Title
Giant spin-splitting and gap renormalization driven by trions in single-layer WS 2 /h-BN heterostructures

Permalink
https://escholarship.org/uc/item/5xh1q06m

Journal
Nature Physics, 14(4)

ISSN
1745-2473

Authors
Katoch, J
Ulstrup, S
Koch, RJ
et al.

Publication Date
2018-04-01

DOI
10.1038/s41567-017-0033-4

Peer reviewed
In two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs), new electronic phenomena such as tunable bandgaps and strongly bound excitons and trions emerge from strong many-body effects, beyond the spin and valley degrees of freedom induced by spin–orbit coupling and by lattice symmetry. Combining single-layer TMDs with other 2D materials in van der Waals heterostructures offers an intriguing means of controlling the electronic properties through these many-body effects, by means of engineered interlayer interactions. Here, we use micro-focused angle-resolved photoemission spectroscopy (microARPES) and in situ surface doping to manipulate the electronic structure of single-layer WS$_2$ on hexagonal boron nitride (WS$_2$/h-BN). Upon electron doping, we observe an unexpected giant renormalization of the spin–orbit splitting of the single-layer WS$_2$ valence band, from 430 meV to 660 meV, together with a bandgap reduction of at least 325 meV, attributed to the formation of trionic quasiparticles. These findings suggest that the electronic, spintronic and excitonic properties are widely tunable in 2D TMD/h-BN heterostructures, as these are intimately linked to the quasiparticle dynamics of the materials.

Coulomb interactions in 2D materials are several times stronger than in their 3D counterparts. In 2D TMDs, this is most directly evidenced by the presence of excitons with binding energies an order of magnitude higher than in the bulk. Although the excitons in these 2D materials have been widely studied by optical techniques, the impact of strong electron–electron interactions on the quasiparticle band structure remains unclear. Theory predicts that many-body effects will influence the spin–orbit splitting around the valence-band maximum (VBM) and conduction-band minimum (CBM). Although these should be observable by ARPES, a direct probe of many-body effects, by means of engineered interlayer interactions, has been too broad for detailed analysis, probably owing to surface roughness and charge impurity scattering. Compared with SiO$_2$ and similar substrates, h-BN has favourable qualities such as atomic flatness, modest screening and a homogeneous charge distribution. This should enable direct investigation of the intrinsic electronic structure and many-body effects of the adjacent TMD. Hexagonal BN is often used as a substrate for graphene heterostructures with high device performance and new exotic electronic states such as quantized Dirac cones. Unfortunately, the lateral size of mechanically assembled heterostructures is usually of the order of 10 μm, much smaller than the beam spot of typical ARPES setups (≥100 μm). Furthermore, sample charging on insulating bulk h-BN substrates would complicate ARPES experiments.

We overcome these challenges as follows. We realize a high-quality 2D semiconductor–insulator interface by mechanically transferring a relatively large (∼100 μm) single-layer WS$_2$ crystal onto a thin flake of h-BN that has itself been transferred onto a degenerately doped TiO$_2$ substrate, as depicted in Fig. 1a. Sample charging is avoided because there is electrical contact from the continuous single-layer WS$_2$ flake to both the h-BN and the conductive TiO$_2$.

