Suppression and emergence of charge-density waves at the surfaces of layered $1T$-TiSe$_2$ and $1T$-TaS$_2$ by \textit{in situ} Rb deposition

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\textbf{Abstract.} \textit{In situ} real-time angle-resolved photoelectron spectroscopy is used to measure the electronic structure changes at the surfaces of the layered charge-density-wave materials $1T$-TiSe$_2$ and $1T$-TaS$_2$ during Rb deposition. For $1T$-TiSe$_2$, Rb adsorption at a sample temperature of 80 K causes a transition from a dirty semiconductor to a metal, in the course of which the $p(2 \times 2 \times 2)$ charge-density wave is completely suppressed. For $1T$-TaS$_2$, Rb adsorption at room temperature is rapidly followed by intercalation, leading to a pronounced metal-to-insulator transition that is correlated with a structural change from the pristine nearly commensurate $p(\sqrt{13} \times \sqrt{13})R13.9^\circ$ superlattice to a commensurate $c(2\sqrt{3} \times 4)$rect. charge-density-wave phase. The implications of the results on the charge-density-wave mechanisms in both compounds are discussed with particular reference to the possible interplay of electron–phonon and electron–electron interactions. It is suggested that strong electron–phonon coupling drives the charge-density wave (CDW) phase transitions in pristine $1T$-TiSe$_2$ as well as in Rb intercalated $1T$-TaS$_2$, i.e. the transitions are interpreted as primarily Peierls-like instabilities or, in other words, Jahn–Teller band instabilities.
1. **Introduction**

The occurrence of standing charge-density waves (CDWs)—periodic modulations of the conduction electron density, which in real materials are always coupled to a periodic lattice distortion—(see [1]) is quite a common phenomenon in transition-metal dichalcogenides (TMDCs) [2], because two important prerequisites are often fulfilled in these layered systems consisting of chemically saturated X–T–X sandwiches (T: transition metal; X: chalcogen): a large electron–phonon coupling and a highly anisotropic band structure with a significant density of occupied states at or near the Fermi level [1]. Yet, despite more than three decades of research, the microscopic mechanism underlying CDW formation in these layer compounds is still not understood. Simple Fermi surface nesting completely fails as an explanation [3] and the more sophisticated models [4] are not fully compatible with the experimental results.

Nevertheless, what has been learned is that a promising strategy toward elucidating the mechanisms of CDW formation might be to modify the properties of the CDW bearing materials in a controlled way, e.g. by application of hydrostatic pressure [5, 6], by substitutional doping [7, 8] or by the intercalation of foreign atoms or molecules in the ‘van der Waals gaps’ between the TX$_2$ sandwiches [9, 10], and then measure how the CDW responds. Among these approaches, in particular intercalation of TMDCs by alkali metals has turned out to be a very simple and powerful method to tune the relevant electronic properties of the host systems [10, 11]. Alkali intercalation facilitates, to a certain degree, control of the transition-metal $d$-band filling and the dimensionality of the electronic structure, while at the same time preserving a high structural integrity of the framework of host layers. Alkali intercalation may specifically result in pronounced changes of the electrical properties. It can turn a semiconductor into a metal [10] or even a superconductor [13, 14] and vice versa and, in the host compounds exhibiting CDWs, it can create novel CDW phases [12] or strengthen superconductivity at the expense of the CDW [10]. Hence, as essentially a tool for tuning the shape, volume and
dimensionality of host Fermi surfaces, alkali intercalation suggests itself as a viable approach
to a better understanding of the notoriously elusive CDW mechanism. However, using alkali
intercalation as a true control parameter requires that the induced changes to the electronic
structure are determined directly and accurately as a function of the alkali concentration and
that they are correlated with the concomitant structural modifications.

Probably the most powerful technique for determining the electronic structure of
condensed matter systems is photoelectron spectroscopy. It is, however, a highly surface-
sensitive technique and puts strict requirements on the samples to be used. This means, in
particular, that traditional ways to achieve bulk alkali intercalation of layered TMDCs, such
as immersion of crystals in solutions or electrochemical methods [10], cannot be applied. These
‘ex situ’ methods generally lead to cracked host lattices with a high impurity density and are
therefore not compatible with the ‘surface science approach’, in which the properties of well-
defined—atomically flat and clean—surfaces are investigated. Fortunately, it has been found
that spontaneous alkali intercalation of the surface layers of TMDCs can occur without major
structural damage, simply when the alkali atoms are deposited on the cleavage surfaces in
ultrahigh vacuum [11, 15]. Since the deposition is usually done immediately before or even
during the measurements, this approach has been termed ‘in situ intercalation’. Its big advantage
is, of course, that the whole arsenal of surface science techniques can be readily applied to study
the electronic and structural changes.

Among the available techniques, photoelectron spectroscopy in fact plays the most
prominent role in in situ alkali intercalation experiments. On the one hand, chemical shifts
and core-hole screening effects in alkali core-level spectroscopy provide direct information
on the state of the alkali atoms, as distinct spectral features corresponding to alkali atoms
dispersed on the surface, condensed into metallic islands or intercalated into the ‘van der Waals
gaps’ can generally be observed. Importantly, surface and subsurface alkali concentrations
can readily be estimated from the measured spectra. On the other hand, the band structures
and Fermi surfaces determined by (synchrotron-radiation-based) angle-resolved photoemission
spectroscopy (ARPES) yield a detailed picture of the electronic structure changes of the host
lattice, including increased band fillings, the possible opening of energy gaps, as well as altered
band dispersions both parallel and perpendicular to the layers.

However, starting with the first in situ alkali intercalation experiments about 20 years
ago [15], the common approach has been to measure the photoemission spectra in a stepwise
fashion, in between short deposition cycles that may involve sample transfer to a preparation
chamber. Naturally, this way of recording the spectral changes as a function of the deposited
amount provides only snapshots so that relevant transient states may be missed, if the sampling
rate is not high enough. With the advent of parallel detection in ARPES [67], however, a
continuous monitoring of the spectral changes on the 1 s time scale—a true ‘photoemission
movie’—has become possible. This is the key experimental advance exploited in this paper.

To demonstrate the full potential of the method, we focus here on Rb as the alkali metal and
on the two prominent CDW compounds $1T$-TiSe$_2$ and $1T$-TaS$_2$ as the host systems. It is shown
that the combination of in situ Rb deposition—leading to adsorption and/or intercalation—and
real-time ARPES is an extremely powerful means of controlling the electronic structure at the
surfaces of layer compounds. In the Rb/TiSe$_2$ system, the CDW is continuously suppressed and
a semiconductor is changed into metal, whereas in Rb/TaS$_2$ it is the other way round: a stronger,
different CDW emerges and a bad metal is turned into a semiconductor with a surprisingly
large energy gap at the Fermi level. An important point is that it is the detailed photoemission
movies of these processes that provide novel insights into the controversial CDW mechanism at work in 1T-TiSe₂ and the intriguing intercalation-induced CDW transition in 1T-TaS₂. In the discussion of the results, the effects of electron–phonon and electron–electron interactions play a central role. In particular, two fascinating interpretations of the ARPES data are considered and discussed in detail: an excitonic insulator instability in pristine 1T-TiSe₂ and a Mott–Hubbard-type metal-to-insulator transition in Rb intercalated 1T-TaS₂.

The paper is structured as follows. In section 2 we review the experimental results on the peculiar CDWs in 1T-TiSe₂ and 1T-TaS₂ and the efforts that were made to control their properties. This is followed by section 3, which provides an overview of the effects of alkali deposition on layered TMDCs. In section 4 we briefly describe the details of the real-time photoemission experiments. The two main parts of this paper are sections 5 and 6. They present the experimental results and their discussion for the two systems Rb/1T-TiSe₂ and Rb/1T-TaS₂. Section 7 closes the paper, summarizing the results and drawing general conclusions.

2. CDWs and their tunability in 1T-TiSe₂ and 1T-TaS₂

When compared to the other TMDCs exhibiting CDWs, pristine 1T-TiSe₂ and 1T-TaS₂ both have their peculiarities. 1T-TiSe₂ is the only group IV–transition-metal compound showing CDW formation. The superlattice unit cell in real space is small, the CDW phase diagram is simple, but the CDW mechanism is not understood. 1T-TaS₂, on the other hand, is the only TMDC showing pronounced interplay of long-range CDW order and local correlation effects. Here, the superlattice unit cell is large, the phase diagram is complex, but the CDW mechanism is hardly questioned. In both compounds, the CDW transition temperatures are high, well above 150 K [16, 17], and the displacements of the transition-metal atoms are large, >2% with respect to the intralayer lattice constant [16, 18].

At room temperature, 1T-TiSe₂ is undistorted and on the border of being semimetallic. If it is cooled, it undergoes only one phase transition to a commensurate p(2 × 2 × 2) CDW state at 202 K [16]. The CDW wave vector connects high-symmetry points at the center and on the faces of the Brillouin zone, thus allowing direct interaction of Se 4p and Ti 3d states and producing a hybridized band structure. This p–d interaction plays a key role in two distinct CDW mechanisms, the excitonic insulator model [19, 20] and the second-order (or pseudo) Jahn–Teller effect [4], [21]–[23]. But it has not yet been settled whether the one or the other model or a combination of both [24]–[26] or even another scenario, an antiferroelectric transition with intrinsic phonon softening [27, 28], is to be preferred.

1T-TaS₂, on the other hand, is structurally undistorted and electronically ungapped only for temperatures above 560 K. Upon cooling, it shows a sequence of CDW phase transitions involving ordering near a $\sqrt{13} \times \sqrt{13}$-type superstructure [2, 29]. The CDW is incommensurate between 543 and 352 K, nearly commensurate (with commensurate domains) from 352 to 183 K (from 221 to 355 K upon heating) and commensurate below 183 K [2, 17, 29]. The final lock-in transition to the commensurate CDW phase leads to a long-range ordered distortion pattern in the Ta plane consisting of star-of-David-shaped 13-atom clusters and, remarkably, the lock-in is coupled to a Mott–Hubbard-type metal-to-insulator transition [30]. Since the CDW wave vector spans large parallel sections across individual Ta 5d Fermi surface pockets, Fermi surface nesting is commonly considered as the driving force of the CDW transition [7]. The metal-to-insulator transition, on the other hand, is usually explained as follows [30]: the combined effects of CDW reconstruction and spin–orbit coupling split the occupied Ta 5d states into three
subband manifolds, the top of which consists of a single band that straddles the Fermi level and is derived mostly from the star center Ta atoms \cite{31, 32}. This band is very narrow and half-filled and therefore susceptible to a Mott–Hubbard transition. The transition to the Mott insulating state, however, does not occur prior to the transition from the nearly commensurate, domain-like phase to the commensurate CDW phase because, as long as domain boundaries are present, free carriers will be available to screen the local Coulomb interaction below the critical value \cite{30, 33}. It should be noted that the CDW ordering in 1T-TaS$_2$ is not purely two dimensional. In the incommensurate and nearly commensurate phases, the sandwich stacking sequence has a period of 3 \cite{29}, whereas for the commensurate phase it is not clear whether the stacking period is 13 \cite{29, 34} or whether the stacking is disordered \cite{35, 36}.

In view of the conspicuous CDWs in 1T-TiSe$_2$ and 1T-TaS$_2$, it is a straightforward idea to try to modify these CDWs in a controlled way by hydrostatic pressure, substitutional doping or intercalation. The motivation is twofold: (i) to learn something about the CDW mechanisms and (ii) to possibly create novel CDW, superconducting or Mott insulating phases, all of which are prevalent in the TMDC family.

As to 1T-TiSe$_2$, the use of all three control parameters generally leads to a continuous suppression of the $p(2 \times 2 \times 2)$ CDW. Table 1 gives an overview of the studied systems together with estimates for the increase in Ti 3d band filling and the change of the Ti 3d–Se 4p overlap at the critical point, at which the superlattice diffraction spots or the resistivity anomaly connected with the CDW transition disappears. In all the listed cases, it is tempting to associate the suppression of the CDW with a change of the p–d interaction as a direct result of an increased carrier concentration (caused by pressure, doping or intercalation), the opening of a p–d gap (due to intercalation or alloying with a semiconductor) or an increase in p–d overlap (caused by pressure). But the overall experimental results are inconclusive. The values for the critical d-band filling (0.03–0.14 e$^-$/TiSe$_2$) and the critical p–d gap (0.11–0.45 eV) are not consistent and the role of disorder in suppressing the CDW is also not clear.

Nevertheless, the suppression of the CDW in 1T-TiSe$_2$ can have an intriguing consequence, as has been shown recently for the intercalation complex Cu$_x$TiSe$_2$ \cite{9}. In this system, a superconducting state emerges near $x = 0.04$ with a maximum transition temperature of about 4 K at $x = 0.08$ and with the CDW being completely suppressed in between, at $x \approx 0.06$ \cite{9}. Evidently, the same strong electron–phonon coupling responsible for CDW formation in 1T-TiSe$_2$ can also drive Cooper pairing as soon as the CDW is weakened, a fact that was known before only for the 2H-TX$_2$ compounds (T = Nb, Ta; X = S, Se) \cite{2}. Very recently, this novel fact for 1T-TiSe$_2$ has been corroborated by the discovery of pressure-induced superconductivity in connection with the CDW meltdown in the pristine material \cite{6}.

Using pressure as the control parameter, the competition between various ground states—CDW, Mott insulator and superconductivity—has recently also been unveiled for 1T-TaS$_2$ \cite{5}. The commensurate CDW/Mott insulating phase disappears at a pressure of 0.8 GPa, the nearly commensurate CDW phase is suppressed at 7 GPa, and superconductivity emerges somewhere in between, at around 3 GPa, with a maximum transition temperature of roughly 5 K \cite{5}. Although fascinating, in terms of CDW control the emergence of superconductivity under pressure is not particularly instructive. In that respect, the results of substitutional doping and intercalation are much more compelling.

