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Electronic Energy States of Tungsten Dichalcogenides by Low Energy Electron Loss Spectroscopy Study

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Low energy electron loss spectroscopy (ELS) was performed on tungsten dichalcogenides (WS_2 and WSe_2) by using incident electron energies of 30–360 eV. The ELS spectra in the second derivative form had considerable structures. Maxima in density of states in the conduction band of the compound were determined from the ELS data due to excitations from different filled states, including core levels, which were studied by X-ray photoelectron spectroscopy. The conduction band of the tungsten disulfide could be divided into two parts. The results are discussed in relation to previous proposals based on band calculations and experimental studies of group VIB dichalcogenides.

§1. Introduction

The transition-metal dichalcogenides (MX_2) constitute a family of layer compounds with a hexagonal network of metal atoms (M) sandwiched between two planes of chalcogen atoms (X).[1] There are about 40 binary layered chalcogenides and the number increases due to polytypes with different stacking of layers. The most striking feature of this family is highly anisotropic structure, which consists of the X–M–X sandwiches within which the bondings are strongly covalent and between which the bondings are weak due to van der Waals forces. The properties of the materials have been extensively reviewed by Wilson and Yoffe,[1] and it is considered that MX_2 is in general semiconducting for group IVB and VIB compounds whereas metallic for group VB compounds. Many optical studies were done mainly to reveal band structures of MX_2.[2,3] In recent years the group VB compounds, *e.g.* TaS_2 or NbS_2, have been studied in the field of superconducting materials with low dimensions, including intercalation of alkali metals or various organic matters.[4] More recently works related to charge density waves, which were observed characteristically in low dimensional materials, have been extended to these layer compounds.[5,6]

Recent progress in electron spectroscopies has enabled one to obtain direct informations on band structures. Experiments by means of photoemission studies such as X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) have directly revealed structures of valence bands of MX_2[7-9] and the results have been compared with theoretical calculations.[10] However, so far informations on empty conduction bands have little been obtained. In contrast with XPS and UPS, low energy electron loss spectroscopy (ELS) is a powerful method to investigate both empty and filled states near surface regions of materials because of small escape length of low energy (~100 eV) electrons.[11-13] However, spectra measured by means of the above electron spectroscopies may be considered to be indicative of appropiate bulk properties because of layer structures in the case of the MX_2 compounds although the escape depth is shallow.[14,15] Since the ELS study yields data on electronic transition energies, it is hoped for the assignment of loss spectra to combine the ELS data with informations about filled states measured by XPS and UPS techniques. In fact several ELS studies have been done to investigate MX_2, mainly MoS_2, to get informations on empty bands.[16] High energy (several tens keV) electron loss spectroscopy, on the other hand, was used for measurements of MX_2,[17,18] which revealed only collective plasmon excitations and dielectric functions of MX_2 but provided little direct informations on single electron excitations, namely on empty bands (states). There have been other attempts to obtain data on unfilled electronic states. Soft-X-ray absorption spectroscopy (XAS), which yields informations about structures of empty band directly, has also been applied to a study on MX_2.[19] From UPS data and the related XAS data, an experimental band model has been derived.[15] However, there is some confusion in different band models proposed by many workers.[1-3,10,14-16,19,20]

In the present paper the ELS spectra of tungsten dichalcogenides (WS_2 and WSe_2 of group VIB compounds) are reported, including the XPS data. The measurements have brought forth informations about conduction bands, mainly that of WS_2. This paper is organized as follows. In §2 experimental procedures are described. Section 3 is devoted to experimental results. In §4 density maxima in conduction band of the group VIB compounds are discussed, followed by conclusions in §5.

