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Density functional theory investigation of the electronic structure and thermoelectric properties of layered MoS_2, $MoSe_2$ and their mixed-layer compound

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ABSTRACT

First principles density functional theory calculations were carried out for the 2H-MoQ_2 (Q=S and Se) and their hypothetical mixed-layer compound. Due to the different electronegativities of S and Se atoms on MoQ_2, the band gap size could be adjusted in mixed-layer compound $MoS_2/MoSe_2$. Also, the indirect band gap in pure MoQ_2 compounds is changed to the pseudo direct band gap in mixed-layer $MoS_2/MoSe_2$ which is similar to the monolayer compound. The layer mixing enhances the thermoelectric properties because of the increased density of states around the Fermi level and the decreased band gap size. Therefore, we suggest that this layer mixing approach should be regarded as a useful way to modulate their electronic structures and to improve their thermoelectric properties.

1. Introduction

The 2H-MoQ_2 (Q=S and Se) compounds are crystallizing in a hexagonal structure with space group $P6_3/mmc$ corresponding to space group number 194 [1]. In detail, their crystal structures result from the layer of hexagonal stacking in Q–Mo–Q sequence. These Q–Mo–Q layers are connected by van der Waals (vdW) interactions. Each of these stable units is referred to as a monolayer, consisting of two hexagonal plane of chalcogen atoms and intermediate hexagonal plane of transition metal atoms coordinated through ionic-covalent bonding, with the Q atoms in trigonal prismatic arrangement as shown in Fig. 1.

Semiconducting layered transition metal dichalcogenides have attracted much interest in their applications due to their wide variety of unique physical and chemical properties such as high anisotropic, optical and thermoelectric properties [2,3]. The weak interaction between the layers and strong bonding within the layers are associated with the charge density wave [4] and superconductivity [5–9]. Also the weak interlayer interaction allows the intercalation of a wide variety of metal atoms and interlayer impurities to control the optical and electrical properties of MQ_2 compounds [10].

The electrical properties of MQ_2 compounds usually show semiconducting behavior [11]. MoS_2 is a semiconducting material with a room temperature conductivity of 0.0012 Ω/cm and activation energy of 0.124 eV in the temperature range 150–300 K [12]. It also shows n- and p-type Seebeck coefficient (S=−275 and 400 μV/K) and diamagnetic behavior. $MoSe_2$ compound was reported [13] to be *n-type* with the Seebeck coefficient and resistivity values being −900 μV/K and 1.0 Ω/cm at room temperature, respectively. Although the transition metal dichalcogenides MoQ_2 (Q=S, Se) are a good candidate for thermoelectric applications because of their high Seebeck coefficients (S) and low thermal conductivities (k), the MQ_2 show large band gap size and low electron density near Fermi level. Therefore, in order to improve thermoelectric properties of MoQ_2 (Q=S and Se), it is necessary decreasing of band gap and increasing of carrier concentration near Fermi level.

In this study, we search for a way to modulate the electronic structures and to enhance thermoelectric properties of layered MoQ_2 compounds. In order to achieve this purpose, hypothetically constructed mixed-layer system of MoS_2 and $MoSe_2$ is considered as shown in Fig. 1c. Because the electronic structures near the band gap

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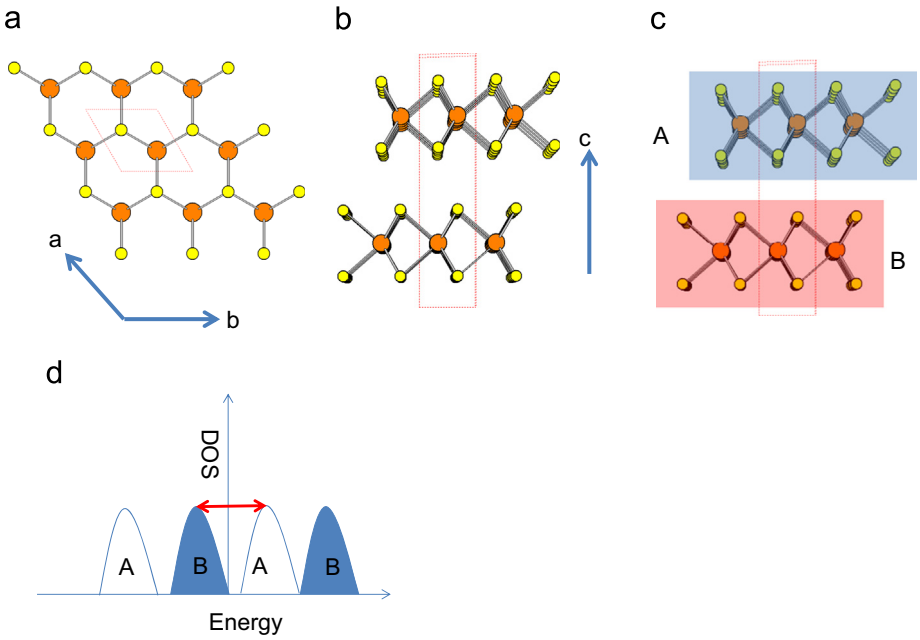