When Ti is substituted for Ta to give the alloy system 1T-Ti$_x$TaS$_2$, the $\sqrt{13} \times \sqrt{13}$ superlattice is suppressed at $x \approx 0.15$, but strong diffuse scattering remains up to $x \approx 0.8$ \cite{7}. Remarkably, the magnitude of the CDW and diffuse scattering wave vectors is observed to

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**Table 1**: Overview of the studied systems together with estimates for the increase in Ti 3d band filling and the change of the Ti 3d–Se 4p overlap at the critical point, at which the superlattice diffraction spots or the resistivity anomaly connected with the CDW transition disappears.

| System         | Ti 3d Band Filling | Ti 3d–Se 4p Overlap |
|----------------|--------------------|---------------------|
| 1T-TiSe$_2$    |                    |                     |
| 1T-TaS$_2$     |                    |                     |

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Table 1. Suppression of the charge-density wave (CDW) in 1\textit{T}-TiSe\textsubscript{2} by intercalation (I), substitutional doping (D) and hydrostatic pressure (P). The critical concentration (or pressure), at which the CDW is suppressed, is denoted by \(x_c\), the corresponding increase in d-band filling by \(\Delta n_d\) (in electrons per unit cell), and the size of the p–d gap by \(\Delta E_{p-d}\) (in eV). A positive (negative) value of \(\Delta E_{p-d}\) indicates a band gap (overlap).

| Method | System | \(x_c\) | \(\Delta n_d\) | \(\Delta E_{p-d}\) |
|--------|--------|---------|----------------|-----------------|
| I      | Cu\textsubscript{x}, TiSe\textsubscript{2} | 0.06\textsuperscript{a} | 0.06\textsuperscript{a} | 0.11\textsuperscript{b} |
| I      | (N\textsubscript{2}H\textsubscript{4})\textsubscript{x}, TiSe\textsubscript{2} | 0.15\textsuperscript{c} | 0.12\textsuperscript{c} | – |
| I      | Ti\textsubscript{1+x}, Se\textsubscript{2} | 0.035\textsuperscript{d} | 0.14\textsuperscript{d} | – |
| D      | Ta\textsubscript{x}, Ti\textsubscript{1-x}, Se\textsubscript{2} | 0.07\textsuperscript{d} | 0.07\textsuperscript{d} | – |
| D      | V\textsubscript{x}, Ti\textsubscript{1-x}, Se\textsubscript{2} | 0.03–0.08\textsuperscript{d,e} | 0.03–0.08\textsuperscript{d,e} | – |
| D      | Zr\textsubscript{x}, Ti\textsubscript{1-x}, Se\textsubscript{2} | 0.15\textsuperscript{e} | – | \(\approx 0.18\textsuperscript{f}\) |
| D      | Hf\textsubscript{x}, Ti\textsubscript{1-x}, Se\textsubscript{2} | 0.4\textsuperscript{f} | – | \(\approx 0.45\textsuperscript{h}\) |
| P      | TiSe\textsubscript{2} | 3.0–4.5 GPa\textsuperscript{a,i} | \(\approx 0.04\textsuperscript{i}\) | \(\approx –0.45\textsuperscript{i}\) |

\textsuperscript{a}Morson et al [9].
\textsuperscript{b}Zhao et al [37].
\textsuperscript{c}Sarma et al [38].
\textsuperscript{d}Di Salvo and Waszczak [8].
\textsuperscript{e}Gaby et al [39].
\textsuperscript{f}Assuming band gaps of 0 eV for TiSe\textsubscript{2} and 1.2 eV for ZrSe\textsubscript{2} [40] and using a linear interpolation.
\textsuperscript{g}Taguchi [41].
\textsuperscript{h}Assuming band gaps of 0 eV for TiSe\textsubscript{2} and 1.13 eV for HfSe\textsubscript{2} [42] and using a linear interpolation.
\textsuperscript{i}Friend et al [43].
\textsuperscript{j}Kusmartseva et al [6].

scale as \(\sqrt{1-x}\) for \(0 \leq x \leq 0.8\), in the same way as the minor axis of the elliptical Ta 5d Fermi surface pocket is expected to change upon hole doping [7]. This result has widely been interpreted as strong evidence for Fermi surface nesting as the driving force of the CDW transition in 1\textit{T}-TaS\textsubscript{2}.

When intercalated with different atomic and molecular species, 1\textit{T}-TaS\textsubscript{2} even exhibits a number of novel superlattice patterns. These are generally not caused by intercalant ordering in the ‘van der Waals gaps’ but by CDW order in the S–Ta–S sandwiches. The various observed superstructures are summarized in table 2, in which the magnitude and direction of the CDW wave vectors are listed for different intercalation complexes and temperatures. Also included are the CDW phases of pristine 1\textit{T}-TaS\textsubscript{2}. The two most common CDWs of 1\textit{T}-TaS\textsubscript{2} intercalation complexes are connected with a \(p(3 \times 3)\) and \(c(2\sqrt{3} \times 4)\) rect. superlattice, respectively. Note that the latter is often termed \(\sqrt{7}a^*/8 \times \sqrt{7}a^*/8\) in the literature and that it involves a change from a primitive hexagonal to a non-primitive centered rectangular superstructure.

In order to understand the observed changes in CDW periodicity upon intercalation of 1\textit{T}-TaS\textsubscript{2}, attempts have been made on the basis of the rigid band model and the concept of Fermi surface nesting [51]. However, as figure 1 illustrates for a simplified Ta 5d tight-binding band structure [32], drawing nesting vectors is not decisive as long as accurate values for the intercalation-induced increase in d-band filling are lacking.
Table 2. CDW superlattices in intercalation complexes of 1T-TaS$_2$. Wood’s notation is used to name commensurate superlattices; incommensurate and nearly commensurate (domain-like) superlattices are labeled as IC and NC, respectively. The magnitude $|\mathbf{q}_0|$ and direction $\varphi$ of the CDW wave vectors relative to the reciprocal lattice vector $a^*$ are given together with the temperatures at which the CDW phases have been observed.

| Intercalant | Superlattice | $|\mathbf{q}_0|/|a^*|$ | $\varphi$ (deg) | $T$ (K) |
|------------|-------------|-----------------|----------------|-------|
| –          | IC$^a$      | 0.283           | 0              | 543–352|
|            | NC$^a$      | 0.285           | $\approx$12    | 352–183|
|            | $p(\sqrt{13} \times \sqrt{13})R13.9^{\pm a}$ | 0.277           | 13.9           | <183  |
| Alkali     | $p(3 \times 3)^b$ | 0.333           | 0              | 350–140|
|            | $c(2\sqrt{3} \times 4)$rect.$^c$ | 0.331           | 19.1           | 300–220|
|            | IC$_1^d$    | 0.385           | 30             | 300   |
|            | IC$_2^d$    | 0.415           | 23.4           | 330–300|
| Cu         | $p(3 \times 3)^e$ | 0.333           | 0              | 300–100|
| N$_2$H$_4$ | IC$_3^f$    | 0.288           | 0              | 360   |
|            | $c(2\sqrt{3} \times 4)$rect.$^f$ | 0.331           | 19.1           | 300   |
|            | $p(3 \times 3)^f$ | 0.333           | 0              | 80    |

$^a$Wilson et al [2], Bayliss et al [17] and Scruby et al [29].
$^b$Clark and Williams [12], Pettenkofer and Jaegermann [44], Crawack and Pettenkofer [45] and Adelung et al [46].
$^c$Clark and Williams [12], Pettenkofer and Jaegermann [44], Adelung et al [46], Crawack et al [47], Rossnagel et al [48] and Schmidt et al [49].
$^d$Clark and Williams [12].
$^e$Pettenkofer et al [50].
$^f$Tatlock and Acrivos [51].

In sections 5 and 6, we will concentrate on two of the scientific challenges mentioned in this section: the role played by the p–d interaction in the CDW transition of 1T-TiSe$_2$ and the origin of one of the novel CDW phases in the intercalation complexes of 1T-TaS$_2$—the one with the $c(2\sqrt{3} \times 4)$rect. superlattice. We will show that in situ alkali deposition—leading to adsorption and/or intercalation—combined with real-time photoemission spectroscopy is an effective tool to address these two issues.

3. In situ alkali deposition on TMDCs

Depending on substrate temperature (typically 30–300 K), deposition rate (typically 0.01–10 monolayer equivalents (MLE) per minute), the alkali–TMDC combination and the quality of the cleavage surface, in situ alkali deposition on layered TMDCs can principally trigger three distinct processes (see figure 2), although combinations of these are also possible [11]:

(i) Formation of alkali metal overlayers on the surface (figure 2(a)): This scenario is typically observed at liquid nitrogen substrate temperatures, at least for the larger alkali metals K, Rb and Cs [52, 53]. It starts with alkali adsorption in a two-dimensionally dispersed phase and ends with alkali metal films growing layer by layer. In between, before the first monolayer
Figure 1. Fermi surface nesting in 1T-TaS$_2$, illustrated in the ΓMK plane of k space with the help of a simple tight-binding model [32]. The solid contours indicate the shape of the Fermi surface for different degrees of Ta d-band filling relative to the stoichiometric d$^1$ state (in electrons per Ta atom). Wave vectors involved in the charge-density-wave phases of intercalation complexes, including the one of the commensurate $p(\sqrt{13} \times \sqrt{13}) \ R13.9^\circ$ phase in pristine 1T-TaS$_2$, are drawn in red; related primitive superlattices are drawn in blue. One group of possible orientations is highlighted by an ellipse.

![Fermi surface diagram](image)

**Figure 2.** Schematic illustration of three distinct outcomes of in situ alkali deposition on TMDC (TX$_2$) surfaces: (a) layer-by-layer growth of the alkali metal, (b) intercalation of the alkali atoms into the interlayer gaps and (c) sandwich-breaking chemical reaction.

is complete, ordered superstructures can form (e.g. 2 × 2 or $\sqrt{3} \times \sqrt{3}$ superlattices at concentrations of 0.25 and 0.33 alkali atoms per transition-metal atom, respectively) and at some coverage the dispersed alkali atoms begin to condense into metallic islands. The observed succession of phases for submonolayer coverages is qualitatively consistent with the idea of a coverage-dependent charge transfer from the alkali atoms to the host.
lattice, an idea that has emerged from extensive studies of the K/graphite system [54]. Initially, the charge transfer is expected to be almost complete (\(\leq 1 \text{e}^-\) per adatom) and the repulsive Coulomb interaction keeps the alkali ions far apart from each other. Then, as the coverage increases and islands are formed, some charge remains on the alkali atoms, is shared in a metallic bond and thus contributes to a net attractive lateral interaction.

(ii) **Alkali intercalation into the topmost ‘van der Waals gaps’** (figure 2(b)): This activated process can start from any of the adsorption states mentioned in (i) and its rate is expected to be higher for higher substrate temperatures and alkali coverages. At liquid nitrogen temperatures, alkali intercalation may require a threshold coverage; at room temperature, it generally occurs more or less spontaneously. Since all possible sites of an alkali atom in the ‘van der Waals gap’ are energetically more favorable than the corresponding sites on the surface [55], there should be a strong tendency toward intercalation from the outset. However, the energy barrier for direct intercalation through an intact sandwich is extremely high [55, 56], leading to the common belief that intercalation proceeds via step or crystal edges or other defects such as cracks or folds, which may even be created in a sort of self-amplifying process [57]. Yet, intercalation is still confronted with a bottleneck because the diffusion barriers in the intersandwich gaps are significantly higher than the ones at the surface [55, 56]. It has been shown experimentally that alkali intercalation into layered TMDCs starts at the surface and propagates gap by gap into the bulk [58]. The expected result is an inhomogeneous alkali distribution within the intersandwich gaps and a concentration gradient from the surface toward the bulk.

(iii) **Chemical reaction with the top surface sandwich** (figure 2(c)): This scenario has been observed, for instance, after Li deposition on group IV transition-metal diselenides at liquid nitrogen temperatures [59]. In this example, the supposedly strong interaction between Li and Se breaks up the top sandwich and leads to the formation of Li\(_2\)Se and metallic transition-metal clusters on the surface. Since such a sandwich decomposing reaction is not observed for the systems and preparation conditions used here, process (iii) will not be considered any further.

Although the processes (i) and (ii)—alkali adsorption and intercalation—are interesting phenomena in themselves, they are only a means to an end in this work, namely to tune the structural and electronic properties of the surface TMDC sandwich.

In view of the layer structure, it is commonly assumed that the surface sandwich of a pure TMDC crystal is fully representative of the bulk. Indeed, low-energy electron diffraction (LEED) on \(1\text{T}-\text{TiSe}_2\) has found only a small vertical expansion of the topmost sandwich (\(\sim 3.5\%\)) and a small contraction of the \(c\) parameter (\(\sim 1\%\)) [60]. And a combined x-ray diffraction and scanning tunneling microscopy study on \(1\text{T}-\text{TaS}_2\) has demonstrated that the periodic lattice distortions in the bulk and at the surface are identical in this system [61].

When alkali atoms are adsorbed on the top sandwich, the structural changes are expected to be weak. Density-functional calculations for submonolayer coverages of Li on \(1\text{T}-\text{TiSe}_2\) predict a small contraction of the \(c\) parameter (\(<3\%\)) as well as a slight weakening of the Ti–Se bond, leading to a small (three-dimensional) expansion of the top Se–Ti–Se sandwich (\(<3\%\)) [55]. As regards the electronic changes, on the other hand, charge transfer from the adsorbate to the adsorbent will surely be significant (in the order of \(0.1 \text{e}^-\) per TX\(_2\), depending on coverage) and it seems reasonable to assume that the charge transfer leads to a rigid-band-like filling
of the transition-metal d band. Unfortunately, quantitative experimental results on alkali metal adsorbed TMDCs are scarce.

