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## XPS and EELS study of the bismuth selenide

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### Abstract

A  $\text{Bi}_2\text{Se}_3$  crystal was studied by XPS (X-Ray Photoelectron Spectroscopy) and EELS (Electron Energy Loss Spectroscopy). Al  $K\alpha$  radiation and an electron beam energy in the range of 0.1 to 2 keV were used, respectively, to probe a Se-terminated (0001) surface. Samples of the constituent elements (Bi and Se) have also been measured with the same setup. The core level chemical shifts obtained show that a charge transfer occurs in  $\text{Bi}_2\text{Se}_3$ . The spectra in the valence band region suggest that the density of states in the compound may be obtained by combining the spectra of the constituent elements, that the electronic states in the vicinity of the gap region consist of a mixture of the metal and calcogen  $p$ -orbitals and that the band arising from the valence  $s$ -orbitals occurs about 12 eV below the valence band maximum. The EELS spectra allow to identify the bulk plasmons for the three materials and the  $\text{Bi}5d3$  and  $\text{Bi}5d5$  interband transitions. Considerations of the energies of the  $\text{Bi}5d$  transitions as measured by XPS and EELS indicate that the bottom of the conduction band of the compound is 1.2 eV above the Fermi level. The EELS results also shows evidence that the losses occurring at 6.4 eV in the compound and at 5.4(5.5) eV in Bi(Se) have their origins in some surface process. We suggest that they may be associated to a surface plasmon. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:**  $\text{V}_2\text{VI}_3$  compounds;  $\text{Bi}_2\text{Se}_3$ ; X-ray photoelectron spectroscopy (XPS); Electron energy loss spectroscopy (EELS); Plasmons; Electronic transitions

### 1. Introduction

The semiconducting  $\text{V}_2\text{VI}_3$  compounds have been studied for more than two decades, mainly because some of these compounds present properties that make them important for technological applications in thermoelectric power conversion and in the fabrication of Hall effect devices. Bismuth selenide, an important member of these  $\text{V}_2\text{VI}_3$  compounds, is a narrow gap semiconductor ( $E_{\text{gap}} = 0.25$  eV) [1] and exhibits an unusual and very anisotropic layer struc-

ture. It crystallizes in a rhombohedral unit cell, where equivalent atoms are arranged in two dimensional, noncompact hexagonal layers perpendicular to the  $c$ -axis. Five such layers – in the sequence of  $\text{Se}^1\text{–Bi–Se}^2\text{–Bi–Se}^1$ , where the Se atoms occupy two different sites – form a tight bound unit whereas these ‘sandwiches’ are kept together by a much weaker  $\text{Se}^1\text{–Se}^1$  interaction. The bonds inside these ‘sandwiches’ are generally considered to be predominantly covalent, and those between them, are due to van der Waals forces [2,3]. This structural arrangement leads to an easy cleavage perpendicular to the  $c$ -axis showing a  $\text{Se}^1$ -terminated surface. Although the  $\text{Bi}_2\text{Se}_3$  has been the subject of a large

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number of investigations in the bulk form [4–7], very little is known about the electronic properties of this compound. The most important work was published by Thuler and co-workers [8] who presented a Synchrotron-Radiation Photoemission study of the valence band density of states and core level binding energies of the  $\text{Bi}_2\text{Se}_3$ . On the other hand, only very recently a band structure calculation for this material was published [1].

More recently, some of the  $\text{V}_2\text{VI}_3$  semiconductors have been investigated in order to understand the effects of doping and intercalation of metal atoms, on their electrical, magnetic, and mechanical properties [9–12]. It has been observed that in the case of intercalation, the metal fills the van der Waals voids in the crystal. Therefore, as the cleavage occurs at the ‘van der Waals gap’, a better knowledge of the (0001) surface properties may be important to understand the mechanism of the intercalation process. So far there is no published work on the properties of this surface.

In this paper we report the results of XPS and EELS studies of the  $\text{Bi}_2\text{Se}_3$  crystal and of its constituent elements Bi and Se. The core level chemical shifts have been determined from XPS spectra of a  $\text{Bi}_2\text{Se}_3$  crystal and of polycrystalline samples of Bismuth and Selenium. EELS were recorded for different primary energies and the surface and bulk plasmons were identified as well as some interband transitions. All spectra were collected with the same experimental setup. In Section 2 we present experimental details and in Section 3 the results are shown and discussed. Finally, in Section 4 a conclusion is presented.

