













## Paramagnetic electronic structure of CrSBr: Comparison between *ab initio* GW theory and angle-resolved photoemission spectroscopy

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We explore the electronic structure of paramagnetic CrSBr by comparative first-principles calculations and angle-resolved photoemission spectroscopy. We theoretically approximate the paramagnetic phase using a supercell hosting spin configurations with broken long-range order and applying quasiparticle self-consistent GW theory, without and with the inclusion of excitonic vertex corrections to the screened Coulomb interaction (QSGW and QSGW̄, respectively). Comparing the quasiparticle band-structure calculations to angle-resolved photoemission data collected at 200 K results in excellent agreement. This allows us to qualitatively explain the significant broadening of some bands as arising from the broken magnetic long-range order and/or electronic dispersion perpendicular to the quasi-two-dimensional layers of the crystal structure. The experimental band gap at 200 K is found to be at least 1.51 eV at 200 K. At lower temperature, no photoemission data can be collected as a result of charging effects, pointing towards a significantly larger gap, which is consistent with the calculated band gap of approximately 2.1 eV.

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### I. INTRODUCTION

Two-dimensional (2D) magnetic materials derived from van der Waals-bonded layered crystals have a wide range of potential applications due to the intricate coupling of spin, charge, and lattice degrees of freedom, and they are fascinating in their own right, in particular since magnetic ordering in a 2D isotropic Heisenberg model is forbidden by the Mermin-Wagner theorem [1]. Several examples of such materials have been discovered in the past few years, such as CrI<sub>3</sub> [2], Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub> [3], and Fe<sub>3</sub>GeTe<sub>2</sub> [4]. Particularly promising properties are found in CrSBr, a layered magnetic semiconductor with an estimated band gap of 1.5 eV at room temperature [5,6]. In CrSBr, the individual layers show ferromagnetic (FM) ordering that persists down to the monolayer limit with a high Curie temperature of approximately 150 K and an in-plane easy axis along the crystallographic *b* direction [5,7]. The alignment of magnetic moments between adjacent layers is antiferromagnetic (AFM) with a Néel temperature of 132 K.

Remarkably, charge transport [8,9] and quasiparticle excitations such as excitons [10] or phonons [11,12] are strongly correlated with the bulk magnetic order with a recent first promising demonstration of quantum transduction via

exciton-magnon coupling [13]. The magnetocorrelated nature of CrSBr is complemented by a highly anisotropic crystal structure with strong implications on physical properties such as the dielectric screening, the exciton spectrum, quasiparticle interactions such as exciton-phonon and electron-phonon coupling [6], and the charge transport [9].

Fundamentally underlying these properties is the electronic band structure of CrSBr for which several predictions have been published, using different approximations [6,9,10,14–19]. All calculations do indeed reflect the expected anisotropy with a strongly anisotropic effective mass around the conduction-band minimum and, to a much lesser degree, also in the valence band. However, existing calculations lack a description of the paramagnetic (PM) phase, and an experimental determination of the band structure is also not reported to the best of our knowledge. Both are important ingredients to provide a clearer picture of the electronic properties and elucidate the intricate interplay of magnetic order and electronic structure in CrSBr with the objective to understand its rich physical properties, quasiparticle excitations, and interactions.

Here we explore the electronic band structure of CrSBr theoretically, with a special emphasis on a consistent treatment of the nontrivial anisotropic screening and its effects on the Cr-*d*/S-*p*/Br-*p* hybridization, and experimentally by angle-resolved photoemission spectroscopy (ARPES). We find that ARPES data cannot be acquired at low temperatures in the AFM ordered state because the sample becomes too

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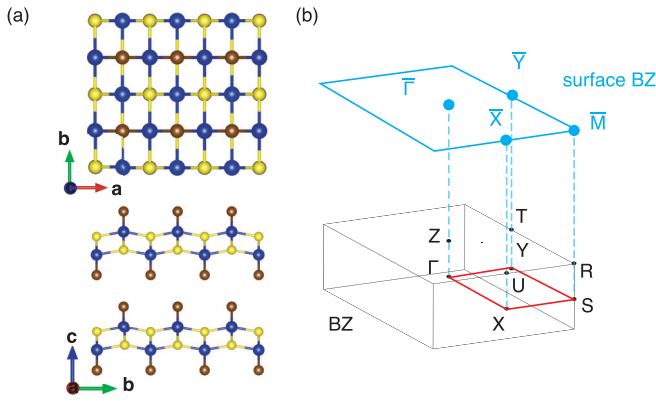


FIG. 1. (a) Structure of the CrSBr unit cell (Cr: blue, S: yellow, Br: brown). (b) Bulk (black) and (001) surface (cyan) Brillouin zones (BZs) for CrSBr with high-symmetry points. Solid red lines indicate the paths along which bands have been calculated.

insulating. The paramagnetic high-temperature phase, on the other hand, is challenging to address by calculations because of the intrinsic spin disorder. However, as it turns out, theoretical aspects such as the role of the long-range Coulomb interaction have a much bigger effect on the band structure than the magnetic ordering such that a comparison between the AFM ground-state calculation and the ARPES results remains meaningful. We obtain very good agreement between the paramagnetic ARPES data and an AFM calculation upon self-consistently including long-range Coulomb interactions and its screening. Our systematic comparison of supercell calculations within the layered FM and AFM states as well as in the paramagnetic phase together with a detailed analysis of the effects of the  $k_z$  dispersion in these states finally allows us to uncover important broadening channels in the ARPES data.

