Multi-peak Electronic Density of States in CrBr₃ Revealed by Scanning Tunneling Microscopy

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CrBr₃ is a layered van der Waals material with magnetic ordering down to the 2D limit. So far, the electronic properties of CrBr₃ are relatively unexplored. Here, we present the scanning tunneling microscopy and spectroscopy (STM/S) results of the CrBr₃ thin flakes exfoliated onto a Highly Ordered Pyrolytic Graphite (HOPG) surfaces. Atomic resolution topography images show the crystal structure and the $dI/dV$ spectra exhibit multiple peak features measured at 77 K. The conduction band – valence band peak pairs in the multi-peak $dI/dV$ spectrum agrees very well with all the reported optical transitions in literature. The density of states (DOS) calculated by the density functional theory (DFT) agrees qualitatively with the experimental $dI/dV$ spectrum, except two small peaks near the Fermi energy. The flake degradation is found at the edges of the mono- and bi-layer flakes. The results shown here pave the way toward the fundamental understanding of the CrBr₃.

Keywords: Chromium trihalides, Van der Waals material, 2D ferromagnetism, STM

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Two-dimensional (2D) materials are the state-of-the-art materials for the paramount goal of engineering in the 21st century - minimizing electronic devices toward the atomic level\textsuperscript{1-5}. Starting from 2004, the realization of monolayer graphene\textsuperscript{1} led to the explosive explorations of various 2D materials. This expands to the entire spectrum of material categories, ranging from insulators, semiconductors, semimetals, metals, to superconductors\textsuperscript{1-5}. In 2017, two groups independently demonstrated stable magnetic ordering in 2D materials (CrI\textsubscript{3} and Cr\textsubscript{2}Ge\textsubscript{2}Te\textsubscript{6})\textsuperscript{6,7}, adding the 2D ferromagnetism as a new member of the 2D material family.

Magnetic and optical properties of CrX\textsubscript{3} (X = Cl, Br, and I) have been studied since 1960s\textsuperscript{8-10}. Previous reports have shown that the magnetic transition temperatures of CrCl\textsubscript{3}, CrBr\textsubscript{3} and CrI\textsubscript{3} are 16.8 K, 32.5 K, and 68 K, respectively\textsuperscript{11,12}. Bulk CrBr\textsubscript{3} has a saturated magnetization of ~3\(\mu_B\) per Cr\textsuperscript{3+} ion\textsuperscript{12-14} and has been confirmed to have ferromagnetic ordering at its monolayer limit\textsuperscript{15,16}. Different optical properties, including absorption, reflectance, photoluminescence (PL) and Kerr rotations, exhibit many specific optical transition energies. For examples, CrBr\textsubscript{3} shows positive and negative Kerr rotation peaks at 23,500 cm\textsuperscript{-1} and 26,700 cm\textsuperscript{-1}, which were assigned to charge transfer (CT) transitions of electrons between Cr and Br atoms in the crystal\textsuperscript{17}. Absorption spectrum measured on CrBr\textsubscript{3} shows peaks corresponding to 13,500 cm\textsuperscript{-1}, 14,400 cm\textsuperscript{-1}, 17,500 cm\textsuperscript{-1}, 18,900 cm\textsuperscript{-1}\textsuperscript{18-20}, 24,500 cm\textsuperscript{-1} and 29,500 cm\textsuperscript{-1}\textsuperscript{17,21}. A photoluminescence (PL) peak with energy of 1.35 eV\textsuperscript{22} and reflectance peaks at 2.9 eV, 3.1 eV and 3.8 eV\textsuperscript{23} were also reported. However, so far, a comprehensive understanding of the electronic properties, which are associated with the optical and magnetic properties of CrBr\textsubscript{3}, does not exist.

So far, the electronic properties of CrX\textsubscript{3} were studied by photoemission spectroscopy\textsuperscript{24} and density functional theory (DFT) calculations\textsuperscript{13,23,25}. The 3d states of the Cr and the p states of
the halogen element contribute to the band structures near Fermi energy. The Cr 3d states are well above the halogen p states\textsuperscript{24,26–29}. Beyond that, the electronic density of states (DOS) of CrBr\textsubscript{3} is not well understood. Density of states of CrBr\textsubscript{3} calculated by DFT using different setups and different magnetic orders can be very different \textsuperscript{30,31}. Thus, a direct comparison with the experimental measurements is needed. Here, by utilizing scanning tunneling microscopy and spectroscopy (STM/S), the electronic DOS of the exfoliated CrBr\textsubscript{3} flakes are reported. A few main observations/conclusions are made: (1) the dI/dV spectra measured at 77 K show multi-peak features; (2) the observed dI/dV spectra agree well with the reported optical measurements; (3) the edge degradation is observed; and (4) DFT calculated DOS agrees with the peak features in the measured dI/dV, except two small peaks near the Fermi energy.