For *in situ* alkali intercalated TMDC surfaces, the two principal and experimentally well-established changes are, structurally, an expansion of the c lattice constant ($\Delta c = 2.0–2.4$ Å in K/VSe$_2$ [62], K/TiS$_2$ [58] and Rb/TaS$_2$ [63]) and, electronically, an increase in the d-band filling due to charge transfer ($\Delta n_d = 0.35–0.5$ e$^-$ per TX$_2$ formula unit for Na/TiS$_2$ [64], Cs/TiS$_2$ [64, 65], and Cs/ZrSe$_2$ [65]). However, the additional and often neglected changes to the geometric and electronic structures are in fact significant. Observed structural modifications include an expansion of the in-plane lattice constant ($\Delta a/a \approx 1.4\%$ in Cu/VSe$_2$ [66]) and a polytype transformation of the surface layers ($1T \rightarrow 3R$ in K/TiS$_2$ [58], Cs/TiS$_2$ [57] and K/VSe$_2$ [62]). And the typical effects on the electronic band structure entail a flattening of the band dispersions perpendicular to the layers, the opening of a gap between the occupied chalcogen p and the transition-metal d states, a decreased occupied chalcogen p band width, as well as a split-off p band at the top of the valence band [11]. All these changes are consistent with an electronic decoupling of the surface sandwiches and they clearly suggest that a rigid-band model cannot be used, except as a first naive approximation.

Although *in situ* alkali intercalation can severely distort the local crystal microstructure by the creation of holes, cracks, folds or other defects [57, 66], it should be pointed out that the electronic bands seen by ARPES generally do not lose any sharpness. This implies that on average the surface sandwiches remain structurally intact on a $\sim 100\,\mu$m scale. As will be demonstrated below, *in situ* alkali adsorption and intercalation indeed provide a powerful way to fine-tune the d-band filling of TMDC surface sandwiches and, in the case of intercalation, also the strength of their electronic coupling to the bulk. The full potential of this approach, however, is not unfolded until it is combined with *in situ* real-time spectroscopy.

### 4. In situ real-time ARPES measurements

The photoemission measurements performed in this work are illustrated in figure 3, together with the important experimental parameters. All experiments were conducted in one experimental chamber under ultrahigh vacuum (UHV) conditions ($p < 5 \times 10^{-10}$ mbar) at beamline 7.0.1 of the Advanced Light Source (Berkeley). High-quality TMDC surfaces were prepared by cleaving the crystalline samples *in situ*. Via liquid helium cooling, the sample temperature could be adjusted between 30 and 300 K. For *in situ* alkali deposition experiments, commercial alkali metal dispensers (SAES Getters), containing a mixture of an alkali metal chromate and a reducing agent, are typically used. By passing a current of 4.5–7.5 A through the dispenser, the mixture is heated to 550 to 850°C and this starts a reduction reaction leading to pure alkali metal evaporation. In our experiments, the dispensers were placed 3–7 cm away from the sample and the resulting deposition rates were of the order of 0.01–1 MLE min$^{-1}$. For the *in situ* real-time photoemission measurements, monochromatic photons with energies between 90 and 150 eV were directed on the sample and the emitted electrons were detected with a Scienta SES-100 hemispherical analyzer with a charge-coupled device (CCD) detector. The overall energy resolution was typically less than 50 meV and the angular resolution was better than 0.5°. The photoemission movies were acquired in an angularly resolved fixed-energy mode, i.e. kinetic energy-versus-emission angle detector images were continuously recorded for selected kinetic energies with a typical exposure time of 1 s. It turned out that the magnetic field induced by the dispenser current caused only a small angular offset in the detector images,
Figure 3. Schematic illustration of the experimental setup. The changes in the electronic structure of the TMDC ($TX_2$) sandwiches upon in situ Rb deposition are monitored in real time by angle-resolved photoelectron spectroscopy (ARPES). Important experimental parameters are indicated.

which could easily be corrected for. Before and after each deposition cycle, a comprehensive characterization of each sample was performed by taking swept-energy photoemission spectra in the relevant energy ranges as well as LEED images.

5. CDW suppression and semiconductor-to-metal transition in Rb/1T-TiSe$_2$

The layered compound 1T-TiSe$_2$ undergoes a $p(2 \times 2 \times 2)$ CDW transition at $T_{\text{CDW}} = 202$ K [16], which involves the softening of a zone-boundary phonon mode [68]. A number of ARPES studies have demonstrated that this transition is accompanied by changes in the dispersion of the Se 4p and Ti 3d derived bands in a narrow energy window around the Fermi level [37], [69]–[75]. From the viewpoint of ARPES, most of the evidence now indicates that 1T-TiSe$_2$ transforms from a (dirty) semiconductor with a small indirect gap (40–150 meV)–[37, 69, 70, 74] between the Se 4p valence band maximum at the center of the Brillouin zone ($\Gamma$ point) and the Ti 3d conduction band minimum at the zone face ($L$ point)–to another (dirty) semiconductor with a larger gap (by 60–120 meV) in the CDW phase [37, 69, 70, 72]. Interaction between Se 4p and Ti 3d states is naturally involved here, as the high-symmetry points $\Gamma$ and $L$ become equivalent in the CDW phase. It should be noted, however, that the ARPES picture is in contrast to optical spectroscopy, which claims to see a semimetal-to-semimetal transition [76], probably due to overlapping band tails.

In order to explain the origin of the CDW, several mechanisms have been proposed and discussed qualitatively [19]–[21], [27, 28, 77] as well as on the basis of a detailed microscopic
theory [4, 22, 23]. Two of them explicitly include the p–d interaction as a key element: the excitonic insulator model [19, 20] and the second-order (or pseudo) Jahn–Teller band instability [4], [21]–[23]. In the first model, exciton formation between holes at \( \Gamma \) and electrons at \( L \) is at the origin of the transition, while in the second model strong electron–phonon coupling is the driving force, in analogy with the well-known Peierls distortion. A third suggestion regards the transition as a pure phonon instability, independent of the details of the electronic structure near the Fermi energy [27, 28]. Note that the canonical explanation of a CDW using the concept of Fermi surface nesting[16], [78]–[80] does not work here, because normal-phase \( 1T\)-TiSe\(_2\) is not in a well-defined metallic state.

As described in section 2, to further elucidate the nature of the CDW transition in \( 1T\)-TiSe\(_2\), three different strategies have been pursued in the past: application of hydrostatic pressure, substitutional doping and bulk intercalation—all of which are directly affecting the p–d interaction by changing the carrier concentrations or the p–d band lineup or both. Although all three approaches have generally resulted in a continuous suppression of the \( p(2 \times 2 \times 2) \) CDW, a coherent microscopic explanation has not emerged. In particular, it has not become clear whether the increased d-band filling, the change of the p–d gap, or disorder is the key factor or even whether the p–d interaction is relevant for the CDW transition at all.

Here, we use in situ Rb adsorption and intercalation in combination with (real-time) ARPES as a novel method to tune the p–d interaction in \( 1T\)-TiSe\(_2\) sandwiches in a very controlled way. We will show that this method reveals important clues as to the role and nature of the p–d interaction in the so far elusive CDW mechanism.

5.1. Photoemission results

To reveal the connection between the electronic structure near the Fermi level and the CDW phase transition in \( 1T\)-TiSe\(_2\), we have performed three different ARPES experiments: (i) a comparison of the band structures in the normal phase and in the low-temperature CDW phase of pristine \( 1T\)-TiSe\(_2\) (figure 4), (ii) a comparison of the band structures of pristine and in situ Rb intercalated \( 1T\)-TiSe\(_2\) at low temperature (figure 5) and (iii) an in situ Rb deposition run at low temperature recorded in real time (figure 6).

A two-dimensional projection of the hexagonal Brillouin zone of layered TMDCs is depicted in figure 6(a). Throughout this section, we will use the k space notation for unreconstructed \( 1T\)-TiSe\(_2\), while keeping in mind that the \( p(2 \times 2 \times 2) \) CDW transition leads to an eight times smaller Brillouin zone and the equivalence of former \( \Gamma \) and \( L \) points. From photon energy dependent ARPES measurements, which essentially expose the band dispersions perpendicular to the layers, we have found that the \( \Gamma \) point of the first Brillouin zone can be probed with a photon energy of 95–100 eV and the \( L \) point with 120–125 eV photons.

A general problem with electronic structure determination in \( 1T\)-TiSe\(_2\) is that this material is on the verge of being semimetallic and that, therefore, ARPES measurements tend to be strongly influenced by the Fermi–Dirac thermal cut-off. As a consequence, clear Fermi-level crossings are not observable and fitting of the energy distribution curves with appropriate model functions including the Fermi–Dirac cut-off typically results in an uncertainty of \( \sim 30 \) meV in the extracted band positions. For the Ti 3d conduction band, the problem is particularly severe because this band is rather flat and largely unoccupied. For convenience, we assume here an anisotropic parabolic band dispersion near the conduction band minimum at \( L \) with effective masses of 3.64 (\( L–A \) direction) and 0.31 (\( L–H \) direction) free-electron masses ±20%,
Figure 4. ARPES $E(k_\parallel)$ band maps of 1T-TiSe$_2$ taken at 300 K (left) and 135 K (right). (a) Near $\Gamma$ ($h\nu = 95$ eV). The dispersion direction is along $M-\Gamma-M$, with zero at $\Gamma$. Solid lines follow the dispersions of the Se 4p valence bands. Each energy distribution curve in the band map is normalized by its average intensity. (b) Near $L$ ($h\nu = 120$ eV). The dispersion direction is along $A-L-A$, with zero at $L$. Solid lines indicate the potential dispersion of the Ti 3d conduction band. Dashed lines represent the Se 4p band dispersions from (a).

respectively. This Ti 3d band structure model is consistent with all the ARPES data presented in the following and, in particular, allows for a straightforward calculation of the population of the Ti 3d band. Unfortunately, the determination of the ‘true’ Se 4p valence band maximum at $\Gamma$ is also problematic. It is hampered by p–d interaction effects that are already present at room temperature, probably due to CDW fluctuations.

We start with a brief reinvestigation of the CDW transition in pristine 1T-TiSe$_2$. Figure 4(a) shows ARPES band maps of 1T-TiSe$_2$ taken near the $\Gamma$ point at temperatures above and below $T_{CDW}$. In the normal phase at room temperature, three bands with hole-like dispersions are resolved. From the comparison with calculated band structures [80, 81, 84], one may conclude that the top two bands are mainly of Se 4p$_{x,y}$ character, while the lowest-lying state is composed primarily of Se 4p$_z$ orbitals. The valence band maximum at $\Gamma$ is located at about 90 meV below the Fermi level. In the CDW phase at 135 K, the top two Se 4p bands are lower in energy by about 50 meV and their maxima are slightly flattened.
Figure 5. ARPES $E(k_f)$ band maps of pristine (left) and in situ Rb intercalated (right) 1T-TiSe$_2$ taken at 135 K. (a) Near $\Gamma$ ($h\nu = 95$ eV). The dispersion direction is along $M-\Gamma-M$, with zero at $\Gamma$. Solid lines follow the dispersions of the Se 4p valence bands. (b) Near $L$ ($h\nu = 120$ eV). The dispersion direction is along $A-L-A$, with zero at $L$. Solid lines indicate the potential dispersion of the Ti 3d conduction band. Dashed lines represent the Se 4p band dispersions from (a).

In figure 4(b) corresponding ARPES maps near the $L$ point are shown. At room temperature, a small electron pocket is detected, originating from a non-stoichiometric population of the Ti 3d-derived states. Due to the Fermi–Dirac cut-off, the bottom of the Ti 3d conduction band at $L$ cannot be unambiguously determined. It is estimated to lie at about 10 meV below the Fermi level (solid line in figure 4(b)(left)). Upon cooling to below $T_{CDW}$, the Ti 3d emission has lost spectral weight and a novel emission feature has appeared around $-200$ meV. Since the new feature faintly displays a hole-like dispersion, it may be attributed to one or some of the Se 4p bands at $\Gamma$ that are now folded onto $L$ due to the $p(2 \times 2 \times 2)$ reconstruction (dashed lines in figure 4(b)(right)). The band edge is at $\sim 140$ meV below $E_F$, consistent with the position of the valence band maximum at $\Gamma$. Again, the location of the Ti 3d band at $L$ cannot be clearly identified. It is possible that it has shifted upward in energy due to p–d band repulsion, but it is equally likely that it is still located at $\sim 10$ meV below the Fermi level (solid line in figure 4(b)(right)).
**Figure 6.** *In situ* real-time photoemission spectroscopy during continuous deposition of Rb on the surface of 1T-TiSe$_2$ ($I = 6$ A, deposition rate $\approx 0.02$ MLE min$^{-1}$, $T = 80$ K, $h\nu = 125$ eV). (a) Schematic Fermi surface of undistorted 1T-TiSe$_2$ (gray lines) in the $\Gamma M K$ plane, under the assumption of a small Se 4p–Ti 3d band overlap. The Brillouin zone boundaries of the normal phase and of the commensurate CDW phase are indicated by thick and thin solid black lines, respectively. (b) Time dependence of the ARPES spectrum at the $L$ point. Peak positions obtained by line-shape fitting are indicated by symbols. (c) Time dependence of the (normalized) photoemission intensity at characteristic energies of $-0.15$ eV (open triangles) and $-0.275$ eV (filled triangles) relative to the Fermi level. (d) Time dependence of the ARPES intensity at $E_F$ along the $H–L–H$ dispersion direction. Fermi-level crossings obtained by fitting are indicated. (e) Time dependence of the Ti 3d band population. Characteristic times are denoted by $t_0$, $t_1$, and $t_2$. At $t_0 = 33$ s, Rb deposition is started; at $t_3 = 425$ s, it is switched off. Near $t_1 = 150$ s, the p–d gap starts to close; near $t_2 = 263$ s, the CDW is suppressed.
These results are in good qualitative agreement with the results of previous ARPES studies \([37], [69]–[72]\). They clearly show that the 1T-TiSe\(_2\) samples investigated in this work undergo a transition from a dirty semiconductor with a \(\sim 80\) meV gap in the normal phase at room temperature to another dirty semiconductor with a larger \(\sim 130\) meV gap in the CDW phase at 135 K. If the bottom of the Ti 3d band is indeed at \(-10\) meV, the non-stoichiometric population of the Ti 3d band will amount to \(n_d = 0.014\) electrons per TiSe\(_2\) formula unit. The non-stoichiometry is probably due to excess titanium and/or iodine atoms incorporated in the crystal growth \([16]\) (samples were grown by chemical vapor transport with iodine as the transport gas).