## II. THEORETICAL AND EXPERIMENTAL DETAILS

We apply three different levels of *ab initio* theory: density functional theory (DFT) within the local-density approximation (LDA), quasiparticle self-consistent *GW* theory (QS*GW*) [20], which, in contrast to conventional *GW* methods, modifies the charge density and is determined by a variational principle [21], and QS*G* $\hat{W}$  [22], in which the screened Coulomb interaction  $W$  is computed including vertex corrections (ladder diagrams) by solving a Bethe-Salpeter equation (BSE) within the Tamm-Dancoff approximation [23]. Crucially, our QS*G* $\hat{W}$  methods are fully self-consistent in both self-energy  $\Sigma$  and the charge density [24].  $G$ ,  $\Sigma$ , and  $\hat{W}$  are updated iteratively until all of them converge. Our results are thus parameter-free and have no starting point bias.

The CrSBr crystal structure is depicted in Fig. 1(a). For all theoretical results, we fix  $a = 3.504$ ,  $b = 4.738$ ,  $c = 2 \times 7.907$  Å (the  $c$ -axis is doubled to treat antiferromagnetic order) to their experimental values [7,25] and relax all atomic positions in the  $z$  direction within VASP [26,27] on the generalized gradient approximation (GGA) [28] level, using a collinear interlayer antiferromagnetic (interlayer ferromagnetic) ordering at a fixed interlayer distance of  $c/2$  and maintaining the orthorhombic crystal structure. This yields

an intralayer nearest-neighbor Cr-Br distance of 2.50 Å, as well as 2.37 and 2.41 Å for the two Cr-S distances, and an interlayer nearest-neighbor Br-Br separation of 3.75 Å in good agreement with Ref. [29]. All *ab initio* band-structure calculations are performed within QUESTAAL using a full-potential linear muffin tin orbital basis set. Single-particle calculations [LDA, and energy band calculations with the static quasiparticle self-energy  $\Sigma^0(k)$ ] are performed for both AFM and FM phases on a  $12 \times 12 \times 6$   $k$ -mesh while the (relatively smooth) dynamical self-energy  $\Sigma(k)$  is constructed using a  $6 \times 6 \times 3$   $k$ -mesh. The QS*GW* and QS*G* $\hat{W}$  cycles are iterated until the rms change in  $\Sigma^0$  reaches  $10^{-5}$  Ry.

For the magnetic configurations, we considered layer-polarized FM and AFM alignments with easy axes along the crystallographic  $a$ ,  $b$ , and  $c$  directions. We refer to these alignments by a notation combining the magnetic state and the easy axis, e.g., AFM- $b$ . As we discuss in detail below, AFM- $b$  and FM- $b$  serve as good proxies for the paramagnetic phase, in which any long-range magnetic order has vanished, while short-range spin correlations persist. We validate this picture with QS*GW* calculations in a paramagnetic  $2 \times 2 \times 2$  supercell (48 atoms; 48 interstitial sites are added to augment the basis with floating orbitals). Local spin orientations are arranged in a quasirandom configuration to minimize the difference between the quasirandom and true random site correlation functions. An objective function composed from 480 pair and 384 triplet functions is minimized, following the approach by Zunger *et al.* [30]. The objective function contained 16 pairs and 24 triplets per Cr site. This corresponds to three shells of Cr neighbors whose length ranged between 0.41 and 0.71 of the lattice constant, and all triples whose sum of lengths did not exceed 1.37 multiples of the lattice constant.

CrSBr crystals were synthesized by chemical vapor phase growth [19]. ARPES experiments were performed at the SGM-3 beamline of ASTRID2 [31]. Energy and angular resolution were 60 meV and  $0.2^\circ$ . The sample temperature was set to 200 K. The synchrotron radiation polarization and the sample-to-analyzer direction were both in the plane of incidence, and the analyzer slit was perpendicular to the plane of incidence. The CrSBr crystals were cleaved *in situ* prior to measurements. The crystal orientation was determined by low-energy electron diffraction and by inspection of the rectangular macroscopic crystal shape.

## III. RESULTS AND DISCUSSION

### A. Self-consistent *GW* AFM results

We start by comparing band-structure calculations for the AFM ground state with the easy axis in the  $b$  crystallographic direction (AFM- $b$ ) within different levels of approximations to assess the role of nonlocal Coulomb interaction and screening together with modifications to the  $d$ - $p$  hybridization, as including these mechanisms turned out to be crucial for a correct description of CrX<sub>3</sub> compounds [32,33]. Figure 1 depicts the structure of CrSBr together with the bulk Brillouin zone (BZ). The projection of the bulk Brillouin zone along the crystallographic  $c$  direction is also shown, as this is the relevant surface BZ for the cleaved crystals used in the ARPES experiment. Figure 2 summarizes the calculated bulk