Figure 1b is an optical microscope image of the sample, including a flake of h-BN, approximately 100 μm wide, surrounded by several transferred flakes of single-layer WS$_2$, on the TiO$_2$ substrate (WS$_2$/TiO$_2$), one of which partially overlaps the h-BN. By using a state-of-the-art spatially resolved microARPES experiment with a 10 μm focused synchrotron beam spot, we are able to collect distinct high-quality band-structure information from the multiple micrometre-scale interfaces. A spatial map of the photoemission intensity around the WS$_2$/h-BN heterostructure is shown in Fig. 1c, which was produced by integrating the intensity over the boxed region of the corresponding k-space band structure shown in Fig. 1d, measured at each spatial point. The crossing single-layer WS$_2$ and h-BN bands in this region ensure strong contrast between WS$_2$/h-BN (white arrow), regions of WS$_2$/TiO$_2$ (light purple) and regions of bare TiO$_2$ (dark purple) in the spatial map. The photoemission map (Fig. 1c) corresponds directly to the optical micrograph (Fig. 1b) with contrasts that reflect the intensity of the WS$_2$ and h-BN features in the red box in Fig. 1d. The band structures from bare TiO$_2$, WS$_2$/TiO$_2$ and several spots within the WS$_2$/h-BN heterostructure are presented in Supplementary Fig. 1. The slight intensity
Fig. 1 | Spatially resolved electronic structure mapping of a WS\textsubscript{2}/h-BN heterostructure supported on TiO\textsubscript{2}. a, Side-view sketch of WS\textsubscript{2}/h-BN on TiO\textsubscript{2}, illustrating single-layer WS\textsubscript{2} regions with direct contacts to h-BN and to TiO\textsubscript{2}. b, Optical microscope image of the sample. The contrast has been strongly enhanced for better visualization of the single-layer WS\textsubscript{2}. Brown patches correspond to bare TiO\textsubscript{2}, light purple to WS\textsubscript{2}/TiO\textsubscript{2} and the darker green/red structure is the h-BN flake. c, Spatial map of photoemission intensity (integrated over the red box in d) for the same region seen in b. d, Measured dispersion along the \( \overline{K}'-\Gamma-\overline{K} \) direction of the single-layer WS\textsubscript{2} Brillouin zone (see green Brillouin zone and dashed red line in the insert) collected at the spatial coordinates marked by a white arrow in c. The rectangular red box marks a region with crossing WS\textsubscript{2} and h-BN bands where the photoemission intensity is integrated to produce the spatial map in c, e, ARPES dispersion in the high-symmetry direction of h-BN (see purple Brillouin zone and dashed black line in the insert). f–h, Constant energy cuts obtained at the given binding energies (see also ticks on the right of panels d,e). Arrows mark distinct energy contours relating to single-layer WS\textsubscript{2} and to h-BN. The red and black dashed lines (insert in d,e) indicate a twist angle of \((23 \pm 1) ^\circ\) in between the single-layer WS\textsubscript{2} and h-BN. VB, valence band. i, j, EDCs obtained along the dotted lines in d,e around the h-BN VBM (i) and single-layer WS\textsubscript{2} VBM (j). The positions of the band edges are given in units of eV and the error bar is 30 meV (and thus smaller than the symbol size).

The impact of electron doping on the electronic structure through in situ surface potassium deposition is shown in Fig. 2a,b (see Supplementary Fig. 2 for core level data on clean and potassium-dosed samples). Doping WS\textsubscript{2}/h-BN leads to the CBM of single-layer WS\textsubscript{2} being populated at the \( \overline{K} \) points of single-layer WS\textsubscript{2}, confirming the expected direct bandgap. A surprising change of the dispersion of the two spin–orbit-split valence bands \( V_{B_{A}} \) and \( V_{B_{B}} \)
Electronic structure of strongly electron-doped WS$_2$/h-BN. a. Dispersion of single-layer WS$_2$/h-BN along the $\Gamma$–$\bar{K}$–$\Gamma$ direction of the single-layer WS$_2$, Brillouin zone, collected from the spot marked by the white arrow in Fig. 1c. b, Corresponding data at the highest achieved electron-doping $N$. c, EDCs (markers) around the VBM and CBM at $\bar{K}$ (see dotted lines and arrows in b) for undoped and electron-doped single-layer WS$_2$, on h-BN. Peak positions extracted from Lorentzian line fits (curves) are shown as vertical dashed lines, and values for the doped case are given in units of eV. Note that the CBM intensity has been scaled by a factor of 0.5 for clearer comparison with the other peaks. d, Schematics of the dispersion change of the valence-band spin–orbit split bands VBA and VBB due to doping and the measured energy gaps between the CBM and VBA (denoted as $E_\text{CBM}$) and VBB (denoted as $E_\text{VBB}$) in the doped case. The energy splitting due to spin–orbit coupling, $\Delta SO$, and the values of $E_\text{CBM}$ and $E_\text{VBB}$ are provided with error bars of 30 meV.

