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Electronic band structure and chemical bonding in the new antiperovskites $AsNMg_3$ and $SbNMg_3$

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Abstract

The electronic properties of the new Mg-based antiperovskites $AsNMg_3$ and $SbNMg_3$ are investigated within the ab initio local-density full-potential LMTO-GGA method. Both compounds are ionic wide-gap semiconductors with a direct energy gap at Γ of 1.332 eV for $AsNMg_3$ and an indirect energy gap ($\Gamma \rightarrow M$ transitions) of 0.623 eV for $SbNMg_3$. The valence bands are composed mainly of N 2*p* and (As,Sb) *np* states. There is some covalent mixing between Mg–N and Mg–(As,Sb) valence states. The equilibrium values of lattice constants and the bulk modulus were also obtained.
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Ternary carbides and nitrides with the cubic antiperovskite structure of the general formula AXM_3, where A are p elements of III–V groups, X is carbon or nitrogen, and M are $s-d$ metals, display a wide range of interesting physical properties, from semiconducting to magnetic and superconducting, see review [1].

Depending on the chemical composition, the distinctions of these compounds are striking: VII-, VIII-group *d*-metal carbides ACM_3 (A = Al, Ga, In, Ge, Sn, etc.) and nitrides ($GaNMn_3$, $SnNFe_3$) exhibit ferro-, antiferromagnetic or more complicated types of spin ordering with temperature-dependent magnetic phase transitions [1–8]. Recently, the new superconductor $MgCNi_3$ ($T_C \sim 8$ K) was discovered and the properties of some quaternary alloys $MgCNi_{3-x}M_x$ (M = VII-, VIII-group *d* metals) [9,10] were studied. It was shown [2–8,11–14] that the electromagnetic properties of those antiperovskite materials are determined mainly by *d* states of transition metals forming the near-Fermi electronic bands.

The second group of AXM_3 involves *s*-metal-based antiperovskites such as $ANCa_3$ (A = Ge, Sn, Pb or P, As, Sb, Bi) [15,16] with filled or partially unfilled *p* bands and an unusual ionic bonding. These materials are narrow-gap semiconductors or non-magnetic ionic metals [17,18].

Recently, the new Mg-based antiperovskites $AsNMg_3$ and $SbNMg_3$ have been synthesized and their structural and transport properties have been reported [19]. Based on structural data, the authors explained these properties by a simple ionic model [20] describing Mg-based antiperovskites as $(As^{3-},Sb^{3-})N^{3-}(Mg^{2+})_3$. According to the semi-empirical band structure calculations [19], $SbNMg_3$ is an insulator with a very wide (~ 9 eV) energy gap. The experimentally observed Pauli paramagnetism and metallic behavior of $SbNMg_3$ are due to possible Mg vacancies.

In this paper, we report the results of *ab initio* calculations of the electronic properties of the above-mentioned new Mg-containing antiperovskites $AsNMg_3$ and $SbNMg_3$, a scalar relativistic self-consistent full-potential linear muffin-tin method (FLMTO) within the local density approximation (LDA) [21,22] with allowance for correlation and exchange effects [23] by using the generalized gradient approximation (GGA). The tetrahedron method was used to calculate the density of states. The results obtained include the band structure, total and site-decomposed local densities of states (DOSs). The equilibrium values of lattice constants, bulk modulus and its derivative were also found. To investigate the chemical bonding, the crystal orbital

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Table 1
Lattice parameter, bulk modulus (B) and its derivative (B') obtained by FP-LMTO GGA calculations for $AsNMg_3$ and $SbNMg_3$ as compared with experiment [19]

Compound		a (Å)	B (Mbar)	B'
$AsNMg_3$	Calc.	4.33325	0.473	5.54
	Exper.	4.21704	—	—
$SbNMg_3$	Calc.	4.47638	0.480	4.38
	Exper.	4.35161	—	—

overlap populations (COOPs) were calculated within the tight-binding method [24].

The ground-state properties of the nitrides (Table 1) are obtained by minimization of the total energy with respect to the unit cell volume (V) by a uniform compression and expansion of the lattice, which were used to carry out an isotropical variation of $V.E(V)'$s curves were fitted by Birch equation of state [25] to obtain the equilibrium lattice constants and evaluate the bulk modulus (B). As can be seen from Table 1, the obtained lattice parameters are in good agreement with the experiment: the difference between numerical and XRD data [19] is less than 2.7% and 2.8% for $AsNMg_3$ and $SbNMg_3$, respectively. The discrepancy may be due to possible Mg-lattice vacancies.

