Probing Magnetism in Exfoliated $\text{VI}_3$ Layers with Magnetotransport

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**ABSTRACT:** We perform magnetotransport experiments on $\text{VI}_3$ multilayers to investigate the relation between ferromagnetism in bulk and in exfoliated layers. The magnetoconductance measured on field-effect transistors and tunnel barriers shows that the Curie temperature of exfoliated multilayers is $T_C = 57 \text{ K}$, larger than in bulk ($T_{C,\text{bulk}} = 50 \text{ K}$). Below $T \approx 40 \text{ K}$, we observe an unusual evolution of the tunneling magnetoconductance, analogous to the phenomenology observed in bulk. Comparing the magnetoconductance measured for fields applied in- or out-of-plane corroborates the analogy, allows us to determine that the orientation of the easy-axis in multilayers is similar to that in bulk, and suggests that the in-plane component of the magnetization points in different directions in different layers. Besides establishing that the magnetic state of bulk and multilayers are similar, our experiments illustrate the complementarity of magnetotransport and magneto-optical measurements to probe magnetism in 2D materials.

**KEYWORDS:** 2D magnetism, Magnetic Tunnel Junction, Magnetotransport, $\text{VI}_3$

Atomically thin layers of many different materials have been produced by exfoliating bulk crystals of van der Waals bonded compounds.\textsuperscript{1,2} The crystalline structure of exfoliated layers is commonly assumed to be the same as that of the bulk parent crystals, and indeed experiments normally confirm this assumption. This is, however, not the case for many recently discovered atomically thin magnetic materials,\textsuperscript{3–9} whose structure in exfoliated form differs from that of the bulk, often resulting in drastically different magnetic properties.\textsuperscript{10–14} Examples are provided by CrI$\textsubscript{3}$, whose multilayers are layered antiferromagnets with $T_C = 51 \text{ K}$, whereas bulk crystals are ferromagnets with $T_C = 60 \text{ K}$,\textsuperscript{4,15,16} and CrI$\textsubscript{3}$, in which the interlayer exchange interaction in multilayers is approximately one order of magnitude larger than in the bulk.\textsuperscript{17}

$\text{VI}_3$ (see Figure 1a) is an example of current interest, which exhibits conspicuous structural differences in bulk and exfoliated multilayers, accompanied by a magnetic response that appears to be strikingly different in the two cases. Bulk $\text{VI}_3$ crystals possess inversion symmetry, and at $T_C = 50 \text{ K}$ undergo a transition into a ferromagnetic state, suggested to be of the Ising type.\textsuperscript{18,19} Recent experiments, however, showcase an unusual evolution of the magnetic properties below 40 K, which is indicative of a more complex magnetic state.\textsuperscript{18,20–26} Experimental observations include the splitting of diffraction peaks measured by neutrons and X-rays techniques;\textsuperscript{20,26} the onset of a disproportionation between the (supposedly) structurally equivalent V atoms, detected by nuclear magnetic resonance;\textsuperscript{22} a pronounced increase in the in-plane magnetic susceptibility found in magnetization measurements,\textsuperscript{18,24,25} (see Figure 1c); and a 30° rotation around the direction normal to the layers of the 6-fold symmetric in-plane easy axis, which occurs upon cooling between 40 and 30 K.\textsuperscript{21} No magnetic state capable to explain all the observed phenomenology has been proposed.

The fewer experiments\textsuperscript{19,27,28} reported on exfoliated layers indicate that the crystalline structure lacks inversion symmetry (for trilayers or thicker layers) and that a ferromagnetic state occurs below $T_C = 57 \text{ K}$, which is a value significantly higher than the bulk $T_C$ (in contrast to expectations\textsuperscript{4,14,29}). Both scanning magnetometry and reflective magnetic circular-dichroism (RMCD) measurements\textsuperscript{19,28} exhibit a behavior consistent with Ising ferromagnetism at all temperatures, with no anomalies. Therefore, it appears that the behavior of multilayers differs from—and is simpler than—that observed in the bulk, but it is unclear whether this conclusion is just a consequence of the few experimental techniques available that offer enough sensitivity to probe magnetism in thin layers.