A detailed evolution of the band extrema with increasing doping is shown in Fig. 3a–e. The dispersions around the VBM as determined from EDC line shape analysis (see Supplementary Fig. 6) are shown by dashed red curves and directly compared in Fig. 3f. We estimate the charge carrier density, $n$, at each dosing step from the CBM position (see Methods). These estimated doping levels are consistent with those achieved in similar experiments$^{10}$ on bulk WS$_2$, and with the intensity of the potassium 3p core level (see Supplementary Fig. 3).

From EDC peak positions at $\bar{K}$ (see Supplementary Fig. 7), we extract the VBM and CBM energies as a function of dosing (Fig. 3g). After the first dosing step ($N = 1.7 \times 10^{13}$ cm$^{-2}$), the CBM becomes occupied, and VBA and VBB rigidly shift to higher binding energy. With further dosing, the CBM moves further down to higher binding energy, while VBA and VBB shift back towards lower binding energy, resulting in a continuous narrowing of the bandgap. In particular, the dispersion of VBA appears to renormalize with increased doping (see Fig. 3d–f), with a strong increase in $\Delta SO$ (Fig. 3g,h). This leads to a corresponding change in the relative energy separation between $E_F$ and $E_\text{CBM}$ (Fig. 3i), implying that the energies of the A and B exciton lines also separate. Data points with different marker shapes and colours in Fig. 3j stem from separate doping experiments on the three different flakes studied in Figs. 2 and 3 and in Supplementary Fig. 8. A reproducible trend is found across all flakes. Note also that in the carrier density range between $2 \times 10^{12}$ cm$^{-2}$ and $1.0 \times 10^{13}$ cm$^{-2}$, we find a more modest bandgap renormalization of $(90 \pm 30)$ meV, which is in excellent agreement with gate device measurements on a similar sample$^6$. Our observations reveal that it is insufficient to consider only rigid band shifts, and that strong dispersion changes can result from doping of single-layer TMDs.

The surprising doping-induced changes in $\Delta SO$ are probably not directly related to the surface potential induced by the potassium deposition (through, for example, the Rashba interaction), which is not expected to affect $\Delta SO$ at $\bar{K}$ for single-layer TMDs. This would introduce a splitting at $\bar{T}$, which we do not observe$^{16,27}$. Furthermore, we can rule out any potassium-induced structural symmetry breaking in our heterostructure, as only minor rigid binding-energy shifts of the S 2p core levels of WS$_2$, and of the underlying h-BN π-band are observed after complete doping (see Supplementary Figs. 4 and 5). The reproducible charge carrier dependence of the spectral changes demonstrated in Figs. 2 and 3 and Supplementary Fig. 8 suggests that these changes originate from Coulomb interactions around the band extrema of single-layer WS$_2$ (refs 1,4–7).

The linewidths of the VB, VBB and CBM peaks exhibit a non-monotonic dependence on doping, which cannot be described by simple scattering on ionized potassium impurities (see further discussion in Supplementary Section 4). Specifically, the observation that VB renormalization coincides with occupation of the CBM suggests that the renormalization is caused by new scattering channels available upon occupation of the conduction band. Previous works using surface potassium deposition for electron-doping of single-layer TMDs on conductive substrates$^{16–19}$, where the Coulomb interactions are already strongly screened in the undoped case, have shown no such changes in $\Delta SO$. We believe that the reduced dielectric constant of the h-BN substrate plays a key role for these observations as it leads to reduced screening of the many-body interactions in the bare single-layer WS$_2$.

An alkali-atom-induced renormalization of the valence band edge at K towards $E_F$ observed in several bulk TMDs, has been attributed to the breaking of the degeneracy of the outermost layers by the doping-induced field$^{25,28}$. This can either be a single-particle effect$^{29}$ or a combination of single- and many-body effects$^{28}$, the latter of which suggests a negative electronic compressibility (NEC), the motion of the chemical potential $\mu$ towards the VBM, i.e. $\mu d\mu/dN < 0$.

In contrast, we observe distinctive effects in single-layer WS$_2$/h-BN, namely (1) a renormalization of $\Delta SO$ within the single layer, (2) an NEC in which $\mu d\mu/dN$ is significantly larger than in the bulk$^{25,28}$, and (3) a VB$_\text{B}$ slope that is discontinuous at $k = (\bar{K}, \bar{\Gamma}) \pm 0.15$ Å$^{-1}$ in Fig. 2b at high doping. This leads to kinks in VB$_\text{B}$, exemplified by the arrow in Fig. 3e, which develop continuously in strength with doping in Fig. 3a–e. Such kinks are common in ARPES when the created ‘photohole’ interacts strongly with well-defined (in energy and/or momentum) excitations$^{10}$.