No experimental data on the bulk modulus of Mg-based ternary nitrides are available. Our estimates of the bulk modulus of $AsNMg_3$ and $SbNMg_3$ (Table 1) can be compared with those of related binary (Mg_3N_2, $B = 1.65$ Mbar [26]) and ternary ionic nitrides ($AsNCa_3$ with orthorhombic $B \sim 66.5$ GPa and simple cubic structures (SC15), $B \sim 83.6$ GPa [18]).

The energy bands for $AsNMg_3$ and $SbNMg_3$ along high-symmetry directions in the BZ are shown in Fig. 1. In Table 2 we summarize our numerical results for the band structure parameters.

The common valence band (VB) for $AsNMg_3$ includes six occupied bands and has a width of about 13.51 eV. The quasi-core N2s and As4s bands are located in the intervals from 13.51 to 12.97 and from 9.99 to 9.23 eV below the Fermi level (E_F), respectively. The DOS curves reveal a three-peak structure, Fig. 2. The lower peak A near -4.4 eV is made of contributions from nitrogen and arsenic p states, which are comparable in values. The middle peak B near ~ 2.9 eV is composed mainly of N2p states. A very sharp peak C near -0.6 eV arises from the As4p-like band that is quasi-flat along $\Gamma - X - M$ symmetry directions. It is seen from Fig. 2 that the VB contains chiefly N2p and As4p states. Mg 3s and 3p states have a density of at least a magnitude lower. Consequently, magnesium is close to its Mg^{2+} cationic configuration. N2p and As4p states overlap along the whole width of the VB. However, the N2p states are principally at the bottom, whereas As4p states are at the top of the VB. This is due to the differences in

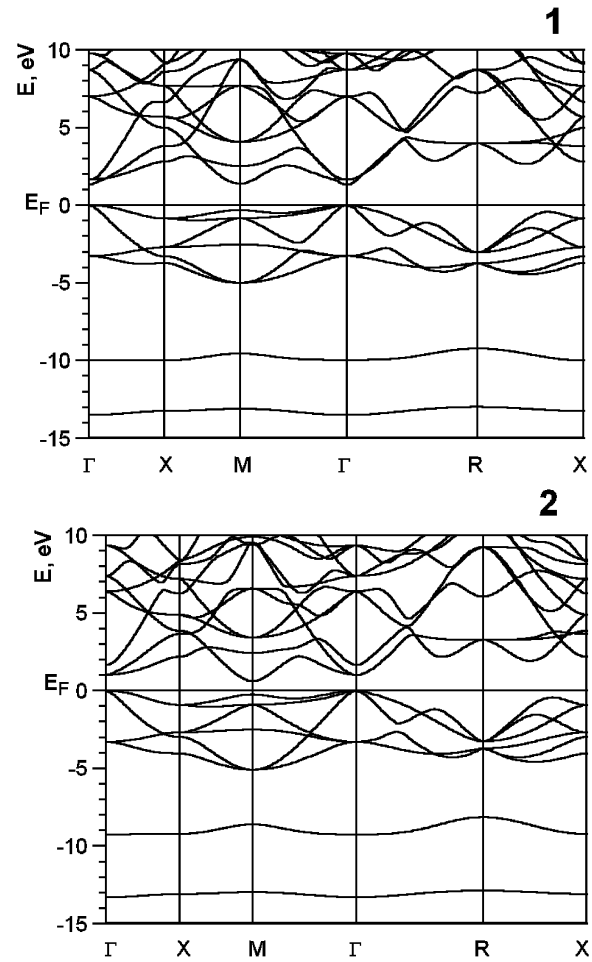

Fig. 1. Energy bands of $AsNMg_3$ and $SbNMg_3$.

the electronegativity of N and As and the types of their coordinations: N atoms are sixfold-, while As atoms are twelvefold-coordinated by Mg^{2+} cations at distances $a/2$ and $a/\sqrt{2}$, respectively. The latter circumstance determines a different character of attractive Madelung potential for N and As electrons.

The calculations show that $AsNMg_3$ has a direct energy gap of 1.332 eV at Γ point between the fully occupied antibonding As4p-like band at the top of the VB and the free bonding band (combined As–Mg-type) at the bottom of the conduction band (CB).