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Here, we investigate exfoliated VI₃ layers by means of magnetotransport experiments and show that—despite their different structural properties and larger critical temperature—their magnetic response is similar to the one observed in bulk crystals, and not consistent with that of an Ising ferromagnet. Magnetotransport was measured using field-effect devices (Figure 1d,e) and in devices in which VI₃ multilayers act as tunnel barriers (Figure 1f–g). In both configurations, a ferromagnetic transition is observed at $T_C = 57$ K, consistent with earlier RMCD measurements. Nevertheless, the tunneling magnetoresistance below $T_C$ deviates qualitatively from that of an Ising ferromagnet and exhibits a behavior in line with that of bulk crystals. Specifically, below 40 K the magnetoresistance measured in a magnetic field perpendicular to the planes becomes negative (whereas it is always positive in an established Ising ferromagnet such as CrBr₃$^{30}$), and the magnetoconductance measured in an in-plane field becomes pronouncedly hysteretic. By analyzing the magnetoconductance measured with the field applied in the two directions, we determine that the easy axis in VI₃ multilayers forms an angle of approximately $30^\circ$ with respect to the normal to the VI₃ planes. Such an angle is close to, but smaller than, the that observed in bulk crystals. Besides showing that the magnetic state of exfoliated VI₃ multilayers and bulk crystals are similar, our results establish that the anomalous magnetic response originates from the in-plane component of the magnetization and illustrate the complementarity of magneto-optical and magneto-transport measurements to probe 2D magnetic materials.

The fabrication of VI₃ devices relies on micromechanical exfoliation of bulk crystals (characterized by magnetization and susceptibility measurements; see Figure 1b,c) to obtain multilayers. The multilayers are processed to form field-effect transistors and tunnel barriers (see Figure 1d–g) using conventional pick-up and transfer techniques based on polymeric stamps. In practice, VI₃ multilayers are contacted with multilayer graphene strips and encapsulated in between exfoliated hBN layers (~20–50 nm thick) to avoid degradation (the exfoliation and assembly of the structures are carried out in the controlled atmosphere of a glovebox). We attach metal contacts to the graphene strips using conventional electron-beam lithography in combination with reactive ion etching, evaporation of a Cr/Au film, and lift-off. All structures are realized on highly doped Si substrates (acting as gates in transistor devices) covered with 285 nm SiO$_2$. We have investigated two transistors and four tunnel junction devices that exhibit fully consistent behavior, and here we present representative data from a selected transistor and a selected tunnel junction (see the Supporting Information Section S2 for data of additional devices).

We first discuss transport measurements performed on a VI₃ transistor (see Figure 2a). Figure 2b shows the transfer curves (i.e., source-drain current $I_{sd}$ as a function of gate voltage $V_{g}$), measured at $T = 90$ K, as $V_{sd}$ is varied from 5 to 1 V. The application of a positive gate voltage—corresponding to accumulating electrons at the surface of VI₃—causes a large increase in current. Even at the largest positive gate voltage, however, the low-temperature resistance is extremely high and increases in a thermally activated fashion upon cooling (see Figure 2c–d), indicating that the accumulated electrons are localized and that transport is mediated by hopping (the activation energy—approximately 50 meV at $V_{g} = +100$ V—corresponds to the distance in the energy of the localized electrons at the Fermi level and the conduction band). Under these conditions, it is unclear whether any magnetococonductance can be measured.

A magnetococonductance $\delta G(H_{\perp}, T) = (G(H_{\perp}, T) - G(0, T))/G(0, T)$ is nevertheless present, and exhibits a systematic evolution as a function of magnetic field applied perpendicular to the layers, $\mu_0 H_{\perp}$, and temperature $T$ (Figure 2e). The magnetococonductance sets in at a lower magnetic field as the temperature $T$ is lowered from 75 to 8 K (see the horizontal dashed line), a manifestation of the critical regime in the paramagnetic state of VI₃ near the ferromagnetic transition. Specifically for a ferromagnet, the conductance is expected to