## 2. Experimental details

The crystals were grown by the Bridgman–Stockbarger method in a vertical arrangement. Pure starting materials, Bismuth (99.999%) and Selenium (99.99%) supplied by Aldrich Chem. Co., were used. After orientation by X-rays the crystals were cleaved perpendicular to the trigonal axis (*c*). Mirror-like surfaces of about  $8 \times 10 \text{ mm}^2$  were obtained although steps could be seen on some of them. The samples were introduced into the ultra high vacuum chamber and after an  $\text{Ar}^+$ -ion sputtering (500 eV; 15 min), a

very clear LEED pattern, with the expected hexagonal symmetry of the (0001) face, was observed.

The XPS and EELS studies were carried out in a VG-ESCALAB 220 i-XL system. Pure Bi and Se (polycrystalline) and  $\text{Bi}_2\text{Se}_3$  (monocrystal) samples were fixed on the same sample holder and submitted to identical cleaning and measurement procedures. The probe region on the surface was controlled by using the imaging facilities of the system. The base pressure in the chamber was about  $6 \times 10^{-8}$  Pa and during the time of measurements the sample showed no contamination. For EELS spectra a VG-LEG62 electron gun was used and no sample charging was observed. The spectra were recorded with the analyzer set to 10 and 20 eV constant pass energy. At these conditions the elastic peaks of the electron spectra showed a nearly constant FWHM of about  $(0.8 \pm 0.1)$  eV. After the XPS and EELS measurements a clear and expected LEED pattern could still be observed showing that the surface has a good stability under argon ion sputtering.

## 3. Results and discussion

The XPS spectra recorded from the Bi and Se polycrystalline samples and the (0001) face of the  $\text{Bi}_2\text{Se}_3$  crystal are shown in Fig. 1. The relative energy peaks were determined from high resolution spectra recorded at a narrow energy range, but large enough to include the peak. At a binding energy of about 160 eV an overlap of peaks involving  $\text{Bi}4f$  and  $\text{Se}3p$  transitions can be observed, but the  $4f$  have much higher intensities than the  $3p$  transitions. The results are presented in Table 1, where the chemical shift represents the difference between the energy peak positions of  $\text{Bi}_2\text{Se}_3$  and those of the pure elements.

From Table 1 one can see that there is no significant difference in the spin-orbit splitting occurring in the compound and that in the pure elements. The  $\text{Bi}5d$  levels show a splitting of 2.9 eV for the compound and 3.1 eV for the Bi metal, and 5.3 eV for the  $\text{Bi}4f$  levels of both samples. The  $\text{Bi}4d$  levels show a splitting of 24.2 eV for Bi metal and 23.5 eV for  $\text{Bi}_2\text{Se}_3$ . For the  $\text{Se}3d$  levels the splitting is 0.8 eV for the Se metal and 0.7 eV for the compound. These