Figures 5(a) and (b) compare the low-temperature photoemission spectra of ‘pristine’ 1T-TiSe\(_2\) near \(\Gamma\) and \(L\) (the same spectra as in figures 4(a)(right) and 4(b)(right)) to spectra of in situ Rb intercalated 1T-TiSe\(_2\) taken at the same temperature with the same photon energies. Spontaneous Rb intercalation of the 1T-TiSe\(_2\) sandwiches near the surface was achieved by Rb deposition at room temperature \((I = 7\) A, \(t = 15\) min, \(d = 3\) cm, see figure 3) and verified by Rb core-level spectroscopy (not shown here). Note that, due to the intercalation-induced lattice expansion in the \(c\) direction, the used photon energies may not probe the \(\Gamma\) and \(L\) points anymore and note also that this is not relevant because any photon energy should give the same result because of the expected lack of band dispersion perpendicular to the layers.

Apparently, the band structure is considerably altered upon Rb intercalation. Near the \(\Gamma\) point, there are now only two Se 4p bands, instead of three, with an energy splitting of \(\sim 250\) meV (figure 5(a)). The valence band maximum is raised in energy to about 90 meV below the Fermi level, back to the normal-phase value of the pristine compound. At the \(L\) point, on the other hand, the bottom of the Ti 3d conduction band is lowered in energy, from \(\sim 10\) meV to about 75 meV below the Fermi energy (figure 5(b)). No Se 4p umklapp bands can be identified, but the Ti 3d-derived emission has a broad tail towards higher binding energies, in the region where the umklapp bands were before.

From the almost complete closing of the Ti 3d–Se 4p gap and the absence of folded Se 4p bands at \(L\), we conclude that the CDW transition in 1T-TiSe\(_2\) is suppressed by in situ Rb intercalation. Only CDW fluctuations may be left over, as suggested by the broad tail of the Ti 3d-derived emission at \(L\). In essence, the dirty semiconductor has been turned into a metal, as the population of the Ti 3d band has changed from \(n_d \approx 0.014\) e\(^-\)/TiSe\(_2\) to \(n_d \approx 0.11\) e\(^-\)/TiSe\(_2\). Assuming complete ionization of the Rb atoms, we can estimate a concentration of \(x \approx 0.1\) for the intercalation complex Rb\(_x\)TiSe\(_2\).

As a consequence of in situ Rb intercalation into TMDCs, the spacing between the sandwiches near the surface is expected to increase by \(\sim 2.4\) Å \([63]\), thus reducing the orbital overlap and the band dispersion perpendicular to the layers \([82, 83]\). For 1T-TiSe\(_2\), this sandwich decoupling should strongly affect the Se 4p\(_x\)-derived band and, to a much lesser extent, the bands of Se 4p\(_{x,y}\) character \([84]\). Indeed, in the ARPES spectra the top of the Se 4p\(_x\) band is depressed in energy so much that it is no longer visible in the energy window of figure 5(b), but the remaining Se 4p\(_{x,y}\) bands are also significantly altered: their near degeneracy is removed—one band shifts up in energy, the other shifts down—and both bands have lower effective masses. These effects are consistent with the observations generally made after in situ alkali intercalation of TMDCs \([11]\) and they vividly demonstrate that a rigid-band model is insufficient to describe the electronic changes.

Finally, figure 6 presents an ARPES movie of the electronic structure changes at the \(L\) point in the course of in situ Rb adsorption at a temperature of 80 K. It has been demonstrated that at
such low substrate temperatures Rb deposition on 1T-TiSe$_2$ leads to adsorption in a dispersed phase, as long as the coverage remains low, and that intercalation does not take place [53]. The motivation for this experiment is to create a situation where charge transfer occurs without the intercalation-induced changes of the band dispersions parallel and perpendicular to the layers.

Figure 6(b) shows that, in the beginning, most of the spectral weight at the $L$ point is concentrated on the backfolded Se 4p states at about $-0.15$ and $-0.28$ eV, while the Ti 3d emission at the Fermi energy is only faintly visible, in agreement with figure 4(b)(right). Along the $H-L-H$ dispersion direction, a very small Ti 3d Fermi surface pocket is detected (figure 6(d)), from which the total extrinsic carrier concentration can be estimated to be less than 0.02 per TiSe$_2$ formula unit.

When Rb adsorption sets in (at time $t_0$), some continuous processes start to evolve: the intensity of the Se 4p emissions decreases, while at the same time the Ti 3d photoemission intensity increases (figures 6(b) and (c)), the corresponding Se 4p and Ti 3d states are slightly and synchronously lowered in energy (figure 6(b)), and the Ti 3d Fermi surface pocket is filled (figures 6(d) and (e)). This combined behavior is consistent with a rigid-band-like filling of the reconstructed band structure.

When a certain electron concentration is reached ($n_d \approx 0.025$ e$^-$/TiSe$_2$ at time $t_1$), however, the movement of the Se 4p states reverses. They are raised in energy and the gap between the top Se 4p states and the Ti 3d states closes, until both emissions merge into one bright feature (figure 6(b)). In this interval ($n_d = 0.025-0.05$ e$^-$/TiSe$_2$ between times $t_1$ and $t_2$), the reconstructed band structure changes non-rigidly, since the relative positions of the band edges are changed. These effects are consistent with a weakening of the p–d interaction. At a concentration $n_d \approx 0.05$ e$^-$/TiSe$_2$ (at time $t_2$), all spectral weight is carried by the Ti 3d states and the CDW is suppressed completely, at least from the point of view of ARPES (figure 6(b)). As soon as the CDW is suppressed, the Ti 3d band filling progresses more rapidly and it is again rigid-band-like.

A look at table 1 reveals that the critical $n_d$ in the Rb adsorption experiment agrees fairly well with the critical d-band fillings ($n_d = 0.03-0.08$ e$^-$/TiSe$_2$) in Cu$_x$TiSe$_2$ [9], Ta$_x$Ti$_{1-x}$Se$_2$ [8] and V$_x$Ti$_{1-x}$Se$_2$ [8, 39]. Hence, the CDW phase transition in 1T-TiSe$_2$ appears to be suppressed at a universal electron doping level of $(0.06 \pm 0.02)$ electrons per TiSe$_2$ formula unit.

Figure 7 summarizes the observed band structure changes in the Se 4p–Ti 3d interaction region that occur as a consequence of Rb adsorption (figure 7(b)) and Rb intercalation (figure 7(c)), in comparison to the low-temperature state of pristine 1T-TiSe$_2$ (figure 7(a)). The major difference between the two Rb/1T-TiSe$_2$ systems lies in the changes to the Se 4p band dispersions. While only the Se 4p band edges are shifted in Rb adsorbed 1T-TiSe$_2$, a novel p band structure emerges in Rb intercalated 1T-TiSe$_2$, with significantly different relative band positions and effective masses. Yet, in both systems, the p–d gap is reduced, the Ti 3d band is filled and the CDW phase transition is suppressed. But what causes the observed suppression of the CDW phase and what do the results tell us about the driving force of the CDW phase transition?

5.2. p–d interaction and CDW suppression

The above ARPES results clearly demonstrate that the interaction between the Se 4p and Ti 3d bands is strong and that this interaction is important in the formation and suppression of the CDW. The magnitude of band interaction effects is generally determined by the ratio between
Figure 7. Schematic band structure of 1T-TiSe$_2$ near the $\Gamma$ and $L$ points. The dispersion direction is along $M-\Gamma-M$ for the Se 4p valence bands (bottom) and along $A-L-A$ for the Ti 3d conduction band (top). The Se 4p band is represented by a dashed curve. (a) Pristine 1T-TiSe$_2$ in the CDW phase. (b) Rb adsorbed 1T-TiSe$_2$ when the CDW is suppressed. (c) Rb intercalated 1T-TiSe$_2$ when the CDW is suppressed.

the matrix element of the interaction potential and the energy difference between the states connected by the matrix element. For pristine 1T-TiSe$_2$, the p–d gap in the normal phase is not too large ($G = 40–150$ meV [37, 69, 70, 74]) and the matrix element of the potential, as given by half of the observed p-band energy lowering in the CDW phase, is not too small ($\Delta = 30–60$ meV [37, 69, 70, 72]). Although the k-space volume over which the mixing of Se 4p and Ti 3d energy levels occurs is rather small, we argue here that the reduction of the total band energy resulting from the p–d interaction is sufficient to overcome the lattice distortion energy and drive the system into the CDW state.

Then, based on simple considerations about the balance between electronic and lattice energies, there are two ways to suppress the CDW phase transition, apart from introducing disorder: (i) by increasing the number of occupied Ti 3d states that are raised in energy or (ii) by decreasing the number of occupied Se 4p states that are lowered in energy in the transition. If the Ti 3d conduction band minimum is filled with additional electrons, previously unoccupied states that could be raised without energy cost are populated and eventually an excess electron concentration will be reached for which the gain in electronic band energy is no longer enough to compensate for the elastic energy cost. If, on the other hand, the density of Se 4p states in the interaction region is reduced, fewer states are lowered in energy and thus also a point may be reached where the transition is completely suppressed. Increasing the normal-phase p–d gap, splitting the top two p states or reducing their effective masses are all possible ways to decrease the Se 4p density of states in the interaction region.

By looking at figure 7, we can conclude that Rb adsorption at liquid nitrogen temperatures suppresses the CDW in 1T-TiSe$_2$ via pathway (i), while Rb intercalation leads to CDW suppression via a combination of pathways (i) and (ii). Since the measured ARPES bands (as well as the LEED reflexes) remain sharp during either process, we believe that disorder effects play only a minor role. We emphasize that particularly in situ Rb adsorption combined with real-time ARPES makes it possible to directly observe in the band structure what previously has
only been speculated upon, namely the continuous suppression of a structural phase transition by excess carriers [27, 85, 86].

An extremely simple model corroborates the above qualitative considerations by giving the right order of magnitude of the effect. The electronic structure near the p valence band maximum and near the d conduction band minimum is mapped onto an electron system with two energy levels coupled by a single phonon mode [85, 87]. The levels are separated by a narrow energy gap \( G \) and the elastic energy is given by \( \frac{1}{2} M \omega_0^2 u^2 \), where \( M \) is the ionic mass, \( \omega_0 \) the phonon frequency and \( u \) a static ion displacement. For this model, it can be shown that a lattice distortion is suppressed when the excess carrier concentration reaches \( n_c = 1 - \frac{M \omega_0^2 G}{2 g^2} \), where \( g \) is the electron–lattice coupling constant [85]. For 1T-TiSe\(_2\), the parameters can be estimated as \( \frac{1}{2} M \omega_0^2 \approx 4.8 \text{ eV Å}^{-2} \) [4] and \( g = \Delta/u_0 \approx 0.6 \text{ eV Å}^{-1} \), where \( \Delta \approx 50 \text{ meV} \) is the interaction matrix element [70] and \( u_0 \approx 0.085 \text{ Å} \) the Ti atom displacement [16] in the CDW phase. With the experimentally determined value for the critical extrinsic electron concentration, \( n_c \approx 0.05 \), we obtain an original band gap \( G \approx 70 \text{ meV} \). Despite the crudeness of the model, this value agrees fairly well with recent ARPES results (see above). We take this as first evidence that the coupling between the p and d states is indeed phononic in origin, as has implicitly been assumed all along in this section. However, it should be emphasized that this is not the only possibility; electronic coupling via direct Coulomb interaction could in principle also be possible.

5.3. Nature of the p–d interaction: electronic or phononic?

The question about the nature of the p–d interaction is intimately connected to the question about the origin of the CDW phase transition in 1T-TiSe\(_2\). As to the driving force of that specific transition, three distinct types of mechanisms have been proposed (and very recently also a combination of two of them [24]–[26]). In the first mechanism, the driving force is primarily electronic; in the second, it is primarily phononic; and in the third, it is a combination of both.

(i) **Excitonic insulator instability** [19, 20]: This fascinating instability can occur in semiconductors (semimetals) with a small band gap (overlap) [88, 89]. It is an instability of the electron subsystem that, in the case of 1T-TiSe\(_2\), would be driven by the direct Coulomb interaction between the Se 4p holes at \( \Gamma \) and the Ti 3d electrons at \( L \). These electron–hole pairs will spontaneously bind into excitons, as soon as the exciton binding energy overcomes the band gap, and this spontaneous exciton formation will be indicated by a complete softening of the corresponding exciton mode. Depending on the spin state of the exciton (singlet or triplet), the outcome can be either a CDW or a spin-density wave. In the case of a CDW and finite electron–phonon coupling, a mixed exciton–phonon mode will soften and a periodic lattice distortion will occur. However, in contrast to the Peierls-like mechanism described below, in the excitonic insulator the lattice distortion can be regarded as an accidental byproduct of a purely electronic instability.

(ii) **Antiferroelectric instability** [27, 28]: In analogy to displacive ferroelectric phase transitions [90], this mechanism regards the structural transition in 1T-TiSe\(_2\) as the result of an instability of the phonon subsystem, independent of the details of the electronic structure. The driving force is an inherent softening of a zone-boundary phonon. However, the origin of the phonon softening remains vague [27, 28] and a purely phononic mechanism cannot explain the observed influence of carrier concentration changes on the phase transition, unless
a finite electron–phonon coupling is included. But then the antiferroelectric instability becomes equivalent to model (iii) [90].

(iii) Jahn–Teller band instability [4], [21]–[23], [77]: This mechanism is the strong-coupling analogue of the weak-coupling Peierls–Fröhlich theory of CDW formation [91, 92]. The basic idea is this: a virtual structural distortion leads to the folding down of the band structure and the opening of energy gaps where original and folded bands cross or come close to each other; if the total energy gain through lowering of the occupied states is larger than the lattice distortion energy, the structural distortion becomes real via complete softening of the relevant phonon mode. From the outset, this instability is an instability of the coupled electron–lattice system and it is driven by strong electron–phonon coupling. The three experimental signatures of the novel state—the periodic modulation of the conduction electron density (the CDW), the periodic lattice distortion and the energy gapping in the band structure—always appear together.

