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Abstract. The electronic structure of the layered semiconductor InSe along Δ is studied by spin resolved photoelectron spectroscopy using circularly polarized radiation from the BESSY 6.5 m normal incidence monochromator beamline. The experiments were performed in the highly symmetric set-up of normal incidence and normal emission. The photon energies were varied between 7.8 eV and 18 eV. The spectra show a pair of weakly dispersing peaks arising via direct transitions from valence-band states with symmetries Δ_9^5, Δ_9^6 and Δ_7^5, Δ_8^6. Our data determine the spin–orbit splitting in the valence bands to be $\Delta E_{so} = 0.3 \pm 0.1$ eV. In addition the existence of a gap in the unoccupied bands along Δ above the fundamental gap is proven. Correlating measured peak positions and calculated bands (by a linearized augmented-plane-wave method) require an energy-dependent correction of the valence-band positions toward higher binding energies. The changing sign of photoelectron spin polarization reveals that between 7.6 eV and 12.5 eV above the valence-band maximum unoccupied states with symmetries Δ_7^5, Δ_8^6 and Δ_9^5, Δ_9^6 exist.

1. Introduction

Spin resolved photoelectron spectroscopy using circularly polarized radiation is an essential tool in the study of the electronic structure of non-magnetic solids and their surfaces [1–4]. The spin-dependent effects observed in this spectroscopy originate from spin–orbit coupling. They depend on the symmetry of the electronic states involved via the relativistic dipole selection rules [5, 6]. Spin resolved photoelectron spectroscopy using circularly polarized radiation has been successfully used to investigate the valence and the conduction bands of Pt(111) [4], Ir(111) [7], Xe(111) [8], Pd(111) [9] and WSe_2(0001) [10]. In these experiments, the advantage of the technique has been demonstrated by determining band symmetries.

In this paper the method is applied to the study of InSe. InSe is a semiconductor with layered crystal structure belonging to the non-symmorphic space group D_{6h}^4 with strong covalent intralayer bonding, but only weak bonding between adjacent layers [11, 12], often

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referred to as van der Waals type. The (0001) surface of InSe is formed by chemically saturated Se layers which are hexagonal closed packed and therefore show C_{6v} point symmetry [13]. Between two Se sandwich layers a covalently bonded In–In layer is introduced. The lattice parameters for InSe are $a = 4.05$ Å and $c = 16.93$ Å [12]. In this paper we report on the experimental and the theoretical study of the relativistic valence-band structure of InSe(0001) along Δ, i.e. perpendicular to the (0001) planes, and on the symmetry characterization of the valence bands as well as the unoccupied bands.

2. Experiment

The experiment was performed at the BESSY 6.5 m normal incidence monochromator beamline using photon energies from 7.8 eV to 18 eV. The apparatus has been described previously [1, 2]. All data were taken in the highly symmetric set-up of normal incidence of the circularly polarized synchrotron radiation and normal emission of the electrons. The overall energy resolution (photons plus photoelectrons) was better than 350 meV. The spin-polarization component P parallel to the spin of the incident photons was measured by Mott scattering at 100 keV.

A clean (0001) surface of InSe was prepared by cleaving in ultra-high vacuum (UHV) (base pressure $p < 2 \times 10^{-10}$ mbar). The surface structure was monitored by low-energy electron diffraction (LEED).

