The study of electronic structure of molybdenum and tungsten trisulfides and their lithium intercalates by x-ray electron and x-ray emission and absorption spectroscopy

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The distribution of electron density in cathode materials MoS_3 and WS_3 during their lithiation has been studied by X-ray electron and X-ray emission and absorption spectroscopies. It is demonstrated that the lithium electrons localize both on metal and on sulfur atoms but mainly on disulfide atoms. Presence of a complementary bond of donor-acceptor nature has been proposed. On a basis of this assumption and X-ray emission spectra the electron structure of MoS_3 has been suggested.

1. Introduction

Intercalation of transition metals trichalcogenides with alkali-metals [1-2] is a well reversible reaction that allows to use these materials to set up high-energy-density and high-cyclereversibility alkali metal battery [3-4]. In the cycle of "charge-discharge" the transition metal trichalcogenides act as the reservoir for the alkali metals electrons. It is of interest to study the distribution of electron density and the change of electronic structure under intercalating of these materials. The results can be useful for the search of promising materials for constructing of highenergy-density current sources.

In our previous work [5,6] electronic structure of trisulfides and triselenides of niobium and their lithium intercalates has been studied. It is shown that during lithiation of these materials the lithium electron density is distributed largely on chalcogen atoms (in great part on atoms of dichalcogenide pair) and partially on metal atoms. In starting niobium trichalcogenides the charge non-equivalency of the chalcogen atoms is observed that is described by ionic formula $Nb^{+4}X^{-2}(X_2)^{-2}$. At a higher degree of lithiation these chalcogen atoms become equivalent.

In contrast to previously studied niobium trichalcogenides the trisulfides of molybdenum and tungsten are amorphous [7]. Until the present time the electronic structure of these materials has been poorly understood. The local structure of MoS_3 and WS_3 has been studied by RDF, EXAFS and XPS [8-10]. The chain (quasi-one-dimensional) model of the structure described by ionic formula $M_2^{+5}(X^{-2})_4(X_2)^{-2}$ has been suggested. The fragment of the proposed MoS_3 structure is displayed in Fig. 1. Metal atoms in MoS_3 are placed along metallic chain at different distances, respectively, 2.75 Å and 3.16 Å from each other. Closely-spaced metal atoms are bound by three bridging sulfur atoms which are in S^{-2} state and form equilateral triangle which is normal to metallic chain. Average M-S distance is 2.44Å. The molybdenum and tungsten trisulfides are diamagnetic semiconductors $(R = 3 \times 10^3 \Omega \times cm)$. No metal pairing are observed in the structure of WS_3 . Average M - M and M - S distance are 2.75 Å and 2.41 A, respectively.

The aim of the present work is to study the distribution of electron density and the change of electron structure of MoS_3 and WS_3 cathode materials during their lithiation.



Figure 1: The fragment of local structure of amorphous MoS_3 [7-9]. -molybdenum, \bigcirc -sulfur

2. Experimental section

Trisulfides of molybdenum and tungsten were prepared from corresponding tetrathiometallates ammonia by decomposition in vacuum by heating to $T = 250^{\circ}C$. The starting tetrathiometallates were obtained according to reported methods [11]. Hexane butyllithium solution was obtained from metallic lithium and n-butylchloride [12]. The concentration of n-butyllithium in solution was determined by direct titration of 0.1N hydrochloric acid from hexane solution of n-butyllithium with phenolphthalein. By interaction of corresponding trisulfides with solution of n-butyllithium, the phases of the following composition 1) $Li_{0.96}MoS_3$, $Li_{1.60}MoS_3$, $Li_{2.00}MoS_3$, 2) $Li_{0.85}WS_3$, $Li_{1.13}WS_3$, $Li_{1.76}WS_3$ were obtained.

Reaction was conducted in sealed evacuated silica ampoules at the room temperature for 7 days. The technique of isolation of intercalation products is described in detail in [13]. The composition of lithium in synthesized samples was determined by flame photometry. The obtained samples were amorphous on evidence derived from XRD analysis.

