

Spin Filtering in CrI₃ Tunnel Junctions

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ABSTRACT: The recently discovered magnetism of two-dimensional (2D) van der Waals crystals have attracted a lot of attention. Among these materials is CrI₃ – a magnetic semiconductor exhibiting transitions between ferromagnetic and antiferromagnetic orderings under the influence of an applied magnetic field. Here, using first-principles methods based on density functional theory, we explore spin-dependent transport in tunnel junctions formed of fcc Cu (111) electrodes and a CrI₃ tunnel barrier. We find about 100% spin polarization of the tunneling current for a ferromagnetically-ordered four-monolayer CrI₃ and tunneling magnetoresistance of about 3,000% associated with a change of magnetic ordering in CrI₃. This behavior is understood in terms of the spin and wave-vector dependent evanescent states in CrI₃ which control the tunneling conductance. We find a sizable charge transfer from Cu to CrI₃ which adds new features to the mechanism of spin-filtering in CrI₃-based tunnel junctions. Our results elucidate the mechanisms of spin filtering in CrI₃ tunnel junctions and provide important insights for the design of magnetoresistive devices based on 2D magnetic crystals.

KEYWORDS: *CrI₃, 2D magnet, tunnel junction, spin filtering, tunneling magnetoresistance, DFT calculations*

INTRODUCTION

The growing family of two-dimensional (2D) materials offers a platform to design novel van der Waals heterostructures with unique electronic and optical properties.^{1,2} Recently, the range of these properties has been expanded to include 2D magnetism.^{3,4,5} Although a magnetic order is prohibited within the 2D isotropic Heisenberg model at finite temperatures,⁶ magnetocrystalline anisotropy lifts this restriction and enables the appearance of 2D Ising ferromagnetism. The discovery of long-range magnetic order in 2D crystals, such as CrI₃,³ opens a new route for the fundamental studies of spin behavior at low dimensions and could lead to novel spintronics applications.

CrI₃ is a semiconductor with easily exfoliating monolayers. The van der Waal's force binds stiff CrI₃ monolayers with a cleavage energy comparable to that of transition metal chalcogenides and graphene.^{7,8} Bulk CrI₃ is a ferromagnet with the Curie temperature of 61K, the magnetic moment of 3.1 μ_B per Cr atom⁹ being oriented out of the layer plane with magnetic anisotropy of about 650 μ eV.¹⁰ When exfoliated, CrI₃ exhibits a magnetic order dependent on layer thickness: whereas a CrI₃ monolayer is an Ising ferromagnet, a CrI₃ bilayer is an antiferromagnet consisting of two ferromagnetic monolayers with antiparallel magnetic moments.³ Under an applied magnetic field of 0.65T,³ a CrI₃ bilayer exhibits a spin-flip transition, which changes the interlayer magnetic alignment from antiferromagnetic (AFM) to ferromagnetic (FM). This indicates a relatively weak interlayer exchange coupling of about 0.2 meV, which allows tuning the spin-flip transition by electric means.^{11,12} The switching of the magnetic order in CrI₃ from AFM to FM has recently been demonstrated by the electric field effect¹³ and electrostatic doping^{11, 14} under a constant magnetic bias.

The existence of magnetism in CrI₃, which can be engineered in a layer-by-layer fashion, expands functional properties of the 2D materials. It makes possible to design van der Waal's heterostructures combining magnetic and non-magnetic components where the electrical and optical properties can be controlled by magnetic ordering of the adjacent layers. A prominent example is a large tunneling magnetoresistance (TMR) effect of 95%, 300%, and 550% which was reported for graphite/CrI₃/graphite tunnel junctions with bilayer, trilayer, and tetralayer CrI₃ barriers.¹⁵ Here, the CrI₃ served as a tunneling barrier and TMR was associated with a change of magnetic ordering of CrI₃ from AFM to FM under the influence of an applied magnetic field. This is different from the conventional TMR effect in magnetic tunnel junctions where two FM electrodes are realigned by an applied magnetic field, resulting in a change of tunneling resistance,¹⁶ and the related effects in ferroelectric tunnel junctions with magnetic electrodes.^{17,18} Even higher values of TMR were demonstrated for other types of tunnel junctions utilizing CrI₃ barrier layers of different thickness: 19,000%,¹⁹ 10,000%,²⁰ and even 1,000,000%²¹ at a finite bias voltage.

