New type of half-metallic antiferromagnet: transition metal pnictides

New type of half-metallic antiferromagnet: transition metal pnictides

N H Long, M Ogura and H Akai

Department of Physics, Graduate School of Science, Osaka University, 1-1 Machikaneyama,
Toyonaka 560-0043, Japan

E-mail: longnh@presto.phys.sci.osaka-u.ac.jp

Abstract
The electronic structures of transition metal pnictides ABX_2, where A and B are the transition
metal elements and X = N, P, As, Sb, and Bi, with the total valence d-electron number of the
transition metal ions being ten, are investigated in the framework of the first-principles KKR
Green's function method. Some possible crystal structures such as NiAs-type, NaCl-type,
chalcopyrite, zinc-blende, wurtzite, and MnP-type structures are assumed. Similarly to
chalcogenides, a new type of spin-compensated half-metallic ferrimagnet is found for the case
of nitrides. The stability and magnetic transition temperature of these nitrides indicate that they
are good candidates for spintronics materials. For other cases of pnictides such as P, As, Sb, and
Bi, the half-metallicity seems not to be realized.

1. Introduction

Half-metallic materials, which show metallic conduction only
for one direction (say, up) of the electron spin, have been
one of the key materials of spintronics due to their possible
applications as spin injection devices. Many new half-metallic
materials have been proposed theoretically, and some of them
have also been confirmed by experiments. Almost all the half-
metallic materials so far known exhibit ferromagnetism. From
a practical point of view, the higher the Curie temperature,
the better the materials for spintronics devices. However, the
magnetic transition temperature of these ferromagnets is rather
low and, moreover, many of them seem not to be chemically
very stable. Obviously these features are not favorable for
applications. To find new half-metals which are chemically
stable and also have a high magnetic transition temperature is
a big issue.

It is well known that antiferromagnetism is the most
common magnetic structure in transition metal compounds.
Many of these antiferromagnets show rather a high Néel
temperature. Unfortunately, because of spin-rotational
symmetry, antiferromagnets cannot be half-metallic. However,
this is not true for ferrimagnets with compensated magnetic
moments. Such systems exhibit no net magnetization but yet
can be half-metallic. In order to widen the possibility of finding
chemically and magnetically stable half-metals, it is important
to examine such a new type of materials. For this purpose,
we have performed the computational materials design on the
basis of the first-principles electronic structure calculation. In
this paper, we propose transition metal pnictides as likely
candidates for materials that are half-metallic and at the same
time compensated ferrimagnets (half-metallic antiferromagnet,
hereafter).

The possibility of half-metallic antiferromagnetic materi-
als was first proposed by van Leuken and de Groot in 1995 [1].
They showed that an intermetallic compound, $V_7MnFe_8Sb_7In$,
could be a fully spin-compensated half-metallic material. In
1996, Pickett found that some double perovskites also might
be possible candidates for half-metallic antiferromagnets [2].
Recently, the Mainz group [3] and Galanakis *et al* [4] searched
on rather simple Heusler alloys such as Mn_3Ga and Cr_2MnZ
as candidates of half-metallic antiferromagnets. Their predic-
tion was based on the Slater–Pauling rule for full-Heusler al-
loys, for which the spin moment of the system $M_t = Z_t - 24$
is equal to zero if the total number of electrons Z_t reaches 24.
On the other hand, Akai and Ogura [5] pointed out the possibil-
ity of half-metallic diluted antiferromagnetic semiconductors.
These are compound semiconductors doped with 3d transition
metal ion pairs. They suggested that antiferromagnetic cou-
pling of two kinds of transition metal ions, one with less-than-
half-filled d states and the other more than half filled, realizes
half-metallicity.

The antiferromagnetic half-metallic materials are sup-
posed to be more advantageous than half-metallic ferromagnets

because of the following reasons: (i) insensitive to an external field and hence non-volatile as a magnetic memory; (ii) high magnetic transition temperature is obtained; (iii) easy to inject spin due to their small shape magnetic anisotropy. Up to now, no experimental evidence of the existence of half-metallic anti-ferromagnets has been reported. The reason might be that their magnetic and crystal structures are not as stable as the theories are asserting.

