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Abhinav Kumar; Alejandro Strachan; Nicolas Onofrio 💿

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Abhinav Kumar,1 Alejandro Strachan,2 and Nicolas Onofrio1,a) 匝

AFFILIATIONS

¹Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Hong Kong ²School of Materials Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47906, USA

^{a)}Author to whom correspondence should be addressed: nicolas.onofrio@polyu.edu.hk

ABSTRACT

Metal-insulator transitions in two dimensional materials represent a great opportunity for fast, low energy, and ultradense switching devices. Due to the small energy difference between its semimetallic and semiconducting crystal phases, phase transition in MoTe₂ can occur with an unprecedented small amount of external perturbations. In this work, we used the density functional theory to predict critical strain and electrostatic voltage required to control the phase transition of 3d and 4d metal doped MoTe₂. We found that small doping contents dramatically affect the relative energies of MoTe₂ crystal phases and can largely reduce the energy input to trigger the transition compared to the pristine case. Moreover, the kinetics corresponding to the phase transition in the proposed doped materials are several January 2025 07:51:27 orders of magnitude faster than in MoTe₂. For example, we predict 6.3% Mn doped MoTe₂ to switch phase under 1.19 V gate voltage in less than 1 μ s with an input energy of 0.048 aJ/nm³. Due to the presence of the dopant, the controlled change of phase is often complemented with a change in magnetic moment leading to multifunctional phase transition.

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I. INTRODUCTION

Materials exhibiting metal-insulator transition, which is characterized by a sudden change in resistance and transmittance near transition, have shown a vast range of applications, including rewritable optical storage media,¹ switches,² thermochromic windows,³ laser protection,⁴ energy harvesting systems,⁵ and memory devices.⁶ For example, transition metal oxides such as VO₂⁷ and chalcogenide glasses8 (e.g., Ge₂Sb₂Te₅) have recently received great attention for their application in resistive switching devices due to their controllable phase transition. However, significant temporal and spatial variations of the switching voltages and resistance states, poor retention time, and thermal disturbances remain major issues to address.7, Moreover, the downscaling limit imposed by current materials is estimated to reach approximately 10 nm, and their high power are far from next-generation nanoelectronics requirements.

Group VI transition metal dichalcogenides (TMDs) represent a special class of fast-growing two dimensional (2D) materials¹⁰ with various electronic properties depending on the number of layers, their composition, and phase. Single-layer TMDs have been used to make atomically thin field effect transistors,¹¹ nanophotonic devices,^{12,13} and optoelectronic devices.^{14,15} Phase transition

in TMDs has been studied for years mostly by thermal and chemical means.^{16,17} Unlike their bulk form, few layered molybdenum dichalcogenides have direct bandgaps in their ground state H-phase, which decreases from sulfur to tellurium.^{18,19} By contrast, tungsten ditelluride exhibits a semimetallic ground state T'-phase.²⁰ A small amount of strain in the range 3%-0.3%, or an electrostatic voltage of 1.8 V, has been predicted to induce phase transition in monolayer MoTe₂ from H to T'-phase.²¹ This semiconductor-to-metal transition was demonstrated experimentally with a reported strain of 0.2%, at room temperature²² and later via an applied gate voltage of 3 V,²³ in good agreement with the theoretical predictions. Although mechanical phase transitions are of interest,^{22,24} electrostatic doping remains the most appealing pathway for electronic device applications. Electrostatically driven phase transition in MoTe₂ has shown potential for high performance switching devices with predicted energy consumption per unit volume 100 to 10 000 times lower than the well-studied Ge₂Sb₂Te₅, at T = 300 K.²⁵ However, the reported energy barrier associated with MoTe₂ phase transition is 0.88 eV/f.u., corresponding to 50 s time scale at room temperature.²¹ This slow kinetics and high voltage operation are still above the standards of today's semiconducting industry.

