**Ultrafast Formation and Annihilation of Strongly Bound Excitons in Bulk CrSBr**

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

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**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 antiferromagnetic 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 lacking. Here, we employ time- and angle-resolved photoemission spectroscopy to map the temperature-dependent band structure and carrier dynamics in bulk CrSBr. Time-resolved measurements reveal a rapid band renormalization of the lower conduction band that occurs during photoexcitation, pointing towards complex many-body effects governing 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 magnet.

**Introduction**

[2D Magnets/Motvation, 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 distribution of bound excitons in a variety of systems. (*8*) Here, we employ time- and angle-resolved photoemission (trARPES) to track the photoinduced femtosecond dynamics and directly probe the excitonic signatures in bulk CrSBr (**Figure 1**).

Physics of exciton Mott transition (*9*)

**Figure 1.** trARPES of bulk CrSBr.(a) (b) trARPES experimental schematic. (c). E = 0 eV is referenced to the valence band maximum (VBM) peak at the point.

**Results and Discussion**

To map the electronic band structure and photoinduced dynamics of bulk CrSBr, we perform time-and angle-resolved photoemission spectroscopy (trARPES) built around a high-repetition rate high-harmonic generation (HHG) XUV source and tunable femtosecond pump pulses. (*10*–*12*) 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 and electronic dynamics in a single experiment (**Figure 1b**). (*13*) **Figure 1d-f** shows a two-dimensional (*kx, ky*) momentum map near the valence band maximum (VBM) and at higher energies (E ~ 1.3 and ~2 eV) above the VBM at room-temperature. While the central (*kx=ky=*0) point of the VBM shows suppressed intensity, the point of the second Brillouin zone is more intense (*14*, *15*).

~~We perform ARPES at temperatures above and below the reported bulk magnetic transition temperature (T~~~~N~~ ~~~ 132 K), at which the system hosts interlayer antiferromagnetic ordering, with intralayer ferromagnetic order persisting to higher temperatures temperature (T~~~~C~~ ~~~ 165 K).~~ (*16*) **F**

After photoexcitation (1.55 eV, ~40 fs), we observe a quasi-flat dispersion along appearing >1 eV above the valence band maximum. (**Figure 1e,f**) Such an anisotropic dispersion has been predicted theoretically and recently observed in ARPES of few-layer CrSBr in contact with metallic substrates (*17*) as well as in alkali-metal dosed bulk CrSBr. (*18*) In particular, we observe two distinct features around E ~ 1.3 eV and E ~ 2.0 eV relative to the valence band maximum, each featuring the quasi-flat dispersion.

While initial experimental studies estimated the electronic band gap of bulk CrSBr to be around 1.5 eV, (*19*) recent ARPES works have suggested a possibly larger band gap of at least roughly 2 eV. (*14*, *18*, *20*) Optical emission measurements have shown the lowest-energy exciton resonance determining the optical band gap to lie around ~1.35 eV. (*1*, *2*, *21*) Taken together, we therefore assign the two features observed in our measurements at E ~ 1.3 eV and E ~ 2 eV (**Figure 1**) to the bound exciton state and the single-particle conduction band minimum of bulk CrSBr, respectively. Notably, our assignment implies an exciton binding energy of roughly 700 meV in bulk CrSBr. This large binding energy is consistent with previous theoretical works (*1*, *21*) [cite]. ~~To date, a direct, momentum- and energetically resolved picture of the exciton, including its binding energy, in CrSBr has so far been lacking.~~

Comparing the momentum maps of these two features, we see subtle differences (**Figures 1e,f and S**). While the upper feature features more intensity near the X points in line with previous works (*17*, *18*), the lower feature is more extended along with most intensity centered around the point. Indeed, in CrSBr, the exciton wavefunction is comprised of mostly the band character near the valence band maximum and conduction band minimum at the point and extending to X. (*21*) This may explain the subtle differences in the momentum maps corresponding to the bound exciton and conduction band states in our measurements. While we detect the electron in photoemission measurements after the breakup of the exciton by the XUV probe pulse, the hole dispersion must also be taken into consideration as it is mapped onto the excitonic signature in trARPES measurements. (*22*, *23*) However, the parabolic dispersion of the valence band itself is not seen in our observations, likely due to our optical excitation of 1.55 eV compared with the exciton resonance near ~1.35 eV in which we create excitons with excess energy and non-zero center-of-mass momentum. (*22*) Such a distribution of hot excitons may also explain the intensity towards and at the X point, compared with calculations of the 1s excitons state.(*21*)

