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Half-metallic and Magnetic Properties of (001) Surfaces of $KCaN_2$ Compound in full-Heusler Structure

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The electronic and the magnetic properties of (001) surface of $KCaN_2$ half-metallic compound with full-Heusler structure are studied with the use of a full-potential linearized augmented plane wave method. Two possible terminations of the surface are considered and only the one with N atoms in the topmost layer is found to retain the half-metallic properties of the bulk. The magnetic properties of N-terminated surface are enhanced compared with the properties of the bulk. The calculated magnetic moments on the N atoms in the $KCaN_2$ are 1.26 μ_B in the bulk and 1.90 μ_B at the surface. The subsurface metal atoms are also slightly polarized. In the surface terminated with metal atoms, not only the half-metallicity is destroyed, but also the magnetic properties of the system are weakened.

Keywords : half-metallicity, electronic structure, surface magnetism

1. Introduction

Full-Heusler compounds have been known for more than a century, but they still attract attention because of their magnetic properties, such as high Curie temperature and high magnetic moments. Additionally, some of full-Heusler as well as half-Heusler alloys were predicted to be half-metallic ferromagnets (HMF) [1, 2]. HMFs, materials with 100 per cent spin polarization at the Fermi level, are demanded by a fast developing spintronics, since they may be perfect spin injectors when used in the form of thin films at the interfaces with semiconductors. Considering application of compounds to electronic devices, one cannot forget about as accurate as possible a description of the surface properties of the materials. Electronic properties of surfaces differ from those of the bulk. How much different the surface properties are from those of the bulk depends, among others factors, on surface termination. Many materials found to be half-metals in their bulk structures lose the property at surfaces. For example, Co_2XY (X=Mn, Cr, Ti; Y=Si, Ge) were all found to be half-metals [3, 4, 5], but most of the materials lost the property at (001) surfaces; only CrAl-terminated Co_2CrAl (001) surface, and CrSi- and TiSi-terminated (001) surfaces of Co_2CrSi and Co_2TiSi, respectively, retained the half-metallicity [6, 7].

Lately, apart from the extensive investigation of the full-Heusler compounds containing 3d elements, several reports informed about the half-metallic ferromagnetic properties of full-Heusler materials not containing transition metals in their structure. Rozale *et al.* reported that $KCaX_2$ (X=C, N, O) are HMFs with a large half-metallic (HM) gap [8]. Their work followed wider study on so called d^0 half-metals in half-Heulser structure, such as GeKCa, SnKCa [9]. Those materials are very promising from an application point of view not only because they have quite large HM energy gap and high Curie temperature, but also because they are robust with respect to the lattice compression. The fact that they retain the half-metallicity even though the lattice constant is contracted by about 10% increases the chance that the materials are epitaxially grown on surfaces of conventional semiconductors without losing the HM properties.

It is still important to predict the surface properties of the materials. Lately, we showed that GeKCa and SnKCa lose their HM properties at KCa-terminated (001) surface and retain the properties at Ge- (or Sn-) terminated one [10]. While the surface atoms in the structures terminated with metal atoms became strongly demagnetized, those at the topmost layer of Ge- (or Sn-) terminated surfaces were found to enhance their magnetic moments. Due to the fact that the (001) surface of a $KCaN_2$ crystal in full-

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Heulser structure may also be terminated with either KCa layer of a layer containing non-metal elements, we expect similar behavior of the two types of the surface. However, because of the differences in the structures as well as in the nature of the non-metal building block of the structures, the properties of Ge(Sn)KCa surfaces cannot be simply extrapolated on $KCaN_2$ surface.

In this paper, we discuss the the half-metallicity at the (001) surfaces of $KCaN_2$ obtained from the results of electronic structure calculations with the use of a first-principles method.

2. Computational Method

As calculated by Rozale *et al.*, the equilibrium lattice constant of bulk $KCaN_2$ in the full-Heulser structure is 6.236 Å [8]. The value was adopted for our calculation of the electronic properties of the $KCaN_2$ (001) surfaces. In order to refer to the existing data on the properties of $KCaN_2$, at the first step we carried out the calculations of the bulk properties on the $KCaN_2$. Next, the calculations were carried out for (001) surface of the compound. The surface has two different terminations. Both of them were considered: one, whose topmost layer consisted of nitrogen atoms, and the other with the uppermost layer built of simple metal atoms. We refer to the two terminations as N-term and KCa-term, respectively. The surfaces were modeled by 13-layers slabs separated one from another by 5 lattice constants, i.e., 31.13 Å. Such a large separation ensures that there is no interaction between the slabs. The interatomic and interlayer distances were in accordance with the lattice constant. The structural parameters were not optimized. The two systems are sketched in Fig. 1; only three near-surface and two bulk-like layers are pictured.

