Dichalcogenides (TMDC) such as NbSe$_2$ resemble the famous Peierls instability [1, 2]. Transition metal and organic salts, the CDW phenomenology often closely resemble typical examples for how CDWs can also occur in quasi-1D systems, such as ZrTe$_2$. The starting point for understanding the instability of the parent phase.

Charge-density waves (CDWs), typically found in low-dimensional metallic systems, are a striking example of how coupling between the electrons and the crystal lattice can lead to novel ground states. In quasi-1D systems, such as ZrTe$_3$ and organic salts, the CDW phenomenology often closely resembles the famous Peierls instability [1, 2]. Transition metal dichalcogenides (TMDC) such as NbSe$_2$ have become prototypical examples for how CDWs can also occur in quasi-2D metals [3–5]. The starting point for understanding the CDW at ≈200 K in the well-known TMDC TiSe$_2$ is, however, an indirect narrow-gap semiconductor. Moreover, both the CDW ordering pattern and the normal state electronic structure are three-dimensional [6, 7], placing the CDW in this system far from the conventional picture, and its origin remains controversial.

Some reports assign TiSe$_2$ as a realisation of the long-predicted ‘exciton insulator’ phase, driven purely by electronic interactions [8–14]. The presence of substantial lattice distortions in the ordered phase, however, also points to an important role of electron-phonon coupling [5, 15–18], which may act cooperatively with electron-hole correlations to stabilise the CDW [19–22]. The emergence of superconductivity in TiSe$_2$ close to the critical point for the suppression of long-range CDW order via pressure [23], charge carrier doping [24], or intercalation [25, 26], further motivates interest in understanding the instability of the parent phase.

In this paper, we revisit the evolution of the electronic structure of TiSe$_2$ through the CDW transition, paying particular attention to $k_z$-dependent variations by employing detailed photon-energy dependent angle-resolved photoemission spectroscopy to probe the full three-dimensional high- and low-temperature electronic structure. Our measurements demonstrate how a mismatch of dimensionality between the 3D conduction bands and the quasi-2D valence bands in this system leads to a hybridisation that is strongly $k_z$-dependent. While such a momentum-selective coupling can provide the energy gain required to form the CDW, we show how additional ‘passenger’ states remain, which couple only weakly to the CDW and thus dominate the low-energy physics in the ordered phase of TiSe$_2$.

We revisit the enduring problem of the 2×2×2 charge density wave (CDW) order in TiSe$_2$, utilising photon energy-dependent angle-resolved photoemission spectroscopy to probe the full three-dimensional high- and low-temperature electronic structure. We show how additional “passenger” states remain, which couple only weakly to the CDW and thus dominate the low-energy electronic structure in the ordered phase.

Single crystals were grown by the iodine vapour transport method, and cleaved in-situ. ARPES measurements were performed at the I05 beamline at Diamond Light Source [28]. We label high-symmetry points of the Brillouin zone according to the notation of the high temperature phase, using the starred Γ$^*$ notation when referring to the 2×2×2 low-temperature unit cell.

The understanding of the CDW instability in TiSe$_2$ rests upon the details of the normal state electronic dispersions, and in particular the dimensionality of the relevant bands. Fig. 1(a) shows an overview of the occupied states, with a pair of Se 4p$_{x,y}$ states forming the low-energy valence bands at the Brillouin zone center, and a Ti 3d-derived conduction band centered at each L point [17, 29]. The conduction bands have an elliptical cross section in the $k_x - k_y$ plane, evident in a constant energy map at $E_F$ measured using a photon energy chosen to probe approximately the A-L-H plane ($k_z \approx \pi/c$, Fig. 1(b)). They are, however, strongly three-dimensional. In Fig. 1(e,g), the ARPES measurements at L points of the Brillouin zone show a clear electron-like conduction band, but the band disperses significantly along $k_z$ such that it is well above $E_F$ at M, in Fig. 1(f). Consistent with the Fermi surface calculated from density functional theory (DFT), shown in Fig. 1(c), our photon energy-dependent measurements (Fig. 1(d) [30]) also indicate that this conduction band pocket substantially tilts away from the $k_z$ axis. In contrast, the uppermost valence bands, of Se 4p$_{x,y}$ character, are found to be almost 2D; measurements with photon energies chosen to probe the high-symmetry Γ and A points (Fig. 1(e-g)) indicate a $k_z$ dispersion of the upper valence band of <10 meV (Fig. 1(h)). A third valence band, of Se 4p$_z$ character, appears only around the Γ point and disperses strongly along $k_z$ (Fig. 1(d)). This band does not play an im-
important role in the CDW ordering and so we do not consider it in detail below.

