Tunable band gap and enhanced ferromagnetism by surface adsorption in monolayer Cr₂Ge₂Te₆

Changsheng Song,^{1,2,*} Wen Xiao,^{1,2,*} Lei Li,² Yi Lu,³ Peiheng Jiang,^{2,†} Chaorong Li,¹ Aixi Chen,^{1,†} and Zhicheng Zhong^{2,4,†} ¹Department of Physics, Zhejiang Sci-Tech University, Hangzhou 310018, China

²Key Laboratory of Magnetic Materials and Devices, Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology,

Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

³Institute for Theoretical Physics, University of Heidelberg, Heidelberg 69120, Germany

⁴China Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

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Two-dimensional (2D) van der Waals (vdW) materials have attracted significant attention for their promising applications in spintronic devices. Here, using first-principles calculations and renormalized spin-wave theory, we investigate the influence of surface adsorption (H and alkali metals) on the bandgap and ferromagnetism of monolayer $Cr_2Ge_2Te_6$. We find that H-atom adsorption maintains the bandgap of $Cr_2Ge_2Te_6$ around 0.95 eV but leads to a nearly indirect-to-direct band gap transition, while alkali-metal adsorption removes the bandgap and induces metallicity. More importantly, both H and alkali-metal adsorption surprisingly make the magnetic anisotropy energy four times larger than that of pristine $Cr_2Ge_2Te_6$, leading to an increase of T_c by about 33%. Our findings of adsorption-controlled bandgap and magnetism in a 2D vdW magnet may open up opportunities for potential applications for new-generation magnetic memory storage, sensors, and spintronics.

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I. INTRODUCTION

In the last decade, two-dimensional (2D) materials such as graphene [1] and transition metal dichalcogenides [2] have been extensively studied for their importance from both fundamental and applicational viewpoints [3,4]. The 2D magnetism, however, has long been absent from the spotlight, as the Mermin-Wagner theorem [5] dictates that it rarely occurs. Very recently, several 2D layered van der Waals (vdW) materials, including CrI₃ [6–10] and Cr₂Ge₂Te₆ [11–20], were found to be intrinsically ferromagnetic. The surprise comes from their strong magnetic anisotropy, which overcomes the thermal fluctuations and stabilizes the magnetic order at finite temperature. While these 2D magnets open up new possibilities for future spintronic devices, their current Curie temperatures are too low for practical applications [11]. In addition, both CrI3 and Cr2Ge2Te6 also exhibit semiconductor characteristics that may also find application in spintronics.

Various efforts have been devoted to manipulating the electronic and magnetic properties in 2D CrI_3 and $Cr_2Ge_2Te_6$ via electric field [7,14] and electrostatic doping [8,9,21]. In a recent study, bipolar tunable magnetization loops below the Curie temperature were realized in $Cr_2Ge_2Te_6$ via electrostatic gating, which was tentatively attributed to the moment rebalance in the spin polarized band structure [15]. A complete and reversible electrical switching between the interlayer antiferromagnetic and ferromagnetic states in bilayer CrI_3 was achieved by applying an electric field [7]. Controlling the electron spins, or more specifically, the magnetism of a system by electric-field tuning has proven challenging [22].

Nevertheless, surface adsorption [23–26], as a modulation method of ionic gating, has been proven to be an attractive approach to control electronic structure and magnetism in 2D vdW materials [21,27]. By adsorption, the external adatoms are adsorbed on the surface of the host material and a charge transfer could be also induced between adatoms and their neighbor atoms, from which an electrostatic doping effect could be realized. Such a doping effect can give rise to a gate-controlled modification of magnetism, e.g., an increase of T_c in 2D magnetic Fe₃GeTe₂ [28].

In this work, by performing first-principles calculations and renormalized spin-wave theory, we study the effects on the electronic structure and magnetic properties in monolayer $Cr_2Ge_2Te_6$ by adsorbing H and alkali metal (Li, Na, and K). With H adsorption, $Cr_2Ge_2Te_6$ maintains the intrinsic ferromagnetic semiconducting with a 0.95 eV bandgap, but an indirect-to-direct band gap transition is induced. On the other hand, the adsorption with alkali-metal turns $Cr_2Ge_2Te_6$ into a ferromagnetic metal. Moreover, surface adsorption can increase the magnetic anisotropy energy up to four times larger in $Cr_2Ge_2Te_6$, leading to a steady increase of T_c . Our findings of surface adsorption-controlled bandgap and magnetism in $Cr_2Ge_2Te_6$ show possibilities for potential applications in new-generation 2D spintronic devices.