On a qualitative level and in analogy to concepts of chemistry [93], two variants of the Jahn–Teller effect can be applied to the CDW transition in $1T$-TiSe$_2$, each linked to different geometrical aspects of the observed lattice distortion pattern [21, 77]. The periodic lattice distortion involves two different environments of a Ti atom, one in which a rotational motion of the TiSe$_6$ octahedron towards a trigonal prism occurs and the other in which the Ti atom and two of its six surrounding Se atoms move closer to each other [16]. Now, in the first variant of the Jahn–Teller effect, a threefold degenerate Ti 3d ground state is presupposed and it is predicted that the $1T$-toward-2H rotational motion in the first Ti environment splits off the Ti 3d$_z$ states to lower energy (first-order Jahn–Teller effect) [77]. Hence, the energy lowering originates in the Ti 3d states and the Se 4p states are irrelevant. By contrast, in the second variant, the Ti–Se bond shortening in the second Ti environment causes a mixing of Se 4p ground states and low-lying Ti 3d excited states and thereby lowers the ground state energy (second-order or pseudo Jahn–Teller effect) [21]. Here, the band energy lowering occurs in the Se 4p bands and it becomes larger as the original separation between the p and d states becomes smaller. Apparently, the second-order Jahn–Teller effect provides a far better description of the situation in $1T$-TiSe$_2$. Note that the first-order Jahn–Teller effect leads to the incorrect prediction that excess electrons in the band Ti 3d band should enhance CDW formation.

Remarkably, on the basis of the band Jahn–Teller mechanism, a detailed microscopic theory for the CDW transition in $1T$-TiSe$_2$ has been developed [4, 22, 23], taking into account the wave vector, mode and temperature dependence of the electron–lattice interaction and ultimately providing quantitative results on the changes to both the electron and phonon dispersions. However, the starting point of this theory is a band structure with a substantial Se 4p–Ti 3d overlap of $\sim 0.2$ eV and it predicts the opening of a p–d gap of $\sim 0.2$ eV in the CDW phase. Both values are not supported by the ARPES results presented above and reported previously [37], [69]–[75].

In view of the peculiar band structure and the undoubtedly strong electron–phonon coupling in $1T$-TiSe$_2$, it should be pointed out that the electron and phonon subsystems will always change simultaneously so that a modified Se 4p–Ti 3d band lineup as well as a lattice distortion will be produced in all three models, independent of the driving force of the transition. Thus, based solely on the electronic structure changes seen by ARPES, one cannot favor one model over the other; the ARPES band mapping results are consistent with all three scenarios. One may even argue that it is impossible to perform a decisive experiment in this situation, because the electron and lattice subsystems are so closely interrelated.
Nevertheless, the question about the driving force of the transition is still legitimate and fascinating. In the absence of any explanation for why there should be a ‘pure’ phonon softening, the two remaining models are the excitonic insulator and the Jahn–Teller band instability and we pose the question in the form: is excitonic insulator formation likely in 1T-TiSe$_2$?

We assume that 1T-TiSe$_2$ in the normal phase is a semiconductor with a small indirect gap $G > 0$ and that the exciton binding energy $E_B$ is of the order of $k_B T_{CDW}$ [89]; thus $E_B \approx 17$ meV. In this context, three major prerequisites for the occurrence of an excitonic insulator are [89]: (i) a small gap, $G \leq E_B$, (ii) a low excess carrier concentration, $E_F \leq E_B$, where $E_F$ is the Fermi energy of the Ti 3d conduction band, and (iii) a long scattering lifetime, $h/\tau \leq E_B$.

At or near room temperature, most of the recent ARPES studies [37, 69, 70, 74] including this one find $G > E_B$. It should be noted, however, that even at room temperature the measured $G$ may not be the true normal-phase $G$ due to fluctuation effects [72]. So, condition (i) may still be fulfilled. Requirement (ii) is clearly satisfied in stoichiometric samples, but not necessarily in ‘doped’ ones. According to figure 6(b), the CDW in Rb adsorbed 1T-TiSe$_2$ is suppressed when $E_F \geq 40$ meV, which corresponds to a critical extrinsic electron concentration of $\sim 0.05$ e$^-$ per TiSe$_2$ formula unit. This value implies that, if exciton formation was indeed responsible for the transition, the excitons would be surprisingly insensitive to screening. Finally, if one takes the full-width at half-maximum of the (deconvoluted) Ti 3d ARPES peaks around the $L$ point as a measure of the inverse scattering lifetime, one finds $h/\tau \geq 75$ meV at room temperature [70, 74]. The major contribution to this value comes from electron–phonon scattering, as can be estimated by the formula $h/\tau = 2\pi \lambda k_B T$ [94], giving $h/\tau \approx 80$ meV for $T = 300$ K and for an estimated electron–phonon coupling constant $\lambda \approx 0.5$. This suggests that condition (iii) is not fulfilled. Hence, the ARPES results are somewhat in conflict with prerequisites (i) and (iii) so that we are led to believe that the tendency toward excitonic insulator formation is very weak in 1T-TiSe$_2$. Also, to our knowledge, there has been no experimental evidence as yet for the presence of p–d excitons in the normal (most probably semiconducting) state of 1T-TiSe$_2$.

Up to now, excitonic insulator formation (not using optical excitation) has only been observed in intermediate valence rare earth compounds, TmSe$_{0.45}$Te$_{0.55}$ being the most extensively studied example [95]–[99]. In these systems, two major prerequisites for p–d exciton formation and condensation have been identified: a free carrier concentration of $\sim 10^{21}$ cm$^{-3}$ and a large effective mass of the holes of $\sim 100 m_0$ [100]. The first number is a compromise between ineffective enough screening and large enough exciton overlap and the second condition leads to heavy excitons with a long lifetime. Both requirements are incompatible with 1T-TiSe$_2$. The first is fulfilled when the extrinsic electron concentration is about 6.5% per TiSe$_2$ formula unit, but then the potential excitonic insulator phase is already suppressed; and the effective electron and hole masses are one to two orders of magnitude smaller than 100 $m_0$.

In conclusion, even if a tendency toward excitonic insulator formation should exist in 1T-TiSe$_2$, it is hard to imagine that the involved electron–electron interaction is the dominant interaction driving the CDW phase transition. It seems more likely that exciton formation is suppressed by the indisputably strong electron–phonon interaction, which is also the hallmark and driving force of the band Jahn–Teller instability. Nonetheless, as mentioned above, the microscopic theory based on the Jahn–Teller mechanism is also not fully convincing yet, since there are inconsistencies with recent high-resolution ARPES results regarding the relative p–d band positions. A refinement of the microscopic theory for the CDW phase transition is clearly desirable.
6. CDW modification and metal-to-insulator transition in Rb/1T-TaS$_2$

As described in section 2, near room temperature, the layered compound 1T-TaS$_2$ is in a nearly commensurate, domain-like CDW phase with a $\sqrt{13} \times \sqrt{13}$-type superlattice (in the following termed the nc–p($\sqrt{13} \times \sqrt{13}$)R13.9° phase). When intercalated with simple foreign species such as alkali metals, Cu, or N$_2$H$_4$, the pristine CDW in the 1T-TaS$_2$ host lattice transforms into several novel CDW phases, some of which are independent of the nature of the intercalant. The most spectacular novel phase is characterized by a c(2$\sqrt{3} \times 4$)rect. superlattice. It involves not only a symmetry change but also the opening of a large energy gap of roughly 1 eV at the Fermi level.

Here, we investigate the nc–p($\sqrt{13} \times \sqrt{13}$)R13.9°-to-c(2$\sqrt{3} \times 4$)rect. transition employing in situ Rb intercalation of 1T-TaS$_2$ monitored in real time by photoemission spectroscopy. Two intriguing questions will be explored: Why does the novel CDW phase occur and how shall the novel phase be classified—as a Peierls band insulator or a Mott–Hubbard correlated insulator?

6.1. Photoemission results

To explore the electronic and structural changes in 1T-TaS$_2$ upon in situ Rb deposition at room temperature, we have performed three experiments on three freshly cleaved 1T-TaS$_2$ surfaces with Rb deposition rates between 0.02 and 0.2 monolayer equivalents (MLE) per minute: two continuous deposition runs, the ‘fast’ run no. 1 (figure 8; ~0.2 MLE min$^{-1}$) and the ‘slow’ run no. 2 (figure 9; ~0.02 MLE min$^{-1}$), both recorded in the form of photoemission intensity movies for selected binding energy intervals, and the ‘stepwise’ deposition run No. 3 (figure 10), consisting of short, consecutive deposition cycles with extensive characterization of the valence electronic structure performed in between.

Since all three Rb deposition runs reveal almost identical effects on the Ta 5d valence states near the Fermi level as well as on the Ta 4f core levels, they are considered as having led to the same reproducible physical processes at the surface of 1T-TaS$_2$. The obtained results are in good overall agreement with the results of previous, less comprehensive photoemission studies on the same compound [46] or on closely related systems [44, 47, 101]. A small part of the results presented here has already been published in [48]. The extensive information contained in figures 8–10 can be summarized as follows:

(i) Ta 5d valence states: In pure 1T-TaS$_2$ at room temperature, ARPES does not observe a well-defined Fermi surface, although the Ta 5d band contains an odd number of electrons per unit cell (see $E(k_\parallel)$ band map no. 1 in figure 10(b)). Due to the nc–p($\sqrt{13} \times \sqrt{13}$)R13.9° CDW, the elliptical Fermi pockets depicted in figure 8(a) are strongly gapped, particularly on the Brillouin zone face between the $M$ and $K$ points, and the only significant spectral weight at the Fermi level is found around the $\Gamma_1$ point at the center of the Brillouin zone. The possible Fermi level crossing at about $\frac{1}{4}\Gamma M$ is not clearly distinguishable. The occupied Ta 5d band width is ~0.95 eV and the band dispersion shows two intensity dips around $\frac{1}{4}\Gamma M$ and $\frac{3}{4}\Gamma M$, which can be considered as a precursor of the splitting into three subbands (centered at about −0.95 eV, −0.4 eV and near $E_F$)—the characteristic signature of the long-range ordered commensurate CDW phase [31, 32]. Apart from the intensity dips, band folding effects due to the superlattice potential are not detectable in the spectral...
Figure 8. *In situ* real-time photoemission spectroscopy during continuous deposition of Rb on the surface of $1T$-TaS$_2$ (‘deposition run no. 1’, $I = 6$ A, deposition rate $\approx 0.2$ MLE min$^{-1}$, $T = 300$ K, $h\nu = 96$ eV). (a) Schematic Fermi surface of undistorted $1T$-TaS$_2$ (gray lines) in the $\Gamma M K$ plane. The Brillouin zone boundaries of the normal phase and of the commensurate CDW phase are indicated by thick and thin solid black lines, respectively. (b, c) Time dependence of the Ta 5d valence-band spectrum at the $\Gamma$ point and of the Ta 5d photoemission intensity at characteristic energies of $-0.09$ eV (black line) and $-0.52$ eV (red line) relative to the Fermi level. (d, e) Time dependence of the Ta 4f$^{7/2}$ core-level spectrum and of the CDW induced Ta 4f$^{7/2}$ splitting. Points 1–7 indicate the corresponding core-level splittings and integrated deposition times of the stepwise deposition run no. 3 (see figure 10). Characteristic times are denoted by $t_0$, $t_1$ and $t_2$. At $t_0 = 93$ s, Rb deposition is started. Between $t_1 = 193$ s and $t_2 = 248$ s, a structural phase transition takes place, as indicated by the LEED patterns in figure 10(d).
Figure 9. *In situ* real-time photoemission spectroscopy during continuous deposition of Rb on the surface of 1T-TaS$_2$ (‘deposition run no. 2’, $I = 6.5$ A, deposition rate $\approx 0.02$ MLE min$^{-1}$, $T = 300$ K, $h\nu = 150$ eV, $U_{\text{bias}} = -25$ V). Rb deposition is started at $t_0 = 114$ s. At $t_1 \approx 1260$ s, major changes in the valence-band and core-level spectra begin to occur. (a, b) Time dependence of the Ta 5d valence-band spectrum at $\Gamma$ and of the Ta 5d photoemission intensity at energies of $-0.1$ eV (black line) and $-0.5$ eV (red line). (c, d) Time dependence of the Ta 4f core-level spectrum and of the average CDW induced Ta 4f splitting. (e–g) Time dependence of the Rb 3d core-level spectrum, of the photoemission intensities associated with Rb atoms adsorbed on the surface (blue line) and intercalated into the intersandwich gaps (red line), and of the estimated Rb concentrations. The Rb photoemission intensities are given relative to the Ta 4f intensity. (h) Time dependence of the position of the spectral onset, reflecting changes in the work function $\phi$. In (a), (c), (e) and (h), spectra plotted on the left.
Figure 9. (Continued) show the state before Rb deposition and spectra on the right depict the state at the end of the deposition run. In (e), a spectral decomposition into peak doublets associated with surface Rb (blue line) and intercalated Rb (red line) is shown.

Figure 10. Evolution of the electronic structure and CDW superlattice, as seen by ARPES and LEED, in the course of stepwise Rb deposition on the surface of $1T$-TaS$_2$ (‘deposition run no. 3’, $I = 6$ A, $T = 300$ K). The deposition cycles are denoted by 1–7; the corresponding integrated deposition times are given in figure 8(e). (a) Normal emission Ta 5d and Ta 4f$_{7/2}$ spectra ($h\nu = 96$ eV). At the top, spectra measured on pristine $1T$-TaS$_2$ at a temperature of 30 K are indicated for comparison (thin solid lines). (b) $E(k)$ band map of the Ta 5d states along $\Gamma\text{MK}$ ($h\nu = 96$ eV). (c) Photon energy dependence of the entire normal emission valence-band spectrum including Ta 5d and S 3p states ($h\nu = 80$–140 eV). (d) LEED patterns and classification of the observed superlattices ($E_{\text{kin}} = 96$ eV).

weight distribution measured by ARPES (at lower photon energies, however, faint effects can be identified [102, 103]).