DFT calculations employing standard local density or generalized gradient approximations incorrectly predict a semimetallic band structure for the undistorted phase, with a substantial band overlap [7, 29], as can be seen from the presence of both hole and electron pockets in our calculated DFT Fermi surface in Fig. 1(c). It is therefore important to experimentally constrain the high temperature band gap, but previous estimates have varied from a gap of 150 meV to a band overlap of 70 meV [8, 29, 31–33]. In Fig. 1(h) we compare energy distribution curves (EDCs) of the valence bands at high-symmetry points, indicating an indirect band gap of 74±8 meV. The data in panels (e-h) are divided by the Fermi function to reveal the spectral weight above $E_F$.

First, the upper valence band at the A point cannot hybridise significantly with the conduction band states, since the pronounced $k_z$ dispersion of the latter renders it at inaccessibly high energies at M (Fig. 2(a,b)). Therefore the dispersion of the valence bands derived from the A point of the high temperature phase will remain largely unchanged through the CDW transition, except for an overall shift of the chemical potential from DFT calculations. In the CDW phase, the valence and conduction bands hybridise according to an interaction $\Delta_{CDW}(k)$. While this depends on the microscopics of the interaction terms being considered, a reasonable assumption for $\Delta_{CDW}(k)$ is a broadly-peaked function centered around $\mathbf{q}_{CDW} = (\pi, 0, \pi) = L$, where phonon modes are known to soften at the CDW transition of TiSe$_2$ [18, 34].

Anticipating the hybridisations allowed by this interaction term, we plot the bands in Fig. 2(a) offset by $\mathbf{q}_{CDW} = (\pi, 0, \pi) = L$. Careful choice of both the photon energy and polarisation ensures that the correct high-symmetry points of the three-dimensional Brillouin zone are probed, with adequate spectral weight at the band extrema to extract their locations directly from EDCs. From this, we assign the smallest indirect band gap as occurring between the $\Gamma$ and L points, with a magnitude of 74±8 meV. Crucially, this energy scale is small enough to be accessible to CDW ordering.

The mismatched dimensionality of the conduction and valence bands does, however, have a major influence on shaping the electronic structure in the ordered state of TiSe$_2$. In Fig. 2(a) we show the normal state conduction and valence band dispersions along the $k_z$ axis. These are based on the data in Fig. 1, except for the $k_z$ dispersion of the conduction band, for which we use a bandwidth of $\sim 200$ meV.
The band hybridisation is thus strongly $k_z$-dependent.

Second, the different orbital components of the conduction band couple inequivalently to the CDW order. The $2 \times 2 \times 2$ lattice distortion in TiSe$_2$ is a 3Q ordering, corresponding to a superposition of the atomic displacements associated with three softened L-point phonon modes [7]. Thus, electron pockets from three L points are backfolded to the $\Gamma^*$ point of the reconstructed Brillouin zone, allowing hybridisation with the valence bands. However, we demonstrate in our tight-binding analysis in the Supplemental Material (SM) [36] that the valence bands. However, we demonstrate in our tight-binding analysis in the Supplemental Material (SM) [36] that the valence bands. However, we demonstrate in our tight-binding analysis in the Supplemental Material (SM) [36] that the valence bands. However, we demonstrate in our tight-binding analysis in the Supplemental Material (SM) [36] that the valence bands.