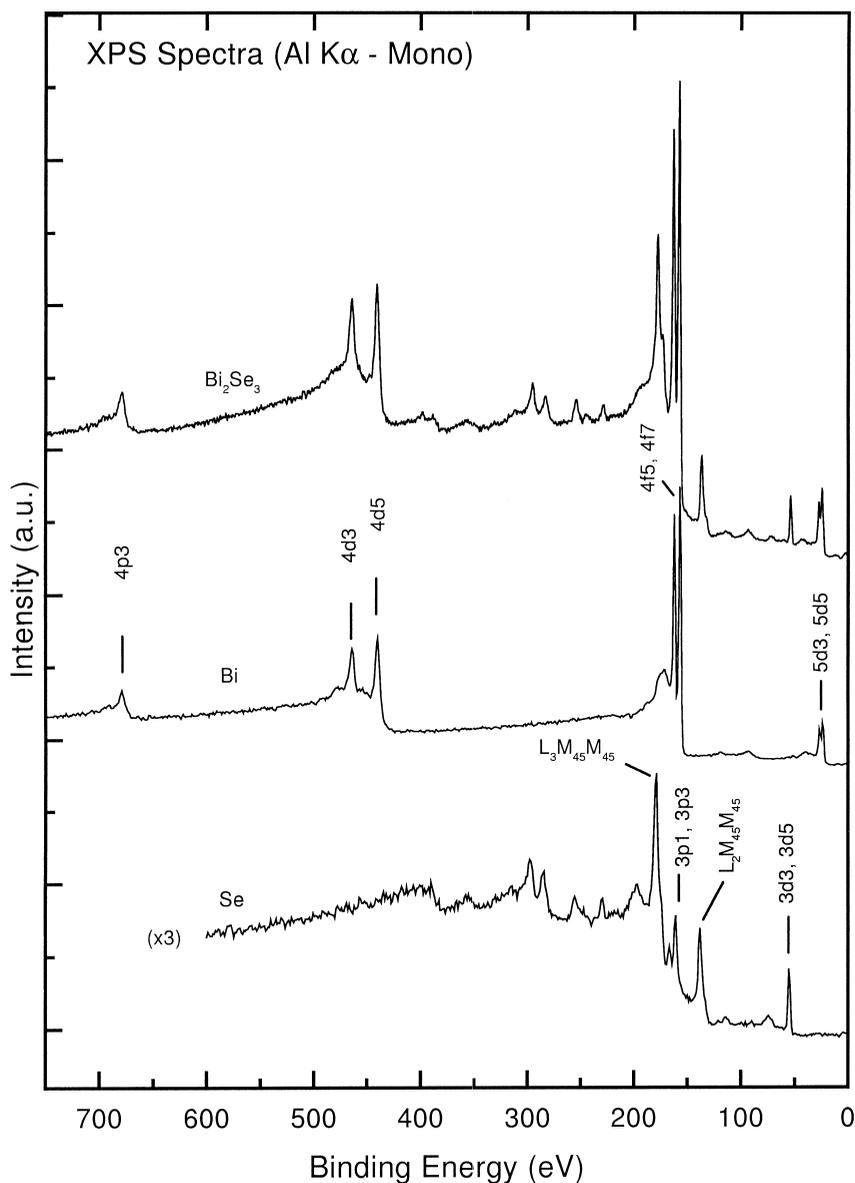


Fig. 1. XPS spectra (Al K $\alpha$ -Mono) of Bi<sub>2</sub>Se<sub>3</sub> (0001) surface and polycrystalline Bi and Se.

results for the Bi5*d* and Se3*d* agree well with those found by Thuler et al. [8].

As it is displayed in Table 1, almost all the Bi core-levels in the Bi<sub>2</sub>Se<sub>3</sub> are shifted by about the same amount (0.8–1.0 eV) with respect to those transitions in the pure metal, except for the Bi4*d*<sub>3</sub> transition which is only 0.2 eV shifted. So far, we have not found any explanation for this anomalous

result. As can be seen in Fig. 1, both Bi4*d* transitions show very well resolved peaks either in the Bi and in the compound spectrum. As the measurements were carried out at the same experimental setup (the samples were fixed together on the sample holder) we believe that this result is not an experimental artifact. The Se3*d* levels show a shift of about –1.3 eV. These results are different from those reported by

Table 1

Peak positions (in eV-binding energy) in the XPS spectra of the Bi, Se and Bi<sub>2</sub>Se<sub>3</sub> samples<sup>a,b,c</sup>

Transitions	Peak position: Bi (±0.1 eV)	Peak position: Se (±0.1 eV)	Peak position: Bi <sub>2</sub> Se <sub>3</sub> (±0.1 eV)	Chemical shift (±0.1 eV)	Data (eV)	Ref. *: Bi <sub>2</sub> Se <sub>3</sub> *: Bi,Se
Bi5d <sub>5</sub>	23.5	–	24.5	1.0	24.55	[8]*
Bi5d <sub>3</sub>	26.6	–	27.4	0.8	27.61	[8]*
Bi4f <sub>7</sub>	156.6	–	157.6	1.0	156.8	[22]*
Bi4f <sub>5</sub>	161.9	–	162.9	1.0	162.1	[22]*
Bi4d <sub>5</sub>	439.8	–	440.7	0.9	440.8	[22]*
Bi4d <sub>3</sub>	464.0	–	464.2	0.2	465.0	[22]*
Bi4p <sub>3</sub>	678.2	–	679.2	1.0	679.7	[22]*
Se3d <sub>5</sub>	–	54.5	53.3	–1.2	52.95	[8]*
Se3d <sub>3</sub>	–	55.3	54.0	–1.3	53.80	[8]*

<sup>a</sup> Monochromatized Al K $\alpha$  radiation was used.<sup>b</sup> The chemical shift was obtained by subtracting the energy peak position of the elements from that of the Selenide.<sup>c</sup> In the last two columns values of binding energies taken from the literature are shown.

