

Valence-band-structure determination of InSb by angle-resolved photoemission

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Angle-resolved photoemission with synchrotron radiation was used for an experimental determination of the valence-band structure of InSb along the high-symmetry directions of the bulk Brillouin zone. Normal-emission photoelectron spectra from the (110), (100), and (111) crystal faces exhibit peaks which show dispersion with photon energy. They are interpreted in terms of direct transitions to a free-electron-like final band. The experimental band structure is in general agreement with calculated bands, but there are deviations on the order of 1 eV at several critical points. The justification for the use of a parabolic final band is discussed, and experimental tests for its validity are described.

I. INTRODUCTION

Angle-resolved photoemission in combination with synchrotron radiation is a unique tool for the determination of electronic energy bands in solids.^{1,2} It has been shown that peaks in the spectra which exhibit shifts with photon energy can be related to direct transitions between occupied and unoccupied bands. A problem arises in determining the appropriate electron momentum \mathbf{k} for a particular transition, since the component of \mathbf{k} normal to the surface (k_{\perp}) is not conserved in the photoemission process due to the potential barrier at the surface. While some effort has been made to rely on calculated unoccupied bands, it has become clear that an interpretation of spectral features in terms of transitions to a free-electron-like final band works very well in many cases; this is particularly true for \mathbf{k} values away from the zone boundaries. At the boundary, final-state gaps occur which are not accounted for by the free-electron final state. These can, however, be estimated by recourse to calculations, or determined experimentally in favorable cases.³ The fact that the free-electron model works so well has recently been explained by Hora and Scheffler,⁴ who performed band-structure calculations for the ground state as well as for a realistic photoemission final state; this point will be taken up again in the discussion.

Most band-structure investigations have been concerned with metals, and particularly with the noble metals.⁵ Recently, it has been shown that the free-electron final-band model may also be applied to semiconductor band structures.⁶⁻¹⁰ Our study of the band structure of InSb provides further evidence that this model is applicable to semiconductor band-structure determination. We also discuss how, from a series of spectra recorded over a large range of photon energies, an unambiguous determination for the only free parameter in the model, the bottom of the parabola, can be achieved. A comparison of our experimental bands with a band-structure calculation shows that while there is good overall agreement between the data, there are significant deviations in some regions of \mathbf{k} space.

II. EXPERIMENTAL

The photoemission experiments were carried out in a commercial angle-resolving photoelectron spectrometer (ADES 400, VG Scientific) with a base pressure of 1×10^{-10} mbar. InSb(110), (100), and (111) crystals were obtained as wafers and bulk material (MCP Ltd., Great Britain), cut to shape, and rinsed in ethanol before introduction into the vacuum chamber. After bakeout, the crystals were cleaned by mild argon-ion bombardment (500-eV ions, current density approximately $5 \mu\text{A}/\text{cm}^2$) and heating to 200°C. It was found that even at low ion doses (about 1–2 h of bombardment under the conditions indicated above), the surfaces developed a slight pitting, which was particularly visible under glancing incidence; this is indicative of surface roughening. The surfaces thus prepared exhibited sharp low-energy electron diffraction (LEED) patterns and were atomically clean as also found in previous experiments.¹¹ In a different set of experiments, spectra were also recorded from InSb(110) surfaces cleaved under ultrahigh vacuum. These were very similar to the ones obtained from the ion bombarded and annealed crystals, but peaks were sharper and more intense with respect to background in the spectra from the cleaved surface.

Synchrotron radiation from the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) storage ring was dispersed by a toroidal grating monochromator¹² with three interchangeable gratings, giving high photon fluxes at energies between 8 and 200 eV. The spherical electron analyzer was set to a pass energy such that overall resolution (electrons plus photons) was between 0.1 eV at the lower photon energies, and 0.45 eV at the highest photon energies.