The appearance of the giant TMR effect in tunnel junctions based on CrI₃ barriers is understood in terms of the spin-filtering effect.¹⁵⁻²¹ According to the density-functional theory (DFT) calculations, the conduction band of CrI₃ is fully spin polarized,^{7,22} so that the band gap for majority-spin electrons is smaller than that for minority-spin electrons. This creates a spin-dependent tunneling barrier which filters electrons according to their spin orientation. Therefore, when the CrI₃ monolayers are FM-ordered under the influence of a sufficiently large magnetic field, the tunneling current is dominated by majority-spin electrons, which encounter a low

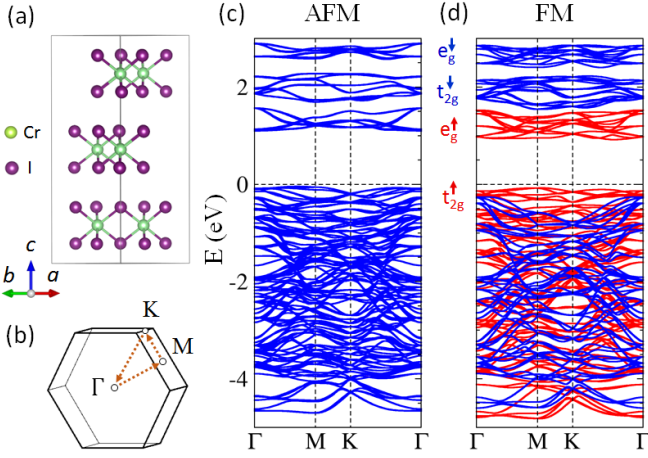


Fig. 1 Atomic and electronic structure of bulk CrI₃. Atomic structure of the unit cell of bulk CrI₃ (a) and the corresponding Brillouin zone with the high-symmetry points indicated (b). Spin projected band structure of bulk FM (c) and AFM (d) CrI₃ calculated along the high symmetry lines indicated in (b) with the Cr orbital character for selected bands shown. Red (blue) color designates the majority (minority)-spin bands.

tunneling barrier, and hence the conductance is high. However, when the CrI₃ monolayers are AFM-ordered at zero magnetic field, both majority- and minority-spin electrons encounter a higher barrier, which height varies across the CrI₃ layer, and the conductance is low. Note, that the detection of the spin-filtering effect in CrI₃-based tunnel junctions is different from that in the conventional spin-filter tunnel junctions, where a FM counter electrode is required to select the tunneling spins.^{23,24}

Although qualitatively the mechanism of the giant TMR in CrI₃-based tunnel junctions has been articulated, the quantitative analysis and detailed physical understanding of the spin-filtering effect is still missing. In this paper, we employ DFT calculations to elucidate the spin-dependent transport properties of the tunnel junctions, which consist of fcc Cu (111) electrodes and a magnetic CrI₃ barrier layer. Cu as an electrode material was chosen because of a small lattice mismatch with CrI₃, a simple free-electron-like Fermi surface, and appropriate band alignment placing the Cu Fermi level within the band gap of the CrI₃. We find a nearly 100% spin polarization of the tunneling current for ferromagnetically-ordered CrI₃ and a giant TMR effect increasing with CrI₃ thickness. This behavior is explained in terms of the spin and wave-vector dependent evanescent states in CrI₃ which control the tunneling conductance. In addition, we find a sizable charge transfer from Cu to CrI₃ which adds a new feature to the mechanism of spin-filtering in CrI₃-based tunnel junctions, as compared to those utilizing graphite electrodes.

RESULTS

Bulk CrI₃

Bulk CrI₃ in hexagonal setting of space group 148 ($R\bar{3}$) contains three CrI₃ layers stacked in the [0001] direction as shown in

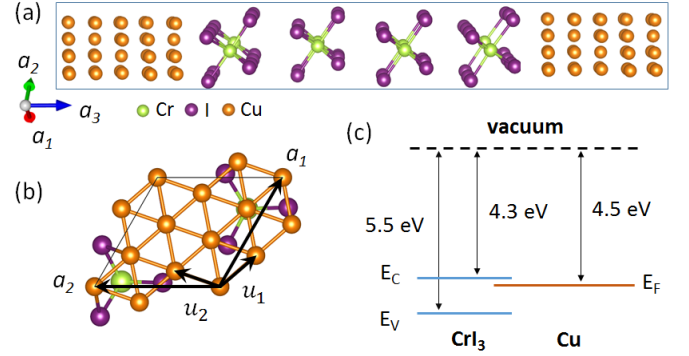


Fig. 2 Side (a) and top (b) views of the atomic structure of the Cu(5ML)/CrI₃(4ML)/Cu(5ML) tunnel junction. (c) Band alignment between bulk CrI₃ (001) and fcc Cu (111).

