

## Core level spectroscopy of MoS<sub>2</sub>

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### Abstract

X-ray photoelectron spectroscopy has been used to study mineral molybdenite, MoS<sub>2</sub>. The fitted core level spectra of sulphur 2p and molybdenum 3d states reveal several photon energy sensitive components. The high binding energy component in both spectra is proposed to originate from the uppermost sulphur or molybdenum atoms of an S–Mo–S sandwich layer of the hexagonal structure, respectively. The other features are suggested to be caused by the edge structures formed during the sample cleavage. The edge facets have much stronger chemical properties than the basal planes and they are known as the active sites of MoS<sub>2</sub> when it is used as a catalyst. The spectral features and the effect of the structure of UHV cleaved MoS<sub>2</sub> on them are discussed.

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### 1. Introduction

Several studies of transition metal dichalcogenide semiconductor, molybdenum disulphide MoS<sub>2</sub> have been carried out during the past few decades. As a layered, anisotropic material it can be exploited in many areas of materials science. 2H–MoS<sub>2</sub> has a graphite like crystal structure where the layer of transition metal between two layers of chalcogen atoms form two-dimensional MoS<sub>2</sub> sheets which belong to the hexagonal space group (D<sub>3h</sub>). Locally six sulphur atoms are coordinated to one molybdenum atom comprising the trigonal prismatic structure. The bonds within these S–Mo–S units are strongly covalent. The two-dimensional sheets are stacked in such a way that the two sulphur atoms of the second MoS<sub>2</sub> layer are beneath the Mo atoms of the first layer. The interaction between these S–Mo–S sheets is due to Van der Waals potentials providing a natural cleavage plane of the crystal. The coordinatively saturated S atoms at the surface and

consequently, the absence of the suitable orbitals for bonding between the MoS<sub>2</sub> sandwiches [1] are the reason for the inertness of basal planes. According to Park et al. [2] neither surface reconstruction nor does relaxation occur in this crystal. The hexagonal structure where the S–Mo–S layers shear over each other in the direction of motion is the origin of good lubricating properties of molybdenum disulphide which has especially many possibilities among space technology [3]. Nanotechnology has become topical when more efficient lubricants than MoS<sub>2</sub> powder have been needed for both economic and environmental reasons. For instance, the lifetime and wear properties of MoS<sub>2</sub> nanoparticles [4], structure and stability of nanotubes [5] or synthesis of nanowires [6] have been studied. Also, calculations for structural models of fullerene-like MoS<sub>2</sub> systems, which have applications both as a lubricant and as a catalyst, have been presented [7]. MoS<sub>2</sub> works well as a catalyst. It has been used, for instance, in catalysis to get rid of sulphur and nitrogen derivatives. The metal–sulphur bond strengths and the ability of MoS<sub>2</sub> to interact with metal atoms [8] or metal containing clusters [9] are studied because of their effect on the catalytic activity. An ion bombardment has been shown to be an effective tool to

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increase the reactivity of the MoS<sub>2</sub> basal planes [10–13]. In addition to the XPS [10,11,13] and UPS [14] studies of MoS<sub>2</sub> other methods like XPD [2,8], STM [1] and TEM [15,16] have been used to characterize this material. Various studies have focused on the band structure [17,18] or valence band and electronic structure of MoS<sub>2</sub> from both, theoretical and experimental point of view [2,14,19–22]. Experimental studies of MoSe<sub>2</sub> and MoTe<sub>2</sub> core level spectra have been published recently [23,24].

## 2. Experimental

The experiments were carried out at the MAX II synchrotron radiation laboratory in Lund, Sweden using beamline I411 equipped with hemispherical electron energy analyzer (Scienta) and modified SX-700 monochromator with an adjustable exit slit. All the MoS<sub>2</sub> single crystals used in this study were in the form of natural mineral molybdenite and they originated from the Wolfram Camp Mines, Queensland, Australia. The pristine (0001) surface was generated by cleaving the sample in UHV conditions. Specimens A, B and C were cleaved by removing part of the sample in one piece with the scraping blade. To facilitate the cleaving procedure of fourth specimen, D, a piece of aluminium which had the same dimensions than the sample was glued on the surface. Then the aluminium and a layer of MoS<sub>2</sub> attached to the glue were removed by the same blade. The latter method was experimented in order to receive a smoother, less terraces and steps containing (0001) surface. The preparation chamber was connected to the analyzer chamber and the pressure stayed below  $6 \times 10^{-9}$  mbar during the sample cleavage, transport and experiments.