§2. Experimental Procedures

2.1 *Sample preparation*

Stoichiometric amount of powdered elements, tungsten W (purity 99.9%) and chalcogens, S and Se (99.999%), were introduced into a silica ampoule, evacuated to $\sim 10^{-6}$ Torr and sealed. In a horizontal furnace the ampoule was heated in several hours to a final temperature between 750 and 850°C and maintained at the temperature about for 3 days, and then removed from the furnace to be cooled. At this stage compounds obtained were in the form of free-flowing black powders. Next, the powder crystals were transported using bromine to grow single crystals. An silica ampoule containing the powdered compound and small amount of liquid bromine (99%) was evacuated and sealed, partly immersed in liquid nitrogen. The ampoule was inserted in a furnace with a suitable temperature gradient and one ampoule end was maintained at the highest temperature of 1000°C within ± 2°C for a few weeks, while the temperature of the other end was 700–800°C. Then the ampoule was removed from the furnace, and partly cooled by water to condense the bromine vapour. Crystals grown were in the form of flat plates as reported in ref. 21.

2.2 *Specimen mounting*

Specimens, soldered on a molybdenum or a tantalum thin plate with indium, were transferred for the ELS study, which was hoped to be performed in a well defined surface region with no contaminants. Auger analysis was used to detect contaminants, and revealed no bromine which was used as a transport agent. The MX_2 compounds can be cleaved easily because of the weak van der Waals forces between layers. Specimens measured were cleaved in air just prior to insertion into a spectrometer since contaminants such as carbon and oxygen were only slightly detected in the air-cleaved samples by the Auger analysis.[14,22] This may be due to electron-impact desorption of weakly bonded contaminants since the pressure in the chamber became slightly higher at the onset of electron irradiations.

2.3 *ELS measurements*

A PHI single-pass cylindrical mirror analyzer (CMA) with a coaxial electron gun was used as the primary beam source and the energy analyzer in the ELS study. The primary beam was incident upon specimen surfaces and backscattered electrons were detected in a cone of half-aperture of 42.3° by the CMA. The Auger analysis was performed in the conventional mode. The ELS study was performed in the region of the primary electron energy E_p of 30–360 eV with the primary current below ~ 1 μA. The spectrum was measured as negative second derivative of electron energy distribution $N(E)$ by means of a lock-in technique (with modulation voltage of 0.8 V peak-to-peak), since a derivative spectrum revealed much finer structures than a non-derivative one. The energy resolution ΔE of the CMA was proportional to the pass energy E of the electrons ($\Delta E/E \sim 0.6\%$). Peak positions of the loss spectrum were almost independent (within $\sim$0.3 eV error) of the angle $\theta (0° \lesssim \theta \lesssim 30°)$ between the specimen normal and the CMA axis. In the case of electron excitations from W-2p core, the measured value of the electron energy contained uncertainty of $\lesssim 1$ eV, but the relative energy positions among the loss peaks could be determined within $\sim$0.3 eV error. The pressure of $\lesssim 10^{-9}$ Torr with beam on did not distort the ELS study of MX_2 because of very slow progress in contaminations, and therefore maintainance of the pressure below 10^{-10} Torr in the experiment was not required in the present case.

2.4 *XPS measurements*

For WS_2 specimens XPS study was also performed with Mg–Kα radiation. The data were taken with a Dupont-ESCA 650B spectrometer, in which the pressure was $\sim 10^{-7}$ Torr. The Fermi level of the specimen was determined by using binding energies of C 1s(285.0 eV) and Au $4f_{7/2}$(83.8 eV) deposited on the specimen in the chamber as references.