Figure 1a. Figures 1c-1d show the calculated band structure of bulk CrI₃ along the high-symmetry directions in the 3D Brillouin zone (Fig. 1b) for AFM (Fig. 1c) and FM (Fig. 1d) CrI₃. The calculated energy gap is 0.92 eV for FM and 1.05 eV for AFM configuration. Both values are smaller than the measured band gap of 1.2 eV,⁹ which is due to well-known deficiency of the standard DFT approach.²⁵ The energy position and the orbital character of the conduction band minimum (CBM) control transport properties of CrI₃. The band structure of CrI₃ is determined by the crystal field splitting of the 3d orbitals of the Cr³⁺ ion ([Ar] 3d³) located at the center of the octahedron formed by the six I⁻ ions (Fig. 1a). The crystal field of octahedral symmetry breaks the Cr 3d orbital state into the triply degenerate t_{2g} state, which lies at a lower energy, and the doubly degenerate e_g state, which lies at a higher energy. According to the Hund's rule, the majority-spin t_{2g} states are fully occupied by the three available Cr³⁺ electrons and form the valence band, while the minority-spin t_{2g} states and the e_g states are empty and form the conduction band (Fig. 1d). The exchange splitting of the spin bands makes the band gap in CrI₃ spin-dependent. While the majority-spin CBM is formed of the e_g states and lies at about 1 eV above the valence band maximum (VBM), the minority-spin CBM is formed of the t_{2g} states and lies at about 1.6 eV above the VBM (Fig. 1d). The spin-dependent band gap is responsible for the spin-dependent barrier height in tunnel junctions based on CrI₃, which is the origin of the spin-filtering effect.

Cu/CrI₃/Cu tunnel junction: Atomic structure

We consider a Cu/CrI₃/Cu tunnel junction which consists of a 4-monolayer CrI₃ (001) tunnel barrier stacked according to the bulk $R\bar{3}$ symmetry and placed between 5 monolayers of Cu (111) as shown in Fig 2a. We assume the in-plane constant of the supercell to be the theoretical bulk lattice constant of CrI₃, $a = 6.81 \text{ \AA}$ (the reported experimental value is $6.87 \text{ \AA}$ ⁸). In the supercell, the lattice vectors corresponding to the CrI₃ slab are $\vec{c}_1 = (a, -\sqrt{3}a/2, 0)$, $\vec{c}_2 = (-a, -\sqrt{3}a/2, 0)$ and $\vec{c}_3 = (0, 0, c)$,

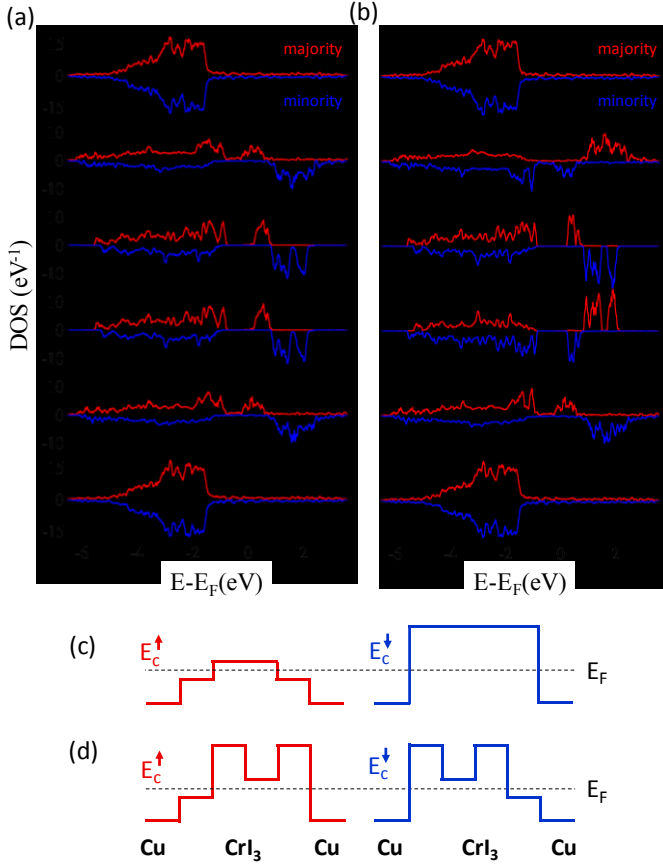


Fig. 3 (a, b) Calculated layer- and spin-resolved density of states (DOS) in a Cu(5ML)/CrI₃(4ML)/Cu(5ML) tunnel junction as a function of energy for FM- (a) and AFM- (b) ordered CrI₃. Top and bottom panels display DOS of the interfacial Cu MLs, central panels display DOS of the four CrI₃ MLs. Majority (minority)-spin DOS are indicated by red (blue) lines. (c, d) Schematics of the spin-dependent potential barrier profile across the junction for FM- (c) and AFM- (d) ordered CrI₃. Majority (minority)-spin channels are indicated by red (blue) lines. The Fermi energy (E_F) is indicated by the dashed line.

