Tunable electronic properties and enhanced ferromagnetism in Cr$_2$Ge$_2$Te$_6$ monolayer by strain engineering

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Abstract

Recently, as a new representative of Heisenberg’s two-dimensional (2D) ferromagnetic materials, 2D Cr$_2$Ge$_2$Te$_6$ (CGT), has attracted much attention due to its intrinsic ferromagnetism. Unfortunately, the Curie temperature ($T_C$) of CGT monolayer is only 22 K, which greatly hampers the development of the applications based on the CGT materials. Herein, by means of density functional theory computations, we explored the electronic and magnetic properties of CGT monolayer under the applied strain. It is demonstrated that the band gap of CGT monolayer can be remarkably modulated by applying the tensile strain, which first increases and then decreases with the increase of tensile strain. In addition, the strain can increase the Curie temperature and magnetic moment, and thus largely enhance the ferromagnetism of CGT monolayer. Notably, the obvious enhancement of $T_C$ by 191% can be achieved at 10% strain. These results demonstrate that strain engineering can not only tune the electronic properties, but also provide a promising avenue to improve the ferromagnetism of CGT monolayer. The remarkable electronic and magnetic response to biaxial strain can also facilitate the development of CGT-based spin devices.

Supplementary material for this article is available online

Keywords: density functional theory calculations, Cr$_2$Ge$_2$Te$_6$, electronic properties, magnetic properties, Curie temperature, strain engineering

(Some figures may appear in colour only in the online journal)
Introduction

The research on two-dimensional (2D) materials has rapidly been progressing due to their rich physico-chemical properties [1–9]. However, many 2D materials such as graphene, black phosphorus, and h-BN, have no magnetism, which limits their applications in spintronics. To add this functionality to nonmagnetic 2D materials, many approaches, such as the introduction of defects [10, 11], doping [12–14], and adsorption of atoms and molecules [15, 16], have been explored. Unfortunately, the coupling of magnetic moments induced by these methods in otherwise nonmagnetic 2D materials was local or strongly dependent on the environment. Therefore, attention has been focused on searching new intrinsically magnetic 2D materials.

Encouragingly, some 2D ferromagnetic materials such as Fe₃GeTe₂, CrI₃, and Cr₂Ge₂Te₆ (CGT), have been successfully synthesized [17–20], and the intrinsic magnetism in these 2D materials has been experimentally confirmed. These exciting findings clearly demonstrate that it is very promising to identify 2D semiconductors with room temperature ferromagnetic order. The Fe₃GeTe₂ monolayer has a Curie temperature of 130 K, but exhibits metallic character [21], while magnetic semiconducting materials are required for spintronics. The CrI₃ monolayer has been reported as a new type of Ising ferromagnet with out-of-plane spin orientation and its Curie temperature is 45 K [17]. Almost at the same time, another intrinsic ferromagnetic semiconductor, CGT bilayer, was successfully prepared in experiments [18]. As a promising Heisenberg’s 2D ferromagnetic with strong magnetic anisotropy energy and magneto-optical effects, CGT has potential applications in spintronic nanodevices [22–24]. Xu et al. predicted that magnetic anisotropy of CGT monolayer is mainly single ion anisotropy [25], however, the Curie temperature of CGT monolayer is only 22 K [18], which greatly hampers the development of CGT materials for spintronic devices. Thus, recent theoretical efforts have been given to explore suitable approaches to enhance the ferromagnetic stability of CGT and modulate the magnetic moment [26–28]. For example, it was predicted that the electromagnetic properties of CGT monolayer significant changes upon adsorption of gas molecules. In particular, NO adsorption increases the Curie temperature by 38% [26]. By H and alkali-metal adsorption, the magnetic anisotropy energy and Curie temperature can be increased by a factor of four and 33%, as compared to the pristine CGT [27]. In addition, it was proposed that Ge vacancies can remarkably enhance the magnetic anisotropy energy of CGT monolayer [28].