We measured the Mo 3d and S 2p spectra using different excitation energies ranging from 200 to 350 eV for sulphur and from 280 to 400 eV for molybdenum. The take-off angle between the photoelectrons and sample surface was the fixed to 45°. The binding energies were calibrated using Au 4f<sub>5/2</sub> peak and the Fermi level. All the experiments were carried out at room temperature. The contamination rate was confirmed by scanning the O 1s energy region. All the spectra were fitted using Voigt line shapes and Shirley's background removal. The energy resolution of the experiments was excellent and the full width at half maximum (FWHM) values of the spectra varied between 0.25 and 0.30 eV for specimens A, B and D and between 0.34 and 0.39 eV for specimen C, respectively. The FWHMs were assumed to be approximately the same for all the components used to fit S 2p or Mo 3d<sub>5/2</sub> spectra. The Lorentzian width was fixed to 0.09 eV. The energy resolution for the S 2p line at photon energies used in our experiments varies from 30 meV to less than 100 meV [25]. The spin-orbit splittings are 1.19 and 3.10 eV for S 2p and Mo 3d, respectively. The S 2s peak exists at the same binding energy area than the Mo 3d one but due to good resolution and thereby very narrow peaks it is clearly separated from Mo 3d<sub>5/2</sub> (Fig. 4a) and does not have to be taken into account in the fitting procedure of the latter one.

## 3. Results

We have cleaved and studied several natural MoS<sub>2</sub> crystals at the same beamline where no major changes have been made to the experimental system between the experiments. The sulphur 2p core level spectra of three studied specimens are shown in Figs. 1–3 and they cover the most surface and the bulk sensitive measurements of our experiments. By comparing these spectra the changes are easiest to detect. In the S 2p spectra three distinct doublets are resolved the most intense feature being at the highest binding energy with all the used surface sensitive excitation

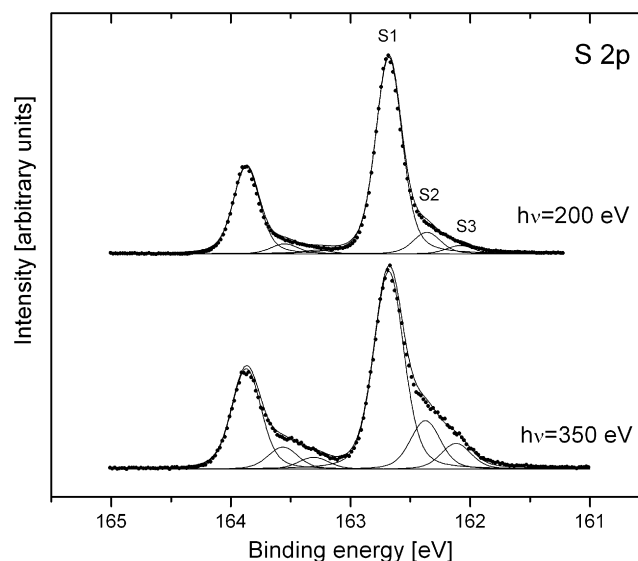


Fig. 1. The sulphur 2p core-level spectra of specimen A. The upper spectrum is the more surface sensitive one and the photon energies are shown on the right side of the spectra. The components are labeled with S1, S2 and S3 and they are explained in the text.

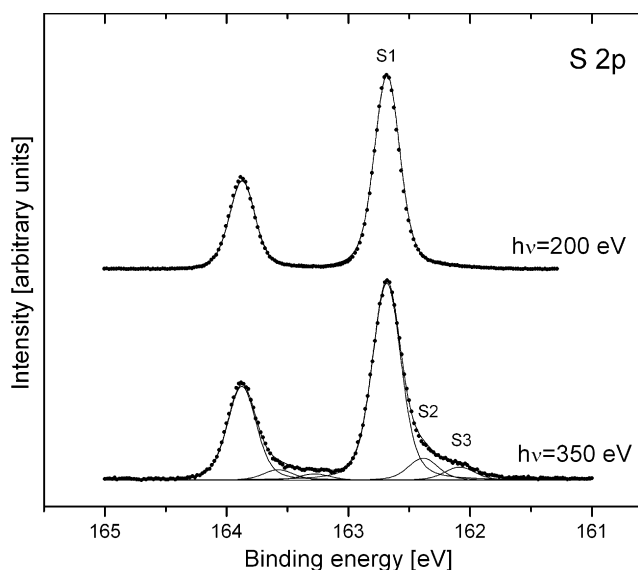


Fig. 2. S 2p spectra of specimen B.