II. CALCULATIONAL DETAILS

Our density functional theory calculations are carried out by using Vienna *ab initio* Simulation Package (VASP) [29,30] with projector augmented wave method. The exchangecorrelation interaction of electrons is treated within the generalized-gradient approximation (GGA) using the form of Perdew-Burke-Ernzerhof (PBE) [31,32]. To improve the description of on-site Coulomb interaction between the localized Cr 3*d* states, we adopt the GGA+U scheme [33] with

^{*}These authors contributed equally to this work.

[†]Authors to whom correspondence should be addressed: jiangph@nimte.ac.cn; chenaixi@zstu.edu.cn; zhong@nimte.ac.cn



FIG. 1. Top view and side view of representative ball-and-stick crystalline structure of (a) relaxed 2D monolayer $Cr_2Ge_2Te_6$ and (b) adsorption configurations. Blue, orange, ochre, and green spheres represent Cr, Ge, Te, and adatom, respectively. Note that one of the Cr atom (unadsorbed one) in each unit cell locates behind another one (the adsorbed one) in the bottom panel of (b).

an effective U = 2.0 eV (see supplemental material for more discussion on the choice of U [36]). A vacuum space of at least 15 Å along the out-of-plane z axis is employed to eliminate the interaction between neighboring structures. The Brillouin zone is sampled using a $9 \times 9 \times 1$ Γ -centered Monkhorst-Pack grid. The in-plane lattice constants of all configurations are fixed at a = b = 6.91 Å [18], and the atomic positions are fully relaxed with the convergence force less than 0.01 eV/Å. The range-separated hybrid functional HSE06 [34] is used for calculating the bandgap, and other properties of electronic and ferromagnetism are calculated using the GGA+U scheme with inclusion of spin-orbit coupling. Finally, we adopt a renormalized spin-wave theory (RSWT) [5,35] to estimate the Curie temperature T_c in monolayer Cr₂Ge₂Te₆, while the exchange interactions used for all calculations are $J_1 = -2.71$ meV, $J_2 = -0.058$ meV and $J_3 = -0.115 \text{ meV} [11,36].$

III. RESULTS AND DISCUSSION

A. Ferromagnetism properties and electronic structure

Cr₂Ge₂Te₆ consists of a 2D honeycomb network of Cr atoms, while the hexagonal vacancies are occupied by edge-sharing Te octahedra and Ge dimers, respectively [see Fig. 1(a)]. One H or alkali-metal (Li, Na, K) atom is adsorbed on the surface in each unit cell (u.c.) of monolayer $Cr_2Ge_2Te_6$, and adsorption percentage of H or alkali atoms is 10%. To find the most energetically favorable adsorbing configuration, we study four different initial positions [37] labeled as top (at the top of Cr atom), hcp (at the top of Te atom), fcc (at the top of Ge), and bridge (above the middle of Cr and Te atoms) (see different configurations in Fig. S2 [36]). Among them, the top configuration has the lowest adsorption energy, which is thus considered as the most stable configuration and will be focused on in our following discussion. In the fully relaxed top configuration, the adatoms are located above one of the two Cr atoms in the unit cell [Fig. 1(b)], which results in a slight

distortion of the associated $CrTe_6$ octahedron and pushes the two Ge atoms down ~0.6 Å along z direction [see Fig. 1(b)].

To investigate the structural stability of pristine monolayer $Cr_2Ge_2Te_6$ and the adsorbed ones, we first calculate the phonon dispersions. The absence of imaginary frequency (as shown in Fig. S3 [36]) confirms the dynamics stability of the pristine and the adsorbed compounds. We next calculate the formation energy for different adatoms (H and alkali metal Li/Na/K) defined as $E_{form} = E_{ads} - E_{Cr_2Ge_2Te_6} - E_{ada}$, where E_{ads} and $E_{Cr_2Ge_2Te_6}$ are the total energies of the adatoms adsorbed and the pristine $Cr_2Ge_2Te_6$ unit cell, respectively. E_{ada} is the chemical potential of the individual adatom. As illustrated in Table I, the much lower formation energy of H adsorption demonstrates that it is easier to adsorb H atoms than alkali metal on the surface of $Cr_2Ge_2Te_6$.