X-ray electron spectra of core levels of metal and sulfur and valence bands of trisulfides of molybdenum and tungsten and their lithium intercalates have been obtained on VG Microtech spectrometer (CLAM-100 analyzer). The samples for investigation were kept in evacuated silica ampoules. The ampoules were opened before experiment in dry nitrogen atmosphere, pressed in tablets and loaded into vacuum chamber. Argon ion etching of the samples was carried out at 3 kV, 20 mA for 3-5 min. The spectra were recorded at 20 eV pass energy using MgK_{α} -irradiation at 300 W. Calibration of energy was performed from hydrocarbon adsorption peak (C 1s=285.0 eV). Data processing and curve fitting was carried out using standard VG software.

X-ray emission spectra $MoL_{\beta2,15}$ and SK_{β} and MoL_3 - and SK- absorption edge in these samples have been obtained on X-ray fluorescent spectrometer "Stearat" using crystal-analyzer quartz (2d=6.67 Å), focused by Iogann (R=500 mm). Spectra were recorded using X-ray copper anode and proportional flow counter. Spectral resolution is ~0.5 eV.

3. Results

With the aim of studying the distribution of the electron density and the electronic structure of molybdenum and tungsten trisulfides during their lithiation X-ray electron spectra of Mo3d, W4f, S2p-core levels and valence band in starting and lithiated molybdenum and tungsten trisulfides and X-ray emission $MoL_{\theta 2.15}$ - and SK_{θ} spectra and MoL₃ and SK-absorption edge spectra in starting and lithiated molybdenum trisulfides were recorded. X-ray electron spectra of Mo3d and W4f-core levels in starting and lithiated MoS_3 and WS_3 are shown in Fig. 2. In spectra of lithiated MoS_3 and WS_3 the Mo3dand W4f doublets are shifted to the lower binding energy. In spectra of lithiated MoS_3 and WS_3 another doublet of lesser intensity is observed. The binding energy of this doublet corresponds to Mo(VI). This doublet can be connected with molybdenum oxides, MoO_3 , on a sample surface. However, successive increasing of the doublet intensity in lithiated samples allows to propose that the occurrence of the Mo(VI) state is the peculiarity of lithiation of MoS_3 . The similar situation is observed in lithiated WS_3 . However, in this case additional doublet arises even in starting WS_3 . Binding energies and relative intensities of these doublets are shown in Table 1.



Figure 2: Mo3d and W4f X-Ray electron spectra of starting and lithiated MoS_3 and WS_3 . a) $Li_x MoS_3$, x: 1. 0.2; 2. 0.97; 3. 1.60; 4. 2.00 b) $Li_x WS_3$, x: 1. 0.2; 2. 0.85; 3. 1.13; 4. 1.76

X-ray electron spectra of S2p-levels in starting and lithiated MoS_3 and WS_3 are shown in Fig. 3.

These spectra are the superposition of two $S2p_{3/2,1/2}$ doublets. The doublet at lower binding energy and that of higher binding energy correspond, respectively, to a bridging ions S^{-2} and to atoms of disulfide pair, $(S - S)^{-2}$. Ratio of intensities of these doublets corresponds to ratio of number of disulfide atoms to that of the S^{-2} ions (1:2 for starting MoS_3 and WS_3). Binding energy of the S^{-2} ions doublet shifts to lower energy. Binding energy of the disulfide pair doublet in addition shifts to that of the S^{-2} ions doublet and its intensity decreases. Binding energies and

Table 1.