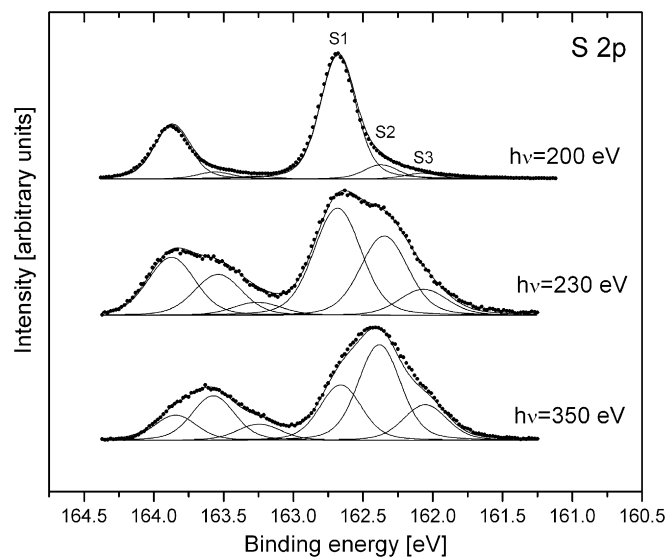
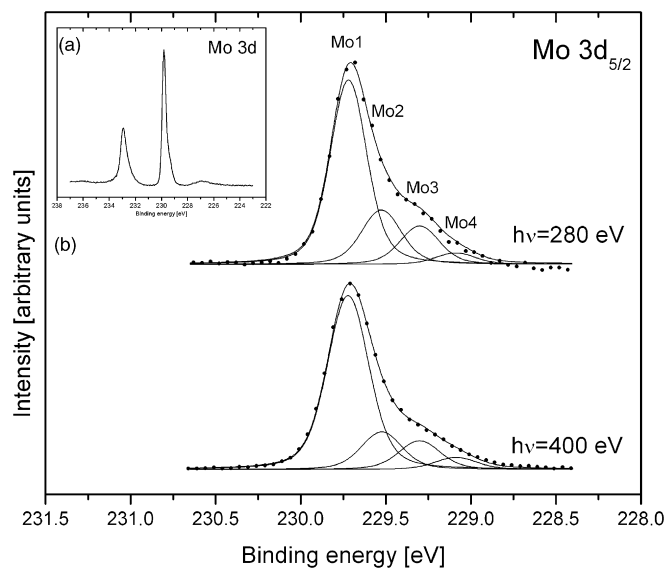
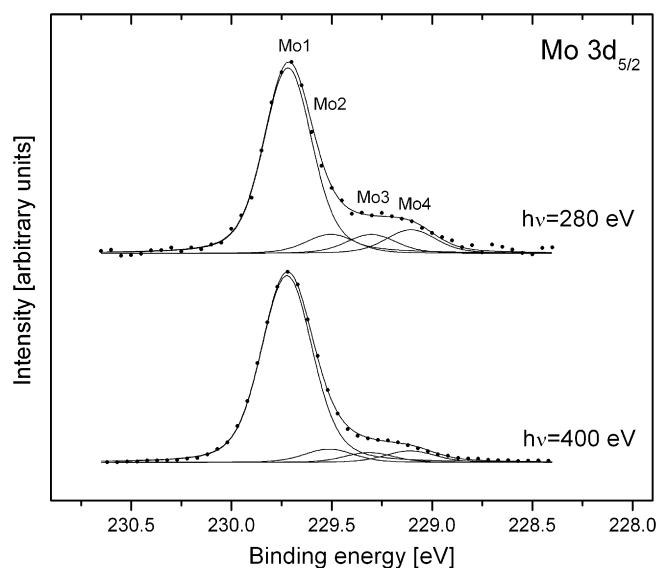


Fig. 3. S 2p spectra of specimen C.

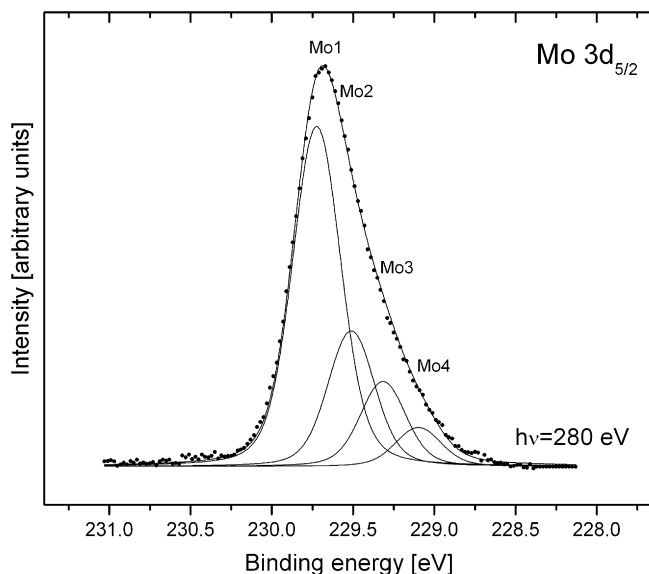
energies. The binding energy shifts of other components are presented as a comparison with the binding energy of this feature S1. The other features of the spectra are shifted towards lower binding energies approximately by 0.3 (S2) and 0.6 eV (S3). In the case of the sample whose spectra are shown in Fig. 2 these features do not appear until the highest photon energy has been used. In Fig. 1 the intensity of the  $-0.31$  and  $-0.58$  eV shifted components will be stronger as the photon energy increases. The intensity changes are very small for those photon energies that correspond to the smallest inelastic mean free path (IMFP) of the photoelectrons originating from the first S–Mo–S layer. When the excitation energy is raised to 350 eV the intensities change more drastically.

