First Principles Phase Diagram Calculation for the 2D TMD system

\( WS_2 - WTe_2 \).

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Abstract

First principles phase diagram calculations, that included van der Waals interactions, were performed for the bulk transition metal dichalcogenide system \((1 - X) \cdot WS_2 - (X) \cdot WTe_2\). To obtain a converged phase diagram, a series of cluster expansion calculations were performed with increasing numbers of structure-energies, \(N_{str}\) up to \(N_{str} = 435\), used to fit the cluster expansion Hamiltonian. All calculated formation energies are positive and all ground-state analyses predict that formation energies for supercells with 16 or fewer anion sites are positive; but when \(\approx 150 N_{str} \leq 376\), false ordered ground-states are predicted. With \(N_{str} \geq 399\), only a miscibility gap is predicted, but one with dramatic asymmetry opposite to what one expects from size-effect considerations; i.e. the calculations predict more solubility on the small-ion S-rich side of the diagram and less on the large-ion Te-rich side. This occurs because S-rich low-energy metastable ordered configurations have lower energies than their Te-rich counterparts.

Keywords: WS\(_2\) – WTe\(_2\); First Principles; Phase diagram calculation; van der Waals; transition metal dichalcogenide, TMD.

1. Introduction

There is great interest in two-dimensional (2D) transition metal dichalcogenide (TMD) materials \(MX_2\), where \(M = \text{Mo, W, Nb, Re, etc. and } X = \text{S, Se, or Te}\). \([1, 2]\). Currently, interest is focused on applications such as: band-gap engineering \([3,4]\); nano-electronic devices \([2,5,6,7]\); photovoltaic devices \([8,9]\); valleytronics applications \([10,11]\); 2D building blocks for electronic heterostructures \([12]\); and as sensors \([13]\).

The bulk 2H crystal structure (P6\(_3\)/mmc space group) has AB-stacking of three-atom-thick 2D-layers that are bonded by van der Waals forces. Hence van der Waals forces influence bulk and multilayer phase relations and therefore anion order-disorder and/or phase separation in TMD solid solutions. The results presented below, for bulk \(WS_2 - WTe_2\), imply that van der Waals interactions may strongly affect phase stabilities, either between adjacent layers in bulk or few-layer samples, or between monolayers and substrates.

Previous work on bulk \((1 - X) \cdot MoS_2 - (X) \cdot MoTe_2\) \([14]\) predicted two entropy stabilized incommensurate phases at \(X \approx 0.46\), and this work was done to see if a similar prediction applies to the structurally analogous \((1 - X) \cdot WS_2 - (X) \cdot WTe_2\) system. In the \(WS_2 - WTe_2\) system, however, only a miscibility gap is predicted, but a very large number of formation energy calculations, \(N_{str} \geq 400\), is required to suppress false ground-states (GS). Also, the asymmetry of the calculated phase diagram is the opposite of what one expects from a size-effect argument; typically there is more solubility of the smaller ion in larger-ion-rich solutions (more S-solubility in Te-rich solutions) than vice versa; \(R_s = 1.84 \text{ Å}; R_{Te} = 2.21 \text{ Å}\). \([15]\)

2. Methodology

2.1. Total Energy Calculations

Total structure energies, \(\Delta E_{str}\) were calculated for fully relaxed \(WS_2\), \(WTe_2\) and for 433 \(W_{4\times 4}\)(S\(_m\)Te\(_n\)) supercells. The Vienna \textit{ab initio} simulation program (VASP, version 5.3.3 \([16,17]\)) was used for all density-functional theory (DFT) calculations, with projector augmented waves (PAW) and a generalized gradient approximation (GGA)
for exchange energies. Electronic degrees of freedom were optimized with a conjugate gradient algorithm. Valence electron configurations were: W_{pv} 5p^65d^6, S_{s} 2s^2, Te_{s} 2s^2. Van der Waals interactions modeled with the non-local correlation functional of Klimes et al.\[18\]. A 500 eV cutoff-energy was used in the "high precision" option, which converges absolute energies to within a few meV/mol (a few tenths of a kJ/mol of exchangeable S- and Te-anions). Precision is at least an order of magnitude better. Residual forces of order 0.02 eV or less were typical.

