First-Principles Calculations of the Exchange Interaction of the CrGeTe₃/NiO Interface

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Two-dimensional (2D) magnetic materials have recently attracted a great attention due to their potential applications in information processing and storage. It was observed in an experiment that the CrGeTe₃/NiO heterostructure shows a higher Curie temperature and a stronger perpendicular anisotropy. This suggests that antiferromagnet NiO can be coupled with ferromagnetic CrGeTe₃ by the proximity effect, which enhances ferromagnetism. However, the mechanism behind the coupling is unknown. In this work, we built a CrGeTe₃/NiO heterostructure model and investigated the electronic structure and magnetic properties of the CrGeTe₃/NiO interface by first-principles calculations. It is shown that the intralayer exchange interaction between the Cr atoms is ferromagnetic, and the interlayer exchange interaction between the Ni atoms and Cr atoms at the interface is antiferromagnetic. The interlayer interaction is equivalent to a magnetic field as strong as \( B = 100.3 \) T applied by the NiO substrate to the CrGeTe₃ layer, which results in the higher Curie temperature of CrGeTe₃ observed in the experiment.

Keywords: 2D materials, first-principles calculation, CrGeTe₃/NiO interface, exchange interaction, heterostructure

INTRODUCTION

Since the discovery of graphene (Novoselov et al., 2004; Geim and Novoselov, 2007; Geim, 2009), two-dimensional materials, such as hexagonal BN (Kubota et al., 2007) and transition metal dihalides (TMDs), have attracted considerable attention due to their novel properties and potential applications (Mak et al., 2010; Fang et al., 2012). Since a van der Waals heterostructure (Geim and Grigorieva, 2013) was proposed, the types of two-dimensional materials have been greatly enriched. The two-dimensional magnetic materials can be used in new spintronic devices with the advantages of high sensitivity and high storage density (Pesin and MacDonald, 2012; Han et al., 2014; Han, 2016). In the traditional isotropic Heisenberg model, any thermal fluctuation caused by finite temperature will destroy the long-range magnetic order in one- or two-dimensional systems, as stated in the so-called Mermin–Wagner theorem. However, recent studies have shown that magnetic anisotropy can bypass the Mermin–Wagner theorem and result in a long-range ferromagnetic order at finite temperature (Mermin and Wagner, 1966).

Both CrGeTe₃ and CrSiTe₃ monolayers are 2D ferromagnetic semiconductors, which makes them promising candidates for further applications in spintronics (Žutić et al., 2004; MacDonald et al., 2005; Geim and Grigorieva, 2013; Liu et al., 2016). The intrinsic ferromagnetism of CrGeTe₃ and CrSiTe₃ monolayers is due to the ferromagnetic superexchange interaction via the 90° Cr-Te-Cr path, which is mediated by the \( t_{2g} \) orbital exchange interaction of adjacent high-spin Cr³⁺ (Casto et al., 2015; Chen et al.,...
spin properties of Cr and Ni atoms. The Hubbard U of Cr and Ni et al., 1998; Han and van Veenendaal, 2012) is applied to tune the atoms, the GGA + U method (Liechtenstein et al., 1995; Dudarev consider the strong localization effect of the d electrons in Cr and Ni strongly impacts the calculated electronic properties. In order to in the perpendicular direction, a vacuum region of 15 Å is added along the c-axis. The atomic positions are completely relaxed until the error of total energy and the residual force within 10^{-5} eV and 0.05 eV/Å, respectively. The energy cutoff of the plane wave basis is 520 eV. The Brillouin zone integral is performed on a Monkhorst–Pack k-mesh of 2 × 2 × 1 size (Monkhorst and Pack, 1976). Along the high symmetry line Γ (0, 0, 0) → M (1/2, 0, 0) → K (1/3, 1/3, 0) → Γ (0, 0, 0), the band structure is calculated.

