Hidden spin-polarized bands in semiconducting 2H-MoTe$_2$

R. Oliva $^a$, T. Woźniak $^b$, F. Dybala $^a$, J. Kopaczek $^a$, P. Scharoch $^b$ and R. Kudrawiec $^a$

$^a$Department of Experimental Physics, Faculty of Fundamental Problems of Technology, Wroclaw University of Science and Technology, Wroclaw, Poland; $^b$Department of Theoretical Physics, Faculty of Fundamental Problems of Technology, Wroclaw University of Science and Technology, Wroclaw, Poland

ABSTRACT
We present experimental and theoretical studies of the electronic band structure of 2H-MoTe$_2$ at high hydrostatic pressures. Photoreflectance measurements allowed the determination of the pressure coefficient of the direct transitions $A$ and $B$, which are 2.40(3) and $-3.42(18)$ meV/kbar, respectively. We attribute the sign difference to a strong splitting of the conduction bands with increasing pressure and the presence of hidden spin-polarized states in bulk MoTe$_2$. These results provide direct experimental evidence that the spin–valley locking effect takes place in centrosymmetric transition metal dichalcogenides.

IMPACT STATEMENT
The experimental confirmation of the presence of spin-polarized states in a centrosymmetric crystal opens the door to explore valleytronic and spintronic phenomena beyond monolayers, including multilayers and heterostructures.

Introduction
Molybdenum ditelluride (2H-MoTe$_2$) is a semiconductor that belongs to the family of transition metal dichalcogenides (TMDCs), which are layered crystals of the form MX$_2$ (M being a transition metal and X a chalcogenide). Amongst all semiconducting TMDCs, MoTe$_2$ is unique because it exhibits the smallest indirect (direct) band gap, around 0.85 eV (1.15 eV) [1]. Hence, the small gap of MoTe$_2$ allows to extend the optoelectronic applications of TMDCs into the near-infrared range, close to the band gap of silicon. Moreover, it has been predicted that the properties present in monolayers, such as valley polarization [2], prevail in the bulk form as a consequence of a strong spin orbit coupling (SOC) and weak interlayer van der Waals forces [3,4]. The presence of spin-polarized bands in bulk TMDCs opens an exciting range of potential applications in spintronics for multilayered TMDCs [5]. However it is crucial to understand the effect of SOC on the band spin–orbit splitting and on the degree of band spin-polarization in order to design novel technological devices. In this regard, MoTe$_2$ is an excellent candidate for investigation since it exhibits the largest splitting of the conduction and valence bands amongst all Mo-containing TMDCs [6].

The electronic band structure of MoX$_2$ has been intensively studied both experimentally and theoretically, and special attention has been paid to the region of the K point in the Brillouin zone (BZ), where the first direct electronic transitions take place (A and B). Spin- and angle-resolved photoemission spectroscopy [7–9] evidenced the presence of spin-polarized states in bulk TMDCs which was previously believed to take place only for non-centrosymmetric materials such as monolayers (MLs). However, since the photoemission spectroscopy mostly probes the outermost layer, it is highly desirable to use alternative optical techniques to confirm the presence...
of spin-polarized states in bulk TMDCs. On the other hand, exploring the optical properties of MoTe2 could help to clarify the ordering of the conduction bands at K or the nature of other interband transitions. For instance, the A* feature, which is \( \approx 50 \) meV above the A transition, has been either assigned to excited excitonic states [10,11] or direct transitions at the H k-point [12–14]. More recently magneto-reflectance measurements showed that such feature could be attributed to an interlayer excitonic transition [15,16]. Hence it is desirable to further investigate the excitonic features present in MX2 to better understand the effect of the SOC on the electronic band structure.

High pressure measurements by means of modulation spectroscopy represents a unique tool to obtain detailed information about the band structure [17]. So far TMDCs have been investigated both at high and ambient pressure by several modulation spectroscopies including photoreflectance (PR). Measurements at ambient pressure resolved many excitonic transitions (including A and B) and assigned most of them to direct transitions in the band structure [1,12,18]. High-pressure PR measurements allowed to establish the pressure coefficients for the A and B transitions and infer the semiconductor to metal transition pressure of MoS2, MoSe2, WS2 and WSe2 [19]. Recent high-pressure optical absorption measurements on MoS2 [20] allowed to indirectly assess the spin-polarized nature of the states of bulk MoS2 and evaluate the pressure dependence of the excitonic binding energies, indirect band gap, effective masses and dielectric constants. Despite these works, MoTe2 has been comparatively less investigated. High pressure PR measurements on MoTe2 would provide useful information to better understand the effect of interlayer distance on the SOC, spin-polarized bulk states and provide hints to stabilize the origin of all measured excitonic transitions.