Fig. 1. ((a) and (b)) The top and side views of the crystal structure of 2H-MoQ_2, where Q=S, Se. The scarlet and yellow circles represent Mo and chalcogen atoms, respectively. (c) The side view of the mixed-layer $MoS_2/MoSe_2$ in which two different layers MoS_2 (A) and $MoSe_2$ (B) alternate along the stacking direction. (d) Schematic diagram illustrating of rearrangement of electronic structure. Here, A and B are DOS of different layer of mixed-layer $MoS_2/MoSe_2$ and the layer A (MoS_2) is having a more electronegative chalcogen atom than does the layer B ($MoSe_2$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

are sensitively affected by the interlayer Q…Q vdW interaction [14], the interlayer S…Se vdW interactions in the mixed layer compound could modify its the band gap properties. The thermoelectric properties of a semiconductor MoQ_2 are strongly connected with its electronic structure around the band gap and hence on the interlayer vdW interactions. Thus, one might expect that the thermoelectric properties of $MoS_2/MoSe_2$ can be considerably changed from those of pure MoQ_2. It is of interest and importance to explore if the construction of a mixed-layer system $MoS_2/MoSe_2$ is a way of improving the thermoelectric property of a layered MQ_2.

In understanding the structures and physical properties of solid state compounds in general, it is essential to know their bonding and the nature of their frontier energy levels. For covalent bonding character compounds, it is generally difficult to predict the nature of their frontier energy levels in the absence of first principles electronic structure calculations. Furthermore, for such compounds, it is often difficult to put forward a simple bonding picture with which to describe the essential features of their calculated electronic structures. It is important to carry out systematic electronic structure studies on closely related systems to gain the insight into the band gap properties. In the present work, we examine the electronic structures of the MQ_2 and its mixed-layer $MoS_2/MoSe_2$ compound on the basis of first principles density functional theory (DFT) calculations to find the effect of layer mixing in their geometrical and electronic structure, by expansion, to seek way of the possibility of the improving their electric properties, especially thermoelectric properties.

2. Computational details

In our density functional calculations, we employed the frozen-core projector augmented wave method [15,16] encoded in the Vienna ab initio simulation package (VASP) [17], and the generalized-gradient approximation (GGA) of Perdew et al. [18] for the exchange–correlation functional with the plane-wave-cut-off energy of 450 eV and a set of 200 k-point in the irreducible Brillouin zone. The interlayer interactions in MQ_2 and mixed-layer compound are vdW interactions in nature, which are not correctly treated in the simple GGA method. Thus, in our study, we employed the vdW-DF scheme [19] to describe their interlayer interactions. The structures of the pure MoQ_2 (Q=S, Se) as well as the mixed-layer $MoS_2/MoSe_2$ compounds were fully optimized, and the self-consistent-field convergence thresholds of 10^{-5} eV and 0.001 eV/Å for the total electronic energy and force, respectively. The optimized structural parameters are listed Table 1, and those of the mixed-layer compound $MoS_2/MoSe_2$ in Table 2. In general, the DFT calculation with the PBE functional underestimates a band gap, we carried out the calculations with the hybrid functional HSE06 [20–22] resulting in band gaps of 1.18 eV for MoS_2, 1.15 eV for $MoSe_2$, and 0.74 eV for $MoS_2/MoSe_2$.

Table 1
The structural parameters a, c and z_Q of MQ_2 (space group $P6_3/mmc$) and their calculated electronic band gaps E_g (eV) obtained by the GGA calculations. Here z_Q refers to the z-coordinate of the chalcogen Q ($4h$ site).

	a (Å)	c (Å)	z_Q	M–Q (Å)	E_g
MoS_2	3.169	12.324	0.6230	2.408	0.89
$MoSe_2$	3.289	12.927	0.6210	2.527	0.83
[a]MoS_2	3.1922	12.5100	0.6245	2.422	0.96
[a]$MoSe_2$	3.3290	13.1547	0.6227	2.550	0.92

[a] The structural parameters of optimized MQ_2 (space group $P6_3/mmc$) and their calculated electronic band gaps E_g (eV) obtained from the J. Klimes's vdW-DF calculations.

The thermoelectric transport coefficients are calculated within the Boltztrap code [23] which solves the semi-classical Boltzmann equation and the rigid band approach [24]. The rigid band approach to conductivity is based on the transport distribution

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N}\sum_{i,\vec{K}} \sigma_{\alpha\beta}(i,\vec{k})\frac{\delta(\varepsilon-\varepsilon_{i,\vec{k}})}{d\varepsilon}, \quad (1)$$