RESULTS AND DISCUSSION

According to the experimental results (Idzuchi et al., 2019), the thickness of CrGeTe3 is 5.5–8 nm, while the thickness of NiO is 20–100 nm. Therefore, when building the model, the thickness of the NiO layer should be relatively large, while the thickness of the CrGeTe3 layer is relatively small. In this work, four layers of NiO are used to simulate the substrate. For simplicity, a single layer of CrGeTe3 is put on the NiO layers. In order to make the lattice match better, we selected the NiO (111) plane. In order to have stronger exchange at the interface, we set the Ni layer right at the interface. The optimized lattice constants of NiO (111) and CrGeTe3 (001) surfaces are 5.895 Å and 6.913 Å, respectively. In the CrGeTe3/NiO heterostructure model, CrGeTe3 (001) is stacked on top of NiO (111) (2 × 2), and the lattice mismatch is about 1.6%. The thickness of the CrGeTe3 (001) monolayer is 3.502 Å, where a unit cell includes 6 Cr, 6 Ge, and 18 Te atoms. The thickness of NiO (111) layers is 8.505 Å, where a unit cell includes 64 Ni and 64 O atoms. In addition, the lattice parameter of the heterojunction is a = b = 11.944 Å and c = 30.697 Å, and the initial interlayer distance (d) is 3.69 Å. The lowermost Ni and O layers are fixed to simulate the NiO substrate, and other atoms are relaxed. Figure 1A shows the atomistic model of the CrGeTe3/NiO heterojunction. In order to obtain the most stable magnetic ordering, two kinds of ferromagnetic (FM1 and FM2) and two kinds of antiferromagnetic (AFM1 and AFM2) orders of CrGeTe3 are considered, as shown in Figure 1B. The magnetization direction of all Cr atoms in the FM1 order is upward, and the magnetization direction of all Cr atoms in the FM2 order is downward. The magnetization directions of the four Ni layers, from top to down, are ↑ ↑ ↑ ↑, and the magnetic order in the same layer of Ni atoms are ferromagnetic. This is called “AFM II” magnetic order of bulk NiO. In the FM1 and FM2 orders, the magnetic coupling between CrGeTe3 layer and NiO layer is ferromagnetic and antiferromagnetic, respectively.

The total energies of FM1, FM2, AFM1, and AFM2 are −744.05, −744.26, −743.97, and −744.14 eV, respectively. It is obvious that the total energy of FM2 state is the lowest. Its total magnetic moment is −18 µB. Therefore, the ground state of CrGeTe3/NiO heterojunction is the FM2 state, where the exchange interaction in the CrGeTe3 monolayer is ferromagnetic and that between the CrGeTe3 monolayer and the NiO layers is antiferromagnetic. In order to investigate the stability of the FM2 interface system, we further calculated the binding energy, which is defined as
$E_f = E_{\text{tot}} - E_{\text{CrGeTe}_3} - E_{\text{NiO}}$. Here, $E_{\text{tot}}$ is the total energy of the heterostructure, $E_{\text{CrGeTe}_3}$ ($E_{\text{NiO}}$) is the total energy of the isolated CrGeTe$_3$ (NiO). The binding energy of the FM2 state is $-0.067$ eV/Å$^2$. The negative binding energy of the FM2 state shows that the heterostructure is energetically preferred and can be realized in the experiment. We calculated the phonon spectra (Xie et al., 2021) of NiO (111) and CrGeTe$_3$ (001) surfaces in the FM2 state. The results showed that there is no virtual frequency, which means that the structures of NiO (111) and CrGeTe$_3$ (001) surfaces are stable.