Thuler et al. [8]. They found a value of  $-1.68$  eV for the Se3d and 0.66 eV for the Bi5d. However, their results were obtained by comparing their measurements with published data. Our results stem from measurements with the same experimental setup and therefore we believe that they are more reliable. The chemical shifts presented in Table 1 show that a charge transfer indeed takes place and therefore, the bonds in the crystal have some ionic character. This is in agreement with a band structure calculation that has predicted the metal atoms to be positively charged and the chalcogen atoms to be negatively charged [1].

The density of valence states (DOVS) of the Bi<sub>2</sub>Se<sub>3</sub> (Fig. 2) exhibits two well defined regions. One is at low binding energy where two features can be distinguished. The most prominent feature in this region is at 2.1 eV. If we assume the suggestion that the valence band spectrum of the compound can be ‘constructed’ from the elemental contributions [8,14] we must point out that in the pure Se the corresponding peak is at 1.9 eV and in Bi it is at 2.3 eV [13]. The curve labelled ‘2Bi+3Se’ in Fig. 2 was obtained by weighing the elemental spectra of Bi and Se and then adding them up. Therefore, it seems reasonable to associate this band to a mixture of *p*-like DOVS of Se and Bi atoms and not only to chalcogen atom lone-pair orbitals, as has been suggested for similar compounds [14,21]. In addition, the shoulder at about 4.4 eV in Bi<sub>2</sub>Se<sub>3</sub> must reflect the Bi6*p* and Se4*p* bonding bands, since the elemen-

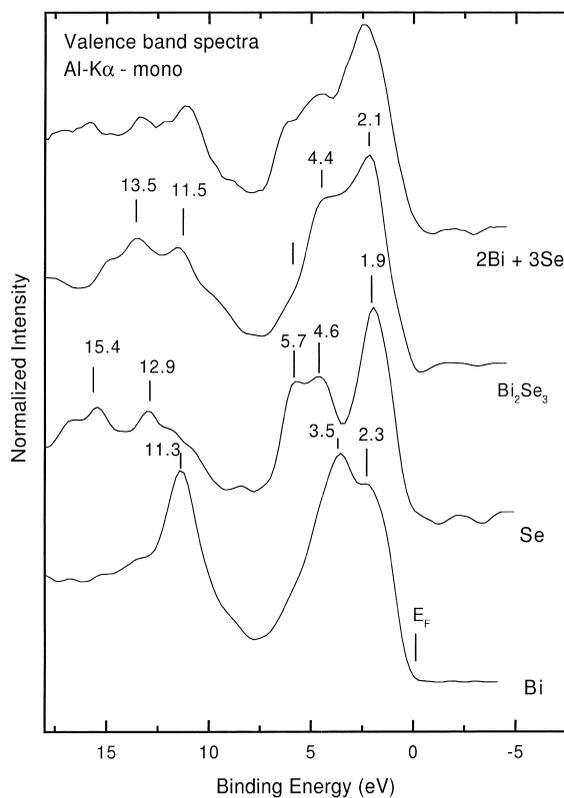


Fig. 2. Photoelectron spectra in the region of the valence band for the compound Bi<sub>2</sub>Se<sub>3</sub> and the elements Bi and Se. The curve ‘2Bi+3Se’ is the result of weighing the Bi and Se spectra.

tal valence band spectra show maxima at 3.6 eV in Bi and at 4.6–5.7 eV in Se. In the high binding energy region of the DOVS the  $\text{Bi}_2\text{Se}_3$  spectrum shows two well defined peaks at 11.5 and 13.5 eV. Again, looking at the valence spectra of the pure elements, we can see that these features must be associated to the  $\text{Bi}6s$  and  $\text{Se}4s$  bonding orbitals, respectively. This interpretation of the DOVS spectra is in agreement with the results from calculations based on a molecular orbital model constructed with the largest  $pp\sigma$  interaction between the closest neighbors [1,15]. These band calculations showed that the valence and conduction bands consist of the metal and calcogen  $p$ -orbitals, while the bands arising from the valence  $s$ -orbitals occur about 10.9 eV below the valence band maximum and that the bottom of the conduction band is about 1.3 eV above the Fermi level. These results agree well with our observations.