Strain engineering is one of the most commonly used routes to tailor the electronic and magnetic properties of 2D materials [29–39]. For example, in our recent theoretical study, we demonstrated that the band gap of zigzag BCN hybrid materials with zigzag arrangement of graphene and h-BN stripes decreases under biaxial tensile strain, while the band gap of armchair BCNs material varies more complicated with strain and is related to C concentration [29]. The band structure of transition metal dichalcogenides can be continuously tuned by applying the uniaxial and biaxial tensile strains [30]. The transition from the direct to the indirect band gap can be achieved under the uniaxial compression and tensile strains in black phosphorus [31]. The transition from ferromagnetic to antiferromagnetic state under compressive strain was recently predicted for CrₓX₃ (X = Cl, Br, I) [32]. External strain can considerably enhance the stability and tune the magnetic moments of the CoB₆ monomolecular layer [33]. It is proposed that because the VX₂ (X = S, Se) monolayer has strong ionic covalent bonds, the tensile strain can remarkably increase its magnetic moment [35]. All these findings inspired us to investigate the strain dependence on the electronic and magnetic properties of CGT.

In this work, by means of systematic density functional theory (DFT) computations, we studied the electronic and magnetic properties of CGT monolayer under a biaxial tensile strain. It is found that the tensile strain can not only effectively tune the band gap of CGT monolayer, but also significantly enhance the ferromagnetism. The Curie temperature increases by 191% under 10% tensile strain. As the strain applied increases, the magnetic moment of Cr atom increases monotonically. These results suggest that strain engineering can effectively tune the band gap and enhance the ferromagnetism of CGT monolayers, which provides a new way to design spin devices based on CGT.

Computational methods

Our calculations were carried out within the framework of the DFT using the Vienna ab initio simulation package [40, 41] and the projector-augmented-wave method [42, 43]. The Perdew–Burke–Ernzerhof (PBE) [44] functional in the generalized gradient approximation (GGA) was used to describe the exchange and correlations. To sample the Brillouin zone, 9 × 9 × 1 k-point grid mesh was used. A vacuum thickness of at least 15 Å was introduced along the z-axis to avoid any artificial interactions between periodic images of slabs. The plane-wave cutoff energy was set to 500 eV. The lattice constants and atom coordinates were fully optimized, the energy and force convergence values were set as 1 × 10⁻⁶ eV and 0.005 eV Å⁻¹, respectively.

Since the GGA-PBE functional may fail to predict the magnetic properties of transition metal-based compounds with 3d electrons, and the PBE + U method is a better choice, we also used PBE + U functional to examine the lattice constants and magnetic moment of CGT monolayer, in which the Hubbard U value of Cr atom was set to 2.0 eV [27]. It is found that the lattice constant and magnetic moment of CGT monolayer are consistent with the results calculated by PBE (table S1 of supporting information (available online at stacks.iop.org/NANO/32/485408/mmedia)). In addition, considering that GGA tends to underestimate the band gaps, we calculated the band structures of CGT monolayer using the hybrid HSE06 functional, which generally gives more accurate band gap values [45]. Though the band gap value increases from 0.37 eV by PBE to 0.68 eV by HSE06, both functionals characterize CGT as an indirect semiconductor.
and give rather similar band structures (figure S2 of supporting information). These results showed that PBE is able to well predict the main features of the geometric, electronic, and magnetic properties of CGT. Thus, we used spin-polarized PBE method throughout the calculations in this work unless stated otherwise.

Results and discussion

We first investigated the pristine CGT monolayer without any external strain. In order to obtain the ground state of CGT monolayer, ferromagnetic (FM), Néel antiferromagnetic (Néel-AFM), stripy-antiferromagnetic (stripy-AFM), and zigzag antiferromagnetic (zigzag-AFM) configurations were considered (figure S1, supporting information). It is found that FM configuration is energetically more favorable than the AFM ones, thus is the ground state. Among the three AFM configurations, the Néel-AFM configuration is lower in energetically than stripy-AFM and zigzag-AFM configurations. In the following we will focus on the FM ground state.

The Cr atoms in CGT monolayer form a 2D honeycomb spin arrangement, while the hexagonal region between them is occupied by Ge dimer and Te octahedron with shared edges, as shown in figure 1(a). Our optimized lattice constants of CGT monolayer are \( a = b = 6.91 \) Å, which are consistent with the previous theoretical studies [22, 27]. The nearest-neighbor bond length \( d_{\text{Cr-Te}} \) is 2.78 Å, which also well agrees with the previous reports [26].

The spin-density distribution analysis reveals that the magnetic moment of CGT monolayer is mainly localized on Cr atom (see figure 1(b)), and the magnetic moment per Cr atom is 3.17 \( \mu_B \). According to the band structure (figure 1(c)), CGT monolayer is an indirect semiconductor with the band gap of 0.37 eV, well consistent with previous studies [46]. The conduction band minimum (CBM) and valence band maximum (VBM) are located at K and \( \Gamma \) points, respectively. Moreover, the projected density of states (PDOS) indicates that the CBM and VBM are mainly localized at the \( d \) orbitals of Cr atoms and the \( p \) orbitals of Te atoms, respectively (figure 1(d)).

