Band symmetries of GaSe(0001) studied by spin-resolved electron spectroscopy using circularly polarized radiation

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We have studied the symmetry properties of the bands of the layered semiconductor GaSe along the Δ direction by means of spin-resolved electron spectroscopy using circularly polarized synchrotron radiation and by means of a relativistic LAPW band-structure calculation. The photoelectron spectra show in the main a pair of weakly dispersing peaks caused by 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 of these valence bands to be $\Delta E_{so}=0.3\pm0.1$ eV. We find a gap in the unoccupied bands along Δ about 8 eV above the fundamental gap. The analysis of the photoelectron spin polarization reveals that also unoccupied states with low symmetries Δ_7^5, Δ_8^6 and Δ_9^5, Δ_9^6 are involved in excitation and emission. Spin resolved spectra measured at Auger electrons following the decay of Ga 3*d* core holes confirm that *p* derived unoccupied states exists below the vacuum level.

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I. INTRODUCTION

Spin-resolved photoemission spectroscopy using circularly polarized radiation has been proven to be an essential tool to study the electronic structure of nonmagnetic solids and their surfaces, especially with respect to band symmetries.[1–4] Spin-dependent effects in these photoemission experiments originate from spin-orbit coupling. Via the relativistic dipole selection rules the spin polarization of excited electrons strongly depends on the symmetry of the initial and final electronic states involved in the photoexcitation.[5,6] Spin-resolved photoemission excited by circularly polarized radiation has been successfully applied to determine the band symmetries of the cubic crystals Pt(111) (Ref. 3), Ir(111) (Ref. 7), Xe(111) (Ref. 8), Pd(111) (Ref. 9), and of the layered semiconductors WSe_2(0001) (Ref. 10) and InSe(0001) (Ref. 11). In these layered materials WSe_2 and InSe the spin-orbit split bands are closely spaced, and even with high-resolution photoemission spectroscopy it is very difficult to identify transitions from different bands. As emission from neighboring bands split by spin-orbit coupling yields for each band out of the pair an electron spin polarization of opposite sign, split bands can be clearly separated by spin-resolved photoemission spectroscopy.[9–11]

As the relativistic dipole selection rules are valid also for photoexcitation of core hole states, the orientation (and with that the spin polarization) of the hole states depends on the symmetry of the final states reached in the photoexcitation, and will vary with the photon energy if the final-state symmetry varies. With an Auger decay of the excited hole states the core hole orientation is transferred to the outgoing Auger electrons.[12–17] Therefore, the Auger-electron spin polarization (measured as a function of the photon energy) is suitable for probing the symmetry of the unoccupied final states being reached by the primary photoexcitation. This is of special interest for unoccupied states below the vacuum level, e.g., with energies between the conduction band minimum and the vacuum level in the case of semiconductors. For these energies, the electronic states are not accessible by direct photoemission.[18] First measurements of spin-dependent Auger emission using excitation by circularly polarized radiation have been performed at nonmagnetic alkaline layers. In these studies the symmetry of unoccupied states with energies below the vacuum level was determined.[15–17]

In this paper we extend the studies of the layered semiconductors to GaSe, a material which shows similarities with InSe but very different band symmetries just above the vacuum level. As with InSe the electronic structure of the semiconducting III-VI compound GaSe is interesting from a fundamental point of view: GaSe also crystallizes in a layered structure with strong covalent bonding within the layer, but only weak van der Waals bonding between adjacent layers and shows quasi-two-dimensional properties.[19–21] GaSe also belongs to the nonsymmorphic space group D_{6h}^4. The (0001) surface of GaSe is formed by chemically saturated Se layers which are hexagonal closed packed and show C_{6v} point symmetry.[22] We use a new relativistic calculation for the empty bands of GaSe and spin-dependent measurements to study the symmetry properties of the band structure of GaSe(0001) along the Δ direction.

II. EXPERIMENT

The experiment was performed at the 6.5-m normal incidence monochromator beamline for circularly polarized off-plane bending-magnet radiation at the BESSY I storage ring in Berlin using an apparatus described previously.[1–3] All data were recorded in the highly symmetric setup of normal incidence of the circularly polarized synchrotron radiation and electron emission within an acceptance cone around the surface normal. Photon energies were used in the range from 7 to 27 eV. The degree of circular polarization was (0.90 ± 0.03),[23] the bandwidth of the radiation about 0.5 nm. The

calibration uncertainty of the monochromator was about 0.1 eV. The emitted electrons were analyzed with respect to their energy using a simulated spherical field 180° spectrometer[24] with an energy resolution of about 150 meV. Due to an acceleration voltage of 5 eV between the sample and the spectrometer entrance optics, the acceptance cone of the spectrometer was slightly dependent on the electron kinetic energy E_{kin}. While electrons with $E_{kin}=1$ eV were accepted within a cone of $\pm 4°$, this cone narrowed to $\pm 3°$ for higher electron energies.[25,26] The spectrometer was followed by an UHV Mott polarimeter operated at 100 keV. The Mott polarimeter recorded the electron spin-polarization component P parallel to the spin of the incident photons.