2.2. The Cluster Expansion Hamiltonian

Cluster expansion Hamiltonians (CEH)\[19\], were fit to sets of 71, 253, 295, 399, and 435 formation energies, \(\Delta E_f\), solid dots (green online) in Figs. 1a-5a:

\[
\Delta E_f = (E_{Str} - mE_{WS_2} - nE_{WTe_2})/(2(m + n))
\]

Here: \(E_{Str}\) is the total energy of the \(W_{m+n}(S_mTe_n)_2\) supercell; \(E_{WS_2}\) is the energy/mol of WS\(_2\); \(E_{WTe_2}\) is the energy/mol of WTe\(_2\).

Fittings of the CEHs were performed with the Alloy Theoretic Automated Toolkit (ATAT)\[17, 20, 21, 22\] which automates most CEH construction tasks\[21\].

3. Results

3.1. Ground-State Analyses

Filled circles (green online) in Figs. 1a - 3a indicate values of \(\Delta E_f\) that were calculated with the VASP package, i.e. \(\Delta E_{VASP}\). Large open squares in Figs. 1a - 5a (red online) indicate the CEH-fit to \(\Delta E_{VASP}\). Smaller open squares (\(\Delta E_{GS}\); blue online) indicate the results of a ground-state (GS) analyses that included all ordered configurations with 16 or fewer anion sites, 151,023 structures. Calculated values for cross validation scores, (CV)\(^2\), and the numbers of structures, \(N_{Str}\), are plotted on the figures.

Additional GS analyses were performed by Monte-Carlo (MC) simulations at fixed bulk compositions, via decreasing temperature (T) scans down to T=0. The 0K \(\Delta E_f\) values from these calculations are plotted as solid (predicted stable) or open-diamonds (metastable; blue online) in Figs. 2a and 3a; and as small filled down-facing triangles (blue online) in Figs. 4a and 5a. Because the calculated formation energies for the ordered configurations in Figs. 2a and 3a are negative, they constitute (false) predicted large-cell ordered-GS. If their formation energies are positive they can be regarded as low-energy microstructures. Note that these formation energies from MC-simulations are always upper bounds, because MC-simulations don’t yield perfectly ordered simulation boxes.

3.2. Phase Diagram Calculations

First principles phase diagram calculations that were performed with the ATAT package\[20, 21, 22\] are plotted in Figs. 1b-5b. Additional symbols on Figs. 2b, 3b, and 4b are used to indicate various phase fields that were identified, by visual inspections of MC-snapshots: large filled down-pointing triangles (orange online) indicate disorder; up-pointing triangles (cyan online) indicate a layer structure (e.g. Fig. 2c); and striped circles (black and red online) indicate two-phase, assemblages, ordered plus disordered or two ordered phases.

4. Discussion

One expects that fitting CEHs to larger and larger sets of \(\Delta E_{VASP}\) ultimately leads to a converged result for the calculated phase diagram. The results presented here indicate that the fits with \(N_{Str} = 71, 253, 295,\) and 376 (not shown) are not sufficient because: false GS are predicted, typically at \(X = 1/3\) and \(X = 1/2\); and qualitatively different phase diagrams are predicted with each increase in \(N_{Str}\). Standard ground-state analyses for the sets with \(N_{Str} = 253, 295,\) and 376 (not shown) predicted no ordered GS with 16 or fewer anion sites, but MC T-scans down to T=0K, predicted false GS based on unit cells with more than 16 anion sites. The diagrams for \(N_{Str} = 399\) or 435 are essentially identical, and may represent a converged result. One can, however, never rule out the possibility that a fit based on \(N_{Str} > 435\), might yield a different result.
Figure 1: For $N_{5p} = 71$: (a) Ground-State analysis; (b) calculated phase diagram. In (a): $\Delta E_{\text{VASP}}$ filled circles (green online); $\Delta E_{\text{Fit}}$ large open squares, (red online) is the CE-fit to the DFT set; $\Delta E_{\text{CE}}$ smaller open squares, (blue online) are the CE-based ground-state analysis; All $\Delta E_f > 0$ implies that there are no ordered GS, with 16 or fewer anion sites, and suggests that the phase diagram will have a miscibility gap. Note the small cross-validation score, $(CV)^2 = 0.00265$, which suggests a very good CEH-fit, and in (b) the near absence of asymmetry in the miscibility gap.