§3. Results

3.1 *Valence electron excitations*

The group VIB specimens of 3R-WS_2 and 2H-WSe_2 had alike loss spectra with each other, as shown in Fig. 1, reflecting the same group with the trigonal unit cell for both polytypes. Therefore the detailed ELS data were shown mainly for the specimen of WS_2 in the rest of this paper. In the region of energy losses below 30 eV all energy loss peaks of WS_2 were positioned at 4.0, 6.5, 9.0, (13.0), 17.6, 19.3 and 23.9 eV [Fig. 2(a)]. The loss denoted by the parenthesis varied from 12.7 to 13.2 eV with the primary electron energy E_p of 50–150 eV. The two transitions at 9.0 and 23.9 eV may come from the excitations of two kinds of plasmons, i.e. that of π-electrons (the lower loss) and that of total valence electrons (the higher one), following Liang and Cundy who measured loss spectra of MX_2 by means of high energy (80 keV) electrons.[17] This assignment was supported by the fact that the intensity of the ELS spectrum at these positions increased more than those of other peaks with the increment of E_p from 150 to 360 eV [Fig. 2(a) and (b)]. The loss peak at 17.6 eV was considered to correspond to the excitation of surface plasmon which might be a collective excitation at vacuum-solid boundary, from the fact that the peak appeared to be clearer than that due to the excitation of the bulk plasmon at 23.9 eV with decreasing E_p [Fig. 2(a)]. The above bulk plasmons were described in dielectric approach as in the case of three dimensional solids.[17] The energy of 17.6 eV was close to that of $23.9/\sqrt{2}$ eV, a value expected in the case of three dimensional solid surface. The above losses due to the collective excitations are excluded from the identification of the loss spectra described in §4. Similar assignments can be done for the loss spectra of WSe_2.

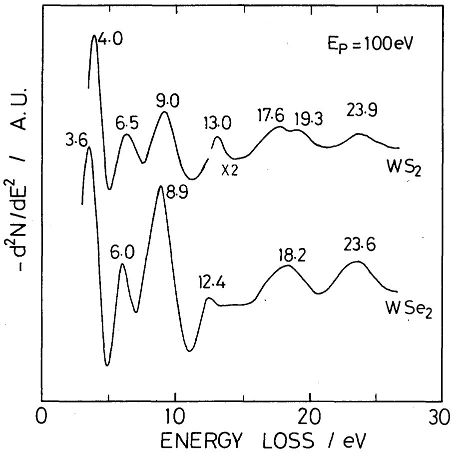
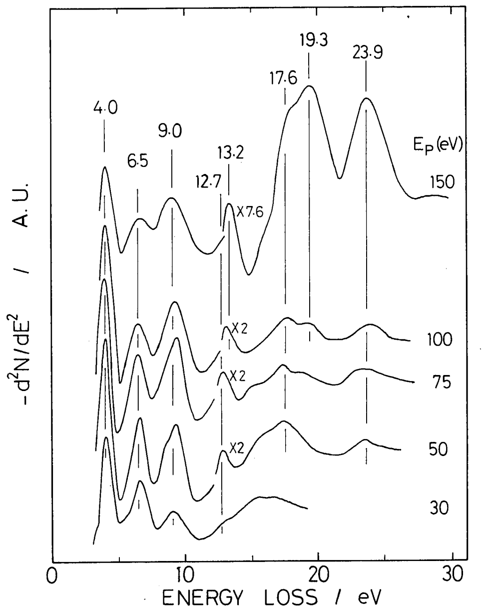
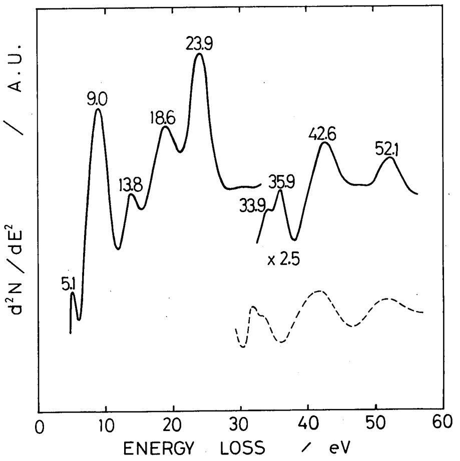


Fig. 1. ELS spectra of 3R-WS_2 and 2H-WSe_2 with primary electron energy E_p of 100 eV.