The EELS spectra of the  $\text{Bi}_2\text{Se}_3$  (0001) surface presented in Fig. 3 show that when increasing the

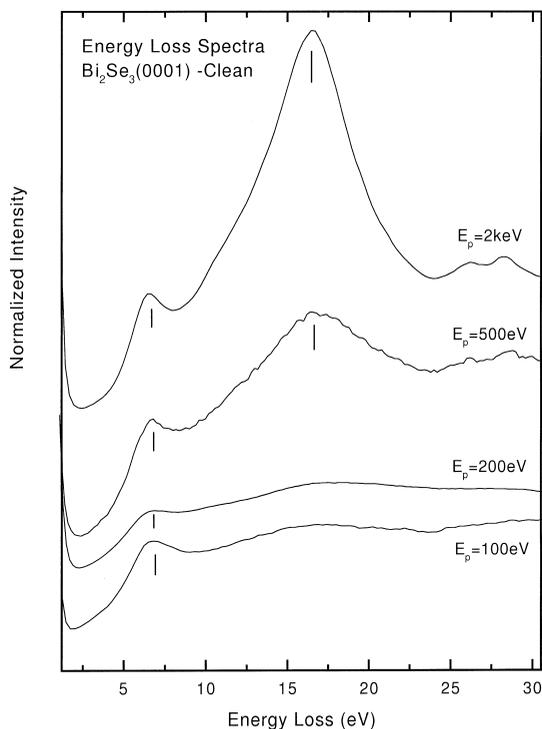


Fig. 3. Energy Loss Spectra in  $\text{Bi}_2\text{Se}_3$  (0001) at different incident electron beam (primary) energies.

primary energy ( $E_p$ ), new loss features appear in the spectrum. The lowest energy loss at 3.2 eV at  $E_p = 2$  keV is better defined as the primary energy is increased from 400 eV (see Fig. 4). It may be associated to a transition from the top of the valence band to the conduction band (Fig. 2). However this loss is not seen at  $E_p = 200$  eV, but one loss feature seems clearly defined at 3.5 eV in the  $E_p = 100$  eV spectrum. This fact suggests that this loss may have a different origin from the loss observed at 2 keV. It may be associated to a surface state transition or a surface resonance. At  $E_p \approx 400$  eV other new losses appear in the spectra that become very well defined as the energy is increased. The feature at about 16.5 eV corresponds to a wide peak in the integrated spectra (Fig. 3) and it is the largest peak at  $E_p = 2$  keV. We assign this loss to a bulk plasmon. Two other losses are observed at about 25.8 and 28.5 eV. These structures correspond to the transitions from the core levels  $\text{Bi}5d5$  and  $\text{Bi}5d3$  to the bottom of the conduction band. The remained observed losses occur at about 10.8 and 6.4 eV. As the former is not present at low primary energy we cannot associate it to a surface loss. In fact, it may come from the interband transition of  $\text{Bi}6s$  to the conduction band.

The loss at 6.4 eV shows an interesting behaviour. In the spectra of Fig. 3 it corresponds to the second most intense peak which seems not to change with increasing  $E_p$ . Looking at Fig. 2, we can see that this loss occurs at an energy corresponding to a minimum in the valence density of states. Then it can not be associated to an interband transition. As it is the only loss that is very well defined at low primary energy, we suggest that this feature has its origin in an excitation occurring at the surface, possibly a surface plasmon. To the authors' knowledge there is no published EELS work on the  $\text{Bi}_2\text{Se}_3$  (0001) surface and therefore we cannot compare our results, but reflectivity measurements [16] show good agreement with the losses at 3.5 and 6.4 eV.