Binding energies of $Mo3d_{5/2}$, $W4f_{7/2}$, $S2p_{3/2}$ and relative intensities of doublets for $Li_x MoS_3$ and $Li_x WS_3$

	M 03d5/2			S2p3/2		
x	$\overline{E_1^b}$	E_2^b	I_2/I_1	E ^b ₁	E_2^{\bullet}	I_2/I_1
0	229.4	-	-	162.7	163.7	.47
0 .96	228.9	234.0	.05	162.0	163.0	.23
1.60	228.6	232.8	.30	161.6	162.3	.20
2.00	228.6	23 2.8	.32	161.5	162.2	.20
	W4f7/2			S2p3/2		
x	$\overline{E_1^{b}}$	E_2^{\flat}	I_2/I_1	E_1^{\flat}	E_2°	I_2/I_1
0	33.3	35.5	.50	162.3	163.7	.67
0. 2	32.6	34 .8	.68	16 1.5	1 62.3	.39
0.85	32.3	34.3	.90	161.2	1 62. 0	.43
1.76	32.3	33 .6	1.31	164.4		

relative intensities of these doublets are shown in Table 1.

X-ray electron spectra of the valence band of starting and lithiated MoS_3 and WS_3 are shown in Fig. 4.

The changes observed in the spectra of lithiated MoS_3 and WS_3 reflect those of density of the electron state in valence band. In lithiated MoS_3 and WS_3 the density of states increases near Fermi level. The deeper part of band reflects states corresponding to M - S bonds. The sulfur 3s-states fill region of 13-16 eV. Splitting of S 3s-states into three subbands corresponds to σ binding and σ^* antibinding energy levels of disulfide and non-binding 3s- states of S^{-2} ion.

X-ray emission SK_{β} - and $MoL_{\beta2,1\delta}$ -spectra, SK- and MoL_3 -absorption edge spectra and Xray electron spectra of valence band in starting and lithiated MoS_3 are represented in Fig. 5 on energy scale relative to Fermi level.

Emission spectra SK_{β} (transition 3p-1s) reflect the contribution of sulfur 3p-electrons to the density of states in valence band. SK_{β} -spectra of starting and lithiated MoS_3 occupy a wide energy region (7-8 eV). The pronounced peculiarities of spectrum shape are not observed except the peak at the bottom of the band. In lithiated samples the width of SK_{β} -spectrum is decreased because of the shift of the bottom of the band and peak at 5 eV shifts consistently to upper part of the band. Contribution of disulfide atoms (S - S)



Figure 3: X-Ray electron spectra of S2p-level in starting and lithiated MoS_3 and WS_3 . a) $Li_x MoS_3$, x: 1. 0.2; 2. 0.97; 3. 1.60; 4. 2.00 b) $Li_x WS_3$, x: 1. 0.2; 2. 0.85; 3. 1.13; 4. 1.76

to SK_{β} -spectrum (33% in MoS_3) is displaced 1.1 eV to lower energy, for aligning to Fermi level was carried out relatively to $3p_{3/2}$ -peak of sulfur atoms in S^{-2} state.

Emission spectra $MoL_{\beta^2,16}$ (transition $4d - 2p_{3/2}$) show the contribution of 4d and 5s electrons of metal to the density of states in valence band. Spectrum of metal states in valence band also occupies wide energy region (9-10 eV) and has pronounced peculiarities. Comparison of valence band spectra and emission spectra of sulfur and molybdenum allows to distinguish four characteristic peculiarities (in Fig. 5 marked as A,B,C,D) that can be related to different MO. In lithiated samples a contribution of Mo atoms to



Figure 4: The valence band X-Ray electron spectra of starting and lithiated MoS_3 and WS_3 . a) Li_xMoS_3 , x: 1. 0.2; 2. 0.97; 3. 1.60; 4. 2.00 b) Li_xWS_3 , x: 1. 0.2; 2. 0.85; 3. 1.13; 4. 1.76

the density of states of bands corresponding to these MO is essentially changed.

SK- and MoL_3 -absorption edge spectra show contribution of sulfur and molybdenum atoms to the density states above Fermi level. In spectra of lithiated samples a series of typical changes are observed.