TABLE I. The formation energy ($E_{\rm form}$), the distance between the adatom and nearest neighboring Cr ($d_{\rm Cr-adatom}$), band gap ($E_{\rm gap}$) with PBE+U and HSE06 calculations, local spin moment of the Cr ($M_{\rm Cr}$), Te ($M_{\rm Te}$), Ge ($M_{\rm Ge}$) (the subscript numbers 1 and 2 stand for the near and far atoms from the adatom), total magnetic moment ($MM_{\rm total}$) and the energy difference per unit cell (two Cr sites) between FM and AFM ($\Delta E = E_{\rm AFM} - E_{\rm FM}$) in monolayer Cr₂Ge₂Te₆ with H, Li, Na, and K adsorption.

	Monolayer	Н	Li	Na	K
$E_{\rm form}$ (eV/u.c.)	_	-1.38	-0.41	-0.48	-0.53
$d_{\rm Cr-adatom}$ (Å)	_	1.58	3.05	3.24	3.93
$E_{gap(PBE+U/HSE)}$ (eV)	0.31/0.96	0.22/0.95	_	_	_
$M_{\rm Cr1}$ ($\mu_{\rm B}$)	3.08	2.45	3.30	2.99	2.96
$M_{\rm Cr2}$ ($\mu_{\rm B}$)	3.08	3.13	3.26	2.88	2.91
$M_{\text{Te1}} (\mu_{\text{B}})$	-0.09	-0.11	-0.10	-0.07	-0.08
M_{Te2} (μ_{B})	-0.09	-0.13	-0.16	-0.14	-0.14
$M_{\text{Ge1}}(\mu_{\text{B}})$	0.04	0.03	0.02	0.02	0.02
$M_{\text{Ge2}}(\mu_{\text{B}})$	0.04	0.01	0.00	0.00	0.00
MM_{total} ($\mu_{\rm B}/{\rm u.c.}$)	6.00	5.00	5.76	5.49	5.47
$\Delta E \text{ (meV/u.c.)}$	92.7	80.5	133.3	128.7	121.4



FIG. 2. Spin-resolved total and partial density of monolayer $Cr_2Ge_2Te_6$ -H. The insets (from top to bottom) demonstrate the difference in charge density (pink and green isosurfaces denote the accumulation and depletion, respectively. The isosurface value is taken to be 0.002 eV/Å³) and the schematic plot of polarized electrons orbital occupation, respectively.

We then investigate the ground state magnetic ordering of monolayer $Cr_2Ge_2Te_6$ with surface adsorption. The energy difference between ferromagnetic (FM) and zigzag-type antiferromagnetic (AFM) ordering [38] ($\Delta E = E_{AFM} - E_{FM}$) are all positive, which suggests that monolayer $Cr_2Ge_2Te_6$ prefers to stay in FM ordering under all the adsorptions we have considered. The H (alkali metal) adsorption weakens (strengthens) the FM ordering, as is evident from the decrease (increase) of both ΔE and the local spin moment of the Cr atom (M_{Cr}) as shown in Table I. As the effects of adsorption are essentially different for H and alkali atoms (Li/Na/K), we discuss them separately hereafter.

To understand the physical mechanism of the change of magnetism under H adsorption, we calculate the projected density of states (DOS) as shown in Fig. 2. One notable feature is that the localized H states mostly act as a deep acceptor energy level and prefer to occupy around $-5.8 \,\mathrm{eV}$ below Fermi energy. As illustrated in the inset of Fig. 2, this leads to one spin-up electron transfering from the $Cr-t_{2\sigma}$ state to H-1s state, which results in the decrease of the total magnetic moments from 6.0 to $5.0 \,\mu_{\rm B}$ in Cr₂Ge₂Te₆-H. The energies of the Cr-d states are also redistributed in the range from -0.5 eV to Fermi energy. In addition, the H-s, Te-p, and Cr-d orbitals couple together and lead to the emergence of more localized Cr t_{2g} spin-down states. Moreover, the adatom H redistributes the charge around its neighboring Te atoms, which indirectly alters the pd hybridization between Cr-d and Te-*p* orbitals in their tetrahedral ligands.

