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Reflectivity, Photoelectric Emission, and Work Function of AlSb

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The reflectivity and photoelectric emission from $h\nu = 2$ to 6 eV, and the work function, have been measured for (110) surfaces of AlSb (p type, $N_A = 2\times10^{17}$ cm^{-3}) cleaved in high vacuum and covered with various amounts of cesium. The yield of the clean surface is similar to that of other measured III-V compounds. The threshold for photoelectric emission is 5.22 ± 0.02 eV, corresponding to excitation from the top of the valence band. With a band gap $E_g = 1.62$ eV, the electron affinity is 3.6 eV. The work function is 4.86 ± 0.05 eV and the Fermi level lies 0.36 ± 0.07 eV above the top of the valence band at the surface. By deposition of cesium, the work function was lowered to 1.37 eV and the resulting yield spectrum shows structure related to that of the reflectivity. The combined results of reflectivity and photoelectric emission are discussed in terms of the band structure of AlSb.

I. INTRODUCTION

THE combination of optical-reflectivity and photoelectric-emission results provides a particularly powerful approach to the determination of band structures.[1–5] The elemental[6,7] and many of the compound semiconductors[8] have now been investigated this way. In the present work the reflectivity and photoelectric emission properties of AlSb have been measured on surfaces that were prepared by cleavage in ultrahigh vacuum. This was necessary to obtain reliable data since chemically polished surfaces of AlSb react rapidly with water vapor in air.[9] The results are interpreted with the assumption that their spectral structure is due to direct optical transitions (i.e., with conservation of the wave vector **k**) at critical points in the joint density of states. These are points in the Brillouin zone where a conduction band $E_c(\mathbf{k})$ and a valence band $E_v(\mathbf{k})$ have the same gradient

$$\nabla_k E_c(\mathbf{k}) = \nabla_k E_v(\mathbf{k}). \tag{1}$$

Around such points there exists an extended region in **k** space available for the optical transition

$$E_c(\mathbf{k}) - E_v(\mathbf{k}) = h\nu. \tag{2}$$

Such points are most likely to be points of high symmetry (i.e., Γ, L, X), where

$$\nabla_k E_c = \nabla_k E_v = 0.$$

There has been experimental evidence suggesting that conservation of the **k** vector during optical transitions is not an important selection rule[5] in some cases. The photoelectric emission data of several metals and semiconductors[10] are interpreted by Spicer and co-workers in terms of nondirect transitions. Conservation of **k** vector has not been questioned with Si, Ge, and the III–V compounds; the photoelectric-yield results[6–8] for these materials as well as the reflectivity data[11] appear to be explained in terms of direct optical transitions. However, difficulties are encountered in understanding the energy distributions of photoemitted electrons from these materials upon the assumption of direct transitions with negligible energy losses through scattering between excitation and escape.[6,7] It is suggested[12,13] that an appreciable fraction of the excited electrons suffer many collisions before their emission and are thus able to lose several tenths of an eV in energy. If this is the case, the measured energy distributions would not yield simple information about the optical transitions. Kane[12] has pointed out that peaks in the energy distribution might then actually correspond to regions of *low* densities of states in the higher band. This could occur because the transition rate with phonon emission is proportional to the density of states; thus electrons at energies with low state density, besides having a higher group velocity, also possess a longer lifetime. Both factors contribute to a greater mean free path and consequently to a higher probability of escape.

Since the present work supplies no new evidence on this problem, we deliberately choose to interpret the results with the hitherto adopted model of direct transitions, leaving experimental findings open to reinterpretation if future evidence should make it necessary.

II. BAND STRUCTURE OF AlSb

Most of the data published so far on the band structure of AlSb deal with the band edges. The most probable value of the band gap, according to measurements of the optical absorption edge, is $E_g = 1.62\pm0.03$

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[2] H. Philipp, E. A. Taft, and L. Apker, Phys. Rev. **120**, 49 (1960).

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[5] W. E. Spicer, Phys. Rev. Letters **11**, 243 (1963).

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[10] C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1044 (1964); and references therein.