Due to an acceleration voltage of 5 eV between the sample and the spectrometer the acceptance cone of our spectrometer depends slightly on the kinetic energy E_{kin} of the electrons. While electrons with $E_{kin} = 1$ eV are accepted within a cone of $\pm 4°$, this cone is narrowed down to $\pm 3°$ for higher electron energies [14, 15].
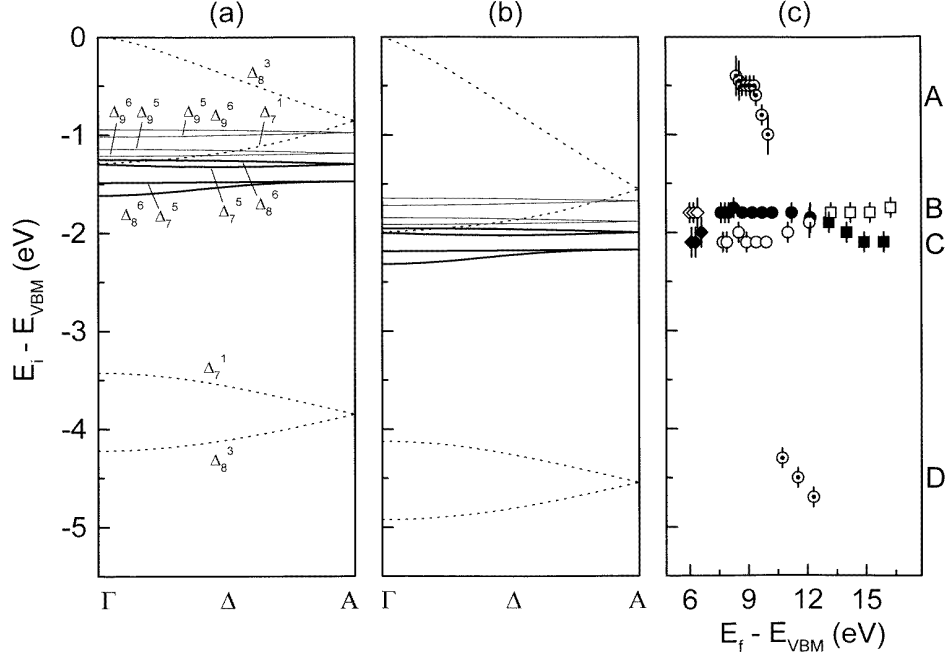
3. Bandstructure calculation

We calculated the valence-band structure of InSe using the full-potential linearized augmented-plane-wave (LAPW) method. We added 'local orbitals' for the high-lying 'semicore' states to improve the linearization and used the WIEN97 package [16]. Exchange and correlation is treated within the generalized gradient approximation [17] and spin–orbit coupling is added in a second variation step. We used the experimental lattice parameters presented in [12], but optimized the internal z-parameters of In ($z = 0.1675$) and Se ($z = 0.0917$), which differ significantly from the old experimental data [11]. It should be noted that the position of the weakly dispersing bands along Δ depends sensitively on those internal parameters.

Figure 1(a) shows the calculated relativistic valence-band structure of InSe (0001) in Δ direction with symmetry labels. The energy zero is set to the valence-band maximum (VBM) (Γ point). The symmetry assignments for these valence bands were obtained by starting with labels of the non-relativistic bandstructure of InSe(0001) and then using a group theoretical treatment. In the non-relativistic valence-band structure the weakly dispersing bands along Δ have been assigned to Δ_5 or Δ_6 symmetry (single-group representation, for the symmetry labels we use the notation of Koster *et al* [18]) while the strongly dispersing bands have been assigned to Δ_1 or Δ_3 symmetry [11]†‡. Due to the spin–orbit coupling bands with symmetries Δ_5 and Δ_6 are split into bands with symmetries Δ_7^5, Δ_9^5 and Δ_8^6, Δ_9^6, respectively (double-group representation). Bands with symmetries Δ_1 and Δ_3 are transformed into Δ_7^1 and Δ_8^3 bands,

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† Symmetry labels in [11] were given in the points Γ and A. Symmetry labels in Δ-direction were obtained by compatibility relations between Γ (A) and Δ.

‡ Our notation Δ_3 in single-group representation corresponds to Δ_2 in [11].

Figure 1. (a) Calculated relativistic valence-band structure of InSe(0001) in Δ-direction. The VBM is chosen as the energy zero. For symmetry assignment see text. Broken curves indicate bands of symmetries Δ_7^1, Δ_8^3. Thin and thick full lines indicate bands with symmetries Δ_9^5, Δ_9^6 and Δ_7^5, Δ_8^6, respectively. (b) The calculated bands have to be shifted by 0.7 eV to higher binding energies. The uppermost band Δ_8^3 is adjusted to connect the band Δ_7^1 at point A with VBM at point Γ. (c) The data points have been obtained from the partial intensities I_+ and I_-, partly shown in figure 2. For peak B and peak C the data points represented by full symbols correspond to measured peaks with positive P while open symbols correspond to measured peaks with negative P. For peaks A and D dotted circles correspond to $P = 0$.

respectively [18, 19]. The subscript and superscript indicate the double- and single-group representations respectively. Broken curves indicate bands with symmetries Δ_8^3, Δ_7^1. Thin and thick full lines indicate bands with symmetries Δ_9^5, Δ_9^6 and Δ_7^5, Δ_8^6 respectively. (Figures 1(b) and (c) will be discussed in the next section.)