We prepared the clean (0001) surface of GaSe by cleaving in ultrahigh vacuum.[27] The surface structure was monitored by low-energy electron diffraction (LEED).

III. BAND STRUCTURE CALCULATION

We calculated a relativistic band structure of GaSe using the full-potential linearized augmented plane-wave method (LAPW). We added ''local orbitals'' for the high-lying ''semicore'' states to improve the linearization and used the WIEN97 package.[28] We treated exchange and correlation within the generalized gradient approximation[29] and added spin-orbit coupling in a second variational step. We used the measured lattice parameters from Ref. 21.

Figure 1 shows the calculated relativistic band structure of GaSe(0001) in the Δ direction with the symmetry labels included. The valence part is on the left and the unoccupied one is on the right. The zero of energy is the valence-band maximum (VBM) (Γ point). The symmetry assignments for the calculated bands have been obtained by applying a group theoretical analysis of the respective wave functions of both relativistic and nonrelativistic bands. An alternative method to obtain the symmetry assignment for the calculated relativistic bands is reported elsewhere.[30] For the symmetry labels we use the notation of Koster.[31,32] Dotted lines indicate total symmetric bands with symmetries Δ_8^3, Δ_7^1, dashed and solid lines indicate bands with symmetries Δ_9^5, Δ_9^6 and Δ_7^5, Δ_8^6, respectively. In each symmetry label the subscript and superscript indicate the double-group representation and single-group representation from which each is derived, respectively. For the symmetry labels of the unoccupied bands we use abbreviations, e.g., Δ_8^3 as 8(3) and Δ_7^1 as 7(1).

It should be noted that in the valence part avoided crossings exist between the Δ_7^1-band and the two Δ_7^5-bands (solid lines). Therefore, the shape of the two Δ_7^5-assigned bands is not identical to the shape of the two Δ_9^5-bands (dashed lines). Indeed, without any avoided crossing the Δ_7^5-bands and the Δ_9^5-bands would have an identical shape because they are spin-orbit split bands.[5]

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows spin-separated photoemission spectra obtained from GaSe(0001) for photon energies ranging from 9 to 19.4 eV. They are measured along the Δ direction in EDC mode (energy distribution curve mode) at normal incidence

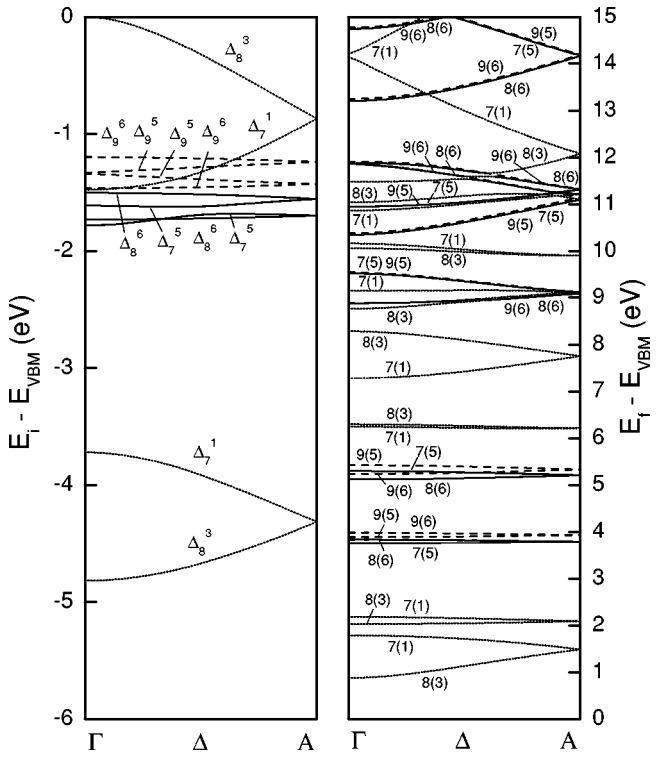

FIG. 1. Calculated relativistic bandstructure of GaSe(0001) along the Δ direction. The valence bands are displayed on the left, The unoccupied bands on the right. The valence-band maximum (VBM) is chosen as the energy zero for both parts. For the symmetries of the unoccupied parts we use abbreviation, e.g., Δ_7^1 is given as 7(1) and Δ_8^3 as 8(3).

of the circularly polarized radiation and normal emission of the electrons. All spectra are normalized by the photon flux. They also are normalized to the circular polarization $P_{circ}=100\%$. The energy scale of the spectra gives the initial-state energy with the VBM defining the zero of the energy.[33] In the spectra, besides the spin-independent total intensity I, the spin-separated partial intensities I_+ and I_- (thick and thin lines in Fig. 2, respectively) totally spin polarized parallel and antiparallel to the photon spin, are given, respectively. I_+ and I_- are related to the electron spin polarization P and the total intensity $I=I_++I_-$ by

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

Positive P corresponds to a preferential spin direction of the electrons parallel to the photon spin.

