**Ultrafast Exciton and Carrier Dynamics in Bulk CrSBr**

Lawson T. Lloyd1, Tommaso Pincelli1,2, Túlio de Castro1, Ferdinand Menzel3, Zdeněk Sofer4, Nathan P. Wilson3, Martin Wolf1, Laurenz Rettig1, and Ralph Ernstorfer\*,1,2

1. Fritz-Haber-Institut der Max Planck Gesellschaft, Berlin, Germany
2. Technische Universität Berlin, Berlin, Germany
3. Walter Schottky Institut, Department of Physics, School of Natural Sciences, Technische Universität München, Garching, Germany
4. Chemistry Department, University of Chemistry and Technology Prague, 16628 Prague, Czech Republic

\* Corresponding author: ernstorfer@fhi-berlin.mpg.de

**ABSTRACT**

Van der Waals (vdW) layered magnets have the potential to enable novel optoelectronic and spintronic applications. Among these, CrSBr is a direct band gap semiconductor that hosts interlayer antiferromag- netic order, a highly anisotropic, quasi-1D electronic structure, and strongly bound excitons. However, understanding how the carrier and exciton dynamics couple to the underlying spin order is currently lack- ing. Here, we employ time- and angle-resolved photoemission spec- troscopy to map the temperature-dependent band structure and car- rier dynamics in bulk CrSBr. We observe an electronic band splitting that emerges below the magnetic transition temperature, which we in- terpret as arising from a super-exchange mechanism giving rise to in- tralayer ferromagnetism. Time-resolved measurements reveal a rapid band renormalization of the lower conduction band that occurs during photoexcitation, pointing towards complex many-body effects govern- ing the excited state dynamics and optical properties. These results provide important experimental observations of the low-temperature electronic band structure and shed further light on the microscopic interactions driving carrier dynamics and spin order in this vdW mag- net.

**Introduction**

[2D Magnets etc]. CrSBr is a van der Waals layered magnetic semiconductor that with a direct electronic band gap, highly anisotropic optical and electronic properties, as well as pronounced many-body exciton physics which couple to the underlying magnetic order. (*1*–*4*) [Ultrfast] Previous time-resolved studies have uncovered coherent exciton-magnon coupling persisting to the nanosecond timescale (*2*, *5*, *6*) and as well as few to sub-picosecond exciton decay dynamics in bulk and monolayer CrSBr. (*7*)

Recently, trARPES has proved an incisive technique to directly probe the energetics and momentum distribtuino of bound excitons in a variety of systems. (*8*)

Here, we employ time- and angle-resolved photoemission (trARPES) to map the photoinduced dynamics and directly probe momentum space excitonic distribution in bulk CrSBr on femtosecond timescales.

**Results and Discussion**

To map the electronic band structure and photoinduced dynamics of bulk CrSBr, we perform time-and angle-resolved photoemission spectroscopy (trARPES) with tunable femtosecond pump pulses. Leveraging momentum microscopy, which allows for the simultaneous acquisition of both in-plane momenta (kx, ky) and provides a global view of the electronic band structure in a single experiment (**Figure 1**). (*9*, *10*) We perform ARPES at temperatures above and below the reported bulk magnetic transition temperature (TN ~ 132 K), at which the system hosts interlayer antiferromagnetic ordering, with intralayer ferromagnetic order persisting to higher temperatures temperature (TC ~ 165 K). (*11*) **Figure 1a** shows a two-dimensional (*kx, ky*) momentum map near the valence band maximum (VBM) at room-temperature. While the central (*kx=ky=*0) point shows suppressed intensity, the point of the second Brillouin zone is more intense, as observed previously. (*12*, *13*). After 800 nm photoexcitation, we observe population above the valence band at higher energies as well, featuring quasi-flat dispersion along -X different to the momentum map of the valence band maximum. Such a quasi-one dimensional band has recently been observed in ARPES of few-layer CrSBr in contact with metallic substrates. (*14*) Our observations of the transient electronic band structure provide further evidence of the quasi-one dimensional nature of this material. (*15*)

In particular, we observe two distinct features at E ~ 1.3 eV and E ~ 2.0 eV, both displaying the characteristic quasi-1D dispersion along -X. … In particular, the observation of the high energy feature at E = 2.0 eV is striking considering the pump excitation energy of 1.5 eV should not lead to direct optical excitation.