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[12] E. O. Kane (unpublished).

[13] H. A. Lettington, Phys. Letters **9**, 98 (1964).

eV.[14,15] This value is confirmed by the temperature dependence of the intrinsic conductivity.[15] Measurements of the pressure dependence of the optical absorption edge[16] suggest that the minimum of the conduction band lies along the [100] axis; the effective mass[17] of the electrons is $m/m_0=0.39\pm0.06$. A broad infrared absorption band around 0.3 eV displaying the behavior of an interband transition was observed in n-type material.[14,15,18] This could be due to either an indirect or a direct X_{1c}-X_{3c} transition (see Fig. 6). The shape of this absorption curve is much more reminiscent of the X_{1c}-X_{3c} transition[19] observed in GaP than of indirect transitions as they are observed, for instance, in GaAs.[20] The intensity of the infrared absorption is proportional to the number of electrons in the conduction band; the proportionality factor in AlSb is about 5 times higher than in GaAs[20] where the transition is known to be indirect, and very nearly equal to that of GaP,[21] where the transition is known to be direct. By an extrapolation of Burdiyan's[22] measurements of the absorption edge in the system $(\mathrm{Ga}_{(1-x)}\mathrm{Al}_x)\mathrm{Sb}$, Ehrenreich[23] suggests a direct gap of 1.8 eV. We therefore have the following picture of the conduction band: The minimum energy of the conduction band is X_{1c}, which lies 1.62 ± 0.03 eV above the valence-band maximum. The X_{1c}-X_{3c} splitting is 0.29 eV. The minimum at the center of the zone Γ_{1c} is 1.8 eV above the valence band. Mead and Spitzer[24] propose another structure for the conduction-band minima where the [100], [111], and [000] minima of the conduction band lie, respectively, 1.5, 1.85, and 2.1 eV above the top of the valence band.

The valence band has a spin-orbit splitting of 0.75 eV at $k=0$.[25] The density-of-states effective mass for the holes is $0.9m_0$.[26] Cardona[9] measured the reflectivity of AlSb up to $h\nu=3.5$ eV and found two peaks at 2.78 and 3.18 eV which he attributed to the L_{3v}-L_{1c} transition, thus finding a value of 0.4 eV for the spin-orbit splitting at the L point.

The present work presents new data on reflectivity, photoelectric yield, and energy distributions at photon energies between 2.2 and 6.2 eV.

III. EXPERIMENTAL METHODS

Measurements of the work function and photoelectric emission properties were carried out using the equipment of Allen and Gobeli, described elsewhere.[27] The work function, photoelectric yield spectrum, and the energy distributions of the emitted electrons for various values of $h\nu$ were measured on two different freshly cleaved (110) surfaces of AlSb. These measurements were repeated as the work function was gradually lowered by deposition of various amounts of Cs on the surface.[28] This makes a progressively larger region of the conduction bands observable by photoemission. These measurements were performed at pressures below 5×10^{-10} Torr.

The reflectivity was measured by comparing the intensities of the reflected and the incident beam, Fig. 1. These measurements were performed in a stainless steel vacuum cell equipped with two sapphire windows. One window was used for the entrance of the primary beam and the exit of the reflected beam. The intensity of the primary beam was measured behind the rear window when the sample was moved out of the path. The primary beam made an angle of 8° with the surface. (The monochromator produces a light cone whose half

