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Ising ferromagnetism and robust half-metallicity in two-dimensional honeycomb-kagome Cr2O3 layer

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In contrast to the current research on two-dimensional (2D) materials, which is mainly focused on graphene and transition metal dichalcogenide-like structures, studies on 2D transition metal oxides are rare. By using ab initio calculations along with Monte Carlo simulations and nonequilibrium Green’s function method, we demonstrate that the transition metal oxide monolayer (ML) of Cr2O3 is an ideal candidate for next-generation spintronics applications. 2D Cr2O3 has honeycomb-kagome lattice, where the Dirac and strongly correlated fermions coexist around the Fermi level. Furthermore, the spin exchange coupling constant shows strong ferromagnetic (FM) interaction between Cr atoms. Cr2O3 ML has a robust half-metallic behavior with a large spin gap of ~3.9 eV and adequate Curie temperature. Interestingly, an intrinsic Ising FM characteristic is observed with a giant perpendicular magnetocrystalline anisotropy energy of ~0.9 meV. Most remarkably, nonequilibrium Green’s function calculations reveal that the Cr2O3 ML exhibits an excellent spin filtering effect.

INTRODUCTION

A tremendous amount of research attention is currently focused on nanomaterials because of their remarkable physical properties and diverse technological applications. While there have been significant progress in the field of two-dimensional (2D) materials displaying a broad range of electronic and optical properties, most of these materials are intrinsically nonmagnetic, thus hindering their application to spintronics. Recent experimental discoveries of ferromagnetic (FM) 2D layers have demonstrated the cleavage of CrI3 and Cr2Ge2Te6 single crystals that possess a FM order even in the monolayer (ML). Moreover, numerous room-temperature FM thin films containing 3d transition metals, such as VSe2 and δ-FeOOH, have been synthesized on van der Waals substrates. These recent experimental recognitions of intrinsic magnetism in 2D materials have instigated the search for 2D magnetic materials that exhibit long-range ferromagnetism.

Spintronics is one of the most promising fields in condensed matter physics owing to the expectation of various applications of innovative technologies by utilizing the spin degree of freedom. In the field of spintronics, half-metallic materials have many advantages because one spin channel is conductive, while the other is insulating. This results in a 100% spin polarization and giant magnetoresistance, which are essential quantities for spintronics. Various materials are known to be half-metallic, but most of them are conventional bulk systems. 2D layers show many peculiar physical properties because of great modifications in their electronic structures at low dimension. Increase in the thickness as compared to ML has a significant effect on its properties, such as change in magnetic ordering, bandgap dependency, and metal–insulator transition. In addition, numerous quantum phases including the quantum spin and quantum anomalous Hall effect etc. are expected to be discovered in 2D layers and their heterostructures. Due to the high demand for next-generation nanoscale spintronic devices, it is necessary to develop 2D half-metallic materials.

In contrast to the current research, which is mainly focused on the 2D graphene and transition metal dichalcogenide-like structures, very few atomically thin metal oxides have been synthesized to date. Experimental study of 2D magnetic layers shows the Cr-based layers have FM state with large spin magnetic moment (≥3 μB) and hydroxides have been synthesized on van der Waals substrates. The exceptionally large spin gap of ~3.9 eV and its distinct honeycomb-kagome structure differentiate Cr2O3 ML from the recent theoretical prediction of 2D magnetic materials. Cr2O3 ML displays not only an adequate Tc (185 K), but also a giant perpendicular MAE as compared to experimentally realized 2D layers. Our results show that the 2D Cr2O3 ML exhibits an intrinsic Ising ferromagnetism and excellent spin filtering effect.

RESULTS AND DISCUSSION

Structural stability

The Cr2O3 ML is a honeycomb-kagome lattice (as shown in Fig. 1a), in which the O atoms form a kagome lattice, while the Cr atoms bonding with the O atoms form a hexagonal lattice. This honeycomb-kagome structure may lead to exotic magnetic properties different from the case of the pure kagome lattice. The stability of Cr2O3 ML was evaluated from the formation energy

\[ E_f = E(Cr_2O_3) - 2E(Cr) - 3/2E(O_2), \]  

where \( E(Cr_2O_3) \) is the formation energy of Cr2O3, \( E(Cr) \) is the formation energy of Cr, and \( E(O_2) \) is the formation energy of O2.
This conventional local density approximation (LDA) 29, generalized various exchange-correlation functionals were used, including temperature. Figure 1c, d shows snapshots of the Cr2O3 ML at the end of 5 ps at 300 K. Note that the structure of the Cr2O3 ML is strongly bonded planar network and can be prepared via well-established soft chemical routes.