To verify that such a $k_z$- and orbital-selective hybridisation underpins the reconfiguration of the low-energy electronic structure at the CDW ordering transition in TiSe$_2$, we search for two indicative spectroscopic signatures. The first is that the upper valence band at low temperatures should show characteristic dips along $k_z$, which can be loosely considered to be the inverse profile of the interaction $\Delta_{CDW}(k_z)$. Such dips are evident in measurements of the $k_z$ dispersion of the bright backfolded valence bands along M-L-M in the low-temperature phase ($T = 10$ K, Fig. 2(c)), very similar to the schematic in Fig. 2(b). The uppermost valence band dips by $\Delta_{CDW} \approx 100$ meV around L points, where primarily the strongly hybridised valence bands derived from $\Gamma$ are being observed, but recovers at M points where the more weakly hybridised valence bands derived from the A point are observed, confirming $k_z$-selective hybridisation.

Second, we consider the relative spectral weight of bands that are backfolded by the periodic lattice distortion. As evident in Fig. 3(a), low-temperature measurements show prominent backfolding of valence bands at the L point. This is a famous feature of ARPES spectra in the CDW phase of TiSe$_2$ [5, 8, 10, 17, 29, 33, 37, 38], where the backfolded intensity is comparable with the original valence bands at the $\Gamma$ point, indicating a strong involvement of these states in the CDW. In contrast, the conduction band appears brightly at the L point, but backfolded copies of this band are not clearly apparent in the spectra measured at $\Gamma$, consistent with previous reports [8, 39]. In fact, careful measurements at the $\Gamma$ point (see Fig. SM1 in SM) do reveal a replica of the conduction band, but with extremely weak spectral weight, showing a striking asymmetry with the remarkably bright intensity of the backfolded valence bands. This is entirely consistent with the assignment of the occupied electron band in the low-temperature phase as the branch with $d_{z^2}$ orbital character which remains unhybridised, since it hardly couples to the new periodicity and is thus only very weakly backfolded.

Having established the basic phenomenology of an orbital and $k_z$-selective hybridisation and the role of passenger states, we now turn to the detailed understanding of the low-temperature electronic structure in TiSe$_2$. Despite the large band shifts associated with the CDW, we stress that TiSe$_2$ retains a well-defined ungapped Fermi surface at low temperature, shown in Fig. 3(b). The population of the $d_{z^2}$-derived conduction band is due to a slight unintentional $n$-doping, which is typical of TiSe$_2$ crystals [6, 17, 40]. This is consistent with the $n$-type metallic transport of TiSe$_2$ at low temperatures [6, 40], although the exact carrier density is sample-dependent [41]. Despite the weak coupling of the states which form the Fermi surface here to the periodic lattice distortion, they must still respect the symmetry of the low-temperature phase, in which the $\Gamma$, M, A and L points become all formally equivalent to $\Gamma^*$ of the $2 \times 2 \times 2$ Brillouin zone. Thus the low temperature conduction band must adhere to 3 symmetry, which is preserved in the CDW phase. This explains their almost circular in-plane dispersion observed experimentally, in contrast to the twofold-symmetric elliptical pockets in the high-temperature phase (Fig. 3(b,c)). Moreover, the slanting of the Fermi pockets away from the $k_z$ axis seen in the high temperature phase in Fig. 1(c,d) is forbidden at low temperatures (Fig. 3(d)). The conduction bands also develop a steeper band dispersion at low temperatures, consistent with recent first-principles cal-
FIG. 3. a) Valence band dispersion along A-L at 10 K (hν=121 eV, p-polarisation). b) Fermi surface map, showing near-circular pockets at the L points. c) Schematic Fermi surfaces at high and low temperatures in the k_z = π/c plane. d) Low-temperature k_z map, equivalent to Fig. 1(d), now showing backfolded valence bands, and the Fermi surface in the inset (top-right). e,f) High symmetry dispersions along Γ-M (31 eV, 100 eV) and A-L (44 eV, 121 eV, all s-polarisation) respectively. g) Schematic band structure at Γ* of the 2×2×2 Brillouin zone, with an estimated band gap of ~15 meV.