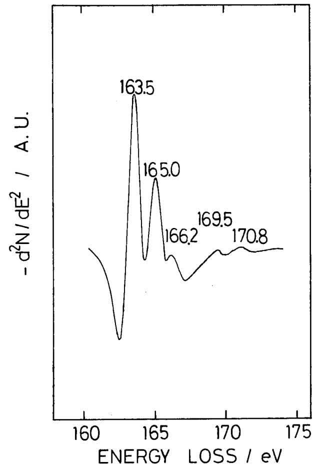
Loss peaks located below 20 eV are in general derived from the transitions from valence states to empty ones above the Fermi level in the absence of surface states, which may be the case with MX_2. The transitions at 4.0, 6.5 and 13.0 eV can be assigned as the excitations from the valence band which is constituted mainly by p-states of chalcogen atoms and located at ~ 5 eV below the Fermi level with the full width of 7–8 eV.[8,9] The losses of 3.6 and 4.0 eV for WSe_2 and WS_2, respectively, were compared with optical transmission spectra.[2] The peak positions in the former (ELS) were located at higher energy site by 0.2–$\sim$1 eV than in the latter (optical transition), which can be explained from the difference in the excitation mechanism in both cases.[12] In other words, for bulk transitions optical absorption measures Im ε, where ε is the complex dielectric function, while ELS measures Im $1/\varepsilon$ in dielectric approach, which seems to be valid for $E_p \sim 100$ eV.[13] In fact it has been reported for MoS_2 that the difference in maximum energies between Im ε and Im $(-1/\varepsilon)$ is about 1 eV in the case of high-energy electron loss measurements.[18] The loss peak at 19.3 eV is considered to be derived from the transition from 3s state of chalcogen atoms (S) to an empty state. (The loss peaks at 5.1, 13.8 and 18.6 in Fig. 2(b) were considered not to indicate correct energies of the transitions mainly



(a)



(b)



(c)

Fig. 2. ELS spectra of WS_2: (a) The dependence of the spectrum on primary electron energy E_p of 30–150 eV in the energy-loss region below 30 eV; (b) The spectrum in the region of the energy losses below 60 eV with $E_p = 360$ eV (solid line), compared with that of clean (Ar^+-sputtered) W with $E_p = 300$ eV (broken line). The peak at 5.1 eV is a specious one due to large background of elastic peak in the $-d^2N/dE^2$ form and is excluded from the assignment; (c) The spectrum derived from excitations of 2p core electrons of sulfur atoms with $E_p = 250$ eV.

because the energy resolution was decreased with E_p and were excluded from the discussion of the loss spectra described in §4.)

3.2 Core electron excitations

The ELS spectra in the region of energy losses above 30 eV [Fig. 2(b) and (c)] are assigned more easily than those in the low energy region described above because the initial states of the transitions are non-dispersive, i.e. located in narrow energy regions. The peak positions in this energy region were 33.9, 35.9, 42.6, 52.1, 163.5, 165.0, 166.2, 169.5 and 170.8eV. It is concluded that the two transitions at 33.9 and 35.9 eV must come from 4f states of tungsten atoms, the binding energies of which were 33.1 and 35.3 eV for $4f_{7/2}$ and $4f_{5/2}$ states, respectively. On the other hand, the last five peaks (163.5–170.8 eV) are assigned to be the transitions from 2p-core states of sulfur atoms located at 163.0 eV($2p_{3/2}$ state) and 164.2 eV($2p_{1/2}$ state) below the Fermi level. The other losses (42.6 and 52.1 eV) can be related to the excitations of electrons in $5p_{3/2}$ and $5p_{1/2}$ states of tungsten atoms. The binding energies of core levels, shown in Fig. 3, were determined by the XPS measurements except for those of W 5p states which were deduced from data[23] of the