Generally, the band structure of $SbNMg_3$ is very similar to those of isostructural and isoelectronic $AsNMg_3$, see Figs. 1 and 2 and Table 2. The VB of $SbNMg_3$ is composed primarily of N2p and Sb5p states localized predominately near the lower and the upper edges of the VB, respectively. The "replacement" of As by Sb in the ternary nitride shows up most vividly in the position of the quasi-core Sb5p band (in the interval 9.26–8.14 eV below the E_F), as well as in the increasing dispersity (in the direction $\Gamma - M$) of the lower free-bonding band with participation of Sb s, p, d states (Fig. 1). As a result, the energy gap of $SbNMg_3$

Table 2
Band structure parameters (in eV) for $AsNMg_3$ and $SbNMg_3$ (FP-LMTO GGA calculations)

Compound	$AsNMg_3$	$SbNMg_3$	Mg_3N_2	
			Ref. [25]	Ref. [26]
Band width				
Total	13.51	13.30	13.1	13.37
Valence	5.00	5.09	4.40	4.21
Top of valence band	Γ	Γ	Γ, H	Γ
Bottom of CB	Γ	M	Γ	N
Position of N2s[a]	13.51–12.97	13.29–12.87	13.1–11.3	
Position of As,Sb ns[a]	9.99–9.23	9.26–8.14	—	—
Energy gap	1.332	0.623	2.35(Γ)	2.06(Γ−N)

[a] Below E_F.

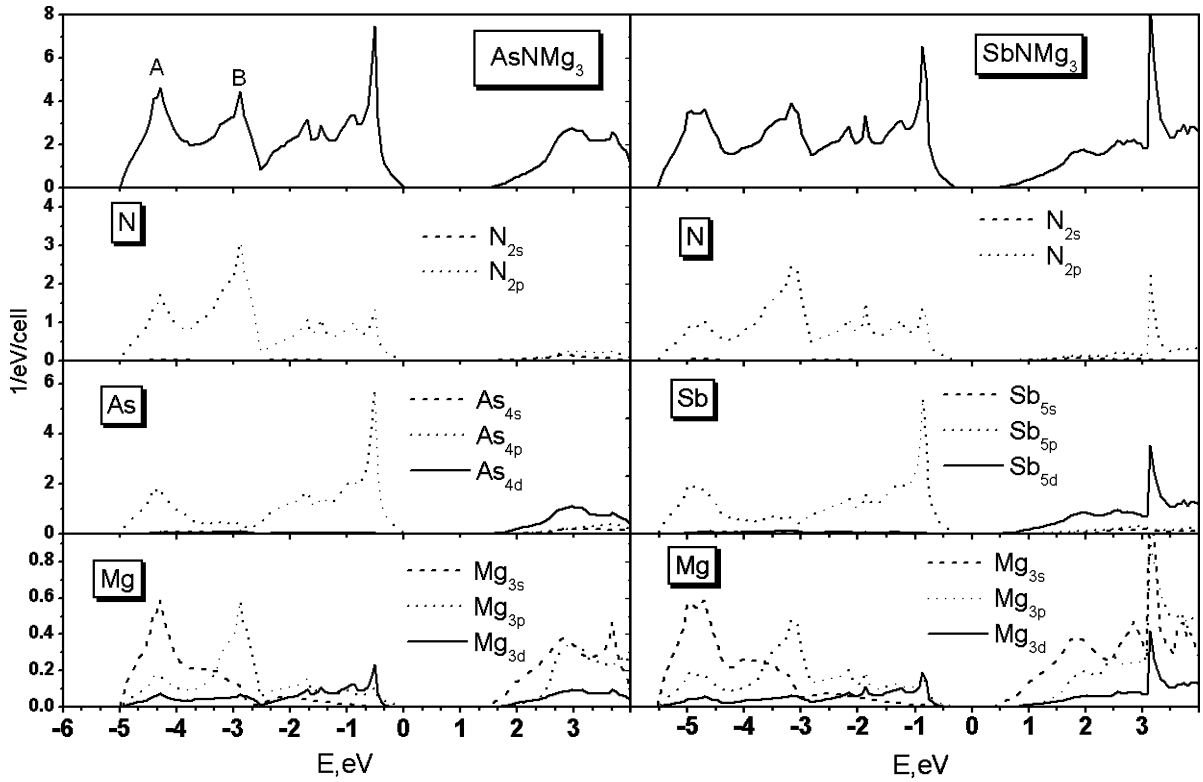

Fig. 2. Total and partial DOSs for $AsNMg_3$ and $SbNMg_3$.

decreases to ~0.623 eV and the nitride is an ionic semiconductor with an indirect gap ($\Gamma \rightarrow M$ transitions).