In our previous work [6], based on the same ideas of constructing the half-metallic diluted antiferromagnetic semiconductors, we found a new type of half-metallic antiferromagnets. These are transition metal chalcogenides with transition metal ions whose total number of d valence electrons is 10, such as $(FeCr)Se_2$. In addition to the advantages that half-metallic antiferromagnets generally have, these compounds could easily be fabricated. In the present paper, we search for the possibilities of transition metal compounds with a pnicogen (N, P, As, Sb, or Bi).

2. Calculation

The basic idea to obtain half-metallic antiferromagnets is described in detail in our previous papers [5, 6]. In the following, we summarize this idea briefly. As mentioned in the previous section, the idea was first proposed for the half-metallic diluted antiferromagnetic semiconductors, and then used in developing ABX_2-type intermetallic compounds. Here, A and B are the transition metal ions, one of them with less than half-filled d states and the other with more than half filled. The total number of valence electrons of A and B should be ten. As a typical example, we choose A and B as two 3d magnetic ions with d^4 and d^6 configurations, respectively. In our previous work on transition metal chalcogenides, one reasonable choice of A and B pairs is Cr and Fe. However, in the present case of pnictides with the valence electron being $+3$, a suitable choice must be a Mn and Co ion pair. Here, the Mn ion has a d^4 configuration and the Co ion has a d^6 configuration. The coupling between Mn and Co can be either ferromagnetic or antiferromagnetic. The electronic structures corresponding to these two magnetic structures are schematically shown in figure 1.

It can be seen that the antiferromagnetic coupling of Mn and Co causes a band gap at the Fermi level in the spin-down band while no gap exists in the spin-up band. On the other hand, the ferromagnetic coupling gives rise to a metallic band for the both spin bands. Total energy calculations revealed that the antiferromagnetic state is more stable than the ferromagnetic one. The difference in the total energies mostly comes from the gain in the band energy. The energy gain due to the band energy is considerably larger for the antiferromagnetic coupling than the ferromagnetic coupling. This is because the antiferromagnetic coupling produces a common d band for Mn and Co and hence causes considerable band broadening. This mechanism of the energy gain is the origin of the so-called double exchange. In contrast, the superexchange mechanism plays a role in the case of the ferromagnetic coupling. This situation is rather different from
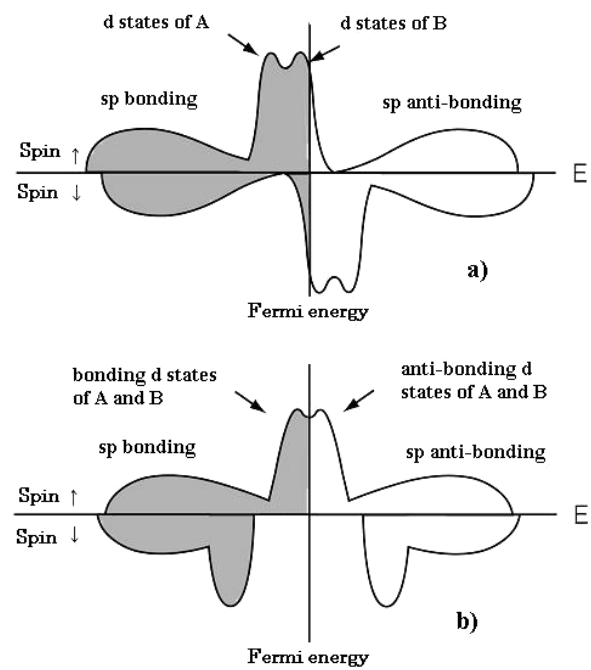

Figure 1. Schematic views of the density of states of Mn and Co in ferromagnetic coupling (a) and antiferromagnetic coupling (b).

usual half-metals, where the double exchange stabilizes the ferromagnetism [7].

To see if this mechanism also works for a wide range of transition metal compounds, we have performed the electronic structure calculations on transition metal pnictides ABX_2 using the KKR Green's function method. The method has been proven to be powerful in investigating the electronic structure of dilute magnetic semiconductors and other spintronics materials [8]. We employ the local density approximation (LDA) for the exchange–correlation potential in most cases. However, because of the non-vanishing self-interaction, the LDA usually underestimates the band gap. In order to examine this effect, we have also employed the self-interaction correction (local SIC) in some specific cases. The implementation of the local SIC is based on the pseudo-SIC idea of Filippetti *et al* [9], though the pseudo-potential scheme is not used in the present study. Such approaches were also used by other authors in the investigation of ferromagnetic half-metals [10]. For the calculation of disordered systems, the coherent potential approximation (CPA) [11] is exploited.