The dynamical properties of the Cr2O3 ML were evaluated by phonon dispersion calculations, as shown in Fig. 1b. Very low-frequency phonon modes mostly originate from Cr atoms, while we observe O dominated phonon modes at 5 THz. The phonon band structure shows extremely small dispersion for these modes, thus indicating that O dominated frequency modes are completely localized. On the other hand, phonon band structures show that high optical modes (~18 THz) are also dominated by O atoms. The phonon band dispersions have no imaginary frequency that indicates the stable FM state of Cr2O3 ML. The values of exchange constants, as listed in Table 2, where J > 0 indicates FM coupling, while J < 0 describes AFM one. All functionals show the positive ΔU(J = J1 + J2 + J3) value, which indicates the stable FM state of Cr2O3 ML. The values of exchange coupling in the larger cell are comparable with the smaller cell that indicates the 2 × 2 cell is enough to describe the magnetic exchange coupling in 2D Cr2O3 ML.

Electronic properties: band structure and density of states

Next, we calculated the spin exchange coupling for Cr2O3 ML. As a matter of fact, applying the isotropic Heisenberg model to a 2D FM system is against the Mermin–Wagner theorem, which claims the absence of long-range magnetic ordering at nonzero temperature 30. Thus, the 2D Ising model is used to describe the spin coupling. Cr atoms are the main magnetic building block in Cr2O3 ML. Cr ions in the 2D layer have the oxidation state of +3 and are expected to give the spin S = 3/2. This has been confirmed by the calculations of magnetic moment where each Cr carrying a spin magnetic moment of 3 μB. The magnetic moments localized on each Cr atom (local spins Sij = 3/2) can be explained with S = 3/2 spin Hamiltonian. For this purpose, we considered a 2 × 2 cell with four different spin configurations, as shown in Fig. 2b-e. To check the effect of supercell size on magnetic exchange coupling, we have also calculated a 4 × 4 cell. With the energies of four ordered spin states, three exchange constants, J1, J2, and J3, between the first, second, and third nearest neighbors, respectively, were determined. The magnetic exchange coupling constants were calculated by

\[ E_{FM} - E_{AFM1} = 9/4(24J_1 + 48J_2 + 48J_3), \]

\[ E_{FM} - E_{AFM2} = 9/4(24J_1 + 48J_3), \]

and

\[ E_{FM} - E_{AFM3} = 9/4(48J_1 + 48J_3). \]

The calculated values of exchange constants J1, J2, and J3 are listed in Table 2, where J > 0 indicates FM coupling, while J < 0 describes AFM one. All functionals display the FM interaction between first nearest neighbors and J1 strongly dominates over others in all functionals except GGA + U. Furthermore, all functionals show the positive ΔU(J = J1 + J2 + J3) value, which indicates the stable FM state of Cr2O3 ML. The values of exchange coupling in the larger cell are comparable with the smaller cell that indicates the 2 × 2 cell is enough to describe the magnetic exchange coupling in 2D Cr2O3 ML.

Electronic properties: band structure and density of states

We now discuss the electronic properties of Cr2O3 ML, which are important in terms of their application to electronic devices. GGA-PBE functional was used to calculate the band structure and partial density of states (DOS). Figure 3a shows that Cr2O3 ML is a half-metallic 2D material with a large spin gap of ~3.9 eV at
We projected the band structure for Cr$_2$O$_3$ ML onto the atomic d orbitals of Cr shown in Fig. 3b, c and the p orbitals of O in Fig. 3d, e. Interestingly, typical kagome band characteristics are observed in the electronic band structure. Below the Fermi level, linearly dispersive band forms a Dirac point at the high symmetry K point and the corresponding two flat bands quadratically contact with the Dirac bands at the Γ point, which are located above and below the Fermi level as marked by circles shown in Fig. 3b. The same feature has been detected in other 2D kagome structures. The single-spin Dirac points below the Fermi level arise from the hybridization of the out-of-plane Cr ($d_{xz}, d_{yz}$) states with slight contributions from the O ($d_z$) states, while the Dirac point above the Fermi level is composed of in-plane Cr ($d_{xy}, d_{x^2-y^2}$) and O ($p_x, p_y$) orbitals, as shown in Fig. 3b, d. The out-of-plane orbitals $d_{xz}, d_{yz}$, and $p_z$ form flat bands below and above the Fermi level. Flat bands are rare and emerge only in a few systems, such as twisted bilayer graphene, kagome lattices, and heavy-fermion compounds. Since the kinetic energy of electron is quenched in the flat band, thus the out-of-plane orbitals $d_{xz}, d_{yz}$, and $p_z$ orbitals which form flat band have special significance. These out-of-plane orbitals indeed are responsible for the FM state in the Cr$_2$O$_3$ layer, which is explained in detail in the next section.

