Prediction of entropy stabilized incommensurate phases in the system $\text{MoS}_2 - \text{MoTe}_2$.

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A first principles phase diagram calculation, that included van der Waals interactions, was performed for the 3D bulk system $(1 - X) \cdot \text{MoS}_2 - (X) \cdot \text{MoTe}_2$. Surprisingly, the predicted phase diagram has at least two ordered phases, at $X \approx 0.46$, even though all calculated formation energies are positive; in a ground-state analysis that examined all configurations with 16 or fewer anion sites. The lower-temperature $I$-phase is predicted to transform to a higher-temperature $I'$-phase at $T \approx 500K$, and $I'$ disorders at $T \approx 730K$. Both these transitions are predicted to be first-order, and there are broad two-phase fields on both sides of the ordered regions. Both the $I$- and $I'$-phases are predicted to be incommensurate i.e. aperiodic: $I$-phase in three dimensions; and $I'$-phase in two dimensions.

I. INTRODUCTION

Recently there has been great interest in two-dimensional (2D) transition metal dichalcogenide (TMD) materials such as $\text{MoS}_2$, $\text{MoSe}_2$ and $\text{MoTe}_2$, their solid solutions, and related 2D materials$^{1,2}$. Traditionally, $\text{MoS}_2$ has been used as a dry lubricant$^3$ that is stable up to 623 K. Currently, interest is focused on applications as: band-gap engineering materials$^{4,5}$; nano-electronic devices$^{2,6-8}$; photovoltaic devices$^{9,10}$; valleytronics applications$^{11,12}$; 2D building blocks for electronic heterostructures$^{13}$; and as sensor materials$^{14}$.

The individual, three-atom-thick, 2D-layers of the bulk system are bonded by van der Waals forces, hence these forces influence bulk and multilayer synthesis and therefore anion order-disorder and/or phase separation in solid solutions. The results presented below, for 3D bulk $\text{MoS}_2 - \text{MoTe}_2$, 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 heterogeneous substrates.

Of the three quasibinary solid solutions $(\text{MoS}_2 - \text{MoSe}_2, \text{MoSe}_2 - \text{MoTe}_2, \text{MoS}_2 - \text{MoTe}_2) (1 - X) \cdot \text{MoS}_2 - (X) \cdot \text{MoTe}_2$ has the greatest difference in anionic radii ($R_S=1.84\,\text{Å}; R_Te=2.21\,\text{Å}$)$^{15}$, which suggests that it is the most likely to exhibit interesting solution behavior. One expects a simple miscibility gap as reported by Kang et al.$^4$ for monolayer $\text{MoS}_2 - \text{MoTe}_2$, hence the prediction of two configurational entropy ($S_{con}$) stabilized incommensurate, i.e. aperiodic, phases is extraordinary (stable phases that have positive formation energies must be entropy stabilized).

II. METHODOLOGY

A. Total Energy Calculations

Total structure energies, $\Delta E_{Str}$, were calculated for fully relaxed $\text{MoS}_2$, $\text{MoTe}_2$ (2H-structure, space group $P6_3/mmc$, AB-stacking of three-atom-thick layers), and for 233 $\text{Mo}_{m+n}(\text{S}_m\text{Te}_n)_2$ supercells. The Vienna $ab\ i initio$ 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: $\text{Mo}^4p^65s^4d; S^3s^2p^4; \text{Te}^4s^2p^4$. Van der Waals interactions that bond the three-atom thick 2D $\text{X}$-$\text{Mo-X}$ layers ($\text{X}=\text{S}, \text{Te}$) together were modeled with the non-local correlation functional of Klimes et al.$^{18}$ Total energies were also calculated without van der Waals interactions, but, up to a basis of 140 structures, ground-state analyses always predicted false ground-states (supplementary material). Convergence with respect to k-point meshes was achieved by increasing the number of k-points until the total energy converged. 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. Often, convergence with respect to hexagonal c-axis length was not automatic, and it was necessary to chose an initial c-axis value that is close to the converged value. Calculated interlayer spacings in $\text{MoS}_2$ and $\text{MoTe}_2$ are 2.992 Å and 3.513 Å, respectively, corresponding experimental values are: 2.977 Å$^{19}$ and 3.382 Å$^{20}$.

