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# Evaluation of TEM methods for their signature of the number of layers in mono- and few-layer TMDs as exemplified by MoS<sub>2</sub> and MoTe<sub>2</sub>

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## ABSTRACT

In mono- and few-layer 2D materials, the exact number of layers is a critical parameter, determining the materials' properties and thus their performance in future nano-devices. Here, we evaluate in a systematic manner the signature of exfoliated free-standing mono- and few-layer MoS<sub>2</sub> and MoTe<sub>2</sub> in TEM experiments such as highresolution transmission electron microscopy, electron energy-loss spectroscopy, and 3D electron diffraction. A reference for the number of layers has been determined by optical contrast and AFM measurements on a substrate. Comparing the results, we discuss strengths and limitations, benchmarking the three TEM methods with respect to their ability to identify the exact number of layers.

## 1. Introduction

Two-dimensional (2D) materials like  $MoS_2$  and  $MoTe_2$  are crystalline solids which are periodic in the lateral directions but their thickness in the vertical direction is confined. The thickness confinement results in a number of unique properties, which make these materials excellent candidates for various novel electronic (Chang et al., 2016) and optical (Liu et al., 2018) applications as well as for spintronics (Sanikop and Sudakar, 2020). By stacking of these materials, targeted van der Waals heterostructures can be formed (Pezeshki et al., 2016; Li et al., 2017; Duong et al., 2019), which provide additional variety in flexible device fabrication (Wang et al., 2011).

Within the family of 2D materials, transition metal dichalcogenides (TMDs) such as  $MoS_2$  and  $MoTe_2$  are promising candidates for applications in future nanodevices. In their bulk form they are often semiconducting with an indirect band gap, which turns gradually into a direct band gap when thinned down from few-layers to a monolayer (Mak et al., 2010; Splendiani et al., 2010; Lezama et al., 2015; Gusakova et al., 2017). While the electronic properties were predominantly studied for bulk materials and monolayers, not many studies report about the properties of few-layer materials. During the transition from the bulk to the few-layer crystal, quantum confinement and the reduced dielectric screening become more and more important for the materials'

properties (Li et al., 2012, 2021; Lee et al., 2019; Liu et al., 2019). For example, few-layer MoS<sub>2</sub> shows different properties in photoluminescence (Mak et al., 2010; Splendiani et al., 2010) and electron energy-loss spectroscopy (Nerl et al., 2017; Moynihan et al., 2020), dependent on the exact number of layers. With respect to applications of 2D materials and their heterostructures, these thickness-dependent properties require precise control over the number of layers (Lin et al., 2016; Lee et al., 2019; Pallecchi et al., 2020; Pawlik et al., 2018).

To date, many methods have been developed to identify the thickness of 2D materials on substrates. The most widely applied are atomic force microscopy (AFM) (Bertolazzi et al., 2013; Shearer et al., 2016), Raman spectroscopy (Chakraborty et al., 2012; Grzeszczyk et al., 2016; Liang et al., 2018), XPS (Zemlyanov et al., 2018), SEM- (Hiura et al., 2010) / LEEM-contrast (Hibino et al., 2010), and optical microscopy (Hutzler et al., 2019; Niu et al., 2018; Ottaviano et al., 2017; Li et al., 2013). AFM, due to its high vertical resolution, is probably the most common method to directly measure the absolute thickness of 2D materials (Shearer et al., 2016; Xiao et al., 2021). However, the identification of the number of layers by AFM is rather time consuming. Optical microscopy, on the other hand, offers the possibility to identify the number of layers quickly through the comparison of the contrast on a SiO<sub>2</sub>/Si substrate of defined SiO<sub>2</sub> thickness, using calculations based on the description of transmission and reflection at the interfaces by the

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Fresnel equations (Li et al., 2013; Blake et al., 2007; Benameur et al., 2011). This requires the knowledge of the dielectric functions of the TMD, which, in turn, is dependent on the number of layers.

Transmission electron microscopy (TEM) is an indispensable tool for studying the structure of freestanding 2D TMDs and it would be of great advantage, if the number of layers could be directly determined in TEM experiments. Despite the broad spectrum of methods available within TEM, the determination of the number of layers is not a trivial task (Yang and Egerton, 1995; Pozsgai, 1997; Diebold et al., 2003; Heo, 2020; Gorelik et al., 2021b). Here we present a methodological study of the influence of the number of layers on data obtained using high-resolution imaging (HRTEM), electron energy-loss spectroscopy (EELS), and electron diffraction (ED). Our test samples are mechanically exfoliated MoS<sub>2</sub> and MoTe<sub>2</sub> of different thicknesses. As a reference for the actual number of layers, each exfoliated flake was first investigated on a substrate by AFM and optical contrast measurements. Subsequently, flakes of the same thickness were prepared as free-standing samples and studied by HRTEM, momentum-resolved EELS (MR-EELS) and three-dimensional ED (3D ED). We evaluate signatures of the actual number of layers and discuss whether they can be used for unambiguous thickness determination by TEM experiments.

## 2. Material and methods

## 2.1. Sample preparation

Bulk crystals of molybdenum disulphide (MoS<sub>2</sub>) and molybdenum ditelluride (MoTe<sub>2</sub>) were obtained from HQ Graphene (Groningen, Netherlands). Few-layer flakes were prepared by mechanical exfoliation, using the scotch-tape procedure (Novoselov et al., 2004; Blake et al., 2007; Benameur et al., 2011). Afterwards, they were transferred onto Si wafers covered with a 90 nm SiO<sub>2</sub> layer. After the optical contrast was measured in reflected light microscopy, a drop of isopropyl alcohol (IPA) was placed on top, and the flake was covered by a Quantifoil "R 1.2/1.3" holey carbon TEM grid [Quantifoil Micro Tools GmbH, Großlöbichau, Germany]. After the IPA has evaporated, the carbon film comes into contact with the flake. Eventually, the underlying SiO<sub>2</sub> substrate was etched off with potassium hydroxide (KOH), thus releasing the grid with MoS<sub>2</sub> flakes. Afterwards, the residues of the preparation components were washed away with double-distilled water using the procedure as described in more detail in (Köster et al., 2021).

## 2.2. Optical microscopy

For optical contrast measurements, we used an Olympus BX51 optical microscope in reflected light illumination mode equipped with an Olympus SC50 camera. In addition, an infrared filter was used to eliminate infrared contributions. The Weber contrast between the bare  $SiO_2$  substrate and the crystal was calculated as

$$C_{Weber} = \frac{I_{\rm SiO_2} - I_{\rm crystal}}{I_{\rm SiO_2}}$$

where  $I_{SiO_2}$  and  $I_{crystal}$  denote the reflected light intensity of the SiO<sub>2</sub> and the crystal, respectively (Blake et al., 2007). More details on the procedure of contrast evaluation can be found in Section 1 of the Supplementary Information (SI).