While there is a rapid rise of the lower energy feature, the upper feature at E = 2.0 eV exhibits a pronounced growth after photoexcitation, pointing to a dynamical process that populates this state after the initiation photoexcitation.

Additionally, the dynamics at different momenta along -X do not change appreciably (Figure ). This observation suggests…

Initial experimental studies estimated the electronic band gap of bulk CrSBr to be around 1.5 eV. However, recent ARPES works imply a larger band gap of nearly 2 eV or greater. (*12*) Recently, ARPES measurements of alkali-dosed samples indeed report a measured electronic band gap of at least 1.84 eV (*16*) while the exciton signatures responsible for the optical gap are found near ~1.35 eV. (*1*, *15*)

While these works therefore suggest an exciton binding energy of well over 0.5 eV based on photoluminescence measurements with exciton signatures of around ~1.35 eV, a direct, momentum- and energetically resolved picture of the excitons in CrsBr is so far lacking. Here, we provided experimental signatures of both the single-particle conduction band and exciton states in bulk CrSBr after photoexcitation, from which we extract an exciton binding energy of > 700 meV at room-temperature.

Exciton formation has been shown to occur in tens of femtoseconds intransition metal dichalcogenides (*17*)

Excitation density and the Mott transition (*18*) in transition metal dichalcogenides. (*19*)

**Methods**

Time- and angle-resolved photoemission measurements were performed Bulk crystals were grown by … []. For ARPES measurements, bulk crystals were mechanically cleaved in ultrahigh vacuum in base pressures better than 10-10 mbar. ARPES OPCPA (*20*) operating at 500 kHz (*9*, *10*) as well as using a helium discharge lamp (21.2 eV).

Previous investigations of two-dimensional semiconductors using ARPES have noted the presence of sample charging due to the photocurrent. In this work, we see clear effects of charging by a shifting of the energy scale at temperatures below T ~ 110 K, and thus we limit our measurements to temperatures above this limit.

To map the electronic band structure of bulk CrSBr, we first perform ARPES based on momentum microscopy, which allows for the simultaneous acquisition of both in-plane momenta (kx, ky), providing a global view of the electronic band structure in a single experiment (**Figure 1**). We perform ARPES at temperatures above and below the reported bulk magnetic transition temperature (TN ~ 132 K), at which the system hosts interlayer antiferromagnetic ordering, with intralayer ferromagnetic order persisting to higher temperatures temperature (TC ~ 165 K). (*11*) **Figure 1** shows a two-dimensional (*kx, ky*) momentum map near the valence band maximum (VBM) at room-temperature and T = 115 K, together with cuts through the annotated high symmetry directions. Both the momentum map and the high symmetry cuts display the anisotropic dispersion along the two orthogonal directions (-X, -Y). While the central (*kx=ky=*0) Gamma point shows suppressed intensity, the Gamma point of the second Brillouin zone is more intense, as observed previously. (*12*, *13*). Interestingly, we observe weak but finite intensity at much higher energies (>1 eV) than the VBM, likely arising from intrinsic sample doping that leads to a weak but finite population in the conduction band (**Figure 2**). Here, we extract an estimated ~1.5 eV single particle band gap for bulk CrSBr at low temperature, in good agreement with previous theoretical and experimental works. () Momentum maps near the conduction band minimum (CBM) display a band with quasi-flat dispersion along -X. Such a flat band is predicted and has recently been observed in ARPES of few-layer CrSBr in contact with metallic substrates. Our observations of the equilibrium band structure of the bulk CrSBr provide further evidence of the quasi-one dimensional nature of this material. (*15*)

Further comparing the data acquired at high and low temperature, … we observe a sharpening of features.

