**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 lackng. Here, we employ time- and angle-resolved photoemission spec- troscopy to map the temperature-dependent band structure and car- rier 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 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 track the photoinduced femtosecond dynamics and directly probe the excitonic signatures in bulk CrSBr (**Figure 1**).

Physics of exciton Mott transition (*9*)

**Figure 1.** (a) 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 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 roughly 2 eV ore greater (*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 (**Figure 1**) at E ~ 1.3 eV and E ~ 2 eV 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 and, to our knowledge, is the first direct measurement. 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. As 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 and is mapped onto the excitonic signature in trARPES measurements. (*22*, *23*) In CrSBr, the valence band maximum is at the point, and this may explain the subtle differences in the momentum-space distribution of the bound exciton and conduction band states. 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*)

**Figure 2.** Real-space Exciton in Bulk CrSBr.

**Figure 3.** Ultrafast dynamics of the aniostropic exciton and conduction band in Bulk CrSBr.

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 exciton Bohr radius as ~ nm and an anisotropy ratio of ~ , in reasonable agreement with previous theoretical studies. (*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**). In particular, we pump with wavelengths close to the exciton resonance (~915 nm) as well as with wavelengths far above the band gap (400 nm). We observe change and reversal in the early-time dynamics and relative intensities of each feature such that the state CB is populated first when exciting with higher photon energies (**Figure 4a**). This supports the interpretation of CB origin as the conduction band of CrSBr. Interestingly, 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. Such a robust exciton formation likely arises from the high exciton binding energy ~ 700 meV in this material and the band structure featuring less energetically favorable dark-excitons compared to *e.g.* WSe2. (*8*)

[FLUENCE DATA] The total population considering both the exciton and conduction band signals continues to decrease, possibly suggesting an Auger-type mechanism or additional relaxation channels. Recent work has uncovered ~1 ps and ~15 ps decay components attributed to exciton recombination and hot exciton relaxation in bulk CrSBr, respectively, as well as a significantly faster sub-picosecond lifetime in monolayer CrSBr. (*7*) Our work uncovers a new, excitation-fluence-dependent exciton decay channel connecting the exciton and quasi-free conduction band electrons in bulk CrSBr. We globally fit the exciton and conduction band electron dynamics presented in **Figure 4b** to a rate-equation model considering exciton recombination and exciton-exciton annihilation as a non-radiative recombination channel, in addition to exciton formation from free carriers. Exciton-exciton annihilation is a second-order, Auger-type decay process in which one exciton non-radiatively recombines and leads to the disassociation of another excition, promoting its electron into the conduction band with excess energy. Overall, this model qualitatively reproduces our observations well, including the evolution of the rise time of the conduction band feature and the faster decay dynamics of the exciton signal with increasing fluence. We extract global time constants of ~ ps, fs, and fs for the exciton recombination, annihilation, and formation, respectively. While we have fit the time constants globally, considering all time traces simultaneously, we choose to independently fit the amplitudes of each curve.

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

**Figure 4.** Ultrafast dynamics of the exciton and conduction band in Bulk CrSBr.

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Strong exciton-phonon coupling in CrSBr (*26*) may also lead to enhanced phonon-assisted Auger-type decay pathways. (*27*, *28*)

Time-resolved photoluminescence: 100s ps decay time as a function of temperature. [slower @ RT?, 10s ps low T] (*26*)

Defect-assoctiated excitons in CrSBr-TMD heterostructures. (*29*)

Exciton formation has been shown to occur in tens of femtoseconds intransition metal dichalcogenides (*30*)

Excitation density and the Mott transition (*31*) in transition metal dichalcogenides. (*32*)

Bistability (*33*)

EEA in TMDs (*34*)

**Conclusions**

**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., 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 analyzed the data and wrote the manuscript with input from all authors.

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