Metamagnetic Transitions in Few-Layer CrOCl Controlled by Magnetic Anisotropy Flipping

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The pivotal role of magnetic anisotropy in stabilising two-dimensional (2D) magnetism has been widely accepted [1,2], however, direct correlation between magnetic anisotropy and long-range magnetic ordering in the 2D limit is yet to be explored. Here, using angle- and temperature-dependent tunnelling magnetoresistance [3,4], we report unprecedented metamagnetic phase transitions in atomically-thin CrOCl triggered by magnetic easy-axis flipping instead of the conventional spin flop mechanism. Few-layer CrOCl tunnelling devices of various thicknesses consistently show an in-plane antiferromagnetic (AFM) ground state with the easy axis aligned along the Cr-O-Cr direction (b-axis). Strikingly, with the presence of a magnetic field perpendicular to the easy-axis (Hc), magnetization of CrOCl does not follow the prevalent spin rotation and saturation pattern, but rather exhibits an easy-axis flipping from the in-plane to out-of-plane directions. Such magnetic anisotropy controlled metamagnetic phase transitions are manifested by a drastic upturn in tunnelling current, which shows anomalous shifts towards higher H when temperature increases. By 2D mapping of tunnelling currents as a function of both temperature and H, we determine a unique ferrimagnetic state with a superstructure periodicity of five unit cells after the field-induced metamagnetic phase transition at ~27 K, possibly corresponding to the formation of an incommensurate magnetic superstructure from the paramagnetic high-T phase [25, 26]. These studies infer the critical importance of the unique quasi-1D staggered lattice of ML CrOCl, which is AA stacked out of plane to form the bulk. As shown in Figure 1, ML CrOCl can be viewed as a staggered CrO double layer sandwiched by two halogen atomic layers. By occupying the same B-site, every two nearest neighbouring Cl and four O atoms form a distorted octahedron surrounding an A-site Cr, creating inequivalent upper and lower quasi-1D Cr chains along the Cl-Cr-CI direction, i.e. the a axis in Fig. 1a. In perpendicular to the 1D chains, Cr atoms are interconnected solely by O atoms, making the b axis significantly longer than a (lower panel of Fig. 1a).

Due to the wide semiconducting band gap of ~ 2.3 eV, we fabricate vertical tunnelling junctions (TJs) to study the layer-dependent magnetism in CrOCl. Fig.
Figure 1. Few-layer tunnelling junctions of CrOCl. a, Side- and top-view of the staggered square lattice of CrOCl consisting of CrOCl octahedrons, imposing cubic crystal field on 3d orbitals in Cr$^{3+}$. b, Schematic cross-section of FLG/CrOCl/FLG tunnelling devices for TMR measurements. c, NCAFM image of a representative CrOCl flake, showing ML steps of ~0.8 nm. Note that ML on SiO$_2$ exhibits an effective thickness of 1.40 nm. d, Fingerprinting Raman red shift in $A_1^y$ for determining CrOCl layer numbers. e, $I_t$ vs $H$ characteristics of representative few-layer CrOCl tunnelling devices with various thicknesses from ML to quintuple layer. Note that high-frequency tunnelling peaks above 4 T are induced by the Shubnikov-de Haas oscillations of FLG electrodes.

Figure 1. illustrates the tunnelling device structure, in which atomically-thin CrOCl channels are sandwiched by two few-layer graphene (FLG) electrodes. In brief, different-layer CrOCl flakes were first exfoliated on SiO$_2$/Si substrates, followed by two dry-transfer steps to assemble a TJ device (see Methods for details). To minimize detrimental leakage current, we use narrow FLG flakes of several $\mu$m in width, and thus, confine the working channel areas to below $1.5 \mu$m$^2$. Typical tunnelling current ($I_t$) vs bias voltage ($V_{bias}$) characteristics are shown in Supplementary Information (SI) Figure S1. After tunnelling experiments, the layer numbers of each device are determined by non-contact atomic force microscopy (NCAFM) using a ML step height of 0.8 nm (Fig. 1c). Equally important, Raman spectroscopy reveals that below six MLs, the $A_1^y$ phonon vibration mode shows monotonic red shift from the bulk value of 207.5 cm$^{-1}$ to the ML wave number of 200.5 cm$^{-1}$, allowing us to unambiguously confirm the layers of our devices in complementary with the NCAFM data (Fig. 1c and extended discussions in SI Note 1).