As in the case of InSe (Ref. 11) all the spin separated spectra show one main peak in each of the two partial intensities I_+ and I_-, e.g., for the photon energy $h\nu=12$ eV in the I_+ spectrum at the binding energy -1.9 eV (peak B) and in the I_- spectrum at the binding energy -2.2 eV (peak C). For these two peaks nearly no dispersion is present over the full range of photon energies. Each of the peaks B and C appears only in one partial intensity. This behavior corresponds to totally spin polarized electrons photoemitted from each of the spin-orbit split valence bands. The binding energies of the peaks B and C differ by 0.3 eV$\pm$0.1 eV which is the spin-orbit splitting ΔE_{so} of the valence-band states.

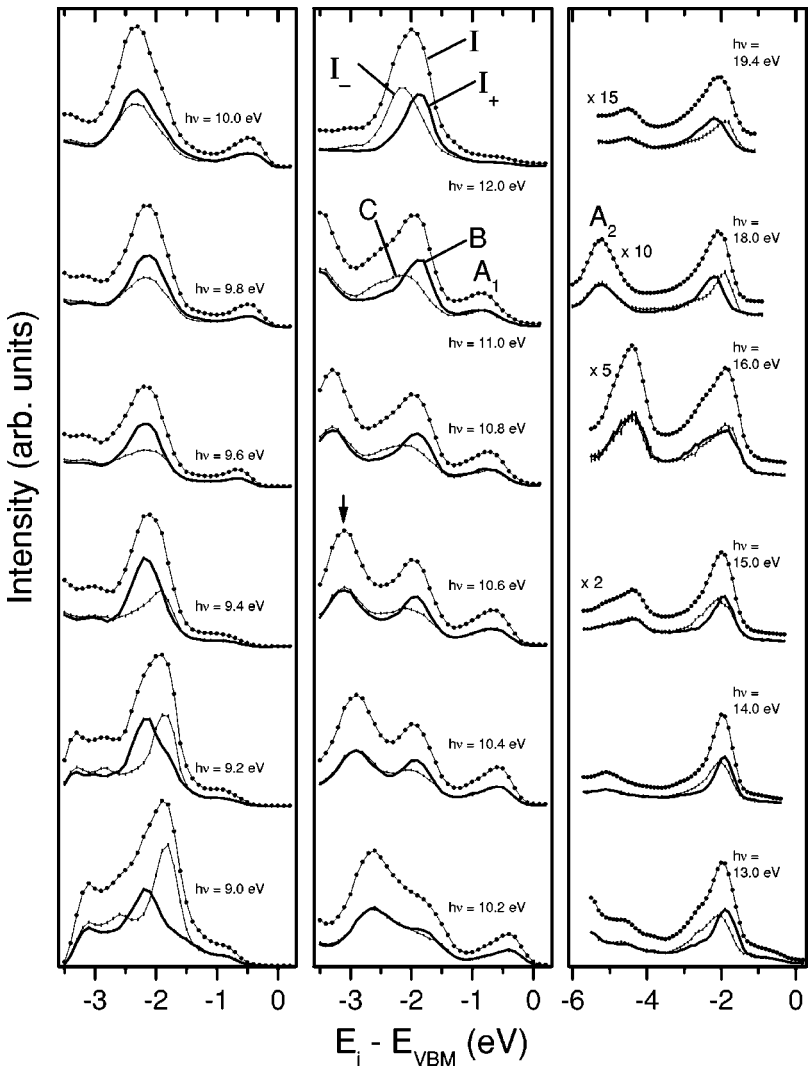

FIG. 2. Spin-separated photoelectron spectra measured in EDC mode from GaSe(0001) for photon energies between 9 eV and 19.4 eV. I is the total intensity, and I_+ and I_- are the two partial intensities. A_1, A_2, B, and C mark observed peaks. The arrow marks a final-state peak. The vertical error bars given in I_+ and I_- represent the single statistical uncertainties in the measured data.