III. RESULTS

A series of valence-band photoelectron spectra from the ion bombarded and annealed InSb(110) surface, recorded in normal emission with light incident under 45°, with respect to the surface normal and the electric field vector

directed along the 110 azimuth, are shown in Fig. 1 for photon energies from 14 to 50 eV. From the top spectrum recorded at $h\nu=50$ eV emission from one group of bands centered around 2 eV below the valence-band maximum (VBM), another around 6 eV below the VBM and a third band close to 10 eV below the VBM are observed. Following these groups of peaks through the spectra recorded at different photon energies, we note that strong peak shifts occur; some of these are marked by lines connecting the peaks. At low photon energies, very strong intensity variations occur, making an assignment of shifts

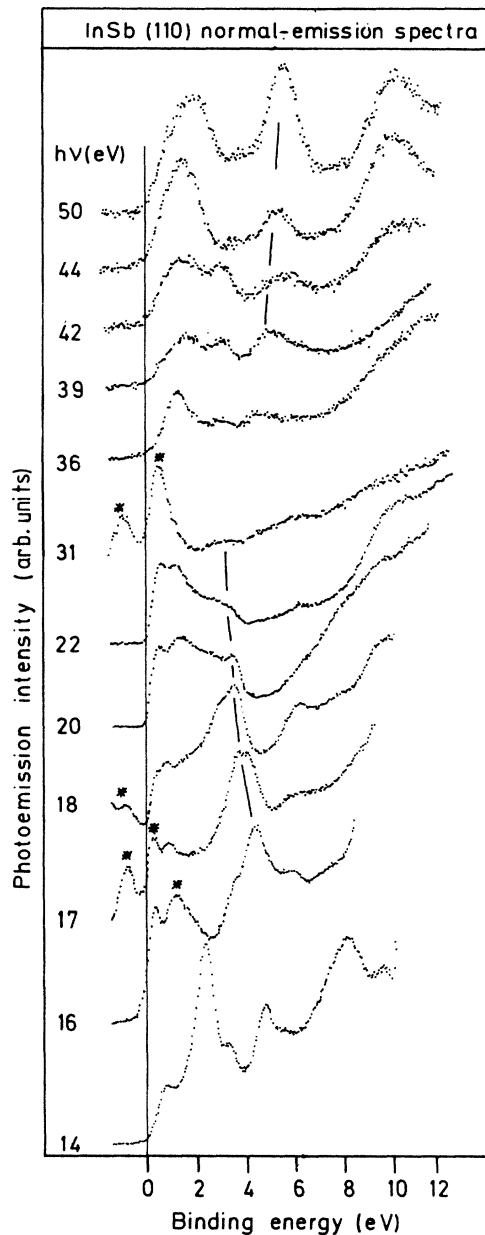


FIG. 1. Set of photoelectron spectra of a clean InSb(110) surface prepared by ion bombardment and annealing, recorded in normal emission with photon energies as indicated. Peaks marked by an asterisk are due to In and Sb 4*d* excitation by second-order light from the diffraction grating.

somewhat more difficult. Apart from the peaks due to excitation of the valence levels, features marked (*) appear in the spectra. These are caused by excitation of the In and Sb 4*d* levels from second-order light present in the monochromator spectrum; although its intensity is rather low (on the order of 2–3 %), the high photoemission cross section of these levels causes the strong appearance of the Sb 4*d* peaks. These peaks, as well as those from the In 4*d* levels, unfortunately mask some interesting regions in the spectra. Despite these effects, it is obvious from the spectra that some of the features (particularly those connected by lines) exhibit shifts with photon energy. In order to interpret the peaks in the spectrum, we apply the model described above in which the final bands in the extended zone scheme are given by

$$E(\mathbf{k}) = (\hbar^2 k^2)/2m + E_0, \quad (1)$$

where \mathbf{k} is the electron momentum perpendicular to the surface and E_0 is the bottom of the parabola, measured from the VBM, and is the only free parameter since we do not adjust for different effective masses in the final state. The energy of the final state is referred to the vacuum level. In order to determine the \mathbf{k} value for a specific transition, we resolve the equation for \mathbf{k} to yield

$$\mathbf{k} = (\hbar/2m_{\text{el}})^{1/2} (E_f - E_0)^{-1/2} - \mathbf{G}_u. \quad (2)$$

This formula holds for direct emission. Since electron momentum inside the solid is only conserved modulo a reciprocal-lattice vector, the possibility of Umklapp processes arises. These occur when an additional reciprocal-lattice vector \mathbf{G}_u is involved in the photoemission process. As described below, some features in our spectra do show evidence for bulk Umklapp processes; these lead to less intense peaks.