The experiments of the S 2p spectra presented in Fig. 3 have been carried out at different time than the experiments of specimens A and B. The measurements with sample C were the first ones of our MoS<sub>2</sub> studies. All the same components can be fitted to these spectra. For specimen C the S1 component at the highest binding energy is the most intense one when the photoelectron energy corresponds to the IMFP within the first S–Mo–S sandwich even though the intensity decreased considerably between photon energies of 200 and 230 eV. The relative intensities of the peaks in the most surface sensitive spectrum are very similar to those of sample A. When the excitation energy was raised to 350 eV the intensity of the S1 component still decreased. The intensities of components S2 and S3 increased in phase the strongest component with this photon energy being the former.

The Mo 3d<sub>5/2</sub> spectra presented in Figs. 4–6 correspond to the specimens whose S 2p spectra are shown in Figs. 1–3, respectively. In the case of Mo 3d the most intense component is at the highest binding energy of the spectrum. This signal is strongest considering all the photon energies we have used. The spectra are fitted using four doublets. The fitting procedure for Mo 3d<sub>5/2</sub> is presented here but the same doublet features fit also for Mo 3d<sub>3/2</sub>. Only the

Fig. 4. The molybdenum 3d (a) and 3d<sub>5/2</sub> (b) spectra of specimen A. The Mo 3d<sub>5/2</sub> spectra measured with 400 eV is part of the spectra in (a).Fig. 5. Mo 3d<sub>5/2</sub> spectra of specimen B.

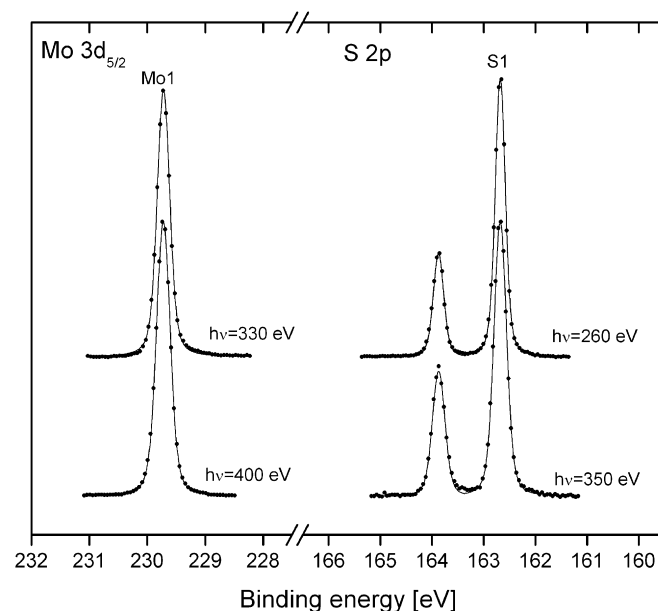
FWHM values are larger for the spin–orbit splitted high binding energy component which is expected to occur. The binding energy shifts relative to the high binding energy peak are about  $-0.2$ ,  $-0.4$  and  $-0.6$  eV. The intensity changes of the components are not very large but the tendency being that the relative intensity of the negatively shifted features decreases and the intensity of the high binding energy component increases as the photon energy will be larger. This is due to the bulk-like surroundings of all Mo atoms on the basal planes. When the photon energy increases the intensity of the bulk Mo atoms between the S atoms will be stronger at the expense of the intensity of the signal originating from the surface edge atoms. The binding energy shifts and relative intensities of the compo-

Fig. 6. Mo 3d<sub>5/2</sub> spectra of specimen C.

nents of S 2p and Mo 3d<sub>5/2</sub> spectra are presented in Tables 1 and 2.