**Experiments**

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the Projector-Augmented Wave (PAW) pseudopotentials. Positions of atoms were calculated using a conjugate gradient algorithm, with cell shape and volume as well as atom positions allowed to change. DOS for bulk and monolayer lattices were calculated. The energy cutoff was set to 500 eV and the criteria for energy convergence was set to be $10^{-6}$ eV. Van der Waals (vdW) correction was considered by DFT-D3 method. A vacuum space of 30 Å was adopted in monolayer case. Spin-orbit interaction was taken into consideration, and both the ferromagnetic and paramagnetic ordering were applied.

**Results and Discussions**

CrBr\textsubscript{3} has a layered structure formed by van der Waals force with high in-plane stiffness making it easier to exfoliate into 2D layers\textsuperscript{32}. The CrBr\textsubscript{3} flakes were exfoliated and transferred
onto a highly oriented pyrolytic graphite (HOPG) substrates\textsuperscript{1}. Figure 1(a) shows the exfoliation procedures. Various flakes with different thicknesses are observed with different colors due to the light interference, as shown in Fig. 1(b). The magnetization vs temperature (M–T) measurement, as shown in Fig. 1(c), shows a Curie-Weiss behavior above the transition temperature of 31.5 K, which agrees with the previously reported work ($T_C = 32.5$ K\textsuperscript{11}). Figure 1(d) exhibits the large scale STM topography image showing step features with the smallest height change to be 5.9 Å, corresponding to the single layer thickness of CrBr\textsubscript{3}\textsuperscript{33}.

With a zoom-in STM measurement at 77 K, as shown in Fig. 2(b), atomic resolution images are revealed. Though there are still noises due to unstable measurements, atomic lattice structures can still be resolved. The low quality of the CrBr\textsubscript{3} topography image is probably a result of the combination of the poor conductivity of the CrBr\textsubscript{3} flakes and the fact that the samples were not degassed after loading to the UHV chamber. The bad tip possibility is ruled out by the atomic resolution STM images on nearby HOPG (the substrate) regions, as shown in Fig. S2. As illustrated in Fig. 2(b), the atomic resolution image of the CrBr\textsubscript{3} agrees well with the crystal structure (space group $R\bar{3}$) overlaid onto it. Note that the overlaid crystal structure model is a bilayer structure of CrBr\textsubscript{3}, indicating the topography images are sensitive to the second layer. This observation is different from the recently reported molecular beam epitaxy (MBE) grown CrBr\textsubscript{3}\textsuperscript{16}, in which only the topmost layer structure dominates the STM topography images. This might be due to the different imaging conditions or different sample preparation methods. More STM studies are needed to clarify the origin of the discrepancy.

On the other hand, $dI/dV$ spectra taken at $T = 77$ K with different bias ranges ($\pm$ 0.8 V, $\pm$ 1 V, $\pm$ 2 V and $\pm$ 3 V with higher sensitivity setting in lock-in amplifier for smaller bias range measurements) are shown in Fig. 2(c). These multi-peak features are further confirmed with the
derivative of the measured $I$-$V$ curve shown in Fig. 2(d). All the peaks in the measured $dI/dV$ curves are consistent with the derivative of the measured $I$-$V$ curves. The nine observed peaks are labeled with numbers, $I$-$4$, and letters, $a$-$e$, for peaks in the conduction and valence bands, respectively. It is worth noting that the $dI/dV$ showed two small peaks near Fermi energy (peak “1” (0.25 ± 0.03 eV) and peak “a” (−0.32 ± 0.02 eV)). This makes the energy gap, the energy difference between peak 1 and peak a, equal to 0.57 ± 0.04 eV. This is much smaller than the reported optical energy gap (~1.8−2.1 eV$^{19,24,25}$) of the CrBr$_3$. This indicates that the transition between peaks “1” and “a” is optically forbidden. Interestingly, these two peaks are not reproduced in the calculated DOS.