In order to evaluate the peaks in the spectrum in terms of direct transitions, one must first make a guess at E_0 . This can be done by comparison with previous studies of similar materials, but the most straightforward way is to consider the shape of the most strongly dispersing band and to equate the energy at which the shift has an extremum with a transition near the zone boundary. By means of a procedure described in the discussion, one can subsequently improve the value of E_0 by an iterative procedure.

An evaluation of peaks in the normal-emission spectra from the (110) surface in terms of direct transitions from the occupied bands to the free-electron parabola with $E_0 = 7.0$ eV is shown in Fig. 2 (direction $\Gamma-K-X$). Here, solid circles denote peak positions taken from spectra with photon energies in the region from 28 to 70 eV, while squares indicate those peaks recorded with photon energies in the range 10–25 eV. Triangles mark those peaks which, when interpreted in terms of Eq. (1), only correspond to reasonable bands under the assumption of bulk Umklapp processes with $\mathbf{G}^{(111)}$. In the figure, solid lines indicate the bands as determined by Chelikowsky and Cohen using an empirical pseudopotential calculation.¹³ A comparison between our experimental data points shows that the overall shape of the bands is very similar, but that there are some deviations from the calculated en-

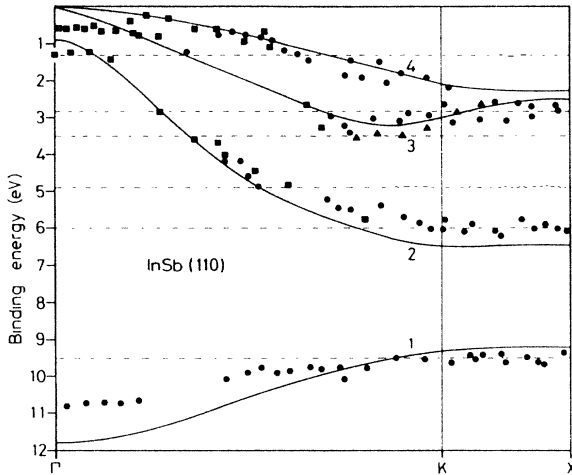


FIG. 2. Experimental band structure of InSb along the Γ -K-X direction of the bulk Brillouin zone, derived from photoelectron spectra as in Fig. 1 and discussed in the text. Squares denote strong peaks, triangles indicate features arising from Umklapp processes.

ergies. The X_6 point of band 2 lies about 0.5 eV above the calculated value, while the X_6 and X_7 points of bands 3 and 4 are situated slightly lower than the theoretical values. This is important since it allows us to determine the so-called heteropolar gap between bands 1 and 2 at the X point, the size of which is a measure of the ionicity of the In-Sb bond. The difference between theory and experiment is strongest for band 1 near Γ ; thus the Γ_6 point lies about 1 eV above the calculated value. At the Γ points, a determination of bands 3 and 4 is difficult because of overlapping peaks. The determination of band 1 over a large region of k is particularly satisfying since these low-lying s -like bands are often difficult to determine due to lifetime broadening and inelastic scattering processes.¹⁴ Our experimental values for critical-point energies are summarized and compared with the calculated values in Table I. It must be kept in mind that some uncertainty in the experimental binding-energy values is introduced by the precision with which we determine the valence-band maximum. In a calculation, the VBM corre-

TABLE I. Energy values of different bands at points of high symmetry as derived from experimental data, and compared with values from the nonlocal pseudopotential band-structure calculation of Chelikowsky and Cohen.¹³ Energies are given below VBM in eV.

		Expt. data (this work)	Theory (Ref. 13)
Band 1	Γ_6	10.8	11.71
	X_6	9.5	9.2
	L_6	10.0	9.95
Band 2	Γ_7	1.3	0.82
	X_6	6.1	6.43
Band 3	X_8	2.8	2.45
			1.44

sponds to the highest-filled band. In order to determine binding energies, we extrapolate the high kinetic-energy part of the spectrum linearly to the baseline, such that any peak binding energy will have a minimum value on the order of 0.2–0.3 eV. If the photoemission peak with the highest binding energy would be taken to represent the VBM, all values in Table I would be reduced by this amount.

