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Surface half-metallicity and stability of zinc-blende sodium monoselenide

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ABSTRACT

The electronic structure and magnetic properties of relaxed (001) surfaces of the *sp*-electron half-metallic ferromagnet NaSe in the zinc-blende phase, are calculated on the basis of first principle density functional theory within the framework of self-consistent field plane wave pseudo-potential method, using the generalized gradient approximation for the exchange-correlation functional. The results of this study reveal that both Na- and Se-terminated surfaces retain the robust bulk half-metallic property. The negative value found for the bulk formation energy indicates that this material is stable against phase separation. We also obtain the surface energies and discuss their stability via the calculated bulk formation energy. The Curie temperature is estimated to be 920 K within mean field approximation, which is well above the room temperature. In the light of the above, zinc-blende NaSe appears to be a good candidate for spintronic applications as spin injection material.

1. Introduction

Attempts to implement the spin degree of freedom in addition to the electronic charge, have given rise to rapid growth of the field of spin electronics [1,2]. Adding the spin degree of freedom to the operation of conventional electronic devices has many advantages like non-volatility of data storage, enhanced data processing speed, reduced electric power consumption, and increased integrated densities [3]. To use the spintronic technology, however, efficient techniques for the injection, transport, manipulation, and detection of spins are required. The generation of spin-polarized current is the primary requirement of spintronic devices, and highly spin-polarized materials are in much demand as spin injection materials. In particular, the half-metallic (HM) materials with characteristic 100% spin polarization at the Fermi level, have been one of the key materials of spintronics due to their possible application as the source of spin-polarized current [4]. Due to the asymmetric electron populations in the two spin channels, half-metals are ferromagnetic with integral total magnetic moments. Following the seminal work of de Groot et al. [5], predicting for the first time the HM property in the intermetallic half-Heusler alloy NiMnSb, much theoretical work has been devoted to the discovery of the transition-metal-based HM ferromagnets, such as the full-Heusler alloy Co_2FeSi [6], perovskite $La_{0.7}Sr_{0.3}MnO_3$ [7], pyrite-type CoS_2 [8], spinel Fe_3O_4 [9], rutile-type CrO_2 [10], and certain transition metal pnictides and chalcogenides in metalstable zinc-blende (ZB) structure [11–13]. In the above, the half-metallicity and the magnetic properties emerge mainly from the hybridization and exchange-splitting of the transition metal *d*-electrons, and are sometimes referred to as *d*-electron HM ferromagnets. The above transition-metal-based HM ferromagnets often present large magnetic moments and stray magnetic fields, which result in considerable energy loss in devices.

Alternatives are the *sp*-electron materials that present half-metallic ferromagnetism with low magnetic moments [14]. The evidence of growth of such materials, has been reported for the self-assembled ultrathin film of CaN in rock salt structure on (001) surface of copper substrate [15]. The possibility of controlled epitaxial growth of the *sp*-electron HM materials on compatible semiconductor substrates, is expected to boost their applicability in spintronic devices, rather similar to the epitaxial growth of the metastable ZB CrAs and CrP ultrathin films on GaAs semiconductor substrate [11,16–18]. In *sp*-electron materials, the half-metallicity originates from the spin-splitting of the anion *p* electrons, and therefore the name *sp*-electron HM ferromagnet. These binary compounds include some of the alkali and alkaline-earth chalcogenides [14,19], and monocarbides in ZB structure [20]. These compounds tend to have lower magnetic moments per formula unit, and therefore reduced stray magnetic fields. They also are predicted to exhibit high Curie temperatures that makes them magnetically

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stable at room temperature, and often present wide half-metallic gaps (energy gap for spin excitation) that makes them more robust against the lattice deformations and the collapse of spin polarization with increasing temperature [21,22].

Since the half-metallic property of bulk materials can be destroyed at the surfaces, due to the formation of surface states, the study of electronic structure and stability of surfaces is of prime importance from the point of view of application feasibility in spintronic devices. Therefore much work has been devoted to studying surface effects in HM materials. For instance in the case of (001) surfaces of CrAs in metastable ZB structure [23], it has been found that the Cr-termination retains the bulk half-metallic property while the As-termination does not. The ZB CrP (110) surface [24], is an example that consists of only one kind of surface termination containing both elements at which the half-metallicity is preserved. As for the *sp*-electron HM monocarbides BaC and SrC in the rock salt structure, it has been found that the anion (C) termination of the (111) surface preserves the bulk half-metallicity while the cation (Ba or Sr) termination loses the HM property [25]. In this paper, we investigate the structural, electronic, and magnetic properties of the (001) surfaces of sodium monoselenide for both the anion (Se) and the cation (Na) termination in metastable zinc-blende structure using the self-consistent field plane wave pseudo-potential method. This is done in the light of the fact that the bulk half-metallicity of ZB NaSe is reported to be preserved up to lattice contractions of about 19.6% [26]. This robustness of half-metallicity with respect to lattice deformation, is crucial for practical epitaxial growth of ultrathin layered structures on compatible semiconductor substrates. Furthermore, the total energy of metastable ZB NaSe is found to be less than an electron volt higher in energy than the corresponding non-magnetic ground state. So, it may very well be possible to grow ultrathin films of metastable ZB NaSe on compatible semiconductor substrates, rather similar to the epitaxial growth of metastable ZB CrAs and CrSb ultrathin films on GaAs substrate. We determine whether the surfaces preserve the robust bulk half-metallicity, and discuss the stability of surfaces via the calculated bulk formation energy. The Curie temperature is estimated within mean field approximation.