Interestingly, it has been shown that alloying $MoTe_2$ with W can reduce transition voltage.^{26–28} Furthermore, doping has the advantage of local control which can be used in homojunction devices²⁹ where the contact and the device are made of the same material. Ground state H-phase $MoTe_2$ has a bandgap similar to that of silicon, and its semimetallic T'-phase exhibits topological properties which can be used as dissipation-free contacts in homojunction devices. However, besides W doped $MoTe_2$, only Re doped $MoSe_2$,³⁰ Sn doped MoS_2 ,³¹ and the effect of chalcogen substitution or vacancy³² have been reported to engineer phase transition. Despite the fact that alloying has the potential to reduce transition voltage, and, therefore, energy consumption over pristine materials,^{26,27} we lack a mechanistic understanding of the effect of dopants on phase transition.

In this paper, we used high-throughput density functional theory (DFT) calculations to explore various 3d and 4d transition metals (TMs) as low concentration dopants in MoTe₂. We show that only a small amount of the TM substituent can lower the phase transition energy, and further application of small external perturbations such as strain or electrostatic doping can trigger a reversible phase transition. For example, we predict T' to H-phase transition in 6.3% Mn-doped MoTe2 with a small amount of strain of only 0.63% along the *a* direction, or a voltage gating of 1.19 V. These values are significantly smaller than those for pristine MoTe₂, which are predicted to be $2.4\%^{21}$ (along b) and $1.8 \text{ V}.^{26}$ The lower transition voltage predicted in Mn doped MoTe₂ compared to that in the pristine case corresponds to an energy consumption reduced by approximately 40%. Moreover, we predict the kinetics of the phase transition for some key dopants to be approximatively 10⁵-10⁷ times faster than in MoTe₂, faster than actual flash memory.³³ To generalize, we propose a simple model to estimate the critical dopant concentration at which phase transition will occur. We further introduce multifunctional phase transition by showing the complementary semiconductor-to-metal electronic transition with magnetic state transition as the magnetic moments in H and T'-phases are different for most of the dopants studied.

II. RESULTS AND DISCUSSION

A. Structural details

The interplay of two mechanisms determines the ground state phase of group VI TMDs, known as ligand field splitting (LFS) and charge density wave (CDW).^{27,34} Monolayer TMDs have a general formula MX₂ and are composed of a layer of TM sandwiched between two layers of chalcogen ions. In the most common H-phase, each metal ion is surrounded by 6 chalcogen ions making a trigonal prismatic environment which splits the d-level of the metal into 1-fold (d_{z^2}) and two 2-fold levels $(d_{xy}, d_{x^2-y^2})$ and d_{yz} , d_{xz}) as shown in Fig. 1(a). As the lowest level is completely occupied by the two d-electrons from the metal, the H-phase of TMDs is semiconducting in nature. The geometry of the T-phase can be visualized as a rotation of one of the chalcogen layers [top layer in Fig. 1(b)] about the *c* direction by 60° . The environment of the TMs changes into octahedral and the corresponding crystal field splitting now becomes 3-fold (d_{xy}, d_{yz}, d_{xz}) and 2-fold $(d_{x^2-y^2}, d_{xz})$ d_{z^2}). Partially filled d-levels result in a metallic state. The energy difference between H and T-phases depends on the strength of the LFS and is usually referred to as ΔE_{LF} . The increased M–X bond lengths, when going from sulfide to telluride, reduce the LFS and hence the bandgap. The high density of state at the Fermi level in the metallic T-phase induces a Peierls-like distortion similar to VO2 in which dimerization and a tilt of dimers have been observed. This new phase which is the ground state for WTe₂ is known as the distorted T-phase or the T'-phase. However, unlike VO2, the T'-phase of TMDs is semimetallic in nature. The energy difference $_{\Re}$ between T and T'-phases is referred to as ΔE_{CDW} . Due to the richbetween T and T'-phases is referred to as ΔE_{CDW} . Due to the richness of energetically close crystal phases, TMDs represent perfect candidates for ultradense phase change memory materials.

Among TMDs, $MoTe_2$ has the smallest H/T' energy difference.²⁷ Various doping types have been discussed as a means to stabilize the semimetallic T'-phase in TMDs. Knowing the fact that the TM dopant prefers Mo substitution in all molybdenum



FIG. 1. Crystal structures and ligand field splitting of H (a), T (b), and (c) T'-phases of monolayer TMDs of formula MX2. The fully and partially occupied d-orbital(s) in the H and T (and T') phases leads to semiconducting and metallic characters. The transition from H to T-phase occurs via a 60° rotation of the upper chalcogen layer and is characterized by a change in the ligand field energy ΔE_{LF} . The transition from T to T'-phase is induced by Peierls-like distortions leading to charge density wave energy stabilization ΔE_{CDW} . Gray and yellow spheres represent metals and chalcogen atoms, respectively.