At this stage, it is interesting to consider the influence of spin-orbit splitting on the band structure of InSb. The empirical pseudopotential calculation gives a value for the Γ_8 - Γ_7 separation at the valence-band maximum of 0.82 eV. Based on the data in Fig. 2 and Table I, we arrive at a splitting of 0.75 ± 0.1 eV if we take the energy separation between the topmost and second line of data points at Γ . This is close to the theoretical value of 0.82 eV, as calculated by Chelikowsky and Cohen.¹³ Since spin-orbit splitting is included in these calculations only via perturbation theory, it is possible that the nonlocal empirical pseudopotential calculation does not sufficiently describe this aspect of the band structure. However, in an experimental band-structure study of GaSb, Chiang and Eastman¹⁵ found a value of 0.76 eV for the Γ_8 - Γ_7 splitting which is identical with the calculated value.¹³ In view of the finite width of the peaks and the difficulties in determining the peak positions close to the Γ point near the VBM, it may not be possible to give the experimental value for the Γ_8 - Γ_7 splitting with sufficient accuracy for a determination of the shortcomings of the calculation.

In addition to peaks which exhibit dispersion with $\hbar\omega$, there are also features in the spectra which do not shift with photon energy. These are ascribed to indirect transitions, in which information on electron momentum is lost because of inelastic scattering, for example, from phonons. The intensity of such features is thought to follow the density of initial states, such that many of them are caused by band maxima and minima at the zone boundary.¹⁶ In the figure, such emission is marked by dashed lines; most but not all of these emissions occur at energies below the VBM which correspond to critical points along Γ -K-X.

We have also recorded spectra in normal emission from the (100) and (111) surfaces in order to determine the band structure of InSb along the Γ -X and Γ -L directions. These surfaces can only be prepared by ion bombardment and annealing or by molecular beam epitaxy. These preparation techniques are known to give rise to surfaces of varying stoichiometry in the case of GaAs.^{17,18} Since we are concerned here with the bulk bands, and surface states or resonances can be readily distinguished in our spectra, our conclusions are not affected by small deviations from the stoichiometric surface. On InSb(100), spectra were recorded in the conventional energy distribution curve (EDC) as well as the constant final state (CFS) mode, in which the electron kinetic energy is held fixed while the photon energy is scanned; in this latter mode all peaks in the spectrum correspond to an identical final state, such that analysis of CFS data is straightforward.

The analysis of InSb(100) spectra in terms of direct transitions along the Γ -X line in k space is shown in Fig. 3. Here, we are able to map band 2 with high precision

over most of the range of k , but are limited to the top of band 1 because of strong indirect emission which masks any dispersing features. This is indicated by the data points at 9.1 eV below the VBM. The shape of the band can, however, be constructed from its position at X determined by the indirect emission feature and its position at Γ , which is known from the data in Fig. 2. The shape of band 2 was determined experimentally over a large range of k , and there is good agreement between the experimental band and the calculation¹³ which is indicated by the line. The upper two bands have a splitting of only 0.3 eV in the calculation, and thus they cannot be separated experimentally. Their common course agrees well with the calculation over a large range of k , however. The branch of experimental data points moving away from the calculated bands near X probably corresponds to direct transitions related to the bulk bands by surface Umklapp because of the reconstruction of this surface.^{7,11}

The results from InSb(100), while resulting in experimental bands over a large portion of k space, are less clear than those from the (110) face. This may be caused by several effects. The (110) face of the zinc-blende semiconductors is the most stable one. It does not reconstruct as heavily as the (100) and (111) faces; on (110) the well-known bond-angle rotation relaxation occurs.¹⁸ Because of the above-mentioned deviations from stoichiometry, stronger inelastic scattering will occur in photoemission from the (100) and (111) surfaces. In the case of GaAs, surfaces prepared by MBE exhibit a variety of LEED structures depending on the relative amounts of gallium or arsenic in the molecular beam, and this also has an effect on the shape of the photoelectron spectra.^{17,19} One method of avoiding difficulties associated with surface preparation is to use a symmetry method for band deter-

mination along different directions in k space, for example, the zero-slope method.³ This requires sharp and strongly dispersing features, however, and may therefore not be easily applicable to the zinc-blende semiconductors.