4. Results and discussion

Typical spin-separated photoemission spectra in energy distribution curve (EDC) mode from InSe(0001) measured at normal incidence and normal emission with photon energies ranging from 7.8 eV to 18 eV are presented in figure 2. All spectra are normalized with respect to the BESSY ring-current and the monochromator transmission. The spectra are given with initial state energies referred to the valence-band maximum defining the zero of the energy [12, 20]†. The spin-separated partial intensities I_+ and I_- given in figure 2 by thick and thin curves, respectively, are connected with the electron spin polarization P and the (spin-independent)

† In [20] all energies are referred to the Fermi energy, $E_F = 0$. For our InSe the valence-band maximum lies 1 eV below E$_F$.
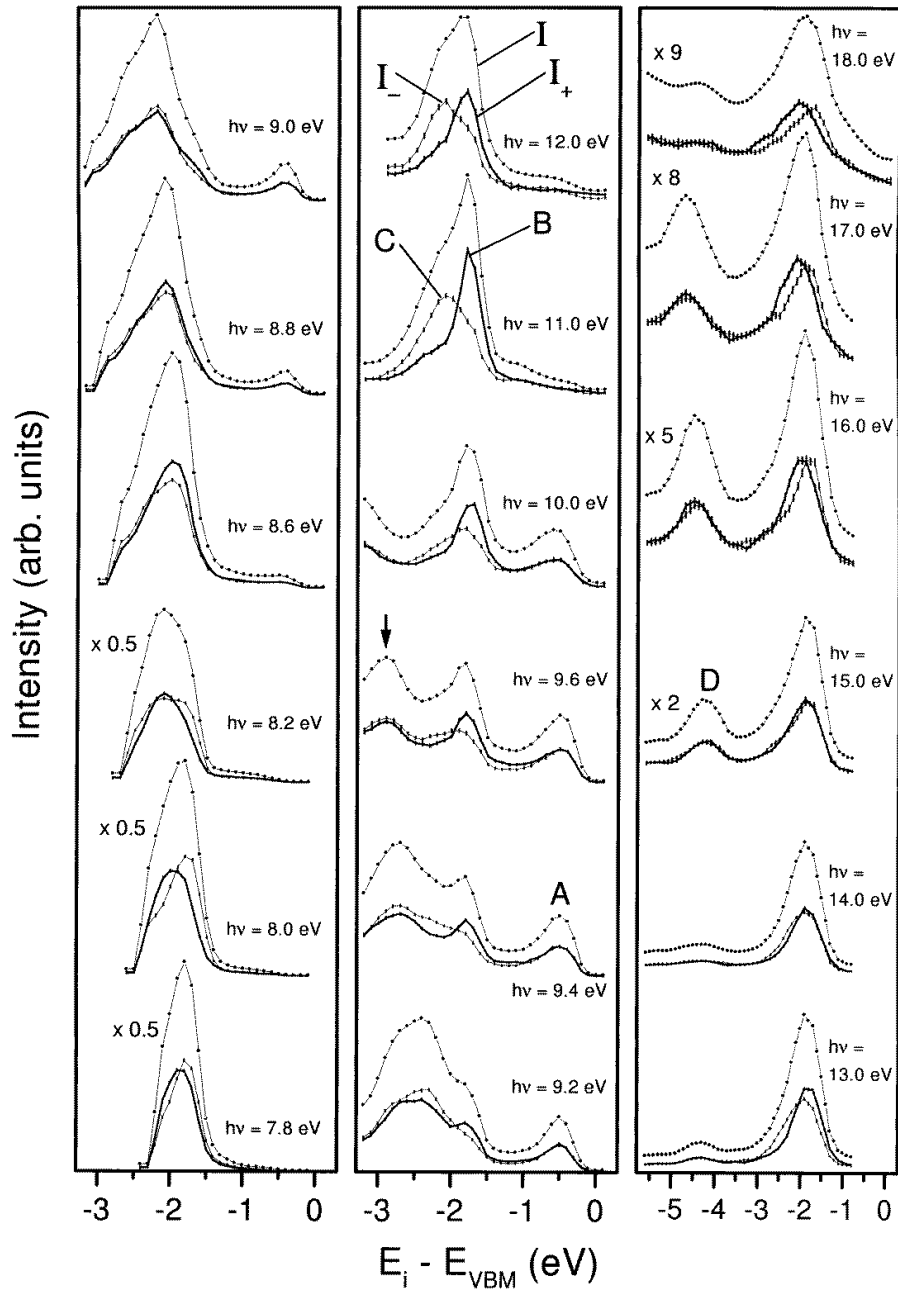
Figure 2. Selected spin-separated photoelectron spectra in EDC-mode from InSe(0001) for photon energies between 7.8 eV and 18 eV. Besides the total intensity $I = I_+ + I_-$ the two partial intensities I_+ and I_- totally spin polarized parallel (bold full curve) and antiparallel (light broken curve) to the photon spin, respectively, are displayed. A–D denote observed peaks. The arrow denotes a final-state peak. The points given in I are data points without error bars. They are connected by lines. The vertical error bars given in I_+ and I_- represent the measured data with the single statistical uncertainties included. Errors due to the calibration of the polarization sensitivity of the Mott detector $S_{eff} = -0.25 \pm 0.01$ are neglected.