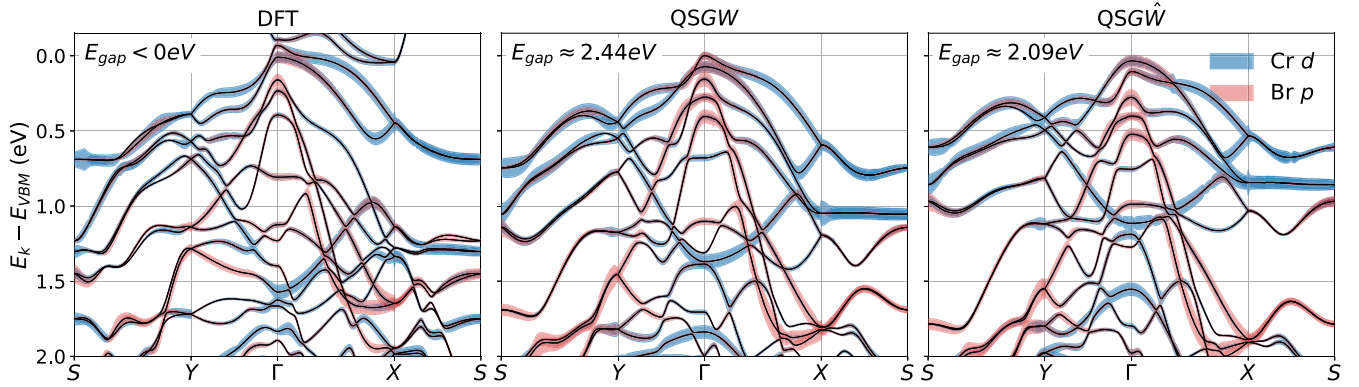


FIG. 2. Orbital-resolved quasiparticle band structures for AFM-*b* CrSBr within DFT, QSGW, and QSGW $\hat{W}$ . The individual (colored) bandwidths indicate Cr *d* orbital (blue) and Br *p* orbital (red) contribution to each state.

band structures obtained within DFT, QSGW, and QSGW $\hat{W}$ . Cr *d* and Br *p* orbital weights in each band are indicated in blue and red, respectively.

The comparison between DFT and QSGW shows striking differences as the DFT result does not show a finite band gap and as the valence-band structures differ quantitatively and to a large extent also qualitatively. The origin of this difference becomes clear upon inspecting the orbital contributions to the individual bands. From this we understand that the *d-p* hybridization is strongly overestimated in DFT resulting in various overestimated avoided crossing gaps. Taking long-range Coulomb interaction renormalizations self-consistently into account narrows the Cr *d* dominated states, as visible at the  $\Gamma$  point, and it reduces most of the avoided crossing gaps. As this is strongly governed by the *d-p* hybridization, which is significantly affected by our *GW* charge self-consistency, we stress that simplified DFT+ $G_0W_0$  calculations, which update neither the charge density nor *W* from changes in screening [34,35], likely result in qualitatively wrong valence bands due to the inappropriate DFT starting point. The qualitative differences in the band structures around  $\Gamma$ , *S*, and *Y* induced by self-consistency are in good agreement with our ARPES data, as we show in more detail below.

Further corrections to the QSGW results in the form of excitonic screening to the Coulomb interaction, as rendered in QSGW $\hat{W}$  calculations, do not qualitatively change the band structure anymore, but they are responsible for quantitative differences mostly notable in all states with significant Cr *d* character.

### B. Impact of magnetic disorder and paramagnetic properties

A comparison to the ARPES data taken in the high-temperature paramagnetic phase should be undertaken using calculations representing the same phase. This is, however, highly challenging for theory due to the complexity resulting from the vanished long-range and residual short-range magnetic order in the paramagnetic phase. Thus, before we discuss our approximate paramagnetic results obtained from supercell calculations, we first compare QSGW $\hat{W}$  calculations for AFM and FM configurations with varying spin easy axes in Fig. 3 as possible proxies for the PM phase. On the level of the quasiparticle energies, we do not find qualitative differences

between the various easy axes reflecting the vanishing impact of magnetocrystalline anisotropy in the ordered phases. There are, however, a few quantitative details, which vary upon rotating the easy axis from AFM-*b* to AFM-*a* or AFM-*c*. This is accompanied by changes to the relative Cr *d* weights. The density of states is nearly unaffected by the easy-axis rotations, and the band gap is not modified at all.

As the AF magnetic exchange interaction between the layers is significantly weaker than the FM in-plane interactions, we expect that the interlayer AFM long-range order is first broken as the temperature increases slightly above the Curie temperature, such that the paramagnetic phase may be approximately seen as a disordered interlayered AFM/FM structure with long-range in-plane FM order. The effect of such a scenario is best tested by comparing QSGW $\hat{W}$  AFM and FM calculations, assuming that the experimental situation lies in between these extremes. The corresponding FM results are shown in the right panel of Fig. 3. Easy-axis rotation has only minor effects, also in the FM ordered phase. However, changing the magnetic polarization between the layers from AFM to FM has a significant impact on the band structure and the density of states. Due to the broken (magnetic) inversion symmetry in the FM phase, all degeneracies of the AFM band structure are lifted, which is most prominently seen in the split highest VBs in the FM case. Upon aligning the AFM and FM band structures with respect to their Fermi level differences ( $\sim 125$  meV), we find a major modification to the two upmost FM VBs, which leak into the AFM band gap and thereby reduce the total gap [as the FM CB position is nearly unaffected; see the supplemental material (SM) [36]]. All other states experience only quantitative renormalizations (next to the broken degeneracies). When comparing the calculations to the experiment, magnetic disorder along the lines calculated here can be expected to result in a significant broadening of the bands. The effect will be especially pronounced in the two bands near the VBM.