The stable structure of transition metal nitrides in nature is either NaCl type or zinc-blende type [12–14]. The transition metal phosphides AP (A are transition metals) are known to take a MnP-type or a NiAs-type structure [15]. On the other hand, the compounds AX (X are As, Sb, Bi) are stabilized in the NiAs-type structure [15]. Therefore, in the present study, we have considered all stable as well as metastable structures, namely NiAs-type, NaCl-type, zinc-blende (ZB), wurtzite, chalcopyrite and MnP-type structures, for transition metal pnictides ABX_2. The details of the calculation for each case will be given in the following section.

In order to estimate magnetic transition temperatures, the magnetic exchange parameters J_{ij} are obtained following
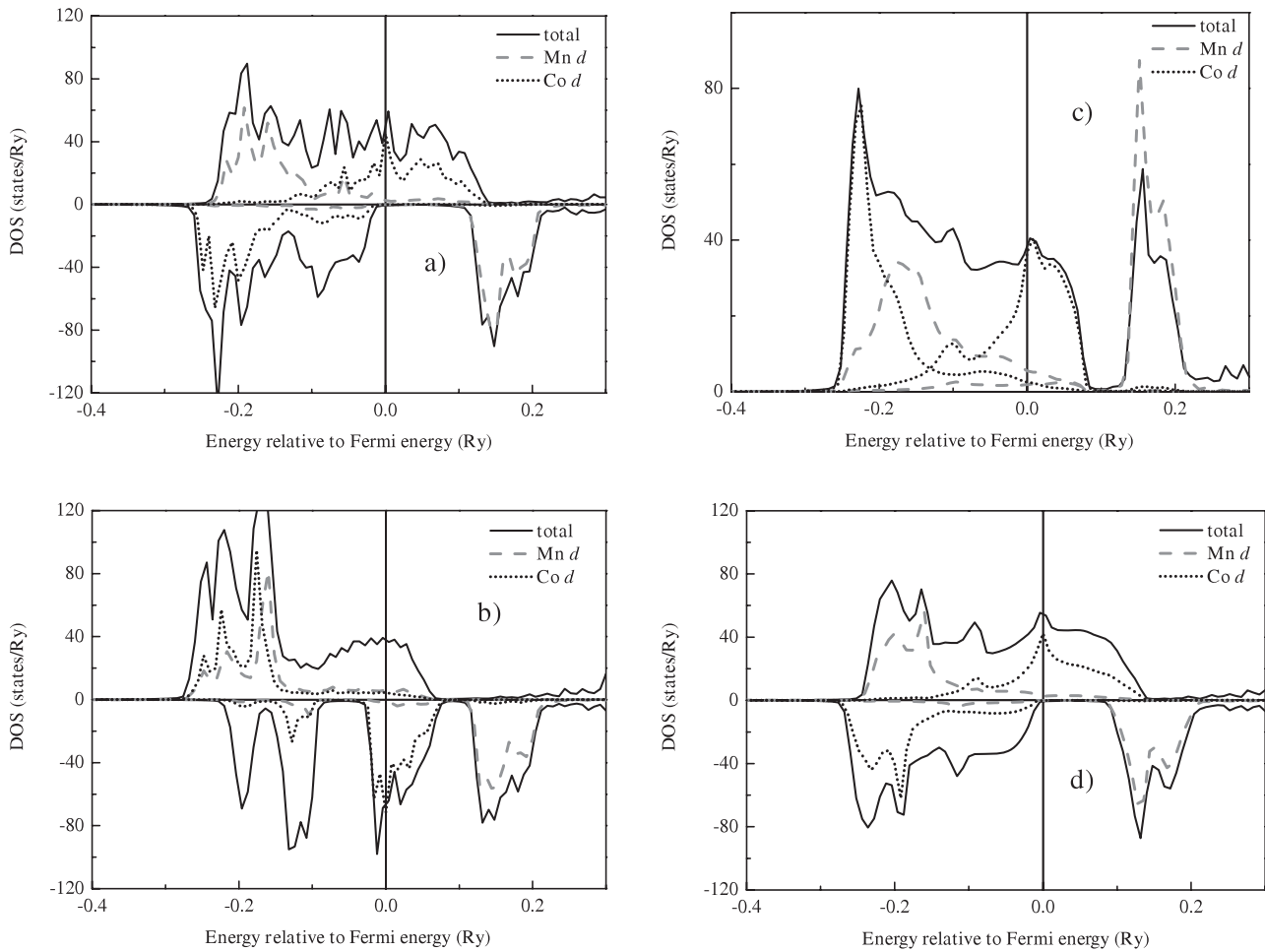
Figure 2. DOS of ZB-type $(MnCo)N_2$ in (a) antiferromagnetic ordered structure (see the text for details); (b) ferromagnetic ordered structure; (c) LMD state; (d) antiferromagnetic disordered structure.