The optical contrast for one to seven layers  $(1-7 \text{ L}) \text{ MoS}_2$  and 1-7 L MoTe<sub>2</sub> was predicted using the formulae described in detail in (Blake et al., 2007) and (Benameur et al., 2011). Simulations were performed with different dielectric functions as input and with the exact wavelength-dependent pixel sensitivity of each CCD channel (red, green, blue), as provided by the manufacturer of the light microscope. Dielectric function data for bulk MoS<sub>2</sub> and thin MoS<sub>2</sub> flakes with 1–7 L were taken from (Song et al., 2019). For MoTe<sub>2</sub>, bulk dielectric constants from (Li et al., 2019) and (Beal and Hughes, 1979) were used.

## 2.3. AFM

The number of layers for the given flakes were identified by atomic force microscopy (AFM). AFM images of the sample were obtained with a NanoWizard 3 Ultra (JPK BioAFM, Bruker Nano GmbH, Berlin) with a piezo z-resolution < 0.9 pm. The measurements were performed at ambient conditions with an Olympus OMCL-AC240TSA-R3E cantilever with gold reflective coating [Olympus Corporation, Tokyo, Japan] and a resonance frequency of 70 kHz using intermittent contact mode. The cantilever has a nominal spring constant of 2 N/m and a sharp tip with a nominal tip radius of 7 nm. Exact layer heights were evaluated by the Gwyddion software (Gwyddion, 2022). For a detailed description of the layer thicknesses identified by AFM see SI Section 1.

## 2.4. HRTEM measurements and image calculation

High-resolution TEM (HRTEM) experiments were carried out at electron acceleration voltages of 60 kV (MoS<sub>2</sub>) and 80 kV (MoTe<sub>2</sub>) using the SALVE instrument with spherical (Cs) and chromatic (Cc) aberration correction and an achievable information limit of 83 pm (60 kV) and 76 pm (80 kV) (Linck et al., 2016). This microscope is based on a FEI Titan Themis<sup>3</sup> column and is equipped with a dedicated Cc/Cs image corrector from CEOS GmbH (Heidelberg, Germany). The Cs and Cc were tuned to values of around -10 µm, respectively. Different electron energies were chosen to be below the predicted knock-on thresholds of the materials (Komsa et al., 2012). For a trade-off between signal-to-noise and beam damage, dose rates in the range of  $2-5 \cdot 10^6 e^{-1}/m^2$  were used. The vacuum in the column of the TEM was in the range of  $10^{-5}$  Pa, therefore chemical etching caused by residual gas in the vacuum chamber (Mølhave et al., 2007) should be sufficiently low. Dose rates of the order of  $10^6 e^{-}/nm^2$ s were used for the acquisition of the HRTEM images, and the images were recorded on a 4k x 4k FEI Ceta CMOS camera with exposure times of about 1 s. The image sampling was below 0.08 Å/px.

HRTEM image calculations for monolayer and few-layer MoS<sub>2</sub> and MoTe<sub>2</sub> were performed using the open source *abTEM* Python Application Programming Interface (API) based on the multislice algorithm (Madsen and Susi, 2021). Within the *abTEM* API, we performed image simulations for a finite electron dose using the Poisson statistics (Graef, 2003). Experimentally acquired values were used as input parameters. In addition, the camera MTF was taken into account.

## 2.5. TEM-EELS measurements

Low-loss TEM-EELS measurements were performed with the SALVE TEM at an acceleration voltage of 60 kV. The microscope is equipped with a Gatan low-voltage GIF Quantum 966 energy filter with a 2048  $\times$  2048 px Ultrascan 1000XP CCD camera. All spectra were acquired in the diffraction mode with parallel sample illumination. The microscope's monochromated X-FEG was mostly operated in the unfiltered mode without excitation of the single-Wien-filter monochromator, in order to avoid detrimental chromatic effects in the diffraction mode. By reduction of the FEG's extraction voltage from 3,900 V to 3,300 V, an energy resolution of 0.65 eV (full width at half maximum, FWHM) was achieved even without monochromator excitation. Only for low-loss EELS measurements of excitonic peaks [see SI Section 6], we used the filtered mode of the monochromator, in which the energy resolution could be improved to 0.15 eV.

The sample thickness was first obtained from EELS using the standard log-ratio method (Malis et al., 1988; Egerton, 2011 pp. 294ff), where the relative thickness  $t/\lambda$  is determined from the ratio between the total intensity of the EELS signal and that of the zero-loss peak (ZLP). For this, we evaluated the EELS signals up to at least 100 eV, with an energy resolution of 0.6 eV and a sampling (dispersion) of 0.05–0.1 eV per channel. The microscope was operated in selected-area diffraction mode, using parallel sample illumination. The collection semi-angle for the EELS data was limited to a value of 11.1 mrad by the energy filter's entrance aperture. Based on the relative sample thicknesses  $t/\lambda$ , absolute thickness values were calculated according to the formulas from Ref. (Egerton, 2011 pp. 294–297), using approximate effective atomic numbers  $Z_{\text{eff}}$  of 26.4 (MoS<sub>2</sub>) and 48.8 (MoTe<sub>2</sub>) as input parameters in the Gatan DigitalMicrograph software (Gatan, Inc., Pleasanton, CA, USA).

For the evaluation of a more specific measure for the sample thickness in terms of the number of MoS2 and MoTe2 layers we applied momentum-resolved (MR-) EELS and evaluated the dispersions of the distinct " $\pi$ " and " $\pi + \sigma$ " peaks in the plasmon-loss regime (0–50 eV). In contrast to standard EELS, energy-loss spectra were recorded for a large range of different momentum transfers  $q \approx \frac{2\pi}{i} \theta$ , where  $\theta$  denotes the scattering angle. The simultaneous acquisition of a large set of *q* values was achieved by recording so-called  $\omega$ -q maps [see, e.g., (Pines, 1956; Watanabe, 1960; Curtis and Silcox, 1971; Midgley, 1999; Kinyanjui et al., 2012)]. Momentum transfers along a single crystallographic direction were selected with a dedicated slit aperture that is commercially available from Gatan, Inc. (Pleasanton, CA, USA). With a special  $\omega$ -q alignment for the parallel EELS mode of the GIF, the spectra for different momentum transfers were spread along the non-dispersive axis of the spectrometer. Using a very large camera length of 2.85 m, a high momentum resolution could be achieved over momentum ranges up to around  $q_{\text{max}} = 0.25 \text{\AA}^{-1}$ . For the evaluation of peak positions in the case  $q \rightarrow 0$ , a zero-loss subtraction was performed by power-law fit (Egerton, 2011, pp. 257–259).