This picture is verified and augmented by our paramagnetic  $2 \times 2 \times 2$  supercell calculation within the QSGW approximation using frozen spins and including spin-orbit coupling shown in Fig. 4 together with the ordered FM-*c* and AFM-*c* band structures for the same supercells. Please note that the indicated high-symmetry points here refer to the ones in the reduced Brillouin zone of the supercell. The resulting band

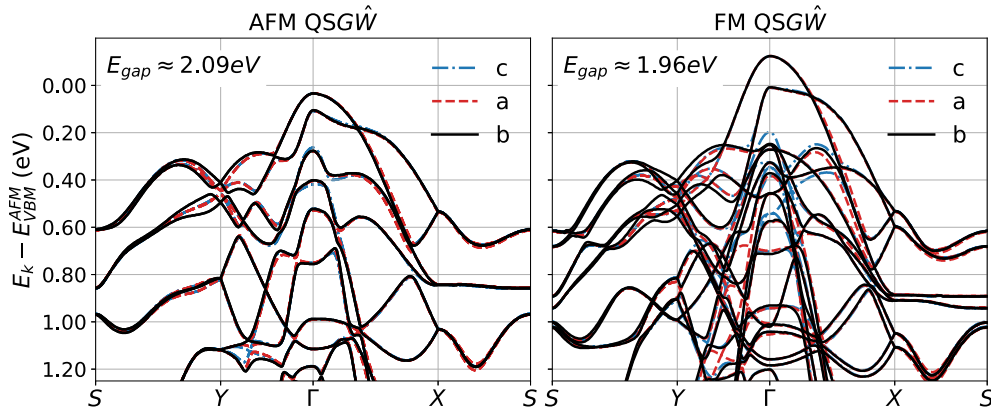


FIG. 3. QSGW band structures for different magnetic easy axes.

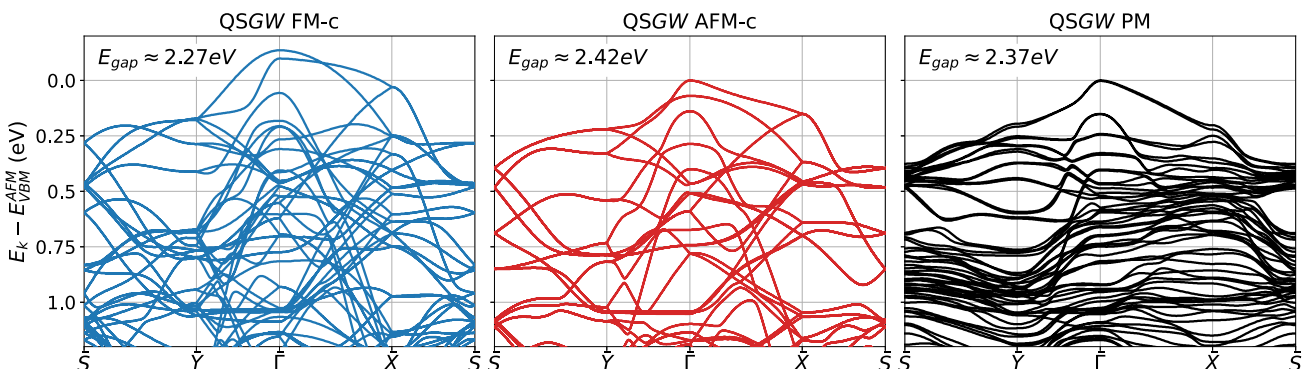
structures are thus folded with respect to those discussed before. The comparison between the the FM-*c* and AFM-*c* band structures resembles the one discussed above. The PM calculation shows many more finely split bands. This is a consequence of the spin disorder, which effectively broadens the states and which can be understood as a static version of spin fluctuations. Throughout the depicted band structures, we find many qualitative similarities between the PM results and both the FM and AFM ones. The most striking features of the PM valence bands are the significant dispersion in  $k_z$  between  $\Gamma$  and Z, which is also present in the FM data, but nearly completely suppressed in the AFM band structure (see the SM [36]) and the strong qualitative difference between the upmost valence bands. In the PM case, these bands do not clearly resemble either the FM or AFM ones, emphasizing that renormalization is a strong signature of the PM phase.

### C. ARPES results

When collecting temperature-dependent ARPES spectra, charging effects were observed below  $T \approx 160$  K. These were sufficiently strong to prevent measurements at low temperatures, and the data reported here were therefore collected at 200 K, i.e., in the PM phase. The effect is illustrated in Fig. 5 by a series of ARPES spectra taken while the sample was cooled down from  $T = 200$  to 100 K. The transition temperature to the insulating state of about 170 K is close

to magnetic ordering temperature [29]. However, the effect is still surprising since the magnetic transition has only a small effect on the conductance determined in bulk transport measurements [5]. Also, depending on the chosen approximation, the magnetic order affects the calculated band gap (see the labels in Fig. 3 and the SM [36]) but the differences are quite small.