Besides the conduction band, there are five low-energy valence bands centered at each Γ* point: three derived from the high temperature Γ point, one of which is the p_z state, and two derived from the A point [7]. These cannot all be observed simultaneously in one geometry, since the spectral weight as seen by ARPES tends to dominantly follow the projection of the states onto the high temperature zone [5]. However by combining the dispersions observed at different photon energies in Fig. 3(e,f), we can identify all five, represented schematically in Fig. 3(g). The upper valence band derived originally from the Γ point is flattened and hybridises so strongly that in fact it is more clearly observed backfolded at the L point in Fig. 3(f). In contrast, the A point dispersion in Fig. 3(f) is very similar to the equivalent measurement at high temperature (Fig. 1(e)) except that the bands are sharper and there is an overall shift of the chemical potential. Thus the in-plane dispersions also reinforce the ideas of k_z-selective hybridisation.

Based on these measurements, we estimate that the low temperature band gap is ~15 meV - much smaller than the 74 meV band gap at high temperatures [43]. This is unexpected, since second order electronic phase transitions typically involve opening up or increasing energy gaps. To rationalise this result, we draw the distinction between the strongly hybridised states which provide the energy gain for the CDW to occur, and the passenger states. The strongly hybridised states originate from the Γ and L points, and are shifted away from E_F by ±Δ_{CDW} ~ 100 meV, a large energy scale consistent with the high T_c ≈ 200 K. However, we identify that the overall band gap at low temperatures is set by other states in the system: the A-derived valence band and the unhybridised Ti-d_{z^2} conduction band branch. Thus the low temperature band gap is between two passenger states, and its magnitude is not directly related to the strength of CDW order.

The observation of a smaller band gap in the ordered phase is not easy to reconcile with a purely excitonic mechanism for the phase transition. Moreover, we have observed an ungapped Fermi surface and a near-continuum of single particle excitations across the energy scale of ±Δ_{CDW}; the existence of these low-energy passenger states would presumably promote the decay of excitons. Nevertheless, the relatively low free carrier density from these passenger states may be insufficient to completely screen the Coulomb interaction between electrons and holes [20], allowing the possibility that excitonic correlations may still play an assistive role in the CDW ordering [19–22, 44]. Irrespective of the precise microscopic origin of the instability, its underlying driving force is an electronic energy gain from band hybridisation. Our measurements highlight how momentum and orbital selectivity can act to decouple such energy gain from the low-energy physics of the ordered state. This is of crucial importance for...
understanding not only the enigmatic CDW state in TiSe$_2$, but also charge ordering instabilities in multi-orbital systems in general.

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FIG. 4. (a) Valence band dispersion, measured using $p$-polarisation at 95 eV, corresponding to a $\Gamma$ point. Note that this is the opposite polarisation to most of the valence band data shown in the main paper, which were mostly measured in $s$-polarisation ($s$- and $p$-polarisations correspond to Linear Vertical and Linear Horizontal polarisations respectively, and the analyser slit is aligned vertically at the I05 beamline.) (b) The same data set, but with a significant overexposure of the colormap, which allows the visual observation of the very weak backfolded conduction band. The MDC at the Fermi level is also plotted, showing weak peaks at $\pm k_F$ of the electron band.

In the main text, we noted that the conduction band can be observed backfolded, but with very weak intensity in ARPES. To understand this effect, we should first remark that although the bandstructure, i.e. the dispersion of the poles in the Green’s function, must obey the symmetry and periodicity of the $2\times2\times2$ unit cell, the spectral weight as probed by ARPES tends to mainly follow the periodicity of the original cell. The spectral weight of “backfolded” features is then typically proportional to the magnitude of their coupling to the new periodicity, though modified matrix elements may also affect the measurements. Theoretically, this problem is treated by projecting (or “unfolding”) the supercell wavefunctions back onto the basis of the original cell [7]. The experimental consequence is that one cannot simply expect to measure all the folded dispersions corresponding to the $\Gamma^*$ point in a single geometry; rather one needs to build a picture by measuring at each of the $\Gamma$,A,M, and L points of the high-temperature cell, and identify the unique dispersions. The low temperature conduction band is not a strongly hybridised state, and derives from the $d_{z^2}$ orbital without significant hybridisation in the CDW phase. Since this conduction band is therefore only weakly coupled to the CDW periodicity, it is observed strongly at the L point (where the conduction band states exist in the undistorted phase) but with only very weak intensity at the $\Gamma$ point, even though both are formally $\Gamma^*$ points of the ordered phase. This asymmetry of spectral weight has been also found in *ab-initio* [7] and tight-binding modelling [19].
Orbital character of conduction bands: tight-binding model calculations

