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Bulk and surface sp half-metallic ferromagnetism in alkali metal pnictides with rocksalt structure: a first-principles calculation

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Abstract
Recently, sp half-metallic ferromagnetism in alkali metal/alkaline earth pnictides (I/II–V) with zinc blende structure was predicted by first-principles calculations (Sieberer *et al* 2006 *Phys. Rev.* B **73** 024404). To search for half-metallic ferromagnets with a more stable structure in alkali metal pnictides MX (M = Li, Na, K; X = N, P, As), we apply here first-principles all-electron and pseudopotential-method-based density functional theory to investigate the electronic and magnetic properties of these compounds with rocksalt structure. Five rocksalt compounds are found to be half-metallic ferromagnets with a magnetic moment of 2.00 μ_B/f.u., and they are more stable energetically than the ones with zinc blende structure, which makes them more promising candidates for the possible growth of half-metallic films or ultrathin films on suitable semiconductor substrates. Furthermore, we show that both lithium- and nitrogen-terminated (111) surfaces of rocksalt lithium nitride retain the bulk half-metallic characteristic, and the surface atomic magnetic moments are enhanced compared to the bulk values.

1. Introduction

Successful realization of spintronics devices requires efficient spin injection from a ferromagnet into a semiconductor for spin control and manipulation [1, 2]. Half-metallic (HM) ferromagnets are seen as the most promising candidates of spin-injector materials because their electronic structures are metallic in only one of the two spin channels, resulting in nearly complete (100%) spin polarization around the Fermi level (the spin–orbit coupling leads to a minor reduction of the spin polarization). The first discovery of HM ferromagnets was in 1983 by de Groot *et al* when calculating the band structure of the half-Heusler compound NiMnSb [3]. So far, many HM ferromagnets have been predicted theoretically or synthesized experimentally in several classes of compounds (see [2] and [4] for recent reviews on HM systems), e.g. full-Heusler alloys such as Co_2MnSi [5], metallic oxides such as CrO_2 [6] and

Fe_3O_4 [7], perovskite compounds such as $La_{0.7}Sr_{0.3}MnO_3$ [8], diluted semiconductors such as Cr-doped ZnTe [9], zinc blende (ZB) transition-metal pnictides and chalcogenides [10–13], and alkaline earth pnictides and carbides [14–16].

Contrary to other HM ferromagnets, the ones with ZB structure are more promising materials for spintronics devices due to their high Curie temperatures and their compatible lattice structures with conventional semiconductors. Furthermore, ZB half-metals have an interesting property that the half-metallicity not only exists in transition-metal pnictides and chalcogenides [10–13] but also exists in alkaline earth pnictides and carbides [14–16]. The former and latter cases are named d and sp HM ferromagnets, respectively, because the ferromagnetic moment is formed mainly by the transition-metal d and anion p electrons, respectively. Contrary to the d HM ferromagnets with ZB structure, on the other hand, the sp ones are more meaningful in realistic applications because they

create lower stray fields and lead to smaller energy losses due to the smaller values of magnetic moment they possess [17].

Therefore, sp HM ferromagnets with ZB structure such as alkaline earth/alkali metal pnictides and alkaline earth carbides were extensively investigated [14–16, 18]. Several research groups used first-principles calculations to predict the possible growth of sp HM films of alkaline earth/alkali metal pnictides and alkaline earth carbides with ZB structure because the ZB structure is not their ground state. The estimated Curie temperatures, exceeding considerably room temperature, make these sp HM systems more promising candidates in spintronics devices [15, 16]. But there have been no experimental reports about these ZB sp HM compounds till now, and thus it is meaningful to find a more stable structure energetically, in contrast to the ZB one for the possible growth of these sp HM ferromagnetic films.

Considering the sp HM ferromagnetism of alkali metal pnictides was investigated only for the ZB structure [15], in this paper we apply first-principles calculations to study the electronic and magnetic properties of these compounds with rocksalt structure, and five sp half-metals with a magnetic moment of 2.00 μ_B/f.u. are found. Importantly, the rocksalt structure of these five half-metals is more stable energetically than the ZB structure. We also show both lithium- and nitrogen-terminated (111) surfaces of rocksalt lithium nitride retain the bulk HM characteristic. This is the first report on the surface sp half-metallicity in binary compounds, and the results are helpful for the possible growth of sp HM films of alkali metal pnictides with rocksalt structure.