Figure 6 provides an overview of the ARPES results collected in an extended zone scheme. The photoemission intensity is shown as cuts through a three-dimensional data set, collected as a function of the energy and a 2D  $\mathbf{k} = (k_x, k_y)$  parallel to the surface. The energy zero has been set to the estimated position of the VBM as observed around the  $\bar{\Gamma}_{10}$  point (the reason for choosing this particular point will become clear later). The Fermi energy of a metal in contact with the sample is at  $E_F = -1.51$  eV. Since no indications of the conduction band are found in ARPES, this implies that the band gap is at least 1.5 eV wide, consistent with the 1.5 eV gap from scanning tunneling spectroscopy at room temperature [5,6]. However, a gap of around 1.5 eV would imply a very strong, essentially degenerate,  $n$  doping of the sample, and one should not expect to observe the aforementioned charging effects, especially if the magnetic transition has only a minor effect on the gap. We thus take this as a strong indication that the band gap of CrSBr is significantly larger. A gap size of  $\approx 2.0$  eV as suggested by the calculations in Fig. 3 could, in combination with high crystalline quality, explain the observed charging


 FIG. 4. QSGW band structures for supercells in FM-*c* and AFM-*c* together with the paramagnetic approximation.

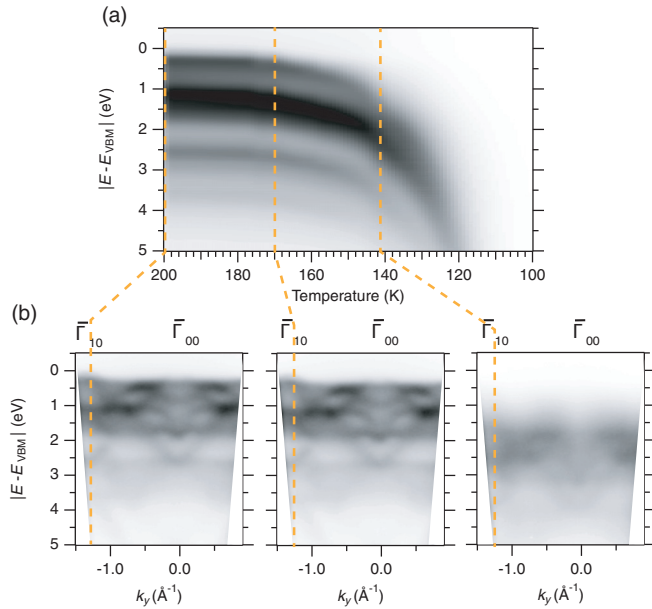


FIG. 5. Illustration of charging at low temperature. (a) Photoemission intensity as a function of energy and temperature at  $\bar{\Gamma}_{10}$  for  $h\nu = 100$  eV (for the definition of the high-symmetry points, see Fig. 6). (b) Photoemission intensity at  $k_x = 0$   $\text{\AA}^{-1}$  for three selected temperatures. Strong charging leads to an energy shift of the spectra below  $T \approx 170$  K.

effects. In this case, the situation would be similar to that in high-quality organic crystals where charging is a well-known issue for ARPES investigations [37].

In Fig. 6(a), the photoemission intensity is shown as a function of the 2D  $\mathbf{k}$ , integrated over an energy range of 30 meV around the VBM. The  $\mathbf{k}$  scan range is wide enough to enclose several surface BZs. The periodicity along  $k_x$  (in the real-space  $a$  direction) is easily identified by the repeated pattern of high-intensity points near  $\bar{\Gamma}_{10}$ ,  $\bar{\Gamma}_{11}$ , and  $\bar{\Gamma}_{12}$ . It agrees with the expected length of a reciprocal-lattice vector in this direction of  $1.79$   $\text{\AA}^{-1}$ . The periodicity in the  $k_y$  direction, in contrast, is not immediately obvious. The size of the BZ in the  $y$  direction is  $1.33$   $\text{\AA}^{-1}$  but the photoemission intensity at the nominally equivalent  $\bar{\Gamma}$  points does not appear to reflect this. In particular, we find local maxima in the photoemission intensity at  $\bar{\Gamma}_{10}$ ,  $\bar{\Gamma}_{11}$ , and  $\bar{\Gamma}_{12}$  but local minima at  $\bar{\Gamma}_{00}$  (corresponding to normal emission) and  $\bar{\Gamma}_{01}$ .

The periodicity is clarified when inspecting cuts through the data set along high-symmetry directions. Cuts in the  $k_x$  direction along the  $\bar{\Gamma}_{10} - \bar{\Gamma}_{11} - \bar{\Gamma}_{12}$  and  $\bar{\Gamma}_{00} - \bar{\Gamma}_{01} - \bar{\Gamma}_{02}$  lines are given in Fig. 6(b). Following the dispersions, it is clear that the assigned  $\bar{\Gamma}$  and  $\bar{X}$  are indeed high-symmetry points and that the VBM is found at  $\bar{\Gamma}$ . However, the apparent dispersion around the  $\bar{\Gamma}$  points is quite different. Around  $\bar{\Gamma}_{10}$ , the intensity of the bands at the highest energy appears to collapse, but a weak intensity disperses to a higher energy than at any other  $\bar{\Gamma}$  point [marked by a red arrow; see also Figs. 6(c) and 6(d) for a magnification of this region]. This is consistent with Fig. 6(a), where the highest overall intensity is observed at  $\bar{\Gamma}_{10}$  and this maximum in the dispersion is taken to be the VBM [defined as the position of the photoemission intensity's leading edge in in Fig. 6(d)]. Near  $\bar{\Gamma}_{11}$  and  $\bar{\Gamma}_{12}$  it is easier to see a