The interpretation of peaks due to direct transitions is even less straightforward for the spectra from InSb(111). Here, as on the (100) face, only band 2 is most clearly distinguished over most of the Brillouin zone. Strong surface-state emission near the top of the valence band (to be discussed elsewhere²⁰) completely masks transitions from bands 3 and 4. The energies of the band maximum and minimum for band 2 along Γ - L are included in Table I, which also summarizes our results for the energies of occupied bands of InSb at the points of high symmetry in the Brillouin zone.

IV. DISCUSSION

In order to get an estimate on the reliability of electronic band-structure determinations by means of the free-electron final-band model, it is appropriate to investigate the dependence of the experimental band structure on the choice of the only free parameter E_0 . It is evident that in a situation in which direct transitions to only one branch of a free-electron final band are considered, a decrease in E_0 such as shown in the schematic representation in Fig. 4 will shift all direct transitions to higher k values, for example, the transition with k_1 to k'_1 . Thus an overall shift of the experimental band structure can be achieved, and one has to rely on other information to achieve a reliable determination of E_0 . In a situation in which spectra over a wide range of photon energies are available, such that transitions to two branches of the free-electron final state are encountered, a change in E_0 will affect transitions to these branches differently, as also shown in Fig. 4. For a decrease in E_0 the value of k for one kind of transitions may decrease (k_2 in the figure), while it increases for the other kind (k_1). Thus for a strongly dispersing initial band, that value of E_0 which lets data points from these different transitions coincide as much as possible obviously represents our best choice. In an iterative procedure, therefore, the value of E_0 was changed in small steps until all $E(k)$ values corresponding to transitions from one (strongly dispersing) band followed the same overall band shape, irrespective of the final band involved. This led to a value of E_0 which produced a contiguous band shape in the most strongly dispersing band. Our error in determining E_0 in this fashion is estimated to be smaller than about 1 eV. For higher deviations, obvious discrepancies occur in the bands, leading to a seemingly random position of points at even larger deviations from the "ideal" E_0 . This determination is not strongly dependent on a calculated band structure since the overall shape of the bands, particularly the strongly dispersing Σ_6 and Σ_7 bands (bands 1 and 2 in Fig. 2), can be guessed without recourse to calculations. While it must be kept in mind that the free-electron final band must have its limitations in the interpretation of photoelectron spectra, its use leads to less ambiguity (at least away from the zone edges) than

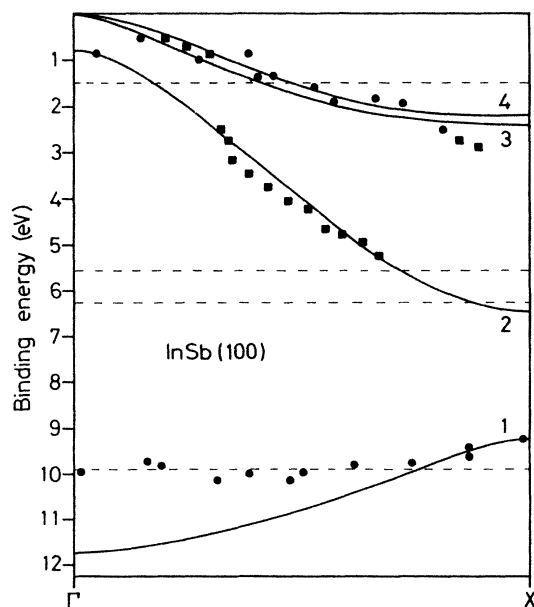


FIG. 3. Experimental band structure of InSb along the Γ - X direction determined through normal emission spectra from an InSb(100) surface.