For the Li (alkali metal) adsorbed system, the distances between adatom and the nearest Cr atom ($d_{Cr-adatom}$) are significantly larger than that of the H adsorbed one as shown in Table I, which will directly influence the strength of surface adsorption and hence the amount of charge transfer. Indeed, the charge distribution in the Li adsorbed system is totally different with the pristine one and the H adsorbed one. In Cr₂Ge₂Te₆-Li, the Li atoms indirectly donate partial



FIG. 3. Spin-resolved total and partial density states of monolayer $Cr_2Ge_2Te_6$ -Li. The insets (from top to bottom) demonstrate the difference in charge density (pink and green isosurface denote the accumulation and depletion, respectively. The isosurface value is taken to be 0.002 eV/Å³) and the schematic plot of polarized electrons orbital occupation, respectively.

electrons (~ 0.2 electron) to the Cr atoms, which results in an electron doping effect as shown in the top panel of the inset in Fig. 3. Thus, a larger magnetic moment of the Cr atom ($\sim 3.30 \,\mu_{\rm B}$) is obtained, which is larger than that of pristine $Cr_2Ge_2Te_6$ (~3.08 μ_B). On the other hand, the absorbed Li also donates electrons to the unoccupied Te-p orbitals as schematically shown in the bottom panel of the inset in Fig. 3, inducing an antiparallel magnetic moment $(\sim -0.26 \,\mu_{\rm B})$, which is slightly larger than the pristine one) on neighboring Te atoms. As a result, the total moment of Cr₂Ge₂Te₆-Li is less influenced. It should be noted that the distance $d_{Cr-adatom}$ between adatom and nearest neighboring Cr varies with different alkalis metals (Li/Na/K) because of their different radius. The electronegativity also varies with elements. Both of $d_{Cr-adatom}$ and electronegativity play key roles in determining the charge transfer and modulating the local magnetic moments of the neighboring Cr, Te, and Ge atoms. Hence the total moment is slightly different for the Li/Na/K adsorbed cases.

The different charge transfer behavior induced by H and Li (alkali metal) adsorption will also result in different electronic properties. As shown in Fig. 4(a), monolayer $Cr_2Ge_2Te_6$ is an intrinsic ferromagnetic semiconductor with an indirect band gap of 0.96 eV under HSE06 calculations, and its valence band maximum (VBM) and conduction band minimum (CBM) locate at Γ and K, respectively. After H adsorption, the bandgap (0.95 eV) is almost the same as that of the pristine $Cr_2Ge_2Te_6$ [see Figs. 4(a) and 4(b)]. However, the previous indirect band gap turns into a nearly direct one with both VBM and CBM locating along Γ -M. It results from a new VBM which is contributed by the absorbed H atom, while the CBM is not influenced. Such a band gap transition will influence the optical properties significantly, i.e., the photoluminescence [2,10,39] or exciton state [40]. For the Cr₂Ge₂Te₆-Li system, a Li atom acts as a typical electronic donor rather than an acceptor like a H atom, and the Fermi level is thus pushed up and



FIG. 4. Band structures of (a) monolayer $Cr_2Ge_2Te_6$, (b) $Cr_2Ge_2Te_6$ -H, and (c) $Cr_2Ge_2Te_6$ -Li with the HSE06 functional. The spin-up (spin-down) bands are marked by the black (red) lines, respectively. The dashed line denotes the Fermi level.

even across the spin-polarized conduction bands [Fig. 4(c)], and turns the Cr₂Ge₂Te₆ [Fig. 4(a)] into a metal.

B. Magnetic anisotropy energy and curie temperatures

Bulk $Cr_2Ge_2Te_6$ is a FM semiconductor with a Curie temperature T_c of 66 K [11], whereas T_c of the monolayer counterpart was calculated to be 21 K [5,11]. As the T_c strongly correlates with the magnetic anisotropy energy (MAE), we further investigate how the surface adsorption can enhance the anisotropy and the T_c .

In the following, we define the MAE as $\Delta E = E_{[100]} - E_{[001]}$ for one unit cell (two Cr sites), whereby a positive (negative) MAE indicates a [001] ([100]) magnetic easy axis. Figure 5(a) shows the MAE with different adatoms. The MAE of pristine Cr₂Ge₂Te₆ is calculated to be 0.094 meV, which is consistent with previous results [5,18]. The positive MAE

also means that the easy axis is along the [001] direction. When H and alkali metals are adsorbed onto $Cr_2Ge_2Te_6$, the MAE is significantly increased to $0.32 \sim 0.38$ meV, up to four times larger than that of the pristine one. We attribute the enlargement of MAE to the doping effect induced by adsorption. To support our conclusion, we calculate the MAE with pure doping by only adding electrons or holes to the pristine $Cr_2Ge_2Te_6$ (as shown in Fig. S8 [36]), the increase of MAE is quite similar to that of adsorbed $Cr_2Ge_2Te_6$, which verifies our conclusion. Here, we should note that the doping effect results from the charge transfer between intrinsic Cr atoms and the dopant atoms as discussed above.