In order to obtain the detailed charge transfer information of the interface, the charge density difference and Bader charge of the CrGeTe$_3$/NiO heterojunction in the FM2 state are calculated. Charge density difference is the redistribution of charge as the CrGeTe$_3$ monolayer is bound to the NiO substrate. In the interface calculation, the bonding of each atom at the interface can be intuitively shown by the charge density difference. The charge density difference can be expressed as

$\Delta \rho = \rho_{\text{CrGeTe}_3/\text{NiO}} - \rho_{\text{CrGeTe}_3} - \rho_{\text{NiO}}$. Among them, $\Delta \rho$ is the difference of charge density, $\rho_{\text{CrGeTe}_3/\text{NiO}}$ is the total charge density of the heterojunction system, and $\rho_{\text{CrGeTe}_3}$ ($\rho_{\text{NiO}}$) is the charge density of CrGeTe$_3$ (NiO) slab alone.

Figure 2A shows the charge density difference of the CrGeTe$_3$/NiO interface in the FM2 state, and Figure 2B zooms in the details of Figure 2A. The cyan area in Figure 2 indicates that the charge density difference is negative, and the yellow region indicates the charge density difference is positive. In Figure 2, the charge transfer
results in Ni and Te weak covalent bonds across the interface. In order to further analyze the mechanism of charge transfer, Bader charge analysis is carried out for the system. The results showed that about 1.166 electron is transferred from NiO to CrGeTe₃. The charge transfer mainly occurs between the Ni, Te, and Cr atoms near the interface. In the binding process, a Te atom near the interface gets 0.098 electron in average, a Cr atom gets 0.060 electron in average, and the charge change of each Ge atom is negligible. However, the charge redistribution of the atoms away from the interface is negligible as they do not participate in the binding process.

In order to study the electronic properties of the CrGeTe₃/NiO interface in the FM2 state, the band structure and density of states of the model are calculated. The band structure of the CrGeTe₃/NiO heterojunction in the FM2 state is shown in Figure 3. The spin-up and spin-down band gaps are 0.578 and 0 eV, respectively. The total band gap is 0 eV. As a comparison, the band gaps of NiO and CrGeTe₃ bulk are calculated to be 2.026 and 0.236 eV, respectively, and those of the NiO (111) surface and CrGeTe₃ (001) monolayer are 0.003 and 0.256 eV, respectively. It is obvious that the band gap of the NiO (111) surface is much smaller than that of NiO bulk, and the band gap of the CrGeTe₃ (001) monolayer is very close to that of CrGeTe₃ bulk. The band gap of the CrGeTe₃/NiO heterojunction in the FM2 state is 0 eV, which is smaller than the NiO (111) surface band gap and CrGeTe₃ (001) monolayer.

The projected density of states of Ni, Te, and Cr atoms near the interface of the CrGeTe₃/NiO heterojunction in the FM2 state is shown in Figure 4A. The projected density of states of Te and Cr atoms of the CrGeTe₃ alone is shown in Figure 4B. From Figure 4A, it is clear that the state near Fermi level is mainly
contributed by the orbitals of Ni, Te, and Cr atoms. Among them, the contribution of the Cr-3d orbital is the largest. The Cr 3d state, the Ni 3d state, and the Te 5p state all pass through the Fermi level. From Figure 4B, it is clear that the state near Fermi level is mainly contributed by the orbitals of Te and Cr atoms. The band gap of CrGeTe₃ alone is 0.236 eV, which is significantly larger than that of CrGeTe₃/NiO heterojunction.

By comparing the PDOS in Figures 4A,B, for the spin-up state, it is seen that some new electronic states appear on the CrGeTe₃/NiO interface from 0.104 to 0.774 eV nearby the Fermi level. Some electronic states disappear from −0.394 to −0.114 eV nearby the Fermi level. These new electronic states lead to the downward movement of the top of the valence band and the bottom of the conduction band. The final result is that the band gap of the spin-up state of the CrGeTe₃/NiO heterojunction becomes smaller. For the spin-down state, it is seen that some new electronic states appear on the CrGeTe₃/NiO interface from −0.002 to 0.236 eV nearby the Fermi level. The appearance of these new electronic states leads to the upward movement of the top of the valence band and the downward movement of the bottom of the conduction band. The end result is that the band gap of the spin-down state of the CrGeTe₃/NiO heterojunction is reduced to zero.