total intensity $I = I_+ + I_-$ by

$$I_\pm = \tfrac{1}{2} I (1 \pm P). \tag{1}$$

A positive P means that the preferential spin direction of the electrons is parallel to the photon spin. Correspondingly, I_+ and I_- are the partial electron intensities totally polarized parallel and antiparallel to the photon spin, respectively.

As a general feature of the spin-separated spectra there is one spin polarized main peak in each of the partial intensities I_+ and I_-: for I_+ at the binding energy -1.8 eV (peak B) and for I_- at the binding energy -2.1 eV (peak C). These two peaks show nearly no dispersion. The difference of the binding energy for correlated peaks in I_+ and I_-, for example 0.3 ± 0.1 eV between peak B and peak C, corresponds to the spin–orbit splitting ΔE_{so} of the valence-band states involved in the emission process. Although the magnitude of this spin–orbit splitting is comparable with the peak width, it is possible to determine this spin–orbit splitting of initial states via the spin resolved photoelectron analysis. Similarly, peaks B and C have been observed at the layered semiconductor GaSe [21] with the same crystal structure as InSe. For GaSe, from the splitting of peak B and peak C, the spin–orbit splitting of the corresponding initial states has also been determined to be $\Delta E_{so} = 0.3$ eV. It is important to note that this identical spin–orbit splitting for InSe and GaSe is due to identical initial states, that is in InSe as well as in GaSe, both peak B and peak C are due to emission from states derived from Se $4p_{xy}$ orbitals [22]. The 0.3 eV spin–orbit splitting in the spin resolved experiments is in good agreement with calculated data [11].

The peak marked by an arrow, for example at $E_i = -2.9$ eV for the photon energy 9.6 eV in figure 2, is a so-called final-state peak. Such peaks arise due to a high density of states in the unoccupied bands. They can easily be distinguished from peaks ascribed to direct transitions from (occupied) valence-band states, as in these peaks the binding energy decreases by amounts equal to the increments of the photon energy [12].

As far as peak B is concerned, it shows negative spin polarization below a photon energy of 8.2 eV which disappears above a photon energy of 8.6 eV. With further increases in photon energy it appears again, when photon energies are above 9.4 eV with positive electron spin polarization. This disappearance of peak B for photon energies ranging from 8.6 eV to 9.4 eV can be explained by a gap of width 0.8 ± 0.3 eV within the unoccupied bands along Δ above the fundamental gap. A further change of sign of the electron spin polarization is observed above a photon energy of 16 eV. Peak C shows the same behaviour with respect to intensity, but with the opposite sign of the spin polarization. The physical mechanism of the changing sign will be discussed later.

