Kinetic mechanism for reversible structural transition in MoTe$_2$ induced by excess charge carriers

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Kinetic of a reversible structural transition between insulating (2H) and metallic (1T') phases in a monolayer MoTe$_2$ due to an electrostatic doping is studied using first-principle calculations. The driving force for the structural transition is the energy gained by transferring excess electrons from the bottom of the conduction band to lower energy gapless states in the metallic phase as have been noticed in earlier studies. The corresponding structural transformation involves dissociation of Mo—Te bonds (one per formula unit), which results in a kinetic energy barrier of 0.83 eV. The transformation involves a consecutive movement of atoms similar to a domain wall motion. The presence of excess charge carriers modifies not only the total energy of the initial and final states, but also lowers an energy of the transition state. An experimentally observed hysteresis in the switching process can be attributed to changes in the kinetic energy barrier due to its dependence on the excess carrier density.

I. INTRODUCTION

The quest for materials with resistivity that can be controlled by passing through a current is driven by their use in data storage and unconventional processing units. Prominent mechanisms realized so far involve formation/dissolution of a conductive filament due to diffusion of ionic species, or tuning the conductivity via a phase change between crystalline/amorphous states induced by Joule heating. Extreme structural transformations associated with low/high resistance states in these materials naturally limit their endurance. Recently, Wang et al. reported an experimentally-observed reversible transition between insulating (2H) and metallic (1T') phases in a monolayer MoTe$_2$ driven by an electrostatic doping. This technique opens up possibilities for developing of new phase-change devices.

The driving force for the 2H→1T' structural transition in doped transition metal dichalcogenides (TMDs) is the energy gained by transferring excess electrons from the bottom of the conduction band to lower energy gapless states in the metallic phases as illustrated in Fig. 1. In general, other TMDs with 2H stable structure (e.g., MoS$_2$) can undergo a charge-mediated phase transition. However, a high energy difference between the 2H and 1T' phases (0.8 eV per formula unit (f.u.) of MoS$_2$) requires a high excess charge density that is beyond practical capabilities of the electrostatic gating.

The advantage of MoTe$_2$ is that 2H and 1T' phases are very close in energy. Li et al. and Zhang et al. calculated the carrier density required to drive the 2H→1T' transition in MoTe$_2$ assuming that the crossover takes place when two phases have the same energy. The threshold excess electron densities of $n_e = 3.7 \times 10^{13}$ cm$^{-2}$ and $6 \times 10^{13}$ cm$^{-2}$ were predicted by these two groups, respectively. The experimental values are $1.2 \times 10^{14}$ cm$^{-2}$ for the 2H→1T' transition and $5 \times 10^{13}$ cm$^{-2}$ for the reverse transformation 1T'→2H. Although the agreement is not perfect, it indicates that first-principle calculations capture the essence of a charge-induced phase transition. What is not addressed so far is a wide hysteresis of $n_e$'s associated with the switching process suggesting a kinetic barrier involved. The goal of this paper is to investigate the energy landscape for 2H→1T' transformation in MoTe$_2$ in the presence of an excess charge.

II. METHOD

Vienna ab-initio simulation program (VASP) density functional theory (DFT) package was employed in this work. A meta-generalized gradient approximation SCAN functional with a revised Vydrov-van Voorhis (rVV10) long-range van der Waals interaction was used for the exchange-correlation functional since it accurately captures both structural properties and the strength of chemical bonds. The inclusion of the van der Waals interaction is essential for layered structures.

Calculations for the bulk MoTe$_2$ were performed using $10 \times 10 \times 2$ and $5 \times 9 \times 2$ $k$-mesh for the primitive Brillouin
zone of hexagonal and monoclinic phases, respectively. The structural relaxation was performed by minimizing Hellmann-Feynman forces and stresses below 20 meV/Å and 0.5 kbar, respectively. The cutoff energy for the plane-wave expansion was set at 280 eV, which is 25% higher than the value recommended in the pseudopotential for molybdenum. These parameters ensure better than 10 meV convergence of the total energy difference between 2H and 1T’ phases of MoTe₂.

The calculated structural parameters for 2H and 1T’ phases are listed in Table S1 (see Supplementary information) along the side with experimental values. Their good agreement gives a confidence in results of calculations.

The monolayers were derived from the bulk structures with a subsequent relaxation of in-plane structural parameters, while maintaining a fixed spacing $c$ between the layers. The separation of $c = 100$ Å was used to represent a monolayer unless otherwise specified.

III. RESULTS AND DISCUSSION

First we discuss the band structure of the 2H and 1T’ phases of MoTe₂ shown in Fig. 2. The monolayer 2H phase features a direct band gap at K point (Fig. 2a) in accord with optical experiments. The magnitude of the band gap 1.1 eV is in good agreement with the experimental 1.1–1.2 eV. The agreement for band gaps is not typical for bare DFT. The likely reason is an error cancelation between an underestimation of the total energy difference between 2H and 1T’ phases of MoTe₂ and a strong excitonic red shift present in optical spectra of 2D materials. The bulk 2H structure exhibits a smaller indirect band gap (see Fig. S1 in the Supplementary information), which follows the experimental trends, namely, the transition from a direct to indirect band gap as the number of layers increases.

The monolayer 1T’ phase has a semimetallic band structure (Fig. 2c) with electron and hole pockets approaching but not touching each other near $\Gamma$ point. In the bulk 1T’ phase the electron and hole pockets penetrate each other (see Fig. S1 in the Supplementary information) giving rise to non-trivial topological states (type-II Weyl semimetal). This result suggests a few layers MoTe₂ as an alternative candidate for a tunable Weyl fermion metallic state that were previously reported for a MoₓW₁₋ₓTe₂ alloy.