## 2.6. Electron diffraction

3D electron diffraction (3D ED) data were collected using a Thermo Fisher Talos 200X TEM at an acceleration voltage of 200 kV. The microscope was operated in nano-diffraction with the C2 condenser aperture of 50 µm, and the effective beam diameter on the sample of 1 µm. The diffraction patterns were recorded on a fast 4k CETA camera with a binning 2 (2048 × 2048 pixels), in continuous rotation mode using a dedicated stage controlling script (Gorelik et al., 2021a). A Fischione Advanced Tomography Holder (E.A. Fischione Instruments, Inc., Export, PA, USA) was used. Diffraction patterns were collected within the tilt range of  $\pm$  60°, with a single-frame exposure of 0.5 s and a rotation speed of 0.04 fraction of the standard speed, giving the effective tilt increment of 0.594°. The total electron dose received by the specimen during a complete tilt series collection was in the range of 3.3  $e'/Å^2$ .

In practice, it is difficult to assure that the crystal stays within the electron beam during the complete tilt series acquisition. The imperfections in the mechanics of the TEM goniometer often led to crystal drift out of the electron beam during the stage tilt. To ensure that 3D ED data were collected from the same specimen area, we recorded several tilt series for each crystal, starting from different positions ( $-60^\circ$  - the most negative tilt position,  $-30^\circ$ ,  $0^\circ$ ,  $30^\circ$ ). When during the processing we noticed, that the data in the second part of the tilt series ( $0-60^\circ$ ) differed between the different runs, we assumed that the specimen had moved out of the beam and replaced the second part of the tilt series by other partial tilts starting at later positions (typically, at  $0^\circ$ ).

The 3D ED tilt series were processed using the EDT Process software (AnaliteX, Stockholm, Sweden) and PETS2 (http://pets.fzu.cz), supported by self-written MATLAB (The MathWorks, Inc., Natick, MA, USA) scripts. Stacks of electron diffraction patterns were centred and rotated to ensure that the tilt axis runs vertically, and intensities of reflections along the relrods (z-direction) were extracted within a small integration box. ED data were simulated using eMap (AnaliteX, Stockholm, Sweden).

Pseudo-periodic artificial crystal structures were created from bulk MoS<sub>2</sub> (Dickinson and Pauling, 1923) and MoTe<sub>2</sub> (Puotinen and Newnham, 1961) with supercell dimensions of a = b = 3.15 Å (for MoS<sub>2</sub>), a = b = 3.52 Å (for MoTe<sub>2</sub>), and c = 1000 Å,  $\gamma = 120^{\circ}$ , containing 1, 2, 3, and 4 layers. For these structures, 3D Bragg reflection data were

calculated in eMap (AnaliteX, Stockholm, Sweden). A finely spaced L index with an increment of 1/c reciprocal distance was used as an approximation for the continuous L coordinate.

## 3. Results

## 3.1. Optical microscopy and AFM

Optical contrast measurements are routinely used for the determination of the number of layers of 2D materials, provided that the required optical parameters are known (Blake et al., 2007; Benameur et al., 2011; Li et al., 2013). Recently, we already used optical contrast measurements for 1–4-layered MoS<sub>2</sub> (Gorelik et al., 2021b). Here we extend this study to a comprehensive work on optical contrast measurements on 90 nm SiO<sub>2</sub> for 1–7 L MoS<sub>2</sub> and MoTe<sub>2</sub>, combined with contrast calculations and thickness validation by AFM. Our focus lies on the interpretation of the optical contrast of MoTe<sub>2</sub>, for which no detailed contrast study is reported in literature. An additional comprehensive AFM study and measured corresponding optical contrasts of 1–5 L MoS<sub>2</sub> can be found in SI Section 1.

Fig. 1 shows results of the AFM and optical contrast analysis of a MoTe<sub>2</sub> flake consisting of regions with different numbers of layers. (a) displays the AFM image, (b) shows the two height profiles marked by red and blue bars in (a). The height differences for areas consisting of different number of layers is clearly visible, allowing to assign a specific thickness to each region of the flakes. Fig. 1(c) shows an optical microscopy image (RGB colour image) together with the corresponding greyscale images of the red, green, and blue channels, shown as insets underneath. (d) The Weber contrast was measured for all positions showing distinctly different contrast. Here, the data points corresponding to the total contrast are coloured in black, and the individual channels are coloured in red, green, and blue. All measured positions show a clear difference in the Weber contrast and could be assigned to different thicknesses between one and seven layers after correlation with the AFM experiments. Furthermore, optical contrast calculations via the Fresnel equations were carried out for MoS2 and MoTe2, presented in detail in SI Section 2, to validate the measured contrast values and, in turn, to get an estimate of the accuracy of the predictions. The pre-characterisation of the number of layers via optical contrast analysis of the TEM flakes, which are analysed in the following sections, is shown in detail in SI Section 3 for both MoS<sub>2</sub> and MoTe<sub>2</sub>.

## 3.2. High-resolution TEM imaging and image calculations

Cc/Cs-corrected HRTEM at low acceleration voltage gives the unique possibility to precisely determine atomic positions (Jia et al., 2003). Therefore, it enables to distinguish atomic columns with varying elemental composition and in particularly to identify distinctly defects in monolayer TMDs (Algara-Siller et al., 2013; Lehnert et al., 2017). Thus, monolayer can be explicitly identified and distinguished from few-layers by the presents of isolated point defects. Here, we use the unique possibilities of HRTEM to study the evolution of the most prominent signatures in 1-4 L MoS<sub>2</sub> and MoTe<sub>2</sub>, and discuss the possibility of using them to discriminate multilayers with 2-4 L.

Fig. 2(a) provides structure models of top and side view of hexagonal (H) mono- and multilayer  $MoS_2$  and  $MoTe_2$ . In the side view, the monolayer consists of three atomic layers, of which the top and bottom layers are aligned and consist solely of chalcogen atoms. The middle layer consists entirely of molybdenum atoms. In a 2H multilayer, the neighbouring layers are arranged in such a way that chalcogen atoms of the following layer lay right above the metal atoms of the previous layer, and vice versa.