Peaks A and D are observed at binding energies between -0.4 eV and -1.0 eV, and between -4.3 eV and -4.7 eV, respectively. While peak A exists only for photon energies between 8.8 eV and 10.5 eV (not shown in figure 2), peak D is present for photon energies between 15 eV and 17 eV. Peaks A and D are present in I_+ as well as in I_- by the same weight, that is the degree of spin polarization $|P|$ is zero in peak A and peak D.

In order to explain our spectra we use the calculated relativistic valence-band structure of InSe displayed in figure 1(a). As a first step, to obtain information about the symmetries of the initial states investigated by our measurements, a comparison between the calculated bands displayed in figure 1(a) and the measured data displayed in figure 1(c) was performed. In figure 1(c) the initial-state energies corresponding to the measured peaks are displayed versus the final-state energy (E_f) above VBM. The data points have been obtained from spin-separated spectra shown in part in figure 2. For the peaks B and C (figure 1(c)) the data points represented by full symbols correspond to measured peaks with positive P while open symbols correspond to measured peaks with negative P. For the peaks A and D given by dotted circles,

no spin polarization is found. To align the measured and calculated data given in figures 1(a) and (c), the calculated valence bands have to be rigidly shifted by 0.7 eV to higher binding energies. The uppermost band Δ_8^3 is adjusted to connect the band Δ_7^1 at point A with VBM at point Γ. The resulting bandstructure is shown in figure 1(b). We attribute the applied shift to the self-energy corrections [3, 23] not considered in the LAPW calculation. It is worth noting that another relativistic valence-band calculation for InSe using a different method [24] shows nearly the same band positions as given in figure 1(a), but the upper Δ_7^1, Δ_8^3 bands are well separated from the flat Δ_7^5, Δ_8^6, Δ_9^5 and Δ_9^6 bands.

Knowledge of the unoccupied part of the band structure is necessary to interpret the photoelectron spin polarization measured in our experiments. As a first step we assume that the unoccupied bands of InSe are free-electron bands [20]. As indicated in [25], the symmetry of the free-electron bands is not unique in the non-symmorphic space group. In the particular case of the Δ-direction the selection of Δ_7^1 and Δ_8^3 as possible symmetries of the final-state bands has been verified.

Firstly, we discuss the spectra measured for photon energies below 8.2 eV and above 16 eV. Peak B is due to excitation from the initial states Δ_9^6, Δ_9^5 (see figures 1(b) and (c)) to the final states Δ_8^3, Δ_7^1 and by the relativistic dipole selection rules [19]† is predicted to have the spin polarization $P = -1$ (excitations from the initial states Δ_7^1, Δ_8^3 to the final states Δ_7^1, Δ_8^3 are not allowed) while peak C is due to excitation from the initial states Δ_8^6, Δ_7^5 to the final states Δ_8^3, Δ_7^1 and is predicted to have the spin polarization $P = +1$. Having in mind that electrons from neighbouring peaks with wrong spin polarization are mixed in, these predictions are satisfied here for both peak B and peak C. For photon energies between 9.4 eV and 16 eV, however, a different behaviour is observed. Δ_7^5, Δ_8^6, Δ_9^5 and Δ_9^6 final states appear to be involved in excitation as well as in emission.

This situation is evident from our spin resolved constant initial-state (CIS) spectra for two different initial states corresponding to peak B and peak C at $E_i = -1.8$ eV and $E_i = -2.1$ eV, respectively. The total intensities I and the corresponding electron spin polarizations P versus the final-state energy (E_f) above VBM are presented in figure 3(a) and in figure 3(b) respectively. The total intensities I are normalized with respect to the BESSY ring-current and the monochromator transmission. As shown in the upper part of figure 3(a) our CIS spectra are divided into three regions by considering the gap in the unoccupied bands, the intensity and the electron spin polarization: region I, from vacuum level (5.75 ± 0.1 eV) to 6.8 eV above VBM; region II, from 7.6 eV to 12.5 eV; region III, above 12.5 eV. In region III all intensities become much flatter. This behaviour corresponds to a nearly free-electron band at energies above 12.5 eV [26]. As shown in figure 3(b) in the regions I and III, the electron spin polarizations for the peaks B and C show good agreement with the group theoretical prediction for total symmetric final-state bands with symmetries Δ_7^1, Δ_8^3 discussed above. However, in region II our measurements for peaks B and C reveal opposite electron spin polarization.