In order to resolve the electronic structure of the $KCaN_2$

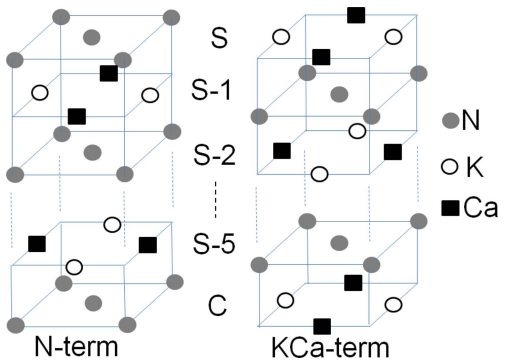

Fig. 1. (Color online) Schematic view of the atomic arrangement in the $KCaN_2$ surface terminated with the layer of (left) nitrogen atoms and (right) simple metals atoms.

bulk and surface, the Kohn-Sham equation [11] was solved self-consistently in terms of the full-potential linearized augmented plane wave (FLAPW) method [12, 13], within generalized gradient approximation of Perdew-Burke-Ernzerh of type [14] to the exchange-correlation potential.

Lattice harmonics with $l \leq 8$ were employed to expand the charge density, the potential, and the wave functions inside the muffin-tin (MT) radius of N was set to 2.0 a.u., while that of metals atoms - to 2.6 a.u. The number of basis functions was about 200 per atom. Integration was performed over a $11 \times 11 \times 11$ mesh of k-points inside the irreducible three dimensional Brillouin zone (BZ) for the bulk $KCaN_2$ and over 7×7 mesh inside the two-dimensional BZ for the two-dimensional systems. All core electrons were treated fully relativistically, while valence states were treated scalar relativistically, without spin-orbit coupling. Self-consistency was assumed when the difference between input and output charge densities was less than 1×10^{-4} electrons/(a.u.)^3.

3. Results and Discussion

We successfully reproduced the half-metallic properties of the full-Heusler $KCaN_2$ bulk reported in [8]. Similarly to the referred data, we found the energy gap in the majority spin channel and evaluated that the width of the half-metallic gap is 0.13 eV. This is slightly narrower than 0.19 eV reported by Rozale *et al.* [8]. The discrepancy may be caused by choosing different MT radii in our calculations. In the other study, the researchers did not differ between the nature of the atoms and the radii were set to 2.5 a.u. for each atom type. One of the consequences of differentiation between metal and non-metal atoms is smaller value of magnetic moment (MM) calculated for N atom in the $KCaN_2$; while Rozale *et al.* obtained the value 1.41 μ_B, our calculation provide a value of 1.26 μ_B. There is also a difference between the MMs calculated by the two groups for K and Ca. The values we obtained for the metal atoms are by about 0.02 μ_B larger than those reported in [4]. Apart from those quantitative results, however, our calculations reveal very similar electronic and magnetic properties, which let us to compare the findings about the surface properties with the properties of the bulk.

In Fig. 2, the total and atom-projected densities of electronic states (DOSs), calculated for the N-term surface, are shown. The spin-down DOSs values are multiplied by negative numbers, and the Fermi levels are set to zero. The total DOS plot indicates that the half-metallicity of the bulk is retained at the $KCaN_2$ surface. In spite of a large energy gap in the spin up electron channel, the half-