which represent the unit cell of bulk hexagonal CrI₃. To match the fcc Cu electrodes to the CrI₃ slab, we enlarge the in-plane Cu lattice parameters to be $\vec{a}_1 \rightarrow \vec{a}_1 + \vec{a}_z$ and $\vec{a}_2 \rightarrow \vec{a}_2 + \vec{a}_z$, where $\vec{a}_1$ and $\vec{a}_2$ are the unit vectors in the Cu (111) plane (Fig. 2b). The estimated in-plane strain between Cu and CrI₃ slabs is $\epsilon \approx 2\%$ ²⁶ suggesting possibility of good epitaxy. The Cu slab is positioned in such a way that one of the Cu atoms lies directly above the Cr atom, as shown in Fig. 2b, so that it has the same distance from the nearest I atoms.

Calculations are performed as described in Methods. The atomic relaxation involves two steps. First, we find the minimum-energy distance, d_{min} , between the Cu (111) slab strained to the CrI₃ (001) lattice constants and the CrI₃ (001) slab, while keeping all the internal coordinates fixed, corresponding to bulk CrI₃ and Cu. Then, we fix d_{min} and relax

all the atomic coordinates in the Cu/CrI₃/Cu supercell. We find that at the interface Cu and I atoms form bonds with the bond length of 2.67 Å. This is not surprising, as iodine is known to form compounds with the noble metals, such as Pt, Au, and Ag. In addition, the relaxation slightly reduces the interlayer spacing between the CrI₃ monolayers to 6.43 Å, as compared to the calculated bulk value of 6.46 Å (the reported experimental value is 6.60 Å⁸). It also makes the Cr-I bonds asymmetric with a longer bond of 2.77 Å next to the interface and a shorter of 2.69 Å bond away from the interface, as compared to the bulk Cr-I bond length of 2.71 Å. These bonds are largely symmetric in the middle CrI₃ monolayers. A tunnel junction with a two-monolayer CrI₃ barrier shows similar relaxation behavior.²⁷

Cu/CrI₃/Cu tunnel junction: Electronic structure

Electronic and transport properties of the Cu/CrI₃/Cu tunnel junction depend critically on the band offset between CrI₃ and Cu. Hence, we first calculate the band offset by analyzing the relative positions of the Fermi level in the Cu (111) slab and the VBM in the CrI₃ (001) slab when the vacuum potentials of the two slabs are matched. Figure 2c shows that the Fermi level in Cu (111) lies about 0.2 eV below the CBM of CrI₃, indicating that CrI₃ layer is expected to produce a tunneling barrier when is used in a Cu/CrI₃/Cu tunnel junction.

This fact agrees with the calculated layer-resolved density of states (DOS) for a Cu/CrI₃/Cu tunnel junction with four monolayers of CrI₃ (Fig. 2a). As seen from Figures 3a and 3b, away from the interface, the Fermi level lies within the band gap of CrI₃ both for FM- (Fig. 3a) and AFM-ordered (Fig. 3b) CrI₃. Therefore, a tunnel barrier exists both for majority- and minority-spin electrons. However, the height of the barrier and its profile across the Cu/CrI₃/Cu tunnel junction are spin-dependent and different for FM- and AFM-ordered CrI₃. In the FM configuration, there is a uniform barrier across the junction with the spin-dependent barrier height of about 0.2 eV in the majority-spin channel and about 0.8 eV in the minority-spin channel (Fig. 3c). In this case, the transmission is expected to be large and dominated by majority-spin electrons. In the AFM configuration, the barrier height changes between low and high values on each consecutive CrI₃ monolayer for both spin channels (Fig. 3d). In this case, the conductance is expected to be low in each spin channel and largely spin independent due to the mirror-symmetry of the barrier profiles between the two spin channels.

There is another important feature in the electronic structure of the Cu/CrI₃/Cu tunnel junction. There is a sizable charge transfer from Cu to the first monolayer of CrI₃ at the Cu/CrI₃ interface. This is evident from the Fermi energy located within the majority-spin e_g conduction band of the interfacial CrI₃ monolayer (Fig. 2a). Such an electron doping effect makes this CrI₃ monolayer “half-metallic,” so that the majority-spin carriers experience no barrier within this monolayer (Fig. 3c, top panel). This feature of the electronic