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Figure 1. (a) Top (left) and side (right) view of the crystal structure of a VI₃ monolayer. The purple and orange balls represent the iodine and vanadium atoms, respectively. (b) Magnetization, $M(H)$, of VI₃ bulk crystals measured at $T = 2$ K as a function of magnetic field applied perpendicular to the layers showing hysteretic behavior. (c) Field-cooled susceptibility $\chi(T) (\mu_0 H = 10$ mT) of our bulk VI₃ crystals, measured in a temperature range between 5 K $< T < 80$ K. The blue and red curves denote measurement configurations where the magnetic field is applied parallel to the c-plane and ab-plane, respectively. Schematic representation (d) of a VI₃ transistor with graphene contacts and optical micrograph (e) of an actual device based on a 18 nm thick multilayer. The highly doped silicon substrate covered by a 285 nm SiO$_2$ layer is used as gate (the scale bar is 10 μm long). Schematic representation (f) and optical micrograph (g) of a tunneling device with graphene contacts on opposite sides of a 18 nm thick VI₃ multilayer (the scale bar is 10 μm long). All structures are encapsulated between hexagonal boron nitride (hBN) crystals to avoid degradation of VI₃.
increase as the VI₃ magnetization increases, i.e., as the spins in the material orient themselves in the same direction. Since the magnetic susceptibility $\chi \propto 1/(T - T_C)$ diverges at $T_C$, a smaller value of $\mu_B H_{\perp}$ is needed to generate the same magnetization as $T$ approaches $T_C$, explaining why the magnetoconductance sets in at lower fields. Indeed, if we plot the spin magnetoconductance measured at different temperatures (Figure 2f) as a function of $T$ (the plot shows an interpolation of data measured at every 2 K as a function of $\mu_B H_{\perp}$). The white dashed line indicates the ferromagnetic transition at $T_C = 57$ K. Figure 2g shows the temperature dependence of the magnetoconductance $\delta G$ for $T > T_C$, as $T$ is varied from 78 to 58 K in 2 K steps. The same data shown in (f) plotted as a function of $\mu_B H_{\perp}/(T - T_C)$. When plotted in this way, all curves collapse on top of each other at small $H_{\perp}$. (h) Temperature dependence of the RMCD signal measured on a VI₃ tunnel barrier device based on a 10 nm thick VI₃ layer. The RMCD was measured in the region between the graphene tunneling electrodes while warming the sample up in the absence of a magnetic field after having cooled down the device down to $\sim 20$ K in an applied perpendicular magnetic field of either +980 mT (red line) or −980 mT (blue line).

For temperatures much lower than $T_C$, the transistor resistance becomes higher than the sensitivity of our instruments, preventing the evolution of the magnetic state to be probed. Out-of-plane transport measurements on VI₃ tunnel barriers do not suffer from this limitation,²⁶,³²−³⁴ and in the remainder of this paper we focus on these measurements to investigate magnetism in exfoliated multilayers. Representative $I$−$V$ characteristics of a VI₃ multilayer tunnel barrier are shown in Figure 3a. They exhibit a very pronounced nonlinearity consistent with Fowler-Nordheim tunneling (see Figure 3b); current flows when the applied bias tilts the bands in the VI₃ barriers and increases the tunneling transmission probability to a level that makes the tunneling current measurable, such that $\ln(I/V^2)$ depends linearly on $1/V$ at high bias.³⁵

Figure 3c represents the tunneling magnetoconductance $\delta G(H_{\perp}, T) = (G(H_{\perp}, T) - G(0, T))/G(0, T)$ as a function of temperature, $T$, and magnetic field applied perpendicular to the layers, $\mu_B H_{\perp}$, measured upon sweeping the field from either negative to positive (left) or from positive to negative (right) values. Because the $I$−$V$ curves are strongly nonlinear, the absolute value of the conductance depends on applied bias, but the features observed in $\delta G(H_{\perp}, T)$ do not; that is, no qualitative aspects of the magnetoconductance temperature and magnetic field dependence changes upon changing bias (see Supporting Information S3). The tunneling magnetoconductance can then be used to probe the properties of the magnetic state, as shown previously for CrH₃, CrCl₃, CrBr₃, and MnPS₃ multilayers.¹¹,¹⁶,²⁷,²⁹,³⁰,³³,³⁴,³⁶,³⁷ Distinct features in
negative upon further cooling, as shown in Figure 4c. The change from positive to negative magnetoconductance is also apparent in Figure 4d, which shows $\delta G$ as a function of $\mu_0 H_L$ for different values of $T$; indeed, the magnetoconductance increases upon increasing $\mu_0 H_L$ for $T > 36$ K and decreases upon increasing $\mu_0 H_L$ for lower temperatures (the data also allow us to determine the coercive field, which is close to 3 T at $T = 4.2$ K, significantly larger than the value measured in bulk crystals, just above 1 T).