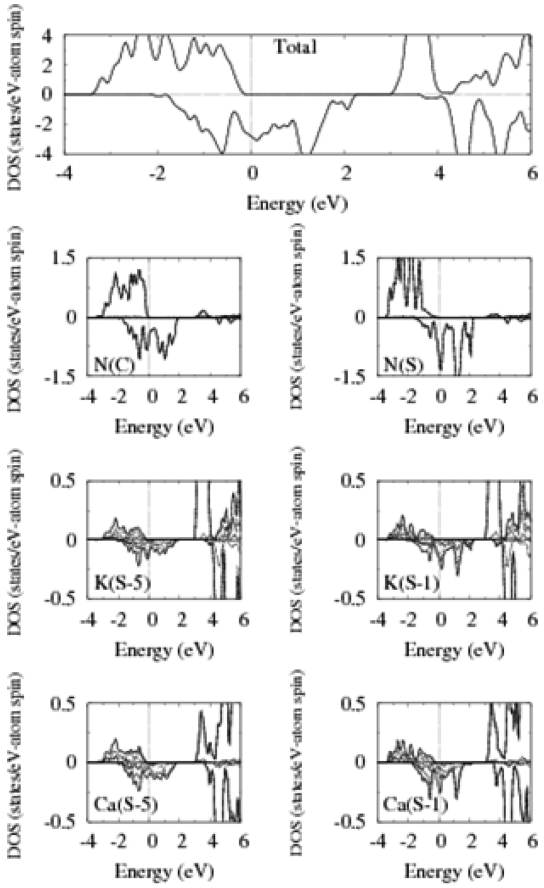

Fig. 2. The total and atom-projected spin-polarized density of states (DOS) calculated for N-terminated $KCaN_2$ surface. The spin-down DOS values are multiplied by negative numbers and the Fermi levels are set to zero.

metallic gap is not wide; it is about 0.10 eV. This is somewhat narrower than the gap in the bulk, which is certainly due to the surface electronic states. The change, however, is not as large as the narrowing of the half-metallic gap at the half-metallic (001) surface of half-Heusler GeKCa and SnKCa [10], which implies that the properties of the N-term $KCaN_2$ surface should be more stable than those of the other two above mentioned compounds. The plots of atom-projected DOSs in Fig. 2 depict the contributions of atoms from the middle (C) and the next to it (S-5) bulk-like layers as well as from the topmost (S) and the subsurface (S-1) layers to the total DOS.

The differences between the DOSs plots in the left and right side columns in the figure mirror the changes that occur in the electronic states distribution in energy scale due to the surface termination. In the bulk, N atom p-electron states are much more delocalized than the states contributed by N atom at the surface. In the S layer, the states contributed by spin-up electrons are split into subbands with distinguishable peaks at −1.2 eV, −2.0 eV, and −2.9 eV. These states are mixed with the valence states of K and Ca of the subsurface layer. The metallic states contributed by the metals atoms in the near-surface region are also more localized than those in S-5 layer, but since the atoms in S-1 do not have unsaturated bonds, the localization of the states is smaller. The number of occupied states of N atom in the spin down channel is smaller for the atoms in S and S-1 layers than it is in the bulk-like area. This implies that the electron density near the surface are spread toward vacuum or regroup and tend to occupy available energy levels supplied by K and Ca atoms of S-1 layer. The calculated total MM for the N-term system is 24.00 $\mu_{B,}$ which confirms that this system is half-metallic. More accurate analysis of the charge transfer between the layers will be given later. The greater number of spin-down states at the Fermi level in the surface region by roughly 60% compared with the bulk suggests an easier excitation of spin-down charge carriers from N-term $KCaN_2$ thin films than from bulk materials.

In Fig. 3, the total and atom-projected densities of electronic states (DOSs), calculated for the KCa-term surface,