During Rb deposition, the Ta 5d electronic structure is strongly modified. At $\Gamma$, the spectral weight close to the Fermi level, near $-0.1$ eV, is transferred to higher binding energies, with a distinct peak emerging at about $-0.5$ eV (figures 8(b), 9(a) and 10(a)). This process is continuous, but it progresses more rapidly once the photoemission intensity curves of the upper and lower peaks have crossed (figure 9(b)). The final result is a clear energy gap with, if symmetric about $E_F$, a width of $\sim 1$ eV and almost zero photoemission.
intensity remaining at \( E_F \) (figures 8(b) and 10(a)). This is in sharp contrast to the temperature-dependent effects in pure \( 1T\)-\( \text{TaS}_2 \), for which only a slight shift of the leading edge is observed at low temperatures (figure 10(a)).

There are, however, more changes to the intralayer Ta 5d band dispersion upon Rb deposition (see \( E(k) \) band map no. 5 in figure 10(b)). The occupied band width is reduced to \( \sim 0.76 \) eV, the bottom of the band at \( M \) is lowered by \( \sim 0.23 \) eV and the dispersion at the top of the band near \( \Gamma \) is remarkably flattened. Moreover, a pronounced ‘kink’ develops around \( \Gamma M \) splitting the Ta 5d band into two subband manifolds centered at about \( -0.5 \) and \( -1.1 \) eV, respectively.

It should be noted that no direct evidence for the expected electron transfer from the Rb to the Ta 5d band is found in the ARPES spectra. Changes in the band filling cannot be determined because, initially, the Fermi surface is not well defined and, later, it is completely destroyed. It is also remarkable that no Fermi edge emerges, even at the end of the ‘fast’ deposition run No. 1, as one would expect for Rb atoms on the surface condensing into metallic islands.

(ii) \( S\) 3\( p\) valence states: Figure 10(c) shows photon energy-dependent measurements at normal emission, which essentially probe the band dispersion perpendicular to the layers, \( E(k_{\|}) \), at the center of the Brillouin zone. Before Rb deposition (\( E(h\nu) \) band map no. 1), the \( S\) 3\( p\) valence bands are located between \(-1.2\) and \(-6.7\) eV, separated from the Ta 5d states by a gap of \( \sim 0.25 \) eV, and their \( k_{\perp}\) dispersion is considerable. After the Rb-induced rearrangement of the Ta 5d states has been completed (\( E(h\nu) \) band map no. 5), the \( S\) 3\( p\) band dispersion perpendicular to the layers is significantly reduced and the p–d gap is larger by \( \sim 0.6 \) eV. Both observations are commonly made in alkali/TMDC intercalation complexes [11].

(iii) Ta 4\( f\) core levels: In pristine \( 1T\)-\( \text{TaS}_2 \), the CDW is rather strong and it has significant effects on the Ta 4\( f\) emissions. Quite generally, inequivalent Ta sites in the distortion pattern will experience different local electron densities, leading to different chemical shifts and also to different line asymmetries due to site-dependent screening effects [104]. Here, we will only be concerned with the CDW-induced line splittings.

In the nc–\( p(\sqrt{3}\times \sqrt{3})R13.9^\circ\) phase at room temperature, each Ta 4\( f\) line is split into a clear doublet with a separation of \( \sim 0.52 \) eV (figures 8(d), 9(c) and 10(a)). During Rb deposition, the Ta 4\( f\) splitting first increases slowly and then more rapidly at the same time when the Ta 5d spectral weight near the Fermi level is heavily redistributed (figures 8(d) and 9(c)). Once the spectral weight at the Fermi level has completely disappeared, the splitting also saturates, at a value of \( \sim 0.82 \) eV (figures 8(d) and 10(a)). Figures 8(e) and 9(d) show the time dependence of the Ta 4\( f\) splitting as obtained by line-shape fitting. Note that the saturated Ta 4\( f\) splitting in Rb/\( 1T\)-\( \text{TaS}_2 \) at room temperature is \( \sim 0.16 \) eV larger than the splitting observed in pristine \( 1T\)-\( \text{TaS}_2 \) at low temperatures (figure 10(a)).

As to the general quality of the measured Ta photoemission spectra, it is apparent that the Ta 5d and Ta 4\( f\) emissions both remain very sharp during Rb deposition and that the intensities are not significantly attenuated, only slightly at the end of the ‘fast’ deposition run no. 1 (figures 8(b) and (d)). This suggests that the Ta layers remain structurally intact and that the Rb adatoms are dispersed.

(iv) Rb 3\( d\) core levels: In \textit{in situ} intercalated alkali/TMDC systems, typically, two distinct features are observed in the alkali core-level spectra: one related to the adsorbed species and the other connected with intercalated alkali ions [11]. Figure 9(e) shows such typical
behavior for the Rb 3d emissions. First, a surface-related Rb 3d spin-orbit doublet is observed with the lower binding energy peak located at $-111.7 \text{ eV}$. Later, a second Rb 3d doublet characteristic of intercalated Rb appears, its lower binding energy peak having an energy of $-110.3 \text{ eV}$.

The intensities of the two Rb 3d emission features relative to the intensity of the Ta 4f emission can be determined by line-shape fitting (figure 9(e)) and from these the Rb concentrations are estimated using calculated values for the photoionization cross sections [105] and for the inelastic mean free paths [106] and assuming that all intercalated Rb atoms are located in the topmost intersandwich gap. The results depicted in figures 9(f) and (g) suggest that Rb intercalation starts right at the beginning of the deposition process and that the intercalation rate increases when a total concentration of $\sim 0.3 \text{ Rb atoms per Ta atom}$ is reached, roughly at the same time $t_1$ when pronounced changes in the Ta 5d and Ta 4f states are occurring (figures 9(a)–(d)). In fact, the overall time dependence of the intercalated Rb concentration (red curve in figure 9(f)) is strongly correlated with the evolution of the Ta 5d intensity at $-0.5 \text{ eV}$ (red curve in figure 9(b)) and the Ta 4f splitting (red curve in figure 9(d)).

(v) **Work function**: The relative change of the work function $\phi$ upon Rb adsorption is reflected in the shift of the spectral cut-off at low kinetic energies, as shown in figure 9(h). When the first Rb atoms adsorb, the work function decreases rapidly until $\Delta \phi$ saturates at a value of about $-1.25 \text{ eV}$. Then, the work function continues to decrease monotonically, at a much slower rate however, as Rb adsorption approaches a coverage of 0.5 MLE. The observed time dependence of the reduction in $\phi$ is clearly correlated with the time dependence of the surface Rb concentration (blue curves in figures 9(f) and (g)). When $\Delta \phi$ is plotted as a function of the concentration of surface Rb atoms (not shown here), an almost linear relationship is revealed indicating that depolarization effects between dipole fields of neighboring Rb atoms have not yet become relevant.

(vi) **LEED**: The LEED patterns that were recorded at different stages of the Rb deposition process (steps 1–7 in deposition run no. 3) reveal a change of the CDW superlattice at some critical point (see figure 10(d)). Before this point, the LEED reflections are consistent with the hexagonal nc–p($\sqrt{13} \times \sqrt{13}$)R13.9° superlattice of pristine $1T$-TaS$_2$ at room temperature. After this point, the superlattice reflections indicate the presence of three orientations of a non-hexagonal $\sqrt{7} \times \sqrt{7}$ unit mesh, correctly classified as the intriguing $c(2\sqrt{3} \times 4)$rect. superstructure. The three domains are rotated by 120° with respect to each other. The structural change occurs between deposition steps 3 and 4, precisely when the dramatic rearrangement of the Ta 5d states near the Fermi level takes place (figures 10(a) and (d)), which in turn is correlated with the increase in both the Ta 4f splitting and the concentration of intercalated Rb (figures 8–10). No further superlattice modification is observed by LEED in the course of the Rb deposition.

Putting these comprehensive surface spectroscopy and diffraction results into context, we arrive at the following scenario. **In situ** deposition of Rb on the surface of $1T$-TaS$_2$ at room temperature results in both dispersed adsorption and intercalation and it is the Rb intercalation that continuously transforms the surface of $1T$-TaS$_2$ into a novel entity with, in the end, dramatically different structural and electronic properties. For extended deposition runs, it can be expected that the intercalation of Rb propagates layer by layer into the bulk. In our cases, however, we assume that most of the intercalated ions end up in the first few ‘van der
Waals gaps’ so that only the uppermost S–Ta–S sandwiches are affected. If we extrapolate the concentrations derived from Rb 3d core-level spectroscopy (figure 9(g)) and consider that each intercalated Rb ion ‘belongs’ to its two neighboring sandwiches, we obtain a saturated chemical composition of Rb$_{0.35}$TaS$_2$ for the topmost sandwich, the one that is primarily seen by photoemission spectroscopy. Note that a concentration of 1/3 Rb atoms per TaS$_2$ formula unit is consistent with a $p(\sqrt{3} \times \sqrt{3})R45^\circ$ superlattice due to Rb ordering but not with the larger unit cell of the observed $c(2\sqrt{3} \times 4)$ rect. superlattice. This is strong evidence for the CDW interpretation of the LEED pattern.

The structural changes in the Rb/1T-TaS$_2$ surface complex at first pertain to the basic lattice parameters. Due to the presence of Rb ions in the first ‘van der Waals gap’, the surface S–Ta–S sandwich will be lifted from the bulk. Scanning tunneling microscopy measurements show that the increase in the $c$ parameter is $\sim 2.4$ Å [63], consistent with $\Delta c = 2.36$–2.41 Å reported for the bulk intercalation complex Rb$_x$TiS$_2$ [107]. Unfortunately, an experimental value for the expansion of the intrasandwich lattice constant $a$ is not available. If bulk intercalated Rb$_x$TiS$_2$ is again used as a reference, one may expect $\Delta a \leq 0.03$ Å [107]. It can be speculated that the compressive strains building up in the surface sandwich are suddenly relaxed at some critical Rb concentration and that the resulting network of nanofolds [66] yields—via the creation of new intercalation channels—the marked increase of the intercalation rate shown in figures 9(f) and (g).

More interesting to us is that the formation of the Rb/1T-TaS$_2$ system is accompanied by a modification of the CDW superstructure in the S–Ta–S sandwich. As evidenced by LEED, the superlattice changes from nc–$p(\sqrt{3} \times \sqrt{3})R13.9^\circ$ to $c(2\sqrt{3} \times 4)$ rect. This involves a symmetry change from a primitive hexagonal to a non-primitive centered rectangular unit mesh, a reduction in the number of Ta atoms per unit cell from 13 to 8, and a shortening of the length of the primitive vectors from $\sqrt{3}a$ to $\sqrt{7}a$. Together with symmetry and periodicity, however, the domain structure of the CDW is also modified. This may be concluded from the evolution of the Ta 4f splitting, which is assumed to reflect the average domain size or, in other words, the coherence of the CDW state [33]. In the nc–$p(\sqrt{3} \times \sqrt{3})R13.9^\circ$ phase, the CDW consists of commensurate hexagonal domains with a relatively small diameter of $\sim 70$ Å [34]; the Ta 4f splitting is correspondingly small. The $c(2\sqrt{3} \times 4)$ rect. phase, on the other hand, exhibits three different domain orientations, but the domain sizes are larger, $\sim 150$–400 Å [46, 49], and the Ta 4f splitting is more pronounced. It is even larger than in the low-temperature commensurate $p(\sqrt{3} \times \sqrt{3})R13.9^\circ$ phase of pristine 1T-TaS$_2$ (figure 10(a)), which may additionally hint at a larger CDW amplitude in Rb/1T-TaS$_2$.

Not surprisingly, a modification of the electronic properties comes along with the observed structural changes. The surprise is the magnitude of the effects, in particular the emergence of the large energy gap of $\sim 1$ eV (assuming a symmetric gap around $E_F$, as confirmed by scanning tunneling spectroscopy [49]) that transforms the system from a poor metal into an insulator. In general, the three hallmarks in the valence electronic structure of in situ alkali intercalated TMDCs are (i) an increased d-band filling due to alkali s-electron transfer, (ii) the opening of a gap between the chalcogen p and transition-metal d states due to the presence of positively charged alkali ions in the intersandwich gaps and (iii) reduced band dispersions perpendicular to the layers due to the enlarged intersandwich separation. In the case of the Rb/1T-TaS$_2$ surface complex, only the latter two effects are clearly seen, but the charge transfer cannot directly be detected because of the opening of the energy gap at $E_F$. It seems, however, reasonable to assume complete ionization of the Rb atoms [10], which would imply a maximum
transfer of $(0.35 \pm 0.1)$ electrons per TaS$_2$ formula unit. Evidently, the rigid-band model, which is commonly used for the electronic structure of intercalation complexes and which assumes that the shape of the transition-metal d band remains the same and that only its filling increases, is completely inappropriate here.

Figure 11 summarizes the major structural and electronic changes involved in the Rb intercalation-driven transition. In essence, the 1T-TaS$_2$ host lattice changes from a quasi-two-dimensional bad metal to a two-dimensional doped insulator and this transition is accompanied by a transformation of a textured nearly commensurate CDW phase with a hexagonal superlattice unit cell and a relatively small average domain size into a three-domain CDW structure with a smaller rectangular superlattice unit cell and a larger average domain size. As to the novel electronic properties, three intertwined questions remain to be answered: Where do the electrons donated by the Rb atoms go, what causes the change of the CDW periodicity and is the energy gap for the most part a Peierls gap or possibly a Mott–Hubbard gap?