The magnetic exchange interaction between Cr atoms strongly depends on the electronic structure of Cr$_2$O$_3$ ML. In the case of FM configuration, O atoms also become spin-polarized, while in AFM case they remain nonmagnetic. Thus, O atom plays a vital role in the half-metallic FM state of Cr$_2$O$_3$ ML. No direct exchange coupling is observed between O and Cr states in AFM case and spin-polarized d-states are turned out to be more localized. On the other hand in FM configuration, we find that O(p) and Cr(d) orbitals hybridize a flat band just above the Fermi level, and this flat band degenerates with the conduction states formed by Cr ($d_{xy}, d_{x^2-y^2}$) orbitals at Γ point (see Fig. 3). Hence it provides an extra channel for indirect coupling between two neighboring Cr atoms through O atom, which is absent in AFM case. This conduction electron mediates indirect spin–spin coupling between Cr atoms through O atom, which is responsible for the FM state between Cr atoms in Cr$_2$O$_3$ ML. Figure 3f displays the partial DOS of the Cr$_2$O$_3$ ML. The major contribution to the magnetic moment originates from the out-of-plane orbitals $|m| = 0(d_{x^2-y^2})$ and $|m| = \pm 1(d_{xz}, d_{yz})$.

\[ J_1 = 11.60 (11.44) \quad 10.33 (10.03) \quad 2.67 (2.53) \quad 7.94 (7.83) \]

\[ J_2 = -0.94 (-1.05) \quad -2.11 (-2.13) \quad 2.40 (2.32) \quad 0.53 (0.49) \]

\[ J_3 = -1.83 (-1.70) \quad -2.68 (-2.52) \quad 1.61 (1.51) \quad -0.34 (-0.30) \]

Values obtained by 4 × 4 cell are presented in parentheses.
Magnetic anisotropy energy and curie temperature
As described before, the Mermin–Wagner theorem prohibits FM order at finite temperatures in 2D materials with continuous spin symmetries due to divergent contributions from gapless spin waves. In order to lift the restriction of continuous spin symmetry, some amount of MAE is required. Figure 4a shows the angular dependence of the MAE at the spin axis \( \phi \), where \( \phi \) is the polar angle which is rotated through the plane of the \( a \) and \( c \) axis of Cr\(_2\)O\(_3\) ML, and \( \theta \) is the azimuthal angle. The MAE is defined as the difference in energy between the system with a given \( \hat{s}(\phi, \theta) \) and the system with spins parallel (P) to the magnetic easy axis. The easy axis is found to be in the out-of-plane direction and the energy of the system with spins parallel along this direction is set to zero. MAE reaches a maximum value of 0.9 meV at \( \phi = 90^{\circ} \), corresponding to an in-plane spin orientation. The value of MAE is significantly higher than bulk transition metals, such as Fe, Co, Ni \((1-3 \text{ meV atom}^{-1})^{25,26}\), and the Cr\(_2\)Ge\(_2\)Te\(_6\) ML \((0.4 \text{ meV cell}^{-1})^{27}\), while it is comparable to the CrI\(_3\) ML \((1.67 \text{ meV cell}^{-1})^{27}\).