For comparison of individual covalent bonds, crystal orbital overlap populations (COOPs) were calculated, see Table 3. COOP analysis reveals a partial covalent character of chemical bonding for all the considered antiperovskites. These findings show that two types of Mg–N and Mg–(As,Sb) covalent bonds exist in both ternary nitrides, whereas Mg–Mg bonding is negligible (0.008–0.007 e/bond) and N–(As,Sb) interactions are antibonding (COOPs < 0). Our results indicate an increase in the order of covalency (by 8%) in NMg_6 octahedra, which is associated with a decrease in the Mg–B distance occurring during $SbNMg_3 \rightarrow AsNMg_3$ transition. COOP values of (Sb,As)–Mg, by contrast, decrease slightly. This can be accounted for by the differences in the radii and intrinsic energies of valence shells of these pnictogens.

The nearest chemical analogue of the considered Mg-based ternary nitrides is the binary nitride Mg_3N_2 used for their preparation [19]. It crystallizes in the anti-bixbyte-type structure, where N arrays are close to ideal cubic packing and each N atom is coordinated by six Mg atoms. The electronic properties of Mg_3N_2 have been recently investigated [1,2], see Table 2. It can be seen that ternary ($AsNMg_3$ and $SbNMg_3$) and binary Mg_3N_2 nitrides exhibit similar characteristics, such as valence band width, optical gap and ionic–covalent bonding type, in spite of different structures and atomic coordination numbers. The experimentally observed

Table 3
Crystal orbital overlap populations (COOPs, e/bond) for $AsNMg_3$ and $SbNMg_3$ obtained in tight-binding calculations

Phase	COOPs			
	Mg–Mg	Mg–N	Mg–(As,Sb)	(As,Sb)–N
$AsNMg_3$	0.008	0.134	0.088	−0.001
$SbNMg_3$	0.007	0.123	0.099	−0.001

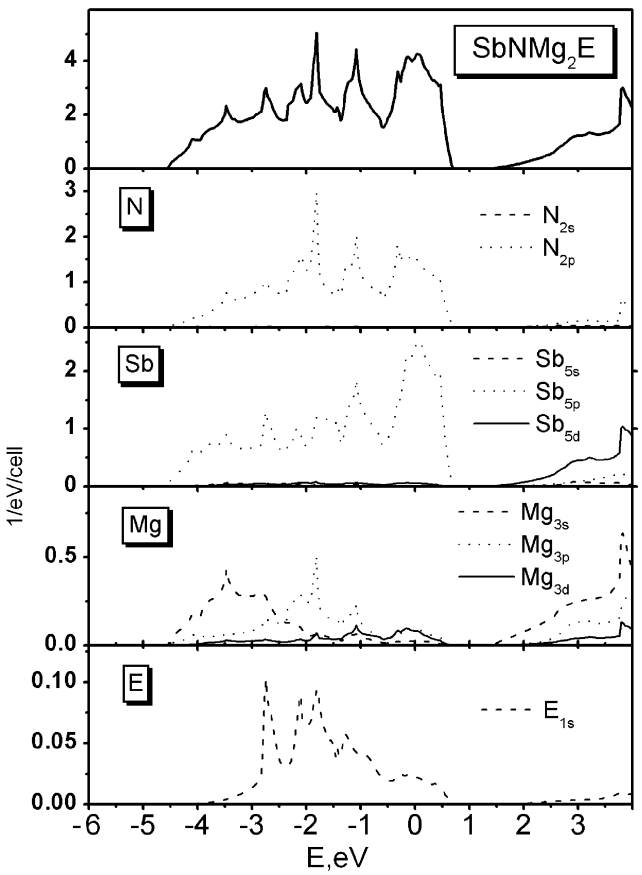

Fig. 3. Total and partial DOSs for $SbNMg_2E$ (E—Mg vacancy).

Pauli paramagnetism and metallic behavior of $SbNMg_3$ are due to possible Mg vacancies (see DOS for $SbNMg_2E$—E is Mg vacancy—Fig. 3).