The strain dependence of the electronic and magnetic properties of the CGT monolayer was investigated by varying the biaxial tensile strain without changing honeycomb-like structures and crystal symmetries. The biaxial tensile strain is defined as \( \varepsilon = \Delta c/c_0 \), where \( c_0 \) and \( c_0 \pm \Delta c \) are the lattice constants of the unstrained and strained CGT monolayer, respectively. \( \Delta c \) is the displacement along the lattice.
10% strain was selected as a representative. As shown in Figure 2(a), the CGT monolayer under 0% strain has an indirect band gap of 0.37 eV. When the strain increases to 0.38 eV at 10% strain, the band gap of CGT monolayer increases from 0.37 to 0.71 eV with tensile strain from 0% to 4%, and then decreases to 0.38 eV at 10% strain.

To better understand the strain-dependent electronic structure of CGT monolayer, we analyze the PDOS under various biaxial strains, as illustrated in Figures 3(d)–(f). For the pristine CGT monolayer, the CBM and VBM mainly originate from the Cr $d$ orbitals and the Te $p$ orbitals, respectively (see Figure 3(d)). As tensile strain increases to 8%, the CBM mainly comes from the Cr $d$ orbitals and the Te $p$ orbitals, while the VBM is always mostly localized at the $p$ orbitals of Te atoms (see Figure 3(f)). Note that with strain increases from 0% to 8%, the Cr $d$ orbitals and the Te $p$ orbitals first move away from the Fermi level and then gets closer to it, consequently, the band gap of CGT monolayer first increases and then decreases. This trend is consistent with the band structure change of CGT monolayer (Figures 3(a)–(c)). Furthermore, the above PDOS analysis is substantiated by partial charge densities of VBM and CBM in CGT monolayer (Figures 3(g)–(i)).

In addition to the modulation of electronic properties, the biaxial tensile strains also have interesting effects to the magnetic moment of CGT monolayer. Figure 4 presents the evolution of atomic magnetic moments in CGT monolayer under different strains, in which the magnetic moments of Cr, Ge and Te atoms in the CGT are denoted as $M_{\text{Cr}}$, $M_{\text{Ge}}$ and $M_{\text{Te}}$, respectively. Our calculations demonstrate that the magnetic moments increase as strain increases from 0% to 10% in CGT monolayer. Specifically, the $M_{\text{Cr}}$ increases from 3.17 $\mu_B$ to 3.40 $\mu_B$ with strain increasing from 0% to 10%. On the other hand, the $M_{\text{Te}}$ and $M_{\text{Ge}}$ increase slightly with increasing biaxial strain in CGT monolayers. These findings indicate that the spin polarizations in CGT monolayer are mainly contributed by Cr atoms with a small contribution from Ge and Te atoms, which can also be seen in the spin-density distributions. Our results suggest that the magnetic properties in CGT monolayer can be significantly controlled by tensile strain. Assuming that the CGT monolayer can remain stable at strain range up to 10%, the tensile strain can provide a promising route for modulating spin state and magnetic properties.

To better understand the strain-dependent magnetic moments in CGT monolayer, we examined the bond lengths, charge transfer, and PDOS under a tensile strain. Figure 5(a) shows the variation of bond lengths as a function of tensile strain. For simplification, the bond lengths of Cr–Te, Ge–Te Ge–Ge are denoted as $d_{\text{Cr-Te}}$, $d_{\text{Ge-Te}}$, and $d_{\text{Ge-Ge}}$. It is found that $d_{\text{Cr-Te}}$ and $d_{\text{Ge-Te}}$ increase with strain, while $d_{\text{Ge-Ge}}$ are almost unchanged. In particular, compared with the unstrained case, at $\varepsilon = 10\%$, $d_{\text{Ge-Te}}$ and $d_{\text{Cr-Te}}$ increase by 4.90% and 3.99%, respectively. The change in bond lengths in the CGT monolayer results in the significant charge