The occupied Cr-3d orbital cannot appear in both spin-up and spin-down directions. For example, when it is found in the spin-down direction, the spin-up Cr-3d orbital is completely unoccupied. These results can be understood by crystal field theory. Cr³⁺ ions are located in an octahedral environment coordinated by six Te anions. The Cr-3d orbital splits into three low energy t₂g orbitals and two high energy e₉ orbitals. According to Pauli’s exclusion principle and Hund’s rule, Cr³⁺ ions will present a high-spin t₂g³e₉⁰ electronic configuration, which means that all occupied 3d orbits must be in one spin direction. Among them, the Cr 3d state also contributes to the spin-down state. Also, higher than the Fermi level, the spin-up state is almost occupied by the Cr 3d state, and the spin-down state is almost occupied by the Ni 3d state.

In order to estimate the magnetic couplings in the CrGeTe₃/NiO heterojunction, we started from the Heisenberg model:

\[ H = - \sum_{i<j} J_{ij} S_i \cdot S_j, \]

and it can be rewritten for our specific model:

\[ H = - \sum_{i<j} J_1 S_i \cdot S_j - \sum_{k<l} J_2 S_k \cdot S_l - \sum_{m<n} J_3 S_m \cdot S_n, \]

where \( J_1 \) is the intralayer exchange interaction between a Cr atom and its nearest-neighbors (NN), \( J_2 \) is the intralayer exchange interaction between a Cr atom and its next-nearest-neighbors (NNN), and \( J_3 \) is the interlayer exchange interaction parameter between a Cr atom and its NN Ni atoms in the top layer of NiO. The Ni atoms in the lower three layers of NiO are not considered in this model because of their weak exchange interaction with the Cr atoms. \( S_i \) is the spin of a Cr atom (S) equal to 3/2, \( S_n \) is the spin of a Ni atom (Sₙi) equal to 1.

In the CrGeTe₃ layer, there are three NN and six NNN Cr atoms for a Cr atom. In FM1 and FM2 structures, there are three NN spin parallel Cr atoms and six NNN spin parallel Cr atoms for a Cr atom. For the interlayer exchange interaction with the NiO substrate, the exchange interaction between a Cr atom and three nearest neighbor Ni atoms is considered. Because the spin directions of Cr and Ni atoms are the same, the interlayer coupling in the FM1 structure is ferromagnetic. Because the spin direction of Cr atom and Ni atom is opposite, the interlayer coupling in the FM2 structure is antiferromagnetic. For an AFM1 structure, there are three NN antiparallel spin Cr atoms and six NNN parallel spin Cr atoms for each Cr atom. In addition, because the sum of the spin of Cr atoms is zero, the summation of the exchange interaction between Cr and Ni atoms is also zero. For the AFM2 structure, the situation is complicated. The interlayer magnetic coupling is the same as AFM1, which is zero. For intralayer magnetic coupling, there are four Cr atoms with one NN parallel spin and two NN antiparallel spin Cr atoms. At the same time, these four Cr atoms also have three NNN parallel spin and three NNN antiparallel spin Cr atoms. The other two Cr atoms have two NN parallel spin and one NNN antiparallel spin Cr atoms. At the same time, these two Cr atoms also have six NNN antiparallel spin Cr atoms. Therefore, the total energies of the CrGeTe₃/NiO heterojunction in four magnetic states can be written as follows:

\[
E_{FM1} = E_0 - 9J_1|S|^2 - 18J_2|S|^2 - 18J_3|S \cdot S_{Ni}|,
E_{FM2} = E_0 - 9J_1|S|^2 - 18J_2|S|^2 + 18J_3|S \cdot S_{Ni}|,
E_{AFM1} = E_0 + 9J_1|S|^2 - 18J_2|S|^2,
E_{AFM2} = E_0 + J_1|S|^2 + 6J_3|S|^2,
\]

where \( E_0 \) is the total energy excluding the magnetic coupling that is insensitive to the magnetic states. By eliminating \( E_0 \), the exchange constants are solved as follows:

\[
J_0 = \frac{E_{FM2} - E_{FM1}}{36|S| \cdot S_{Ni}}
J_1 = \frac{E_{AFM1} - E_{FM2}}{18|S|^2},
J_2 = \frac{E_{AFM1} - E_{AFM2}}{24|S|^2}.
\]