Liechtenstein's formula [16]. Using thus obtained magnetic exchange parameters and assuming the Heisenberg Hamiltonian, the magnetic transition temperature is calculated in the framework of the mean-field approximation or the cluster approximation (CA) that was used by Ogura *et al* [17].

3. Results and discussion

The results of the calculation indicated that transition metal nitrides showed half-metallic antiferromagnetism, similar to chalcogenides, in many cases. However, other transition metal pnictides (P, As, Sb, and Bi) did not exhibit half-metallicity. Therefore, the cases of nitrides will be discussed separately.

3.1. Nitrides

The experimental analyses showed that the 3d transition metal nitrides AN (A = Sc, Ti, V, Cr, and Mn) have a stable NaCl-type structure [13]. For FeN and CoN, some authors concluded that they could take either NaCl-type or ZB structure [12, 13]. Though there are no experimental results for NiN and CuN, their stable structures were predicted theoretically as a ZB-type structure by Wang *et al* [14]. In the present calculation, since

there is no experimental evidence for the whole statement, we have performed the calculation for ABN_2 in different types of structures such as the NaCl-type, ZB, wurtzite, NiAs-type and chalcopyrite structures. Since for systems of open structure the determination of the lattice parameters is not reliable with the muffin-tin potential model that was exploited in the present calculation, plausible lattice constants estimated from ionic radii of pure systems are used in the present study.