Finally, Figure 5a shows the dependence of the magnetoconductance $\delta G(\mu_0 H_\|, T)$ with magnetic field $\mu_0 H_\|$ applied parallel to the VI$_3$ planes. Even in this case, we observe the characteristic manifestation of the critical regime near the ferromagnetic transition (see the lobes of enhanced magnetoconductance for $T$ close to $T_C = 57$ K in Figure 5a), and the low-field collapse of the magnetoconductance curves plotted versus $\mu_0 H_\|/(T - T_C)$ (see Figure 5b). Correspondingly, $\delta G(\mu_0 H_\|, T)$ measured at a fixed field as a function of $T$ peaks at $T_C$ reaching values of 25%, comparable to, but smaller than the values measured when the field is applied perpendicular to the layers (see Figure 5c). This difference carries important information because the relative intensity of the magnetoconductance peaks near $T_C$ measured with field applied perpendicular or parallel to the VI$_3$ layers allows determining the angle between the easy axis and the normal to the planes. For a strongly anisotropic easy-axis ferromagnetic tunnel barrier just above $T_C$ (i.e., in the paramagnetic state), the low-field magnetoconductance is proportional to the square of the magnetization, given by the magnetic susceptibility multiplied by the component of the applied field along the easy axis.\textsuperscript{30} For the same value of magnetic field applied either in-plane or perpendicular to the plane, the ratio $\delta G(H_\|)/\delta G(H_\perp)$ is thus given by the square of the ratio of the projections of the magnetic field along the easy axis, and can be used to calculate the angle $\Theta = \tan^{-1}\left(\sqrt{\frac{\delta G(H_\|)}{\delta G(H_\perp)}}\right)$ between the easy axis and the direction normal to the VI$_3$ planes. The measurements should ideally be performed at a small magnetic field (to ensure that the linear relation between $M$ and $H$ holds true), but with a field sufficiently large to have a signal well above the noise. In Figure 5d we show the derived angle for fields between 1 and 4 T, for two different devices, giving virtually identical results. We see that the angle between the easy axis and the direction normal to the VI$_3$ layers depends only weakly on field and approaches 30° at 1 T, close to (but slightly smaller than) the one obtained from magnetization measurements performed on as-grown bulk crystals.\textsuperscript{31}

Upon cooling below $T_C$, the magnetoconductance measured with field applied parallel to the plane decreases monotonously and remains positive down to $T = 4$ K. However, just under 40 K a pronounced increase in hysteresis sets in (Figure 5e,f), which was not reported for CrBr$_3$ tunnel barriers.\textsuperscript{30} We conclude that for temperatures below 40 K, magnetotransport measurements indicate a crossover to a regime qualitatively different from that of an established Ising ferromagnet such as CrBr$_3$.\textsuperscript{30} This crossover is signaled by a change in the sign of the magnetoconductance in perpendicular magnetic field and by a concomitant pronounced increase in the hysteresis of the magnetization. Upon cooling below $T_C$, the magnetoconductance measured versus in-plane magnetic field.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{(a) Current, $I$, across the tunnel barrier measured at $T = 4$ K as a function of voltage. (b) Similar to what is found in barriers made of different Chromium trihalides, at sufficiently large bias the current behaves as expected for Fowler-Nordheim tunneling, with $\ln(I/V^2)$ linearly proportional to $1/V$. The green solid line ($V = 0.5$ V) indicates the voltage at which the magnetoresistance data shown in (c) (and in Figure 4) were measured. (c) Color plot of tunneling magnetoconductance as a function of applied field $\mu_0 H_L$ and temperature $T$. Left and right panels represent the magnetoconductance measured while sweeping the field from $-4$ T to $+4$ T or from $+4$ T to $-4$ T, respectively. The red dashed line in both panels indicates the Curie temperature $T_C$ determined from the magnetoconductance data. The green dashed line in both panels denotes the temperature at which the magnetoconductance becomes negative ($T \approx 36$ K).}
\end{figure}
the differences in structural properties, critical temperature, and coercive field).

The comparison of magnetotransport and magneto-optical experiments allows us to conclude that the observed phenomenology originates from the evolution of the in-plane component of the magnetization of VI₃. Indeed, tunneling magnetotransport through ferromagnetic barriers probes the alignment of spins in the material, such that configurations of

Figure 4. (a) Magetoconductance curves δG(μ₀H⊥) for the temperature range between 76 and 58 K in 2 K steps. (b) Same data as in panel (a) plotted as a function of μ₀H⊥/(T − T_C). At low magnetic fields, all of the curves overlap, confirming the value of T_C determined from transistor measurements. (c) Magnetoconductance as a function of temperature for different fixed magnetic fields μ₀H⊥ = 1, 2, 3, and 4 T. The red dashed line marks the value at which the magnetoconductance is maximum, corresponding to T_C = 57 K. The black dashed line marks the transition from positive to negative magnetoconductance (T = 36 K). (d) Magnetoconductance traces as a function of magnetic field μ₀H⊥ for temperatures between T = 44 K to T = 28 K in 4 K steps. The traces are offset for clarity and the gray dashed line indicates the zero line for each trace, respectively. Red curves correspond to measurements performed with the magnetic field swept from negative to positive values; blue curves correspond to data taken by sweeping the field in the opposite direction.