Substituting the calculated total energies of the four magnetic states into Eq. 4, we can get the following exchange interaction parameters: \( J_0 = -3.87 \text{ meV} \), \( J_1 = +4.76 \text{ meV} \), and \( J_2 = -1.73 \text{ meV} \). It is clear that the intralayer exchange interaction between the NN Cr atoms is ferromagnetic, which is consistent with the previous experimental result that the CrGeTe₃ monolayer is a two-dimensional intrinsic ferromagnet (Gong et al., 2017). In addition, the interlayer exchange interaction between the Ni and Cr atoms is antiferromagnetic. An intralayer ferromagnetic interaction between the nearest Cr atoms is produced close to the 90° Cr-Te-Cr superexchange channel. At the same time, the interlayer antiferromagnetic interaction between Cr and Ni atoms is produced by approaching the 120° Cr-Te-Ni superexchange channel.

Magnets with large magnetic anisotropy energy (MAE) have potential applications in magnetic storage. Magnetic anisotropy can avoid the Mermin–Wagner theorem and make a detour to long-
range magnetic order in two-dimensional magnets at a non-zero temperature (Mermin and Wagner, 1966; Torelli et al., 2019). MAE is defined as the energy difference when magnetization is in-plane and out-of-plane, respectively (MAE = E∥ - E⊥), where E∥ is the total energy with the in-plane magnetization direction, and E⊥ is that with out-of-plane magnetization direction. The positive (negative) value of MAE represents that the out-of-plane (in-plane) is energetically preferred. The MAE of the CrGeTe3/NiO heterojunction is calculated by enabling spin-orbit coupling (SOC). The easy axis is in-plane with a MAE of −0.094 meV/Å².

The previous experimental result indicates that the CrGeTe3/NiO heterostructure shows a higher Curie temperature than the free-standing CrGeTe3 monolayer (Idzuchi et al., 2019). Therefore, we showed that the Ni–Cr interlayer exchange leads to the increase in Curie temperature of CrGeTe3.

The total exchange energy (Zhong et al., 2017) between the Cr and Ni atoms is \( \Delta E = \frac{E_{\text{CrNi}} - E_{\text{CrCr}}}{2} = 104.54 \, \text{meV} \) by the \textit{ab initio} calculations. Because there are six Cr atoms in the cell, the average exchange energy of each Cr atom is \( \bar{E} = 17.42 \, \text{meV} \).

In the Zeeman effect, it is written as follows:

\[
\bar{E} = -g\mu_B S \cdot B ,
\]

(5)

where \( g \) is the g factor (\( g \approx 2 \)), \( \mu_B \) is the Bohr magneton, \( S \) is the spin of Cr\(^{3+} \) ion (\( S = 3/2 \)), and \( B \) is the magnetic induction intensity. Substituting the \textit{ab initio} value into Eq. 5, we obtained \( B = 100.3 \, \text{T} \),

![Figure 5](image-url)
which is the equivalent magnetic field exerted by the NiO substrate on to the CrGeTe₃ layer. The influence of the NiO substrate on the Curie temperature of the CrGeTe₃ monolayer by the interlayer magnetic coupling is analyzed by means of mean field theory. 

