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First-Principles Research on the Structural and Electric Properties of the Graphene-Like Alkali-Metal Absorbed InSe-M

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Abstract.The structural and electric properties of the alkali-metalabsorbedmonolayer InSe-M (M=Li, Na, K and Rb) are studied by the first-principles calculations. The absorption energies of the monolayer InSe-M are negative so that theyhave stableabsorption structures,indicating that it is possible to prepare them in experiments.The pristinemonolayer InSe is typical conductor, but the alkali-metalabsorbedmonolayer InSe-Mare electronically conductive. Therefore, the alkali-metal absorption causes important influence on the electric properties of the monolayer InSe. However, too little calculated magnetic moments show that the alkali-metal absorption causes little influence on the magnetic properties of the monolayer InSe.

1.Introduction

The discovery of the Graphenein 2004 has been viewed as thevery important finding in new materials in that the Graphenehave muchnewpotential application in photonics, nonlinear optics, flexible transparent electrodes, sensors, conductive composites, and gas separation membranes[1]. Since then thetwo-dimension (2D) materials which have unusual electric, mechanical and optical properties have drawn much attention, and then caused extensive interest on experimental, theoretical and application researches.Especially, the III-VI group van der Waals layered materials such as GaS[2] and InSe[3], have become the material focus recently. InSe is a typical semiconductor. For InSe layers, each layer has hexagonalstructure and the interaction between In and Se-ions is the covalent bond[4]. On the other hand, the interaction between layers is weak Van der Waals-type interaction. InSe is attracting much attention because of its much new possible application in photonics, nonlinear optics, spintronics, etc. More recently, few-layer InSe exhibits promising characteristics for optoelectronic application [4-6].Furthermore, a few layers of InSe flakes had been prepared by using the mechanical exfoliation technique established by Novoselov et al[7].The transport properties of InSe along the layers have been widely investigated over the past twenty-five years[8]. Moreover, InSe nanosheetsused to design field effect transistors (FET) show high electron mobility values such as 4.7, 27.6, 74 and 162 (cm^2 $V^{-1}s^{-1}$) for Al, Ti, Cr and In contacts, respectively[9]. Besides, the on-off ratios of the FET are up to 10^7–10^8[10].

Recently, there is increasing interest to study the influence of metal absorption or doping on the physical properties of Graphene-like materials. In order to realize the miniaturization of electronic devices, magnetic materials with single atom-layer thickness have caused extensive researches, such as the boron nitride single-layer[11,12]with the honeycomb structure. Nonmetal-doped metal oxide semiconductorshaveimportant effect on the application of magnetic devices in that they represent a

new class of d^0-type magnetic materials. It was found that zinc oxide doped by the non-metallic elements such as carbon and nitrogen even can show ferromagnetismat room temperature [13]. The cavitation doping in the layered GaSe can induce the change of ferromagnetic phase. The average magnetic moments of the carrier increase with the increase of the hole density[14]. With the sharp decline of the magnetic moments, the system appears half-metallic. Besides, Ashwin Kishore studied the effect of Te on the monolayer InSe for the photocatalytic water splitting via the density functional calculations.They found that Te-doped InSe is more favorable for the hydrogen reduction reaction than the pristine monolayer InSe.Therefore, doped Te can improve the photocatalytic water ability in InSe monolayer[14, 15].However, there are few studies on alkali-metal absorbed InSe (InSe-M). Therefore, in this paper, based on the calculationof the absorption energies, we systematically investigate the stable crystal structures and electric properties of alkali-metal absorbed InSe monolayer.