FIG. 2. Energy difference between T' and H phases per formula unit of MoTe₂ for various (6.3%) dopants computed with (red circles) and without (blue squares) spin-orbit coupling. Each phase has been fully relaxed including ions and lattice parameters.

dichalcogenides,^{35–37} we have doped 3d and 4d TMs in MoTe₂ and studied the effect of doping on the stability of H and T'-phases. We started from a supercell with 16 MoTe₂, as shown in Fig. 1, and replaced one Mo with various TMs, corresponding to 6.3% of doping ($\sim 6 \times 10^{13} \text{ cm}^{-2}$). This doping concentration is routinely achieved via chemical vapor deposition for various electronic applications.^{38–41} Figure 2 shows the energy difference $E_{T'} - E_H$ per formula unit for various dopants computed with DFT (at the PBE level) with (red solid circles) and without (blue solid squares) spin-orbit coupling (SOC). Details on the calculations are provided in Sec. IV. Maxima in the curves indicate pristine MoTe₂ followed by the isovalent Cr doped at a slightly lower energy difference. The right side of a maximum, which has a steeper slope, corresponds to dopants having more electrons than the pristine case, and the left side corresponds to dopants having less electrons. The shape of the curve can be explained on the basis of the difference in the electronic structure of the two phases. The extra electrons added to the H-phase must cross the bandgap to reach the available conduction band. This costs more energy than the extra electrons added to the T'-phase which accumulate near the Fermi energy, due to its semimetallic nature. By contrast, removal of electrons reduces the energy of the T'-phase more than that of the H-phase, but this effect is smaller and so the slope is less steep. The inclusion of SOC lowers the H/T' energy differences by approximately 7-10 meV for the various dopants. The effect of SOC is critical, especially for Mn and Tc doped systems, for which its inclusion switches the ground state structure from H to T'. Interestingly, Fig. 2 shows that only a small amount of TM dopants (e.g., 6.3% Sc or Y) can dramatically affect the phase stability of MoTe₂ by contrast with the large amount of 33% W predicted (Ref. 27). This can be explained by the isovalent nature of W which induces only small LFS and contributes to the energy transition via CDW. Only Ti, Zr, V, Nb, and Cr dopants stabilize the H-phase, while all the other TM tested show the T'-phase thermodynamically more stable. Because of the low doping concentration, the effect of orbital rearrangement can be ruled out,³⁴ and the interplay between LFS and CDW controls the phase transition. TMs represent a unique group of dopants to finely tune the phase transition in MoTe₂ as suggested by the almost continuous spectrum of energy differences. We now predict

the critical voltage and strain to trigger the phase transition for each doped MoTe₂ and discuss the consequences.

B. Charge doping

A way to dynamically control the phase transition in MoTe₂, which has been discussed in detail in Ref. 28, relies on electrostatic gating of a capacitorlike structure, where the MoTe₂ monolayer has been deposited to one of the two plates. We performed charge doping calculations for all TM doped systems and evaluated the constant stress phase stability of the materials. The constant stress condition corresponds experimentally to low friction between the monolayer TMD and the substrate.²⁸ The number of electrons in these doped materials was varied within the range from -0.08 to +0.08 e/f.u. (by a step of 0.02 e/f.u.). Section S1 of the supplementary material describes how one can convert the charge density to the applied voltage. Figure 3 shows the H/T' energy difference as a function of charge density doping for all TM doped MoTe₂ without SOC. For clarity and readability, we did not represent the data points, and an extended version of the graph is provided in Fig. S21 of the supplementary material. As charge is added or withdrawn from the compounds, the corresponding H/T' energy difference adjusts through the relative stabilization of each phase, similar to the mechanism described above upon doping. Isovalent Nb and V have maxima shifted by -0.06 e/f.u., which corresponds to $\sim 1/16$ e withdrawn from pristine MoTe₂ (i.e., one of the 16 Mo substituted). Similarly, Mn and Tc are shifted to +0.06 e/f.u., corresponding to the addition of an electron per \Im supercell. Therefore, charge doping is equivalent to substitutional doping without the effect of the local strain of the substituent