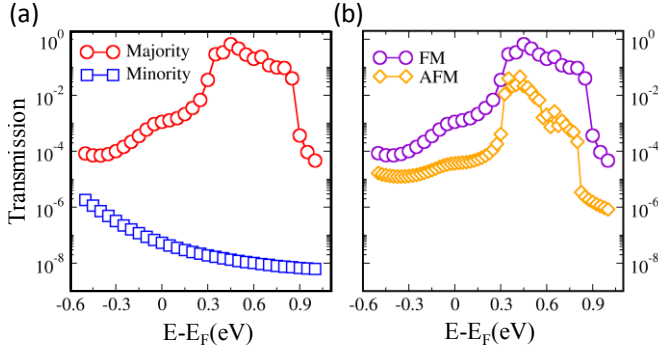


Fig. 4 Spin-resolved transmission per lateral unit cell area across the Cu/CrI₃/Cu tunnel junction as a function of energy for FM-ordered CrI₃ (a) and total transmission for FM- and AFM-ordered CrI₃ (b).

band structure at the Cu/CrI₃ interface adds additional contribution to the spin-filtering effect, as discussed below. For a two-monolayer CrI₃ tunnel junction, this “half-metallic” behavior becomes dominating and results in a large TMR of $\sim 1,500\%$.²⁷

Cu/CrI₃/Cu tunnel junction: Transmission

The transmission function is calculated as described in Methods by considering the Cu/CrI₃/Cu (111) supercell (Fig. 2a) as the scattering region ideally attached on both sides to semi-infinite Cu (111) electrodes. Figure 4a shows the calculated spin-resolved transmission $T_\sigma(E)$ ($\sigma = \uparrow, \downarrow$) across the FM-ordered Cu/CrI₃/Cu tunnel junction as a function of energy. There is several orders of magnitude difference in the transmission values between the majority- and minority-spin conduction channels over the whole range of energies. Relevant to experiment, the transmission value at the Fermi energy $T_\sigma(E_F)$ is four orders of magnitude higher for the majority-spin electrons as compared to the minority-spin electrons. The spin polarization of the tunneling conductance $SP = (T_\uparrow - T_\downarrow)/(T_\uparrow + T_\downarrow)$ is virtually 100%. This manifests a perfect spin-filtering effect resulting from the spin-dependent potential barrier in CrI₃ (Fig. 3c).

Spin filtering is also responsible for the large TMR effect associated with the change in the magnetic ordering of CrI₃ by an applied magnetic field. For FM-aligned CrI₃, the total transmission, $T_{FM} = T_\uparrow + T_\downarrow$, is nearly the same as the majority-spin transmission $T_\uparrow$ (due to $T_\uparrow \gg T_\downarrow$), which is shown in Fig. 4a by red dots. For AFM-aligned CrI₃, the total transmission, T_{AFM} , is twice that per spin (due to symmetry of the considered tunnel junction making the spin transmission for each spin channel to be equal), which is shown in Fig. 4b. By comparing Figs. 4a and 4b, it is seen that T_{AFM} as a function of energy exhibits similar features as T_{FM} , but T_{AFM} is more than an order of magnitude lower than T_{FM} over the whole range of energies. This is explained by the spin-dependent potential profiles shown in Figs. 3c and 3d for the FM- and AFM-ordered tunnel

junction, respectively. While T_{FM} is dominated by the majority-spin electrons encountering a low potential barrier across the whole CrI₃ layer (Fig. 3c, top panel), the AFM ordering makes the tunneling barrier high for either spin channel in those regions where the tunneling electrons have their spin antiparallel to the magnetic moment of the CrI₃ monolayer (Fig. 3d). Thus, while the spin filtering selects a highly transmittive majority-spin channel for the FM configuration, it suppresses the transmission in either spin channel for the AFM configuration by the consecutive filtering of the majority- and minority-spin carriers when they are tunneling across the barrier. The TMR value calculated at the Fermi energy (corresponding to the low bias voltage regime) is $(T_{FM} - T_{AFM})/T_{AFM} \sim 3,000\%$, which reveals a very large TMR effect in line with the experimental observations.¹⁵⁻²¹

As seen from Figs. 4a and 4b, the spin filtering and TMR effects become even larger at higher energies. At about 0.3 eV above the Fermi energy, the majority-spin transmission across the FM-ordered CrI₃ is strongly enhanced (Fig. 4a). A similar feature is seen for transmission across the AFM-ordered CrI₃ (Fig. 4b). This behavior is due to the electron energy entering the majority-spin conduction band of CrI₃. At these energies, the enhanced spin filtering and TMR result from the essentially “metallic” conduction of the majority-spin electrons, in contrast to the tunneling conduction of the minority-spin electrons. The predicted enhancement of the spin filtering at higher energies is likely responsible for the experimentally observed enhancement of TMR with applied bias voltage.^{3,19,21} Similar behavior is predicted for a tunnel junction with a two-monolayer CrI₃ barrier (Fig. S1).