As noted above, the band renormalization coincides with the occupation of the conduction band, suggesting that such excitations are associated with electron–hole (e–h) pairs near $E_F$ in the conduction band, induced in response to the valence-band hole created during photoemission. In the undoped situation sketched in Fig. 4a, such interactions are not possible. At high carrier densities where the conduction band is occupied, an e–h excitation around $\bar{K}$ (or $\bar{\Gamma}$) can interact with the valance-band photohole, forming a positively charged, bound electron–hole–hole complex denoted as...
Fig. 3 | Evolution of single-layer WS₂ VBM and CBM dispersion with charge-carrier density. a–e, microARPES measurements around the K-point of single-layer WS₂/h-BN for clean (a) and increasingly potassium-dosed cases (b–e). The red curves are the fitted VB₀ and VB₁ dispersions determined from double Lorentzian fits of EDCs (see Supplementary Fig. 6). The arrow in e points to a possible kink in VB₁, f, VB₁ and VB₂ dispersions extracted from the EDC analysis in the strongly electron-doped cases. g, ARPES intensity at the K-point and peak positions (red markers) at each potassium-dosing step (see corresponding EDC analysis in Supplementary Fig. 7). h,i, Spin-orbit splitting (h) and bandgap values (i) determined from the VB₂, VB₁ and CBM positions, combining data from K-doping experiments on the different WS₂/h-BN flakes investigated here, in Fig. 2 and in Supplementary Fig. 8. The lines in h,i are provided as guides to the eye. N, charge carrier density. E_g, bandgap energy.

Fig. 4 | Quasiparticle dynamics in doped single-layer WS₂. a, Band diagram illustrating the generated photohole (open blue circle) in VB₁ and the photoemitted free electron (filled red circle) in the undoped situation. b, Illustration of an e⁺h⁻ trionic quasiparticle generated in doped single-layer WS₂. The photohole binding energy is lowered and the VB₁ dispersion renormalizes with respect to the bare band (green dashed curve) by the trion binding energy ΔE_{trionic}. c, A photohole generated in VB₁ in the doped situation undergoes a process that is analogous to the undoped situation in a, owing to the absence of strong trion interactions with photoholes in this band.
consequences of forming trionic quasiparticles around the VB₄ and conduction-band extrema.

The assignment of trions in optical measurements of semiconducting TMDs is currently being debated, as a recent theoretical study points towards the possibility of interactions between e–h pairs and the remaining charge density forming other types of quasiparticles such as exciton–polarons⁵⁰. Our ARPES measurements provide direct evidence for such multi-component excitations in single-layer TMDs and give access to both their energy and momentum dependence that is lacking from momentum-integrating transport, optical or tunnelling measurements. We envisage further theoretical and experimental studies to disentangle such many-body effects in the spectral function of single-layer TMDs. The charge-carrier-dependent electronic bandgap and spin-splitting that arise from these many-body effects will profoundly impact the charge-, spin- and valley-dependent dynamics and transport properties of devices, as well as the interpretation of excitonic effects.

Received: 26 April 2017; Accepted: 7 December 2017; Published online: 22 January 2018