4. Discussion

4.1. Charge state of atoms in MoS_3 and WS_3

The obtained results demonstrate that the intercalation of molybdenum and tungsten trisul-



Figure 5: $MoL_{\beta2,15}$ (solid line on the left) and SK_{β} X-Ray emission spectra (dashed line on the left), MoL_3 (solid line on the right) and SK-edge absorption spectra (dashed line on the right) and XPS of valence band (dotted line) of starting and lithiated MoS_3 . a) MoS_3 , b) $Li_{0.97}MoS_3$, c) $Li_{1.60}MoS_3$, d) $Li_{2.00}MoS_3$.

fides with lithium essentially changes the electronic structure of these compounds. First of all, we observe the change of core level energies of sulfur and molybdenum displayed in Table 1. The change of core level energy of an atom can be caused by three factors: the change of charge state of atom, the change of crystalline potential in the vicinity of core atom resulted from change of chemical environment, and the change of Fermi level position. During intercalation in MoS_3 and WS_3 the lithium ions occupy the cen-

ter of van der Waals cavities measured ~6- 7Å and the impact of lithium ions on potential in the vicinity of metal chain atoms and its ligands can be considered insignificant. The change of Fermi level as a result of free bands occupation by lithium electrons can result in increasing the value of core level energy. Consequently, decreasing of core level energy can be caused by the change of the charge state of molybdenum and sulfur atoms as a result of occupation of free bands composed from contribution of molybdenum and sulfur atoms. In addition, we point out the good correlation (Fig. 6) between the shifts of core levels obtained in this work and "charge-discharge" curve of cathode- anode cell [2] characterizing the voltages on the cell as a function of degree of its discharge, i.e. number of lithium ions inserted into cathode matrix.



Figure 6: Correlation between the change of $Mo3d_{5/2}$ -energy in MoS_3 and "the discharge curve" of cathode-anode cell at different lithiation degree [9].

The displacement of disulfide pair doublet to S^{-2} ions doublet in SK_{β} -spectrum shows that the lithium loses electrons mainly to the disulfide pair atoms. They occupy the antibonding σ^* -orbital of $(S-S)^{-2}$ pair. The charge state of the disulfide pair is displaced to S^{-2} -state when σ^* -orbitals has been occupied.

The experience of the study of the charge state of atoms by XPS suggests that an intimate relationship between core level energy of atom and the oxidation degree is observed [14,15]. By then the charge states of sulfur atoms have been investigated sufficiently [16,17]. It is known that the energies of S2p-levels of S^{-2} -state (for example, M_2S , where M is one-valent metal or MS, where M is two-valent metal) span 161.5-162.7 eV, the values of neutral sulfur (for example, in S_8 , R_2S , R_2S_2 , where R is neutral radical) do 163.6-164.5 eV. Consequently, the energy of S2p-level of disulfide sulfur atoms in MoS_3 obtained in this work (163.7 eV) is close to $(S-S)^0$ -state rather than $(S-S)^{-2}$ -state.

Similar difficulty occurs in studies of charge state of metal. The energy of Mo3d-level in MoS_3 is less than that in MoS_2 where the metal atoms are in Mo^{+4} -state, and these data disagree with ionic formula suggested for MoS_3 structure [8]. In reference [8] it was proposed that the low value of Mo3d-level energy in MoS_3 can be accounted for by the change of the metal charge state at M - M bond formation (pairing of electron of d_{x^2} -orbitals). However, the bond M - M is pure covalent and hardly can change the oxidation degree of metal. Another way of looking at this fact based on decreasing ionicity Mo - S bonding (for example in ZrS_3 [16]) is not sufficiently advanced, for the coordination of sulfur atoms by metal and distances M - S in MoS_2 and MoS_3 appeared to be closely allied.

These difficulties may be resolved by suggestion that disulfide pair in MoS_3 forms supplementary M - S bond of donor- acceptor type with the participation of disulfide pair π -orbital (electrons of lone pair of sulfur atoms) and free metal orbital. In this case MoS_3 structure can be formulated as $Mo_2^{+4}(S^{-2})_4(S_2)^0$.