As a typical example, in figure 2, the densities of states (DOSs) for ZB-$(MnCo)N_2$ are shown in four cases: the antiferromagnetic (chemically) ordered structure, ferromagnetic ordered structure and the local-moment-disordered (LMD) state in figures 2(a)–(c), respectively, as well as the antiferromagnetic (chemically) disordered structure in figure 2(d). The chemically ordered structure here means that the Mn and Co ions are located in different sublattice layers stacked along the z direction. Meanwhile, in the disordered structure with chemical formula $(Mn_{0.5}Co_{0.5})N$, Mn and Co atoms are located randomly in the transition metal sites. It is interesting that the antiferromagnetic coupling between d states of Mn and Co realizes half-metallicity in both ordered and disordered structures. In addition, the total energies of the antiferromagnetic ordered structure and
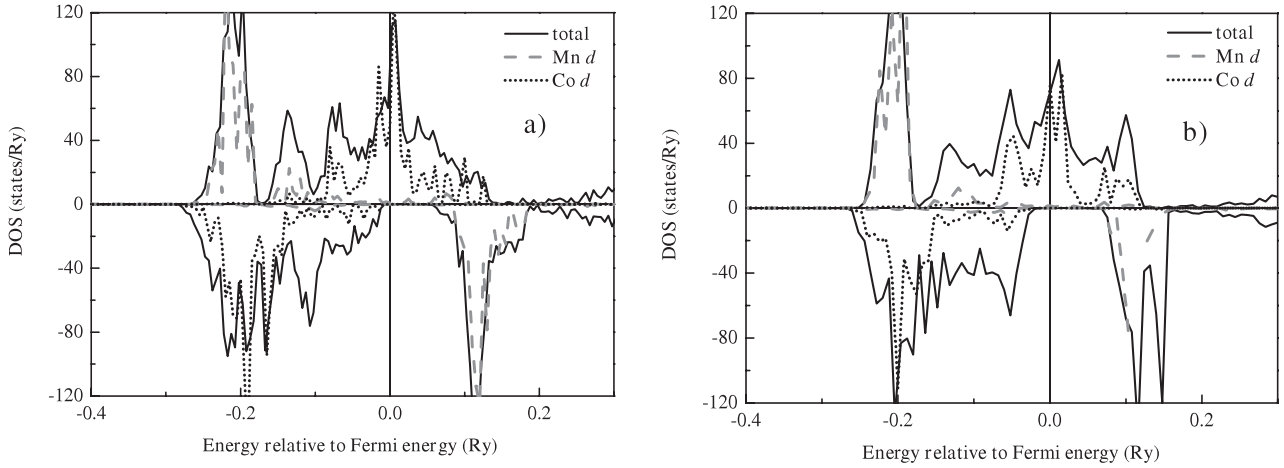
Figure 3. DOS of (MnCo)N$_2$ in (a) NaCl type and (b) NiAs type, both in the antiferromagnetic ordered structure.
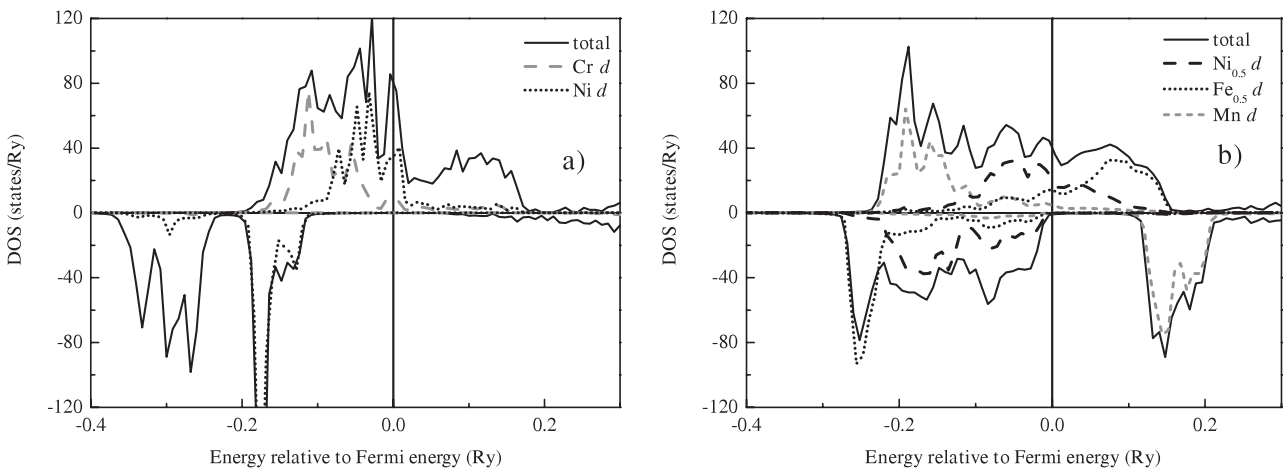

Figure 4. DOS of (a) NaCl-type (NiCr)N$_2$ and (b) ZB-type (MnFe$_{0.5}$Ni$_{0.5}$)N$_2$, all in the antiferromagnetic ordered structure.

ferromagnetic ordered structure are -29.3 and 9.7 mRyd, respectively, compared with the LMD state. Moreover, the total energy of the antiferromagnetic disordered structure is 10.0 mRyd higher than that of the ordered structure. Therefore, we can conclude that the antiferromagnetic ordered structure should be the most stable structure among others considered here.

In figure 3, the DOSs of (MnCo)N$_2$ in the antiferromagnetic ordered structure of NaCl-type and NiAs-type structures are presented. It is seen that the half-metallicity is realized, similarly to ZB-(MnCo)N$_2$. Also in the chalcopyrite and wurtzite structures the half-metallic antiferromagnetism is stable (not shown here).

In table 1, we summarize the total magnetizations of (MnCo)N$_2$ in the antiferromagnetic ordered structure in various types of crystal structures. In all cases, the different signs of local magnetic moments of Mn and Co lead to vanishing total magnetic moment. The magnetic transition temperatures (Néel temperatures T_N) are also given in the last two columns. The Néel temperatures calculated by the mean-field theory are not much different from those calculated by the cluster approximation (CA). The estimated T_N values are

Table 1. Magnetic moments and transition temperature (T_N) for (MnCo)N$_2$ for various types of structure.

(MnCo)N$_2$ structure	Moment (μ_B)			T_N (K)	
	Mn	Co	Total	Mean field	CA
Zinc-blende	3.856	-2.503	0.034	519	420
NaCl type	4.309	-2.483	0.002	196	143
NiAs type	4.259	-2.456	0.002	347	327
Chalcopyrite	3.850	-2.555	0.007	530	445
Wurtzite	4.018	-2.530	0.004	295	268

around room temperature, leading to the applicability of these materials to spintronics devices.