Since the MAE is strongly correlated with T_c , we further calculate the T_c by using renormalized spin-wave theory, which has been proven to be a rather accurate estimation [5,35]. Figure 5(b) shows the T_c as a function of MAE. While the MAE of the pristine $Cr_2Ge_2Te_6$ corresponds to a T_c of 21 K, the fourfold increase of MAE in adsorbed systems corresponds to a $T_c \sim 28$ K. Thus, our theoretical results show that the T_c of monolayer $Cr_2Ge_2Te_6$ can be significantly enhanced by surface adsorption.

IV. CONCLUSIONS

In summary, we have proposed an adsorbent-atom-tuned modification of electronic structure and magnetism in a monolayer $Cr_2Ge_2Te_6$. Our results show that adsorbing $Cr_2Ge_2Te_6$ with an H atom leads to a nearly indirect-to-direct band gap transition, and reduces the magnetic moments of Cr atoms via the Cr-H charge transfer. On the contrary, alkali-metal adsorption turns the semiconducting $Cr_2Ge_2Te_6$ into a metal. More importantly, we found that the MAE is dramatically increased by adsorbing both H and Li (Na, K), leading to a significant increase of T_c . Our work is a step forward for an understanding of the ferromagnetic behaviors in 2D vdW crystals, and may provide useful guidelines for future experimental and theoretical works on surface adsorption-driven magnetic spintronic devices.



FIG. 5. (a) Variation of magnetic anisotropy energy in monolayer pristine $Cr_2Ge_2Te_6$ and with H, Li, Na, and K adsorption. The magnitude of the magnetic anisotropy energy is equal to 0.094, 0.324, 0.350, 0.368, and 0.392 meV. (b) Magnetic anisotropy energy dependent of transition temperature T_c in monolayer $Cr_2Ge_2Te_6$.

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- K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
- [2] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105, 136805 (2010).
- [3] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, and S. Sorgenfrei, Nat. Nanotech. 7, 699 (2012).
- [4] S. Manzeli, D. Ovchinnikov, D. Pasquier, V. Y. Oleg, and K. Andras. Nat. Rev. Mater. 2, 17033 (2017).
- [5] Z. Li, T. Cao, and S. G. Louie, J. Magn. Magn. Mater. 463, 28 (2018).
- [6] B. Huang, G. Clark, E. Navarro-Moratalla, R. K. Dahlia, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, H. C. David, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. D. Xu, Nature (London) 546, 270 (2017).
- [7] S. W. Jiang, J. Shan, and K. F. Mak. Nat. Mater. 17, 406 (2018).
- [8] S. W. Jiang, L. Z. Li, Z. F. Wang, K. F. Mak, and J. Shan, Nat. Nanotechnol. 13, 549 (2018).
- [9] T. Song, X. Cai, M. W.-Y. Tu, X. Zhang, B. Huang, N. P. Wilson, K. L. Seyler, L. Zhu, T. Taniguchi, K. Watanabe, M. A. McGuire, D. H. Cobden, D. Xiao, W. Yao, and X. Xu, Science 360, 1214 (2018).
- [10] P. Jiang, L. Li, Z. Liao, Y. X. Zhao, and Z. Zhong, Nano. Lett. 18, 3844 (2018).
- [11] C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z. Q. Qiu, R. J. Cava, S. Louie, J. Xia, and X. Zhang, Nature (London) 546, 265 (2017).
- [12] Y. F. Li, W. Wang, W. Guo, C. Y. Gu, H. Y. Sun, L. He, J. Zhou, Z. B. Gu, Y. F. Nie, and X. Q. Pan, Phys. Rev. B 98, 125127 (2018).
- [13] J. Liu, S. Y. Park, K. F. Garrity, and D. Vanderbilt, Phys. Rev. Lett. 117, 257201 (2016).
- [14] W. Xing, Y. Chen, P. M. Odenthal, X. Zhang, W. Yuan, T. Su, Q. Song, T. Wang, J. Zhong, S. Jia, X. C. Xie, Y. Li, and W. Han, 2D Mater. 4, 024009 (2017).
- [15] W. Zhi, T. Y. Zhang, M. Ding, B. J. Dong, Y. X. Li, M. L. Chen, X. X. Li, J. Q. Huang, H. W. Wang, X. T. Zhao, Y. Li, D. Li, C. K. Jia, L. D. Sun, H. H. Guo, Y. Ye, D. M. Sun, Y. S. Chen, T. Yang, J. Zhang, S. P. Ono, Z. Han, and Z. D. Zhang. Nat. Nanotechnol. **13**, 554 (2018).
- [16] Y. Liu, and C. Petrovic, Phys. Rev. Mater. 3, 014001 (2019).
- [17] V. Carteaux, D. Brunet, G. Ouvrard, and G. Andre, J. Phys. Condens. Matter 7, 69 (1995).
- [18] Y. Fang, S. Wu, Z.-Z. Zhu, and G.-Y. Guo, Phys. Rev. B 98, 125416 (2018).
- [19] K. Y. Wang, T. Hu, F. H. Jia, G. D. Zhao, Y. Y. Liu, I. V. Solovyev, A. P. Pyatakov, A. K. Zvezdin, and W. Ren, Appl. Phys. Lett. **114**, 092405 (2019).

