Stable monolayer honeycomb like structures of RuX_2 (X=S, Se)

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(Dated: September 21, 2016)

PACS numbers: 31.15.A-, 71.15.Mb, 73.20.-r, 81.05.Zx

I. BULK RUX_2

For the sake of comparison, we optimize the bulk forms of RuX_2 structures. The obtained structural and electronic parameters are presented in Table 1. The structural parameters of pyrite RuX_2 systems are in excellent agreement with the experimental results. We find E_g values, the energy gaps of bulk RuX_2, as the half of the experimental results due to standard PBE calculations, but their band characteristics are the same with the literature as illustrated in Fig.1.

II. $T^{'}$-RUX_2

Kuc et al. present that the estimation of electronic properties of TMDs within PBE0 or B3LYP give much worse results than HSE06 calculations[2,3]. Since the experimental results of $T^{'}$-RuX_2 structures are not available, we also calculate the bandgap of $T^{'}$-RuX_2 structures by using different DFT+HF methods. Fig.2 illustrates the obtained band dispersions of $T^{'}$-RuX_2 structures by B3LYP and PBE0 calculations. The band structures have similar characteristics with different bandgap values.

In Table 2, we present some additional crystallographic parameters including bond lengths and angles of T and $T^{'}$ forms of 2D-RuX_2 structures.

Fig.3 displays the thermodynamic variables of $T^{'}$-RuX_2 structures as a function of the temperature in the range of 0-1000 K. All of these functions are extracted from the calculated phonon dispersion relations at zero pressure by using PHONOPY programme[4]. As can be seen in Fig.3, the thermodynamic variables show dramatic changes specially at low temperatures below 200 K. For instance, while $T^{'}$-RuX_2 has almost fixed free energy below 100 K with low entropic contributions, it goes to negative values with increasing temperature. Entropy of $T^{'}$-RuX_2 also increases with temperature as expected. And finally, we present volumetric specific heat C_v of $T^{'}$-RuX_2. It is seen that the heat capacity depends on temperature at T<400 K and C_v goes to zero while the temperature goes to zero in accordance with the third law of thermodynamics. At high temperatures, C_v tends to the Dulong-Petit limit, especially over the 400 K all of the $T^{'}$-RuX_2 heat capacities have same values.

III. OPTICAL PROPERTIES

From the dynamical dielectric response functions $\varepsilon(\omega)$, the main optical spectra; such as reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, energy loss spectrum $L(\omega)$ can be obtained. We calculate them by using the following equations;

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2 \quad (1)$$

$$\alpha(\omega) = (\sqrt{2})\omega[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)]^{1/2} \quad (2)$$

$$L(\omega) = \varepsilon_2(\omega)/[\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2] \quad (3)$$

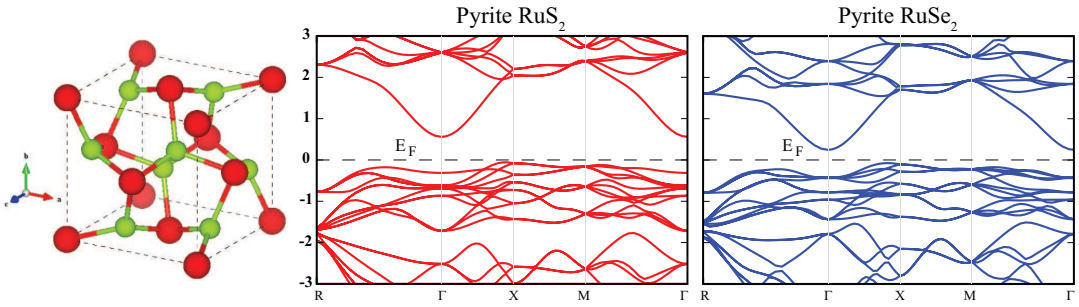

FIG. 1. Bulk pyrite structure of RuX_2 (X=S, Se) and electronic band dispersions.

TABLE I. The obtained parameters for bulk RuX_2; lattice constants [experimental[1]], Ru-Ru and Ru-X distances, band gap energies [experimental[1]].