With these resolved peaks in the $dI/dV$ spectra of CrBr$_3$, the reported optical measurements can be matched to certain conduction-valence band peak pairs. The peak positions are analyzed from a total of eight measured $dI/dV$ spectra and the results are shown in a histogram in Fig. S3(b) and summarized in Table 1. Table S1 shows the energy differences of all possible conduction-valence band peak pairs. And finally, Table 2 lists the reported low temperature optical measurements, including PL$^{22}$, absorption$^{17−21}$ Kerr rotation$^{17,34}$, reflection$^{23}$, and dielectric measurements$^{17}$, and compared with the conduction-valence band peak pairs from Table S1. It is clear from Table 2 that all the reported optical transition energies are matched with certain measured $dI/dV$ conduction-valence band peak pairs. The extremely good agreements between the reported optical transition energies and the measured $dI/dV$ conduction-valence band peak pairs indicate that the measured $dI/dV$ is closely representing the CrBr$_3$ electronic DOS, including the two small peaks near zero bias (peak 1 and a).

Figure 3 shows the DFT calculated DOS of the CrBr$_3$ with the crystal structure shown in Fig. 2(a). Two magnetic phases are considered, ferromagnetic (FM) and paramagnetic (PM). First, it
is found that the DOS for the two phases are very similar (roughly the same energy gaps) with a small difference at the conduction band side and they qualitatively agree with the dI/dV spectra shown in Fig. 2(c). This similarity explains why the comparison between our dI/dV spectra measured at 77 K agrees well with the reported optical transitions measured at much lower temperature (see Table 2). Second, the calculated DOS agrees qualitatively with the dI/dV spectra (Fig. 2(c)). However, the peaks “I” and “a” in the dI/dV spectrum are not reproduced in the DFT calculated DOS (Fig. 3). The calculated DOS in literature also does not show any sign of these two peaks. This discrepancy is directly related to the energy gap value of the CrBr$_3$. The energy gap in the DFT calculated DOS (Fig. 3) is 1.4 – 1.5 eV, much higher than the energy gap (0.57 eV) revealed in the dI/dV spectrum (Fig. 2(c)). The reported DFT calculated DOS exhibit the energy gap in the range of 1.15 eV – 2.7 eV$^{30-32,35}$ and with various overall shape of DOS, as summarized in Fig. S4. The differences in the DOS among different calculated results originate from the different settings. However, the differences compared to the dI/dV spectra shown here infer that there might be some interesting mechanisms not captured by any of these reported DFT calculations. Thus, the results here call for more exploration of the DOS calculations.

Next, let’s move our attention to the CrBr$_3$ monolayer. Figures 4 (a) and (b) show the topography and dI/dV mapping of a CrBr$_3$ monolayer measured at 77 K. The clear dI/dV contrast (Fig. 4(b)) unambiguously distinguishes the substrate HOPG and the CrBr$_3$ monolayer flake. The dI/dV spectrum (Fig. 4(c)) measured on the CrBr$_3$ monolayer exhibits a similar shape as the dI/dV spectrum measured on HOPG (Fig. S2(d)) with additional humps in the positive bias side matching the measured peaks on the bulk CrBr$_3$ dI/dV spectrum (Fig. 2(c)). We believe that the combined spectral features are due to the interactions between the monolayer CrBr$_3$ and the
underneath HOPG layer. This observation further confirms that the STM measurements on CrBr$_3$ are sensitive to the second layer materials.

The monolayer thickness is confirmed and measured by the line profile across the substrate (HOPG) and the monolayer flake (Fig. 4(d)) as ~4.8 Å, which is smaller than the step height (5.9 Å) found in the bulk region (Fig. 1(d)). This smaller apparent height is most likely due to the electronic contrast between the CrBr$_3$ and HOPG. As the HOPG is more conductive than CrBr$_3$, under the constant current scanning mode, the tip-sample distance will be smaller for tip-CrBr$_3$ compared to the tip-HOPG case, which leads to ~1 Å lower apparent height. On the CrBr$_3$ monolayer flake, there are a few small islands, which are the second layer CrBr$_3$, judged by the similar dI/dV contrast. The height of the second layer on top of the CrBr$_3$ monolayer is measured to be 3.8 Å (Fig. 4(e)), which is even smaller than the monolayer case (4.8 Å). We believe this is because of the incomplete CrBr$_3$ second layer due to the edge degradation and the small island size. The round shape, instead of flat top shape, topography profile (Fig. 4(e)) is a clear evidence of this. The degradation, due to the short air exposure prior to the loading into the UHV chamber, is also clearly seen in Fig. 4(b). The edge of the monolayer is curved and exhibits high dI/dV contrast with uniform lateral length scale of ~2.3 nm. Similar degradation is also observed at the edge of the second layer with ~1.5 nm lateral length scale. The smaller lateral length scale of the degradation in the second layer indicates either (i) the edge in the multilayer is relatively more stable than that of the monolayer edge; or (ii) the smaller lateral sizes of the second layer islands measured here limiting the degradation process.