The determination of oxidation state of metal in other transition metal chalcogenides also presents difficulties and it may be connected with the presence of dichalcogenide pair $(X-X)^{-2}$.

4.2. Electronic structure of MoS₃

As far as we know to the present day any theoretical or experimental results of investigation of the molybdenum or tungsten trisulfides electronic structure has not been published. For lack of supplementary information, it is very difficult to give well-grounded interpretation of experimental spectra shown in Fig. 5. Nevertheless, it will be useful to describe in qualitative sense an electronic structure of MoS_3 on the basis of these results. It is needless to say that the proposed model of electronic structure must be regarded as a tentative one.

Emission $MoL_{\theta 2.15}$ -spectra reflect the contribution of an 4d- and 5s-electron density of Moto the valence band. The spectra occupy a wide energy region (from 0 to 10 eV) and on the whole overlap an energy region of SK_{θ} -spectra which reflect the contribution of the sulfur 3d electrons. This means that M - S bond has appreciably a covalent character. Widely used at the present time, ionic model of the electronic structure of trichalcogenides and dichalcogenides of transition metals in which it is assumed that the metal dbands are higher than the anion 3p-band and binding electrons on the whole occupy lower levels but upper levels remain empty, fails in this case. The presence of covalent component in M - Sbond leads to formation of bonding (deeper) and anti-bonding (upper) orbitals containing contribution both of metal and sulfur atoms. The M - M bond $(d_{12} - d_{12})$ is completely covalent, resulting in significant displacement of bonding orbitals downwards. The essential covalent bond takes place in a number of other trichalcogenides and dichalcogenides of transition metals, such as Fe. Co. Ni. Mn [19,20]. For MoS_2 this fact was demonstrated in work [21].¹

In MoS_3 structure the environment of metal atom is a distorted trigonal antiprism. For a regular trigonal antiprism (D_{3d} symmetry), splitting of d-orbitals can be characterized by angle β between z axis and the metal-ligand bond [18]. For $\beta = \arccos 1/\sqrt{3} \ (\beta = 55^{\circ})$, the antiprism is distorted to octahedron (z axis goes through the centers of opposite faces) and d-orbitals split into doubly degenerate level $e_u(d_{xy}, d_{yz})$ and triply degenerate level $a_{1q}(d_s) + e_q(d_{sy}, d_{s^2-y^2})$. When there is a departure of the symmetry from octahedron, the deeper (triply degenerate) level splits into a_{1g} and e_{g} [18]. In MoS₃ the angle β is close to $(\beta \approx 53^{\circ})$ the angle in octahedron (about the center of antiprism). The metal atom is displaced from the prism center by 0.2 Å, however, the crystalline potential is slightly varied $(\approx 5 \times 10^{-3})$. Thus, the deeper metal levels are d_{x^2} and $(d_{xy}, d_{x^2-y^2})$ -orbitals and the upper level

¹In this work Dr. D.S.Urch emphasized: "The simple electronic model for MoS_3 of a narrow Mod band and then, at aslightly higher binding energy, a Sp band is quite wrong."

consists of the d_{xx} and d_{yx} -orbitals.

Because of high ionic bonds the *d*-orbitals of metal split in wide energy region. In this case it is possible a considerable mixture of upper *d*-bands and 5*p*-bands of metals, this is, hybridized wave functions of valence electrons are s - p - d character and include nine energy bands. In connection with quasi-one-dimensional MoS_3 structure the energy bands, as for other closely related structures, can be considered narrow enough (0.5-1.5 eV) [22,23], this is, the valence electrons are sufficiently well localized on the bonds.



Figure 7: The bond groups and distributions of electrons on the bonds in MoS_3 . •-molybdenum, O-sulfur

The possible distribution of electrons on the bonds in terms of localized MO corresponding to the directional valence σ -bonds is shown in Fig. 7.