Here we report on the photoreflectance (PR) measurements performed at high hydrostatic pressures on the semiconducting 2H polytype of MoTe2. Our measurements allowed tracking the pressure dependence of several excitonic transitions, including A and B. The experimental results are discussed in the light of \textit{ab initio} band structure calculations based on density functional theory (DFT). Good agreement is found between the experimental and calculated pressure coefficients for the A and B excitonic transitions. Other features observed in the PR spectra were assigned to direct transitions at the H k-point of the BZ and the presence of interlayer and excited states is discussed. Finally, we provide direct evidence of spin-valley locked bands in bulk MoTe2.

### Materials and methods

#### Samples

High purity (99.9999% confirmed) molybdenum ditelluride (2H-MoTe2) were synthesized by the flux zone method by the commercially available 2D Semiconductor company. Raman, XRD and PL characterization showed high crystallinity, details can be found elsewhere [21].

#### Computational methods

DFT calculations were performed with the use of ABINIT code [22]. Fully relativistic PAW datasets with the GGA (PBE) approximation were used for geometry optimization along with the D-3 correction for the van der Waals interaction [23]. Geometrical parameters were optimized for interatomic forces lower than 10\(^{-8}\) Hartree/Bohr. HGH pseudopotentials with the spin–orbit interactions included were used for the band structures calculations [24]. The MBJ/LDA (TB09) [25] functional, which consists of the modified Becke–Johnson exchange potential combined with the LDA correlation, has been used. For the band structure convergence criteria we took a total energy difference of 10\(^{-9}\) Ha and a wavefunction squared residual of 10\(^{-16}\). In all calculations the \( 8 \times 8 \times 4 \) Monkhorst–Pack mesh and the plane wave basis energy cutoff of 30 Ha for geometry optimization and 60 Ha for band structure calculations were used.

#### Experimental methods

A MoTe2 sample (400-μm-thick) was mounted inside a UNIPRESS piston cylinder cell, where high pressure was generated using a press. Daphne 7474 was used as hydrostatic medium. The pressure was determined by measuring the resistivity of a InSb probe. A sapphire window in the cell provided optical access to the sample. For the PR measurements we used a single grating of 0.55 m focal length to disperse the light reflected from the samples. The signal was measured using an InGaAs (Si) detector for energies below (above) 1.25 eV. A chopped (270 Hz) 405 nm laser line was pumped into the sample together with a probe tungsten lamp (power of 150 W). Phase-sensitivity detection of the PR signal was processed with a lock-in amplifier. The principle of photoreflectance spectroscopy is to modulate the built-in electric field of the sample and measure changes in the reflectivity associated with direct optical transitions [26]. Combined with high-pressure techniques, PR can provide a highly useful benchmark to test computational models (such as those based on DFT) for the calculation of the electronic band structure of TMDCs [19,27].
Figure 1. Electronic dispersion curves for MoTe$_2$ at zero pressure (black curves) and 20 kbar (red curves). Electronic bands have been labeled at relevant wave vectors. Direct transitions are expected at the K and H k-points and an indirect gap is defined from K2 to Q.

**Results**

The calculated electronic band structure of 2H-MoTe$_2$ is shown in Figure 1 along the high symmetry points of the BZ for ambient pressure (black curves) and a pressure of 20 kbar (red curves). As it can be seen in the figure, bulk MoTe$_2$ is an indirect band gap semiconductor. The valence band maximum (VBM) is located at the K high-symmetry point of the BZ and the conduction band minimum (CBM) at an arbitrary point between K and $\Gamma$ (labeled Q) \[16\]. Previous DFT calculations reported pressure coefficient of the indirect band gap around $\Delta E \approx -7.3$ meV/kbar, corresponding to a transition between k-points away from K or $\Gamma$ \[28\]. Our calculations provide a different picture of the electronic dispersion, in consistency with angle-resolved photoemission spectroscopy (ARPES) measurements \[29\], and predict an indirect band gap pressure coefficient around $\Delta E \approx -4.76$ meV/kbar. While no experimental data for the pressure coefficient of the indirect band gap of MoTe$_2$ are available to date, our calculated pressure coefficient is similar to that measured for MoS$_2$ by means of optical absorption, $\Delta E \approx -3.29$ meV/kbar \[20\].