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- [20] J. Zeisner, A. Alfonsov, S. Selter, S. Aswartham, M. P. Ghimire, M. Richter, J. van den Brink, B. Büchner, and V. Kataev, Phys. Rev. B 99, 165109 (2019).
- [21] D. R. Klein, D. MacNeill, J. L. Lado, D. Soriano, E. Navarro-Moratalla, K. Watanabe, T. Taniguchi, S. Manni, P. Canfield, J. Fernández-Rossier, and P. Jarillo-Herrero, Science 360, 1218 (2018).
- [22] F. Matsukura and T. Y. O. Hideo, Nat. Nanotechnol. 10, 209 (2015).
- [23] C. Tsai, F. Abild-Pedersen, and J. K. Nrskov, Nano. Lett. 14, 1381 (2014).
- [24] J. Wellendorff, K. T. Lundgaard, A. Møgelhøj, V. Petzold, D. D. Landis, J. K. Nørskov, T. Bligaard, and K. W. Jacobsen, Phys. Rev. B 85, 235149 (2012).
- [25] F. Mittendorfer, A. Garhofer, J. Redinger, J. Klimes, J. Harl, and G. Kresse, Phys. Rev. B 84, 201401 (2011).
- [26] D. Sander, J. Phys. Condens. Matter 16, R603 (2004).
- [27] J. C. V. Klimes, D. R. Bowler, and A. Michaelides, Phys. Rev. B 83, 195131 (2011).
- [28] Y. J. Deng, Y. J. Yu, Y. C. Song, J. Z. Zhang, N. Z. Wang, Z. Y. Sun, Y. F. Yi, Y. Z. Wu, S. W. Wu, J. Y. Zhu, J. Wang, X. H. Chen and Y. B. Zhang, Nature (London) 563, 94 (2018).
- [29] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
- [30] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- [31] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
- [32] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. 64, 1045 (1992).
- [33] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
- [34] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003).
- [35] M. Bloch, Phys. Rev. Lett. 9, 286 (1962).
- [36] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.99.214435 for detailed information about the choice of value of U, renormalized spin-wave theory (RSWT) parameters, crystalline structure of four different initial absorbed positions, phonon dispersions, band structures of monolayer Cr₂Ge₂Te₆ and Cr₂Ge₂Te₆-H by using PBE+U, PBE+vdW, PBE+SOC, and HSE06 calculations, and the site-, orbital-, and spin-projected densities of states (DOS) of monolayer Cr₂Ge₂Te₆.
- [37] Z. Fu, B. Yang, N. Zhang, D. Ma, and Z. Yang, Appl. Surf. Sci. 436, 419 (2018).
- [38] Y. Zhu, X. Kong, T. D. Rhone, and H. Guo, Phys. Rev. Mater. 2, 081001 (2018).
- [39] A. Splendian, L. Sun, Y. B. Zhang, T. S. Li, J. Kim, C-Y. Chim, G. Galli, and F. Wang, Nano. Lett. 10, 1271 (2010).
- [40] D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Phys. Rev. Lett. 111, 216805 (2013).