Conclusions
Using STM/S, atomic resolution image and electronic properties of CrBr$_3$ flakes have been explored. The electronic band gap of CrBr$_3$ measured at 77 K is observed to be $0.57 \pm 0.04$ eV and it is argued that this energy gap may not be optically active. Atomic resolution image fits the bilayer structure, indicating the second layer crystal also has influences on the STM measurements. Same effects are observed for the monolayer on the HOPG substrate. Multiple peak features in $dI/dV$ spectrum are observed at 77 K and match well with all the reported optical measurements of the CrBr$_3$. The DOS calculated by DFT exhibits a band gap of $1.4-1.5$ eV, which is much higher than the experimental energy gap (0.57 eV). This deviation is mainly due to the missing peaks (peaks “$I$” and “$a$”) in the DFT calculations. Further investigation is needed to understand the origin of such discrepancy. All these observations provide solid information regarding the experimental electronic properties of the bulk and monolayer CrBr$_3$. It can also be the basis of further understanding of the magnetic and optical properties of this material.

**Methods**

The magnetization measurement was carried out with a Quantum Design Physical Property Measurement System (PPMS) on a single crystal CrBr$_3$ with a DC magnetic field of 500 Oe. CrBr$_3$ has a layered structure formed by van der Waals force with high in-plane stiffness making it easier to exfoliate into 2D layers$^{32}$. In this study, the “scotch-tape” method$^{1}$ was used to directly exfoliate the CrBr$_3$ flakes (single crystals CrBr$_3$ bought from hq graphene) onto a highly oriented pyrolytic graphite (HOPG) or Si wafer substrates$^1$. First, a blue industrial tape is attached onto the top surface of a CrBr$_3$ crystal. When the blue tape is removed from the crystal, many CrBr$_3$ flakes were exfoliated from the crystal. A polydimethylsiloxane (PMDS) stamp is then in contact with the blue tape for the second exfoliation. Finally, the CrBr$_3$ flakes are transferred onto the desired substrate. It is worth noting that a slow peeling rate of PDMS could
get more flakes transferred onto the target substrate. HOPG substrate is used for STM measurements; while Si wafer is used for scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

This exfoliation process was done in an ambient environment and the sample was transferred to the ultra-high vacuum (UHV) chamber within ~15 minutes of the air exposure. No annealing procedure has been carried out after loading CrBr$_3$/HOPG into UHV prior to STM measurements to avoid any possible evaporation of the atoms. The STM measurements were conducted with a base pressure ~ $10^{-11}$ mbar. $dI/dV$ signals were recorded with 997 Hz modulation frequency and 1 ms time constant in lock-in setup. STM imaging was done with 450 $\times$ 450 points for each topography and $dI/dV$ images.

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the Projector-Augmented Wave (PAW) pseudopotentials. Positions of atoms were calculated using a conjugate gradient algorithm, with cell shape and volume as well as atom positions allowed to change. DOS for bulk and monolayer lattices were calculated. The energy cutoff was set to 500 eV and the criteria for energy convergence was set to be $10^{-6}$ eV. Van der Waals (vdW) correction was considered by DFT-D3 method. A vacuum space of 30 Å was adopted in monolayer case. Spin-orbit interaction was taken into consideration, and both the ferromagnetic and paramagnetic ordering were applied.

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**Author Contributions**

D.B performed STM measurements. Z.F performed EDS. A. S. Z. calculated DOS from DFT calculations. N.S and U.E provide PPMS measurements. All authors contributed to the manuscript writing and discussion for the conclusions.

**Competing Interests statement**

The authors declare no competing interests.