Calculations of a Fermi energy alignment for a monolayer 2H and 1T’ phases of undoped MoTe₂ indicate a validity of the energy argument shown schematically in Fig. 1. Specifically, the Fermi energy of the 1T’ phase is located in the middle between highest occupied and lowest unoccupied states of the 2H structure. The total energy of the 2H phase is 40 meV/f.u. lower than that of the 1T’ phase in the bulk and only 5 meV/f.u. lower at the monolayer level.

Stability of 2H vs 1T’ phase in the presence of excess electrons of the areal density $n_e$ added to the monolayer MoTe₂ to simulate an electrostatic gating, was used to generate intermediate states. Here $a$ stands for lattice vectors or fractional coordinates of atomic positions, and $\xi$ is the reaction coordinate. Figures 3a and 3b illustrate the initial 2H structure ($\xi = 0$) and the final 1T’ structure ($\xi = 1$). A nudged elastic band method was employed to explore the reaction coordinate space for internal degrees of freedom and find the lowest energy transition state (Fig. 3). An evolution of the total energy as a function of the reaction coordinate exhibits two plateaus that implies a two-step trans-
The formation process. The first plateau at $\xi = 0.5$ corresponds to the transition state. It involves contraction of two raw of Mo-atoms along $x$-axis and simultaneous “squeezing” of the first Te-atom between two Mo-atoms (Fig. 4b). The transformation is accompanied by dissociation of one Mo–Te bonds, which explains a relatively high magnitude of the barrier, 0.83 eV/f.u. The calculated kinetic barrier can be compared to the literature values of 0.9 eV/f.u. for MoTe$_2$ and 1.6 eV for MoS$_2$, which is indicative of a stronger Mo–S bond.

The second plateau in the energy landscape occurs near $\xi = 0.7$ (Fig. 5). At this point, the second Te-atom transitions between two Mo-atoms (Fig. 4c) and completes the structural transformation. An importance of a correlated movement between Te and Mo atoms during the 2H$\rightarrow$1T’ structural transition was emphasized by Huang et al.31,32 Furthermore, the transitions steps in Fig. 4 show that Te-atoms do not move simultaneously, but rather overcome the barrier in two consecutive steps. As a result, the phase boundary moves from left to right along $x$-axis in Fig. 4. This process is reminiscent of a domain wall motion during polarization switching in ferroelectric materials.31,32 By analogy, the 2H$\rightarrow$1T’ phase transition in MoTe$_2$ does not happen concurrently, but rather involves propagation of a wave front of a finite width (significantly greater than the simulation cell used here), which requires overcoming a much lower energy barrier. Similar to ferroelectric materials, the 2H$\rightarrow$1T’ switching process also features a wide hysteresis with respect to the driving force (the excess charge carrier density).2

The presence of an excess charge modifies not only the total energy of the final states (Fig. 3), but also affects the energy of a transition state (Fig. 5). The kinetic energy barrier is lowered by $\Delta E_k = -60$ meV at the doping level of $n_e = 1.4 \times 10^{14}$ cm$^{-2}$. This result can be attributed to the metallic nature of electronic structure at the transition state ($\xi = 0.5$ in Fig. 5) and its lower energy in the charge state (Fig. 3) with respect to the 2H structure ($\xi = 0$). To estimate the effect of doping on the 2H$\rightarrow$1T’ transition rate, we assume that it can
be described by the Arrhenius equation \( \nu_0 \exp(-E_a/k_B T) \) with \( \nu_0 \) being the attempt frequency, \( k_B \) being the Boltzmann’s constant, and \( T \) being the temperature. A doping-induced modification of the kinetic barrier results in increasing of the transition rate by a factor of \( \exp(-\Delta E_a/k_B T) \). Here a 10-fold rate increase is expected at the room temperature and the doping level of \( n_e = 1.4 \times 10^{14} \text{ cm}^{-2} \). It should be noted that the electrostatic doping has a similar effect on the energy barrier for the 1T'\( \rightarrow \)1T' structural transition in MoTe\(_2\), but the energy scale is much smaller (in the order of 1−2 meV).

Note added during publication: Krishnamoorthy et al. recently reported a similar study of the kinetic energy barrier and its change due to the presence of electronic excitations on the monolayer MoTe\(_2\). Their energy barrier of 0.77 eV/f.u. is comparable to 0.83 eV/f.u. reported here in the absence of the excess charge. A qualitatively similar reduction of the energy barrier in the presence of excitation is noticed.

**IV. CONCLUSION**

The density functional theory with a van der Waals correction was used to study a kinetic barrier in the phase transition between stable insulating (2H) and metastable metallic (1T') phases of MoTe\(_2\). In bulk, the total energy of 2H phase is 40 meV/f.u. lower than that for the 1T' phase. The energy difference reduces down to 5 meV/f.u. for the monolayer structures indicating that exfoliation stabilizes the 1T' phase. This balance can be further shifted in favor of the 1T' phase by adding excess charge carriers (electrons). The 2H\( \rightarrow \)1T' structural transformation requires overcoming the energy barrier of 0.83 eV/f.u., which is reduced by 60 meV/f.u. at the excess carrier density of \( n_e = 1.4 \times 10^{14} \text{ cm}^{-2} \) that corresponds to adding 0.15 electrons per formula unit of MoTe\(_2\). The structural transformation takes place in two steps during which two Te-atoms transit between 2H and 1T' equilibrium positions in a consecutive manner. This finding suggests existence of commonalities between the 2H\( \rightarrow \)1T' phase transition in MoTe\(_2\) and a domain wall motion, thereby explaining the presence of a hysteresis in the reversible 2H\( \leftrightarrow \)1T' phase transition.

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