Figure 2: For $N_{5p} = 253$: (a) ground-state analysis; (b) calculated phase diagram. Filled diamond symbols in (a) indicate predicted GS structures as shown in the MC-snapshots of: (c) honeycomb structure at $X = 1/3$, and (d) a striped-phase at $X = 1/2$. The open diamond symbol at $X = 2/3$ indicates a low-energy metastable honeycomb-ordered structure. Additional symbols in (b): large filled down-pointing triangles (orange online) indicate disorder; up-pointing triangles (cyan online) indicate a layer structure (d); large checkered circles (red online) indicate a honeycomb structure (c); and striped circles (black and red online) indicate two-phase, assemblages, ordered plus disordered or two ordered phases.
Figure 3: For $N_{SD}=295$: (a) ground-state analysis; (b) calculated phase diagram. Open diamonds in (a) (blue online) indicate: (c) an ordered structure at $X=1/3$; and low-energy, mostly striped, microstructures at $X=1/2$ and $X=2/3$. Note however, that the $X=1/3$- and $X=1/2$-phases appear to be stable at elevated temperatures.

Figure 4: For $N_{SD}=399$: (a) ground-state analysis; (b) calculated phase diagram. Small down-pointing triangles in (a) are $\Delta E_{CE}$ values for MC-simulation T-scans from a low-T value to $T=0$. Note the asymmetry in these values. Additional symbols in (b) have the same meanings as in Fig. 3.
Figure 5: For $N_{St} = 435$: (a) ground-state analysis; (b) calculated phase diagram. Down-pointing triangles in (a) are $\Delta E_{CS}$ values for MC-simulation $T$-scans from a low-$T$ value to $T=0$. Note the asymmetry in these values, which is opposite to what one expects from a size-effect argument. Compare the nearly symmetric miscibility gap in Fig. [1] with the dramatic asymmetries of Figs. [4] and [5].

Two generalizations apply to all calculated phase diagrams for models with $150 < N_{St} < 376$: (1) When false GS are predicted, they are always in the S-rich bulk composition range $0 < X < 0.5$; (2) The range range $0.5 < X < 1.0$ is dominated by phase separation at $T > 1050K$. (1) above indicates that low-energy ordered configurations on the S-rich side of the system drive the asymmetry of phase separation that is noted in (2).

Kang et al. [3] performed first principles phase diagram calculations (with ATAT; $N_{St} \approx 40$) for monolayer $WS_2 - WTe_2$, and reported a phase diagram with its’ consolute point at $(X, T) \approx (0.55, 680K)$; i.e. without the dramatic asymmetry exhibited in Figs. [4] and [5] where $(X, T) \approx (0.7, 1075K)$.

5. Conclusions

A CEH-fit to at least $N_{St} \approx 400$ is required to calculate a realistic phase diagram for the $WS_2 - WTe_2$ TMD system. Low cross-validation scores, and routine GS analyses are not sufficient for systems such as TMDs because very low-energy metastable ordered states imply that an apparently well-fit CEH can predict false GS phases. It is likely that the $WS_2 - WTe_2$ system has a highly asymmetric miscibility gap as shown in Fig. [5] and that the predicted asymmetry is driven by low-energy metastable ordered states on the S-rich side of the system.

6. ACKNOWLEDGEMENTS

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