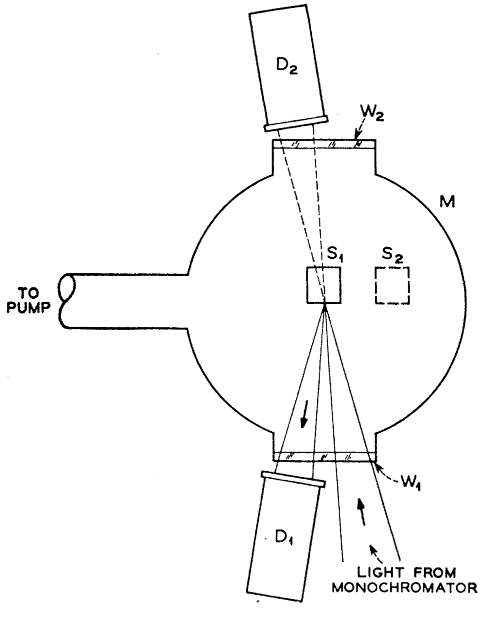

FIG. 1. Experimental setup for the measurement of the reflectivity of AlSb *in vacuo*. M = cylindrical metal envelope; W_1, W_2 = sapphire windows; S_1 = sample in position for the measurement of the reflected light intensity with photomultiplier in position D_1; S_2 = sample in position for the measurement of the incident light intensity with photomultiplier in position D_2.

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[22] I. I. Burdiyan, Fiz. Tverd. Tela **1**, 1360 (1959) [English transl.: Soviet Phys.—Solid State **1**, 1246 (1960).

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[24] C. A. Mead and W. G. Spitzer, Phys. Rev. Letters **11**, 358 (1963).

[25] R. Braunstein, Bull. Am. Phys. Soc. **4**, 133 (1959).

[26] D. N. Nasledov, S. V. Slobodchikov, Zh. Tekhn. Fiz. **28**, 715 (1958) [English transl.: Soviet Phys.—Tech. Phys. **3**, 669 (1958)].

[27] G. W. Gobeli and F. G. Allen, J. Phys. Chem. Solids **14**, 23 (1960); also, later papers.

[28] F. G. Allen and G. W. Gobeli, Rev. Sci. Instr. **34**, 184 (1963).

angle is 5°.) The monochromatic light was produced by a Bausch and Lomb monochromator and a stabilized hydrogen lamp. A photomultiplier covered with sodium salicylate was used to measure the light intensities. The intensity variations of the light source did not exceed 1%, which gives a precision of $\Delta R/R \approx 3\%$. The cleavage apparatus for the reflectivity measurements was similar to that described by Lander, Gobeli, and Morrison.[29] The sample could be cooled crudely by filling the bellows with liquid nitrogen. This allowed the sample to reach a temperature of 130±1°K determined with a copper-constantan thermocouple.

A pressure in the reflectivity cell of 10^{-8} Torr was achieved without bakeout by pumping with a high-speed Vac-Ion pump.

While most of the III–V compounds have very good cleavage properties,[30] it is difficult to obtain satisfactory cleavage planes with AlSb. The surfaces investigated in this work consisted of flat regions of approximately 0.5 mm in extent separated by steps of the order of 0.1 mm. Examination with an optical microscope showed that the planar regions were good (110) cleavage planes. It is concluded from this that the structure in the reflectivity and photoemission data are characteristic of a nearly perfect (110) surface of AlSb. Also, the work function measured with the Kelvin method did not scatter by more than 10 mV when measured at various points of the clean surface. However, the absolute values of the yield may be wrong by as much as 30%.

IV. EXPERIMENTAL RESULTS

(A) Reflectivity

The reflectivity R of solids is determined by their complex index of refraction $N=n-ik$.[31] Since the imaginary part of the dielectric constant $\epsilon_2=2nk$ is proportional to the joint density of states, measurements of the spectral dependence of R will yield information about optical transitions and band structure. In particular, peaks in R will occur at nearly the same photon energies as peaks in absorption. Corresponding maxima in R and ϵ_2 will be displaced with respect to each other by energies in the order of 0.1 eV.

TABLE I. Optical and photoemissive properties of AlSb and their interpretation in terms of band structure. α=absorption, R=reflectivity, Y=photoelectric yield.