To focus on the effect of magnetic order on the electronic structure, we perform ARPES measurements using a hemispherical electron energy analyzer, both which XUV ionizing radiation laser based high-harmonic generation as well as a He discharge lamp and a which provides a much higher energy resolution. In **Figure 3**, energy-momentum cuts along the high symmetry S-Y-S direction are shown for room-temperature and T = 115 K. At low temperature, two distinct features separated by ~few hundred meV appear together at Y roughly ~1.5 eV below the VBM. However, these features are not resolvable at elevated temperatures (**Figures 3b,c**). Instead only a single, broad peak appears visible, possibly correlated to the transition to the magnetically ordered state at low temperature. Energy distribution curves (EDCs) at Y for both temperatures highlight these features likely arise from a splitting of the single feature present at room-temperature, and do not arise solely from, e.g., a linewidth narrowing with reduction in temperature.

To better understand the effect of temperature on the band structure, we track the band evolution from T = 120 K to room-temperature (**Figure 4**), through both relevant magnetic transition temperatures of T ~ 132 K and T ~ 165 K. The two separated features (**Figure 3**) are clearly resolvable for temperatures up to T ~ 140K, above the antiferromagnetic ordering. While these peaks begin to converge at higher temperatures, an asymmetry persists to temperatures in proximity to T ~ 165K, suggesting the separation of these features is related to the intralayer ferromagnetic ordering of bulk CrSBr at low temperatures.

The ferromagnetic ordering in CrSBr has been proposed to be driven by a superexchange between Cr ions mechanism mediated by halide ions, as both Cr-S-Cr and Cr-Br-Cr bond angles are near 90. [] We compare our experimental band structure to theoretical calculations by Bianchi *et al* [], which reveal a dominant Br and Cr character of the relevant bands at Y that we observe to evolve as a function of temperature (**Figure 5**). Thus, our experimental results provide strong evidence for a dominating Cr-Br-Cr superexchange mechanism giving rise to ferromagnetism. These results indicate a marker for the effect of spin order on the electronic band structure and as well as a driving mechanism for intralayer ferromagnetic magnetic ordering bulk CrSBr.

**Figure 1**. Schematic of (a) bulk CrSBr displaying interlayer antiferromagnetism, and (b) the experimental configuration combining a momentum microscope and hemispherical analyzer for ARPES measurements. (c) Two-dimensional (*kx, ky*) momentum map at the valence band maximum of bulk CrSBr acquired at T = 120 K. (d) Cuts along the high-symmetry path annotated in (a). The data is acquired by averaging a continuous modulation of the XUV linear polarization between s- and p-polarization.

**Figure 2**. S-Y-S cuts at (a) T = 330 K and (b) T = 115 K show a splitting of a feature centered at Y below the magnetic transition temperature (TN = 132 K). Energy distribution curves (c) reveal a splitting of ~500 meV between the two temperatures. (d) Tracking the splitting as a function of temperature across the phase transitions…

**Figure 3**. A near-900 Cr-Br-Cr bond angle (a) supports a potential superexchange mechanism driving the intralayer ferromagnetism in CrSBr. (b)

**Figure x**. A momentum map (a) resolves the lower conduction bands due to the intrinsic sample doping.

(*12*)

**Author Contributions**

L.T.L, T.P., and T.d.C. performed ARPES experiments. F.M., N.P.W, Z.S. provided bulk crystal samples. M.W., L.R., and R.E. provided funding and infrastructure. L.T.L wrote the manuscript with input from all authors.

**Acknowledgements**

This work was funded […]. L.T.L acknowledges financial support from the Alexander von Humboldt Foundation.

**References**

1. N. P. Wilson, K. Lee, J. Cenker, K. Xie, A. H. Dismukes, E. J. Telford, J. Fonseca, S. Sivakumar, C. Dean, T. Cao, X. Roy, X. Xu, X. Zhu, Interlayer electronic coupling on demand in a 2D magnetic semiconductor. *Nat. Mater.* **20**, 1657–1662 (2021).