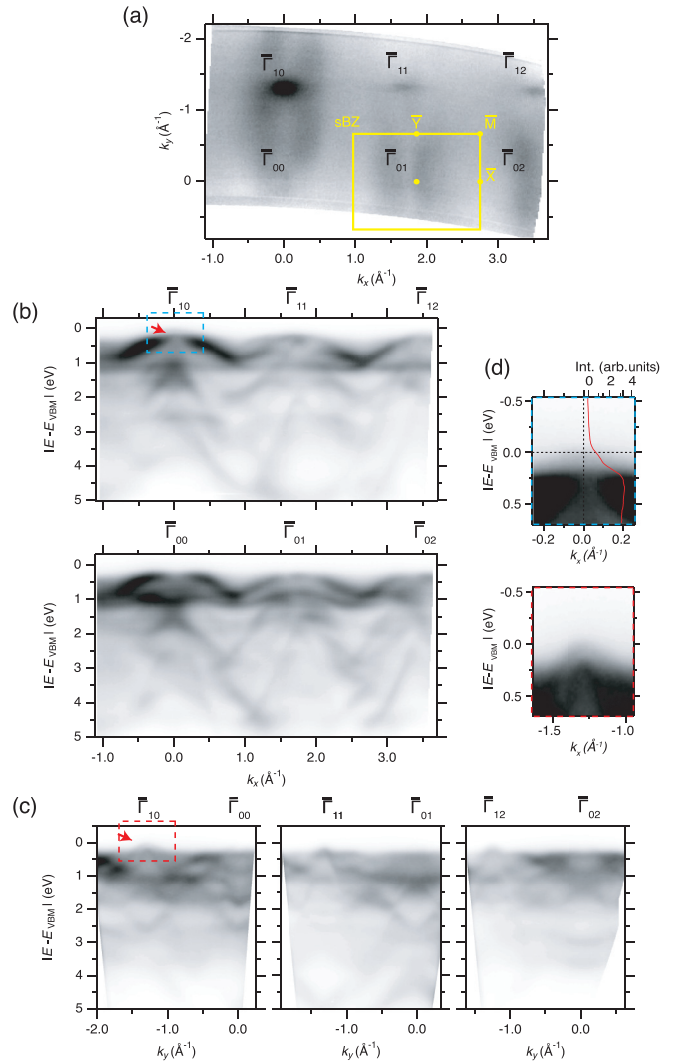


FIG. 6. Electronic structure of CrSBr determined by ARPES at a photon energy of  $h\nu = 100$  eV. (a) Photoemission intensity integrated in a 30 meV window around the VBM. (b) Photoemission intensity in the  $k_x$  direction along  $\bar{\Gamma}_{10} - \bar{\Gamma}_{11} - \bar{\Gamma}_{12}$  and  $\bar{\Gamma}_{00} - \bar{\Gamma}_{01} - \bar{\Gamma}_{02}$ . (c) Corresponding cuts in the  $k_y$  direction along the  $\bar{\Gamma}_{10} - \bar{\Gamma}_{00}$ ,  $\bar{\Gamma}_{11} - \bar{\Gamma}_{01}$ , and  $\bar{\Gamma}_{12} - \bar{\Gamma}_{02}$  directions. The red arrows mark the point at which the VBM is observed. (d) Magnification of the VBM region in panels (b) and (c). The red curve in the upper panel is the photoemission intensity at  $\bar{\Gamma}_{10}$  as a function of energy.

local maximum in the dispersion, but this is found at a slightly lower energy than at  $\bar{\Gamma}_{10}$ . In fact, the same band is also visible at  $\bar{\Gamma}_{10}$ ,  $\approx 170$  meV below the very faint band forming the VBM. This is best seen in the magnification of the dispersion around the VBM at  $\bar{\Gamma}_{10}$  shown in Fig. 6(d). An extreme case is normal emission,  $\bar{\Gamma}_{00}$ , where the photoemission intensity around the VBM appears to be strongly suppressed. A similar picture presents itself at lower energy where the observable bands around equivalent high-symmetry points do not appear to be the same with some exceptions, e.g., the band crossing at the  $\bar{X}$  points at about 2 eV that is clearly observed between  $\bar{\Gamma}_{10}$  and  $\bar{\Gamma}_{11}$  and between  $\bar{\Gamma}_{11}$  and  $\bar{\Gamma}_{12}$ .

The dispersion in the  $k_y$  direction shows similar effects. Again, the local symmetry around the  $\bar{\Gamma}$  and  $\bar{Y}$  points in

Fig. 6(c) is clear, confirming the expected periodicity. But also here, the local band structure around the symmetry points appears different for symmetry-equivalent points apart from some bands, for example a pronounced feature at 2.6 eV that is observed around  $\bar{\Gamma}_{00}$ ,  $\bar{\Gamma}_{01}$ , and  $\bar{\Gamma}_{10}$ .