$h\nu$ eV	$(dh\nu/dT)$ $\times 10^4$ (eV/°K)	Experiment	Transition (tentative)	Source
1.62 (1.5)	−3.5	α	$\Gamma_{15v}-X_{1c}$	17, 18, 19 (27[b])
1.8 (2.1)		α	$\Gamma_{15v}-\Gamma_{1c}$	25, 26 (27[b])
0.29	−0.2	α	$X_{1c}-X_{3c}(X_{1c}-\Gamma_{1c})$	a, 17, 18 (21[b])
0.75		α	Δ_0	28
2.42	−4.4	R	?	c
2.82	−3.1	R	$\Lambda_{3v}-\Lambda_{1c}(L_{3v}'-L_{1c})$	c, (9[b])
3.22	−3.2	R	$\Lambda_{3v}-\Lambda_{1c}(L_{3v}'-L_{1c})$	c, (9[b])
0.4		R	Δ_1	c, 9
3.55 (3.67)	(0)	Y (R)	?	c
4.22 (4.35)	(−4.2)	Y (R)	$X_{5v}-X_{1c}$	c
4.85		Y	$L_3^1-L_{3c}$	c
5.3 (5.4)	(−4.4)	Y (R)	$L_3^1-L_{3c}$	c

[a] After reinterpretation in Sec. II of this work.
[b] Alternate value, or interpretation.
[c] This work.

The optical reflectivity of the freshly cleaved surface of AlSb is shown in Fig. 4(a). The photon energies corresponding to the maxima of peaks are shown in Table I, together with their temperature dependence, assuming linearity with temperature.

(B) Surface Properties

The work function of the freshly cleaved (110) face of AlSb, measured by the Kelvin method, is $\varphi=4.86 \pm 0.05$ eV. This value represents the difference between the potential energy of an electron in vacuum and the Fermi level, as shown in Fig. 2.

The photoelectric yield Y of the freshly cleaved surface is shown in Fig. 3. It is similar to that of Si, Ge, and the measured III-V compounds.[32] Near threshold, Y varies with the cube of the excess photon energy. This is shown by the insert of Fig. 3, where the cubic root of the yield is plotted versus $h\nu$. The extrapolated threshold is 5.22±0.02 eV. The evidence that this threshold corresponds to emission from states at the valence band maximum at the surface in the case of Ge, Si, and several III-V compounds has been summarized by Gobeli and Allen.[32] The over-all similarity between the photoelectric properties of AlSb and these other materials suggests that the same arguments can be applied here. With this model, the Fermi level at the clean (110) surface of AlSb lies 0.36±0.05 eV above the top of the valence band. Since the energy gap is 1.62 eV at room temperature, the electron affinity is 5.22−1.62=3.60±0.04 eV. However, as pointed out for the other materials,[32] the possibility remains that part of the cubic tail is due to emission from surface states above the valence-band maximum.[33] In this case the energy bands would be located a few tenths of an eV lower relative to the Fermi level than indicated on Fig. 2. For photon energies ≥6.1 eV, the yield is linear in $h\nu$.[32] The present measurements do not determine this linearity with any precision, nor can we

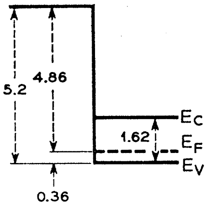

FIG. 2. Energy diagram of the clean surface of AlSb.

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[29] J. J. Lander, G. W. Gobeli and J. Morrison, J. Appl. Phys. 34, 2298 (1963).

[30] A. U. MacRae and G. W. Gobeli, J. Appl. Phys. 35, 1629 (1964).

[31] See, for instance, T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications Ltd., London, 1959).

[32] G. W. Gobeli and F. G. Allen, Phys. Rev. 137, A245 (1965).

decide whether AlSb displays the single linear behavior like Si, GaAs, and InAs or two linear branches like Ge, InSb, and GaSb.[32] The linear portion begins at photon energies too close to the limits of the instrument (6.4 eV). However, based on the evidence from these other materials, it is probably safe to assume that a linear portion of the curve does exist as shown in Fig. 3 and corresponds to direct excitation followed by escape without scattering. Such a transition [which must lie in or close to the direction normal to the (110) surface] is shown as D in Fig. 6.

Since the bulk of the sample is *p* type, with $N_A \sim 2\times10^{17}$ cm^{-3}, there is little band-bending in this particular instance.