To obtain a deeper insight into the mechanism of spin-dependent tunneling we calculate transmission $T(\mathbf{k}_\parallel)$ for different wave vectors $\mathbf{k}_\parallel$ in the two-dimensional Brillouin zone. Due to periodicity of the system in the plane perpendicular to the transport direction, wave vector $\mathbf{k}_\parallel$ in that plane is conserved during the tunneling process. Figures 5 a-c show the calculated $\mathbf{k}_\parallel$ resolved transmission across the Cu/CrI₃/Cu tunnel junction for FM (Figs. 5 a,b) and AFM (Fig. 5c) aligned CrI₃. As is seen from the figures, in all cases the transmission is somewhat reduced around the high symmetry $\bar{\Gamma}$ point and enhanced in certain peripheral regions of the 2D Brillouin zone.

In order to understand this behavior, we analyze the complex band structure of bulk CrI₃. It is known that tunneling through insulators can be interpreted in terms of evanescent states,²⁸ and the method to investigate them is the complex band structure in the energy gap region.^{29,30,31} To obtain the complex band structure, for each $\mathbf{k}_\parallel$, we calculate the dispersion relation $E = E(k_z)$, allowing complex $k_z = q + i\kappa$. The imaginary part κ is the decay rate, so that the corresponding wave functions decay as $\sim e^{-\kappa z}$. The evanescent states with the lowest decay rate are expected to be most efficient in the tunneling process

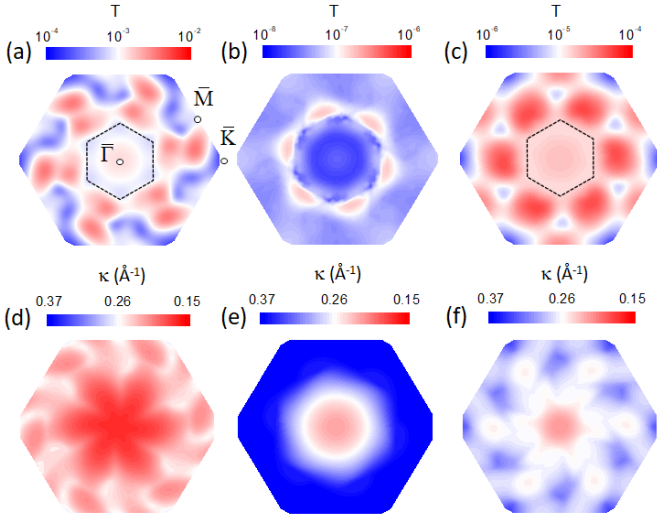


Fig. 5 (a-c) $k_{\parallel}$ -resolved transmission (T) across the Cu/CrI₃/Cu tunnel junction in the 2D Brillouin zone for majority (a) and minority (b) spin for FM and AFM (c) ordered CrI₃. The transmission is plotted in a logarithmic scale (note different scales for (a), (b), and (c)). The high symmetry points in the 2D Brillouin zone are shown. Dashed lines in (a) and (c) indicate the region where there are no available propagating states in the interface monolayer of CrI₃. (d-f) $k_{\parallel}$ -resolved lowest decay rate for majority (a) and minority (b) spin for FM and AFM (c) ordered bulk CrI₃ calculated at 0.2 eV below the CBM.

and hence to control the transmission. In Figs. 5d-f, we plot the lowest decay rate $\kappa(k_{\parallel})$ for the energy in the band gap of bulk CrI₃, corresponding to the Fermi energy in the Cu/CrI₃/Cu tunnel junction. Below we discuss the relationship between the $k_{\parallel}$ dependent transmission (Figs. 5a-c) and the lowest decay rate (Figs. 5d-f).

First, we consider the majority-spin conduction channel for the FM aligned CrI₃. Comparing Figures 5a and 5d, we see that away from $\bar{\Gamma}$ point closer to the edges of the 2D Brillouin zone (beyond the hexagon indicated by the dashed line in Fig. 5a), there is a clear resemblance between the high values of $T(k_{\parallel})$ and the low decay rates $\kappa(k_{\parallel})$. This behavior is consistent with the expectation that the slowest decaying evanescent states produce the highest transmission. However, the six-petal flower feature with the lowest decay rate centered at the $\bar{\Gamma}$ point seen in the color plot of $\kappa(k_{\parallel})$ (Fig. 5d) is not reproduced in the color plot of $T(k_{\parallel})$ (Fig. 5a).