Finally, we present the S 2p and Mo 3d<sub>5/2</sub> core-level spectra of fourth sample (Fig. 7) which was cleaved using the piece of aluminium glued on the sample. With all the photon energies we used only one doublet and no surface core level shifts were detected in the spectra.

The intensity changes between the comparable components of different specimens measured with the same excitation energies indicate that the detected surfaces somehow deviate from each other. Because of the weak Van der

Fig. 7. S 2p and Mo 3d<sub>5/2</sub> spectra of sample D, showing no additional surface features.

Waals forces between the S–Mo–S layers the inert (0001) basal plane is expected to be revealed in the cleavage process. However, there are always unknown concentration of defects and steps on the surface. Since the origin of the samples is the same and conditions at the moment of cleavage and experiments were comparable, we suggest that the structure of the cleaved surface has an effect on the shape of the spectra. In those areas where the steps and terraces exist the shift should appear. It is often shown that the more close-packed the surface is the smaller are the

Table 1

The binding energies (BE) and relative intensities of the components fitted in the S 2p spectra

Excitation energy (eV)	BE of S1 (±0.02 eV)/ relative intensity of S1 (±0.1%)	ΔBE of S2 (±0.02 eV)/ relative intensity of S2 (±0.1%)	ΔBE of S3 (±0.02 eV)/ relative intensity of S3 (±0.1%)
200 (specimen A)	162.68/86.2	−0.31/9.9	−0.59/3.9
350 (specimen A)	162.68/73.3	−0.31/17.4	−0.59/9.3
200 (specimen B)	162.68/100.0	–	–
350 (specimen B)	162.68/84.4	−0.30/9.7	−0.60/5.9
200 (specimen C)	162.68/86.0	−0.30/10.0	−0.60/4.0
230 (specimen C)	162.68/50.8	−0.32/37.0	−0.61/12.2
350 (specimen C)	162.68/29.1	−0.30/51.5	−0.60/19.4

The S1 feature corresponds to the high binding energy component and the components S2 and S3 shift towards lower binding energies.

Table 2

The binding energies (BE) and relative intensities of the components fitted in the Mo 3d<sub>5/2</sub> spectra

Excitation energy (eV)	BE of Mo1 (±0.02 eV)/ relative intensity of Mo1 (±0.1%)	ΔBE of Mo2 (±0.02 eV)/ relative intensity of Mo2 (±0.1%)	ΔBE of Mo3 (±0.02 eV)/ relative intensity of Mo3 (±0.1%)	ΔBE of Mo4 (±0.02 eV)/ relative intensity of Mo4 (±0.1%)
280 (specimen A)	229.72/62.5	−0.19/19.7	−0.42/13.7	−0.63/4.1
400 (specimen A)	229.72/69.3	−0.20/14.7	−0.42/11.3	−0.63/4.7
280 (specimen B)	229.72/74.5	−0.21/7.9	−0.41/7.8	−0.61/9.8
400 (specimen B)	229.72/84.7	−0.21/5.9	−0.41/4.3	−0.61/5.1
280 (specimen C)	229.72/57.7	−0.21/22.4	−0.41/13.6	−0.62/6.2

The Mo1 feature corresponds to the high binding energy component and the components Mo2, Mo3 and Mo4 shift towards lower binding energies.