**Figure 2.** Retrieval of the anisotropic real-space exciton wavefunction in bulk CrSBr.

**Figure 3.** Ultrafast dynamics of the exciton and conduction band electrons in bulk CrSBr.

**Figure 4.** Excitation fluence-dependent dynamics.

In recent years, momentum microscopy, by resolving both in-plane momenta simultaneously, has provided powerful insights into the orbital and real-space character of excitons in both molecular and inorganic semiconductors. (*24*) Leveraging the two-dimensional momentum space information, we retrieve the real-space exciton wavefunction of bulk CrSBr by Fourier transformation of the momentum maps corresponding to the exciton state at E ~ 1.3 eV (**Figure 2**). From this, we estimate the oval-shaped exciton’s Bohr radii as ~1 nm and ~0.25 nm, in reasonable agreement with previous theoretical studies (~1.4 nm). (*25*) Our observations provide a direct and powerful insight into the strongly bound ( ~ 700 meV) and anistropic nature of the exciton in bulk CrSBr.

The observation of the higher energy feature at E ~ 2.0 eV is striking considering the pump excitation energy of 1.55 eV is well below our assignment of the electronic band gap. **Figure 3b,c** shows the kx dispersion and the ultrafast dynamics of these two features, X and CB. 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 on the few hundreds of femtosecond timescale. Additionally, the dynamics of the exciton feature at different *kx* momenta along are largely indistinguishable (**Figure S**), suggesting that this feature arises from a single state, i.e. the exciton.

To better understand the relationship between the X and CB features and the dynamics leading to the population of CB after photoexcitation, we perform further trARPES measurements with varying excitation fluence and wavelength. **Figure 4** shows dynamics integrated along the direction with ~915 nm excitation (1.355 eV, 50 fs), close to the exciton resonance, and with varying excitation densities. With this excitation wavelength, we again observe two spectral features separated by ~0.7 eV as in **Figure 1** with 1.55 eV excitation, in addition to a dynamical rise of the higher energy feature relative to the lower. Interestingly, we also observe a strong excitation fluence dependence in both the initial decay dynamics of the exciton population as well as the rise time and relative intensity of the conduction band feature. These observations indicate an initial many-body interaction mechanism dominating the sub-picosecond dynamics. Meineke *et al*. recently uncovered ~1 ps and ~15 ps decay components attributed to hot exciton relaxation and exciton recombination in bulk CrSBr, respectively, as well as a significantly faster sub-picosecond lifetime in monolayer CrSBr. (*7*) Our work uncovers a novel, excitation-fluence-dependent ultrafast exciton decay channel in bulk CrSBr. Notably, this pathway leads to a strong competition between quasi-free conduction band electrons and bound excitons on sub-picosecond timescales after photoexcitation. On longer time scales of few tens of picoseconds, we indeed observe dynamics consistent with a longer ~15 ps decay component (**Figure S**) as reported in the recent work of Meineke *et al*. (*7*)

For excitation with shorter excitation wavelengths, we observe a reversal in the early-time dynamics and relative intensities of the CB and X features such that the CB state is populated first when exciting with higher photon energies (**Figure 4a**). This observation is most prominent with 400 nm excitation, which results in hot electrons populated far above the band edge, and we observe a reversal at 700 nm (~1.77 eV) and especially at ~680-640 nm (~1.8-1.9 eV) as well, consistent with conduction band energy in our ARPES data and recent estimates of the band gap by previous ARPES measurements. (*14*, *18*, *20*) Indeed, Meineke *et al*. observe a distinct change in the initial dynamics with excitation of ~1.8 eV compared to lower energies. (*7*) These observations further support the interpretation of the CB feature origin as the conduction band of bulk CrSBr in our measurements. An excitonic signature at 700 nm has also previously been noted. [?] However, It is also interesting to note that the exciton X state, while featuring a slightly delayed rise time with respect to the CB state with high pump photon energies, is very quickly populated even with very above-gap excitation, e.g. 400 nm. Such a robust exciton formation is consistent with the very high exciton binding energy ~ 700 meV that we measure in this material, as well as the distinct quasi-flat conduction band which features less energetically favorable local minima for carriers to relax to or, for example, for dark excitons compared to *e.g.* WSe2. (*8*)

[MOTT OR NOT?]