This behavior can be understood in terms of the $k_{\parallel}$ dependent density of states (DOS) at the interfacial monolayer of CrI₃. As was discussed in conjunction with the DOS plotted in Fig. 3a, due to the charge transfer from Cu, this monolayer of CrI₃ has a non-zero majority-spin DOS at the Fermi energy and thus serves as the termination of the metal electrode rather

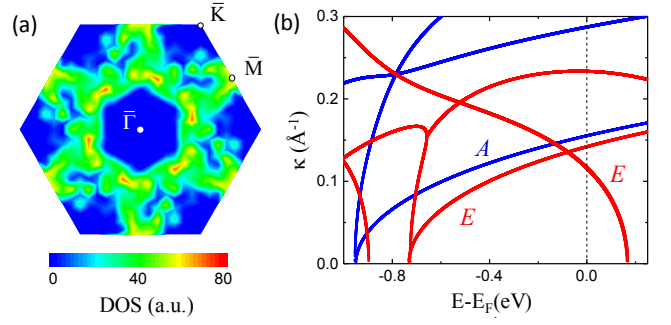


Fig. 6 (a) $k_{\parallel}$ -resolved majority-spin density of states (DOS) of bulk FM-ordered CrI₃ plotted in the 2D Brillouin zone at $E = 0.23$ eV above the CBM. (b) The complex band structure of CrI₃ for majority- (red curves) and minority- (blue curves) spin electrons. The dashed line indicates the Fermi energy in the Cu/CrI₃/Cu tunnel junction.

than a tunneling barrier. The $k_{\parallel}$ dependent DOS determines the efficiency of transmission across this monolayer from the Cu electrode further into the tunneling region of CrI₃. Figure 6a shows the $k_{\parallel}$ dependent majority-spin DOS of bulk CrI₃ at $E = 0.23$ eV above the CBM corresponding to the Fermi energy in the interfacial CrI₃ monolayer (see Fig. 3a). The key feature of this plot is the absence of electronic states within the hexagon region around the $\bar{\Gamma}$ point. Thus, while the electronic states are available in the most peripheral region of the 2D Brillouin zone, supporting the metallic-like transmission across this area, there are no propagating state in the central hexagon region, which implies that the transmission through this area is suppressed. This fact explains the reduced transmission seen within the hexagon region in Fig. 5a indicated by the dashed line. The similar behavior is observed for the Cu/CrI₃(2ML)/Cu tunnel junction (Fig. S1d). The six-petal flower feature, showing the lowest decay rates in CrI₃ (Fig. 5d), reveals itself only at the edges of the petals where the enhanced transmission is seen in Fig. 5a.

For AFM-ordered CrI₃, the $k_{\parallel}$ -resolved transmission across the Cu/CrI₃/Cu tunnel junction (Fig. 5c) shows a qualitatively similar behavior, although it is lower by about two orders in magnitude than the transmission for FM-ordered CrI₃. Comparing Figures 5c and 5f, we see a qualitative similarity between the high values of $T(k_{\parallel})$ and the low decay rates $\kappa(k_{\parallel})$ in the peripheral region of the 2D Brillouin zone. The transmission is suppressed however within the hexagon area (indicated by the dashed line in Fig. 5c) due to the absence of electronic states at one of the interfaces (left or right depending on the spin channel) in this region of the Brillouin zone (Fig. 6a).

The situation is different for the minority-spin transmission $T(k_{\parallel})$ across the FM-ordered Cu/CrI₃/Cu tunnel junction. First, as seen from Figure 5b, the transmission values are about four orders in magnitude smaller than those for the majority spin

(Fig. 5a). Second, there is virtually no correlation between $T(\mathbf{k}_{\parallel})$ and $\kappa(\mathbf{k}_{\parallel})$. According to Figure 5e, the expected high transmission should occur at the $\bar{\Gamma}$ point. However, as seen from Figure 5b, transmission is suppressed in the hexagon area around this point. This disparity is due to the symmetry mismatch between the states available at the Fermi energy in Cu and the evanescent states in CrI₃ at the $\bar{\Gamma}$ point. This can be understood from Figure 6b, where we plot the imaginary part of the wave vector κ in bulk CrI₃ as a function of energy at the $\bar{\Gamma}$ point. There are several majority- and minority-spin evanescent bands crossing the Fermi energy (indicated by the vertical dashed line in Fig. 6b). The states with the lowest decay rate have the E symmetry representation for the majority-spin electrons and the A symmetry representation for the minority-spin electrons, corresponding the group of the wave vector along the Γ -Z direction in the Brillouin zone of bulk CrI₃. In terms of atomic orbitals, the A symmetry state transforms as s , p_z and d_{z^2} orbitals, while the E symmetry state transforms as p_x , p_y , $d_{x^2-y^2}$, d_{xy} , d_{yz} , and d_{xz} orbitals. The incoming Cu states at the $\bar{\Gamma}$ point contain the mixture of the Cu s , p , and d atomic orbitals; however, the contribution of the A symmetry states is much smaller ($\sim 5\%$) compared to the contribution of the E symmetry states. Thus, the symmetry mismatch between the in-coming and evanescent states suppresses the transmission around the $\bar{\Gamma}$ point and makes the overall transmission of the minority-spin electrons low.