**References**

1. Novoselov, K. S. *et al.* Electric Field Effect in Atomically Thin Carbon Films. *Science* **306**, 666–669 (2004).

2. Novoselov, K. S., Mishchenko, A., Carvalho, A. & Castro Neto, A. H. 2D materials and van der Waals heterostructures. *Science* **353**, aac9439 (2016).

3. Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. *Nature* **499**, 419–425 (2013).

4. Fiori, G. *et al.* Electronics based on two-dimensional materials. *Nat. Nanotechnol.* **9**, 768–779 (2014).

5. Ajayan, P., Kim, P. & Banerjee, K. Two-dimensional van der Waals materials. *Phys. Today* **69**, 38–44 (2016).

6. Huang, B. *et al.* Layer-dependent ferromagnetism in a van der Waals crystal down to the
monolayer limit. *Nature* **546**, 270–273 (2017).

7. Gong, C. *et al.* Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals. *Nature* **546**, 265–269 (2017).

8. Tsubokawa, I. On the Magnetic Properties of a CrBr$_3$ Single Crystal. *J. Phys. Soc. Japan* **15**, 1664–1668 (1960).

9. Gossard, A. C., Jaccarino, V. & Remeika, J. P. Experimental Test of the Spin-Wave Theory of a Ferromagnet. *Phys. Rev. Lett.* **7**, 122–124 (1961).

10. Davis, H. L. & Narath, A. Spin-wave renormalization applied to ferromagnetic CrBr$_3$. *Phys. Rev.* **134**, A433–A441 (1964).

11. Bené, R. W. Electron-Paramagnetic-Resonance study of Cr ions and exchange-coupled Cr ion pairs in the BiI$_3$ structure. *Phys. Rev.* **178**, 497–513 (1969).

12. Senturia, S. D. & Benedek, G. B. Nuclear Resonance in Ferromagnetic Chromium Tribromide from 4.2 K to the Curie Point. *Phys. Rev. Lett.* **17**, 475–478 (1966).

13. Wang, H., Eyert, V. & Schwingenschlögl, U. Electronic structure and magnetic ordering of the semiconducting chromium trihalides CrCl$_3$, CrBr$_3$, and CrI$_3$. *J. Phys. Condens. Matter* **23**, 116003 (2011).

14. Radhakrishna, P. & Brown, P. J. Polarized neutron-diffraction study of spin-density distribution in chromium tribromide. *Phys. Rev. B* **36**, 8765–8771 (1987).

15. Kim, M. *et al.* Hall micromagnetometry of individual two-dimensional ferromagnets. *arXiv* arXiv:1902.06988 (2019).

16. Chen, A. W. *et al.* Direct observation of van der Waals stacking governed interlayer
magnetism. *arXiv* arXiv:1906.03383 (2019).

17. Jung, W. Dielectric Constant and Magneto-Optical Kerr Rotation of Ferromagnetic Chromium Tribromide above the Absorption Band Edge. *J. Appl. Phys.* **36**, 2422–2426 (1965).

18. Wood, D. L., Ferguson, J., Knox, K. & Dillon, J. F. Crystal-Field Spectra of $d^{3-7}$ Ions. III. Spectrum of Cr$^{3+}$ in Various Octahedral Crystal Fields. *J. Chem. Phys.* **39**, 890–898 (1963).

19. Kanazawa, K. K. & Street, G. B. The Electrical Properties of Chromium Tribromide. *Phys. Status Solidi* **38**, 445–450 (1970).

20. Dillon, J. F., Kamimura, H. & Remeika, J. P. Magneto-Optical Studies of Chromium Tribromide. *J. Appl. Phys.* **34**, 1240–1245 (1963).

21. Dillon, J. F., Kamimura, H. & Remeika, J. P. Magneto-Optical Properties of Ferromagnetic Chromium Trihalides. *J. Phys. Chem. Solids* **27**, 1531–1549 (1966).

22. Zhang, Z. *et al.* Direct photoluminescence probing of ferromagnetism in monolayer two-dimensional CrBr$_3$. *Nano Lett.* **19**, 3138–3142 (2019).

23. Pollini, I., Thomas, J., Carricaburu, B. & Mamy, R. Optical and electron energy loss experiments in ionic CrBr$_3$ crystals. *J. Phys. Condens. Matter* **1**, 7695–7704 (1989).