The d_{y^2} -electrons are localized on M - Mbonds. The closely-spaced metal atoms are bound through bridging S^{-2} ligands by electrons of s-, d_{xy} -, $d_{x^2-y^2}$ -orbitals. The widely spaced metal atoms are bound through (S - S) and S^{-2} ligands by electrons of $5p_x$ -, d_{xx} -, d_{yx} -orbitals. These orbitals are occupied by two electrons and form valence bonds with two sulfur atoms whereas the bond with third sulfur atom has donor-acceptor character with participation of the lone pair of sulfur atoms and free metal orbital. Two bands formed by p_x - and p_y -orbitals remain empty and can take part in the interchain bonds. The character and occupancy of bonds in MoS_3 are listed in Table 2.

Comparing these bond groups with the peculiarities of the experimental spectra shown in Fig. 5, one can assume the simple qualitative model of electronic structure of MoS_3 presented in Fig. 8.

However, it should be pointed out that the location of the energy levels, component set and degeneracy of MO and type of bonding are dictated rigidly by the symmetry of the metal atoms environment, the peculiarities of experimental spectra, proposed model of arrangement of local structure and a number of other factors, in particular, the change of structure characteristics during lithiation. For example, peak A in $MoL_{62.15}$ spectra cannot be related to MO corresponding to M - M and M - S bonds, for this peak is decreased and disappeared at x = 2 during lithiation of MoS_3 , whereas results of EXAFS [2] have shown that M - M distance is decreased and M-S distance is increased. An origin of peak A and its decrease during lithiation can be understood if the presence of donor-acceptor bond is proposed in which the lone pair of disulfide sulfur atoms takes part and transfers electrons to metals. Lithiation of MoS_3 weakens this bond or, may be, breaks it. As mentioned above, the contribution of sulfur atoms of disulfide pair to SK_B -spectrum is displaced by 1.1 eV to Fermi level and, correspondingly, the anion component to donor-acceptor bond is shifted upward as shown in Fig. 8.

Peak C in $MoL_{\beta 2,15}$ -spectrum corresponds to bonds $M - S_2$, $M - S_3$ of metal with ligands

Table 2: Character and occupancy of bonds of MoS_3 structure (per two formula units)

bonds	char.	AO set	occup.
Mo - S1	i-c	3p-s, d=n d=2-v2	12
Mo - S2, S3	i-c	$3p - d_{xx}, d_{yx}$	8
Mo - 53	d-a	$3p - 5p_{s}$	4
M - M	с	$d_{x^2} - d_{x^2}$	2
S - S	с	3p - 3p	2
Lone pair	nb	S3p	8
Upper bands	u	$\sigma^*, 5p_{\pi,y}$ etc.	-

i-c-ionic-covalent, d-a-donor-acceptor, c-covalent, nb-nonbonding, u-unoccupied. (S-S) and S^{-2} . Peak B corresponds to bond $(M-S_1)$ of metal with three bridging S^{-2} ions and to bond M-M $(d_{s^2}-d_{s^2})$, that is placed deep within the valence band, contrary to other transition metals trichalcogenides [24,25]. By assuming that the metal contribution to the bands A, B, C is in the ratio of 2:3.5:1, Fig.8, and the donor-acceptor bond transfers to metal two electrons, the covalency of bond can be obtained as the ratio of electrons remained on the metal to the total number of electrons on the bond. Accvalent character of ~25% for B and C bonds was estimated, that agrees with covalency of M-Sbonds calculated from electronegativity by Pauling.