An important issue is the prediction of the structure, stability factors, and electronic properties of as yet unfamiliar ternary nitrides $PNMg_3$ and $BiNMg_3$. Another problem is the investigation of regular features of formation of the electronic structure and phase conditions in the series Mg_3N_2–"$PNMg_3$"–$AsNMg_3$–$SbNMg_3$–"$BiNMg_3$", as well as possible effects of structural relaxation from the simple antiperovskite structure for Mg-based ternary nitrides. For example, according to Ref. [18], for related Ca-based nitrides, the stable structures of $PNCa_3$ and $AsPCa_3$ at zero pressure and zero temperature are orthorhombic (space group *Pbmn*). At high pressures, they may undergo phase transitions to a simple cubic SC15 structure. Our preliminary estimates of elastic constants for $AsNMg_3$ and $SbNMg_3$ point to tetragonal distortions of the ideal cubic perovskite-like structure, suggesting a probable phase transition in the region of lower temperatures. *Ab initio* ivestigations of these effects are now in progress.

In summary, *ab initio* band structure calculations were performed for the new ternary nitrides $AsNMg_3$ and $SbNMg_3$. The calculations showed that both Mg-based antiperovskites are wide-gap ionic semiconductors with a direct energy gap of 1.332 eV for $AsNMg_3$ and an indirect gap of 0.623 eV ($\Gamma \rightarrow M$ transitions) for $SbNMg_3$. The near-Fermi region is determined by N–(As,Sb) p states. The numerical estimations of individual inter-atomic overlap population reveal a partial covalent character of the nitrides. The main contributions are observed from the valence *sp* shells for Mg–N and Mg–(As,Sb) atoms; N–(As,Sb) interactions are antibonding.

References

[1] A.L. Ivanovskii, Russ. Chem. Rev. 64 (1995) 499.
[2] K. Motizuki, H. Nagai, J. Phys. C 21 (1988) 5251.
[3] K. Motizuki, H. Nagai, T. Tanimoto, J. Phys. C 49 (1988) 8–161.
[4] M. Shirai, Y. Okata, N. Suzuki, K. Motizuki, Jpn. J. Appl. Phys. 32 (3) (1993) 250.
[5] S. Iskida, S. Fujii, M. Maeda, S. Asano, Jpn. J. Appl. Phys. 32 (3) (1993) 248.
[6] S. Iskida, S. Fujii, M. Maeda, S. Asano, Jpn. J. Appl. Phys. 32 (3) (1993) 282.
[7] C.A. Kuhnen, A.V. dos Santos, Solid State Commun. 85 (1993) 273.
[8] A.L. Ivanovskii, Russ. J. Inorgan. Chem. 41 (1996) 650.
[9] N. He, Q. Huang, A.P. Ramirez, Y. Wang, K.A. Regan, N. Rogado, M.A. Hayward, M.K. Haas, J.S. Slusky, K. Inumara, H.W. Zandbergen, N.P. Ong, R.J. Cava, Nature 411 (2001) 54.
[10] M.A. Hayward, M.K. Haas, A.P. Ramirez, T. He, K.A. Regan, N. Rogado, K. Inumaru, Solid State Commun. 119 (2001) 491.
[11] I.R. Shein, A.L. Ivanovskii, N.I. Medvedeva, JETP Lett. 74 (2001) 122.
[12] A. Szajek, J. Phys.: Condens. Matter 13 (2001) L595.
[13] D.J. Singh, I.I. Mazin, Phys. Rev. B 64 (2001) 140507R.
[14] I.G. Kim, J.I. Lee, A.J. Freeman, Phys. Rev. B 65 (2002) 64525.
[15] F.J. Di Salvo, Science 247 (1990) 649.
[16] M.Y. Chern, D.A. Vennos, F.J. Di Salvo, Solid State Chem. 96 (1992) 415.
[17] D.A. Papaconstantopoulos, W.E. Pickett, Phys. Rev. B 45 (1992) 4008.
[18] P.R. Vansant, P.E. Van Camp, V.E. Van Doren, J.L. Martins, Phys. Rev. B 57 (1998) 5615.
[19] E.O. Chi, W.S. Kim, N.S. Hur, D. Jung, Solid State Commun. 121 (2002) 309.
[20] D.E. Partin, D.J. Williams, M. O'Keefe, J. Solid State Chem. 132 (1992) 56.
[21] S.Y. Savrasov, Phys. Rev. B 54 (1996) 16470.
[22] M. Methfessel, M. Scheffler, Physica B 172 (1991) 175.
[23] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
[24] H. Whangbo, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 6093.
[25] F. Birch, J. Geophys. Res. 83 (1978) 1257;
C.M. Fang, R.A. de Groot, R.J. Bruls, H.T. Hintzen, G. De With, J. Phys.: Condens. Matter 11 (1999) 4833.
[26] M.G.M. Armenta, A. Reyes-Serrato, M.A. Borja, Phys. Rev. B 62 (2000) 4890.