The rest of this paper is organized as follows. The computational procedure is described in Section 2. In Section 3, the bulk electronic and magnetic properties of NaSe in the zinc-blende phase are revisited using the self-consistent field plane wave pseudo-potential method. The electronic structure and magnetic properties of (001) surfaces of ZB NaSe, are presented in Section 4. The surface stability assessments are given in Section 5, and the paper is concluded with a discussion and summary in Section 6.

2. Computational method

Our calculations are performed on the basis of spin-polarized density functional theory (DFT) [27] within the framework of the self-consistent field plane wave pseudo-potential (PW-PP) method as implemented by the PWscf code in the Quantum Espresso package for solving Kohn-Sham equations through self-consistency [28]. We used the generalized gradient approximation (GGA) with ultrasoft pseudo-potentials in the scheme of Perdew, Burke, and Ernzerhof (PBE) [29]. The relativistic effects are treated within the scalar approximation. The reciprocal space integrations were carried out using optimized Monkhorst-Pack method [30]. We also performed convergency tests in order to obtain optimized cut-off energies, and the appropriate number of *k*-points for Brillouin zone integration. Hence, the optimized kinetic energy cut-offs of 35 Ry and 350 Ry were applied to the plane wave expansion of wave functions and the Fourier expansion of charge density, respectively. The (001) plane is modeled using an optimized nano-slab of thirteen

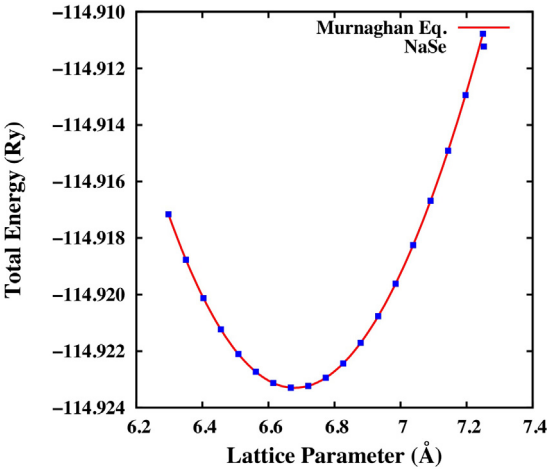

Fig. 1. The total energy vs. lattice parameter for NaSe in the zinc-blende structure. The data points are fitted by the Murnaghan equation of state.

Table 1
The lattice constant a (in Å), the half-metallic energy gap E_{HM} (in eV), and the atomic as well as the total magnetic moment per formula unit (in μ_B) for the bulk ZB NaSe structure. The corresponding values obtained by the FP-LAPW method [26], also are given for comparison.

Compound		a	E_{HM}	μ_{tot}	μ_{Na}	μ_{Se}	μ_{int}
NaSe	Present	6.66	0.47	1.00	−0.02	1.02	–
	Others [26]	6.67	0.39	1.00	0.01	0.66	0.33

atomic layers in the ZB structure and for the Brillouin zone integration, we used a $13 \times 13 \times 13$ *k*-mesh for the bulk, and a $13 \times 13 \times 1$ *k*-mesh for the (001) surfaces. Self-consistency is considered to be achieved when the total energy difference between consecutive iterations is less than 10^{-6} Ry/f.u. (Rydberg per formula unit).

3. Bulk properties

The equilibrium lattice constant of ZB NaSe is obtained using the total energy versus lattice parameter curve by fitting the Murnaghan equation of state, as shown in Fig. 1. The equilibrium lattice constant thus obtained is $a = 6.66$ Å, which is in very good agreement with the lattice parameter reported previously within the framework of full-potential linearized augmented plane wave (FP-LAPW) method for ZB NaSe (see, Table 1) [26]. More importantly, the total magnetic moment per formula unit is found to be $\mu_{tot} = 1\ \mu_B$ that is integer-valued with respect to the Bohr magneton μ_B, a necessary condition for the materials to be HM ferromagnets. The magnetic moment of $1\ \mu_B$ per formula unit, may be understood in terms of transfer of one valence 3*s* electron from the cation Na to the anion Se, thus leaving one unpaired electron in the anion 4*p* state.

The bulk properties such as the lattice parameter, the half-metallic gap, the total as well as the atomic magnetic moments for the bulk NaSe, are compared in Table 1 with their previously obtained values within the framework of FP-LAPW method [26]. It should be, however, noted that there is no interstitial quantity such as μ_{int} in our self-consistent field PW-PP method of solution as it does not employ the muffin tin potentials used in FP-LAPW method. Thus, the observed difference between the atomic magnetic moments in Table 1, must be viewed in the light of the above. The total magnetic moments (per formula unit), however, are in excellent agreement as expected.

The spin-resolved density of states (DOS) near the Fermi level for NaSe in the zinc-blende phase, are shown in Fig. 2. According to Fig. 2, ZB NaSe is half-metallic as there is an energy gap at