System	Structure	lattice (Å) a=b=c	d_{Ru-Ru} (Å)	d_{Ru-X} (Å)	E_g (eV)
RuS_2	Pyrite	5.596 [5.609]	3.957	2.343	0.62 [1.22]
$RuSe_2$	Pyrite	5.942 [5.934]	4.202	2.427	0.33 [0.76]

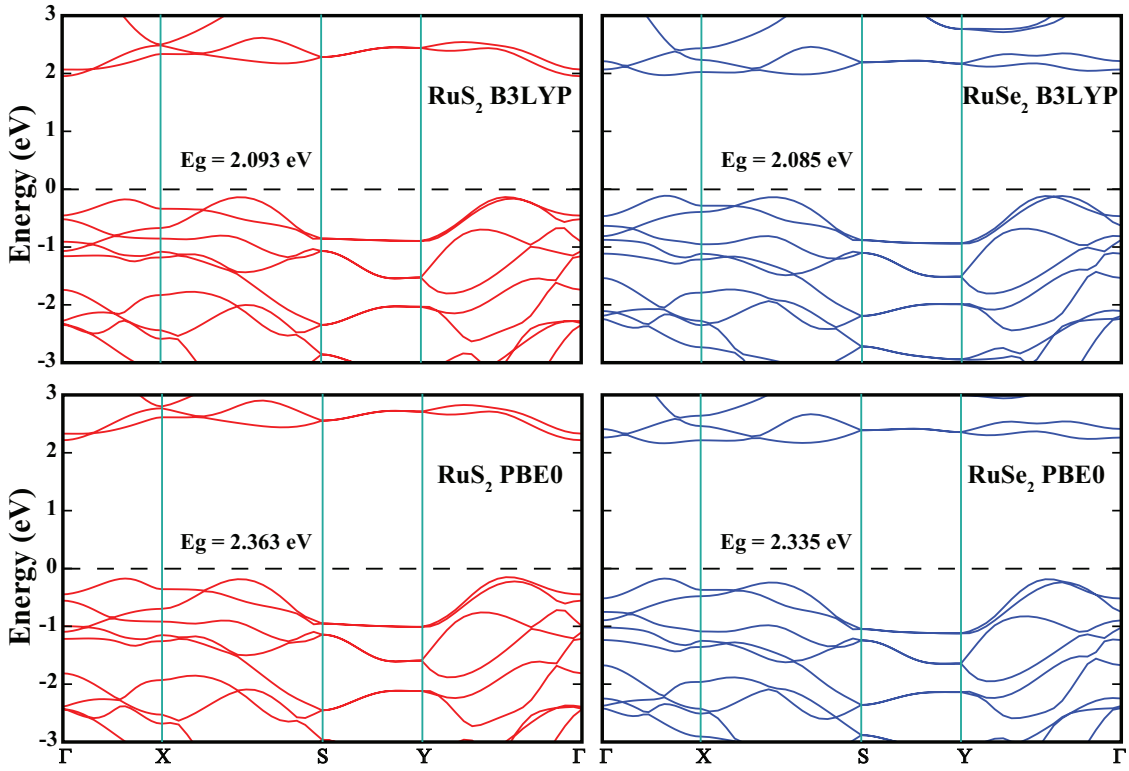

FIG. 2. Band dispersions of $T^{'}$-RuX_2 structures according to B3LYP and PBE0 calculations.

TABLE II. The equilibrium optimized structural parameters of 2D RuX_2 (X=S, Se) systems in T and $T^{'}$ forms: lattice constants, Ru-Ru and Ru-X distances, bond angles.

System	Lattice (Å)	d_{Ru-Ru} (Å)	d_{Ru-X} (Å)	Θ (deg)
T-RuS_2	a=b=3.338	Ru-Ru=3.338	Ru-S=2.390	SRuS=91.48
T-$RuSe_2$	a=b=3.475	Ru-Ru=3.475	Ru-Se=2.515	SeRuSe=92.66
$T^{'}$-RuS_2	a=5.561 b=3.450	Ru_1-Ru_2=2.829	Ru_2-S_2=2.384 Ru_1-S_1=2.384 Ru_2-S_3=2.381 Ru_1-S_2=2.258	$Ru_1Ru_2Ru_1$=75.15 $Ru_1S_1Ru_1$=92.68 $Ru_1S_2Ru_2$=75.03
$T^{'}$-$RuSe_2$	a=5.789 b=3.597	Ru_1-Ru_2=2.910	Ru_2-Se_2=2.506 Ru_1-Se_1=2.506 Ru_2-Se_3=2.513 Ru_1-Se_2=2.382	$Ru_1Ru_2Ru_1$=76.35 $Ru_1Se_1Ru_1$=91.75 $Ru_1Se_2Ru_2$=73.02