2.Model and Method

The calculated supercell of the monolayer InSe-M is shown in Figure.1. The structure of the monolayer InSe consists of In-Se-Se-In layers as depicted in Figure.1a (side view) and Figure.1b (top view). 'M' represents the absorbed alkali-metals (M=Li, Na, K and Rb). Each layer has the hexagonal structure and the D3h symmetry from Figure.1b.The structural relaxing and electronic structure calculation of the pristine and adsorbed monolayer InSe are carried out by using Vienna Abinitio Simulation Package (VASP) based on the spin-polarized density functional theory (DFT)[16,17]. The projector augmented wave method (PAW) is used to describe the ion-electron potential[18]. The Perdew–Burke–Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) is employed as the exchange–correlation function[19].In order to avoid the interlayer interaction, the Van der Waals force is considered.Here,a 3×3×1supercell is set with avacuum layer with the thickness 20Åalong the z direction to prevent interaction between slabs. Thecutoff energy is set as 400 eV and the Monkhorst-Pack k-grid meshis 7 × 7× 1 in slab (and monolayer) calculations. The lattice constant of the monolayer InSeare 12.225Å, 12.225Å and 20 Å,respectively.The valence electronic structures of isolated atoms are $5s^25p^1$,$4s^24p^4$,$(n-1)s^2(n-1)p^6ns^1$ (n=1, 2, 3 and 4) for In, Se and alkali-metals, respectively.

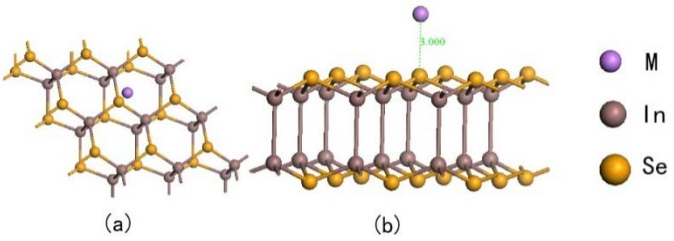

Figure.1.Ball-and-stick model for InSe-M monolayer, where subfigures (a)and (b)show side view and top view, respectively.

3 Results and Discussions

The band structure of the pristine monolayerInSeis showninFigure.2. From Figure.2, the pristinemonolayerInSeis a typical semiconductor with indirect band gap. Its valence band maximum (Ev=-0.0021eV) is between the K and M-points, but the conduction band minimum (Ec=1.4960 eV)is situatedat the Γ-point. Thus, there is an evident energy gap 1.4981eV, which is in excellent agreement with previous report[20].

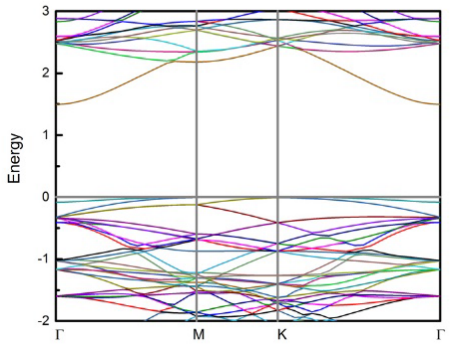

Figure.2The band structure of thepristine monolayerInSe.

From Figure.1, the calculatedsupercell of the alkali-absorbedInSe-Mmonolayer has 37 atoms including 18 In-atoms, 18 Se-atoms and one absorbed alkali-atom.In order to get the preferredabsorptionsite,the alkali-atom is placed above the Se and In-atom, respectively, and then corresponding absorption energy is calculated by the followed formula.

$$E_a = E_{total} - (E_{atom} + E_{InSe})$$

Here the E_{total}, E_{atom}, and $E_{InSe}$are the total energy of the alkali-absorbed monolayerInSe-M, the alkali-atom, and the pristine monolayerInSe, respectively. Based on our calculated results and the energy minimum principle, the alkali-atom prefers the top site above the Se-atom.According to the above formula, the absorption energies for Li, Na, K and Rb-absorbed monolayerInSe-Mare-1.38, -1.16, -1.58 and -1.63, respectively. These energies are negative, implying that the absorption process is exothermic, so that the above absorption process is possible in experiments.The absorption energy of the Rb-absorbed monolayer is lowest, implying that Rb absorption above the Se-ion is easier than other atoms. The main reason is possibly that the radius of Rb-5s orbital is larger than Li-2s, Na-3s and K-4s orbitalso that the Coulomb interaction between the Rb-5s electron and the nucleus is less than that between Li-2s, Na-3s and K-4s electrons and their nucleus.Less Coulomb interaction will result in that the 5s-electron is more easilytransferred to the Se-ion, and then form a more stable absorption structure.