6.2. Possible origin of the $c(2\sqrt{3} \times 4)\text{rect. CDW}$

When a novel CDW occurs, a simple explanation in terms of Fermi surface nesting is always tempting. The doping dependence of the undistorted Ta 5d Fermi surface is sketched in figure 1 and, indeed, the spanning wave vector of the $c(2\sqrt{3} \times 4)\text{rect.}$ CDW indicates rather strong nesting for a band filling of the order of the estimated Rb-induced charge transfer to the Ta 5d band. Although this argument has commonly been used to explain the CDW superlattices of 1T-TaS$_2$ intercalation complexes [10, 12, 38, 44, 51], it is not really applicable here. Firstly, the initial electronic structure is that of the nc–$p(\sqrt{13} \times \sqrt{13})R13.9^\circ$ phase and not that of the normal phase. Secondly, in both the initial nc–$p(\sqrt{13} \times \sqrt{13})R13.9^\circ$ phase and the final $c(2\sqrt{3} \times 4)\text{rect.}$ phase the distortions are large so that the electronic energy gain is not concentrated on the states near the Fermi surface but is spread over the entire Brillouin zone. In such strong-coupling CDWs with large energy gapping, a local bonding picture is often more appropriate than the concept of Fermi surface nesting. In the specific case of 1T-TaS$_2$, the CDW distortion is then regarded as being due to a tendency of the Ta atoms to form metal–metal bonds and some kind of quasimolecule or cluster [21, 30, 109].

In the commensurate and nearly commensurate CDW phase of pristine 1T-TaS$_2$, the basic structural unit in the Ta plane is a star-of-David-shaped 13-atom cluster with three types of inequivalent Ta atoms in the ratio 1 : 6 : 6; 12 atoms in two hexagonal rings around the 13th central atom move toward that atom (figure 11(b)(left)) [30]. For such a distortion pattern, the occupied Ta 5d states are calculated to collapse into three subband manifolds: 12 Ta d electrons completely occupy two lower-lying three-band manifolds and the remaining Ta d electron resides in an upper one-band manifold straddling the Fermi level [31, 32]. Figure 11(d)(left) shows an experimental density-of-states curve obtained by integrating an ARPES $E(k_\parallel)$ band map over the $k_\parallel$ interval $[\Gamma, M]$. The indicated tentative decomposition into Gaussian peaks confirms the predicted density-of-states scheme. If the distortion amplitude increases, the gaps between the manifolds will increase, but the upper manifold will remain pinned at $E_F$. Hence, the electronic energy lowering that gives rise to the structural distortion in the commensurate and nearly commensurate CDW phases of pristine 1T-TaS$_2$ primarily occurs in the lower two subband manifolds, together containing $\sim 0.92$ electrons per TaS$_2$ formula unit.

For the $c(2\sqrt{3} \times 4)\text{rect.}$ phase of Rb/1T-TaS$_2$, the atomic displacement pattern and resulting changes to the Ta bonding interactions are not known. Nevertheless, we propose the
Figure 11. Schematic illustration of structural and electronic effects following in situ Rb deposition on the surface of 1T-TaS$_2$. Pristine 1T-TaS$_2$ in the nearly commensurate CDW phase is shown on the left and the Rb/1T-TaS$_2$ intercalation complex on the right. (a) Layer structure of 1T-TaS$_2$. On the right, plus adsorbed and intercalated Rb atoms. (b) CDW superlattice unit cells (solid red lines) and inequivalent Ta atoms (open, filled and colored symbols) forming clusters in the Ta plane. On the right, a primitive unit cell is indicated by a dashed red line. (c) Possible CDW domain structures. On the left: a simple model for the nearly commensurate phase of 1T-TaS$_2$ (after [108]). Hexagonal commensurate areas are separated by ‘discommensurate corridors’. Between neighboring domains, there is a small lateral offset (thin solid line), which is the origin of the near commensurability. On the right: three domains ($\alpha$, $\beta$, $\gamma$) with different orientations compatible with the rectangular symmetry. (d) Occupied electronic structure near the Fermi level in a density-of-states scheme. The dashed curves denote angle-integrated ARPES spectra. The indicated spectral decompositions are used to illustrate possible groupings into subband manifolds. The numbers give the occupation in electrons per superlattice unit cell. On the left, an additional splitting into Hubbard subbands above and below the Fermi level is indicated. On the right, a charge transfer of $\Delta n = 1/4$ e$^-$ per TaS$_2$ formula unit is assumed.
density-of-states scheme depicted in figure 11(d)(right). The indicated experimental curve was obtained by integrating the $E(k_p)$ band map in figure 10(b)(top) over the $k_p$ interval $[\Gamma, M]$. We assume that the lowest Ta 5d bands are grouped into two completely filled manifolds, the lower one containing six electrons, similar to the $p(\sqrt{3} \times \sqrt{3})R13.9^\circ$ phase of pristine $1T$-TaS$_2$, and the upper one filled with four electrons. Note that this implies a charge transfer of $0.25$ e$^-$ per TaS$_2$ formula unit, because the superlattice unit cell contains only eight nominally d$^1$ Ta atoms. One can readily understand why this configuration is energetically more favorable than a rigid-band filling of the electronic structure in the $p(\sqrt{3} \times \sqrt{3})R13.9^\circ$ phase. Since the Fermi surface is completely destroyed, all electrons (i.e. 1.25 per TaS$_2$ formula unit) will contribute to the electronic energy gain when the distortion amplitude is increased. Such a scenario, however, requires a large enough energy gap and lattice distortion from the outset. In that respect, we note that an extra energy gain associated with the formation of the $c(2\sqrt{3} \times 4)$ rect. superlattice comes from locking-in to the underlying crystal lattice [113]. The lock-in energy generally increases with decreasing superlattice wavelength [114]. Hence, it is larger for the $c(2\sqrt{3} \times 4)$ rect. superlattice ($\lambda_0 = \sqrt{3}a$) than for the $p(\sqrt{3} \times \sqrt{3})R13.9^\circ$ superlattice ($\lambda_0 = \sqrt{13}a$).

In short, we argue here that the charge transfer to the Ta 5d band in the Rb/$1T$-TaS$_2$ complex is exactly 0.25 electrons per TaS$_2$ formula unit. This value represents a large part of the maximum possible electron transfer estimated from Rb core-level spectroscopy and it is consistent with the emergence of a complete energy gap at the Fermi level. The $c(2\sqrt{3} \times 4)$ rect. superlattice basically occurs in the electron doped system because it allows for a substantial band-energy lowering due to the creation of a two-dimensional band insulator.

6.3. Nature of the energy gap: Peierls or Mott–Hubbard?

Since the dramatic rearrangement of the electronic states in Rb intercalated $1T$-TaS$_2$ is clearly correlated with a change of the superlattice, it is natural to attribute the electronic changes to a Peierls-type transition, as has been done in the previous section. Nevertheless, the magnitude and completeness of the energy gap at the Fermi level are surprising, and pristine $1T$-TaS$_2$ is a material on the verge of a Mott–Hubbard transition that may well be fully realized by small perturbations. Moreover, there is some degree of localization of the Ta 5d states, since the bands are rather dispersionless at the center of the Brillouin zone (figure 10(b)(top)) and, indeed, an ARPES intensity map that looks intriguingly similar to the one at the top of figure 10(b) has been used to identify a Mott–Hubbard transition at the surface of the closely related compound $1T$-TaSe$_2$ [110]. Hence, it could also be argued that the energy gap in Rb/$1T$-TaS$_2$ is not a Peierls band gap but a Mott–Hubbard correlation gap [47]–[49], [101]. The question then is: Does the $c(2\sqrt{3} \times 4)$ rect. CDW state in Rb/$1T$-TaS$_2$ create a favorable situation in which a Mott–Hubbard transition becomes possible? If such a transition actually occurred, the upper peak in the density-of-states curve in figure 11(d)(right) would not correspond to a completely filled subgroup of uncorrelated bands but to a correlated lower Hubbard subband manifold.

The description of correlated electron behavior is commonly reduced to three parameters: the on-site Coulomb interaction $U$, the one-electron bandwidth $W$ and the band filling $n$ (number of electrons per unit cell). In a generalized Hubbard model with degenerate bands, which we tentatively regard as an appropriate physical model here, systems will become Mott–Hubbard insulators for all integer fillings $n = 1, 2, \ldots, 2M - 1$, where $M$ is the band degeneracy, if the ratio $U/W$ is larger than a critical $(U/W)_c$. In general, $(U/W)_c$ increases.
with $M$ and decreases away from half-filling $n/M = 1$ [111]. For the single-band Hubbard model ($n = M = 1$) on a triangular lattice, it is found that $(U/W)_{c} \approx 1.3$ [112].

Before discussing the possibility of Mott–Hubbard transitions in CDW distorted 1T-TaS$_2$ sandwiches, we remark that it is helpful to think separately about the contributions to the bandwidth $W$ arising from $k_{\|}$ and $k_{\perp}$ dispersion. For $W_{\|}$ the important control parameters are the wavelength and amplitude of the periodic lattice distortion, and for $W_{\perp}$ it is the intersandwich separation.

In the commensurate CDW phase of pristine 1T-TaS$_2$, the low-energy physics can be mapped on the single-band Hubbard model at half-filling. The relevant band is the one that is associated with the star-center Ta atoms and split off in a gap at $E_{F}$ [32]. The Coulomb interaction $U$ is estimated from experiment and theory to be about 0.25–0.7 eV [33, 113, 115] and density-functional calculations predict a total bandwidth of $\sim 0.5$ eV, mostly arising from dispersion in the $k_{\perp}$ direction [115, 116]. The calculated intrasandwich bandwidth $W_{\|}$ is only less than 0.1 eV [32, 115, 116], in good agreement with ARPES results [103]. Note, however, that ARPES has not yet detected the supposedly stronger interlayer interactions [102, 103]. The position and full-width at half-maximum of the topmost occupied peak in figure 11(d)(left), when interpreted as the lower Hubbard band, suggest $U/2 \approx 0.1$ eV and $W \approx 0.15$ eV. Hence, we end up with estimates of 0.2–0.7 eV for $U$ and 0.1–0.5 eV for $W$. According to these numbers, $U/W > 1.3$ is probably but not clearly fulfilled, as might have been anticipated from the marginal stability of the Mott insulating state seen in experiment [33, 117]. In the nearly commensurate phase, the free carriers available from the discommensurate corridors between the commensurate domains (figure 11(c)) are already sufficient to screen $U$ below the critical value.

How might $n$, $W$ and $U$ change in the $c(2\sqrt{3} \times 4)$ rect. phase of Rb/1T-TaS$_2$? The new superlattice unit cell contains eight Ta atoms, each on average in a 5d configuration before charge transfer. Hence, the requirement of integral band filling limits the possible charge transfer from Rb to the Ta 5d band to integer multiples of $1/8 \, e^{-}$ per TaS$_2$ formula unit. Although charge transfers of 0.125, 0.25 and 0.375 $e^{-}$/TaS$_2$ would all be consistent with the upper limit of $(0.35 \pm 0.1) \, e^{-}$/TaS$_2$ estimated from Rb core-level spectroscopy, we tentatively assume 0.25 transferred electrons per formula unit here, as in the previous section. Then, if we stick to the proposed density-of-states scheme depicted in figure 11(d)(right), the band filling will be $n = 4$ and the possible band degeneracies $M = 3, 4, 5$. This implicates a larger critical ratio $(U/W)_{c}$ as compared to the $n = M = 1$ case of pristine 1T-TaS$_2$. Extrapolating the values of the critical interaction that were obtained for a triangular lattice for $M = 1, 2$ [112, 118], we estimate $(U/W)_{c}$ to be about 2.7.

The lattice expansion caused by Rb intercalation, both perpendicular and parallel to the sandwiches, will decrease $W_{\perp}$ and, to a lesser extent, also $W_{\|}$. One may even foresee that the 40% increase of the $c$ parameter causes a complete electronic decoupling of the sandwiches, i.e. $W_{\perp} \approx 0$. By contrast, the reduced size of the $c(2\sqrt{3} \times 4)$ rect. unit cell will probably lead to an effective increase of $W_{\|}$, since the distance between potential localization centers on neighboring clusters necessarily becomes smaller. As for the Hubbard $U$, one may also expect an increased value because the average Ta valency changes from 4+ to 3.75+, making the Ta sites more negative [119] and because screening may be less efficient in the $c(2\sqrt{3} \times 4)$ rect. phase due to reduced dimensionality (increased intersandwich separation) and the more long-range ordered domain structure with fewer free electrons released from domain walls [33]. Quantitative predictions of these effects are, however, difficult. A pragmatic way out is, again,
to use the width and position of the upper peak in figure 11(d)(right) as estimates for the bandwidth and the Coulomb interaction, respectively. The obtained values are $W \approx 0.3–0.4$ eV and $U/2 \approx 0.5$ eV, implying an effective increase of both $W$ and $U$ and a ratio $U/W$ of about 3. Hence, in view of the estimated $(U/W)_c \approx 2.7$, a Mott–Hubbard metal-to-insulator transition could still be possible.

The rather unsatisfactory conclusion then is that, from the view of photoemission spectroscopy, the nature of the $c(2\sqrt{3} \times 4)$ rect. phase in the intercalation complex Rb/1T-TaS$_2$ cannot be unambiguously identified. It can be a Peierls-type band insulator with an energy gap mostly determined by the structural distortion and with electron correlation effects playing a minor role. Or it can be a Mott–Hubbard-type correlated insulator resulting from a delicate interplay of CDW periodicity and commensurability, interlayer coupling, electron doping and electron–electron repulsion. In both cases, the charge transfer from the Rb atoms to the Ta 5d band is expected to adjust to exactly 0.25 electrons per TaS$_2$ formula unit, in the Peierls insulator to produce a completely filled subband manifold and in the Mott–Hubbard insulator to have integral band filling.