Figure 1 summarizes layer-dependent $I_t$ as a function of out-of-plane $H$ at 1.6 K in few-layer CrOCl TJs with thicknesses from ML to quintuple layers, all consistently showing a drastic upturn in tunnelling current at around 3 T. At first glance, the results seem to suggest field induced spin-flop (SF) transitions for $H||c$, which are expected for a $c$-easy axis AFM ground state with negligible interlayer magnetic coupling. However, by rotating $H||c$ towards the $a$ and $b$ axes respectively, angle ($\theta$)-dependent $I_t$-$H$ curves unfold a distinct AFM magnetic ordering for few-layer CrOCl crystals. As shown in Figure 2a, abrupt $I_t$ upturns are observed for both $H||c$ and $H||a$, contradicting with the uniaxial $c$-easy axis AFM in the bulk. Because the $I_t$ upturn thresholds monotonically increase when $H$ rotates from the $c$- to $a$-axis (SI Figure S2), we can also exclude an easy-plane AFM configuration for few-layer CrOCl, which would show a maximum SF threshold when $H$ is aligned with the canting direction of Cr magnetic moments ($\theta \sim 30^\circ$; see extended discussions in SI Note 2). To get insight into the magnetic ground state of few-layer CrOCl TJs, we further investigated the tunnelling behaviour with in-plane $H$ rotation. As shown in Figure 2b, when $H$ rotates from the $a$- to $b$-axis, there is an inverse cosine scaling in the $I_t$ transition thresholds, indicating that the effective magnetic field along the $a$-axis is solely responsible for the magnetic phase transitions. Using polar plotting, it is clear to see that $I_t$, which is nearly isotropic in low $H$, is characterized by a distinctive butterfly-shaped two fold symmetry after the phase transitions (Figure 2b).

These self-contradicting experimental observations with the presumable bulk-like $c$-easy axis AFM ordering for few-layer CrOCl, however, can be consistently ex-
plained by an in-plane AFM ground state with its easy axis aligned along the b crystallographic direction. In this easy-axis configuration, H∥c causes out-of-plane spin rotation in low fields, and eventually induces a magnetic phase transition which flips the easy magnetization direction from the b- to c-axis. Using $T$-dependent tunnelling, we can clearly see that the $I_\parallel$ thresholds substantially increase when TJ devices are warmed up (Figure 3a). Such an anomalous $T$ dependence is opposite to the trend of SF transition-controlled tunnelling, which also cannot explain the low-field hysteresis in all CrOCl TJs with different thicknesses (Figure 3a and Figure 1a).

To appreciate such a field-induced MAE flipping mechanism, it is crucial to comprehend intralayer competition between in-plane exchange anisotropy (EA) and out-of-plane magnetocrystalline anisotropy (MCA), rooted in the unique staggered square lattice of CrOCl. In particular, an in-plane AFM ordering in CrOCl requires a monoclinic lattice distortion by the rotation of the a axis within the $a-c$ plane [21], rather different from the in-plane monoclinic transition in VOCl [23]. Despite sharing the same octahedron crystal field symmetry as CrOCl, V$^{3+}$ in VOCl has only two 3d electrons occupying $d_{xy}$ and $d_{yz}$ orbitals respectively (Figure 3b and SI Note 3). By in-plane monoclinic distortion, AFM ordering between neighbouring upper and lower V$^{3+}$ atoms along the compressed diagonal direction ($\frac{1}{2}a + \frac{1}{2}b$) is induced by enhanced direct exchange interactions to avoid geometrical frustration associated with a rhombic unit cell (see SI Figure S3). Along the quasi-1D V-Cl-V atomic chains, direct exchange of filled $d_{xy}$ orbitals also enforce AFM coupling, leaving V$^{3+}$ atoms along the elongated ($\frac{1}{2}a - \frac{1}{2}b$) direction inevitably FM aligned.