As mentioned in section 2, A and B of ABX$_2$ are transition metal ions whose total valence electron number is ten. Therefore, beside the Mn and Co pair, the Ni and Cr pair is also an adequate choice. However, in the present case, it is revealed that there occurs no band gap at the Fermi level in the spin-down band within the LDA. In order to examine a possible overscreening effect due to the LDA, we introduce the local SIC treatment. This procedure is introduced only to estimate a possible band gap on the safe side. In figure 4(a),
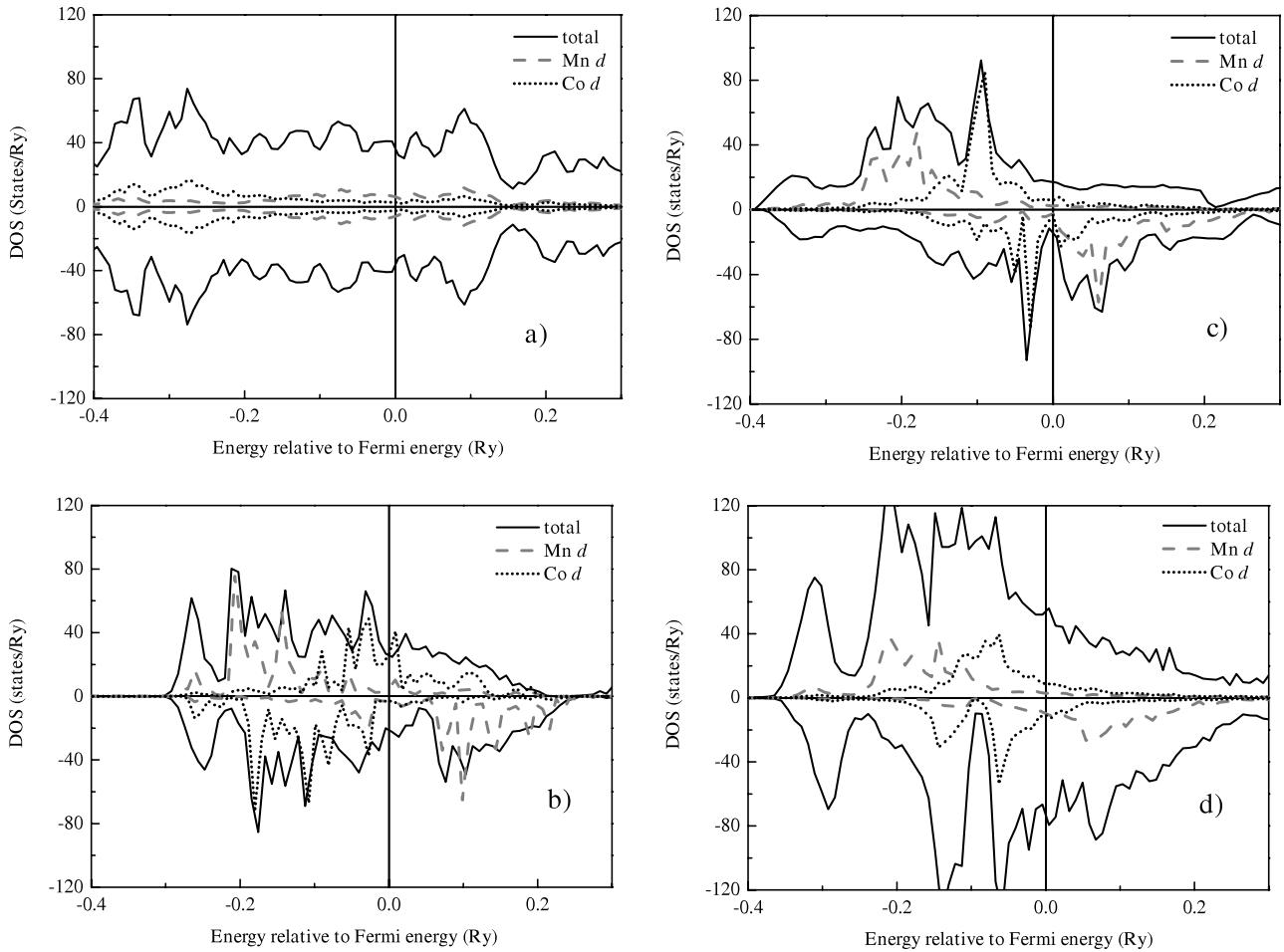
Figure 5. DOS of (a) MnP-type $(MnCo)P_2$; (b) ZB-type $(MnCo)As_2$; (c) NiAs-type $(MnCo)Sb_2$; (d) chalcopyrite $(MnCo)Bi_2$ all in the antiferromagnetic ordered structure.