Though the widths of the two peaks are comparable with the spin-orbit splitting of the initial states, the splitting can be determined via the spin separated partial intensities resulting from spin-resolved photoelectron spectroscopy. It is worth noting that similar peaks B and C appear in photoemission from InSe, and that the splitting of these peaks reveals an identical spin-orbit splitting. As GaSe and InSe have the same crystal structure, the valence-band states which show up in the peaks B and C must be derived from atomic orbitals of Se, the atomic constituent which is identical in both materials. In accordance with Ref. 19 these orbitals are the Se $4p_{xy}$ orbitals.

At photon energies below 9.4 eV peak B is present in the partial intensity I_- only and so is due to excitations resulting in negative spin polarization of the photoelectrons. At a photon energy of about 9.6 eV peak B disappears, but with the photon energy increasing above 10.2 eV it reappears in the partial intensity I_+ and so is due to excitations resulting in positive spin polarization. At photon energies above 16 eV peak B disappears in I_+ and reappears in I_-, i.e., the electron spin polarization of peak B again changes the sign. These changes of sign will be discussed later. The disappearance of peak B for photon energies ranging from 9.6 to 10.2 eV corresponds to a gap of width 0.6 ± 0.3 eV within the unoccupied bands along Δ above the fundamental gap. Peak C behaves identically to peak B, but with the partial intensities I_+ and I_- exchanged, i.e., with opposite sign of the spin polarization.

A peak A_1 appears at binding energies between -0.4 eV and -1.0 eV, and a peak A_2 between -4.3 eV and -5.2 eV. While peak A_1 exists only for photon energies between 9.6 and 11.5 eV, peak A_2 is present for photon energies between 15 and 18 eV. Peak A_1 and peak A_2 are present in I_+ as well as in I_- with nearly identical weight, so the spin polarization P approaches zero in each of the two peaks.

There is a so-called final-state peak at about 7.4 eV above the VBM. It appears significantly in the 10.6 eV spectrum of Fig. 2 and is marked by an arrow. Final-state peaks are caused by a high density of states of the unoccupied bands. They can be distinguished from direct photoemission peaks by their kinetic energy being constant, i.e., the appearing binding energy changes by amounts equal to the change of the photon energy.[34,35] Final-state peaks usually show no spin polarization.[30]

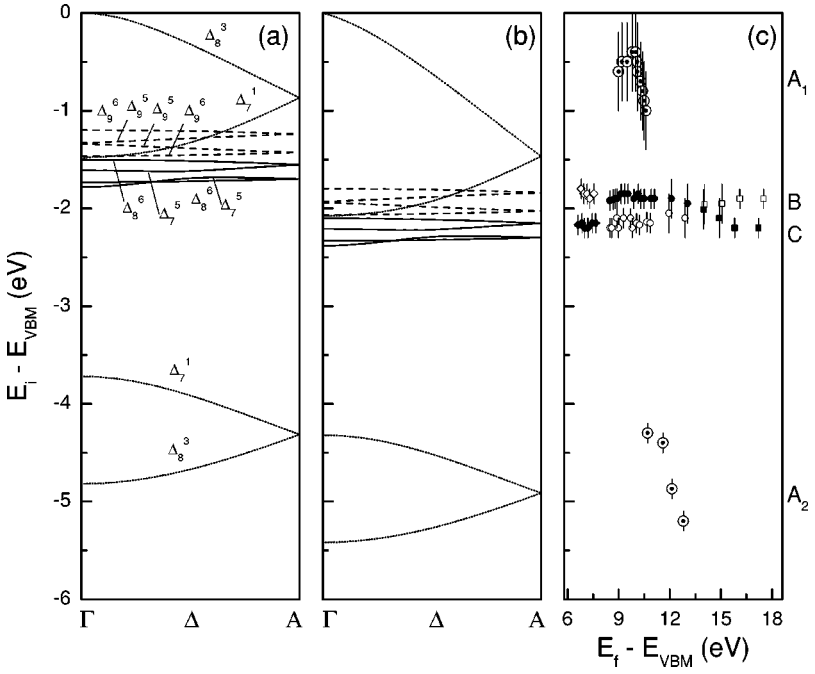

FIG. 3. (a) Calculated relativistic valence-band structure of GaSe(0001) in the Δ direction taken from Fig. 1. (b) calculated bands shifted by 0.6 eV to higher binding energies. The uppermost band Δ_8^3 is adjusted to connect the band Δ_7^1 at the point A with the VBM at the point Γ. (c) data points obtained from the partial intensities I_+ and I_-, partly shown in Fig. 2. For *B* and *C* the data points represented by closed symbols correspond to measured peaks appearing in I_+ (connected with $P=1$) while open symbols correspond to measured peaks appearing in I_- (connected with $P=-1$). The unpolarized peaks A_1 and A_2 are given by partly filled circles.