However, once $d_{yz}$ is occupied in the case of CrOCl, in-plane lattice distortion becomes unfavourable because lattice compression along the ($\frac{1}{2}a + \frac{1}{2}b$) direction directly increases head-on overlapping between $3d_{yz}$ orbitals (Figure 3b). Instead, CrOCl undergoes an out-of-plane lattice distortion by rotating the a axis towards c, which produces a c-axis monoclinic lattice of 90.06° as well as zigzagging in the Cr-Cl-Cr atomic chains [24]. This unique type of monoclinic lattice distortion, which weakens direct exchange along the a-axis while leaving Cr-Cl-Cr superexchange interaction unchanged, makes the in-plane AFM ordering feasible in few-layer CrOCl when device encapsulations slightly reduce the monoclinic angle.

Using 2D mapping of $I_\parallel$ as a function of both $T$ and $H$, it is illuminating to see that few-layer CrOCl exhibits four distinctive magnetic phases. As shown in Figure 4a and 4b for two representative devices (TL-S17 and QL-S27 respectively), few-layer CrOCl TJs in zero field make phase transitions at ~12.5 K from an intermediate para-magnetic state (PM') to the AFM ground state, in good agreement with the bulk $T_N \sim 13.5$ K. By applying $H||c$, the PM'-to-AFM transitions are gradually suppressed, producing a magnetic dome structure which is typical for an AFM magnet. Above 4 T, there emerges a second magnetic dome with a distinct nature from a SF phase, i.e. canted AFM [17][19][21][22]. As shown in Figure 4c-4f, by fixing $T$ and sweeping $H$, well-defined phase boundaries between the AFM ground state and the MAE-flipped domain only exist below 7 K, above which the two magnetic domes are separated by the PM' phase. It is also conspicuous that, for fixed field of $H = 8$ T, the MAE-flipped dome has a maximum phase transition $T_\parallel$ of 17.5 K, which is significantly higher even when compared with the bulk $T_N$. Utilizing first-principle density functional theory (DFT) calculations (See detailed discussions in SI Note 4), we determine the magnetic ordering for the AFM ground state and the MAE-flipped phase, respectively. For the AFM ground state, we compare different in-plane magnetic configurations with zigzagging Cr-Cl-Cr atomic chains along the a-axis and varying c-axis monoclinic angles from 90° to 90.06°. To meet the two criteria of minimized magnetic coupling energy and a b-easy axis AFM, we determine the a unique in-plane AFM state with a periodicity of four unit cells and quasi-
Figure 3. **Temperature-dependent tunnelling in few-layer CrOCl devices.**  

**a.** $T$-dependent tunnelling of few-layer CrOCl devices reveal an opposite $T$ dependence to the trend of SF transition-controlled tunnelling, which should shift $I_t$ transition thresholds to lower $H$ when TJ devices are warmed up. **b.** Schematic of partial density of states of three occupied $t_{2g}$ orbitals in CrOCl. Due to the Cr$^{3+}$ valence state and an octahedron crystal field, $d_{zx}$, $d_{xy}$ and $d_{yz}$ orbitals of the $t_{2g}$ manifold are half-filled. Note that the conventional octahedron coordinates, in which $x$ and $y$ axes are defined by two Cr-Cl axes within the CrO$_2$Cl$_2$ basal plane, are used here for clarity.

Although atomically thin 2D materials in general exhibit distinctive physical properties from the bulk counterparts, e.g. interlayer coupling driven dimensional crossover in mechanical properties from ML to BL graphene and MoS$_2$ [28, 29], the fascinating MAE flipping controlled magnetic ordering and divergent metamagnetism in few-layer CrOCl unfold the great promises of exploring 2D magnetism in a wide range of vdW layered AFM materials. Being isostructural compounds, it will be appealing to compare 2D magnetism in few-layer TiOCl, VOCl and FeOCl with CrOCl, considering that different numbers of $d$ electrons can drastically change the competition between in-plane EA and out-of-plane MCA. There may be other exotic magnetic mechanism in the 2D limit, such as spin-phonon coupling and magnetostriction in these unique systems with staggered lattices.

**METHODS**

**Single Crystal Synthesis.** High-quality CrOCl single crystals were synthesised by chemical vapour transport of stoichiometrically mixed high-purity $\text{Cr}_2\text{O}_3$ and $\text{CrCl}_3$ powder (Alpha Esar, 99.9%). The containing quartz tube was evacuated to a base pressure of $10^{-2}$ Pa when flame-sealed before loading into a tube furnace.
Single crystals were grown for 7 days in a temperature gradient of 1073 K to 1213 K. Then, the furnace was naturally cooled down to room temperature.