Figure 4b illustrates the in-plane magnetization as the spin axis rotates through \( ab \) plane. MAE exhibits a strong dependence on the polar angle \( \phi \) and is independent of the azimuthal angle \( \theta \), which is a remarkable characteristic of stable intrinsic Ising ferromagnetism. Figure 4c, d depict the orbital-resolved MAE of Cr\((d)\) and O\((p)\), respectively. Spin–orbit coupling (SOC) allows to calculate the matrix elements \( E_{\text{SOC}} \) for the angular momentum \((l = 1, 2)\). Following the second-order perturbation theory, the MAE can be approximately determined by matrix elements of the angular momentum operator. The matrix element difference is taken between easy axis [001] and hard axis [100]. Positive and negative values indicate the out-of-plane and in-plane contributions in MAE, respectively. For Cr atoms, the differences of the matrix elements of \( d_x - d_y \) between in-plane and out-of-plane magnetization show large contribution for out-of-plane magnetization, while the others show negligible. For O atoms, the major matrix element difference of \( p_x - p_y \) shows negative value, which results in the in-plane magnetization.

For practical spintronics applications, it is necessary to explore the change in magnetism of Cr\(_2\)O\(_3\) ML with respect to temperature. \( T_c \) is a critical point at which the FM system becomes paramagnetic, and this is an important parameter to evaluate magnetic properties. We simulated the temperature-dependent magnetization curve of Cr\(_2\)O\(_3\) ML by carrying out Monte Carlo (MC) simulations\(^{36}\). Our model includes the MAE term in the Hamiltonian equation and can be written as

\[
\hat{H} = -\sum_{ij} m_i m_j - k_2 \sum_{i} m_i^2,
\]

where \( m_i \) and \( m_j \) are the magnetic moments (in \( \mu_B \)) at sites \( i \) and \( j \), respectively, \( k_2 \) is the anisotropy constant (MAE per atom), \( m \) is the spin lying along a single preferred axis (known as the easy axis), and \( J \) is the exchange parameter. For MC simulations, a 50 \times 50 supercell was used to mimic the 2D lattice; this is found to be large enough to minimize the periodic constraints. The MC simulations used 10,000 equilibrations and averaging steps. These MC simulations allow us to calculate variations in the mean magnetization per unit cell with temperature. To validate our method, we have calculated the \( T_c \) of CrI\(_3\) ML then compared it with the experimental value and the value obtained by the spin-wave theory\(^{37}\). Spin-wave theory gives \( T_c = 33 \text{ K} \), underestimating the experimental value of 45 K by 20%. In contrast, our calculated value 46 K is in perfect agreement with the experimental value.
proving the reliability of our method. The calculated mean magnetization as a function of temperature for Cr$_2$O$_3$ ML is illustrated in Fig. 5. Note that the magnetization decreases to 0.77 $\mu_B$ at 100 K and the paramagnetic state is found at the temperature of ~185 K. The value of $T_c$ is significantly higher than those of the Cr$_2$Ge$_2$Te$_6$ (30 K)$^5$, CrI$_3$ (45 K)$^5$, and even Fe$_2$GeTe$_2$ (130 K)$^{38}$ layers.

Nonequilibrium Green's function transport properties
Lastly, to explore the spin-filtering effect at magnetic domains in half-metallic Cr$_2$O$_3$ ML, we calculated the spin transport properties at zero bias voltage of the device based on Cr$_2$O$_3$ ML (inset in Fig. 6d). The corresponding position-dependent distributions of DOS for the Cr$_2$O$_3$ electrode are shown in Fig. 6a, b. It is clear from Fig. 6a that the majority spin dominates the whole energy range. On the other hand, the minority spin is concentrated away from the Fermi level. We compared the transport properties between the P and antiparallel (AP) magnetization configurations, where the spin orientations of Cr atoms in the left and right electrodes are the same and inverse, respectively. Spin-dependent conductance for P and AP configurations at zero bias can be seen in Fig. 6c, d. P configuration of the two-probe systems (as shown in Fig. 6c) is periodic with translational symmetry and the conductance for each spin takes a step form given by the number of transport channels times the conductance quantum $G_0 = e^2/h$. The spin-up current is surpassed while the spin-down current is completely inhibited. In the AP configuration, as shown in Fig. 6d, the conductance spectra show no transport channel over a wide range of energy, and extremely small conductance is found away from the Fermi level in both spin-up and spin-down channels due to the similarity of the energy bands of opposite spins. Thus, both the spin-up and spin-down conductances in the AP configuration are ignorable compared to the spin-down conductance in the P configuration. Our findings demonstrate that the perfect spin filtering can be achieved in a device based on Cr$_2$O$_3$ ML in a wide energy range around the Fermi level.