**FIG. 5.** Monolayer TiSe$_2$ tight-binding simulations. a) Bandstructure in the undistorted phase. Distinct bandwidths arising from primarily the Se 4p, Ti 3d : $t_{2g}$ and 3d : $e_g$ orbitals are identified. (b) Fermi surface in the undistorted phase. (c) Backfolding of the bands, in the CDW phase at infinitesimal distortion, and d) for a realistic value of the CDW distortion/interaction. e) Detailed band dispersions at the $\Gamma$ point of the reconstructed phase, identifying the strongly hybridised doubly-degenerate $d_z$ branch and the singly-degenerate $d_l$ unhybridised branch. Dashed lines correspond to infinitesimal distortion (i.e. dispersions are shown backfolded, but not hybridised). (f-j) Orbital character projections. In (f), one can see the extra Se weight appearing on the upper, hybridised branch of the conduction band, while the lower, unhybridised branch, does not gain Se weight. (g) The $d_l$ conduction band is clearly identified with the $d_{z^2}$ orbital, whereas in (h) the doubly-degenerate $d_z$ branch corresponds to the projections of $t_{2g}$ orthogonal to $d_{z^2}$. (i,j) Moving away from the high-symmetry point and the hybridised region, the natural orbital basis are the rotated basis functions where $x^*$, $y^*$, $z^*$ correspond to the idealised octahedral environment of Ti (colored arrows in inset).

In the main text it was stated that the observed conduction band, the singly-degenerate and apparently unhybridised branch which we label as $d_{1s}$, has $d_{z^2}$ orbital character. Here, we justify this statement with a tight-binding model analysis. We use the model recently developed by Kaneko et al. [19]. This model was developed for monolayer TiSe$_2$, and therefore does not capture the $k_z$-dependent physics we report in the main text; however it provides a useful simplification to allow discussion of structure and orbital content of the conduction bands. Notably, the $p_z$ orbital which disperses strongly along $k_z$ in the bulk is confined in the monolayer case, thus only the $p_x$, $p_y$ valence bands appear at low energies. Moreover our tight-binding implementation does not include spin-orbit coupling, meaning that these states form a doublet at the $\Gamma$ point.

Kaneko et al. [19] fitted the band dispersions obtained from DFT calculations of the monolayer to obtain their Slater-Koster parameters. However, since their parameters give a small band overlap (negative band gap), we adjust the $p$-orbital energy down by 100 meV in order to yield a band gap comparable with the bulk value, keeping other parameters constant. We do not claim this parameter set is in any way optimized compared with the experimental dispersions for either bulk or monolayer TiSe$_2$, only that the model is sufficiently realistic to make statements regarding the orbital character of bands. In a similar spirit, we implement the CDW distortions in a rather simplified manner, where only the Ti displacements are considered, and the nearest-neighbour $p-d$ hopping terms are simply rescaled by the ratio of the new bond length in the $2 \times 2$ phase to that in the undistorted phase. The actual atomic positions are not displaced for the calculation, and the non-radial components of the displacements are ignored. Although this is therefore only a first approximation, it can be justified by the fact that we obtain similar results to the complete but technically complex implementation performed by Kaneko et al. [19].