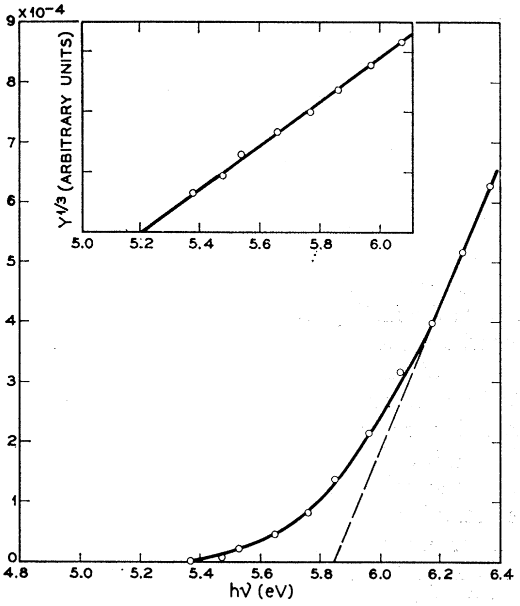

FIG. 3. Photoelectric yield, in electrons emitted per absorbed photon, of the freshly cleaved (110) surface of AlSb. Insert: Cubic root of the same yield displaying the law $Y=a(h\nu-5.22)^3$.

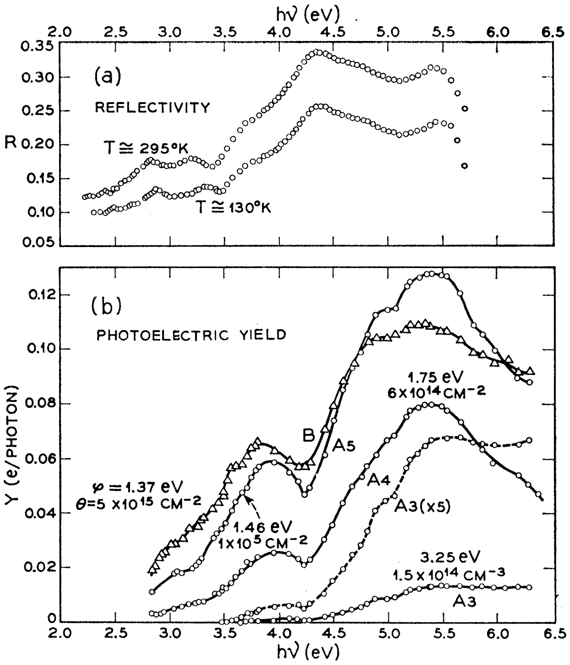

FIG. 4. (a) Reflectivity of AlSb cleaved in high vacuum. The scale for R is arbitrary. (b) Photoelectric yield of AlSb surface covered with various layers of Cs. Curves A3 to A5 are measurements on one surface. Curve B is a measurement on a different surface. θ = cesium coverage in Cs ions/cm^2; φ = work function measured by the Kelvin method.

(C) Photoelectric Emission from Cs-Covered Surfaces

The range of photon energies available without going to the vacuum ultraviolet is too small to allow an investigation of the band structure by photoemission from the clean surface. Also, at photon energies close to the threshold, the emission is mainly determined by the probability of escape, and the effect of variations in absorption coefficient could hardly be observed. Furthermore, the energy necessary for emission is so high that electrons excited to the interesting levels (Fig. 6) cannot escape. As the work function of the crystal is lowered, the photoelectric-yield spectrum will give information about optical transitions, densities of states, and scattering mechanisms. Since the descriptions of the theory of photoemission have been published,[34,35] we shall only summarize qualitatively what one expects:

(a) Strong transitions to final states lying below the vacuum level will produce a dip in the yield spectrum.

(b) As the final state moves above the vacuum level, the dip will gradually disappear and change into a peak, because of increasing escape probability.

(c) For a high absorption coefficient, the transitions take place close to the surface; consequently the electron losses by scattering will be less important and the yield higher.

Figure 4 (b) shows the photoelectric yield in electrons emitted per absorbed photon for successive cesium coverages. The amount of cesium deposited on the surface and the resulting work functions measured by the Kelvin method are shown in the figure. The letters A and B refer to two different surfaces. The correlation between the yield curves and the reflectivity will be discussed in Sec. V.