2. Computational method

We use the first-principles full-potential linearized augmented plane-wave (FP-LAPW) (Wien2k code) [19] and the plane-wave pseudopotential (PWPP) method-(CASTEP code) [20] based density functional theory to calculate the electronic and magnetic properties of alkali metal pnictides MX (M = Li, Na, K; X = N, P, As). In the FP-LAPW calculations, the radii R_{mt} of the muffin tins for Li, N, Na, P, K and As are chosen to be 1.5, 1.8, 2.0, 2.0, 2.3 and 2.3 a.u., respectively. The $R_{mt}K_{max}$ is set as 8.0. The self-consistency calculations are considered to be converged only when the energy difference between input and output energy was less than 10^{-5} Ryd/f.u.. In the PWPP calculations, the ultrasoft pseudopotentials for M and X atoms are adopted, and the plane-wave energy cutoff is taken as 500 eV. For both methods of FP-LAPW and PWPP, the Brillouin zone integration is carried out by using the $10 \times 10 \times 10$ and $10 \times 10 \times 1$ k-point meshes for the bulk and surface calculations, respectively, and the generalized gradient approximation in the scheme of Perdew, Burke and Ernzerhof (GGA-PBE) [21] is used for the electronic exchange–correlation functional.
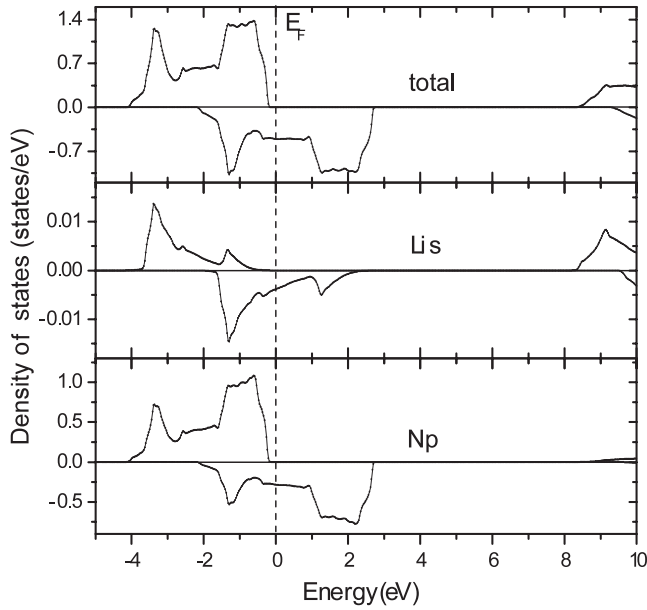
3. Results and discussion

We begin with the geometry optimization for rocksalt MX with both the FP-LAPW and PWPP methods in order to determine the equilibrium lattice constants in the ferromagnetic state. The

Table 1. The optimized lattice constants (a_0) of I–V compounds with rocksalt structure in the ferromagnetic state and total magnetic moments (M) per formula unit. For each compound, FP-LAPW results are listed on the first line, with PWPP results on the second line.

	a_0 (Å)			M (μ_B)		
	N	P	As	N	P	As
Li	4.33	5.00	5.20	2.00	0.00	0.00
	4.35	5.00	5.19	2.00	0.00	0.00
Na	5.03	5.87	5.90	2.00	1.55	0.65
	5.02	5.89	5.94	2.00	1.72	1.03
K	5.82	6.74	6.90	2.00	2.00	2.00
	5.76	6.67	6.85	2.00	2.00	2.00