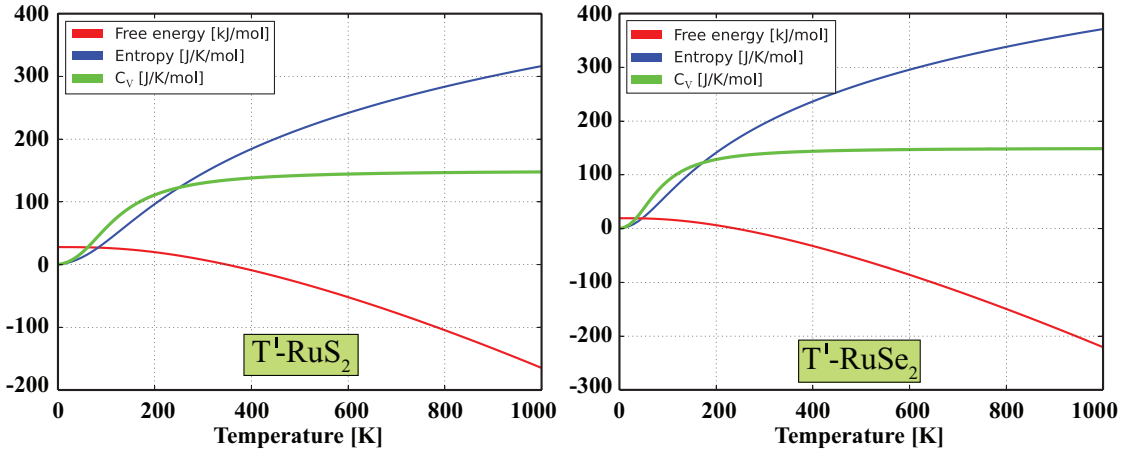

FIG. 3. Thermodynamic properties as a function of temperature of $T^{'}$ structures of RuS_2 and $RuSe_2$ systems.

TABLE III. Calculated Born-effective-charge tensor elements (Z_{ij}) for the constituents of $T^{'}$-RuS_2 structures.

		Z_X	Z_Y	Z_Z
Ru1	Z_X	-1.46469	0.00000	0.99581
	Z_Y	-0.00085	-2.96063	-0.00165
	Z_Z	0.04141	0.00000	-0.07716
		Z_X	Z_Y	Z_Z
Ru2	Z_X	-1.46589	0.00000	0.99429
	Z_Y	0.00085	-2.96063	0.00165
	Z_Z	0.04152	0.00000	-0.07718
		Z_X	Z_Y	Z_Z
S1	Z_X	0.79368	0.00000	0.00949
	Z_Y	-0.00102	1.64258	-0.00055
	Z_Z	-0.00914	0.00000	0.04704
		Z_X	Z_Y	Z_Z
S2	Z_X	0.67275	0.00000	-1.00241
	Z_Y	0.00041	1.31798	0.00053
	Z_Z	-0.03193	0.00000	0.02985
		Z_X	Z_Y	Z_Z
S3	Z_X	0.67224	0.00000	-1.00136
	Z_Y	-0.00041	1.31798	-0.00053
	Z_Z	-0.03178	0.00000	0.03020
		Z_X	Z_Y	Z_Z
S4	Z_X	0.79478	0.00000	0.00637
	Z_Y	0.00102	1.64258	0.00055
	Z_Z	-0.01010	0.00000	0.04801

TABLE IV. Calculated Born-effective-charge tensor elements (Z_{ij}) for the constituents of $T^{'}$-$RuSe_2$ structures.

		Z_X	Z_Y	Z_Z
Ru1	Z_X	-2.60505	0.00000	0.93282
	Z_Y	-0.00179	-3.24731	-0.00115
	Z_Z	0.04830	0.00000	-0.10569
		Z_X	Z_Y	Z_Z
Ru2	Z_X	-2.60506	0.00000	0.93126
	Z_Y	0.00179	-3.24731	0.00115
	Z_Z	0.04816	0.00000	-0.10596
		Z_X	Z_Y	Z_Z
Se1	Z_X	0.97291	0.00000	0.12451
	Z_Y	-0.00144	1.58367	-0.00039
	Z_Z	-0.01626	0.00000	0.05778
		Z_X	Z_Y	Z_Z
Se2	Z_X	1.63268	0.00000	-1.05497
	Z_Y	0.00049	1.66368	0.00089
	Z_Z	-0.03160	0.00000	0.04960
		Z_X	Z_Y	Z_Z
Se3	Z_X	1.63156	0.00000	-1.05304
	Z_Y	-0.00049	1.66368	-0.00089
	Z_Z	-0.03053	0.00000	0.04964
Se4		Z_X	Z_Y	Z_Z
	Z_X	0.97468	0.00000	0.12123
	Z_Y	0.00144	1.58367	0.00039
	Z_Z	-0.01741	0.00000	0.05765

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