Along with the structure models in Fig. 2(a), we provide the respective AC-HRTEM images and multislice calculations for  $MoS_2$  in Fig. 2(b) and for  $MoTe_2$  in Fig. 2(c). In order to compare the image intensities between monolayers and bilayers, we extracted line profiles of



**Fig. 1.** Atomic force microscopy (AFM) image of a  $MOTe_2$  flake with regions of different number of layers (a), two lines are marked by red and blue were used to measure the height profiles; height profiles of red and blue lines (b); optical microscopy image (RGB) of the same flake (c), inserts below show greyscale images of individual channels; measured Weber contrast of the total and individual (red, green, and blue) channels of the 1–7 L MoTe<sub>2</sub> (d).

the intensities along the atomic rows as shown in Fig. 2(b, c) by red and blue arrows in experimental and calculated images. For a monolaver of MoS<sub>2</sub>, the peaks in the intensity profile correspond to the single molybdenum [Z(Mo) = 42] and two sulfur atoms [Z(S) = 16]. The difference in the scattering power of these species is not very high (42:32) and thus the difference in the height of the peaks is relatively low, as seen in both the experimental and calculated data (red). For the bilayers, every column contains the same atomic species and thus the pairs of the peaks have almost the same height (blue). The relative ratio between the neighboring peaks is very low and becomes indistinguishable in the presence of noise in the images [cf. line scans in Fig. 2]. As a result, the image contrast cannot be used as a reliable criterion to differentiate 2-4 L of MoS<sub>2</sub> [cf. SI Fig. S5]. The situation is different for MoTe<sub>2</sub>. In contrast to sulfur, the scattering power of one tellurium atom [Z(Te) = 52] is stronger than that of molybdenum, and thus, a row of two tellurium atoms has a higher contrast than a single molybdenum atom [see Fig. 2 (c)]. With a further increase in the number of layers, the differences in the intensity profiles disappear. This makes it impossible to distinguish between the different atomic columns and thus between the different number of layers [cf. Fig. 2(c) and SI Fig. S5]. Nevertheless, a discrimination of 2H phases from other occurring stacking types is feasible, see SI Section 4 Fig. S6.

Additionally, for MoTe<sub>2</sub>, we noticed a peak in the middle of the hexagons in the HRTEM images, which not associated with an atomic species. As can be seen in Fig. 2(c), the contrast of these peaks increases as the sample thickness increases. This can be explained by multiple scattering in a periodical structure: interference between the scattered waves leads to the formation of additional features (Haider et al., 2010), which are not associated with atomic positions in the structure. In general, our image calculations are in good quantitative agreement with the experimentally acquired images. Small discrepancies can be explained by uncertainties in the defocus, minor uncertainties of the other aberration coefficients, and local corrugation and strain in the material.

## 3.3. EELS measurements

## 3.3.1. The log-ratio method

First, we discuss the applicability of the standard log-ratio method for the determination of the number of layers by EELS. While this method was shown to give accurate results for the determination of relative thickness changes of a specimen (Malis et al., 1988), it can reach its limit for very thin samples. Especially in terms of the absolute thickness, the method is only expected to yield an accuracy of 10 % or 2 nm, as has been observed for samples with thicknesses of 10–200 nm [see, e.g., (Malis et al., 1988; Heo, 2020)]. Nevertheless, the question rises whether the log-ratio method can still provide some information for few-layer samples, as the method has been applied in literature to estimate the thickness of thin TMD flakes below 10 layers (Nerl et al., 2017; Pelaez-Fernandez et al., 2021).

For log-ratio thickness measurements of 1–4 L MoS<sub>2</sub> and MoTe<sub>2</sub>, we recorded EELS spectra from freestanding sample areas of 1  $\mu$ m in diameter, as limited by a selected-area aperture. For various sample areas in both materials, the resulting  $t/\lambda$  values and corresponding absolute thicknesses are shown in Fig. 3(a) and (b), respectively. While we can observe a general trend to higher thickness measurements between 1 and 4 layers of MoS<sub>2</sub> or MoTe<sub>2</sub>, there are two particular issues that render a layer-accurate thickness determination with the log-ratio method impossible.

Firstly, we observe that the log-ratio results differ significantly for sample positions with the same number of layers. These variations can even be larger than those between sample positions with different number of layers. This can be partly explained by varying hydrocarbon contamination between individual sample areas, as more contamination will increase the resulting sample thickness [c.f. (Heo, 2020)]. As a result, a single log-ratio measurement for the absolute thickness of a few-layer sample does not allow to reliably determine the number of layers. Secondly, the absolute sample thicknesses of both materials are generally overestimated by the log-ratio results. This can again be partly explained by the effect of surface contamination which should lead to a general offset of all data points. However, we also measure a significantly higher sample thickness for MoTe<sub>2</sub> than for MoS<sub>2</sub>. While this is



**Fig. 2.** (a-c) Comparison between experimental and calculated Cc/Cs-corrected HRTEM images for mono-, bi-, three-, and four-layer MoS<sub>2</sub> and MoTe<sub>2</sub>. (a) Structure models representing the top- and side-view atomic arrangements of metal and chalcogen atoms are aligned to the HRTEM images. (b, c) 60 kV MoS<sub>2</sub> and 80 kV MoTe<sub>2</sub> experimental HRTEM images (1st rows) are shown (dose rates of  $2-5\cdot10^6e^-/\text{nm}^2$  s) together with the corresponding calculated image (2nd rows). In addition, positions of contrast line scans are marked by red (monolayer) and blue (bilayer) arrows. Besides, comparison of the experimental and simulated contrast profiles is presented.



**Fig. 3.** Estimation of sample thickness with the log-ratio method at 60 kV: (a) Relative thickness  $t/\lambda$  values for 1 – 4 layers of MoTe<sub>2</sub> and MoS<sub>2</sub> as determined from the EELS spectra up to energy losses of around 200 eV (energy sampling: 0.05 eV/channel). (b) Corresponding absolute sample thickness based on the approximation from Refs. (Malis et al., 1988; Egerton, 2011 pp. 294ff) and a collection semiangle of  $\beta = 11.1$  mrad.

expected for the *relative thickness*  $t/\lambda$  due to the smaller inelastic mean free path for MoTe<sub>2</sub>, a correct measurement of the absolute thickness should result in similar values for MoS<sub>2</sub> and MoTe<sub>2</sub>, as they have very similar lattice constants. However, our results show that the thickness increase per layer is in the same order of magnitude as AFM measurements reported in literature [MoS<sub>2</sub>: 0.65 nm, (Radisavljevic et al., 2011; Song et al., 2019); MoTe<sub>2</sub>: 0.7 nm, (Wang et al., 2019)]. This can be partly explained by the higher surface contamination in MoTe<sub>2</sub> in comparison to MoS<sub>2</sub> (Mirabelli et al., 2016).