SUMMARY

Using first-principles methods based on density functional theory, we have explored the mechanisms of the spin filtering effect in tunnel junctions with a 2D ferromagnetic insulator CrI₃ used as a tunneling barrier. Our results demonstrate that a four-monolayer CrI₃ barrier provides virtually a fully spin-polarized transmission in a tunnel junction utilizing fcc Cu (111) electrodes. The predicted tunneling magnetoresistance effect is about 5,000%, associated with the change of magnetic ordering in CrI₃ from ferromagnetic to antiferromagnetic. A simple qualitative picture of the spin filtering effect is based on the exchange splitting of the spin bands in CrI₃ producing different barrier heights for majority- and minority-spin carriers. The detailed analysis of the spin-dependent electronic band structure and the spin and wave-vector resolved transmission in Cu/CrI₃/Cu tunnel junctions show however a more multifaceted behavior. We find, in particular, that there is a sizable charge transfer from Cu to the interfacial monolayer of CrI₃ at the Cu/CrI₃ interface. This makes this CrI₃ monolayer “half-metallic,” i.e. such that the majority spins experience no barrier within this monolayer, whereas the minority spins encounter a tunnel barrier. Furthermore, the detailed analysis of the complex band structure of CrI₃ shows that the spin filtering effect cannot be quantitatively understood based on a simple model of the spin-dependent barrier heights. The important

roles are played by the $\mathbf{k}_{\parallel}$ - and spin-dependent evanescent states, their symmetries and matching to the propagating states in the electrodes. These effects add new important features to the mechanism of spin-filtering in CrI₃-based tunnel junctions. Our results provide important insights into the understanding of spin-filtering produced ferromagnetic insulators, such as CrI₃, and may be useful for the design of novel magnetoresistive devices based on 2D magnetic crystals.

METHODS

The atomic and electronic structure of the system is calculated using density functional theory (DFT) as implemented in Vienna *ab initio* simulation package (VASP).^{32,33} The projected augmented plane wave (PAW) method is used to approximate the electron-ion potential.³⁴ The exchange-correlation potential is described within generalized density approximation (GGA). In the calculations, we use a kinetic energy cutoff of 340 eV for the plane wave expansion of the PAWs and $6 \times 6 \times 1$ grid of k points for the Brillouin zone integration. For the accurate description of the interlayer separation in CrI₃, the van der Waals interaction is included in the calculations.³⁵ The in-plane lattice constant is fixed to the theoretical value of the bulk CrI₃ lattice constant of 6.81 Å, which is close to the experimental value of 6.88 Å. With this in-plane lattice constant, the out-of-plane lattice constant and all the internal coordinates of the supercells are relaxed until the Hellman-Feynman force on each atom is less than 0.01 eV/Å. Under these conditions, the inter-plane separation of the CrI₃ monolayers is found to be 6.45 Å. All the calculations are spin-polarized with the Cr moment aligned parallel within the CrI₃ monolayers. The FM (AFM) phase of CrI₃ is described by assuming parallel (antiparallel) alignment of the magnetic moments of the adjacent CrI₃ monolayers. For the AFM structure, three monolayers of CrI₃ are not compatible with the periodic boundary conditions, and hence we increase the lattice by a factor of two in the c -direction. The band offset calculations are performed using 6 layers thick Cu slab (equivalent to two unit cells of Cu(111)) padded with 16 Å vacuum and 8 monolayer-thick AFM-ordered CrI₃ slab padded with 16 Å of vacuum. The work function is defined by the potential energy difference between the vacuum and the Fermi level for the Cu slab and the valence band maximum for the CrI₃ slab.

The transmission and complex band structure calculations are carried out using the Atomistic Simulation Toolkit (ATK) with the PBE pseudopotentials distributed in the QuantumWise package (Version 2015.1).^{36,37} As implemented in the code, the transmission is calculated using the non-equilibrium Green's function approach.³⁸ The Cu/CrI₃/Cu (111) supercell is used as the scattering region, ideally attached on both sides to semi-infinite Cu (111) leads.³⁶ This structure has open boundary conditions in the c -direction but is periodic in the a - b plane. The latter property makes the in-plane Bloch wave vector $\mathbf{k}_{\parallel}$ a good quantum number, so that transmission T is a function of $\mathbf{k}_{\parallel}$. For

calculating transmission, the two-dimensional Brillouin zone is sampled using a uniform 51×51 $k_{\parallel}$ mesh.

The atomic structure of the Cu/CrI₃/Cu(111) junctions is designed with the help VNL distributed with Atomistic toolkit.³⁹

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