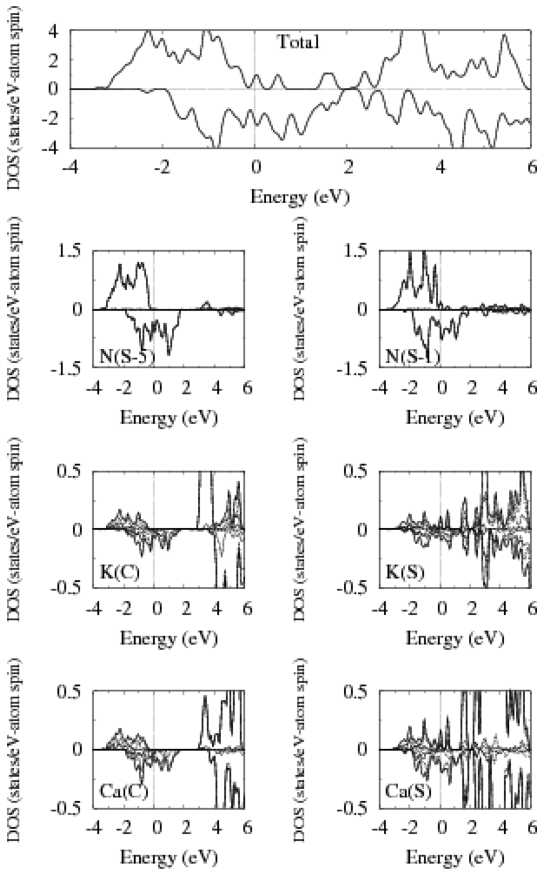

Fig. 3. The total and atom-projected spin-polarized density of states (DOS) calculated for KCa-terminated $KCaN_2$ surface. The spin-down DOS values are multiplied by negative numbers and the Fermi levels are set to zero.

are shown. The outline of Fig. 3 is the same as that of Fig. 2. Clearly, at the surface terminated with simple metals atoms the half-metallic properties of the bulk are lost. This is similar to what we know about the surface properties of half-Heusler GeKCa: (001) surface terminated with K and Ca atoms exhibits metallic behavior, as well [10]. However, the loss of the half-metallicity found in the $KCaN_2$ cannot be explained the same way as it was in the GeKCa. In the latter, the distribution of the surface states contributed by K and Ca atoms of S layer implied that the electrons at the surface behave nearly as free electrons in metals. In the KCa-term $KCaN_2$, electronic states are found at the Fermi level in spin up electron channel, but the DOS spectra have several distinguishable peaks in both occupied and unoccupied regions. The differences may come from the different structures of the compounds; yet, in half-Heusler compound the subsurface layer contains "voids" where N atoms reside in full-Heusler structure. Additionally, electrons of N interact stronger with K and Ca than the electrons of Ge do because of a much greater difference in their electronegativity.

In Table 1 and in Table 2, data concerning number of charges within MT spheres of the atoms from C, S-5, S-1 and S layers of the investigated systems are collected together with the calculated values of the magnetic moments (MMs) on the individual atoms.

In the bulk-like layers of the $KCaN_2$ surface, regardless its termination, the charge distribution between N, K, and Ca atoms is the same. Strong polarization of p electrons of N leads to a small polarization of K electrons and a very weak polarization of Ca electrons, which is well understood on the basis of the electronic structure of the individual atoms. The largest value of MM is calculated for N atom and equals 1.24 μ_B. As far as the atoms in the near-surface region are concerned, the situation depends on the surface termination.

As the data in Table 1 show, the value of MM on N atom of S layer is increased to 1.90 μ_B. This is due to the change of the number density of electrons in N p orbitals. In the bulk, not filled p orbitals of N atoms accept electrons of K and Ca atoms of subsequent layers; they populate p↓ orbitals. Since the p_z atomic orbitals of N atoms of S layer are not involved into forming bonds, their occupancy is decreasing. At the same time, p↑ orbitals become occupied by a slightly larger number of electrons than the N atoms of C layer, since the electrons are not interacting with the electrons of metals atoms. The K and Ca atoms of S-1 layer rather weakly respond to the changes of the properties of the S layer. The Ca atom is not at all polarized, and the MM of the K atom is only 0.08 μ_B. The ferromagnetic properties of the surface are enhanced compared with the bulk.

The total MM calculated for the KCa-term system has non-integer value of 15.95 μ_B, which confirms that the surface is not half-metallic.

The polarization of atoms of the $KCaN_2$ KCa-term surface show different tendency: The metal atoms of S layer become demagnetized and the MM on N atom of S-1 layer is considerably decreased. Even though the distribution of the electrons between spin-up and spin-down orbitals changes significantly from N of C to N of S-1 layer, the total number density is nearly the same in both atoms

Table 1. *l*-decomposed electrons within muffin-tin spheres on the atoms in the surface, subsurface, and center layers of the (001) surface of N-term $KCaN_2$ together with the calculated values of the total magnetic moments (MMs).