The apparently different dispersion around symmetry-equivalent points could have several reasons. The first is that scanning the parallel crystal momentum  $\mathbf{k}$  across the surface also leads to a change of the probed  $k_z$ . The different high-symmetry points thus have the same  $\mathbf{k}$  modulo a surface reciprocal-lattice vector, but they do not have the same  $k_z$ . Any dispersion along  $k_z$  would thus lead to a different observed band structure around equivalent high-symmetry points in the extended surface BZ. While this explanation might play a role, the effect is likely to be minor because a pronounced  $k_z$  dispersion is not expected for a layered van der Waals material such as CrSBr. Moreover, very similar band dispersions are made when using different photon energies, also supporting the 2D character of the band structure [36]. On the other hand, both calculations and ARPES results show a small degree of  $k_z$  dispersion for the lower-lying bands which could contribute to a broadening, as discussed below.

A more likely explanation for the observed differences in apparent dispersion are strong matrix element effects that completely suppress some bands in certain regions of reciprocal space. A particularly interesting example is the VBM, which is most clearly observed around the  $\bar{\Gamma}_{10}$  point and not at all around normal emission at  $\bar{\Gamma}_{00}$ . Such pronounced matrix element variations are most likely explained by sublattice interference effects due to the presence of two equivalent atoms (of each kind) in the unit cell, similar to what is seen in the  $\pi$ ,  $\sigma$ , and core-level states of graphene [38,39], and in particular near the top of the graphite and graphene  $\sigma$  band that shows an intensity collapse exactly at normal emission, but not for the  $\Gamma$  points in the neighboring BZs [38,40,41]. In the case of CrSBr, the situation is more complex because of the change of orbital character very near to the VBM (see Fig. 2). In any event, the strong matrix element effects call for some care when comparing the ARPES results to calculations because the absence of dispersive features in the experiment does not necessarily indicate poor agreement with a calculation—the features might just be suppressed by matrix element effects. In fact, the predicted state might be observable along an equivalent path in another BZ.

Keeping these considerations in mind, we proceed to a comparison between the measured and calculated band structures. To this end, we use the AFM-*b* QSGW calculation. Figure 7 shows this comparison for experimental data along two different but equivalent paths in the extended zone scheme, one including the  $\bar{\Gamma}_{10}$  point and one including the  $\bar{\Gamma}_{11}$  point. The energy zero in the experimental bands is still the estimated position of the VBM as observed around  $\bar{\Gamma}_{10}$ . The experimental bands are quite broad so that structures often contain more than one calculated band. The overall agreement is, however, excellent, and we find QSGW states at all locations with increased ARPES intensity, as well as clearly vanishing ARPES intensity in regions with no QSGW states. We stress that this is so for the entire wide energy range studied, not only near the VBM. This would clearly not be the case for a comparison with the metallic DFT band structure,

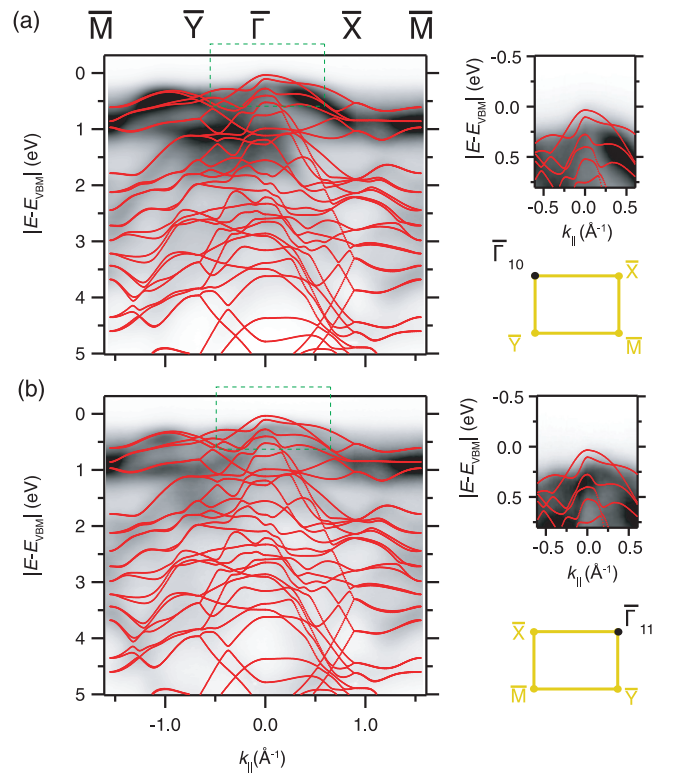


FIG. 7. Photoemission intensity and AFM-*b* QSGW calculation ( $h\nu = 100$  eV) for two equivalent but different paths in the extended zone scheme (indicated on the right-hand side).

and the agreement thus strongly supports the necessity to go beyond DFT for this material.

The situation around the VBM deserves special attention. As already seen in Fig. 6, the highest energy band is observed at  $\bar{\Gamma}_{10}$  and this is assigned to the VBM. The band is broad and has a very low intensity. Indeed, it is only clearly visible in the magnification of Fig. 6(d). Keeping in mind the discussion accompanying Figs. 3 and 4, this observation is consistent with the expectation of a strongly broadened VBM in the presence of magnetic disorder in the paramagnetic state. The band is too broad and weak for a quantitative determination of the dispersion, and it is thus not possible to verify the predicted anisotropy of the effective mass. The local band maxima at  $\bar{\Gamma}_{11}$  and  $\bar{\Gamma}_{12}$  appear at a slightly lower energy ( $\approx 170$  meV) and are therefore assigned to the lower-lying maximum. This also appears to match very well with the superimposed calculations.