In summary, the log-ratio method for thickness determination by EELS is not a reliable technique to obtain the number of layers in fewlayer 2D TMDs such as MoS<sub>2</sub> and MoTe<sub>2</sub>. Especially for MoTe<sub>2</sub>, the method systematically overestimates the absolute thickness. In addition, for the same number of layers, log-ratio results can yield very different results for the relative thickness  $t/\lambda$  which can also vary with only minor changes in the experimental parameters such as the energy sampling [dispersion of the spectrometer, see SI Section 5].

## 3.3.2. Momentum-resolved EELS analysis

Instead of the total intensities of elastically and inelastically scattered electrons, we now consider energy losses of individual features in the low-loss EELS signal. Starting in the band-gap region, the first peaks that could be used for thickness determination are the A and B exciton peaks, which were investigated in numerous recent publications EELS of TMDs (Tizei et al., 2015, 2016; Nerl et al., 2017; Gogoi et al., 2019; Hong et al., 2020, 2021; Susarla et al., 2021). However, these peaks change only very little with the number of layers (Nerl et al., 2017), and these energy shifts are difficult to detect even with a monochromated energy source [cf. SI Section 6]. We therefore focus on the two main features in the energy range of 0-50 eV, which are easy to resolve. These are commonly referred to as the  $\pi$  and  $\pi + \sigma$  plasmon peaks (Johari and Shenoy, 2011; Kumar and Ahluwalia, 2012; Mohn et al., 2018; Moynihan et al., 2020), although they might not always be of plasmonic nature in 2D materials (Nelson et al., 2014; Novko et al., 2015). In few-layer 2D materials of different thickness, these  $\pi$  and  $\pi+\sigma$  peaks both show a shift in energy as well as a change in intensity (Eberlein et al., 2008; Nerl et al., 2017; Moynihan et al., 2020). Moreover, their dispersion changes with the number of layers; thus, the peak positions have a different dependence on the momentum transfer q. In the following, we discuss the prospects of momentum-resolved (MR) (low-loss) EELS for the determination of the number of layers of MoS<sub>2</sub> and MoTe<sub>2</sub>. For collective excitation (plasmon) of an electron gas, we expect that in the optical limit  $q \rightarrow 0$ , perfectly two-dimensional systems show a square-root dispersion, while in the three-dimensional case, the dispersion is quadratic (Raether, 1980; Nagao et al., 2001; Liu et al., 2008). We analyse the plasmon dispersion for small, finite nonzero momentum transfers of up to around 0.25 Å<sup>-1</sup>. With this momentum range, we avoid problems with the subtraction of the very dominant ZLP for q = 0 and

with the  $1/q^2$  dependence of the EELS signal. The latter results in very low SNR at high q, which can only be compensated to a limited extend by longer exposure times. With longer exposure times, the 2D samples suffer electron-beam-induced damage and contamination, which will both alter the EELS signal.

Fig. 4 shows experimental MR-EELS data for few-layer MoS<sub>2</sub> for a thickness of 1–4 layers. From the raw  $\omega$ -q data [cf. Fig. 4(a)], we extracted individual MR-EELS signals via vertical line scans over a small momentum range  $\Delta q_r$ , as indicated by the red dashed frame. In Fig. 4(b), the resulting spectra are exemplarily shown for a momentum transfer of q = 0.06 Å<sup>-1</sup>, with solid black, red, blue, and orange curves for 1–4 L, respectively. The  $\pi$  and  $\pi + \sigma$  peaks are labelled and the shifts of the peak positions for different layers are indicated by arrows. Fig. 4(c, d) show the extracted peak dispersion for momentum transfers up to 0.15  ${\rm \AA}^{\text{-}1}$ ( $\Gamma$ M direction), where the spectra could still be obtained with reasonable signal-to-noise ratio (SNR). The results show clearly that both the  $\pi$  and  $\pi+\sigma$  peak shift to higher energies with increasing number of layers and increasing momentum transfer. Square-root fits (solid lines) show the general course of the  $\pi$  and  $\pi + \sigma$  peak dispersions, with the largest energy differences for 1-4 L occurring at the highest recorded momentum transfers. As demonstrated in SI Fig. S9, these differences will decrease again for very high momentum transfers q, which makes spectra for intermediate q the ideal choice for MoS<sub>2</sub> thickness measurements by MR-EELS.

In analogy to Fig. 4, MR-EELS data for 1–4 layers of MoTe<sub>2</sub> are displayed in Fig. 5. With MoTe<sub>2</sub> being a stronger scatterer than MoS<sub>2</sub>, we were still able to record the  $\pi \pm_1 \sigma$  peak dispersion of MoTe<sub>2</sub> with very good SNR up to q = 0.25 Å<sup>-1</sup>. In contrast to MoS<sub>2</sub>, however, the extracted peak dispersions in Fig. 5(c, d) do not match the expected square-root behaviour, which becomes more pronounced for larger q values and higher number of layers, see SI Fig. S10 - S11. Moreover, across the whole range of momentum transfers, 2 and 3 layers of MoTe<sub>2</sub> have very similar peak positions, which makes MoTe<sub>2</sub> thickness measurements by MR-EELS very challenging. While the  $\pi + \sigma$  peaks are far enough apart for q = 0.11 to 0.13 Å<sup>-1</sup>, the differences between 1 and 4 L decrease very quickly for higher momentum transfers. The peak posi-

tions already converge for around  $q = 0.2 \text{ Å}^{-1}$ , where they become indistinguishable from the peak positions in thick flakes (number of layers larger than 18) of MoTe<sub>2</sub> (maroon curve). For the discrimination between thin (1–4 L) and thick flakes of MoTe<sub>2</sub>, however, our data clearly demonstrates that MR-EELS data should be recorded for the smallest possible q, where the spectra for few-layer MoTe<sub>2</sub> can be easily distinguished from a bulk material with its nearly flat dispersion in the optical limit  $q \rightarrow 0$  (Raether, 1980; Egri, 1985). Eventually, the discrepancy from the square-root behaviour in the optical limit of the dispersion of the  $\pi + \sigma$  peak for higher number of layers in MoTe<sub>2</sub> indicates the transition from the two-dimensional towards the three-dimensional



**Fig. 4.** Momentum-resolved EELS data for freestanding MoS<sub>2</sub> with 1–4 layers. (a) Experimentally obtained  $\omega$ -q map (4 L) with indicated energy axis  $E = \hbar \omega$  and momentum axis  $q_x$ . (b) Extracted EELS signal from the red framed area in (a) for  $q = 0.06 \text{ Å}^{-1}$ . (c, d) Dispersions of the  $\pi$  and  $\pi + \sigma$  peaks for the individual 1–4 L. The error bars mark the uncertainties from the finite momentum resolution and from the determination of the peak positions, respectively. Square-root fits to the data points are shown as solid curves.