FIG. 3. Energy difference between T' and H phases per formula unit of MoTe₂ without SOC for various TM dopants (except Cu, Ag, Zn, and Cd) as a function of excess charge density per MoTe₂. Pristine MoTe₂ and potential low energy phase transition dopants are represented with thicker lines.

is related to the detailed electronic structure of the doped materials as suggested by the difference in the slope between pristine MoTe₂ and the Cr-doped (isovalent) compound.

As discussed above, the inclusion of SOC is important for quantitative predictions. To reduce the computational cost of SOC calculations, we first made the assumption that the effect of SOC in charged materials is similar to that in the neutral case. We note that this assumption is valid because of the low charge doping content achieved in the present study with a maximum of 0.08 e/f.u. This will be later validated by including fully the effect of SOC to each charge doping content for some selected dopants. Therefore, as a preliminary screening, we added the difference between SOC and non-SOC (nSOC) energies of the neutral system for each phase and each dopant to the corresponding nSOC energies of each charged system. A comparison of critical excess charge density (the charge density required to trigger the phase transition) for nSOC and SOC-corrected calculations (SOC*) is reported in Table I. We found critical charge densities of +0.160 and -0.051 e/f.u. for pristine MoTe₂ without SOC. These values were reduced to +0.120 and -0.038 e/f.u. with SOC* approximation, consistent with previous reports^{27,28} as well as our validation batch, fully including the SOC effect (SOC column of Table I) corresponding to +0.112 and -0.040 e/f.u., respectively.

Based on this, we predict that V, Mn, and Tc dopants require lower positive critical charge densities to change phase compared to pristine MoTe₂. Both H and T' ground state phases are observed, depending on the dopant. Interestingly, we found that small positive critical excess charges of only +0.011 and +0.018 e/f.u. would trigger the phase transition in 6.3% Tc and Mn-doped MoTe₂, respectively, which is in good agreement with the validation batch including fully the SOC effect of +0.012 and +0.019 e/f.u. These small excess charges correspond to critical (constant voltage mode) voltages of 1.20 and 1.19 V, respectively, and lower than our predictions for pristine MoTe₂ of +3.75 and -1.29 V. These voltages (1.20 V) are significantly lower than gate voltages achieved experimentally.^{23,42} The corresponding energy consumption to trigger the phase transition are 0.11, 0.048, and 0.062 aJ/nm^3 for pristine, Mn, and Tc doped MoTe₂, respectively (details given in Sec. S1 of the supplementary material). Moreover, Ti-, Fe-, and Ru-doped materials also show small critical charge densities (< 0.1 e/f.u.) and represent additional candidates to tune the H/T' phase transition. The isovalent Cr dopant exhibits similar electrostatic behavior than the pristine case with a predicted phase transition at a slightly larger negative charge density value. All TM dopants are predicted to require larger negative charge density to trigger the transition compared to that for pristine MoTe₂. It is worth mentioning that these critical charge densities do not account for any thermal effect and should, therefore, be considered an upper limit. A recent discussion of such effects in MoTe2 and the consequence on the energy consumption can be found in Ref. 25.

We performed additional simulations to evaluate the effect of dopant concentration on the H/T' energy difference. Figure S7 in the supplementary material shows H/T' nSOC energy differences as a function of the dopant type corresponding to 12.5%, 6.3%, and 4.2% doping concentrations. As expected, the energies are dramatically affected by the concentration of the dopant. This provides g

TABLE I. Positive (σ_+) and negative (σ_-) critical charge density per formula unit required to switch the phase of various doped MoTe₂ with (SOC) and without SOC (nSOC). The column SOC* corresponds to an approximation of the SOC case, as described in the text. nSOC values were extracted from Fig. 3 and SOC from Figs. S3 and S6 in the superimentary material via linear interrolation of the intersecting curves. Boldface highlights small values of the critical charge density (smaller than 0.1 eff u.) supplementary material via linear interpolation of the intersecting curves. Boldface highlights small values of the critical charge density (smaller than 0.1 e/f.u.).