24. Pollini, I. Electronic structure of CrBr$_3$ studied by x-ray photoelectron spectroscopy. *Phys. Rev. B* **60**, 16170–16175 (1999).

25. Huang, C. *et al.* Prediction of Intrinsic Ferromagnetic Ferroelectricity in a Transition-Metal Halide Monolayer. *Phys. Rev. Lett.* **120**, 147601 (2018).
26. Pollini, I. Photoemission study of the electronic structure of CrCl$_3$ and RuCl$_3$ compounds. 
   *Phys. Rev. B* **50**, 2095–2103 (1994).

27. Pollini, I. Multiplet splitting of core-electron binding energies in chromium compounds. 
   *Phys. Rev. B* **67**, 155111 (2003).

28. Carricaburu, B., Mamy, R. & Pollini, I. Valence band photoelectron spectra of CrBr$_3$ insulators. *J. Phys. Condens. Matter* **3**, 8511–8517 (1991).

29. Antoci, S. & Mihich, L. Determination of the self-consistent band structure of CrCl$_3$, CrBr$_3$, NiCl$_2$, and NiBr$_2$ by the intersecting-spheres model. *Phys. Rev. B* **18**, 18 (1978).

30. Li, H., Xu, Y.-K., Lai, K. & Zhang, W.-B. The enhanced ferromagnetism of single-layer CrX$_3$ (X = Br and I) via van der Waals engineering. *Phys. Chem. Chem. Phys.* **21**, 11949 (2019).

31. Liu, J., Sun, Q., Kawazoe, Y. & Jena, P. Exfoliating biocompatible ferromagnetic Cr-trihalide monolayers. *Phys. Chem. Chem. Phys.* **18**, 8777–8784 (2016).

32. Zhang, W., Qu, Q., Zhu, P. & Lam, C. Robust intrinsic ferromagnetism and half semiconductivity in stable two-dimensional single-layer chromium trihalides. *J. Mater. Chem. C* **3**, 12457–12468 (2015).

33. Richter, N. *et al.* Temperature-dependent magnetic anisotropy in the layered magnetic semiconductors CrI$_3$ and CrBr$_3$. *Phys. Rev. Mater.* **2**, 024004 (2018).

34. Shinagawa, K., Suzuki, T., Saito, T. & Tsushima, T. Magnetic Kerr effect and charge transfer transitions in ferromagnetic chromium tribromide. *J. Magn. Magn. Mater.* **140–144**, 171–172 (1995).
35. Wang, H., Eyert, V. & Schwingenschlögl, U. Electronic structure and magnetic ordering of the semiconducting chromium trihalides CrCl$_3$, CrBr$_3$, and CrI$_3$. *J. Phys. Condens. Matter* **23**, 116003 (2011).
Figure 1. Device fabrication and sample confirmation: a, Schematic of “scotch-tape” technique used to exfoliate CrBr$_3$ flakes onto a HOPG substrate. b, Optical image of transferred CrBr$_3$ flakes on a HOPG substrate. c, Magnetization (M) vs temperature (T) measurement showing a transition temperature of 31.5 K. d, STM topography image of CrBr$_3$ multilayers at room temperature (Bias: 2 V, setpoint current: 400 pA) with height profile corresponding to monolayer thickness.
Figure 2. STM/S studies of multilayer CrBr$_3$: a, Crystal structure of CrBr$_3$ (ML: monolayer, BL: bilayer). In BL structure, green represents Cr atom at top layer, blue represents Cr at bottom layer and sky-blue represents Cr atoms on both layers. b, Atomic resolution STM image of CrBr$_3$ multilayer sample (Bias: 1 V, set current: 1 nA). Magnified view of the region marked by blue dashed box overlaid with BL crystal structure of CrBr$_3$. c, dI/dV spectra of CrBr$_3$ taken at 77 K with different bias ranges. d, Comparison between the numerical derived dI/dV spectrum (blue) calculated from the I-V curve (red) and the lock-in amplifier measured dI/dV spectrum (green). Insets are the magnified view to show features underlying in the bias range of ±0.5 V.
Figure 3. DOS of bulk CrBr₃: Comparison of DFT calculation (black for FM phase and blue for PM phase) with the $dI/dV$ spectra (green and red).
Figure 4. Monolayer and bilayer CrBr$_3$ topography and $dI/dV$ measured at 77 K.: a, Topography and b, $dI/dV$ images of the monolayer CrBr$_3$ on HOPG and small second layer islands on top of the monolayer CrBr$_3$. Imaging condition: bias = 4 V; set current = 400 pA. c, $dI/dV$ spectrum of the monolayer CrBr$_3$ on HOPG. d and e, Line profiles of the topography and $dI/dV$ mappings across the HOPG/monolayer (line 1) and monolayer/bilayer/monolayer (line 2), as indicated with green lines in (a) and (b).
Table 1. Peak positions of the labeled peaks in Fig. 2(c).