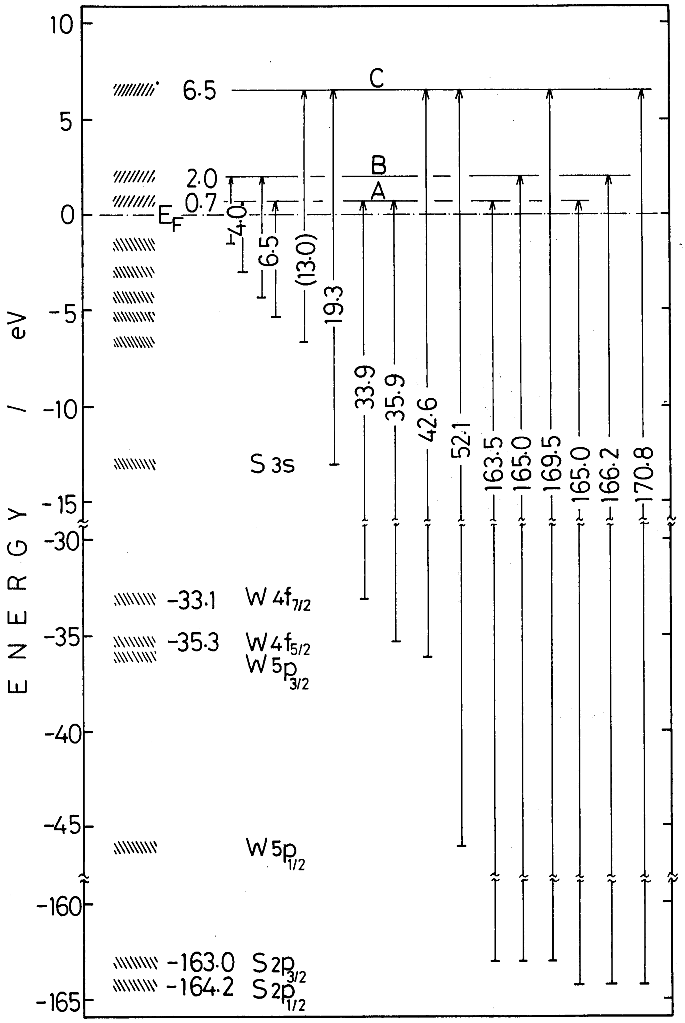


Fig. 3. Assignment of ELS spectra for WS_2. Three final states are deduced to explain all loss lines observed in Fig. 2, except for losses due to plasmon excitations. The Fermi level E_F and core binding energies (W 4f and S 2p states) were determined by XPS study.

binding energies of the states for pure tungsten because of the fact that the energies of the W 5p states could not be measured in the present XPS study due to rather small cross sections for photo-ionizations of the states. The difference in sensitivity between ELS and XPS cases may be due to the difference of the spectral forms, i.e. $-d^2N/dE^2$ and N, partly reflecting the difference in excitation probability between both cases. The details of the assignments will be described in the following section.

§4. Discussion

As for the single electron excitations, final states can be identified from the knowledge about initial states since a loss spectrum gives informations on the transition energies between initial and final states. Selection of initial states with narrow width in energy, i.e. core states, makes easy the assignment of final states, since in the case of core-excitations the transition energies can be associated directly with the energy positions of the final states. For WS_2, final states can be determined as three levels located at 0.7, 2.0 and 6.5 eV above the Fermi level E_F (which we name A, B and C, respectively), by using the ELS data in the energy-loss regions of 30–40 eV [Fig. 2(b)] and 160–175 eV [Fig. 2(c)] and the binding energies of W 4f and S 2p cores obtained from the XPS study. In Fig. 3 are identified the corresponding transitions in the loss spectra shown in Fig. 2 by using the final states thus deduced.