Furthermore, one can get some information about the bottom of the conduction band in the compound by considering the energies of the  $\text{Bi}5d$  transitions as measured by XPS and EELS. XPS gives the energy with respect to the Fermi level and the EELS gives the energy for the transition of the  $\text{Bi}5d$  level to the bottom of the conduction band. Therefore, the difference between these two energies gives the position

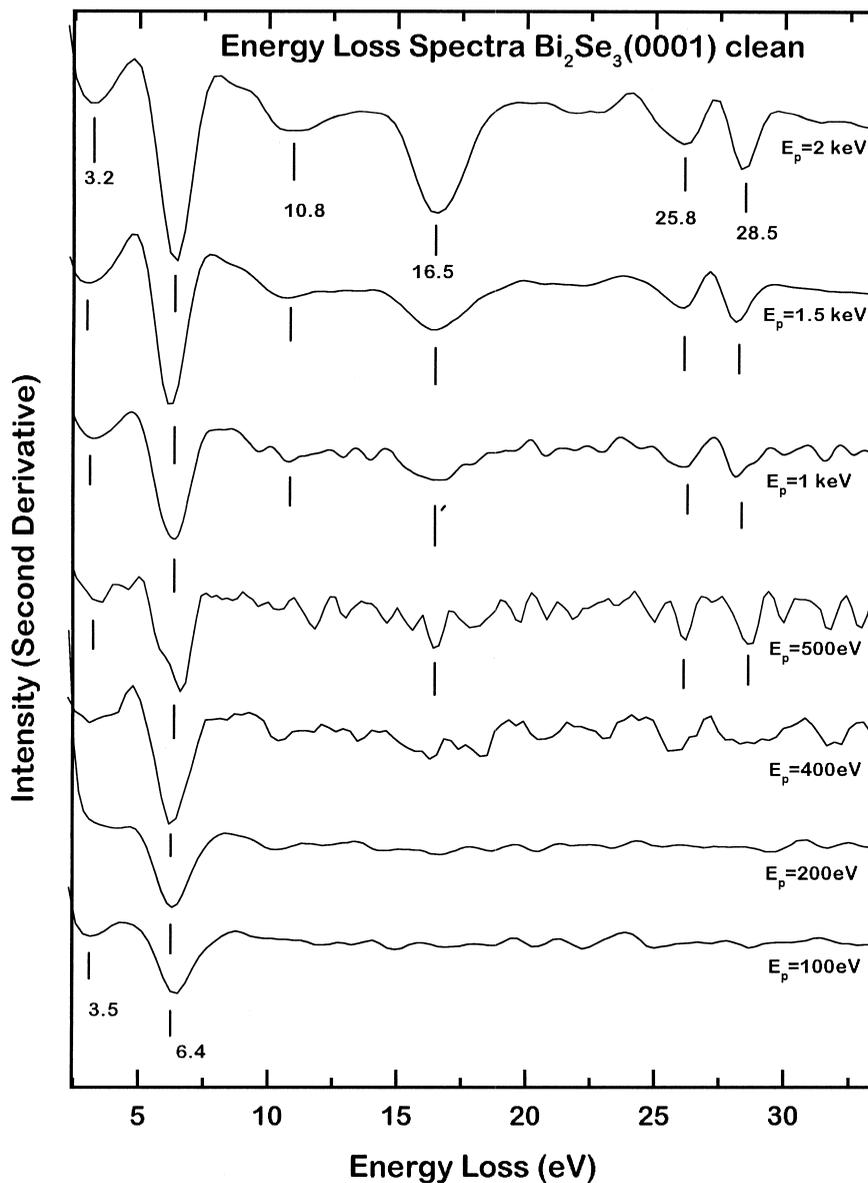


Fig. 4. Second derivative of Energy Loss Spectra in  $\text{Bi}_2\text{Se}_3(0001)$  at different incident electron beam (primary) energies. The loss at 16.5 eV is the bulk plasmon and the loss at 6.4 eV is the surface plasmon.

of the minimum of the conduction band above the Fermi level. The values of the present work result in a mean difference of 1.2 eV that should correspond to the bottom of the conduction band in  $\text{Bi}_2\text{Se}_3$ . This result is in good agreement with that obtained in band calculations [1] where it was found that the conduction band consists only of the metal  $p$ -orbitals

and its minimum is about 1.3 eV above the Fermi level. This result is also consistent with the loss feature observed at 3.2 eV (Fig. 4) that may be due to the transitions from the top of the valence band to the bottom of the conduction band. As can be seen in Fig. 2 the main feature in the top of the valence band occurs at 2.1 eV below the Fermi level. Then the

transition from this state to the bottom of the conduction band requires an energy of 3.3 eV. This value corresponds to the loss occurring at low energy in the Loss spectrum (Fig. 4).