To correlate the calculated valence-band structure with the measured data, Fig. 3(c) shows the initial-state energies corresponding to the measured peaks versus the final-state energy (E_f) with the VBM used as energy zero. The data points are obtained from the spin-separated spectra shown in part in Fig. 2. For peaks *B* and *C* the data points represented by filled symbols correspond to peaks appearing in I_+ while open symbols correspond to peaks appearing in I_-. The crossing of the data points for peak *B* and peak *C* reflects the changing preferential spin direction in these peaks. The unpolarized peaks A_1 and A_2, they are present in I_+ and in I_- with identical weight, are shown by partly filled circles. To improve the alignment of the calculated and the measured data given in Fig. 3(a) and Fig. 3(c), respectively, in Fig. 3(b) the calculated valence bands are rigidly shifted by 0.6 eV to higher binding energies. However, to keep the VBM at the Γ point,[27,36] the uppermost Δ_8^3-band is adjusted to connect the correlated Δ_7^1-band at the point A with the VBM at the Γ-point. The shift could be due to a self-energy correction[4,37] not considered in our LAPW calculation. Comparison of Figs. 3(b) and 3(c) shows that the peaks *B* and *C* originate from the initial states with the symmetries Δ_9^6, Δ_9^5 and Δ_8^6, Δ_7^5, respectively, while peaks A_1 and A_2 originate from initial states with symmetries Δ_8^3, Δ_7^1.

An assignment of the measured peaks with direct transitions between the calculated occupied and unoccupied bands of different symmetry is hard to perform, because especially the calculated unoccupied bands shown on the right side of Fig. 1 are too complex. Starting with the possible symmetries of the occupied bands given in Fig. 3 and assuming the final states to be totally symmetric, the relativistic dipole selection rules given in Table I allow proving the existence of the states involved in the photoemission process.[5,6] The final states should be totally symmetric, because in the normal emission geometry of our experiment other states should not couple to the outgoing plane waves in the vacuum. It is worth noting that the symmetry of the totally symmetric (free-electron-like) bands is not unique in the nonsymmorphic space group.[38,39] Along the Δ direction the selection of Δ_7^1 and Δ_8^3 as possible symmetries of the unoccupied states has been verified.[38] Such unoccupied states also result in our LAPW band-structure calculation (see Fig. 1).

First the spectra measured for photon energies below 9.4 eV and above 16 eV shown in Fig. 2 must be considered. For these energies peak *B* appears in I_- (spin polarization $P=-1$), peak *C* in I_+ (spin polarization $P=+1$). According to the relativistic dipole selection rules, peak *B* is due to excitations from the initial states Δ_9^6, Δ_9^5 to the final states of symmetries Δ_8^3, Δ_7^1, while peak *C* appearing in I_+ is due to excitations from the initial states Δ_8^6, Δ_7^5 to the identical final states of symmetries Δ_8^3, Δ_7^1. The changed sign of the electron spin polarization at photon energies between 10.2 eV

TABLE I. Group theoretical prediction for the electron spin polarization following for transitions between states with symmetries out of the point group C_{6v} excited by circularly polarized radiation.[32] Initial states are given on the left, final states are on the top. α and β mean polarization $P=1$ and $P=-1$, respectively. For the sign "−" the transition is not allowed. The definition of $P>0$ in Ref. 32 is contrary to the definition applied in this table and throughout this paper. It should be noted that Δ_7^2 is omitted in Table I because dipole transitions from or to Δ_7^2 cannot occur.

	Δ_7^1	Δ_8^3	Δ_8^4	Δ_7^5	Δ_9^5	Δ_8^6	Δ_9^6
Δ_7^1	−	−	−	β	α	−	−
Δ_8^3	−	−	−	−	−	β	α
Δ_8^4	−	−	−	−	−	β	α
Δ_7^5	α	−	−	−	−	−	β
Δ_9^5	β	−	−	−	−	α	−
Δ_8^6	−	α	α	−	β	−	−
Δ_9^6	−	β	β	α	−	−	−