**Fig. 5.** Momentum-resolved EELS data for freestanding MoTe<sub>2</sub> with 1–4 layers and for a thicker flake (>18 L). (a) Experimentally obtained  $\omega$ -q map (>18 L) with indicated energy axis  $E = \hbar \omega$  and momentum axis  $q_x$ . (b) Extracted EELS signal from the red framed area in (a) for q = 0.09 Å<sup>-1</sup>. (c, d) Dispersions of the  $\pi$  and  $\pi + \sigma$  peaks, as determined from the maxima in blurred spectra (filled circles). The general course of the dispersions is illustrated by smoothed curves (open circles and connecting lines), using a Savitzky-Golay filter with linear fits over windows of 3 data points.

case.

Regarding the reliability of the results by MR-EELS, it has to be noted that contamination of the 2D layers can alter the measured dispersions significantly, as demonstrated in SI Fig. S12 for MoTe<sub>2</sub>. Unless the cleanliness is assessed by a different TEM method such as HRTEM imaging, MR-EELS measurements from a single sample position or thickness will not provide sufficient information for a reliable thickness measurement. From our experience, this is a problem especially for MoTe<sub>2</sub>, which is known to be more prone to oxidation and contamination (Mirabelli et al., 2016). Nevertheless, the cleanliness of the sample can be improved by careful annealing (Lin et al., 2012; Tripathi et al., 2017) or mechanical cleaning (Kim and Kim, 2020; Schweizer et al., 2020) in vacuum.

## 3.4. 3D ED

A decrease of the crystal's size in one direction in direct space causes an elongation of the reflections in the corresponding direction in reciprocal space. In the extreme of 2D materials a continuous intensity distribution along the reflection rows – so-called *relrods* – are formed. In normal incidence, an electron diffraction pattern of a 2D crystal consists of discrete Bragg spots corresponding to the [0001] orientation of the bulk crystal structure [Fig. 6(a)]. Orthogonal to this plane (Fig. 6(a)), continuous relrods are formed (Fig. 6(b)). For the relrods notation we will follow the nomenclature proposed by (Gorelik et al., 2021b).

Note that the relrods are not thin lines but have a complex shape and appear broader at higher *L*, best seen for the 10*L* rod [Fig. 6(b)]. This effect is associated with the intrinsic waviness of free-standing 2D materials (Meyer et al., 2007a, 2007b; Brivio et al., 2011). The effective broadening of reflections at high tilt positions makes the classical crystallographic box integration with a fixed box size unreliable. We therefore decided to use the maximal value of the peak intensity instead. The data were collected in continuous rotation mode, thus each value for the peak intensity is a physical integration over a small wedge with a width of the effective tilt increment. We are aware that the present geometry of the data collection may lead to an overemphasis of the intensity for reflections with smaller *q* over those with larger *q*. However, we keep this point open, leaving the discussion on the quantitative interpretation of the intensities for future studies.

The main finding of our previous study on 3D ED of 1–4 layered hexagonal MoS<sub>2</sub> (Gorelik et al., 2021b) was that crystals consisting of an odd number of layers have Laue class 6/mmm, while crystals with an even number of layers have Laue class  $\overline{3}m1$ . The most prominent difference between these two Laue classes is the presence (6/mmm) or absence ( $\overline{3}m1$ ) of a mirror plane within the L = 0 plane.

Three types of relrods were analysed in this work — 10L, 11L, and 20L (Fig. 6(a)). In order to evaluate difference in diffraction data, intensities distribution along the selected relrods were calculated

(kinematic scattering) for MoS<sub>2</sub> and MoTe<sub>2</sub> for 1–8 layers (simulated data for 1–4 layers of MoS<sub>2</sub> were already presented in (Gorelik et al., 2021b)). The results are summarized in Figs. 7 and 8. Different distance between single atomic planes 3.173 Å between two sulphur layers, and 3.491 Å between tellurium layers (in monolayer MoS<sub>2</sub> and MoTe<sub>2</sub>, respectively) and different scattering factors of corresponding atomic species lead to slightly different intensities distribution along the relrods. Therefore, the two strongest peaks of the 10*L* relrod of a MoS<sub>2</sub> monolayer (at 0.3 Å<sup>-1</sup>, see Fig. 7(a), red plot) move closer to the centre for MoTe<sub>2</sub> (Fig. 8(a), red plot). The intensity of the central peak at *L* = 0, for MoTe<sub>2</sub> (Fig. 7(b), red plot) is stronger than that of MoS<sub>2</sub> (Fig. 8(b), red plot).

The symmetry of the MoTe<sub>2</sub> relrods follows the same scheme that was established for MoS<sub>2</sub> crystals (Gorelik et al., 2021b): crystals with odd number of layers show relrods which are symmetric with respect to the base (L = 0), while crystals with even number of layers have asymmetric intensity distributions. An asymmetry in the relrods is clearly seen for bilayers (Fig. 7(b), 8(b)) and for 4-layers (Fig. 7(d), 8 (d)).

The differences between the relrods corresponding to different number of layers can be expressed by two quantitative factors: the *asymmetry* of the relrods regarding their base (L = 0) and the *characteristic width* of the intensity oscillations of the relrods. The asymmetry factor (*AF*) can be defined as following:

$$AF = var[I(L) - I(-L)]$$

Here, *var* stands for the variance, and I(L) stands for the intensity distribution along a relrod. For the analysis of the asymmetry factor, we used 10*L* relrods, as they are showing the most distinct differences. The characteristic width of the oscillations was measured as the full width at half maximum (FWHM) of the central peak (strong peak closest to L = 0) in 10*L* relrods. For monolayer MoS<sub>2</sub>, the central peak is not well defined. Here, we measured the FWHM of the peak at  $L = 0.3 \text{ Å}^{-1}$  instead.