The upper part of valence band is filled by sulfur lone pair states and states of $M - S_2$, $M - S_3$ bonds. The lower part of conduction band (peak E) consists of disulfide pair σ^* -states overlapping with antibonding bands of $(M-S_1)^*$ and $(M - S_2, S_3)^*$ bonds in the upper part. The lower part of antibonding bands M - S is overlapped with vacant $5p_{x,y}$ metal bands of bonding character (with respect to interchain interactions). The M-S bands and σ^* are presented in MoL_3 and SK-absorption spectra as the intense and narrow peak E near absorption edge that supports assumption about localization of electrons. Note that in absorption spectrum of elemental sulfur this peculiarity is not observed (delocalization of electrons). The antibonding d_{2}^* and $5p - \pi$ bands are placed considerably above and appeared as peculiarities F and G in MoL_3 -edge absorption spectra. The contributions of metal and sulfur atoms to the density of states in the valence and conductivity bands are depicted by bars in emission and absorption spectra of Mo and S. It should be pointed out that to occupied MO the sulfur atoms contribute essentially whereas free MO are composed mainly of contributions of metal atoms. This clearly demonstrates sufficiently high ionic bonds and characterizes range of feasibility of ionic models.

4.3. The Change of the electronic structure upon intercalation

The ions of alkali metals during intercalation of the transition metals trichalcogenides are placed in structural cavities of matrix (van der Waals cavities). The excess electron occupies free matrix band above Fermi level. However, a consideration of electronic structure of intercalated trichalcogenides of transition metals in terms of "rigid band" model is not sufficiently correct. The occupation of the free levels of matrix leads to the change of the bond character and, consequently, to change of the structure that, in its turn, results in change of the structure of valence band. In work [2] the changes of structural characteristics of molybdenum and tungsten trisulfides during lithium intercalation has been studied by EXAFS. It is shown that at high degree of intercalation considerable structural rearrangement of starting host occurs, in particular, the distance M - M is decreased and number of bonds M - M is increased whereas distance M - Sis increased and the number of these bonds is decreased. Under intercalation above 3 atoms per formula units, irreversible structural changes take place and repeated charge of the cell is impossible. The metal-cluster groups is suggested to be formed typical for chalcogenides at low degree of oxidation. The most probable transition to structures like Chevrel phases M', MaXa has been proposed.

The behavior of MoS_3 during intercalation is explained in our model. According to proposed tentative model of the electronic structure of MoS_3 , during lithiation first antibonding σ^* orbital of dichalcogenide pair and overlapping antibonding bands $M - S_{2,3}$ and $M - S_1$ are being occupied. This results in increasing of distances M - S and S - S and in the change of contribution of metal and sulfur atoms to valence band, that manifests itself as the change of ratio of intensity of peak B to that of C in $MoL_{\theta 2,15}$ spectrum.In the first stage of intercalation considerable changes occur in C peak region that can be connected with weakening or breaking of $M - S_{2,3}$ bond. The further increasing of intercalation degree results in changes in region of A and B peaks that is connected with attenuation or disruption of M - S bonding and, if possible, the part of donor-acceptor bonds is replaced by valence bond M - S that leads to increase the degree of oxidation of metal to Mo(VI).

Near Fermi level the density of states is in-



Figure 8: The qualitative schematic representation of electronic structure of MoS_3

creased (peak D), that is clearly associated with the occupation of the lower-lying free bands. Fermi level is not shifted, on the contrary, occupied part of band is displaced below Fermi level that is connected with splitting into bonding and antibonding bands (relative to lithium atom) resulted from weak overlapping with lithium 2slevel. Splitting of occupied bands is evidenced by displacement of peak E in SK and MoL_3 absorption edge spectra to higher energy. A contribution to peak E in SK-absorption spectrum is given by σ^* -band (displaced from true position to higher energy by 1.1.eV), $(M - S_1)^*$ -band and $(M - S_2, M - S_3)^*$ -band. The occupation of these bands by lithium electrons under lithiation results in change of shape and displacement to higher energy of peak E. At $x \approx 1 \sigma^*$ -band has been occupied practically, in this case occupation and displacement of other bands is being continued that leads to formation of shoulders onto the peak. $(M - S_1)^*$ and $(M - S_2, M - S_3)^*$ -bands correspond to peak E in MoL3-absorption spectrum. In the initial stage of intercalation only lower $(M - S_1)^*$ -band is occupied that causes splitting of peak E slightly, on further intercalation both bands are occupied and peak E is shifted as a whole. At intercalation degree less than 6 atoms of lithium per two formula units these changes are reversible (see Fig. 6) [2]. At higher intercalation degree it begins the filling of free bonding metal $p_{x,y}$ -bands participating in interchain bonding that leads to the formation of metal-cluster groups and, consequently, to irreversible changes of matrix structure.