optimized lattice constants are listed in table 1. We find the differences of lattice constants between the two computational methods are small. Table 1 gives the calculated total magnetic moments per formula unit (f.u.) for rocksalt MX at equilibrium lattice constants. Both calculated methods show that there is no spin polarization in rocksalt LiP and LiAs, which is the same as that of ZB LiP and LiAs [15]. In contrast, only five rocksalt compounds LiN, NaN, KN, PK and KAs have an integer magnetic moment of 2.00 μ_B/f.u., but this phenomenon of integer moment exists in all ZB MX except LiP and LiAs [15]. Note that the difference in calculated magnetic moments between the FP-LAPW and PWPP methods is small except for NaAs. This can be explained from the dependence of magnetic moment on the lattice constant of NaAs. From table 1 we know the magnetic moments of NaAs are 0.65 and 1.03 μ_B at the optimized equilibrium lattice constants (5.90 and 5.94 Å) with Wien2k and CASTEP codes, respectively. But our further calculated magnetic moment with CASTEP at the lattice constant of 5.90 Å is 0.88 μ_B, which indicates the magnetic moment is sensitive to the change of lattice constant, and the difference in magnetic moment between the two calculated codes becomes small at the same lattice constant. So the difference in magnetic moment between the two codes mainly originates from the different equilibrium lattice constants. The following results are presented with the FP-LAPW method.

Considering an integer magnetic moment is the characteristic of HM ferromagnets, we have performed the electronic structure calculations for five rocksalt compounds LiN, NaN, KN, KP and KAs. We find these five compounds exhibit half-metallicity. As an example, the spin-polarized total and main partial density of states (DOS) of rocksalt LiN are shown in figure 1. We only give the partial DOS of Li s and N p states because the values of other states around the Fermi level are very small. The total DOS indicates that the minority spin (spin down) electrons are metallic, while there is an energy gap around the Fermi level for the majority spin (spin up) electrons of rocksalt LiN. Thus rocksalt LiN exhibits an HM characteristic. Comparing the total DOS and the partial DOS, one can see that the total DOS around the Fermi level of rocksalt LiN originates mainly from the N p states with a small contribution from the Li s states. The spin splitting mainly occurs to the N 2p states, which provides the main magnetic moment. This

Figure 1. Spin-polarized total and main partial DOS of rocksalt LiN.

Figure 2. Total energies as a function of volume per formula unit for LiN with rocksalt and zinc blende structures. FM and AFM represent ferromagnetic and antiferromagnetic states, respectively.

can be seen from the calculated magnetic moment. The total magnetic moment of 2.00 μ_B/f.u. for rocksalt LiN consists of three parts: the Li atom (0.01 μ_B), the N atom (1.58 μ_B) and the interstitial area (0.41 μ_B). The small moment of the Li atom results from the hybridization between the Li s states and the N p states.

To determine the magnetic ground state of rocksalt LiN, we also calculate the total energy of LiN in the antiferromagnetic state. Because the above ferromagnetic calculations have shown that the magnetic moments are mainly carried by the N p electrons, in the antiferromagnetic calculations we refer to [15], i.e. we consider an eight-atom cell with cubic primitive lattice vectors and a layer geometry along the [001] direction, where two anions N are situated in the $z = 0$ plane and two in the plane $z = a/2$, which can be assumed during the calculations to have an antiparallel magnetization. Figure 2 gives the calculated total energy as a function of volume per formula unit of LiN in antiferromagnetic and ferromagnetic states. Obviously, the ferromagnetic energy is lower than that of the antiferromagnetic state, and the total energy difference between the antiferromagnetic and ferromagnetic states at equilibrium lattice constants is about 150 meV/f.u. So the ferromagnetic state is the magnetic ground state of rocksalt LiN. The calculated total magnetic moment in the LiN cell with antiferromagnetic state is 0 μ_B and the antiparallel N magnetic moments are 1.35 and -1.35 μ_B, which indicates the success of the antiferromagnetic calculations. We also note that the absolute values of N magnetic moments in the antiferromagnetic state are a little smaller than that in the ferromagnetic state (1.58 μ_B) due to the different equilibrium lattice constants between the antiferromagnetic and ferromagnetic states (see figure 2). For the other four half-metals of rocksalt NaN, KN, KP and KAs, our further calculations show that the ferromagnetic state is also their ground state, and the total energy differences
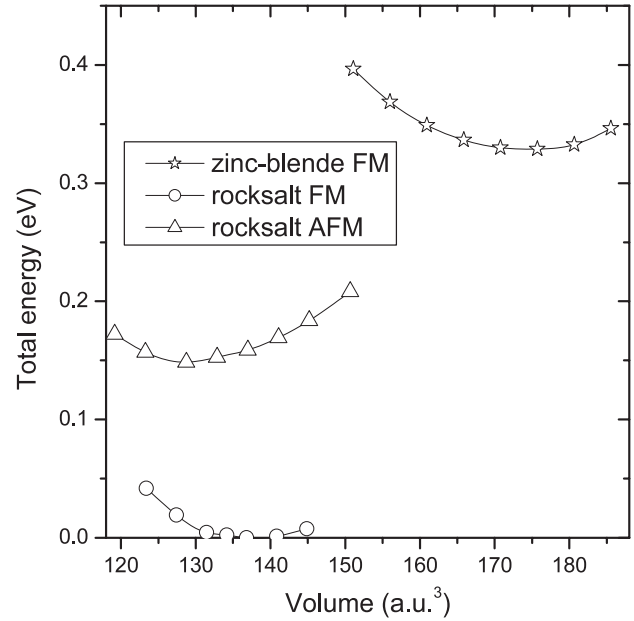
between the antiferromagnetic and ferromagnetic states are about 240, 172, 139 and 198 eV/f.u., respectively. The large energy differences stabilize strongly the ferromagnetic ground state.