Formation energies ($\Delta E_f$) for 233 $\text{Mo}_{m+n}(\text{S}_m\text{Te}_n)_2$ supercells are plotted in Fig. 1, in which values for $\Delta E_f$ are normalized per mol of exchangeable anions, S and Te:

$$\Delta E_f = (E_{Str} - mE_{\text{MoS}_2} - nE_{\text{MoTe}_2})/(2(m+n)) \quad (1)$$

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FIG. 1. Comparison of formation energies $\Delta E_f$ for the 235 DFT calculations (solid circles, green online) to Cluster Expansion (CE) formation energies: $\Delta E_{\text{Fit}}$ (large open squares, red online) are the CE-fit to the DFT set; $\Delta E_{\text{GS}}$ (smaller open squares, blue online) are the CE-based ground-state analysis; $\Delta E_l$ (solid black diamond at $X = 0.46$, $\Delta E_l \approx 0.03$ eV) is the $I$-phase formation energy. All $\Delta E_f > 0$ implies that there are no ordered ground-states, and suggests that the phase diagram will have a miscibility gap.

Here: $E_{\text{Str}}$ is the total energy of the $\text{Mo}_i(\text{S}_{m}\text{Te}_n)_2$ supercell; $E_{\text{MoS}_2}$ is the energy/mol of MoS$_2$; $E_{\text{MoTe}_2}$ is the energy/mol of MoTe$_2$.

All supercell energies are positive which suggests a miscibility gap system, unless one or more entropy stabilized phases are stable.

B. The Cluster Expansion Hamiltonian

A cluster expansion Hamiltonian (CEH)$^{21}$, for the (1-X)-MoS$_2$-(X)-MoTe$_2$ quasibinary system was fit to the set of 235 formation energies, $\Delta E_{\text{ASP}}$, solid dots (green online) in Fig. 1 with a cross validation score of (CV) $Q^2 = 0.00723896$. Fitting of the CEH was performed with the Alloy Theoretic Automated Toolkit (ATAT)$^{17,22–24}$ which automates most of the tasks associated with CEH construction. A complete description of the algorithms underlying the code can be found in$^{23}$. Large open squares in Fig. 1 (red online) indicate values of the 235 $\Delta E_{\text{Fit}}$ that were calculated with the CEH. Smaller open squares ($\Delta E_{\text{GS}}$, blue online) indicate the results of a ground-state analysis in which the CE was used to calculate formation energies for all ordered configurations with 16 or fewer anion sites, 151,023 structures.

III. RESULTS AND DISCUSSION

A first principles phase diagram (FPPD) calculation was performed with grand-canonical, and canonical, Monte Carlo (MC) simulations using the emc2 and phb codes which are part of the ATAT package$^{22–24}$. Most phase boundaries were calculated with the phb program which uses equilibration tests to set the numbers of equilibration- and MC-passes$^{24}$. To draw high-T extensions of the two-phase fields, and to locate the $I \equiv I'$ transition, a 48x48x12 unit cell simulation box was used, with 2000 equilibration passes and 2000 MC-passes (see suplimentary material for comparisons of various equilibration- and MC-pass settings in calculations of the $I \equiv I'$ phase transition). The predicted phase diagram is shown in Fig. 2; where $\text{(MoS}_2)$ denotes an MoS$_2$-rich solution phase, and similarly for $\text{(MoTe}_2$).

Kang et al.$^4$ performed first principles phase diagram calculations for four dichalcogenide monolayer systems: $\text{MoSe}_{2(1-x)}\text{Te}_{2x}$, $\text{WS}_{2(1-x)}\text{Te}_{2x}$, $\text{MoS}_{2(1-x)}\text{Te}_{2x}$ and $\text{WSe}_{2(1-x)}\text{Te}_{2x}$. van der Waals interactions, and fitting Their CEs wer fit to about 40 structures per system, and van der Waals interactions (with substrate) omitted. All systems were predicted to have miscibility gaps, and surprisingly, all consolute points are on the Te-rich sides. One expects the consolute point to be on the S-rich side, because it typically requires less energy to substitute a smaller S-ion into a larger Te-ion site, than vice versa. Figure 2 also has reduced solubility on the Te-rich side, but this is related to immiscibility between the $I$ ($I'$) phase, and the Te-rich phase.