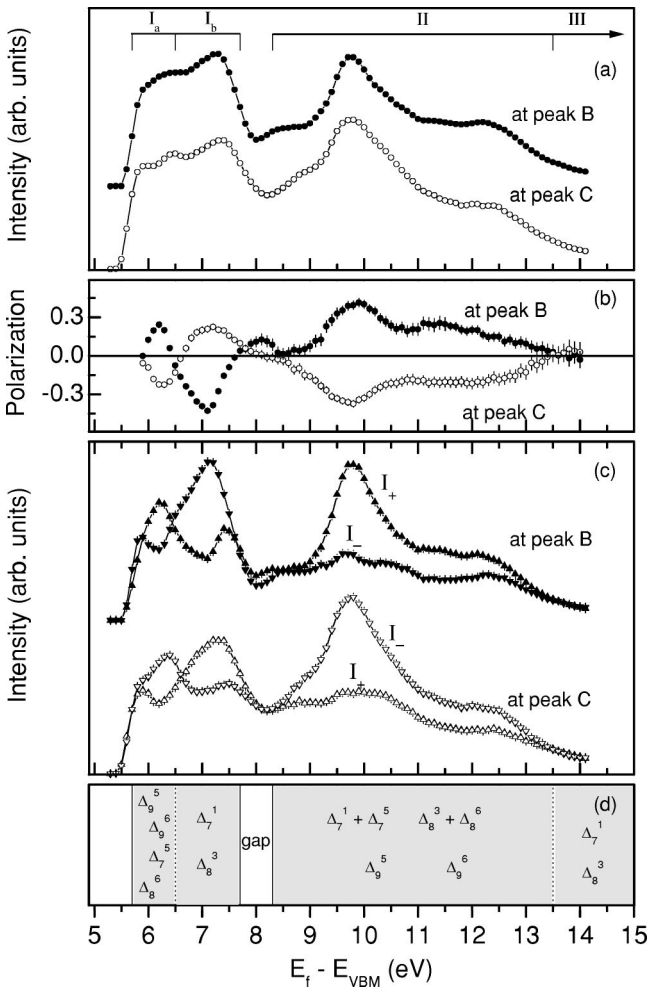

FIG. 4. Constant initial state (CIS) spectra from GaSe(0001) for two different initial states, corresponding to the peaks *B* and *C* in Fig. 2. (a) total intensities, (b) electron spin polarizations, (c) partial intensities, (d) assumed symmetries of the unoccupied bands. The energy interval is divided into several regions on the basis of the intensity and the electron spin polarization, region I_a: from vacuum level (5.7 ± 0.1 eV above the VBM) to 6.5 eV, region I_b: from 6.5 to 7.7 eV, region II: from 8.3 to 13.5 eV, region III: above 13.5 eV. In addition to the statistical uncertainties represented by the error bars the spin polarization has a scaling uncertainty of 5% of the given values. The measured spin polarization does not reach $P=\pm1$ because peak *B* and peak *C* are partly mixed and an inelastic background cannot be removed.

and 15 eV, however, implicates the low-symmetric final states Δ_7^5, Δ_8^6 and Δ_9^5, Δ_9^6 in excitation as well as in emission.

This situation is more closely demonstrated in our spin resolved CIS (constant initial state) spectra. Figure 4 shows CIS spectra measured for two the different initial states energies $E_i=-1.9$ eV and $E_i=-2.2$ eV, corresponding to the binding energies of peak *B* and peak *C*, respectively. The total intensity *I* and the corresponding electron spin polarization *P* versus the final state energy (E_f) above VBM appear in Figs. 4(a) and 4(b), respectively, and the partial intensities I_+ and I_- appear in Fig. 4(c). As shown in the upper part of Fig. 4(a) our CIS spectra are divided into several regions according to the gap in the unoccupied bands along the Δ direction, the intensities, and the electron spin polarization, region I_a: from vacuum level [5.7 ± 0.1 eV (Ref. 40)] to 6.5 eV above VBM, region I_b: from 6.5 to 7.7 eV, region II: from 8.3 to 13.5 eV, region III: above 13.5 eV. In regions I_b and III the electron spin polarizations for the peaks *B* and *C* is in accordance with the group theoretical prediction for total symmetric unoccupied bands with the symmetries Δ_7^1, Δ_8^3 as discussed above. But in regions I_a and II our measurements for peaks *B* and *C* reveal opposite electron spin polarization. This discrepancy indicates that the often used model of free electron final state bands[33] does not apply to GaSe. In order to obtain positive electron spin polarization for peak *B*, relativistic dipole selection rules demand transitions from the initial states Δ_9^6, Δ_9^5 to final states with low symmetries Δ_7^5, Δ_8^6 as shown in Table I. Normal emission out of these states is not allowed as they are not totally symmetric. But, emission out of such states is possible inside the acceptance cone of our spectrometer, as shown for Xe(111) (Ref. 25), WSe_2(0001) (Ref. 10), and InSe(0001) (Ref. 11). We measure this off-normal emission results in the peaks and spin polarizations the regions I_a and II. Correspondingly, peak *C* requires the final states of the symmetries Δ_9^5, Δ_9^6 to obtain the measured negative electron spin polarization. Therefore, flat unoccupied bands of symmetries Δ_7^5, Δ_8^6 or Δ_9^5, Δ_9^6 have to be supposed in the regions I_a and II. A scheme of these regions and their corresponding symmetries is shown in Fig. 4(d).