Motivated by the experimental observation of 2D Ising FM in MLs, we used first-principle calculations to systemically investigate the electronic and magnetic properties of Cr$_2$O$_3$ ML. We

Fig. 4 Magnetocrystalline anisotropy. a Angular dependence of the MAE of Cr$_2$O$_3$ on polar angle $\phi$, while azimuthal angle $\theta$ is 0. Inset shows the out-of-plane $\phi = 0$ [001] direction. b Angular dependence of the MAE of Cr$_2$O$_3$ on $\theta$, while $\phi$ is $\pi/2$. Inset displays the in-plane $\theta = 0$ [100] and $\theta = 2\pi/3$ [010] directions. Atom-resolved MAE of Cr$_2$O$_3$ ML, c dresolved MAE of Cr atom, and d presolved MAE of O atom.

Fig. 5 Curie temperature. Temperature-dependent magnetization curve of 2D Cr$_2$O$_3$ FM layer obtained by MC simulation.
demonstrated that the honeycomb-kagome lattice of Cr$_2$O$_3$ ML is thermodynamically stable at room temperature. Cr$_2$O$_3$ ML has a honeycomb-kagome structure characterized by a kagome band with an unusually large gap in one spin channel. MAE exhibits a strong dependence on the polar angle $\phi$ and is independent of the azimuthal angle $\theta$, which is the characteristic of a stable intrinsic Ising ferromagnetism. Calculations of the magnetic anisotropy revealed a giant MAE of ~0.9 meV. The MC simulations demonstrated that the $T_c$ of the Cr$_2$O$_3$ ML is estimated to be 185 K.

We also investigated the spin transport properties by using the nonequilibrium Green's function method, and found that the Cr$_2$O$_3$ ML exhibits an excellent spin filtering. We anticipate that our work will stimulate experimental studies to validate and extend our findings.

**METHODS**

First-principles calculations details

The structural, electronic, and magnetic properties were calculated by using the Vienna ab initio simulation package (VASP)$^{39,40}$ The interaction between valence electrons and ionic cores was described within the framework of the projector augmented wave method$^{41}$. The energy cutoff for the plane wave basis expansion was set to 500 eV. The ground state optimized lattice constants of the Cr$_2$O$_3$ ML were $a = b = 6.175$ Å. Self-consistent calculations were carried out with an $11 \times 11 \times 1$ k-mesh and a vacuum distance of 15 Å was utilized in the direction normal to the layer. The convergence criterion of energy was set to 0.01 meV for unit cell and the atomic positions were fully relaxed until the force on each atom was smaller than 0.001 eV Å$^{-1}$.

Phonon and ab initio molecular dynamics

To investigate the dynamical stability, we also calculated the phonon dispersion curve by using PHONOPY code$^{42}$. The energy cutoff for the plane wave basis expansion was set to 500 eV. The ground state optimized lattice constants of the Cr$_2$O$_3$ ML were $a = b = 6.175$ Å. Self-consistent calculations were carried out with an $11 \times 11 \times 1$ k-mesh and a vacuum distance of 15 Å was utilized in the direction normal to the layer. The convergence criterion of energy was set to 0.01 meV for unit cell and the atomic positions were fully relaxed until the force on each atom was smaller than 0.001 eV Å$^{-1}$.

Magnetic anisotropy calculations details

MAEs were calculated by including SOC. A very strict criterion of $10^{-8}$ eV atom$^{-1}$ for the total energy convergence was set and the converged MAE results were obtained at high $41 \times 41 \times 1$ k-points. The detailed information on the MAE calculations and the influence of different approximations using VASP can be seen in ref. 45.

Nonequilibrium green's function method

For the transport calculations, we used the nonequilibrium Green's function method based on DFT. All the electron transport calculations were carried out using RSPACE code$^{46-50}$, which is based on the real-space finite-difference method$^{51,52}$. Exchange-correlation interactions were treated by LDA, and the norm-conserving pseudopotentials$^{53}$ of Troullier and Martins$^{54}$ were used for the core electrons with a grid spacing of 0.15 Å. The relative spin directions of two electrodes were changed to obtain zero bias-dependent transmission.

**DATA AVAILABILITY**

The data that supports the findings of this study are available within the article.

**CODE AVAILABILITY**

The calculations were implemented using the VASP, Vampire, Phonopy, and RSPACE packages.

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COMPETING INTERESTS
The authors declare no competing interests.

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