The energy distributions measured with the surface labeled B are shown in Fig. 5. These energy distributions are normalized, that is, the area under each

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[33] J. J. Scheer and J. van Laar, Phys. Letters 3, 246 (1962).

[34] E. O. Kane, Phys. Rev. **127**, 131 (1962).

[35] C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1030 (1964).

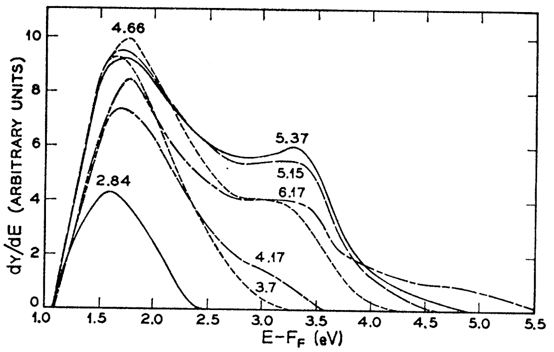

FIG. 5. Energy distributions measured on surface B of Fig. 4. The figures indicate the photon energies in eV. The distributions are normalized so that the area under each curve is proportional to the yield (Fig. 4).

curve is proportional to the yield at the corresponding photon energy. These photon energies are labeled on Fig. 5. The abscissa shows the energy of the electrons with respect to the Fermi level since this is the energy measured with the retarding field method once the work function of the collector is known. The latter is determined from the saturation point of the energy distributions from the clean surface for which the work function is independently measured and remains constant over the emitting area.

The energy distributions display two peaks, the maxima of which lie at $E-E_F=1.75$ and 3.3 eV, respectively. The low-energy maximum is not significant since it results from the fact that the number of electrons moving towards the surface inside the crystal grows with decreasing energy while the probability for escape decreases and is zero at $E-E_F=\varphi$, where φ is the work function.

The high-energy limit of the main part of the distributions obeys the relation

$$E-E_F=h\nu-0.6\text{ eV}. \qquad (3)$$

In fact the distributions do not vanish at this energy but display an exponentially decreasing tail which finally vanishes at an energy close to $E-E_F=h\nu$. This high-energy tail will be discussed in a later publication together with photoelectric emission from InP and CdSe.

In order to locate the final energy of the transition giving rise to the peak at $E-E_F=3.3$ eV in the band structure, it is necessary to determine the position of the Fermi level with respect to the energy bands of AlSb. The simplest conclusion to be drawn from the energy distributions would be that the maximum energy (3) corresponds to excitation from the top of the valence band. In this case, the Fermi level would lie 0.6 eV above the valence band at the cesium-covered surface; band-bending would be unimportant since surface and bulk would be *p* type.

However, deposition of a monolayer of cesium on silicon produces a degenerate *n*-type surface,[6,7,36] bringing the Fermi level close to the edge of the conduction band.

If the same situation prevails for AlSb, the energy bands will bend by more than 1 eV over a depth of approximately 1000 Å. Electrons excited at various depths will possess different final energies with respect to the Fermi level. The energy distributions (Fig. 5) will be smeared by approximately one volt and conclusions about the final states of optical transitions will be uncertain by the same amount.

The available experimental evidence does not allow us to rule out the possibility of an *n*-type surface.

V. DISCUSSION

In this section we shall try to identify the important optical transitions in AlSb by comparing the reflectivity [Fig. 4(a)], the photoelectric yield spectrum [Fig. 4(b)], and the energy-distributions (Fig. 5) under the assumptions outlined in Sec. I. The results, including tentative assignments in terms of critical points, are reported in Table I; these results are being used for a detailed computation of the band structure with the pseudopotential method by Cohen and Bergstresser.[37] The purpose of Fig. 6 is merely to illustrate the findings reported in Table I; it should not be considered an accurate representation of the band-structure of AlSb.