2. Y. J. Bae, J. Wang, A. Scheie, J. Xu, D. G. Chica, G. M. Diederich, J. Cenker, M. E. Ziebel, Y. Bai, H. Ren, C. R. Dean, M. Delor, X. Xu, X. Roy, A. D. Kent, X. Zhu, Exciton-coupled coherent magnons in a 2D semiconductor. *Nature* **609**, 282–286 (2022).

3. M. E. Ziebel, M. L. Feuer, J. Cox, X. Zhu, C. R. Dean, X. Roy, CrSBr: An Air-Stable, Two-Dimensional Magnetic Semiconductor. *Nano Lett.* **24**, 4319–4329 (2024).

4. N. J. Brennan, C. A. Noble, J. Tang, M. E. Ziebel, Y. J. Bae, Important Elements of Spin-Exciton and Magnon-Exciton Coupling. *ACS Phys. Chem Au* **4**, 322–327 (2024).

5. G. M. Diederich, J. Cenker, Y. Ren, J. Fonseca, D. G. Chica, Y. J. Bae, X. Zhu, X. Roy, T. Cao, D. Xiao, X. Xu, Tunable interaction between excitons and hybridized magnons in a layered semiconductor. *Nat. Nanotechnol.*, 1–6 (2022).

6. Y. Sun, F. Meng, C. Lee, A. Soll, H. Zhang, R. Ramesh, J. Yao, Z. Sofer, J. Orenstein, Dipolar spin wave packet transport in a van der Waals antiferromagnet. *Nat. Phys.*, 1–7 (2024).

7. C. Meineke, J. Schlosser, M. Zizlsperger, M. Liebich, N. Nilforoushan, K. Mosina, S. Terres, A. Chernikov, Z. Sofer, M. A. Huber, M. Florian, M. Kira, F. Dirnberger, R. Huber, Ultrafast Exciton Dynamics in the Atomically Thin van der Waals Magnet CrSBr. *Nano Lett.* **24**, 4101–4107 (2024).

8. S. Dong, M. Puppin, T. Pincelli, S. Beaulieu, D. Christiansen, H. Hübener, C. W. Nicholson, R. P. Xian, M. Dendzik, Y. Deng, Y. W. Windsor, M. Selig, E. Malic, A. Rubio, A. Knorr, M. Wolf, L. Rettig, R. Ernstorfer, Direct measurement of key exciton properties: Energy, dynamics, and spatial distribution of the wave function. *Natural Sciences* **1**, e10010 (2021).

9. M. Puppin, Y. Deng, C. W. Nicholson, J. Feldl, N. B. M. Schröter, H. Vita, P. S. Kirchmann, C. Monney, L. Rettig, M. Wolf, R. Ernstorfer, Time- and angle-resolved photoemission spectroscopy of solids in the extreme ultraviolet at 500 kHz repetition rate. *Review of Scientific Instruments* **90**, 023104 (2019).

10. J. Maklar, S. Dong, S. Beaulieu, T. Pincelli, M. Dendzik, Y. W. Windsor, R. P. Xian, M. Wolf, R. Ernstorfer, L. Rettig, A quantitative comparison of time-of-flight momentum microscopes and hemispherical analyzers for time- and angle-resolved photoemission spectroscopy experiments. *Review of Scientific Instruments* **91**, 123112 (2020).

11. F. Pei, J. Yu, J. Zhou, S. Wang, D. Liu, Y. Yuan, L. Xi, F. Jin, X. Kan, C. Wang, L. Wang, W. Yan, Y. Wu, S. Wang, K. Chen, T. Ma, X. Liu, M. Yang, Q. Li, Surface-Sensitive Detection of Magnetic Phase Transition in Van Der Waals Magnet CrSBr. *Advanced Functional Materials* **n/a**, 2309335.