The K point in the BZ has received intensive research since at this point the first direct transition takes place for both, bulk and monolayer materials. However, it is important to note that while the first direct transition takes place at K, a similar dispersion takes place around H. At high pressure a strong conduction band splitting takes place in K but remains unchanged in H. As it can be seen in Figure 1, our calculations reveal that such splitting lacks a band crossing and is driven by a strong decrease in the energy of the band with the lowest effective mass. This result is consistent with previous calculations at ambient pressure, which do not reveal a band crossing along the $\Gamma$-K direction \[6\].

The photoreflectance spectra measured at different pressures are shown in Figure 2. Six PR features can be observed in the spectra, labeled A, A*, B, B*, C and C*. Since the A*, B* and C features are rather weak and somewhat difficult to resolve, colored dashed lines have been plotted as a guide to the eye. The red dotted curves are fit to the spectra assuming six excitonic transitions and employing the Aspnes formula \[30\],

$$\frac{\Delta R}{R}(E) = \text{Re} \left[ \sum_{j=1}^{n} C_j e^{i\theta_j} (E - E_j + i\Gamma_j)^{-m} \right], \quad (1)$$

where $n$, $C_j$ and $\theta_j$ are the number of transitions, amplitude and phase of the resonance, $E_j$ and $\Gamma_j$ are the energy and broadening parameter of the transition, respectively. For excitonic transitions we take $m = 2$. As it can be seen in the figure, the agreement between the experimentally measured spectra and the line shape of the fit is excellent. The moduli of each individually fitted resonances ($\rho_j$) for the spectra measured at 16.8 kbar has been plotted below as colored solid curves. For the calculation, we used the following expression,

$$\rho_j(E) = \frac{|C_j|}{\left((\hbar \omega - E_j + \Gamma_j^2)^{m/2}\right)}.$$
**Figure 2.** Photoreflectance spectra acquired at different pressures (solid black lines). Fittings are shown as red dotted curves. Colored dashed lines around the fitted transition energies are shown as guide to the eye. The moduli of fitted resonances at 16.8 kbar are shown at the bottom (colored peaks).

**Figure 3.** The energies of the transitions fitted to the PR experimental data are plotted as function of pressure (colored symbols). All the calculated energies of direct transitions are plotted as lines; the transitions assigned to fitted PR features have been colored and labeled accordingly (colored solid lines); the calculated direct transitions that are absent in the PR spectra are shown as dotted lines. Note: All the theoretical lines have been upshifted by 80 meV for the sake of clarity.
where all the parameters were taken from the fitted values in Equation (1). As it can be seen in Figure 2, The modulus of the C resonance is very broad and partially resembles that of resonance B*. However, it was necessary to include such resonance in the fitting procedure in order to accurately reproduce the experimental line-shape. The pressure dependence of the fitted energies for each transition is plotted in Figure 3.

Figure 3 shows the pressure dependence of the transition energies fitted to the PR spectra (full symbols) and all the calculated direct transitions at high-symmetry k-points (dotted and solid lines). The solid lines and full symbols are colored accordingly to our assignation and the dotted lines represent the calculated transitions not resolved in the PR spectra. The energetic difference between experiments and calculations can be attributed to two factors: (i) intrinsic inaccuracies in the band gap calculations within DFT [31] and (ii) the excitonic binding energies (up to \(\approx 16\) meV [32]), not considered in the calculations. On the other hand, it is important to note that the lowest calculated direct transition (see the lowest dashed line in the figure) is clearly split from the A transition (200 meV at 20 kbar) but is not observed experimentally (see Figure 2). The absence of this transition in the PR spectra is a direct evidence of the band spin polarization in bulk MoTe2. Interestingly, an interlayer exciton with the same energy has been observed in the high-field magneto-reflectance measurements at a temperature of 4 K [16], but such feature is absent in the PR spectra measured at ambient pressure.