At present, however, we favor the Peierls insulator with a large band (pseudo-)gap of $\sim 1$ eV, in which the very few remaining charge carriers at the Fermi level will readily be localized by defect potentials (Anderson localization as opposed to collective Mott localization). Such a scenario is corroborated by a suggestive analogy to the intercalation complex N$_2$H$_4$/1T-TaS$_2$. In this system, an optical gap of $\sim 1$ eV [38] comes along with a concentration of about 1 localized $S = 1/2$ Ta state per 400 Ta atoms [113, 120], a value consistent with Anderson localization but too low for Mott localization for which one would expect at least 1/8 of all Ta sites to have a localized spin. Unfortunately, magnetic susceptibility measurements for the Rb/1T-TaS$_2$ intercalation complex are not available. Clearly, it would also be interesting to see whether realistic band structure calculations using the local-density approximation can find a large enough energy gap. If they did, it would be a strong indication that the electronic structure is indeed more band-like than correlated. Before such calculations can be done, however, a detailed structural characterization of the $c(2\sqrt{3} \times 4)$ rect. phase needs to be performed.

7. Conclusions

It was known before that in situ alkali adsorption and intercalation is a powerful method to modify the electronic and structural properties of layered transition-metal dichalcogenides near their surfaces in an easily controlled and largely non-destructive way. In this work, the key experimental advance has been to combine this approach with real-time ARPES so that the electronic structure changes, in particular those occurring near the Fermi level, can be monitored continuously during the alkali deposition process.

This work has focused on a large alkali metal, Rb, and two fascinating layered CDW compounds, 1T-TiSe$_2$ and 1T-TaS$_2$. It has been verified that in situ Rb adsorption (without intercalation) is a method to fill the transition-metal d band of the topmost sandwich in a rigid-band sense, whereas in situ Rb intercalation provides a way to add more electrons to the d band and additionally decouple the top sandwiches from each other and from the bulk. For the intercalated systems, the rigid-band model cannot adequately describe the observed changes. At the moderate deposition rates used in this work ($\ll 1$ monolayer equivalent per minute), the important control parameter is substrate temperature. At liquid-nitrogen temperatures, Rb intercalation is generally suppressed; at room temperature, it occurs very rapidly.

New Journal of Physics 12 (2010) 125018 (http://www.njp.org/)
The charge transfer associated with alkali adsorption and intercalation is expected to make the host lattice more metallic. This is indeed what is observed for 1\textit{T}-TiSe$_2$, which undergoes a transition from a (dirty) semiconductor to a metal upon Rb adsorption as well as upon Rb intercalation. During this transition, the $p(2 \times 2 \times 2)$ CDW is continuously suppressed, in clear correlation with a gradual weakening of the interaction between the Se 4p and Ti 3d states. Upon Rb intercalation into 1\textit{T}-TaS$_2$, on the other hand and counterintuitively at first, a transition from a (bad) metal to an insulator is observed. This transition is correlated with a structural change from the pristine nearly commensurate $p(\sqrt{13} \times \sqrt{13})$R13.9° superlattice to a novel commensurate $c(2\sqrt{3} \times 4)$ rect. CDW phase.

The presented \textit{in situ} ARPES results lend strong support to the hypothesis that strong electron–phonon coupling drives the CDW phase transitions in pristine 1\textit{T}-TiSe$_2$ and in Rb intercalated 1\textit{T}-TaS$_2$. Accordingly, these two transitions are interpreted as Peierls-like instabilities or, in other words, Jahn–Teller band instabilities. As in all real materials, however, electron–lattice and electron–electron interactions are simultaneously present so that the identification of a dominant interaction is not unambiguous. In the two investigated CDW phase transitions, strong electron–phonon coupling may drive the transition, but the Coulomb interaction between the electrons may be important too. For pristine 1\textit{T}-TiSe$_2$ the possibility of an excitonic insulator instability cannot be completely excluded and for Rb intercalated 1\textit{T}-TaS$_2$ it is not fully unreasonable that the nature of the insulating ground state is of the Mott–Hubbard type. Further experimental and (particularly) theoretical scrutiny of the role played by electron–electron interactions in these transitions is clearly desirable [24]–[26], [115].

One may speculate that the same strong electron–phonon coupling driving the formation of CDWs could also lead to the emergence of superconductivity in Rb intercalated 1\textit{T}-TiSe$_2$ and 1\textit{T}-TaS$_2$. The possibility of superconductivity in Rb$_x$TaS$_2$ can be ruled out, however, because the Fermi surface is completely destroyed. But for Rb$_x$TiSe$_2$ an obvious similarity exists with the intercalation complex Cu$_x$TiSe$_2$, in which a superconducting state emerges near $x = 0.04$ with a maximum transition temperature of $\sim 4.2$ K at $x = 0.08$ [9]. For both systems, the CDW transition is completely suppressed at a concentration level $x = 0.05$–0.06 and the ARPES spectra are very much alike [37, 71]. We therefore predict that Rb$_x$TiSe$_2$ becomes a superconductor at $x \approx 0.05$. The challenge then is to perform an \textit{in situ} intercalation experiment below 4 K and see the emergence of superconductivity, for example, by (real-time) ARPES or scanning tunneling spectroscopy.

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References

[1] Grünér G 2000 \textit{Density Waves in Solids} (Cambridge, MA: Perseus)
[2] Wilson J A, Di Salvo F J and Mahajan S 1975 \textit{Adv. Phys.} \textit{24} 117
[3] Johannes M D and Mazin I I 2008 \textit{Phys. Rev.} B \textit{77} 165135
[46] Adelung R, Brandt J, Kipp L and Skibowski M 2001 Phys. Rev. B 63 165327
[47] Crawack H J, Tomm Y and Pettenkofer C 2000 Surf. Sci. 465 301
[48] Rossnagel K, Rotenberg E, Koh H, Smith N V and Kipp L 2005 Phys. Rev. Lett. 95 126403
[49] Schmidt P, Kröger J, Murphy B M and Berndt R 2008 New J. Phys. 10 013022
[50] Pettenkofer C, Jaegermann W and Parkinson B A 1991 Surf. Sci. 251–2 583
[51] Tatlock G J and Acrivos A V 1978 Phil. Mag. B 38 81
[52] Starnberg H I, Brauer H E and Strocov V N 2005 Phys. Rev. Lett. 95 126403
[53] Schmidt P, Kröger J, Murphy B M and Berndt R 2008 New J. Phys. 10 013022
[54] Pettenkofer C, Jaegermann W and Parkinson B A 1991 Surf. Sci. 251–2 583
[55] Tatlock G J and Acrivos A V 1978 Phil. Mag. B 38 81
[56] Starnberg H I, Brauer H E and Strocov V N 1999 J. Phys.: Condens. Matter 11 8957
[57] Starnberg H I, Brauer H E and Hughes H P 1993 Phys. Rev. Lett. 71 101 237602
[58] Liang W Y , Lucovsky G, White R M, Stutius W and Pisharody K R 1976 Phil. Mag. 33 493
[59] Zunger A and Freeman A J 1978 Phys. Rev. B 17 1839
[60] Benesh G A, Woolley A M and Umrigar C 1985 J. Phys. C: Solid State Phys. 18 1595
[61] Adelung R, Brandt J, Rossnagel K, Seifarth O, Kipp L and Skibowski M 2001 Phys. Rev. Lett. 86 1303
[62] Starnberg H I, Brauer H E, Holleboom L J and Hughes H P 1999 J. Phys.: Condens. Matter 11 8957
[63] Starnberg H I, Brauer H E and Hughes H P 1996 J. Phys.: Condens. Matter 8 1229
[64] Spiecker E, Schmid A K, Minor A M, Dahmen U, Hollensteiner S and Jäger W 2006 Phys. Rev. Lett. 96 086401
[65] Mårtensson N, Baltzer P, Brühwiler P A, Forsell J-O, Nilsson A, Stenborg A and Wannberg B 1994 J. Electron Spectrosc. Relat. Phenom. 70 117
[66] Holt M, Zschack P, Hong H, Chou M Y and Chiang T-C 2001 Phys. Rev. Lett. 86 3799
[67] Rossnagel K, Kipp L and Skibowski M 2001 Phys. Rev. B 65 235101
[68] Kidd T E, Miller T, Chou M Y and Chiang T-C 2002 Phys. Rev. Lett. 88 226402
[69] Li G, Hu W Z, Qian D, Hsieh D, Hasan M Z, Morosan E, Cava R J and Wang N L 2007 Phys. Rev. Lett. 98 117007
[70] Burka B, Thomson R E, Clarke J and Zettl A 1992 Science 257 362
[71] Fang C M, de Groot R A and Haas C 1997 Phys. Rev. B 56 4455
[72] Watarai S and Matsubara T 1975 Prog. Theor. Phys. 53 1214
[73] Woo K C, Brown F C, McMillan W L, Miller R J, Schaffman M J and Sears M P 1976 Phys. Rev. B 14 3242
[74] Liang W Y , Lucovsky G, White R M, Stutius W and Pisharody K R 1976 Phil. Mag. 33 493
[75] Zunger A and Freeman A J 1978 Phys. Rev. B 17 1839
[76] Benesh G A, Woolley A M and Umrigar C 1985 J. Phys. C: Solid State Phys. 18 1595
[77] Adelung R, Brandt J, Rossnagel K, Seifarth O, Kipp L and Skibowski M 2001 Phys. Rev. Lett. 86 1303
[78] Starnberg H I, Brauer H E, Holleboom L J and Hughes H P 1993 Phys. Rev. Lett. 70 3112
[79] Fang C M, de Groot R A and Haas C 1997 Phys. Rev. B 56 4455
[80] Watarai S and Matsubara T 1975 Prog. Theor. Phys. 53 1214
[81] Natori A 1976 J. Phys. Soc. Japan 40 163

New Journal of Physics 12 (2010) 125018 (http://www.njp.org/)
[87] Kristoffel N and Konsin P 1967 Phys. Status Solidi b \textbf{21} K39
[88] Kohn W 1968 \textit{Many Body Physics} ed C DeWitt and R Balian (New York: Gordon and Breach) p 353
[89] Halperin B I and Rice T M 1968 \textit{Solid State Phys.} \textbf{21} 115
Halperin B I and Rice T M 1968 Rev. Mod. Phys. \textbf{40} 755
[90] Kristoffel N and Konsin P 1988 \textit{Phys. Status Solidi} B \textbf{149} 11
[91] Peierls R E 1955 \textit{Quantum Theory of Solids} (Oxford: Clarendon) pp 108–12
Peierls R E 1991 \textit{More Surprises in Theoretical Physics} (Princeton: Princeton University Press) pp 27–30
[92] Fröhlich H 1954 \textit{Proc. Soc R. A} \textbf{233} 296
Minkin V I 1999 Pure Appl. Chem. \textbf{71} 1919
[93] Grimvall G 1981 \textit{The Electron–Phonon Interaction in Metals} (Amsterdam: North-Holland)
[94] Neuenschwander J and Wachter P 1990 Phys. Rev. B \textbf{41} 12693
[95] Wachter P, Bucher B and Malar J 2004 Phys. Rev. B \textbf{69} 094502
[96] Wachter P and Bucher B 2005 \textit{Solid State Commun.} \textbf{134} 73
[97] Bronold F X and Fehske H 2006 Phys. Rev. B \textbf{74} 165107
[98] Bronold F X, Fehske H and Röpke G 2007 \textit{J. Phys. Soc. Japan Suppl.} A \textbf{76} 27
[99] Wachter P, Jung A and Pfunder F 2006 Phys. Lett. A \textbf{359} 528
[100] Stoltz S E, Starnberg H I and Holleboom L J 2003 Phys. Rev. B \textbf{67} 125107
[101] Pillo Th, Hayoz J, Naumović D, Berger H, Perfetti L, Gavioli L, Taleb-Ibrahimi A, Schlapbach L and Aebi P 2001 Phys. Rev. B \textbf{64} 245105
[102] Perfetti L, Gloo T A, Mila F, Berger H and Grioni M 2005 Phys. Rev. B \textbf{71} 153101
[103] Hughes H P and Scarfe J A 1995 Phys. Rev. Lett. \textbf{74} 3069
[104] Yeh J J and Lin C J 1995 \textit{At. Data Nucl. Data Tables} \textbf{32} 1
[105] Tanuma S, Powell C J and Penn D R 1994 \textit{Surf. Interface Anal.} \textbf{21} 165
[106] Rouxel J 1979 \textit{Intercalated Layered Materials} ed F Lévy (Dordrecht: Reidel) p 201
[107] Ishiguro T and Sato H 1995 Phys. Rev. B \textbf{52} 759
[108] Haas C 1978 \textit{Solid State Commun.} \textbf{26} 709
[109] Perfetti L, Georges A, Florens S, Biermann S, Mitrovic S, Berger H, Tomm Y, Höchst H and Grioni M 2003 Phys. Rev. Lett. \textbf{90} 166401
[110] Ono Y, Potthoff M and Bulla R 2003 Phys. Rev. B \textbf{67} 035119
[111] Aryanpour K, Pickett W E and Scalettar R T 2006 Phys. Rev. B \textbf{74} 085117
[112] Klipstein P C, Friend R H and Yoffe A D 1985 Phil. Mag. B \textbf{52} 611
[113] Lee P A, Rice T M and Anderson P W 1974 \textit{Solide State Commun.} \textbf{14} 703
[114] Freericks J K, Krishnamurthy H R, Ge Y, Liu A Y and Pruschke Th 2009 Phys. Status Solidi B \textbf{246} 948
[115] Bovet M, van Smalalen S, Berger H, Gaal R, Forró L, Schlapbach L and Aebi P 2003 Phys. Rev. B \textbf{67} 125105
[116] Dardel B, Grioni M, Malterre D, Weibel P, Baer Y and Lévy F 1992 Phys. Rev. B \textbf{45} 1462
Dardel B, Grioni M, Malterre D, Weibel P, Baer Y and Lévy F 1992 Phys. Rev. B \textbf{46} 7407
[117] Lu F, Wang W-H and Zou L-J 2008 Phys. Rev. B \textbf{77} 125117
[118] Sánchez K, Palacios P and Wahnón P 2008 Phys. Rev. B \textbf{78} 235121
[119] Guy D R P, Friend R H, Harrison M R, Johnson D C and Sienko M J 1982 \textit{J. Phys. C: Solid State Phys.} \textbf{15} L1245

New Journal of Physics 12 (2010) 125018 (http://www.njp.org/)