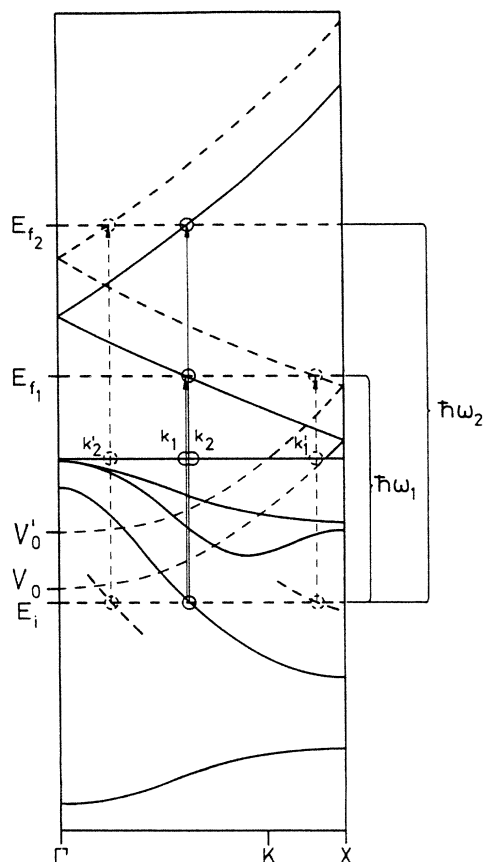


FIG. 4. Schematic representation of the free-electron final bands with different E_0 . Note how the transition to E_{f1} is moved to a larger value of k as E_0 is decreased, while the transition to E_{f2} is moved to a smaller value of k , since the transitions occur to different branches of the parabola.

one would guess at first glance.

This point can be well illustrated by comparing our evaluation with a recent photoemission study of various III-V compound semiconductors by Williams *et al.*²¹ These authors compare their photoelectron spectra, recorded with photon energies up to 22 eV, with a band-structure calculation by Pandey (Ref. 3 in Ref. 21) for the unoccupied bands up to energies of 20 eV above the vacuum level. In their analysis, they find that the majority of transitions take place on those branches of the final states which are closely related to the free-electron final-state parabola. For the case of InSb(110) our free-electron parabola with $E_0 = 7$ eV matches the calculated final band (which was additionally strongly modified by Williams *et al.* to improve agreement between theory and experi-

ment) to within about 2 eV over the full range of k from Γ to X . Other branches of the calculated final bands which were also included in the analysis of Williams *et al.* turn out to be those related to Umklapp processes, which are automatically included in a calculated final band. The limited number of data points in the study of InSb by Williams *et al.* do not enable us to compare the precision with which the occupied bands were determined. It is likely that an evaluation based on calculated ground-state final bands may be more realistic near zone boundaries since gaps are included; the size of these gaps is bound to change when a realistic final state is included, however. This point has recently been studied in detail by Hora and Scheffler for valence-level photoemission from a Pd surface.⁴ These authors performed a theoretical study of the occupied and unoccupied band structure as well as a calculation of photoemission within the one-step approach, i.e., with realistic excited-state final bands. Their main findings can be summarized as follows: the ground-state unoccupied bands strongly differ from those calculated in the one-step model. In particular, the gaps in the final bands close, flat bands become less important, and the s - p derived final bands show a dispersion practically identical to a free-electron parabola (see Fig. 9 of Ref. 4). As a result of their calculations, Hora and Scheffler also found that this band was the only one that contributed to the photoemission intensity. While these results, obtained for Pd, may not be directly applied to other materials, the message is significant in that it indicates that the use of a free-electron parabola may be a very good approximation to a realistic final state.

Höchst and Hernandez-Calderon⁷ have also evaluated the band structure of InSb from spectra taken with resonance lamp photon energies over the range 11.83–40.8 eV photon energy. While this limited set of photon energies leads to a remarkable number of data points for bands 2, 3, and 4, it must be pointed out that, because of this limited range, the size of the heteropolar gap could not be evaluated nor could the course of the lowest band be determined. Because of the above-mentioned difficulty of determining E_0 from one single branch of the final band, the authors also have to rely more heavily on a calculated band structure. This may explain the discrepancy between their value for E_0 of 4.5 eV and our value of 7.0 eV.

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