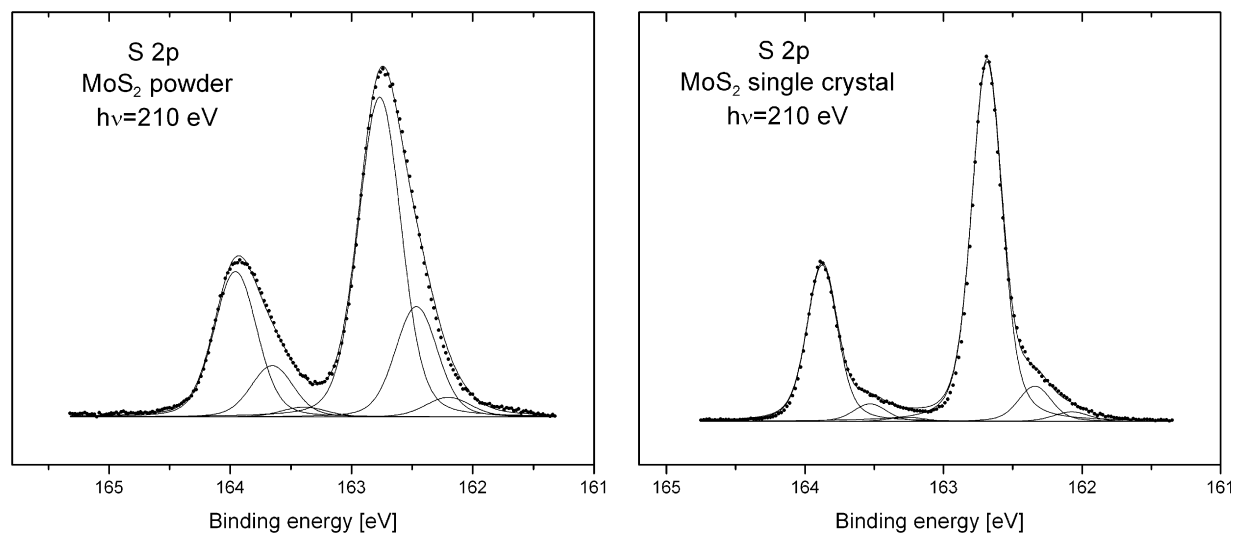


Fig. 8. Sulphur 2p spectra of MoS<sub>2</sub> powder (left side) and single crystal show that the same components can be fitted in both spectra. The binding energy shifts are approximately  $-0.3$  and  $-0.6$  eV relative to the high binding energy peak.

shifts between detected components in the spectra. The intensity changes of the components as a function of the photon energy can be contributed by the photoelectron diffraction, since the effect has been reported to occur for MoS<sub>2</sub> single crystals [2,8].

The core-level spectra of the powder MoS<sub>2</sub> had approximately the same shape than the corresponding spectra of the crystal samples. Both S 2p and Mo 3d spectra were possible to fit with the similar number of components on the low binding energy side than the comparable spectra of the single crystal. Only the peak widths were slightly larger for the powder specimen as can be seen in Fig. 8. Following S 2p FWHM values were detected: 0.42–0.44 eV for powder specimen and 0.28–0.30 eV for single crystal, respectively.

#### 4. Discussion

In all the surface sensitive spectra of S 2p and Mo 3d the most intense component was at the highest binding energy. In the case of sulphur, the signals of the negatively shifted components S2 and S3 increased as the experiment became more bulk sensitive. The situation with Mo 3d was the opposite. The intensities of Mo2, Mo3 and Mo4 decreased when the excitation energy increased. We suggest that signal S1 originates from the first S atom layer of S–Mo–S sandwich. The existence of other features (S2 and S3) with surface sensitive photon energies would reflect how the (0001) cleavage has occurred. The more intense components in the spectra, the more steps and terraces appear in the area where the photoelectrons are emitted from.

When comparing the spectra detected for samples A, B and C it can be seen that when there are more intense features on the low binding energy side of the S 2p spectra the intensity of the low binding energy side components of Mo 3d has also increased. For specimen A the intensities of components S2 and S3 are the smallest and so they are for Mo2, Mo3 and Mo4. The strongest S2, S3, Mo2,

Mo3 and Mo4 components have been detected in the measurements for specimen C. This tendency supports the idea that the more intense components on the low binding energy side of the spectra consist of the more step edges and terraces the analyzed area contains. The interpretation is also promoted by the core level spectra of sample D which was cleaved in a way that nearest small number of terraces and steps were formed on the surface. The sulphur and molybdenum spectra measured from that surface revealed only one doublet indicating that this experiment excludes the possibility for other components on the low binding energy side being due to signals from the second or third atom layer meaning that no surface core-level shifts for MoS<sub>2</sub> are seen.

In the case of molybdenum the signal Mo1 is supposed to be caused by the first Mo atom layer between the sulphur atoms. The surroundings of these atoms are similar in all sandwich layers but the situation changes when the atoms appear on the step edges. The catalytic activity of layered-structure MoS<sub>2</sub> is generally believed to depend on the step edges or defects on the surface [26–28]. The presence of coordinately unsaturated Mo and S sites have been shown to exist on the pristine basal surface of MoS<sub>2</sub> due to, for instance, the edge planes  $(\bar{1}010)$  (S-edge),  $(10\bar{1}0)$  (Mo-edge) and  $(1\bar{2}10)$  [29,30]. There are several theoretical studies based on DFT calculations focusing on the edge structures [26,29–31]. According to them the Mo-atom of the Mo-edge is not energetically stable because of its coordination to only four S atoms instead of six like in bulk structure. The edge facets have been observed to be much more catalytically active ones than the basal planes [23] and the surface energy of the edges is estimated to be about hundred times larger than it is for the (0001) planes [30]. The theoretical calculations of the reconstructions of the S–Mo–S sandwich edges seem to depend largely on the models [31,32]. Raybaud et al. [32] who have calculated the electronic structure of relaxed surface show that there