The asymmetry factor plotted against the FWHM forms a *detectability map* for the number of layers (Fig. 9). Here, clearly separated points correspond to crystals that are likely to be distinguished from experimental data, whereas points nesting close to each other may be difficult or impossible to differentiate. As a result, MoS<sub>2</sub> and MoTe<sub>2</sub> crystals with thicknesses above 5 layers will practically show the same signature in 3D ED data, and therefore, cannot be identified.

Experimentally obtained 10*L* relrods for 1–4 layers  $MOTe_2$  are shown in Fig. 10. Fig. 10 (a) shows the overlay of the simulated and experimental relrods for monolayer  $MOTe_2$ . The overall intensity distribution is well reproduced. The widths of the peaks and their positions in the experimental profiles agree well with the simulations.

The intensity of neighbouring relrods 10L and 01L of monolayer MoTe<sub>2</sub>, although having the same shape, differ in their scale by approximately 20 %. Systematic difference in the intensities of

(a)

**Fig. 6.** Electron diffraction data of monolayer MoTe<sub>2</sub>: normal incidence zone pattern (a) and a section of the reconstructed reciprocal space, oriented orthogonal to the normal incidence plane and passing through 10*L*, 20*L*, and 30*L* relrods. In the normal incidence pattern (a), the symmetry-equivalent reflections (10 $\overline{1}$ , 01 $\overline{1}$ , etc.) are marked by dashed circles, the position of the section shown in (b) is marked by the red rectangular. In (b) the normal incidence direction is oriented vertically, the base plane with *L* = 0, roughly corresponding to the normal incidence pattern<sup>21</sup> is marked by a blue line.



Normal incidence

101L

30<u>3</u>L

2021

(b)

I = 0

202

112

022

101

011

Fig. 7. Kinematically simulated electron diffraction data for 10*L*, 11*L*, and 20*L* relrods, shown in red, green, and blue correspondingly, for MoS<sub>2</sub>: (a) monolayer, (b) bilayer, (c) 3-layer, (d) 4-layer, (e) 5-layer, (g) 7-layer, (h) 8-layer.

neighbouring relrods was already observed for monolayer MoS<sub>2</sub> (Gorelik et al., 2021b) and is associated with the dynamical scattering of non-centrosymmetric structure (Deb et al., 2020). Interestingly, for MoTe<sub>2</sub> the shape of the neighbouring relrods is the same, but the scale is different. The following pair of neighbouring relrods — 11*L* and  $\overline{1}2L$ (Fig. S13), does not show any disagreement in the intensities, while the third pair – 20*L* and 02*L* (Fig. S13) again shows a significant difference at L = 0.

The difference in intensities of reflections within Friedel pairs can be used for identification of monolayers (Brivio et al., 2011; Deb et al., 2020). As we have observed, for MoTe<sub>2</sub> monolayer, intensities of symmetry equivalent reflections  $10\overline{1}$ ,  $01\overline{1}$ ,  $\overline{100}$ ,  $0\overline{11}$ ,  $1\overline{10}$ , should show systematic variation of about 20 %. This technique allows identification of a monolayer from a single normal incidence electron diffraction zone pattern. Yet, higher number of layers cannot be distinguished this way.

Fig. 10 (b) shows the overlay of the simulated and experimental relrods for bilayer MoTe<sub>2</sub>. The peaks' widths in the experimental and simulated data match quite well, also the positions of the peaks are well reproduced. The relative intensities of the peaks follow the general trend, yet disagree significantly for the first 10*L* rod (Fig. 10 (b)) at L = 0. Fig. 10 (c) presents the relrods for 3-layer MoTe<sub>2</sub>. The intensity distribution is symmetric, the peaks' widths fit well. For 10*L* and 11*L* rods (Fig. S15), the experimental intensity at L = 0 is underestimated. The data for 4-layer MoTe<sub>2</sub> is shown in Fig. 10 (d). The relrods are asymmetric, as expected from the number of layers, the best fit is achieved for the 20*L* rod (Fig. S16).

For all crystals, with number of layers ranging from 1 to 4, we systematically observed a deviation of the experimentally measured plots from the simulated data. For a monolayer, in the simulated profile of 10*L* relrod the peak at L = 0 is significantly lower than those at L = 0.27 Å<sup>-1</sup>, in the experimental data the peaks have roughly the same intensity



Fig. 8. Kinematically simulated electron diffraction data for 10*L*, 11*L*, and 20*L* relrods, shown in red, green, and blue correspondingly, for MoTe<sub>2</sub>: (a) monolayer, (b) bilayer, (c) 3-layer, (d) 4-layer, (e) 5-layer, (f) 6-layer, (g) 7-layer, (h) 8-layer.



Fig. 9. Detectability map calculated for  $MoS_2$  and  $MoTe_2$  crystals with different number of layers (1–8) from 3D ED data: asymmetry factor vs. characteristic FWHM of relrods oscillations. The map is based on simulated 3D ED data.

(Fig. 10 (a)). For thicker crystals with 2-4 layers, the intensity of the

central peak at L = 0 measured experimentally is underestimated.

For a monolayer, the overestimation of the peak at L = 0 can be explained by significant layer corrugation. The angular spread of orientations of different parts of a crystal result in the broadening of relrods at higher *L*, leaving less scattered intensity in the centre of the rod, where it is measured.

<sup>&</sup>lt;sup>2</sup> Strictly speaking, the normal incidence pattern is not equal to the base plane with L = 0. Depending on the radius of the Ewald sphere, the normal incidence zone deviates from the base plane, with relrods being cut at a certain height with  $L \neq 0$ .



**Fig. 10.** Experimental (scatter plots) and simulated (solid line) scattering intensity distribution profiles along the 10*L* relrods for a monolayer MoTe<sub>2</sub> (a), bilayer (b), 3-layer (c), and 4-layer (d). The experimental plots of bi-, 3- and 4-layered crystals are constructed from partial tilt sequences  $-60^{\circ}...0^{\circ}$  (circles) and  $0...60^{\circ}$  (stars).

The situation with thicker crystals is less clear. Scattering angles for electrons are very low, meaning that *q*-dependent deviation of intensities can hardly be explained by a Lorentz factor (Buerger and Klein, 1945). We leave these effects for further investigations and focus on two parameters quantifying the number of layers — the asymmetry factor and the characteristic oscillations width.