the local SIC calculations for DOS of NaCl-type $(NiCr)N_2$ are shown as typical examples. It is apparent that a wide insulator gap appears in the spin-down band due to the large exchange splitting of Ni and Cr. Hence, the half-metallicity of $(NiCr)N_2$ is realized within the local SIC scheme.

The A and B atoms are not necessary strictly chosen to form a pair. For example, if we substitute Co in $(MnCo)N_2$ with 50% Fe and 50% Ni, the compound becomes $(MnFe_{0.5}Ni_{0.5})N_2$. The total number of valence electrons remains ten. It can be seen in figure 4(b) for ZB-type $(MnFe_{0.5}Ni_{0.5})N_2$ that half-metallicity is also realized because of the antiferromagnetic couplings of Mn–Fe and Mn–Ni. This idea can be equally applied for other cases such as $(Fe_{0.5}Cr_{0.5}Co)N_2$ or $(Fe_{0.5\uparrow}Cr_{0.5\uparrow}Ni_{0.5\downarrow}Fe_{0.5\downarrow})N_2$.

3.2. Compounds with P, As, Sb, and Bi

Most of the transition metal phosphides have a MnP-type structure. Other transition metal pnictides (i.e. As, Sb, and Bi) have a stable phase of NiAs-type structure and a metastable phase of ZB structure [15]. In the following, we show the DOS of ABX_2 with X as P, As, Sb, and Bi in some structures to see their electronic structure as well as the magnetic properties. In these calculations, the lattice constants are taken from the experimental values of manganese pnictides MnX.

In the MnP-type crystal structure, the transition metal pnictides are nonmagnetic. In figure 5(a), the DOS of the MnP-type $(MnCo)P_2$ is shown as an example. In figures 5(b)–(d), the DOSs of ZB-type $(MnCo)As_2$, NiAs-type $(MnCo)Sb_2$ and chalcopyrite-type $(MnCo)Bi_2$ are illustrated, respectively. It can be seen that the exchange splitting of the more-than-half-filled transition metal ion (here is Co) is not enough to create an insulator gap in the spin-down band in all the cases. In order to estimate a possible correction to the band gap, we have performed the local SIC calculation for these systems. The calculated results for the DOS of ZB-type $(MnCo)As_2$ and NiAs-type $(MnCo)Sb_2$ are plotted in figure 6.

For ZB-type $(MnCo)As_2$ (figure 6(a)), although the exchange splitting of d states of transition metals is large within the local SIC calculation, the hybridization between d states of Co and p states of pnictide ions is still considerable. As a result, there remain still some holes in the spin-down band at the Fermi level, leading to metallic bands in both spin directions. Therefore, the system is not appropriate as a candidate for a half-metallic antiferromagnet. For NiAs-type $(MnCo)Sb_2$ (figure 6(b)), the system is even a ferromagnet. Consequently, these systems are unlikely to be half-metallic. We have also searched for other possible transition metals such as a Ni–Cr pair. The results for these systems are quite similar to the Mn–Co cases.
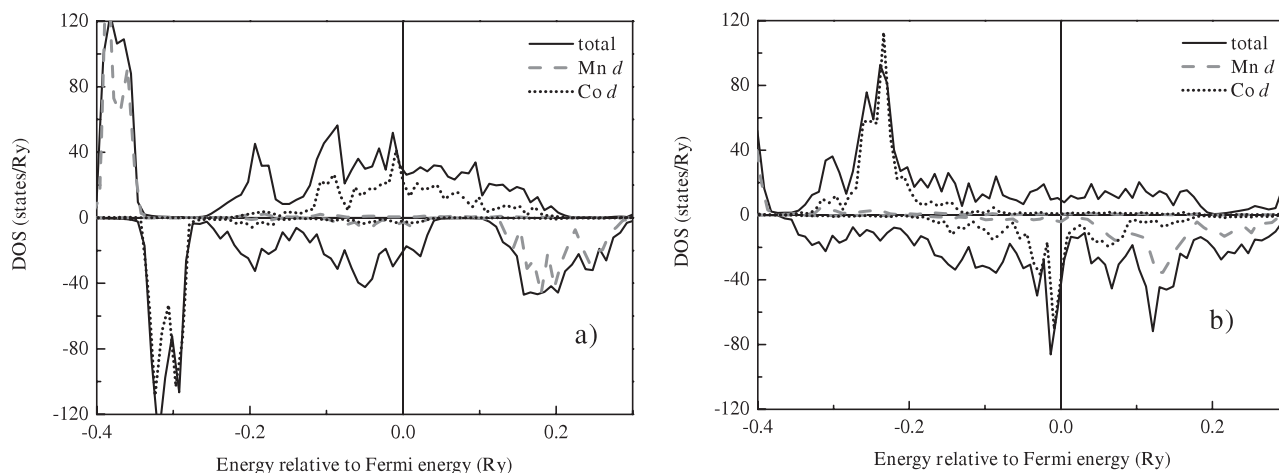
Figure 6. DOS of (a) ZB-type $(MnCo)As_2$ and (b) NiAs-type $(MnCo)Sb_2$ in the antiferromagnetic ordered state calculated by the pseudo-SIC.