The transitions from unknown valence states constructed by W 5d and S 3p states together with those from unidentified core states, i.e. S 3s and W 5p states, are also included in Fig. 3. For these initial states, well structured data were absent in the present XPS study or other studies, so their binding energies were determined as follows. As for the core levels of W 5p, the binding energies are considered to be lower energy sites by ~ 1 eV in WS_2 than in pure W since the difference in the binding energies of W 4f states between WS_2 and pure W are about 1 eV.[23] This consideration yields the binding energies of ~ 36 and ~ 46 eV for W $5p_{3/2}$ and $5p_{1/2}$ states, respectively, which can explain well the losses at 42.6 and 52.1 eV as the transitions from the W 5p states to the highest final level C. Next, the S 3s state is estimated to be located at ~ 13 eV below E_F, from the identification of the 19.3 eV loss to the transition from the S 3s state to the empty state C. The estimated energy position of the S 3s state is reasonable, compared to UPS data of group VIB compounds, *e.g.* MoS_2 and $MoTe_2$.[8] Finally, we will discuss the density of state of the valence band. As for the transitions from valence bands one should note that in the dielectric theory loss spectra may be proportional to $-\mathrm{Im}\ 1/\varepsilon$ for valence electron excitations while for core electron excitations they may reflect $\mathrm{Im}\ \varepsilon$,* peaks of which may give direct informations on energies of electronic transitions. This may yield a slight difference in the procedure for the assignment of the loss spectra between both cases since peak positions usually locate at higher energy side by ~ 1 eV, at most, in $-\mathrm{Im}\ 1/\varepsilon$ than in $\mathrm{Im}\ \varepsilon$ as described above.[12] From the assumption that WS_2 has similar electronic structures of the valence band to those of other group VIB compounds, *e.g.* MoS_2, maxima of the density of state in the valence band of WS_2 are determined as shown in Fig. 3. For molybdenum compounds (MoS_2 and $MoSe_2$), UPS data[9] indicated that most of the valence-band maxima of the sulfide located at higher energy positions by ~ 0.4 eV than those of the selenide due to difference in spin-orbit interactions, whilst maxima in ELS spectra for the sulfide positioned in higher energy sites by about 0.4 eV than for the selenide.[16] The present ELS data for the tungsten compounds (Fig. 1) indicate that peak energies of WS_2 are shifted to higher energy sites by ~ 0.4 eV than the corresponding peaks of WSe_2. From these situations the valence-band maxima of WS_2 are deduced by shifting the energy positions of those in WSe[9] by the same energies (0.2–0.5 eV) as the energy differences between the molybdenum compounds (MoS_2 and $MoSe_2$). The result shows that the maxima locate at 1.5, 3.0, 4.3, 5.3 and 6.6 eV below E_F. Such five maxima are associated with the metal d_{z^2}-state (the top maximum) and the outermost chalcogen p-states (the other four maxima come roughly from bonding and antibonding states of the p_z and p_x/p_y states).[9] By using the estimated density maxima in the valence band, the transitions at 4.0, 6.5 and 13.0 eV can be assigned with uncertainty less than the energy difference in peak positions between $-\mathrm{Im}\ 1/\varepsilon$ and $\mathrm{Im}\ \varepsilon$ as described in §3.1.

The final states thus obtained can not be related to surface states because it is almost evident as mentioned already for the surface states not to exist in the case of the MX_2 compounds. So, these final levels must represent electronic states of the bulk material. Since the transition probabilities depend on both the initial and the final states, electronic characters of free atoms may partly be reflected in the loss spectra for the core excitations.[24] However, the levels deduced above are considered not to correspond completely to atomic excited levels because the excitations from the various cores with different electronic characters are associated with the same final level. Therefore the final states obtained are considered in connection with the electronic band structures of WS_2: they must indicate special parts of the conduction band of WS_2, probably density maxima in the conduction band. The likeness of the loss spectrum of WS_2, as shown in Fig. 2(b), to that of pure W, where the final

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* The loss data from core electron excitations may reflect absorption spectra similar to optical data because in the dielectric approximation $\mathrm{Im}\ \varepsilon \ll 1$ and $\mathrm{Re}\ \varepsilon \approx 1$, so that $-\mathrm{Im}\ 1/\varepsilon \approx \mathrm{Im}\ \varepsilon$.[24] For MoS_2, Koma *et al.*[16] showed that ELS spectrum of core-excitation in as low E_p region as in the present study was in good agreement with soft X-ray absorption spectrum.[19] This indicates that the dielectric approximation may be valid in the present E_p region.