Dopant	Critical charge density (e/f.u.)								
		σ_+		σ_					
	nSOC	SOC*	SOC	nSOC	SOC*	SOC			
Sc	n/a	n/a		-0.004	n/a				
Y	+0.002	n/a		n/a	n/a				
Ti	n/a	n/a		n/a	n/a				
Zr	n/a	n/a		n/a	n/a				
V	n/a	+0.067		n/a	n/a				
Nb	n/a	n/a		n/a	n/a				
Cr	n/a	n/a		-0.072	-0.051				
Mo	+0.160	+0.120	$+0.112^{a}$	-0.051	-0.038	-0.040^{a}			
Mn	n/a	+0.018	$+0.019^{a}$	-0.014	n/a				
Тс	n/a	+0.011	$+0.012^{a}$	-0.008	n/a				
Fe	+0.035	+0.080		n/a	n/a				
Ru	+0.052	+ 0.079		n/a	n/a				
Со	n/a	n/a		n/a	n/a				
Rh	n/a	n/a		n/a	n/a				
Ni	n/a	n/a		n/a	n/a				
Pd	n/a	n/a		n/a	n/a				

^aFrom Figs. S3 and S6 in the supplementary material.

additional candidates exhibiting small critical charge density to trigger the phase transition. For example, at 4.2% dopant, Sc, Y, Mn, Tc, Fe, and Ru appear now to be in the ground state H-phase, approximately 10 meV above the T'-phase. However, the inclusion of SOC shows that 4.2% Mn doped MoTe₂ is the T'-phase ground state, and we predict a small critical charge of 0.009 e/f.u. to switch to the H-phase. By contrast, 4.2% Ti doped MoTe₂ is the H-phase ground state and requires only 0.007 e/f.u. to switch to the T'-phase. To generalize, we show in Figs. S8–S9 in the supplementary material that the H/T' energy differences are approximately proportional to the dopant concentration, providing a simple way to estimate the critical doping concentration. Table S1 in the supplementary material summarizes (nSOC) critical doping concentrations required to trigger the phase transition in various doped MoTe₂. This can be easily extended to include the SOC effect.

Although Figs. 2 and S7 (supplementary material) provide important information related to the thermodynamic stability of each phase, they lack kinetic information. We performed nudged elastic band (NEB) calculations to evaluate the energy barriers between H and T' phases of some key dopants. The corresponding potential energy surfaces are reported in the supplementary material (Fig. S10). We found activation energies of 0.54, 0.41, and 0.34 eV for 6.3% Tc, Mn, and Sc doped MoTe₂, respectively. If we consider a characteristic frequency of 10 THz,²¹ these barriers correspond to $101.0\,\mu$ s, $0.9\,\mu$ s, and $40.8\,$ ns transition time scales, respectively, 6-8 orders of magnitude faster than the pristine case (details given in Sec. S3 of the supplementary material). We note that influencing factors such as interface, substrate, impurities, and vacancies can affect these kinetics.^{43,44} Nevertheless, these transition speeds are faster than state-of-the-art flash nonvolatile memory and approach that of DRAM.³

C. Strain effect

Another way to induce phase transition in these materials, discussed in Ref. 21, is based on strain. To investigate the effect of strain on the stability of each doped MoTe₂ compound, we calculated the energy of the corresponding H and T' phases on a 5×5 grid of strain ranging between -8% and +8%, around the ground state relaxed cell. The corresponding energies were interpolated and the intersection of the H and T' surfaces, normalized with respect to zero strain lattice parameter of the ground state doped system, is reported in Fig. 4. All doped materials with the H-phase ground state cluster together in the upper quadrants of the figure. The intersection contours corresponding to these H-phase ground state materials cut the positive region of the b-axis and that of the negative a-axis. Similarly, the intersection curves of dopants with the T'-phase ground state cluster together, lie in the lower quadrants of the figure, and cut the negative values of the b-axis and positive values of the a-axis. This suggests that a tensile strain (positive) along b or a compressive strain (negative) along the a direction is required to switch phases for H-phase ground state compounds, while a tensile strain along a or a compressive strain along the b direction is needed to trigger transition of the T'-phase ground state systems.