Vibrating-Sample Magnetometer. The bulk magnetisation of CrOCl single crystals were characterised using a vibrating sample magnetometer (VSM) module in a Quantum Design Physical Properties Measurement System (PPMS-9T). During the experiments, a CrOCl single crystal was vibrated sinusoidally, which causes an electrical signal proportional to the sample magnetisation in a stationary signal pick-up coil. The VSM results confirm the high quality of our single crystals, which are in excellent agreement with the literature reports [24].

Magnetic Torque. Magnetic torque measurements are based on a metal-cantilever capacitor geometry. During the torque experiment, a CrOCl single crystal was mounted on a cantilever made of Au foil, which has a thickness of 25 μm. The width of cantilever is 0.3 mm and the vacuum gap between cantilever and the bottom Au electrode is 0.5 mm. By applying an external magnetic field to the sample, torque exerted on the cantilever (τ = μ₀m × H) are detected by measuring the capacitance signals, which are used to deduce the magnetisations of the sample.

Tunnelling Device Fabrication. Few-layer CrOCl flakes were exfoliated from single crystals in an argon-filled glove box to protect the samples from air degradation. Different layer numbers of CrOCl samples were first selected by optical contrast, which were cross-checked by complementary non-contact atomic force microscopy and Raman spectroscopy. During tunnelling junction preparation, top graphene electrodes, few-layer CrOCl and bottom graphene electrodes were picked up sequentially using PC on PDMS, followed by a final transferring step onto pre-patterned Cr/Au electrodes on Si/SiO₂ substrate. The resulting junction are free of interfacial contaminations, which is crucial for probing the intrinsic magnetism of few-layer CrOCl.

Tunnelling Magnetoresistance Measurements. Tunnelling measurements were performed in an Oxford-14 T cryostat. The system is equipped with a sample rotator for angle-dependent measurements with in-plane or out-of-plane magnetic field. The field- and T-dependent TMR and I–V curves were measured using a Keithley 2400.

DFT Calculations. To get the electronic structure of CrOCl, the Vienna ab initio simulation package (VASP) [30, 31] is used, by the method of the projector augmented wave [32] and the generalized gradient approximation (GGA-PBE) [33], in which the exchange-correlation potential was taken into account. The plane-wave cutoff energy is set at about 500 eV and the k-point...
sampling is performed by the Monkhorst-Pack scheme. The total energy is ensured to be converged within $1 \times 10^{-6}$ eV per unit cell and the force threshold is 0.005 eV/Å. For multilayer, the method of SCAN+rVV10 is adopted to describe the Van der Waals (vdW) interaction. The magnetic ground states of CrOCl are calculated using the method of PBE plus effective $U$.[36]

For magnetic anisotropy energy (MAE) calculation, spin-orbit coupling was added as a perturbation term in VASP.

Atomic Force Microscopy. We use a multi-mode Park NX10 AFM to characterise the surface morphology and measure thin-film thicknesses of freshly exfoliated CrOCl crystals adn CrOCl TJ devices after tunnelling experiments. Few-layer microflakes were transferred onto a SiO$_2$/Si substrate and baked in-situ for a few minutes in order to enhance the contact between samples and the substrate.

Raman Spectroscopy. A Witec Alpha-300R Raman system with 532 nm laser excitation was used to perform Raman spectroscopy. The laser power was set to be below 5 mW to avoid excessive heating damage to the samples.

DATA AVAILABILITY

The authors declare that the main data supporting the findings of this study are available within the paper and its Supporting Information files. Extra data are available from the corresponding authors upon request.

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AUTHOR CONTRIBUTIONS

Y.Z. initiated and supervised the project. M.J.Z. and Q.F.H. synthesised and characterised COC crystals, fabricated COC devices and carried out all the measurements, assisted by M.C., Z. L. and F. W.. C.Q.H and Y.H.L. carried out the DFT calculations. M.J.Z., Q.F.H., C.Q.H., J.B.Y., Y.H.L. and Y.Z. analysed the data and wrote the paper with inputs from all authors.

COMPETING FINANCIAL INTERESTS:

The authors declare no competing financial interests.

DATA AVAILABILITY:

The authors declare that the main data supporting the findings of this study are available within the paper and the Supplementary Information file. Extra data are available from the corresponding authors upon reasonable request.