The EELS spectra at  $E_p = 2$  keV of polycrystalline Bi and Se have some similarities with that of the  $\text{Bi}_2\text{Se}_3$ . As is shown in Fig. 5, the Bi5*d* transitions are observed at 24.8 and 28.1 eV and a loss due to a

bulk plasmon excitation, occurs at 14.7 eV. In the Se spectrum a bulk plasmon loss is observed at 19.8 eV. These plasmon losses agree well with results in Refs. [17–20]. Although the losses associated to the Bi5*d* transitions occur at loss energies higher than the binding energy observed in the XPS experiment, the spin-orbit splitting is almost the same. In  $\text{Bi}_2\text{Se}_3$  the spin-orbit splitting measured by XPS is 2.9 eV (Table

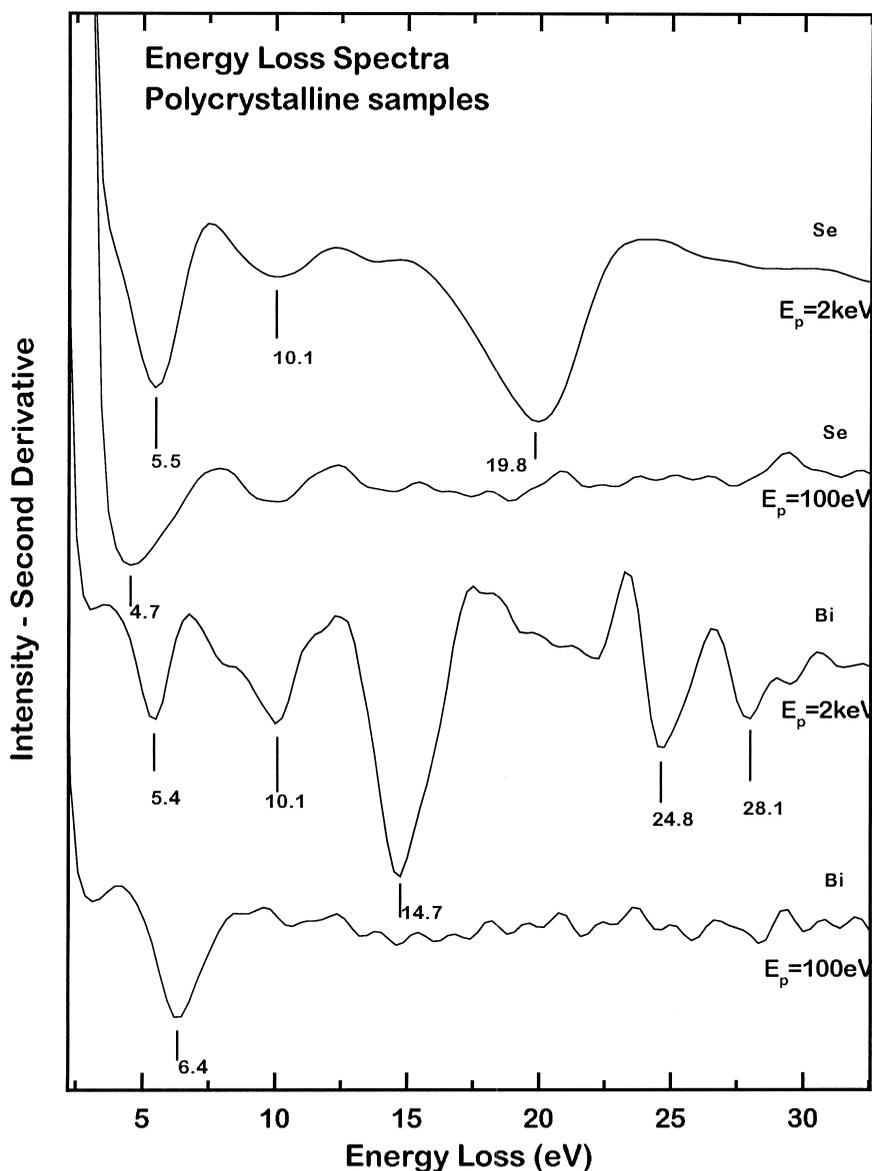


Fig. 5. Second derivative of Energy Loss Spectra of polycrystalline Bi and Se at different incident electron beam (primary) energies.