References
1. Chernikov, A. et al. Electrical tuning of exciton binding energies in monolayer WS₂, Phys. Rev. Lett. 115, 126802 (2015).
2. Liang, Y. & Yang, L. Carrier plasmon induced nonlinear band gap renormalization in two-dimensional semiconductors, Phys. Rev. Lett. 114, 063001 (2015).
3. Chernikov, A., Ruppert, C., Hill, H., Rigosi, A. & Heinz, T. Population inversion and giant bandgap renormalization in atomically thin WS₂ layers, Nat. Photon. 9, 466–470 (2015).
4. Ramasubramaniam, A. Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides. Phys. Rev. B 86, 115409 (2012).
5. Qiu, D., Jornada, F. & Louie, S. Optical spectrum of MoS₂: many-body effects and diversity of excition states. Phys. Rev. Lett. 111, 216805 (2013).
6. Maé, K. et al. Tight-binding trions in monolayer MoS₂, Nat. Mater. 12, 207–211 (2013).
7. Xiao, D., Liu, G., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS₂ and other Group-VI dichalcogenides. Phys. Rev. Lett. 108, 196802 (2012).
8. Goni, A. & Grigorieva, I. Van der Waals heterostructures. Nature 499, 419–425 (2013).
9. Ugeda, M. et al. Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor. Nat. Mater. 13, 1091–1095 (2014).
10. Larentis, S. et al. Band offset and negative compressibility in graphene–MoS₂ heterostructures. Nano Lett. 14, 2039–2045 (2014).
11. Xu, X., Yao, W., Xiao, D. & Heinz, T. Spin and pseudospins in layered transition metal dichalcogenides. Nat. Phys. 10, 343–350 (2014).
12. Kormányos, A. k·p theory for two-dimensional transition metal dichalcogenide semiconductors. 2D Mater. 2, 049501 (2015).
13. Maé, K. F. & Shan, J. Phonons and optoelectronics of 2D semiconductor transition metal dichalcogenides. Nat. Photon. 10, 216–226 (2016).
14. Ferreira, Y. & Cortijo, A. Large conduction band and Fermi velocity spin splitting due to Coulomb interactions in single-layer MoSe₂. Phys. Rev. B 90, 195426 (2014).
15. Bostwick, A., Ohta, T., Seyller, T., Horn, K. & Rotenberg, E. Quasiparticle dynamics in graphene. Nat. Phys. 3, 36–40 (2007).
16. Zhang, Y. et al. Direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial MoSe₂. Nat. Nanotechnol. 9, 111–115 (2014).
17. Zhang, Y. et al. Electronic structure, surface doping, and optical response in epitaxial WSe₂, thin films. Nano Lett. 16, 2485–2491 (2016).
18. Miwa, J. et al. Electronic structure of epitaxial single-layer MoSe₂. Phys. Rev. Lett. 114, 046802 (2015).
19. Jin, W. et al. Direct measurement of the thickness–dependent electronic band structure of MoS₂ using angle–resolved photoemission spectroscopy. Phys. Rev. Lett. 111, 106801 (2013).
20. Dean, C. et al. Boron nitride substrates for high-quality graphene electronics. Nat. Nanotechnol. 5, 722–726 (2010).
21. Wang, L. et al. One-dimensional electrical contact to a two-dimensional material. Science 342, 614–617 (2013).
22. Wang, E. et al. Gaps induced by inversion symmetry breaking and second–generation Dirac cones in graphene/hexagonal boron nitride. Nat. Phys. 12, 1111–1115 (2016).
23. Ustru, S. et al. Spatially resolved electronic properties of single-layer WS₂ on transition metal oxides. ACS Nano 10, 10058–10067 (2016).
24. Denisenko, M. et al. Growth and electronic structure of epitaxial single-layer WS₂ on Au(111). Phys. Rev. B 92, 245442 (2015).
25. Riley, J. et al. Negative electronic compressibility and tunable spin splitting in WSe₂, Nat. Nanotechnol. 10, 1043–1047 (2015).
26. Yuan, H. et al. Zeeman–type spin splitting controlled by an electric field. Nat. Phys. 9, 563–569 (2013).
27. Shanavas, K. V. & Satpathy, S. Effective tight–binding model for MX₂ under electric and magnetic fields. Phys. Rev. B 91, 235145 (2015).
28. Kang, M. et al. Universal mechanism of band–gap engineering in transition–metal dichalcogenides. Nano Lett. 17, 1610–1615 (2017).
29. Zhu, B., Chen, X. & Cui, X. Exciton binding energy of monolayer WS₂. Sci. Rep. 5, 9218 (2015).
30. Efimkin, D. K. & MacDonald, A. H. Many–body theory of trion absorption features in two–dimensional semiconductors. Phys. Rev. B 95, 035417 (2017).