Excitons in semiconductors… Recent two-dimensional semiconductors with exciton binding energies of few hundred meV have… In particular, work has focused on the excitonic Mott transition. Here, … [Signatures of MOTT?] In addition, a separate Auger-type, two-exciton non-radiative decay pathway called exciton-exciton annihilation (EEA) may occur at lower excitation densities below the Mott transition. (*26*) In this scenario, one exciton non-radiatively recombines and leads to the disassociation of another excition, promoting its electron into the conduction band with excess energy. Exciton-exciton annihilation has been observed in …, in TMDs (*26*, *27*), as well as layered perovskites. (*28*)

In particular, debate has arisen over the abrupt or continuous nature of the excitonic Mott transition. While we observe a more-or-less continuous evolution of the dynamics and feature amplitudes, we do not resolve an appreciable shift of either the exciton or conduction band features with either time delay or excitation fluence in our measurements (**Figure S**).

Strong exciton-phonon coupling in CrSBr (*29*) may also lead to enhanced phonon-assisted Auger-type decay pathways. (*30*, *31*)

To gain further insight into the observed dynamics and test our theory of EEA and exciton formation in bulk CrSBr CrSBr, we develop a coupled rate-equation model considering exciton recombination, exciton-exciton annihilation, and exciton formation from free carriers after photoexcitation (Eq. 1). (*28*) We globally fit the exciton and conduction band electron dynamics for a range of excitation fluences to this EEA-based model, considering both resonant (910 nm) and above-gap (400 nm) excitation (**Figure 5**). Overall, we are able to qualitatively reproduce our observations very well, including the evolution of the rise time of the conduction band feature and the faster initial decay dynamics of the exciton signal with increasing excitation fluence when resonantly exciting excitons, and the reversal when considering above-gap excitation. We extract global time constants of ~ ps, fs, and fs for the exciton recombination, exciton-exciton annihilation, and exciton formation, respectively. While we have fit the time constants globally, considering the time traces of both features for all relevant fluences and wavelengths simultaneously, we include independent free parameters to correct the relative amplitudes of each curve (**Figure S**). Leveraging our ability to observe both the CB and exciton states simultaneously, we have uncovered strong EEA in bulk CrSBr as a prominent decay pathway for photoexcited excitons competing with excited state relaxation processes

**Conclusions**

In this work, we have provided for the first time a direct, momentum-resolved view of the strongly bound, anisotropic excitons in the bulk van der Waals magnet CrSBr. From this, we have extracted the excitonic wavefunction as well as an exceedingly large exciton binding energy of ~700 meV. Furthermore, our work has uncovered a novel many-body decay pathway for these photo-generated excitons. Upon near-resonant excitation of the exciton, an Auger-type two-body process, exciton-exciton annihilation, dominates at higher excitation fluences, leading to the generation of quasi-free carriers in the conduction band. With substantially higher, above-gap excitation, we observe the relaxation of hot carriers to the band edge before the formation of strongly bound excitons. The competition between these processes dominate the femtosecond and picosecond dynamics after photoexcitation, which we reproduce well with a coupled rate equation model.

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Exciton formation has been shown to occur in tens of femtoseconds intransition metal dichalcogenides (*32*)

The excitonic Mott transition has been a subject a large investigation. After the initial ~100 fs dynamics, the ionization ratio saturates to roughly 0.4 in our measurements.

Excitation density and the Mott transition (*33*) in transition metal dichalcogenides. (*34*)

Bistability (*35*)

We do not observe any noticeable shift in the X or CB peak positions as a function of delay time (**Figure S**).

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LITERATURE:

Time-resolved photoluminescence: 100s ps decay time as a function of temperature. [slower @ RT?, 10s ps low T] (*29*)

Defect-assoctiated excitons in CrSBr-TMD heterostructures. (*36*)

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**Methods**

trARPES were performed on bulk CrSBr crystals were grown by … []. For ARPES measurements, bulk crystals were mechanically cleaved in ultrahigh vacuum in base pressures better than 10-10 mbar.

trARPES measurements were performed using both a momentum microscope and a hemispherical analyzer. For the momentum microscope measurements. using a high-repetition rate OPCPA (*11*) operating at ~500 kHz (*10*, *12*)

~~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.~~

**Author Contributions**

L.T.L, T.P., M.A.W, 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, supervision, and infrastructure. L.T.L analyzed the data and wrote the manuscript with input from all authors.

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**Supplementary Information**

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**I. Additional trARPES Data**

**II. Fitting the Data**

**III.**