Brillouin function is defined by Yosida (1996) as follows:

\[ B_S(x) = \frac{2S + 1}{2S} \coth\left(\frac{2S + 1}{2S}x\right) - \frac{1}{2S} \coth\left(\frac{1}{2S}x\right), \]

where \( S \) is the spin of Cr atom, and the value of \( x \) is as follows:

\[ x = \frac{2S\sigma J(0) + g\mu_BSB}{k_BT}, \]

where \( \sigma \) is the thermo average magnetic moment of Cr atom, \( k_B \) is Boltzmann’s constant, \( T \) is temperature, and \( J(0) \) is defined as:

\[ J(q) = \sum_n J(R_n)e^{-iqR_n}, \]

where \( J(R_n) \) is the exchange interaction between the lattice sites, and \( q \) is the vector in the reciprocal space. Substituting the exchange constant obtained before, the value of \( J(0) \) is approximately calculated as follows:

\[ J(0) = \sum_n J(R_n) = 3J_1 + 6J_2 = 3.90 \text{ meV} = 6.25 \times 10^{-22} J. \]

At thermo equilibrium, the following equation can be obtained as follows:

\[ \sigma = SB_S\left(\frac{2S\sigma J(0)}{k_BT} + \frac{g\mu_BS B}{k_BT}\right). \]

The left and right sides of Eq. 9 are two functions, respectively, as follows:

\[ \begin{align*}
   y &= \sigma, \\
   y &= SB_S\left(\frac{2S\sigma J(0)}{k_BT} + \frac{g\mu_BS B}{k_BT}\right).
\end{align*} \]

At fixed temperature \( T \) and magnetic induction intensity \( B \), the solutions of Eq. 9 are the intersection points of the two curves of Eq. 10, as shown in Figure 5.

In Figures 5A,C, there is no equivalent external field, while there is in Figures 5B,D. In Figure 5A, two functions crossover in the first quadrant, indicating that Eq. 9 has a non-zero solution of \( \sigma \), which is the average magnetic moment of Cr atom below Curie temperature. In Figure 5C, there is only one intersection point at the origin, which indicates that the spontaneous magnetization vanishes when the temperature is above the Curie temperature. However, when the external field is not zero, as shown in Figures 5B,D, even if the temperature is higher than the Curie temperature at zero extra field, there is still a non-zero solution of \( \sigma \), which implies the rise of Curie temperature.

By taking different \( T \) values under \( B = 0 \text{ T}, 10 \text{ T}, 100 \text{ T}, \) and \( 200 \text{ T} \) and solving Eq. 9, the \( \sigma - T \) figure is platted in Figure 6:

It is noticeable that the decrease of \( \sigma \) with the increase of \( T \) is much slower at \( B = 100 \text{ T} \) than at \( B = 0 \text{ T} \). It indicates that the heterostructure of CrGeTe₃ and NiO is equivalent to applying a strong magnetic field on the CrGeTe₃ monolayer. Thus, the Curie temperature is boosted.

**CONCLUSION**

In summary, we built the CrGeTe₃/NiO heterojunction model and discovered that the interlayer exchange interaction between the Cr atoms and Ni atoms is antiferromagnetic using the first-principles calculations. We further calculated the electrical and magnetic properties of the CrGeTe₃/NiO interface. We inferred that the NiO substrate is equivalent to applying a strong magnetic field of \( B = 100.3 \text{ T} \) on the CrGeTe₃ layer, which is the reason for the increase of Curie temperature. In addition, the easy axis is in-plane with a MAE of \(-0.094 \text{ meV/Å}^2\).

**DATA AVAILABILITY STATEMENT**

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

**AUTHOR CONTRIBUTIONS**

XuL and XZ conceived and implemented the review process. XuL was responsible for the main writing of the manuscript. XZ was responsible for the modification of the manuscript. ZL helped process and check the data part. WZ and HZ helped to build the structure model and provide ideas on magnetic calculation. PY and XJL provided ideas on electronic structure calculation. All authors contributed to the manuscript and approved the submitted version.

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