This discrepancy indicates that limitations of the model of free-electron, final-state bands exist for the system studied here. For the peak B, in order to obtain positive electron spin polarization transitions from the initial states Δ_9^6, Δ_9^5 to pure final states or parts of hybridized final states with symmetries Δ_7^5, Δ_8^6 are demanded by relativistic dipole selection rules [19]. Normal emission out of these states is not allowed as they are not totally symmetric. But as it was shown for Xe(111) crystals emission from such states is possible inside the acceptance cone of our spectrometer [14]. This off-normal emission process results in the measured peaks and spin polarizations present in region II. For peak C correspondingly final states of the symmetries Δ_9^5, Δ_9^6 are required to obtain the measured negative electron spin polarization.

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† In using table 2 of [19] it must be recognized that their definition of $P > 0$ is opposite to our definition.
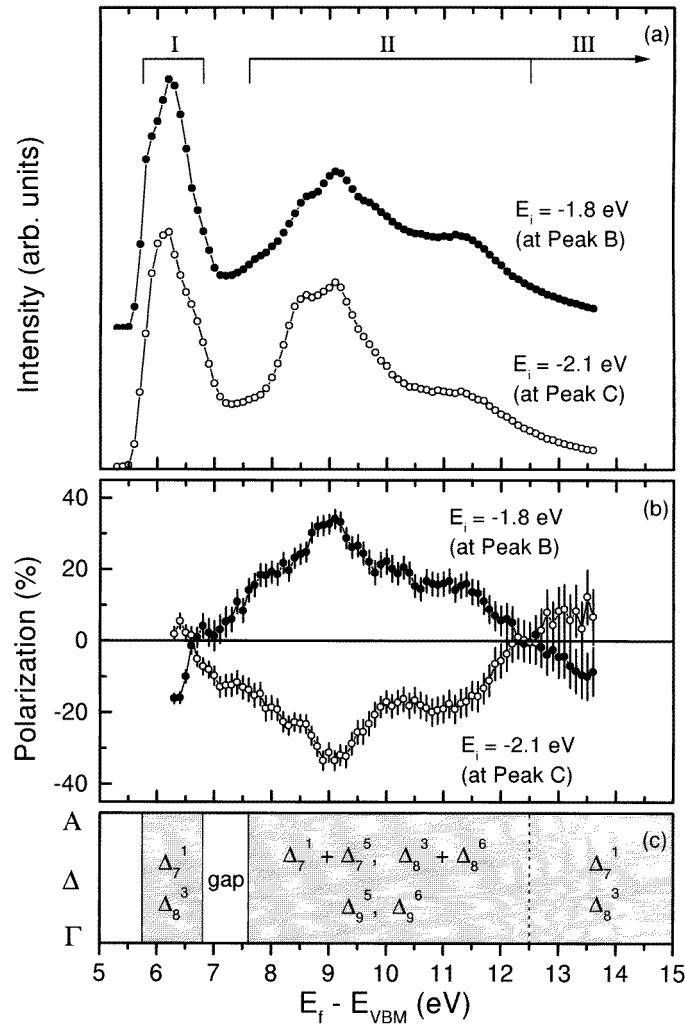
Figure 3. Constant initial-state spectra from InSe(0001) for two different initial states, peaks B and C in the EDC's of figure 2. The uncertainty in energy of our data is ± 0.2 eV. (a) Total intensity. (b) Electron spin polarization. (c) Assumed symmetries of the unoccupied bands for InSe (0001) in Δ-direction. With respect to the discussion the energy interval is divided into three regions on the base of the gap, the intensity and the electron spin polarization: region I, from vacuum level 5.75 ± 0.1 eV above VBM to 6.8 eV; region II, from 7.6 eV to 12.5 eV and region III, above 12.5 eV. The full and open circles in the total intensity (a) represent the measured data. They are connected by lines. In (b) the vertical error bars give the single statistical uncertainties of the measured spin polarization. In addition there is a calibration error of 4% of the given values.