Acknowledgements
We thank A. H. MacDonald for discussions. S.U. acknowledges financial support from the Danish Council for Independent Research, Natural Sciences, under the Sapere Aude programme (grant no. DFF-4090-00125) and from VILLUM FONDEN (grant no. 15375). R.J.K. is supported by a fellowship within the postdoctoral programme of the German Academic Exchange Service (DAAD). S.M. acknowledges support by the Swiss National Science Foundation (grant no. PZELP2-155377). The work at Ohio State was primarily supported by NSF-MRSEC (grant DMR-1420454). Work at the US Naval Research Laboratory (NRL) was supported by core programmes and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research under contract number AOARD 1400108-134414. This research used resources of the Advanced Light Source, which is a US Department of Energy Office of Science User Facility under contract no. DE-AC02-05CH11231.

Author contributions
J.K. and S.U. conceived and planned the experiments. K.M.M. and B.T.J. synthesized the single-layer WS₂ flakes on SiO₂, J.K., S.S., I.J. and R.K.K. assembled the WS₂/b–BN heterostructures on TiO₂, S.U., R.J.K., S.M., J.K., A.B., E.R. and C.J. performed the microARPES experiments. The microARPES set-up was developed and maintained by C.J., A.B. and E.R. S.U. analysed the experimental data with inputs from C.J. and E.R. All authors contributed to the interpretation and writing of the manuscript.

Competing interests
The authors declare no competing financial interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41567-017-0033-4.
Reprints and permissions information is available at www.nature.com/reprints.
Correspondence and requests for materials should be addressed to C.J.
Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
Methods

Fabrication of WS₂/h-BN heterostructures. The heterostructures were prepared by successively transferring few-layer h-BN (commercial crystal from HQ Graphene) and then single-layer WS₂ onto 0.5 wt% Nb-doped rutile TiO₂(100) (Shinkosha Co., Ltd). A thin film of polycarbonate (PC) was mounted onto polydimethylsiloxane (PDMS) on a glass slide to prepare a PC/PDMS stamp. This stamp was first used to pick up h-BN flakes from a SiO₂ substrate and then dropped onto the TiO₂ substrate under a microscope. The transferred h-BN flakes were cleaned of any polymer residue by annealing at 625 K in ultrahigh vacuum (UHV) for 1 h. Next, single-layer WS₂ flakes were picked up from the SiO₂ growth substrate and aligned to drop onto h-BN, such that a part of the flake made contact with the TiO₂ substrate. The process was followed by another annealing step in UHV to clean off any remaining residues.

Experimental details of microARPES. The samples were transported through air to the Microscopic and Electronic Structure Observatory (MAESTRO) at the Advanced Light Source where they were inserted in the microARPES UHV end-station with a base pressure better than 5 × 10⁻¹¹ mbar. The samples were given a mild anneal at 600 K prior to measurements, in order to desorb adsorbates from air. The synchrotron beam-spot size was on the order of 10 μm for the photon energies of 145 eV and 76.5 eV used to obtain the microARPES data. The data were collected using a hemispherical Scienta R4000 electron analyser equipped with custom-made deflectors that enable collecting ARPES spectra over a full Brillouin zone without moving the sample. Potassium-dosing experiments were carried out by evaporating potassium in situ from a SAES getter source mounted in the analysis chamber such that dosing is performed in an optimum sample measurement position without moving the sample. Core level data of undoped and potassium-dosed samples are presented in Supplementary Fig. 2 to document the cleanliness of the samples. The data in Figs. 1 and 2 are from the same sample, whereas the data in Fig. 3 and Supplementary Fig. 8 were obtained on fresh samples. The charge carrier density \( N \) is estimated using a simple model of a 2D parabolic band given by \( N = \frac{g_v g_s m^*_c}{2k_B^2 T} \ln(1 + e^{E - E_F}/k_B T) \), where the factors \( g_v = 2 \) and \( g_s = 2 \) take spin- and valley-degeneracy into account, \( m^*_c \) is the effective mass of the single-layer WS₂ conduction band obtained from ref. 12, \( k_B \) is Boltzmann’s constant, \( h \) is the reduced Planck constant, \( T \) is the sample temperature and \( E - E_F \) is determined from the fitted CBM position. The total energy resolution and momentum resolution in the microARPES data were better than 20 meV and 0.01 Å⁻¹, respectively. Measurements and dosing experiments were carried out at both 85 K and at 20 K, without any noticeable change in behaviour between the two temperatures.

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.