The assumed symmetries of the unoccupied states are supported by the data for the peaks A_1 and A_2. Transitions from the bands with symmetries Δ_7^1, Δ_8^3 located in the vicinity of the binding energies assigned to the peaks A_1 and A_2 are allowed only to bands with symmetries Δ_7^5, Δ_8^6 or Δ_9^5, Δ_9^6. Therefore, the assumption of unoccupied bands of symmetries Δ_7^5, Δ_9^5 or Δ_8^6, Δ_9^6 in region II also explains the observation of peaks A_1 and A_2. The vanishing spin polarization within the peaks A_1 and A_2 is caused by the mixing of transitions to final state bands Δ_7^5, Δ_9^5 and Δ_8^6, Δ_9^6, respectively.

To characterize the unoccupied states with energies below the vacuum level, we applied spin dependent Auger electron spectroscopy following the photoexcitation of Ga 3d core hole states by circularly polarized radiation. Figure 5 shows spin separated constant final state (CFS) spectra measured for photon energies from 19.4 eV to 27.0 eV at the two fixed kinetic energies $E_{kin}=0.5$ eV±0.2 eV (upper panel) and $E_{kin}=1.7$ eV±0.2 eV (lower panel), respectively. With the vacuum level $E_{vac}=5.7$ eV above VBM the kinetic energies $E_{kin}=0.5$ eV and $E_{kin}=1.7$ eV correspond to energies of 6.2 eV and 7.4 eV above VBM, respectively. For $E_{kin}=0.5$ eV three significant peaks *D*, *F*, and *G* are observed at photon energies of about 20.7 eV, 22.9 eV, and 25.1 eV, respectively. A weak peak *E* is present around 22.1 eV. While for $E_{kin}=1.7$ eV the peaks *D*, *E*, and *F* appear at the same photon energy, peak G is shifted by 1.2 eV. With reference to VBM the binding energies of the Ga $3d_{5/2}$ and $3d_{3/2}$ states are $E_i=-18.85$ eV and $E_i=-19.2$ eV, respectively.[41] Thus peak *G* appearing at about 25.1 eV turns out to be due to direct

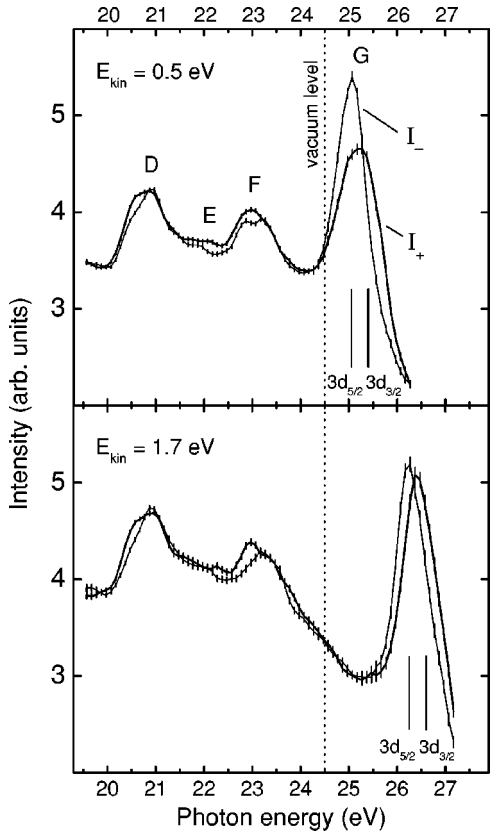

FIG. 5. Spin resolved constant final state (CFS) spectra of GaSe(0001) at two different kinetic energies of 0.5 eV (upper panel) and 1.7 eV (lower panel). Peaks *D*, *E*, and *F* are due to the Auger decay of Ga 3*d* core holes while peak *G* is due to direct photoemission from Ga 3*d* core states. The thin and the thick vertical lines indicate the expected positions for direct photoemission from the $3d_{5/2}$- and $3d_{3/2}$-core states, respectively.