Sieberer *et al* [15] presented the prediction of the growth of HM films of alkali metal pnictides MX with ZB structure because the ZB structure is not their ground state. We now make a comparison of structural stability between the ZB and rocksalt structures. The total energy as a function of volume per formula unit of ferromagnetic LiN with ZB structure is shown in figure 2. It shows that the rocksalt structure has lower energy than the ZB structure, and the total energy difference between ZB and rocksalt structures is about 0.33 eV/f.u.. This value is considerable, and thus compared to the ZB structure of LiN the rocksalt structure is more possibly stabilized on suitable semiconductor substrates. Similar behaviors are also obtained for the other four HM alkali metal pnictides, and the total energy differences between ZB and rocksalt structures for NaN, KN, KP and KAs are about 0.37, 0.27, 0.37 and 0.38 eV/f.u., respectively.

Although the five HM compounds with rocksalt structure are more stable energetically than the ones with zinc blende structure, for the possible growth of HM films, it is important to calculate the formation energies of them. For LiN, NaN and KN, the formation energy $E_{for} = E_{tot} - (E_{cat} + \frac{1}{2}E_{N_2})$. Here, E_{tot} is the ferromagnetic total energy of rocksalt LiN (NaN, KN) per formula unit. E_{cat} is the total energy of bulk Li (Na, K) per atom, and bulk Li, Na and K are bcc structure. E_{N_2} is the total energy per gaseous N_2 molecule. To obtain the total energy of the gaseous N_2 molecule, we use a large cubic cell of 15 Å, which is large enough to avoid interaction with other molecules in the neighboring cells [22, 23]. Similarly, for rocksalt KP, $E_{for} = E_{KP} - (E_K + \frac{1}{4}E_{P_4})$. Here, E_{P_4} is the total energy of the white phosphorus molecule P_4 and
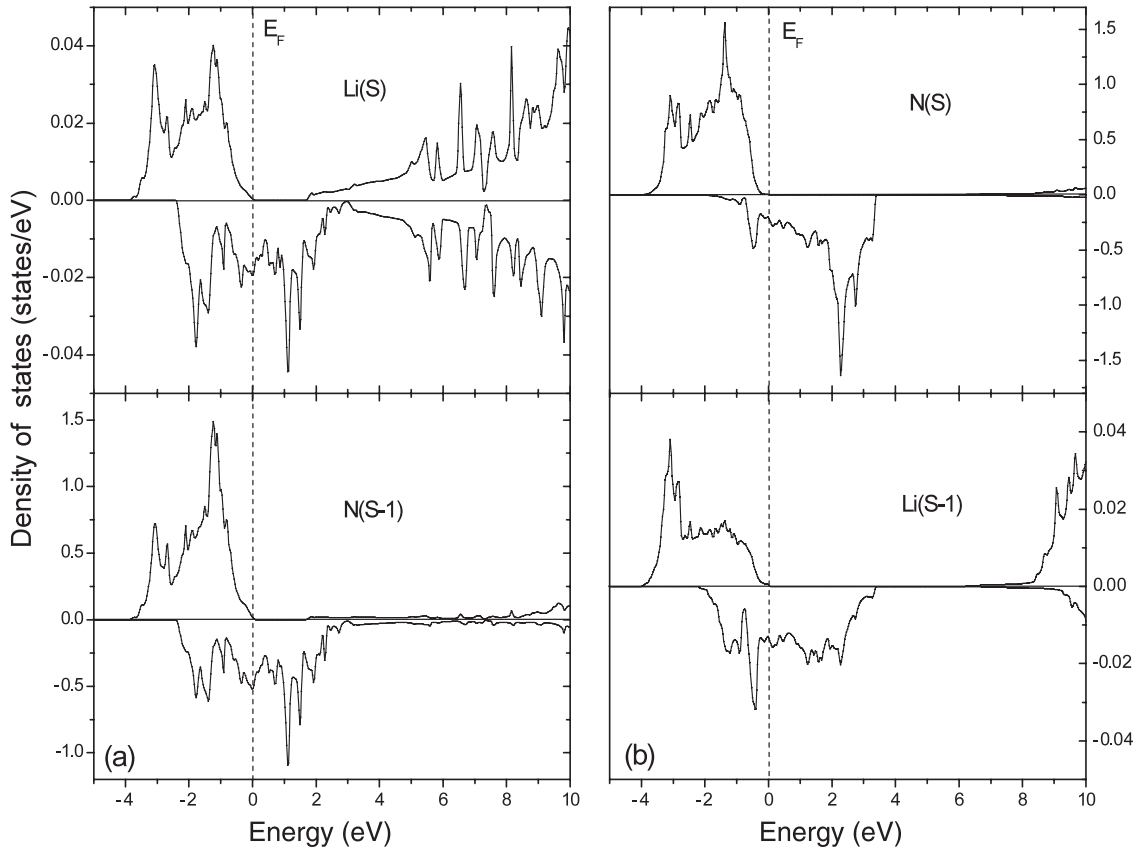
Figure 3. Spin- and atom-resolved DOS of surface (S) and subsurface (S-1) atoms for both Li- and N-terminated (111) surfaces of rocksalt LiN. (a) Li termination, (b) N termination.