1) and in the Loss spectrum it is 2.7 eV. There exist two other loss features in the EELS spectra of Bi and Se. The first one appears at 5.4(5.5) eV in Bi(Se). This loss has been also observed in Electron Energy Loss experiments in the transmission mode, but it has never been interpreted [17–19]. As in  $\text{Bi}_2\text{Se}_3$ , this loss corresponds to a prominent peak in the EELS spectrum. In the case of Bi, according to the valence density of states, there is no possible interband transition at this energy. Based on the arguments used in the interpretation of the  $\text{Bi}_2\text{Se}_3$  spectrum (see above) we believe that this loss in both Bi and Se comes from some surface process. Wehenkel and Gauthe [19] have suggested that for Bi, in spite of the surface plasmon condition (real part of the dielectric constant = -1) being fulfilled at 6 eV, a surface plasmon must occur at 11 eV due to an important contribution of the imaginary part of the dielectric constant. We also observe a loss feature at 10.1 eV in Bi, but this loss does not appear at low primary energy and therefore it can not be associated to a surface process. In the EELS spectrum it appears only as a shoulder on the left hand side of the bulk plasmon peak. Therefore, we suggest that in fact, the loss at about 5.5 eV in both Bi and Se corresponds to an excitation of a surface plasmon as the classical surface plasmon condition predicts.

#### 4. Conclusions

In summary, we have presented results of XPS and EELS measurements of the  $\text{Bi}_2\text{Se}_3$  (0001) surface and of Bi and Se (polycrystalline) carried out at the same experimental setup. The core level chemical shifts obtained show that a charge transfer occurs in  $\text{Bi}_2\text{Se}_3$  that makes the metal atoms more positive and the chalcogen atoms more negative. The density of valence states in  $\text{Bi}_2\text{Se}_3$ , as measured by XPS, seems to support the suggestion of Bishop and Shevchik [14] that it can be constructed by combining the spectra of the constituent elements, as can be easily seen in Fig 2. The EELS spectra allows us to identify the bulk plasmon for all the three materials: 16.5 eV for  $\text{Bi}_2\text{Se}_3$ , 14.7 eV for Bi and 19.8 eV for Se. The  $\text{Bi}5d5$  and  $\text{Bi}5d3$  interband transitions in  $\text{Bi}_2\text{Se}_3$  have been also identified. By comparison of the energies of these transitions as measured by XPS

and EELS it was possible to determine the position of the bottom of the conduction band of the compound to be 1.2 eV above the Fermi level. In addition, the EELS spectra shows evidence that the losses at 6.4 eV in the compound and at 5.4(5.5) eV in Bi(Se) have their origins in some surface process, and probably they can be associated to surface plasmons. Also, the loss feature observed at 3.2–3.5 eV in the  $\text{Bi}_2\text{Se}_3$  spectra may result from an overlap of an interband and a surface state (or surface resonance) transition. On the other hand, the EELS spectra of the compound did not show any other feature that could be clearly associated to the (0001) surface. This may be a consequence of the fact that this surface, at room temperature, does not show reconstruction and it is expected that only a very small relaxation of the surface atoms may occur [18]. In fact, the properties of the (0001) surface of the  $\text{Bi}_2\text{Se}_3$  have not been yet investigated and what is known is that it is a very stable surface and it shows a very sharp LEED pattern with the expected symmetry. However, in spite of the stability this surface must have important properties since experiments of metal intercalation in the van der Waals gap of this compound have shown different behaviours for different metals [9–12]. As the van der Waals gaps are limited by two (0001) surfaces (Se-terminated) the properties of this surface must play an important role in the metal intercalation process. Therefore, more studies on this surface are necessary. An atomic structure determination of this surface by LEED analysis and a calculation of the loss function for the three materials are underway.

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