Figure 5. (a) Color plot of the tunneling magnetoconductance δG as a function of temperature T and magnetic field applied parallel μ₀H∥ to the VI₃ planes (the data are interpolated from magnetoconductance curves measured every 5 K). The two magnetoconductance lobes centered around the Curie temperature (white dashed line indicates T = 57 K) also develop in this case. (b) Magnetocoeuductance δG as a function of μ₀H∥/(T − T_C), measured at temperatures above the ferromagnetic transition (from 60 to 80 K), showing the collapse of all curves at small applied field. (c) Magnetocoeductance as a function of temperature δG(T) for fixed positive magnetic fields μ₀H∥. The dashed line marks the Curie temperature T_C = 57 K. In contrast with the out-plane magnetoconductance, the in-plane magnetoconductance remains always positive down to the lowest temperature investigated. (d) Calculated angle of the easy-axis Θ from measured values of δG(μ₀H∥) and δG(μ₀H⊥) at T ∼ T_C as a function of the applied magnetic field μ₀H. Blue and red filled circles represent the angle for the 7 and 11 nm, respectively. (e) δG(μ₀H∥) curves for representative temperatures T, ranging from above to well below the Curie temperature (60, 30, 20, and 4 K; the traces are offset for clarity). Solid red and blue curves represent the magnetoconductance measured while sweeping the magnetic field μ₀H∥ from negative to positive values or from positive to negative values, respectively. A small hysteresis is present at all temperatures below T_C, and it becomes very pronounced for temperatures close to 40 K, as shown in the color plot in (f), which shows the difference between magnetoconductance (δG_up − δG_down) measured while sweeping the field in opposite directions (the green dashed line corresponds to T = 36 K, that is, the temperature at which the magnetoconductance measured as a function of perpendicular field becomes negative, see Figure 2; the plot shows an interpolation of magnetoconductance traces taken every 5 K).
more aligned spins lead to larger tunneling conductance. The negative magnetococonductance observed in a perpendicular magnetic field, therefore, indicates that below 40 K the misalignment of the spins in the VI₃ multilayers increases upon increasing $\mu_0 H_z$. Because RMCD measurements (the ones in ref 19 and ours, which are only sensitive to the $M_z$ component of the magnetization) find that $M_z$ keeps increasing when lowering $T$ below 40 K and upon applying a perpendicular magnetic field, the increased spin misalignment necessarily originates from the in-plane component of the magnetization.

The simplest scenario that we can envision is that the in-plane component of the magnetization in different VI₃ layers is not pointing in the same direction and that the relative angle between the in-plane component of the magnetization in adjacent layers depends on the applied perpendicular magnetic field and on temperature. In such a scenario, when $T$ is lowered below $T_C$, the total spontaneous magnetization is small and is enhanced by the application of a magnetic field, leading to a positive magnetococonductance. However, as the temperature is lowered and the spontaneous magnetization builds up, this effect of the perpendicular magnetic field decreases and for $T \ll T_C$ its influence on the magnetococonductance becomes negligible (as found in CrBr₃ tunnel barriers). At that point, any misalignment of the in-plane component of the magnetization in different layers may start to dominate magnetotransport. Interestingly, this scenario provides a mechanism that may explain why the critical temperatures of mono- and bilayer VI₃ (60–61 K) are slightly larger than that of thicker multilayers. Indeed, if the in-plane component of the magnetization in adjacent layers points in different directions, the effect of the intralayer exchange interaction responsible for the value of $T_C$ measured in isolated monolayers would be slightly weakened in multilayers, by the competition with the interlayer exchange interaction (the microscopic mechanism mediating the coupling between perpendicular magnetic field and in-plane component of the magnetization, implicit in the proposed scenario, remains to be determined).

In summary, tunneling magnetococonductance measurements show that, despite having distinct crystallographic structures, exfoliated thin VI₃ crystals exhibit a magnetic state which resembles the one observed in bulk crystals with the magnetic easy axis canted away from the normal of the VI₃ layers by a large angle. Even though our measurements do not allow the magnetic state to be determined, they show that an Ising ferromagnetic state is not compatible with experimental observations and that deviations originate from the evolution of the in-plane component of the magnetization. These results illustrate the complementarity of magneto-optical and magnetotransport measurements to probe atomically thin 2D magnetic materials, since the commonly employed geometries of RMCD measurements are only sensitive to the component of the magnetization perpendicular to the layers, whereas tunneling magnetococonductance probe phenomena associated with the total magnetization. This conclusion is worth emphasizing because only a few techniques currently have sufficient sensitivity to probe the magnetic properties of atomically thin layers, and it is important to understand which magnetic properties are probed by different measurements.

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**Notes**

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