Analysis of simulated data (Fig. 9) showed that both for  $MoS_2$  and  $MoTe_2$  crystals with 1–4 layers should give clearly distinguishable signatures. Crystals consisting of 5-layers will likely produce patterns identical to thicker crystals or bulk material, and thus, cannot be identified. Experimental data of crystals consisting of 1–4 layers showed good agreement with the simulated data. Thus, in total, we can say that, despite spotted differences between the simulated and experimental intensity distribution along the relrods, the overall pattern is quite recognizable, and that the combination of the asymmetry factor and peak widths can serve as an unambiguous fingerprint for a  $MoTe_2$  crystal with a given number of layers in the range of 1–4.

In our experiments, we recorded a relatively large fraction of the reciprocal space within the tilt range of  $\pm 60^{\circ}$ . We demonstrated that the most remarkable differences in the relrods of crystals with different thickness appear relatively close to L = 0 (Fig. 10). In principle, the central part of the 10*L* relrod in the range of  $\pm 0.2 \text{ Å}^{-1}$  would be sufficient to assign the number of layers. This limits the required tilt range to  $\pm 30^{\circ}$ , meaning that when the expected profiles of the relrods are known, a short tilt sequence of minimum  $\pm 30^{\circ}$  of electron diffraction patterns will be sufficient to determine the number of layers. Furthermore, other occurring phases can be discriminated by 3D ED from the presented 2H TMDs, see SI Section 9 Figs. S17-S18.

## 4. Discussion

In the following, the observed HRTEM, (MR-)EELS and 3D ED signatures of hexagonal mono- and few-layer  $MoS_2$  and  $MoTe_2$  are

evaluated with respect to the identification of the number of layers. In particular, we review each technique regarding the assignable number of layers, unambiguity of the assignment, and required experimental and computational effort. We discuss the influence of sample contamination on the reliability of thickness determination, as well as the typical electron dose required for each technique.

In HRTEM at optimal imaging conditions, it is possible to unambiguously identify monolayers of both MoS<sub>2</sub> and MoTe<sub>2</sub>. They can be distinguished from 2 to 4 L either by the presence of chalcogen vacancies, or from the contrast between metal and chalcogen atom columns. However, starting from bilayers, the assignment becomes unreliable in both calculated and experimental images, as the much weaker contrast differences are below the noise level. Precise image calculations are crucial for the interpretation of the experimental data, which in turn require exact knowledge of the aberration coefficients during the acquisition of the images. In general, optimal HRTEM images of 2D materials can only be acquired from atomically clean sample regions, free of any contamination. This is particularly difficult for samples such as MoTe<sub>2</sub>, which are prone to oxidation. Of the three analyzed methods, HRTEM needs the highest electron doses, which causes severe beam damage.

The prospects of thickness measurements by TEM-EELS are first evaluated for the standard log-ratio method. While log-ratio thickness measurements show an overall increase in the relative thickness  $t/\lambda$  with the number of layers, the calculated values for the absolute sample thickness are incorrect and no direct assignment to a certain number of MoS<sub>2</sub> or MoTe<sub>2</sub> layers can be made. Log-ratio measurements can routinely be performed with very low experimental effort, but are unreliable mainly due to the large influence of sample contamination. In particular, we have observed strong variations in the log-ratio results for different sample positions on the same 2D flake. In principle,  $t/\lambda$  is a low-dose thickness measurement technique, if the signal is collected from large sample areas. However, this is hampered by the necessity to

measure only on very clean sample areas.

A more sensitive indication of sample thickness is given by momentum-resolved low-loss EELS, using the dispersions of the  $\pi$  and  $\pi + \sigma$  peaks. For both MoS<sub>2</sub> and MoTe<sub>2</sub>, there is a systematic change in the dispersions for 1-4 L, and the energy separation between the peak positions can be as large as several eV for intermediate momentum transfers of around  $q = 0.1 \text{ Å}^{-1}$ . However, a direct assignment of the momentum-resolved EELS data to a certain number of lavers is only possible with high experimental or computational effort, using reference measurements or simulations for each thickness. This adds to the fact that thickness determination by MR-EELS is a rather laborious technique. Eventually, just like the log-ratio method, the MR-EELS technique can also be strongly affected by contamination, so that a reliable thickness measurement at a single sample position is not possible. This again limits the thickness measurements to small clean sample areas and, due to the strong decrease of the MR-EELS signal with increasing momentum transfer q, requires a relatively high electron dose, promoting electron-beam-induced damage.

3D ED data for thin  $MoS_2$  and  $MoTe_2$  crystals showed only slight differences in the appearance of the relrods due to the difference in the atomic scattering factors, so that similar conclusions can be drawn in respect to the identification of the number of layers. A combination of symmetry of the relrods with the width of the oscillations allows to unambiguously assign the number of layers in  $MoS_2$  and  $MoTe_2$  crystals in the range of 1–4. Crystals with a higher number of layers appear too similar (see the detectability map, Fig. 9) and do not allow the assignment. In order to extend the analysis to other 2H TMDs, it would be sufficient to run simulation of electron diffraction intensities in order to estimate the oscillation's width (Fig. S19). The symmetry switch with increase of the number of layers would apply for all 2H TMDs.

Thus, 3D ED data seems to be the most reliable technique in respect to the identification of number of layers. However, the experiment based on acquisition of electron diffraction tilt series from the same sample area is a non-trivial task and requires a certain level of expertise. In addition, the data interpretation requires simulated reference data, bringing the technique to the same level of complexity as MR-EELS. Finally, electron diffraction data suffers much less from sample contamination, compared to high-resolution imaging and spectroscopic techniques and requires significantly much lower electron dose, and, therefore, is the least damaging technique. No beam damage effect was observed in 3D ED data even when multiple datasets were collected from the same sample area.

## 5. Conclusion

In this work, a systematic study of high-resolution TEM contrast, (momentum resolved) low-loss EELS signal and 3D electron diffraction was carried out for MoS<sub>2</sub> and MoTe<sub>2</sub> with different numbers of layers. For our investigation, we intentionally selected the two materials composed of light and heavy elements as representatives for twodimensional 2H TMDs. Before the TEM experiments, the number of layers for each TMD was determined using optical contrast correlated with AFM measurements. Signatures of different number of layers were observed and analysed in every TEM method for samples consisting of 1-4 layers. Eventually, the signatures present in MR-EELS and 3D ED can be used to unambiguously identify up to 4-layers, while in HRTEM imaging under optimal conditions, only monolayer could be clearly identified. Moreover, 3D ED is less affected by sample contamination and beam damage, and is therefore the most feasible method for thickness determination. Finally, the suggested 3D ED data collection and processing scheme can be used for the thickness determination of all 2H TMDs.

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## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.micron.2022.103303.

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