5. Conclusions

In this work the change of the electronic density distribution on the atoms in MoS_3 and WS_3 during lithium intercalation and electronic structure of the starting and intercalating MoS_3 has been investigated by X-ray electron and Xray emission and absorption spectroscopies. Xray electron spectra of core levels characterizing charge state of atoms, valence band spectra characterizing the distribution of full electronic density and $Mo(4d, 5s - 3p_{3/2})$ and S(3p - 1s) Xray emission spectra characterizing partial contribution of atoms to electronic states density of valence band are obtained. It is demonstrated that during lithiation of MoS_3 and WS_3 the lithium electronic density is distributed among metal and sulfur (mainly on disulfide pair atoms). At present it is suggested that chemical bond in transition metal trichalcogenides is almost entirely ionic and the number of ionic bands and the degrees of oxidation of atoms are described by ionic formula. As for MoS_3 , assumed ionic formula is $Mo_2^{+5}(X^{-2})_4(X_2)^{-2}$, from that it follows that lone pair of disulfide (as well as another sulfur atom) are not involved significantly in the formaton of chemical bond. Our work demonstrates that this approach is unsuitable for description of the electronic structure of MoS_3 . Analysis of obtained experimental results taking into consideration some physico-chemical properties allows to make the following conclusion:

1. Character of chemical bond in MoS_3 is appreciably covalent, part of covalency is approximately ~25%.

2. "Covalent component" of electronic density is sufficiently localized on directional two-atoms bonds and, hence, the description of electronic structure in terms of valence bonds and localized MO in the first stage is valid.

3. The charge state of sulfur atoms in disulfide pair is close to $(S - S)^0$ rather than $(S - S)^{-2}$ that can be connected with the participation of lone pair in chemical bond.

4. The degree of oxidation of the metal atoms in MoS_3 proved to be M^{+4} rather than M^{+5} that can be connected with the participation of free metal orbital in donor-acceptor bond instead of breaking of one of five valence bonds with sulfur atom.

5. The above-mentioned peculiarities allows to suggest that there is the additional donoracceptor M - S bond involving free metal orbital and lone pair of disulfide atoms of sulfur in MoS_3 . Then ionic formula is $M_2^{+4}(X^{-2})_4(X_2)^0$ and problems of determination of charge state of metal and disulfide pair do not arise.

6. Using the model of local structure of MoS_3 [7] and obtained experimental spectra, based on covalent character of M-S bonds and suggestion about additional donor-acceptor M-S bond, the tentative model of MoS_3 electronic structure is proposed as shown in Fig. 5.

7. The proposed model of electronic structure

of MoS_3 is supported by the agreement found between "discharge curve" of cathode-anode cell $Li - Li_x MoS_3$ and changing of peculiarities of Xray emission and absorption spectra when changing value x and allows to explain the character of "discharge curve" and chemical behavior of MoS_3 during intercalation.

8. The proposed model of electron structure of MoS_3 allows to determine the requirements which cathode materials for high-energy-density current sources have to satisfy. First, in these materials the energy of free bonding levels resulting in irreversible structural reconstruction of matrix must be as higher as possible. Second, the electron capacity of unoccupied bands lying lower than bonding level must be as higher as possible. The low-dimensional materials having a wealth of M - L bonds and high energy splitting between transition metal *d*-orbitals are best suited for this purpose.

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