| Assigned peak symbols | Peak positions (eV) |  
|-----------------------|---------------------|
| 4                     | 2.38 ± 0.06         |
| 3                     | 1.82 ± 0.04         |
| 2                     | 0.95 ± 0.04         |
| 1                     | 0.25 ± 0.03         |
| a                     | − 0.32 ± 0.02       |
| b                     | − 0.83 ± 0.04       |
| c                     | − 1.43 ± 0.02       |
| d                     | − 2.06 ± 0.01       |
| e                     | − 2.72 ± 0.01       |

Conduction band

Valance band
**Table 2.** Comparison between the energies of the reported optical transitions and the conduction-valence peak pairs.

| Measurement | Measurement temperature | Assigned transition | Reported energy gap (eV) | Corresponding energy gap (eV) | Peak pair | Peak pair energy (eV) | Ref. |
|-------------|-------------------------|---------------------|--------------------------|------------------------------|-----------|----------------------|------|
| PL          | 2.7 K                   |                     | 1.35                     | 1.35                         | 2 – a     | 1.27 ± 0.04          | 22   |
| Abs.        | 4.2 K                   | $^2T_2$             | 13500 cm$^{-1}$          | 1.68                         | 1 – c     | 1.68 ± 0.04          | 18,20 |
| Abs.        | 4.2 K                   | $^2T_1$             | 14400 cm$^{-1}$          | 1.79                         | 2 – b     | 1.78 ± 0.06          | 18,20 |
| Abs.        | 4.2 K                   | $^4T_1$             | 17500 cm$^{-1}$          | 2.17                         | 3 – a     | 2.14 ± 0.04          | 18,20 |
| Abs.        | 4.2 K                   | $^2T_2$             | 18900 cm$^{-1}$          | 2.36                         | 2 – c or 1 – d | 2.38 ± 0.04 or 2.31 ± 0.03 | 20   |
| Abs.        | 4.2 K                   |                     | 19200 cm$^{-1}$          | 2.38                         | 1 – d     | 2.31 ± 0.03          | 18   |
| Kerr (+ max)| 1.5 K                   | $t_{uu} \rightarrow e_g^*$ | 23500 cm$^{-1}$          | 2.92                         | 1 – e or 2 – d | 2.97 ± 0.03 or 3.01 ± 0.04 | 17,21,36 |
| Abs.        | 1.5 K                   | $t_{uu} \rightarrow e_g^*$ | 24500 cm$^{-1}$          | 3.04                         |           |                      | 21   |
| Abs.        | 1.5 K                   |                     | 24310 cm$^{-1}$          | 3.02                         |           |                      | 17   |
| Refl.       | 30 K                    |                     | 3.1 eV                   | 3.1                          |           |                      | 23   |
| Dielectric  | 1.5 K                   |                     | 25000 cm$^{-1}$          | 3.1                          |           |                      | 17   |
| Kerr (− max)| 1.5 K                   | $t_{uu} \rightarrow e_g^*$ | 26700 cm$^{-1}$          | 3.29                         | 3 – c or 4 – b | 3.25 ± 0.04 or 3.21 ± 0.07 | 17,36 |
| Kerr (− max)| 1.5 K                   | $t_{uu} \rightarrow e_g^*$ | 26500 cm$^{-1}$          | 3.29                         | 3 – c or 4 – b | 3.25 ± 0.04 or 3.21 ± 0.07 | 36   |
| Abs.        | 1.5 K                   |                     | 29500 cm$^{-1}$          | 3.66                         | 2 – e     | 3.67 ± 0.04          | 21   |
| Abs.        | 1.5 K                   |                     | 29580 cm$^{-1}$          | 3.67                         |           |                      | 17   |
| Refl.       | 30 K                    |                     | 3.8 eV                   | 3.8                          | 4 – c or 3 – d | 3.81 ± 0.06 or 3.88 ± 0.04 | 23   |