Considering first the undistorted phase in Fig. 5(a), we find a clear hierarchy of bandwidths; the Se 4p states form the strongly dispersive valence bands, while Ti 3d orbitals form relatively weakly dispersing distinct $t_{2g}$ and $e_g$ manifolds, split by the crystal field environment of the octahedral coordination of Ti. The $t_{2g}$ bands are further split at the $\Gamma$ point due to trigonal distortions of the octahedral environment in the 1T phase, but this is only a small effect. The term $t_{2g}$ in this context corresponds to the
\( d_{xz}, d_{yz}, d_{xy} \) orbitals, defined in a rotated reference frame corresponding to the idealised octahedral axes, i.e. the \( x^*, y^*, z^* \) axes point approximately along each of the Ti-Se bond directions (insets of Fig. 5(i,j)). Thus the \( t_{2g} \) orbitals determine the Fermi surface shown in Fig. 5(b), with the chemical potential set to slight electron-doping as is experimentally the case. These Fermi surfaces form ellipses centered at the M points.

In the distorted phase, three copies of the elliptical Fermi surface are backfolded to the \( \Gamma \) point, shown in Fig. 5(c). Thus these bands would be triply-degenerate at the \( \Gamma \) point of the distorted phase at infinitesimal displacement. However, when switching on the hybridisation with the valence bands due to the interaction term introduced by the symmetry-breaking atomic displacements, this triplet splits into a doublet which strongly hybridises with the valence bands, and a singlet representation which is unaffected by the CDW distortion, as seen in in Fig. 5(e).

It is useful to break down the orbital content of these separate dispersions, and in Fig. 5(g) we show that the singlet unhybridised state derives from the \( d_{z^2} \) orbital. Care must be taken on the nomenclature; here the \( d_{z^2} \) orbital corresponds to the crystallographic reference frame where the \( d_{z^2} \) orbital points out of the plane, i.e. not the rotated reference frame. Formally it can be shown that \( d_{z^2} \) is equivalent to the symmetric linear combination of \( d_{xz}^*, d_{yz}^*, \) and \( d_{xy}^* \). These results therefore demonstrate that the component of the \( t_{2g} \) manifold which projects onto the \( d_{z^2} \) orbital does not hybridise with the Se \( p \)-states at \( \Gamma \). This behavior is related to the high-symmetry of the \( d_{z^2} \) orbital in the CDW phase; since the atomic displacements are in-plane only [6], the extra hybridisation terms associated with the CDW distortion cancel as a first approximation for the \( d_{z^2} \) orbital, at least exactly at \( \Gamma \). Thus as the hybridisation is switched on, this singlet branch remains, while the doublet conduction band, corresponding to the non-\( d_{z^2} \) projections of the \( t_{2g} \) orbitals, hybridise with the valence bands and are mutually repelled from the Fermi level. Away from the \( \Gamma \) point and the region of hybridisation, the bands revert to their dispersions in the undistorted phase, where again the natural orbital basis is that of the rotated reference frame (Fig. 5(i,j)).

The appearance of a singlet representation that remains essentially unhybridised appears also in DFT calculations in the CDW phase. For example, the existence of this band, separate from the twofold degenerate hybridised band, was noted by Hellgren et al. [42], who assigned it as having “dominant \( d_{z^2} \) character derived from the Ti atom in the supercell that does not move with the distortion”. However in our view, the essential ingredient is the \( d_{z^2} \) orbital character of this band, rather than a distinction based on the atomic site.

Although this tight-binding analysis gives us confidence on the identification of the conduction band, experimentally we find that in bulk TiSe\(_2\) this band appears to sink to higher binding energies at low temperatures, causing the total band gap of the system to reduce. In our model this feature is not reproduced; the energy of the singlet \( d_{z^2} \) band at \( \Gamma \) simply remains constant as a function of increasing hybridisation. A possible explanation is that, because of the fact that this band is constituted from the \( d_{z^2} \) orbital with lobes of the wavefunction pointing out of the plane, there may be an associated change in the inter-layer hopping for this band in the bulk case, not captured in our monolayer tight-binding model. This is, however, a subtle feature, and it remains to be seen if any \textit{ab-initio} or 3D tight-binding analysis can account for it.