Finally, we experimentally explore the dimensionality of the electronic structure in CrSBr by a photon energy scan to systematically vary  $k_z$ . Figure 8(a) shows the photoemission intensity integrated in an energy window of 30 meV around the VBM as a function of  $k_y$  and  $k_z$ . A cut through the bulk BZ is superimposed, and the bulk  $\Gamma$  points are indicated by black markers. The  $k_z$  values have been obtained from the photon energy under the assumption of free-electron final states, using an inner potential of 12.8 eV. The vertical streak of photoemission intensity around  $\bar{\Gamma}_{10}$  indicates a two-dimensional electronic structure around the VBM. The situation around  $\bar{\Gamma}_{00}$  is inconclusive because the VBM is not observed there

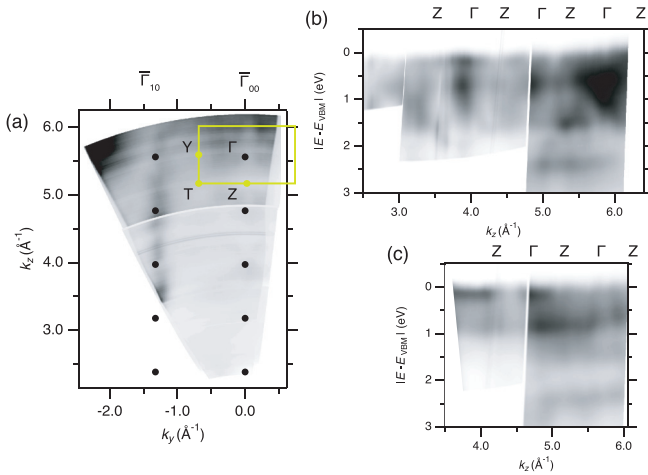


FIG. 8. Dispersion along  $k_z$ . (a) Constant energy surface in a range of 30 meV around the VBM as a function of  $k_z$  and  $k_y$ . Consecutive  $\Gamma$  points are marked in blue, while the BZ is shown in green. (b),(c) Energy dispersion as a function of  $k_z$  at  $k_y = 0 \text{ \AA}^{-1}$  (i.e.,  $\bar{\Gamma}_{00}$ ) and  $k_y = 1.33 \text{ \AA}^{-1}$  (i.e.,  $\bar{\Gamma}_{10}$ ), respectively.

(see Fig. 6). Figures 8(b) and 8(c) show the photoemission intensity as a function of energy and  $k_z$  for  $k_y$  fixed to  $\bar{\Gamma}_{00}$  and  $\bar{\Gamma}_{10}$ , respectively. There is very little evidence of dispersion in the  $k_z$  direction here as well. The most intense features do not show any  $k_z$  dependence of their binding energy and can be easily identified with the most intense features seen for a photon energy of 100 eV ( $k_z \approx 5.29 \text{ \AA}^{-1}$ ) in Fig. 6(c). The lack of  $k_z$  dispersion is also confirmed by a data set showing a very similar  $\mathbf{k}$  dispersion throughout the extended zone, obtained using a different photon energy and shown in the SM [36]. On the other hand, some degree of  $k_z$  dispersion appears to be present at higher-lying bands. In Fig. 8(b), for instance, a dispersing state is visible around 1 eV between 4 and 5  $\text{\AA}^{-1}$  and another one around 2 eV between 5 and 5.7  $\text{\AA}^{-1}$ . Such a dispersion in the lower-lying bands is consistent with the calculated  $k_z$ -dependent band structures in the paramagnetic phase in Fig. S4, and this  $k_z$  can thus be expected to contribute to the energy broadening of the lower-lying bands.

#### IV. CONCLUSIONS

When describing the electronic structure of CrSBr theoretically, it is essential to include the long-range Coulomb interaction and its impact on the charge-density self-consistently, as is done within the QSGW and QSG $\hat{W}$  approximations. The quasiparticle band structures calculated in this way are in excellent agreement with ARPES results. DFT as well

as non-self-consistent DFT+ $G_0W_0$  calculations, on the other hand, result in band structures that are significantly different from our experimental data.

Both ARPES measurements and QSG $\hat{W}$  calculations show a small degree of dispersion along  $k_z$  for states close to the VBM, and we find that AFM- $b$  and FM- $b$  configurations are good proxies for describing the paramagnetic phase. The comparison of these calculations suggests that magnetic disorder in the paramagnetic phase would have a particularly strong effect on the bands forming the VBM, giving rise to substantial energy broadening. This is indeed observed in the experiment. Other effects, such as photoemission matrix elements, could also contribute to suppressing the intensity of these bands, as they are clearly important and responsible for a strong variation in the observable bands throughout the extended BZ scheme.

Finally, ARPES indicates that the crystals have a band gap of at least 1.5 eV. The strong charging below  $T = 160 \text{ K}$ , however, suggests that the low-temperature band gap is significantly larger than that, more in line with the approximately 2.1 eV expected from the calculations.

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