E^{\mathrm{FM-PM}}$ for rs and zb structures and differences in energies $\Delta E^{\mathrm{FM-AFM}}$ of FM and AFM phases (all in meV per 2 atoms). The last column gives energies of spin polarization of isolated group V atoms (in eV)

	$\Delta E^{\mathrm{FM-PM}}$ (crystal)		$\Delta E^{\mathrm{FM-AFM}}$ (crystal)		$\Delta E^{\mathrm{PM-FM}}$ (anion)
	rs	zb	rs	zb	
BaN	−90	−125	−5	−45	
SrN	−135	−185	−35	−50	
CaN	−140	−195	−65	−50	−2.45
CaP	−3	−55	0		−1.37
CaAs	0	−40			−1.24
CaSb	0	−5			−1.02

The relative stability of FM and AFM phases for rs and zb structures of IIA–N nitrides was also checked. To this end, the type I AFM ordering in which spins of anions in every (001) plane are parallel but the sign of the polarization of consecutive planes alternates, was assumed[*]. The differences between energies of FM and AFM phases, $\Delta E^{\mathrm{FM-AFM}}$, given in Table 1 show that in all crystals the FM phase is the ground state magnetic order.

The origin of ferromagnetism may be identified based on the results given in Table 1, from which it follows that in the series of Ca compounds in the zb phase the energy of spin polarization is the highest for CaN, −195 meV, it decreases with the increasing atomic number of the anion, and almost vanishes for CaSb. This indicates

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[*] We do not consider other AFM phases since, e. g., in zb-MnTe energies of type-I and type-III AFM orders differ by 2 meV/atom only, see DJEMIA P., ROUSSIGNE Y., STASHKEVICH A., SZUSZKIEWICZ W., GONZALEZ SZWACKI N., DYNOWSKA E., JANIK E., KOWALSKI B.J., KARCZEWSKI G., BOGUSLAWSKI P., JOUANNE M.,, MORHANGE J.F., Acta Phys. Polonica A, 106 (2004), 239. Similar results are expected for II–V compounds. This value is by an order of magnitude smaller than $\Delta E^{\mathrm{FM-AFM}}$ for CaN and SrN, and thus does not affect our conclusions.

that anions play a dominant role in determining the spin polarization of compounds. This hypothesis is confirmed by the analysis of the density of states (DOS) shown in Fig. 2 for rs-SrN, and by projection of wave functions on atomic orbitals. In all cases the top of the valence band is mainly formed from the *p* orbitals of anions, which contribute ca. 75%. The contribution of d orbitals of cations to the valence bands is about five times smaller. These orbitals contribute mainly to the higher conduction states, and in particular to d(Sr)-derived bands at about 4–8 eV above the bottom of the conduction band. The spin polarization of SrN is clearly visible. Similar results are obtained for other II–V compounds in both the zb and the rs phases.

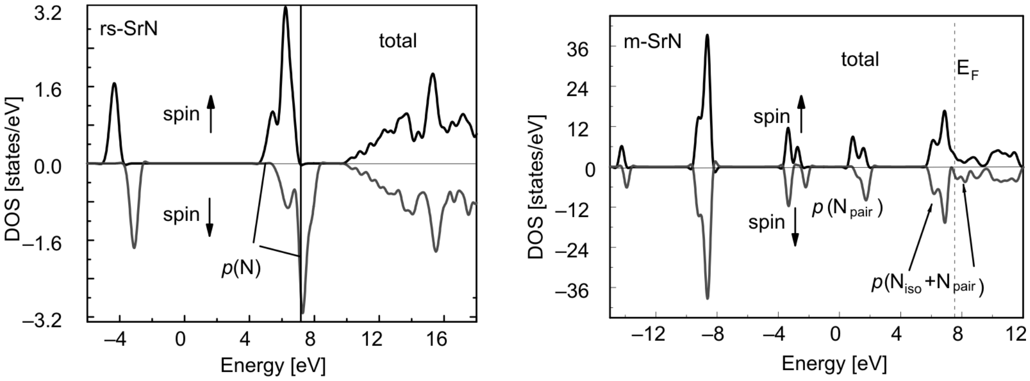

Fig. 2. Density of states per unit cell of rs-SrN and m-SrN; vertical lines show the Fermi energy; positive and negative values of DOS hold for spin-up and spin-down states, respectively

We now turn to m-SrN. Different coordinations of two types of N ions in this structure result in their different properties reflected in charge density and the density of states. In particular, charge states of the two types of N ions, N_{iso} and N_{pair}, are different, and thus m-SrN is a mixed valence compound. DOS at the Fermi level is non-vanishing, and thus m-SrN is metallic. Moreover, the difference between spin-up and spin-down DOS shows the presence of spin polarization with the magnetic moment of 2.2 μ_B per cell. Lower valence bands, displayed by peaks in the DOS, are predominately formed by one kind of atomic (or molecular) orbitals, as indicated in Fig. 2.

Analysis of the contribution of individual atoms to DOS shows that the upper valence band is formed of (i) *p* states of isolated N, $p(N_{iso})$, located about 2 eV below the top of the valence band. These orbitals are fully occupied electrons, (ii) *d*(Sr), which contributes to the valence bands at 2 eV below the Fermi level, as well as to the conduction states at 1−4 eV above E_F, and finally (iii) the states at E_F are dominated by $p(N_{pair})$. These molecular orbitals are partially filled, and give rise to a non-vanishing spin polarization of m-SrN.

Comparing the rs with the monoclinic phase of SrN we see that both structures are ionic because of the large electronegativity difference between Sr cations and N anions. In the rs structure, the odd number of valence electrons results in the half-metallic total spin polarization of free holes, driven by the robust spin polarization of isolated

N atoms. In m-SrN, there are two kinds of N ions which are in different charge states, which imply that they are in a different spin state as well. For this reason, in the notation used by chemists [10], in the monoclinic phase SrN is denoted by $Sr_4[2N^{3-}][N_2^{2-}]$, pointing out the fact that N_{iso} in the 3– state are non-magnetic and closed-shell ions, while N_{pair} are partially spin polarized. The most important result is that SrN in both structures is magnetic in spite of the absence of transition metal atoms.

4. Summary

Using *ab initio* calculations we have studied magnetic and electronic structure of a number of IIA–V compounds in the zb and rs structures. The calculated spin polarization owns its origin to the spin polarization of group V anions. The atomic spin polarization is the strongest for nitrogen, which explains stability of magnetization in CaN, SrN, and BaN nitrides, and the lack of magnetization in rs phosphides and arsenides. SrN was found to be magnetic in both rs and monoclinic structures. In the latter case, magnetism stems from the mixed valence character of m-SrN.

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