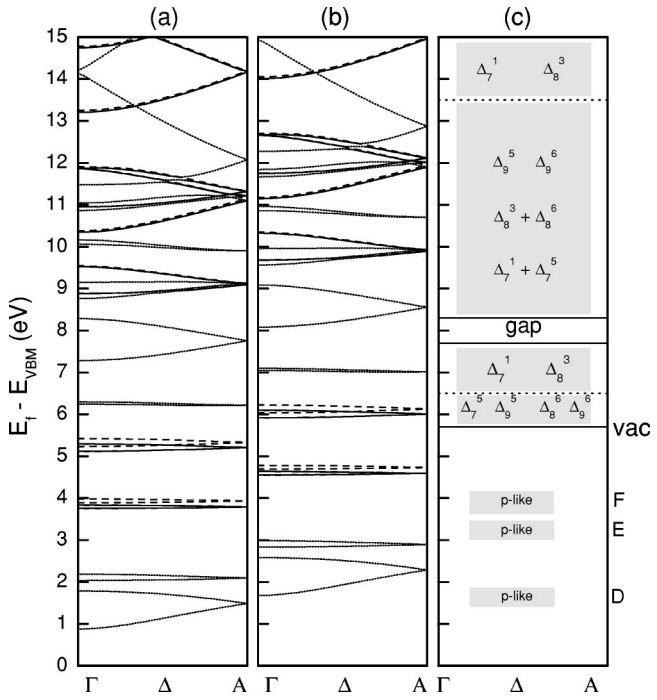

FIG. 6. Comparison between calculated symmetries and measured ones for GaSe(0001) in the Δ direction. (a) Calculated relativistic unoccupied bandstructure taken from Fig. 1. (b) Calculated bands shifted by 0.8 eV to higher energies. (c) Measured symmetry properties of the unoccupied bands taken from Fig. 4(d) for energies above vacuum level and taken from Fig. 5 for energies below vacuum level. The shaded areas below vacuum level present just the energetic positions of the bands revealed from the Auger peaks *D*, *E*, and *F* of Fig. 5 and it does not mean that they have any dependency along the Δ-direction.

photoemission involving excitation from 3*d*-core states into *p*-derived conduction-band states. The partial intensities I_- and I_+ preferred at the low- and the high-energy edge of peak *G* are in accordance with the relativistic dipole selection rules,[5,6] respectively. The peaks *D*, *E*, and *F* appear at photon energies for which direct transitions into the observed constant final states at $E_{kin}=0.5$ eV and $E_{kin}=1.7$ eV do not exist. However, inverse photoemission measurements for GaSe give lower band edges at about 2.1 eV, 2.4 eV, 3.1 eV, 3.4 eV, 4.3 eV, and 4.8 eV above VBM.[36,42] Transition from the 3*d*-core states must not necessarily be allowed to all the corresponding bands. However, the band-edge energies 2.1 eV, 3.1 eV, and 4.3 eV added to the Ga 3*d* binding energies correspond to the appearance energies of the peaks *D*, *E*, and *F*. Thus by transitions from Ga 3*d* states to these unoccupied states, $3d_{5/2}$ and $3d_{3/2}$ holes can be created which in the case of *p*-derived unoccupied states will be spin polarized antiparallel and parallel to the photon spin, respectively.[15,17] These holes will decay by CVV-Auger processes resulting in the Auger electrons which we have observed at $E_{kin}=0.5$ eV and 1.7 eV. The significant preference of I_+ at the low-energy edge of the peaks *D*, *E*, and *F* clearly confirms the primary excitation into *p*-derived states if the Auger decay of the $3d_{5/2}$ core holes is supposed to be a process with the spin polarization transferred to outgoing electrons by the involved valence-band electrons coupled to a singlet.[16]

In Fig. 6 the calculated relativistic band structure and the measured results are compared for the unoccupied part. Figure 6(c) shows the measured symmetry properties taken from Fig. 4(d) for the energies above the vacuum level and taken from Fig. 5 for the energies below the vacuum level. We shifted the calculated bands by 0.8 eV rigidly to higher energies to align the calculated bands and the measured one as shown in Figs. 6(b) and 6(c). Again the physical reason for the shift is a self-energy correction[4,37] not considered in our LAPW calculation as we mentioned for the case of the valence bands. From a comparison between Figs. 6(b) and 6(c) the general agreement between the calculated band symmetries and measured ones is good. Especially, in the regions I_a and II the calculation reveals bands with the low symmetries Δ_7^5, Δ_8^6, Δ_9^5, and Δ_9^6 and these bands allow the change of the sign of electron spin polarization measured in our measurement. We also calculated the partial density of states from the relativistic band structure (not shown in this paper) and it shows that GaSe has a strong *p*-like density of states (DOS) up to about 10 eV above VBM and *d*-like thereafter. The strong *p*-like DOS was also revealed in a recent (nonrelativistic) band structure calculation.[43] This *p*-like DOS allows the measured Auger peaks *D*, *E*, and *F* with preferential posi-

tive spin polarization. The results show similarities with the results revealed from InSe, a material with identical crystal structure and also Se as one of its constituents. But the important difference is that in GaSe just above the vacuum level the bands with the low symmetries Δ_7^5, Δ_8^6, Δ_9^5, and Δ_9^6 exist.

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