We evaluated the uniaxial load required along a and b directions to switch phase in the 6.3% doped MoTe₂ monolayers.



FIG. 4. Intersection contours of the H and T' energy surfaces when varying the lattice constants a and b of various doped $MoTe_2$ monolayers. The lattice constants a and b are represented as percent engineering strains, normalized over the equilibrium lattice constants of the ground state phase a_0 and b_0 . Pristine $MoTe_2$ and potential low energy phase transition dopants are represented with thicker lines. These calculations do not include SOC.

The procedure to extract uniaxial loads is detailed in Sec. S4 of the supplementary material. We also evaluated the effect of SOC on the critical uniaxial load by considering a constant correction from the unstrained crystal phase, in the same spirit as the correction on critical excess charge described before. Details are provided in 3 Sec. IV. The critical values of strain along a and b directions are $\frac{1}{2}$ presented in Table II. Keeping in mind that the experimental realization of a negative load can be challenging, we tried to identify cases with a small positive load. We found a critical load value of 2.49% for pristine MoTe2 along the b-axis without SOC which matches well with a previous study finding of 2.40%.²¹ This value reduces to 1.88% by including the approximated SOC correction (SOC*), which is in perfect agreement with the fully SOC calculations we performed leading to the critical strain of 1.84%. Our simulations predict small critical uniaxial strains of -0.35% and -0.55% along *a* and 0.30% and 0.46% along *b* to trigger the phase transition of Ti and V doped MoTe2, respectively. The T'-phase ground state Tc and Mn compounds exhibit phase transition upon 0.56% and 0.53% along a and -0.25% and -0.34% along b, respectively. This was validated with SOC calculations and we found between 0.03% and 0.47% error in the SOC* predictions. These strain values are significantly lower than that for pristine MoTe₂, and the corresponding materials represent appealing low energy phase transition compounds. Further thermal and vibrational effects can be evaluated by adding the contribution of vibrational frequencies to the free energy of each phase.²¹ Similar to charge doping, one can predict additional low strain phase transition materials by adjusting the concentration of the dopant according to the linear dependency of the concentration with energy.

TABLE II. Critical uniaxial load (in %) along a and b directions required to switch
the phase of various doped MoTe ₂ with (SOC) and without SOC (nSOC). The
column SOC* corresponds to an approximation of the SOC case, as described in
the text and in Sec. IV. Boldface highlights small values of the critical load (smaller
than 0.9% in absolute value).

		Critical uniaxial load (%)								
	Along a			Along b						
Dopant	nSOC	SOC*	SOC	nSOC	SOC*	SOC				
Sc	+0.50	+1.22		-0.39	-0.91					
Y	+0.43	+1.12		-0.48	-0.91					
Ti	-0.97	-0.35		+0.89	+0.30					
Zr	-1.59	-0.97		+1.75	+0.98					
V	-1.25	-0.55		+1.09	+0.46					
Nb	-1.82	-1.22		+1.61	+1.02					
Cr	-2.13	-1.65		+2.25	+1.64					
Mo	-2.28	-1.89	-1.89	+2.49	+1.88	+1.92				
Mn	-0.50	+0.56	+0.63	+0.26	-0.25	-0.28				
Тс	-0.38	+0.53	+0.90	+0.24	-0.34	-0.48				
Fe	+0.51	+2.39		-0.23	-0.94					
Ru	+1.84	+3.23		-0.82	-1.33					
Со	+2.70	+4.00		-1.49	-2.30					
Rh	+4.71	n/a		-2.06	-2.94					
Ni	+2.04	+3.18		-1.11	-1.58					
Pd	+3.78	n/a		-2.04	-2.70					