It is not clear that the Kang et al. Mo$_2$S$_2$ – Mo$_2$Te$_2$ phase diagram would still be a simple miscibility gap had they included hundreds of structures in their CE-fit rather than about 40. Hence the monolayer vs. bulk comparison is uncertain.

Surprisingly, the phase diagram predicted here has multiple two-phase fields, separated by two ordered incommensurate phases, neither of which is a ground state.
To seven digits, the calculated bulk composition of the I-phase, just above its 82.5 K minimum temperature of stability, is X = 0.4642857 = 13/28; i.e. Mo_{14}S_{15}Te_{13}. Stability of the I-phases is a robust result, in Monte-Carlo simulations: (1) CEH fits to 128, 153, 162, 182, 225 and 235 formation energies all predict I-type ordering; (2) I-phase forms spontaneously on cooling of the I’-phase at T \lesssim 500 K, and on heating of a low-T equilibrium (MoS_{2}) + (MoTe_{2}) assemble to T \gtrsim 82 K; (3) I-phase forms spontaneously on heating of the I-phase, or cooling of a disordered solid solution with X \approx 0.46. This calculation considers only S_{con}, and ignores excess vibrational entropy, S_{vib}, which could conceivably destabilize the I-phases. In light of (1) above, however, this seems highly unlikely. Also, there is no fully satisfactory way to model S_{vib} for an aperiodic phase, and a reasonable approximate structure (with I-phase like ordering) would require at least a low symmetry 84-atom cell; which is beyond the scope of this study.

FIG. 3. Minimum energies for various Monte-Carlo super-cells; N_{c} is the length of the supercell, in c-axis units of the P6_{3}/mmc disordered-phase cell constants. The flat minimum at \Delta E_{f} \equiv \Delta E_{I} \approx 0.03 \text{ eV/anion} is interpreted as the I-phase formation energy.

Figure 3 shows how the CE-calculated I-phase formation energy \Delta E_{f}(I - \text{phase}) \equiv \Delta E_{I}, varies as a function of MC-super-cell size and shape. The flat minimum at \Delta E_{I} \lesssim 0.03 \text{ eV/anion} is the calculated I-phase formation energy which is plotted as the solid black diamond in Fig. 1. Supercell dimensions were chosen to accommodate Mo_{14}S_{15}Te_{13} stoichiometry and I-phase ordering. Note that many of the \Delta E_{f} plotted in Figs. 1, are lower in energy than \Delta E_{I}, but that they are for periodic structures with 16 or fewer anion sites in which S_{con} \rightarrow 0 as T \rightarrow 0 K, and clearly (Figs. 4) the I-phase is incommensurate, i.e. aperiodic with S_{con} > 0. Figures 4 exhibit the S:Te (yellow:brown online, respectively) ordering at: (a) 200 K; and (b) 575 K, i.e. below and above the I \rightarrow I’ phase transition. Mo-atoms are omitted for clarity, and labels (001)_{D}, (100)_{D}, and (010)_{D} refer to corresponding crystallographic planes in the high-T P6_{3}/mmc disordered-phase.

In the (001)_{D}- and (100)_{D}-planes, ...S_{m}Te_{n}... chains in the <010>_{D} direction, most often have m = 5 or 6 and n = 4 or 5. Also, in (100)_{D}, the ...S_{m}Te_{n}... chains exhibit irregular alignments relative to one another. Note however, that S_{m}Te_{n}-chains in (001)_{D}-planes order along the <001>_{D} direction, such that S_{m}-units alternate with Te_{n}-units in adjacent 3-atom thick 2D-layers; i.e. ...S_{m}Te_{n}S_{m}Te_{n}...chains are stacked on top of ...Te_{n}S_{m}Te_{n}S_{m}...chains with inescapable misfits, owing to the different and variable values of m and n. Thus I-phase ordering is inevitably imperfect, aperiodic, and incommensurate, which suggests that the I \rightarrow I’ phase transition is first-order.