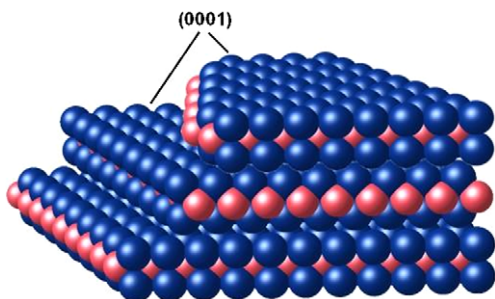


Fig. 9. An outline how the S–Mo–S steps and (0001) terraces could appear on the UHV cleaved hexagonal close-packed MoS<sub>2</sub>. The blue (dark) atoms correspond to the S atoms and red (lighter) ones to Mo atoms, respectively. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

are number of surface states on unsaturated S and Mo surface atoms. They also note that the difficulty of creating well-defined surface is an important reason why the experimental studies of structural and electronic properties of edges are so scarce. This uncertainty of the cleaving process is well elucidated in our work. A potential example of cleaved MoS<sub>2</sub> surface with (0001) terraces and S–Mo–S steps is presented in Fig. 9.

McIntyre et al. [13] have studied the effect of argon ion bombardment on the basal plane of MoS<sub>2</sub> using high resolution X-ray photoelectron spectroscopy. As a comparison with the air-cleaved surface the bombardment clearly had an effect on the spectra. For the Mo 3d spectrum one component on the low binding energy side appeared. However, the shift of the component identified to originate from MoS<sub>1-x</sub> species is larger than any of the shifts we measured. In the case of the S 2p spectra three new components were seen after bombardment. One of them, MoS<sub>2-x</sub>, is in the binding energy area where also we detected spectral features. Also, an XPS study of an ion-sputtered MoSe<sub>2</sub> single crystal surface, where the effect of sputtering was seen on the high binding energy side of the Mo 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks, has been presented [23].

Photoemission studies of a highly oriented pyrolytic graphite by Balasubramanian et al. [33] reveal two carbon 1s components separated by 120 meV binding energy. They presented that the high binding energy component is due to atoms in the surface layer and the other ones to deeper layers. Core level studies published for beryllium (0001) also present signals originating from the few uppermost atom layers on the surface. Bulk signal and three surface shifted components have been experimentally [34] and theoretically [35] shown to exist in beryllium 1s photoemission spectra. The surface sensitive components are interpreted to originate from the first, second and third Be layers.

The intensity changes between the bulk and surface signals for Be 1s and graphite C 1s spectra are more obvious and they can be seen within smaller photon energy changes than in the case of MoS<sub>2</sub>. The changes between the MoS<sub>2</sub> spectra measured with photon energies 200 and 230 eV for S 2p and 280 and 300 eV for Mo 3d, respectively are

very minor at least for specimens A and B. We suppose that fairly small intensity changes in all the detected spectra and the lack of spectral structures caused by second or lower atom layers largely result from the structure of MoS<sub>2</sub>. The distance between the sulphur layers is 0.316 nm and for molybdenum it is even larger, 0.616 nm [12]. Fleischauer et al. [12] have estimated the escape depths for the emitted photoelectrons using the formula presented by Tanuma et al. [36]. They evaluated that the signal with kinetic energy of 40–60 eV originates from the uppermost S–Mo–S sandwich. The IMFP would be comparable to the depth of the second sandwich layer if the kinetic energy of the photoelectron is approximately 225 eV. However, it has been shown that the elastic-scattering effects can contribute to the signal intensities in certain emission directions [37,38], suggesting that the actual signal depth would slightly differ from the results by Fleischauer et al. [12].

The intensity changes of the low binding energy components of specimen C S 2p spectra are larger than the changes of other specimens. In addition, the intensities change more considerably between the photon energies 200 and 230 eV than between energies 230 and 350 eV. We believe that the most important reason to this is the photoelectron diffraction. The XPS spectra of MoS<sub>2</sub> powder specimen (Fig. 8) consist of components similar to the single crystal spectra but the intensity changes are not so strong and thus the fact that photoelectron diffraction can not be detected for polycrystals supports the interpretation. The study of the powder sample shows that the diffraction does not have an effect on the number of the components of the spectra but it can affect the intensities of the components as a function of photon energy. Between photon energies 210 and 350 eV, the relative intensity changes for S1 and S2 components of the S 2p spectra of powder sample are following: from 69.5% to 64.4% for S1 and from 25.7% to 32.2% for S2. The relative intensity of the component S3 changes only approximately 1% between the mentioned photon energies. The same kind of phenomena was detected also for galena PbS (100) surface [39]. The effect was not so strong which could be explained by the different crystal structures of PbS and MoS<sub>2</sub>.