### Discussion

The assignation of different transitions was done by comparing the calculated and the experimental pressure coefficients. As it can be seen in Table 1, transitions A, B and C are assigned to direct transitions at the K point

| Transition name | Assigned transition | \(E(P = 0)\) exp. (eV) | \(E(P = 0)\) calc. (eV) | \(dE/dP\) exp. (meV/kbar) | \(dE/dP\) calc. (meV/kbar) |
|-----------------|---------------------|-------------------------|--------------------------|---------------------------|---------------------------|
| A               | K2—K4               | 1.060(1)                | 0.975(2)                 | 2.40(3)                   | 2.35(18)                  |
| A*              | H2—H3               | 1.117(6)                | 1.079(1)                 | 5.65(55)                  | 6.02(10)                  |
| B               | K1—K3               | 1.362(2)                | 1.280(9)                 | -3.42(18)                 | -3.21(78)                 |
| B*              | H1—H4               | 1.348(5)                | 1.253(1)                 | 4.87(36)                  | 5.52(8)                   |
| C               | K1—K5               | 1.522(20)               | 1.401(10)                | -0.02(93)                 | 1.49(82)                  |
| C*              | H2—H5               | 1.659(1)                | 1.569(1)                 | -2.35(12)                 | -1.08(11)                 |

Table 1. Assignment of each measured direct transition, together with the experimental and calculated transition energies at zero pressure and pressure coefficients.
the BZ, while transitions $A^*$, $B^*$ and $C^*$ are tentatively assigned to ground state exciton transitions at the H point. Additional PR signal is expected to arise from a band nesting contribution located at $\Lambda$ (see Figure 1) [33]. Such feature was previously observed for MoS$_2$ [18], but owing to its broad nature, it is not clearly visible in MoTe$_2$. In the assignation procedure the transitions with calculated zero transition matrix elements were discarded. The degree of spin-polarization was also taken into account at both K and H points.

As it can be seen in the table, after the assignation a good agreement is found between calculated and measured pressure coefficients. Note that calculations do not consider excitonic effects, the impact of the excitonic binding energy, $E_b$, on the optical pressure coefficient, $dE_{\text{opt}}/dP = dE_b/dP + dE_b/dP$, is below our experimental uncertainty ($dE_b/dP \approx -0.4 \text{ meV/kbar}$ for MoS$_2$ [20]).

Figure 4 shows the electronic dispersion around the K $k$-point of the BZ at ambient pressure (left) and 20 kbar (right). As it can be seen in the figure, the two spin-allowed transitions take place; these are the A and B transitions. At high pressures ($P > 1$ kbar), our calculations predict a strong splitting of the conduction band, and the band anticrossing. Hence, the conduction band with the lowest effective mass becomes the CBM at pressures above 1 kbar. This exchange of conduction bands should result in the reversing of the spin polarization ordering at high pressures. In order to validate such hypothesis, we calculated the spin-layer polarization parameter (SLP) [20], which qualitatively provides the degree of spin-layer polarization of states. The calculated values of SLP are shown in Figure 4 as blue and red arrows for each band. The calculated spin configuration confirms the exchange of spin polarization ordering at high pressures. The calculated spin polarizations imply that the transition A (B) exhibits a blueshift (redshift) with increasing pressure, in good agreement with present experiments. Owing to these properties, MoTe$_2$ is an excellent material for investigating the spin-polarization phenomena at high hydrostatic pressures. For instance, it has been shown that bulk MoTe$_2$ exhibits magnetic properties that can be strongly tuned by pressure [34], but the underlying physical mechanism is not yet fully understood. Further investigation on the layer and valley pseudospins in centrosymmetric TMDCs at high pressure could shed new light on the understanding of the pressure-dependent magnetic properties of MoTe$_2$.

**Conclusions**

In conclusion, the present results provide direct evidence that the spin–valley locking effect takes place in centrosymmetric MoTe$_2$, retaining the spin sequence of its monolayer form. This extends the range of potential applications to valleytronics and spintronics for bilayer and bulk MoTe$_2$. Density functional calculations revealed that a strong splitting of the conduction band takes place at high pressure, which result in positive and negative pressure coefficients for the A ($2.40 \text{ meV/kbar}$) and B ($-3.42 \text{ meV/kbar}$) transitions. The good agreement between our calculations and experiments allowed assigning all the measured features to direct excitonic transitions at the K and H points of the BZ and discuss the presence of excited and interlayer states.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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**ORCID**

R. Oliva doi: http://orcid.org/0000-0002-9378-4048

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