P_4 is simulated by constructing a large cubic cell of 15 Å. For rocksalt KAs, $E_{for} = E_{KAs} - (E_K + E_{As})$, and bulk As is a hexagonal structure. Based on the above equations, we obtain the calculated energies of -9.80, -9.23, -9.10, -4.27 and -4.00 eV/f.u. for LiN, NaN, KN, KP and KAs, respectively. One can see that the absolute values of formation energies of the three rocksalt nitrides are considerable, which are comparable with those of rocksalt CaN (-11.2 eV) and SrN (-10.8 eV) [24].

Another aspect of structural stability is the comparison of total energies between the rocksalt structure and the existing phases of these compounds. In the five HM compounds with proposed rocksalt structure, KP and KAs have been realized experimentally, but their experimental structure is orthorhombic with the space group of $P2_12_12_1$ (no. 19) [25, 26]. We perform total energy calculations for orthorhombic KP and KAs with the same computational conditions as that of the rocksalt structure. The results show that the rocksalt structure is about 1.95 and 1.65 eV/f.u. unstable with respect to the orthorhombic structure of KP and KAs. Both values are larger compared to those of 1.0 and 0.9 eV for CrAs and CrSb, respectively [11], which are the energy differences between the ZB and the ground state NiAs structure (note that the ZB CrAs and CrSb films have been grown on appropriate semiconductor substrates [13]). So the experimental growth of rocksalt KP and KAs films or ultrathin films may be difficult to some extent. But we still expect

the experimental efforts especially for rocksalt LiN, NaN and KN because of the high formation energies. The appropriate substrates for the possible growth of films or ultrathin films are ZB SiC (4.35 Å), BeSe (5.14 Å) and InP (5.87 Å) [27] for rocksalt LiN (4.33 Å), NaN (5.03 Å) and KN (5.82 Å), respectively.