Spin-polarized energy band structuresand state densities of themonolayerInSe-M (M= Li, Na, K and Rb) are shown in Figure. 3, where subfigure(1), (2), (3) and (4) are for Li, Na, K and Rb absorbed monolayer, respectively.There are spin-down(left) and spin-up (right) sub-band structures and spin-polarized densities ofstates (middle) in every subfigure, respectively. From Figure.3, both the spin-down sub-bands and the spin-up sub-bands of the monolayer InSe-M (M= Li, Na, K, Rb)go through the Fermi level, indicating that these materials are electrically conductive. However, from Figure.2, the pristine monolayer InSeis semi-conductor. Therefore, the absorbed alkali metals can improve the electrically conductive properties of the pristine monolayerInSe.

On the other hand, the magnetic properties are also calculated in this paper. The total magnetic moments of the monolayer InSe-M are 0.0001, 0.0006, 0.0008 and 0.0009 μ_B for M=Li, Na, K and Rb, respectively, indicating the absorbed alkali-metalscause little influence on the magnetic properties the monolayer InSe. In fact, from Figure.3 the spin-up sub-bands are very similar to spin-down sub-bands totally. Furthermore, the spin-up andthe spin-down TDOS are almost axially symmetric about theenergy axial. These resultsalso indicate that there is no spin-polarization in the monolayer InSe-M.

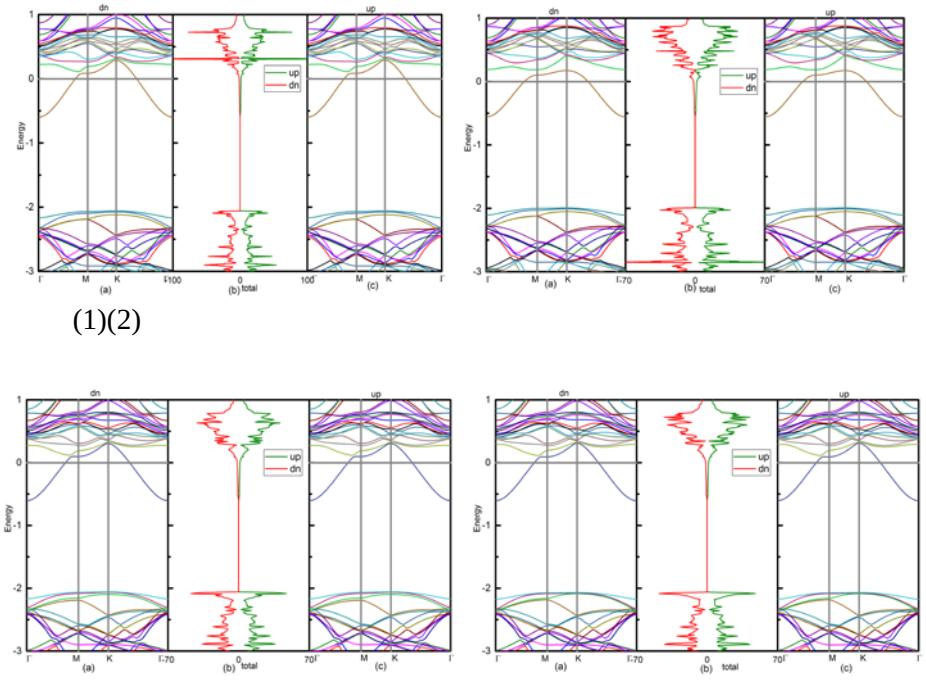

Figure.3.The spin-polarized band structures and the total densities of states of the alkali-metal absorbedmonolayer InSe-M (M=Li, Na, K and Rb), where the spin-down (left) and spin-up (right) sub-band and spin-polarized TDOS (middle) are in every subfigures, respectively.

4.Conclusions

In this paper, the structural and electronic properties of the alkali-metal absorbedmonolayer InSe-M (M=Li, Na, K, Rb) are studied by the first-principles calculations. Results show that the monolayer InSe-M (M=Li, Na, K, Rb) have stable absorption structures so that it is possible to prepare them in experiments. The absorbed alkalimetal can cause important influence on the electric properties, but little influence on the magnetic properties of the monolayer InSe.

5.Acknowledgements

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6.References

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