states must be derived only from tungsten 4d and 5s/5p orbitals, suggests that the final states deduced are constructed mainly by d and s/p character states. In fact it follows from APW band calculations by Mattheiss[10)] that conduction bands of MX_2 for group IVB and VB compounds are divided into three parts, i.e. two subbands ($C_{1\alpha}$, $C_{1\beta}$) derived from d wave functions and an s/p derived one (C_2). Near Γ-point the $C_{1\alpha}$ and $C_{1\beta}$ subbands are deduced mainly from the d_{z^2} orbitals ($C_{1\alpha}$ band) and from the other d orbitals hybridized with the s/p orbitals ($C_{1\beta}$ band). The Fermi level is located between the $C_{1\alpha}$ and the $C_{1\beta}$ subbands for the group VIB compounds, which corresponds to the fact that in general the group VIB compounds are semiconducting. Provided that WS_2 has almost same structures in electronic bands as MoS_2, it is considered from the results of the calculations[10)] that the two final (empty) levels of A and B correspond to the two maxima in the upper subband $C_{1\beta}$ of the d-derived ones hybridized with the s/p character orbitals and that the highest one C must come from the s/p character band C_2. From the theoretical calculations[10)] the s/p band C_2 is expected to be much wider than the d subband $C_{1\beta}$.

Then we briefly discuss the E_p-dependent loss peak at ~13 eV, which may be assigned as the transition from one valence-band maximum at ~ -6.6 eV to the highest final state C(C_2 band). For the origin of the peak, surface states or surface contamination can be excluded since no surface states were observed or no loss peaks were appeared at the corresponding energy position for much contaminated specimens. An E_p-dependent loss may be expected to come from the transition between wide conduction band and broad valence band when it is derived from E_p dependences of the transition probability on momentum and energy. In the case of core-excitations, where atomic character may increase, these effects may be less than in the case of valence-excitation. This explanation for the E_p-dependent loss seems to be plausible, although it can not be excluded completely that the origin may be derived from change of the signal background in second derivative spectrum and/or from a superposition of two different peaks.

The presently obtained levels for WS_2 are compared with proposed band models for MoS_2, which has extensively been studied. The levels are in qualitative agreement with the recent models of MoS_2,[15),16)] as expected from the bond structures of MX_2, but the energy positions are different from each other: the d-derived band $C_{1\beta}$ (the levels A and B) of WS_2 positioned at lower energy site than in the case of MoS_2. This difference may be due to the effects of heavy atoms (W) on spin-orbit interactions. For WSe_2 the empty energy positions are expected to be lowered, which is associated with lower transition energies and lower energy positions of the valence-band maxima than for WS_2. This estimation may be consistent with the difference in energy position between the d-character subband $C_{1\beta}$ of WS_2 and that of MoS_2, namely the difference in the spin-orbit interactions between W and Mo atoms.

Although electronic transitions observed in ELS and XPS studies may be related to each other, in determination of energy positions as against E_F it should be noted that relaxation energies and polarizations are generally different between both cases. However, the present ELS spectra of core-electron excitations can be assigned within the experimental uncertainty by using the corresponding XPS data, which indicates that the difference in these effects between electron excitations from core states due to electron impacts and electron ejections from core states due to photon absorptions may be as small as the present experimental uncertainty for the tungsten dichalcogenides. In the case of valence-electron excitation, the difference in energy positions between maxima of $-\mathrm{Im}\, 1/\varepsilon$ and $\mathrm{Im}\, \varepsilon$ may be expected to be ~1 eV as in the case of MoS_2, but the difference appears to be decreased to $\lesssim 0.5$ eV for the present assignment. This may be due to the difference in relaxation energies between core- and valence-excitations and due to the fact that from core- and valence-loss-spectra different information on density-of-state may be obtained, i.e. on empty states of conduction band and on joint-density-of-state between conduction and valence bands. If these effects are deduced, then the present assignment of the valence-excitations may be changed slightly, including valence-band maxima. However, the relative energy positions of the deduced final levels may be meaningful, anyway.

§5. Conclusions

The ELS measurements of the tungsten dichalcogenides have brought us infomation on the conduction band of the compounds. In the case of core-electron excitations the loss spectra show the structures of the empty band almost directly although they may contain atomic characters partly. From the assignment of the ELS spectra, supported by XPS study, it is concluded that the derived final states correspond to density-of-state maxima in the conduction band proposed theoretically and experimentally. The conduction band of the tungsten disulfide is constructed by two parts: the energy separation of the two parts may be about 4 eV, and the lower band may be more than about 2 eV in width with two maxima in the density of state. All of the ELS peaks, including those from unidentified initial states, can also be assigned consistently.

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