Figure 2. (a) Top and side views of the snapshots of CGT monolayer taken after 5 ps ab initio MD simulations at 300 K. (b) strain effect on the band gap of CGT monolayer. The inset schematically shows strain directions.
transfer as shown in figure 5(b). Note that as biaxial strain increases, the amount of charge transferred from the Cr and Te atoms increases. At the same time, the charge transfer is not obvious for Ge atoms. Specifically, Cr atoms lose about 0.25 electron charge, whereas Te atoms gain about 0.24 electron charge at $\varepsilon = 10\%$. The charge transfer trends for Cr and Te are completely opposite, indicating that the charge transfer mainly occurs between Cr and Te atoms. In addition,
Figure 4. Strain effects on magnetic moment (a) Cr atoms, (b) Ge and Te atoms in the CGT monolayer. The inset schematically shows the spin-density distribution of the CGT monolayer under 0% and 10% biaxial strains. The isovalue is set to be $2 \times 10^{-2}$ e Å$^{-3}$.

The shifts of the $a$ and $b$ states of PDOS in figure 5(c) clearly demonstrates that the spin polarization of $d$ orbital of the Cr atom near the Fermi level increases with the increase of strain from 2% to 8%, leading to an increase in $M_{Cr}$ from 3.21 $\mu_B$ to 3.35 $\mu_B$. Our results suggest that the charge transfer between Cr and Te atoms is very important for the change of magnetic moment with strain in CGT monolayer.

To further understand the impact of biaxial tensile strains on the FM stability of CGT monolayer, we examined the energy difference $\Delta E$ ($\Delta E = E_{AFM} - E_{FM}$) at various tensile strains. Here, $E_{FM}$ and $E_{AFM}$ are the total energies of FM and Néel-AFM configurations in CGT monolayer, respectively. As shown in figure 6(a), the energy difference presents a monotonous increase as the biaxial tensile increases. Specifically, the energy difference increases by nearly a factor of three with the tensile strain increasing to 10%, as compared to that of the unstretched CGT (from 350 to 1025 meV). Thus, with increasing strain, the stability of the FM configuration is considerably enhanced, which is beneficial for applications of CGT monolayer in spintronics devices.

Moreover, the Curie temperature ($T_C$) is one of the critical properties for ferromagnetic materials in nanoelectronics applications. The Curie temperature of CGT monolayer can be calculated by performing Monte Carlo (MC) simulations based on the 2D Heisenberg Hamiltonian model [48, 49].

\[
H = -\sum_{i,j} J_{ij} \cdot \mathbf{S}_i \cdot \mathbf{S}_j
\]

is the Heisenberg spin Hamiltonian, where $i$ and $j$ stand for the nearest Cr atoms, $S$ is the spin operator of Cr site, and $J$ is the spin exchange parameter. The exchange energy between the FM state and the AFM state is calculated by using the following formulas, $E_{FM} = E_0 + E_{ex}$ and $E_{AFM} = E_0 - E_{ex}$ [26], where $E_0$ represents the non-spin-polarized energy of the CGT monolayer per unit cell, $E_{FM}$ and $E_{AFM}$ are the energies of CGT per unit cell in the FM and Néel-AFM states, respectively. The exchange energy $E_{ex}$ is mapped to the Ising model to obtain the values of the $J$ parameter (table 1) as follows, $J = -E_{ex}/6S^2$. Here, $S$ is the spin of each Cr atom, which is $3/2$.

Based on the above method, the Curie temperature of the pristine CGT monolayer is estimated to be 58 K (figure S4, supporting information), which is consistent with the previous MC simulation (57.2 K) [48]. However, the experimentally measured $T_C$ of CGT monolayer is 22 K, which is lower than the values obtained from the MC simulations. In order to compare with the experimental data, we corrected the MC-simulated $T_C$ with the following formula, $T_C^{(strain)} = \frac{T_C}{T_{0}^{(strain)}}$, where $T_C$ and $T_C^{(strain)}$ represent the experimental Curie temperature of CGT and the experimental Curie temperature applied to the strain, respectively; $T_{0}^{(strain)}$ and $T_{0}^{(MC(strain))}$ represent the calculated Curie temperature without considering strain and upon applying the strain based on MC simulations (table 1). Figure 6(a) presents the variation of the enhanced $T_C$ ratio as a function of strain. Clearly, the tensile strain can effectively modulate the $T_C$. The change trend of $T_C$ is the same as that of energy difference, which increases as the strain increases. Notably, at 8% and 10% strains, the experimental Curie temperatures are expected to be 58.7 and 64.3 K, which correspond to enhancements of 166% and 191%, respectively.