4. Conclusion

We have considered the possibilities of half-metallic antiferro-magnets consisting of transition metal ions and pnicogens (N, P, As, Sb, and Bi). For transition metal nitrides, a new type of half-metallic antiferromagnet is realized. These systems contain transition metal ions, either as pairs such as Mn–Co and Ni–Cr or as combinations of more than two types of ions, whose total valence electron number is ten. The 100% spin polarization at the Fermi level, that is the half-metallicity, is predicted in various kinds of structures such as NiAs-type, NaCl-type, zinc-blende, chalcopyrite, and wurtzite crystal structures. The estimated magnetic transition temperatures of these materials (T_N) are around room temperature, leading to possible applications to spintronics devices.

On the other hand, for other transition metal pnictides (P, As, Sb, and Bi), because of strong hybridization between the transition metal and pnictide ions, we could not find any similar kind of half-metallic antiferromagnets. This implies that the half-metallic antiferromagnetism is rather difficult in the intermetallic compounds of transition pnictides, except nitrides.

Acknowledgments

References

[1] van Luken H and de Groot R A 1995 *Phys. Rev. Lett.* **74** 1171
[2] Pickett W E 1996 *Phys. Rev. Lett.* **77** 3185
[3] Wurmehl S, Kandpal H C, Fecher G H and Felser C 2006 *J. Phys.: Condens. Matter* **18** 6171
[4] Galanakis I, Ozdogan K, Sasioglu E and Aktas B 2007 arXiv:cond-mat/0703078v1
[5] Akai H and Ogura M 2006 *Phys. Rev. Lett.* **97** 026401
[6] Akai H, Long N H and Ogura M 2008 *Phys. Rev. Lett.* submitted
[7] Akai H 1998 *Phys. Rev. Lett.* **81** 3002
[8] Akai H http://sham.phys.sci.osaka-u.ac.jp/kkr/
[9] Filippetti A and Spaldin N A 2003 *Phys. Rev.* B **67** 125109
[10] Toyoda M, Akai H, Sato K and Katayama-Yoshida H 2006 *Physica* B **376/377** 647
[11] Akai H 1989 *J. Phys.: Condens. Matter* **1** 8045
[12] Suzuki K, Yamaguchi Y, Kanoko T, Yoshida H, Obi Y, Fujimmori H and Morita H 2001 *J. Phys. Soc. Japan* **70** 1084
[13] Suzuki K, Shinohara T, Wagatsuma F, Kaneko T, Yoshida H, Obi Y and Tomiyoshi S 2003 *J. Phys. Soc. Japan* **72** 1175
[14] Wang H B and Xue D-S 2004 *Chin. Phys. Lett.* **21** 1612
[15] Adachi K and Ogawa S 1988 *Magnetic Properties of Non-Metallic Inorganic Compounds Based on Transition Elements: Pnictides and Chalcogenides* (Berlin: Springer)
[16] Liechtenstein A I, Katsnelson M I, Antropov V P and Gubanov V A 1987 *J. Magn. Magn. Mater.* **67** 65
[17] Ogura M, Takahashi C and Akai H 2007 *J. Phys.: Condens. Matter* **19** 365226