12. M. Bianchi, S. Acharya, F. Dirnberger, J. Klein, D. Pashov, K. Mosina, Z. Sofer, A. N. Rudenko, M. I. Katsnelson, M. van Schilfgaarde, M. Rösner, P. Hofmann, Paramagnetic Electronic Structure of CrSBr: Comparison between Ab Initio GW Theory and Angle-Resolved Photoemission Spectroscopy. *Phys. Rev. B* **107**, 235107 (2023).

13. M. Bianchi, K. Hsieh, E. J. Porat, F. Dirnberger, J. Klein, K. Mosina, Z. Sofer, A. N. Rudenko, M. I. Katsnelson, Y. P. Chen, M. Rösner, P. Hofmann, Charge transfer-induced Lifshitz transition and magnetic symmetry breaking in ultrathin CrSBr crystals. arXiv arXiv:2307.12675 [Preprint] (2023). https://doi.org/10.48550/arXiv.2307.12675.

14. M. Bianchi, K. Hsieh, E. J. Porat, F. Dirnberger, J. Klein, K. Mosina, Z. Sofer, A. N. Rudenko, M. I. Katsnelson, Y. P. Chen, M. Rösner, P. Hofmann, Charge transfer induced Lifshitz transition and magnetic symmetry breaking in ultrathin CrSBr crystals. *Phys. Rev. B* **108**, 195410 (2023).

15. J. Klein, B. Pingault, M. Florian, M.-C. Heißenbüttel, A. Steinhoff, Z. Song, K. Torres, F. Dirnberger, J. B. Curtis, M. Weile, A. Penn, T. Deilmann, R. Dana, R. Bushati, J. Quan, J. Luxa, Z. Sofer, A. Alù, V. M. Menon, U. Wurstbauer, M. Rohlfing, P. Narang, M. Lončar, F. M. Ross, The Bulk van der Waals Layered Magnet CrSBr is a Quasi-1D Material. *ACS Nano* **17**, 5316–5328 (2023).

16. S. Smolenski, M. Wen, Q. Li, E. Downey, A. Alfrey, W. Liu, A. L. N. Kondusamy, A. Bostwick, C. Jozwiak, E. Rotenberg, L. Zhao, H. Deng, B. Lv, D. Zgid, E. Gull, N. H. Jo, Large Exciton Binding Energy in the Bulk van der Waals Magnet CrSBr. arXiv arXiv:2403.13897 [Preprint] (2024). http://arxiv.org/abs/2403.13897.

17. C. Trovatello, F. Katsch, N. J. Borys, M. Selig, K. Yao, R. Borrego-Varillas, F. Scotognella, I. Kriegel, A. Yan, A. Zettl, P. J. Schuck, A. Knorr, G. Cerullo, S. D. Conte, The ultrafast onset of exciton formation in 2D semiconductors. *Nat Commun* **11**, 5277 (2020).

18. A. Steinhoff, M. Florian, M. Rösner, G. Schönhoff, T. O. Wehling, F. Jahnke, Exciton fission in monolayer transition metal dichalcogenide semiconductors. *Nat Commun* **8**, 1166 (2017).

19. M. Dendzik, R. P. Xian, E. Perfetto, D. Sangalli, D. Kutnyakhov, S. Dong, S. Beaulieu, T. Pincelli, F. Pressacco, D. Curcio, S. Y. Agustsson, M. Heber, J. Hauer, W. Wurth, G. Brenner, Y. Acremann, P. Hofmann, M. Wolf, A. Marini, G. Stefanucci, L. Rettig, R. Ernstorfer, Observation of an Excitonic Mott Transition Through Ultrafast Core- *cum* -Conduction Photoemission Spectroscopy. *Phys. Rev. Lett.* **125**, 096401 (2020).

20. M. Puppin, Y. Deng, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Krenz, M. Wolf, R. Ernstorfer, 500 kHz OPCPA delivering tunable sub-20 fs pulses with 15 W average power based on an all-ytterbium laser. *Opt. Express* **23**, 1491 (2015).