The increase in $T_C$ caused by strain can be explained by Goodenough–Kanamori–Anderson (GKA) rule [50–52]. There is a competition between direct exchange interactions and the superexchange interactions in the magnetic ground state of CGT monolayer. Following the geometric features (figure 6(b)), the direct exchange interaction is the direct overlap of the $d$ orbitals on the nearest-neighbor Cr atom, which results in the AFM coupling. The superexchange interaction, where the $d$ orbitals of Cr and the $p$ orbitals of Te atoms overlap, produces FM coupling. The former is mainly determined by the distance between neighboring Cr atoms, while the latter is mainly influenced by the bond angle Cr–Te–Cr ($\theta$). As shown in figure 6(b), the bond angle ($\theta$) of the pristine CGT monolayer is close to 90$^\circ$ (92$^\circ$), which prefers FM coupling according to the GKA rules. Figure 6(b) shows the distance ($d$) between Cr atoms and bond angle Cr–Te–Cr ($\theta$) as a function of strain. Note that the bond angle $\theta$ increases from 92$^\circ$ to 99$^\circ$ as the tensile strain increases, which would lead to the weakness of the superexchange interaction (FM coupling). However, the distance $d$ monotonically increases with increasing the tensile strain. Specifically, the distance $d$ can be increased by more than 10% compared to the pristine CGT monolayer at the strain of 10%, which could significantly weaken the direct exchange interaction, i.e. AFM coupling. Thus, as the tensile strain increases, both the superexchange interaction and the direct exchange interaction become
weak. It can be concluded that the enhancement of the ferromagnetism in CGT monolayer under the tensile strain is attributed to the competition and delicate balance between the superexchange interaction and the direct exchange interaction.

**Conclusions**

In summary, the effects of strain on the electronic and magnetic properties of CGT monolayers were systematically studied by means of DFT computations. Our calculations demonstrated that the band gap of CGT monolayer initially increases and then decreases almost linearly with increasing tensile strain, which is due to the shift of CBM and VBM. More surprisingly, the Curie temperature of CGT monolayer increases by 191% upon 10% tensile strain. The magnetic moment of CGT originates mainly from Cr atoms, and the magnetic moment of Cr atom increases with the increase of tensile strain. This study provides another example of using external strain to modulate electronic and magnetic properties.

**Table 1.** The exchange energy \( E_{\text{ex}} \), spin exchange parameter \( J \), the calculated Curie temperature \( T_{\text{C}}^{\text{MC(strain)}} \), experimental Curie temperature \( T_{\text{C}}^{\text{MC}} \), strain and the band gap \( E_{\text{Gap}} \) of the CGT monolayer upon applying the strain.

<table>
<thead>
<tr>
<th>Strain (%)</th>
<th>( E_{\text{ex}} ) (meV)</th>
<th>( J ) (meV)</th>
<th>( T_{\text{C}}^{\text{MC(strain)}} ) (K)</th>
<th>( T_{\text{C}}^{\text{MC}} ) (K)</th>
<th>( E_{\text{Gap}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>43.83</td>
<td>3.25</td>
<td>58</td>
<td>22.0</td>
<td>0.37</td>
</tr>
<tr>
<td>2</td>
<td>67.42</td>
<td>4.99</td>
<td>89</td>
<td>33.8</td>
<td>0.59</td>
</tr>
<tr>
<td>4</td>
<td>87.10</td>
<td>6.45</td>
<td>115</td>
<td>43.7</td>
<td>0.71</td>
</tr>
<tr>
<td>6</td>
<td>103.50</td>
<td>7.67</td>
<td>136</td>
<td>51.9</td>
<td>0.66</td>
</tr>
<tr>
<td>8</td>
<td>117.02</td>
<td>8.67</td>
<td>154</td>
<td>58.7</td>
<td>0.54</td>
</tr>
<tr>
<td>10</td>
<td>128.12</td>
<td>9.49</td>
<td>169</td>
<td>64.3</td>
<td>0.38</td>
</tr>
</tbody>
</table>

**Figure 5.** Strain effects on (a) the bond length and (b) the electron transfer of Cr and Te atoms in the CGT monolayer. (c) The PDOS of Cr atom in CGT monolayer under 2%, 4% and 8% biaxial strain, respectively.
of 2D materials, and identifies strain engineering as a simple but effective method to improve the ferromagnetism of CGT monolayer. We hope that these results can facilitate the development of CGT-based spin devices, and fully release of the potential of these 2D ferromagnetic materials in the field of strain-tunable electromagnetism.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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