In the following part, we consider some other possible structural properties of the pristine, UHV cleaved MoS<sub>2</sub> surface in addition to the steps and terraces that could contribute to the shape of the core level spectra. As a result of cleaving the sample stacking faults can appear to the layers close to the pristine surface. Shiojiri et al. [16] have reported three different kinds of dislocations. Two of those are given rise by the Mo/S or S/S glides. The formation of third kind of stacking fault is more complicated than a simple slipping. Takahashi et al. [15,40] have observed the hcp stacking order of MoS<sub>2</sub> to transform into the rhombohedral or fcc order in the region just above the slip plane. The rhombohedral order is shown to extend to three S–Mo–S layers. On the surface of graphite sheets, which have the same kind of hexagonal structure than MoS<sub>2</sub>, it has been reported folds of one or two layers. Folding has

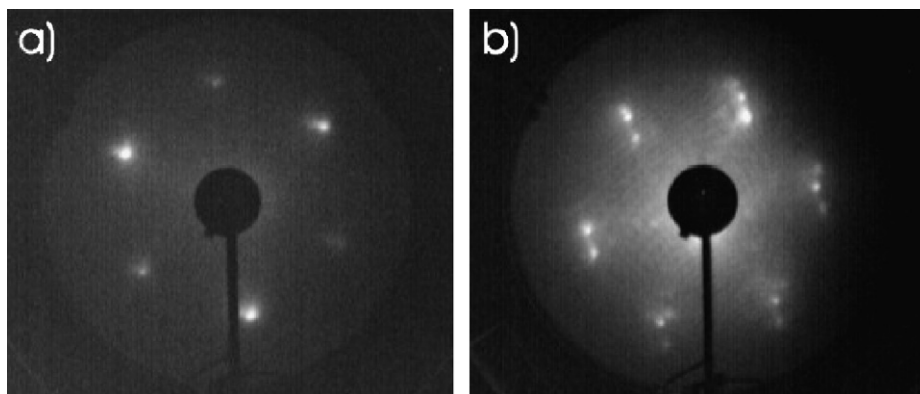


Fig. 10. LEED patterns of UHV cleaved MoS<sub>2</sub> (0001) surfaces. Pattern (a) was received from the surface which contains less steps and terraces than surface shown by pattern (b). The electron energy is 90 eV in both cases.

been detected near to the step edges. It has occurred spontaneously during the sample cleaving [41,42].

We have performed also LEED studies on the UHV cleaved pristine MoS<sub>2</sub> surface. The pattern is detected from the hexagonal surface but there are some reflections from the same spot. The stepped surfaces are well-known to produce spot-splitting in the LEED pattern. Streaking of spots is caused by irregularly stepped surfaces. The LEED patterns of (0001) surfaces of specimens, being cleaved using different ways, are shown in Fig. 10. The p(1 × 1) pattern (b) was obtained from the crystal which was cleaved using only the scraping blade (comparable to the way samples A–C were cleaved) and pattern (a) was detected from the sample which was cleaved using a piece of aluminium glued on the sample (sample D). Consequently, these LEED patterns still confirm our explanation concerning the core level spectra of MoS<sub>2</sub>.

## 5. Conclusions

Only a few core level spectra of molybdenum disulphide have been presented during over the decades of studying MoS<sub>2</sub>. In the presented sulphur and molybdenum photoemission spectra several components were detected. For samples A–C the S 2p spectra consisted of three and Mo 3d of four doublets, respectively. Due to the S–Mo–S layered structure the photon energy dependent changes were more easily observed in the S 2p spectra where the strongest contribution to the surface sensitive spectra was caused by the first sulphur atom layer of the basal plane. We suggest that the high binding energy feature in all the fitted S 2p and Mo 3d spectra originates from the uppermost sulphur and molybdenum atom layer, respectively. The negatively shifted components and the differences between the spectra presented in Figs. 1–6 can be explained to be caused by the steps and terraces formed on the surface during the cleavage process.

The existence of usual surface core level shifted components is excluded by analyzing the core-level spectra of sample D. Only one doublet can be resolved in all the

S 2p and Mo 3d spectra. These doublets are most likely caused by the uppermost S and bulk Mo atoms of the layered S–Mo–S structure.

To be catalytically useful, the surface has to contain active atom sites. In studies of MoS<sub>2</sub> it is often mentioned that some physical or chemical treatment is needed to get a reactive surface. However, our study points out that the active sites can also appear on untreated, UHV cleaved surfaces. Thus the high resolution core level spectroscopy works as a promising tool to observe the possible catalytic activity. The LEED pattern is able to show the catalytically active stepped surface of single crystals but the XPS can also be used for revealing the same thing in the case of polycrystalline samples.

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