Therefore flat unoccupied bands of symmetry Δ_7^5, Δ_9^5 or Δ_8^6, Δ_9^6 have to be supposed at energies between 7.6 eV and 12.5 eV above VBM. It is worth noting that in figure 2, for example in the spectrum measured at the photon energy 11 eV, peak C in the partial intensity I_- has a significant shoulder at the position of peak B. This shoulder may be an evidence for the final states to be hybrids with parts of symmetry Δ_7^1, Δ_7^5 or Δ_8^3, Δ_8^6. In a two-step model the mechanism resulting in the shoulder may be as follows. In the first step electrons from initial

states with symmetries Δ_9^5 or Δ_9^6 are excited to these hybridized final states. In the second step off-normal emission via the acceptance cone from the part Δ_7^5 or Δ_8^6 in the hybrids results in peak B present in I_+. In addition, the total symmetric part Δ_7^1 or Δ_8^3 via normal and off-normal emission results in a (small) peak present in I_- just at the binding energy of peak B. However, the shoulder may also be due to the excitations starting from the Δ_7^1 band rigidly shifted with the flat bands Δ_9^5, Δ_9^6.

The measured peaks A and D located between initial energies of -0.4 eV and -1.0 eV and -4.3 eV and -4.7 eV, respectively, display similar effects. Transitions from the bands Δ_8^3, Δ_7^1 located in the vicinity of the binding energies assigned to the peaks A and D are allowed only for bands with symmety Δ_7^5, Δ_8^6 or Δ_9^5, Δ_9^6. Therefore, the influence of the flat unoccupied bands of symmetry Δ_7^5, Δ_9^5 or Δ_8^6, Δ_9^6 assumed for energies ranging from 7.6 eV and 12.5 eV above VBM also could explain the existence of peaks A and D.

This situation is schematically summarized in figure 3(c). While in regions I and III, bands with symmetry Δ_7^1 or Δ_8^3 are sufficient to explain the measured P, in region II hybridized bands with symmetry Δ_7^1, Δ_7^5 and Δ_8^3, Δ_8^6 and the bands with symmetry Δ_9^5 or Δ_9^6 have to play an important role. A similar behaviour of the peaks A–D has been observed at the layered semiconductor GaSe [21] having identical crystal structure. In particular, in the energy range II where the change of sign is also observed, no intensities have been detected in photoemission from GaSe(0001) for Ga $3d_{5/2}$ and $3d_{3/2}$ initial states [21], which further supports the assumption of d-derived flat bands with symmetries Δ_7^5, Δ_9^5 or Δ_8^6, Δ_9^6 dominating in the region II.

From the experimental point of view, comparison with a calculated, relativistic bandstructure for the unoccupied bands is of great interest. Bandstructure calculations for the unoccupied bands give spatial parts (single-group representation) Δ_1, Δ_3 as well as Δ_5, Δ_6 for energies between 7.6 eV and 12.5 eV. However, a quantitative comparison is not possible at the present state of calculation and experiment.

5. Conclusion

In conclusion, the bandstructure of InSe(0001) in Δ-direction has been investigated by means of spin resolved photoemission using circularly polarized synchrotron radiation. The spectra show a pair of weakly dispersing peaks arising via direct transitions from valence-band states with symmetries Δ_9^5, Δ_9^6 and Δ_7^5, Δ_8^6. Our data give direct information about the spin–orbit splitting ΔE_{so} between pairs of split valence bands with symmetries Δ_7^5, Δ_9^5 or Δ_8^6, Δ_9^6. Our data also prove the existence of a gap of width 0.8 ± 0.3 eV in the unoccupied bands along Δ above the fundamental gap. Our spin resolved measurements demonstrate that flat unoccupied bands with the symmetries Δ_7^5, Δ_8^6 and Δ_9^5, Δ_9^6 have to exist in the energy range between 7.6 eV and 12.5 eV above the valence-band maximum. They are partly hybridized with Δ_7^1 and Δ_8^3 bands.

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