atom	s	p	d	total	MM (μ_B)
	total (↑/↓)	total (↑/↓)	total (↑/↓)	total (↑/↓)	
N (S)	1.71 (0.87/0.84)	2.65 (2.26/0.39)	0.00 (0.00/0.00)	4.36 (3.13/1.23)	1.90
N (C)	1.68 (0.85/0.83)	2.92 (2.06/0.85)	0.00 (0.00/0.00)	4.60 (2.92/1.68)	1.24
K (S-1)	0.07 (0.03/0.03)	0.18 (0.11/0.06)	0.14 (0.08/0.06)	0.41 (0.25/0.16)	0.08
K (S-5)	0.07 (0.03/0.04)	0.21 (0.12/0.09)	0.15 (0.08/0.07)	0.46 (0.25/0.21)	0.05
Ca (S-1)	0.10 (0.05/0.06)	0.12 (0.07/0.05)	0.29 (0.15/0.13)	0.53 (0.29/0.25)	0.04
Ca (S-5)	0.10 (0.05/0.06)	0.13 (0.07/0.06)	0.28 (0.16/0.13)	0.54 (0.29/0.25)	0.04

Table 2. *l*-decomposed electrons within muffin-tin spheres on the atoms in the surface, subsurface, and center layers of the (001) surface of KCa-term $KCaN_2$ together with the calculated values of the total magnetic moments (MMs).

atom	s	p	d	total	MM (μ_B)
	total (↑/↓)	total (↑/↓)	total (↑/↓)	total (↑/↓)	
N (S-1)	1.67 (0.85/0.83)	2.95 (1.91/1.04)	0.00 (0.00/0.00)	4.63 (2.76/1.87)	0.89
N (S-5)	1.68 (0.85/0.83)	2.93 (2.07/0.85)	0.00 (0.00/0.00)	4.61 (2.93/1.68)	1.25
K (S)	0.08 0.04/0.04	0.12 0.06/0.06	0.14 0.07/0.07	0.39 0.20/0.19	0.01
K (C)	0.07 (0.03/0.04)	0.21 (0.12/0.09)	0.15 (0.08/0.07)	0.46 (0.25/0.21)	0.05
Ca (S)	0.13 (0.06/0.08)	0.09 (0.05/0.04)	0.31 (0.16/0.16)	0.55 (0.27/0.28)	-0.01
Ca (C)	0.10 (0.05/0.06)	0.12 (0.07/0.06)	0.29 (0.15/0.13)	0.54 (0.29/0.26)	0.03

types. This is unlike the N-term layer, where the total charge on N atom of C layer is 4.46 and that on N atom of S layer is 4.36. As a result, the calculated MM on the strongest polarized N atom is 0.89 μ_B. The values of the MMs on K and Ca atoms of S layer are almost zero. The K(S) atom is positively polarized and MM on the atom is 0.01 μ_B, while Ca(S) is negatively polarized and the value of MM on the atom is −0.01 μ_B.

Comparing with the full-Heusler alloys containing 3d metals, especially those, who retain half-metallic properties at (001) surface, such as Co_2TiSi [7], or Mn_2CoAl [15], we notice that the N-term surface of $KCaN_2$ that retain HM properties are characterized with a smaller, relative to the bulk value, reduction of the HM gap. The value of MM on the surface N atom increase, as it is the case in the other compounds.

4. Conclusions

We investigated the electronic and the magnetic properties of (001) surfaces of $KCaN_2$ in the full-Heusler structure. Two terminations were considered: N- term and KCa-term. The half-metallic properties of the bulk $KCaN_2$ are retained only at the surface terminated with N atoms. The KCa-term surface was found have metallic properties. Ferromagnetic properties of the KCa-term surface are weakened compared with the bulk of $KCaN_2$ because of the demagnetization of the surface atoms. Only N atoms in the subsurface layer remain polarized and their MM is 0.89 μ_B. In contrast the magnetic properties of the half-metallic N-term surface are enhanced compared with the bulk $KCaN_2$. The calculated value of MM on N atom at the surface is 1.90 μ_B, which is 54% greater than the MM on N atom in the bulk. The polarization of N atoms at the surface causes an increase in polarization of electrons localized on K atoms in the subsurface layer, leading to MM of 0.08 μ_B.

The $KCaN_2$ are promising candidates for application to spintronics as d^0 half-metallic ferromagnets. The N-term surface has enhanced magnetic properties compared with the bulk, but its half-metallic band gap does not change dramatically due to surface effects. Therefore, as expected the properties will be stable and predictable when the compound is be used to form interfaces with other materials.

Acknowledgement

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