D. Magnetization

The introduction of 3d and 4d TMs in MoTe₂ can also induce magnetism in the materials due to their localized d-electrons. Figure 5 shows the magnetic moment of each 6.3% doped material in both H and T'-phases. Ti, V, Nb, Cr, Ru, Ni, and Pd doped materials as well as pristine MoTe₂ have zero magnetic moments which indicates the nonmagnetic nature of these materials. Mn doped materials show a magnetic moment of approximately 1 bohr magneton for both phases, while Fe doped MoTe₂ shows magnetic moments 2-1 bohr in the H-phase and the T'-phase, respectively. The most exciting compounds correspond to Sc, Y, Co, Rh, Cu, Ag, Zn, and Cd doped MoTe₂, which show no sign of magnetism in



the T'-phase but a significant magnetic moment in the H-phase. This suggests the possibility not only to tune the semiconductorto-metal transition but also the magnetic property via electrostatic voltage or strain. Moreover, it should be possible to design the device to magnetically trigger the phase transition in these materials.

III. CONCLUSION

To summarize, we systematically investigated the stability of H and T' phases of 3d and 4d TM doped MoTe₂ using first principle calculations. We found that doping can be used to tune the phase transition in MoTe₂ and that the mechanism relies on the interplay between LFS and CDW. A small amount of dopant can lower the energy difference between semimetallic T' and semiconducting H phases, and we predict the additional perturbation to trigger the transition via strain and electrostatic voltage. Compounds such as 6.3% Mn or Tc and 4.2% Mn or Ti doped MoTe₂ appear as promising candidates for low energy and fast switching materials. Moreover, we described a simple procedure to predict the critical dopant concentration and, hence, additional potential dopants. Interestingly, the introduction of TM dopants significantly lowers the phase transition kinetics and introduces a phase dependent magnetic moment. This last property can have important implications in nanoelectronics where structural phase transition could be induced by an electrostatic or magnetic field.⁴⁵ This work provides a guideline to experimentalists to explore the possibility of phase engineering in MoTe₂ and can be extended to other 2D materials.

IV. METHODS

All calculations were based on DFT as implemented in ⁴⁸ using plane wave projected-augmented wave (PAW) vertication wave projected-augmented wave (PAW) vertication wave the generalized gradient approxima-VASP⁴⁶⁻ pseudopotentials.49 tion (GGA) proposed by Perdew, Burke, and Ernzerhof⁵⁰ with an 35 energy cutoff of 350 eV. Previous GGA based studies on doped 2D is materials have demonstrated the validity of the method including Refs. 51-54. It has been shown that the introduction of Hubbard U parameter does not affect the structural and magnetic properties of Ni and Mn doped monolayer MoS₂.⁵⁴ We further validated our GGA approach by including the effect of an average U value of 2.5 eV to each TM dopant and found negligible differences to the energy and magnetic moment (excluding the Cr dopant). This is summarized as Figs. S19 and S20 in the supplementary material. The Brillouin zone was sampled on a $2 \times 2 \times 1$ Monkhorst–Pack⁵⁵ type mesh to describe the $4 \times 2 \times 1$ supercell (based on 6 atoms rectangular unit cell). To avoid any interaction between layers, we added a vacuum space of 36 Å. Lattice parameters and internal coordinates of the ions were relaxed until energy and force of charged supercells reached values of 0.5×10^{-7} and $0.5 \times$ 10^{-6} eV/f.u. , while we used the looser criteria of 0.01 eV/Å to converge forces in strained supercells. All calculations were spinpolarized. For charge doping, the total number of electrons was changed and ions relaxed within the lattice parameters of the uncharged ground state structure, corresponding to constant stress case. Critical excess charges were extracted by linearly fitting the H/T' energy difference as a function of the excess charge around the zero energy intersection point. We did not correct for the background charge since this has been demonstrated to cancel when

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energy differences are considered.²⁷ We have further validated this in the supplementary material. H and T' strain surfaces were interpolated with a 2D cubic surface and the intersection contours with cubic curves. Uniaxial loads were extracted from successive cubic fits of the strain data as described in the supplementary material of Ref. 21 and reported in Sec. S4 of the supplementary material.

SUPPLEMENTARY MATERIAL

See the supplementary material for details on the charge doping procedure, how to convert critical excess charge to voltage, validation cases, and energy calculations, as well as the effect of doping content, the kinetics of the phase transition, and uniaxial load procedure and corresponding figures. We also provide the effect of Hubbard U parameter to the H/T' energy difference for all the TM doped MoTe₂ materials.

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