It is necessary to investigate the surface electronic structure for the growth of HM films, because some materials in the form of films lose their half-metallicity although the bulk is HM. For instance, both bulk ZB MnAs and MnSe are HM at the InAs lattice constant, but both their (001) surfaces lose the half-metallicity due to the large surface magnetic moment [10]. So we investigate here the electronic and magnetic properties of the (111) surface of rocksalt LiN. Using the optimized bulk lattice constant, the (111) surface is simulated by constructing a slab of 15-atom layers and 10 Å vacuum above the surface, and both the Li- and N-terminated (111) surfaces are considered. Therefore, for the Li-terminated (111) surface, the slab includes eight Li- and seven N-atom layers, and in the case of the N-terminated (111) surface, the slab includes seven Li- and eight N-atom layers.

We first determine the equilibrium structures for both termination types by allowing the topmost four atomic layers to relax. After relaxation we find the topmost atom moves inward for the Li-terminated (111) surface, while the move is outward for the N-terminated case because of the charge transfer from the cations to the anions [28]. This results in the decrease of

Table 2. *l*-decomposed majority (maj-) and minority (min-) spin electrons inside each muffin tin sphere, and magnetic moments (M in μ_B) of each atom for bulk and (111) surface (S) and subsurface (S-1) layers of rocksalt LiN.

		s (maj-/min-)	p (maj-/min-)	Total (maj-/min-)	*M*
Bulk	Li	0.99/0.99	0.03/0.02	1.02/1.01	0.01
	N	0.80/0.76	2.06/0.52	2.86/1.28	1.58
Li-term	Li(S)	1.00/1.00	0.05/0.03	1.05/1.03	0.02
	N(S-1)	0.78/0.76	1.93/0.78	2.71/1.54	1.17
N-term	N(S)	0.81/0.78	2.17/0.23	2.98/1.01	1.97
	Li(S-1)	0.99/0.99	0.04/0.02	1.03/1.01	0.02

0.25 Å for the Li–N bond (the distance between the surface Li and subsurface N atoms) for the Li-terminated (111) surface, and the increase of 0.05 Å for the Li–N bond (the distance between the surface N and subsurface Li atoms) for the case of N termination. We further show the DOS of surface and subsurface atoms in figure 3, which indicates both the Li- and N-terminated (111) surfaces maintain the half-metallicity of bulk LiN. This is different from that of the (001) surface of ZB CrAs, where the Cr-terminated (001) surface is HM while the As-terminated case loses half-metallicity due to the existence of surface states [29]. We also note that for both terminations the surface atomic energy gaps of majority spin electrons are decreased compared to that in the bulk system. In addition, from figure 3 we see that the subsurface atoms also exhibit half-metallicity. To our knowledge, the present study is the first report on surface sp half-metallicity of binary compounds, and it is helpful for the possible growth of rocksalt sp HM films of alkali metal pnictides.

In table 2, we further present the *l*-decomposed majority and minority spin electrons inside muffin tin spheres and the calculated magnetic moments of surface and subsurface atoms for both Li and N terminations. Note that the corresponding bulk values are also listed in order to compare the difference between the surface and bulk systems. From table 2 one can see that the calculated magnetic moments of surface atoms are 0.02 μ_B for Li and 1.97 μ_B for N, which is larger than those in the bulk system. In particular, the surface N magnetic moment increases considerably by about 0.39 μ_B, because the N atom at the surface loses electron charge towards the vacuum. Moreover, the decrease and increase of electron charge in the majority and minority spin channels, respectively, reduces the N magnetic moment in the subsurface layer by about 0.41 μ_B compared to the bulk value.

4. Conclusion

In summary, we have used the first-principles FP-LAPW and PWPP methods to investigate the electronic and magnetic properties of alkali metal pnictides with rocksalt structure. Five rocksalt compounds are found to be HM ferromagnets with a magnetic moment of 2.00 μ_B/f.u., and the large spin splitting of anion p states provides the main magnetic moment. The large energy differences between the ferromagnetic and antiferromagnetic states stabilize strongly the ferromagnetic

ground state. We also find the rocksalt structure is more stable energetically than the ZB structure, which makes them more promising candidates for the possible growth of half-metallic films or ultrathin films on suitable semiconductor substrates. The formation energies are also calculated for the five rocksalt HM compounds, and we find the formation energies of LiN, NaN and KN are comparable with those of CaN and SrN. Finally, the surface calculations show that both Li- and N-terminated (111) surfaces of rocksalt LiN retain the bulk half-metallic characteristic, and the surface atomic magnetic moments are enhanced compared to the bulk values.

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