The difference between I- and I’-phases appears to be a distinction between 3D-ordering in the low-T I-phase and 2D-ordering in the high-T I’-phase. Clearly, ordering is stronger in the basal (001)_{D}-plane than in the (100)_{D}- or (010)_{D}-planes, and striped order within (001)_{D} persists above the I \rightarrow I’ transition.

Figure 5a is a Monte-Carlo T-scan (heating) of the total energy E_{TOT}(T), which confirms first-order character for the I \rightarrow I’ transition: a critical (continuous) transition would not exhibit the sharp change
at $T \approx 503K$; also a transition from the lower-T, higher-$E_{TOT}$ phase to the higher-T, lower-$E_{TOT}$ phase requires that the the lower-T phase be superheated, i.e. metastable before it transforms. Figure 5b is an idealized schematic that compares equilibrium- and metastable-transition paths (solid black line, and blue line with red dots, online respectively). This transition is more subtle in cooling simulations, but still evident in snapshots. In the Fig. 5 inset, no change of slope at the transition is evident in the Helmholtz energy, $F(T)$, which suggests that the transition is weakly first-order\textsuperscript{27}. Also, when the MC temperature-increment was decreased from 1.0 K/MC-step to 0.1 K/MC-step (not shown), the predicted transition temperature decreased by about 10 K, which indicates more superheating at 1.0 K/MC-step than at 0.1 K/MC-step, hence first-order character. This transition is shown as a dotted line in Fig. 2 because the two-phase fields that a first-order transition implies are too narrow to resolve in the MC-simulations.

IV. CONCLUSIONS

To summarize, a first principles phase diagram calculation for the 3D bulk system $(1-X)\cdot MoS_2-(X)\cdot MoTe_2$, that includes van der Waals interactions, predicts the formation of two entropy stabilized incommensurate, i.e. aperiodic phases: the $I$- and $I'$-phases, at $X \approx 0.46$. Above the minimum temperature for stability of the $I$-phase, $T \approx 82K$, the calculation predicts broad two-phase fields between the $I$- or $I'$-phase and disordered S- or Te-rich solution phases, $(MoS_2)$ and $(MoTe_2)$, respectively. Both the $I \leftarrow I'$ and $I' \leftarrow disordered$ transitions are predicted to be first-order. Dramatic changes in phase relations can be induced by arbitrarily small differences in energy, hence van der Waals interactions should not be ignored in layered 2D-systems such as $MoS_2-MoTe_2$.

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The phrase ‘weakly first-order’ is used to describe a transition with a sufficiently small discontinuity in order parameter that some first-order characteristics are undetectable: e.g. a kink in $F(T)$, or $I+I'$ two-phase fields.
FIG. 1. Ground state analyses for cluster expansions based on fits to 102, 110, 120 and 140 formation energies, that were calculated without including van der Waals interactions. Note the presence of false ground-states in each fit; i.e. blue squares below the zero-energy line.
FIG. 2. Calculated $I \leftrightarrow I'$ transition points (solid up-pointing triangles, red online). Scatter in these results reflect MC-simulation fluctuations. The phase boundaries, $(MoS_2) + I(I') \leftrightarrow I(I')$ and $I(I') \leftrightarrow I(I') + (MoTe_2)$, were calculated with the phb program in the ATAT package.
FIG. 3. Calculated \( I \leftrightarrow I' \) transition \( E_{TOT}(T) \) curves as functions of the numbers of MC- and equilibration-passes (\( n \) and \( \text{eq} \), respectively) with a 48x48x12 MC-simulation box (solid circles), and a 56x56x12 MC-box (solid diamonds).

FIG. 3. Calculated \( I \leftrightarrow I' \) transition \( E_{TOT}(T) \) curves as functions of the numbers of MC- and equilibration-passes (\( n \) and \( \text{eq} \), respectively) with a 48x48x12 MC-simulation box (solid circles), and a 56x56x12 MC-box (solid diamonds).