At $h\nu=2.82$ and 3.25 eV we observe two peaks in the reflectivity previously reported by Cardona and labeled as L_{3v}-L_{1c} transitions. The separation of the two peaks is due to the spin-orbit splitting in the valence band.[9] Theoretically,[37] it is more likely that the observed peaks correspond to transitions Λ_{3v}-Λ_{1c} at a saddle point along the [111] direction. The photoelectric yield does not reflect these transitions clearly. (The slight dip in curve A5 might reflect the fact that the final state of the transition is below the vacuum level.) Since the position of these peaks is determined from the reflectivity, the photon energies indicated in Table I must be considered approximate (see Sec. IV A.)

Next, consider the rise in yield between 2.9 and 3.8 eV, a magnitude that increases rapidly with decreasing work function. This rise is not related to structure in the reflectivity. The energy distributions (Fig. 5) show that the electrons emitted at these wavelengths form a broad low-energy group extending up to 2.3 eV above the Fermi level, that is, approximately 2.9 eV above the top of the valence band. It is probable that this yield corresponds to transitions from the valence band to the lower conduction band at noncritical points.

The reflectivity displays a broad peak around $h\nu=3.7$ eV. The yield curves with the lowest work

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[36] J. van Laar and J. J. Scheer, Philips Res. Rept. **17**, 101 (1963).

[37] M. L. Cohen and T. K. Bergstresser (to be published).

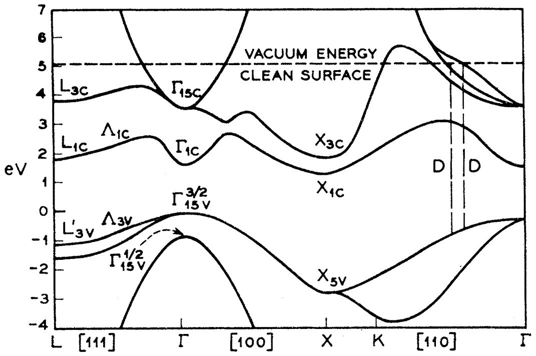

FIG. 6. Schematic sketch of a band structure similar to those computed (M. L. Cohen, to be published) for III–V compounds. Its purpose is to illustrate the transitions described in the text. It is not an accurate band structure for AlSb.

functions show a related structure at 3.55 eV. It is difficult to decide whether this corresponds to $\Gamma_{15v}^{3/2}$-Γ_{15c} transitions or to optical critical points $(\nabla_k E_c = \nabla_k E_v)$ along the [100] and [110] directions in the Brillouin zone.

The most striking feature is the sharp dip in the yield at 4.22 eV corresponding to the high peak at 4.32 in the reflectivity. This is a strong transition to a level below the vacuum potential. In analogy to the other III-V compounds,[8] we label this as X_{5v}-X_{1c} transition. With the X_{1c}-X_{3c} splitting of 0.25 eV (see Sec. II), we should expect evidence of a transition at 4.47 eV. This is not observed in the yield. However, Phillips[8] points out that because of the smaller effective mass at X_{3c} this transition is weaker. Also, the upper level lies just barely above the vacuum potential so that a small fraction of the excited electrons could escape. Thus the absence of a dip or a peak at 4.47 eV, while it does not support the idea of the position of the X_{3c} point, does not contradict it either. In the reflectivity [Fig. 4(a)] this X_{5v}-X_{3c} transition should be observed at 4.6 eV. This may be suggested by the shape of the curve above 4.35 eV. Since the conduction band minimum X_{1c} lies 1.62 eV above the valence band edge, we are able to place $X_{5v} = 1.62 - 4.22 = -2.6$ eV below Γ_{15v}.

The photoelectric yield rises again very sharply at $h\nu > 4.25$ eV. This is due partly to a "recovery" from the 4.22-eV dip as evidenced by the fact that the amplitude of the original low-energy group is low at $h\nu = 4.17$ eV and rises again for $h\nu = 4.6$ eV. At the same time, a high-energy group of electrons rapidly gains in amplitude (Fig. 5). The yield curves exhibit structure between 4.9 and 5.5 eV and the question arises whether this is due to a dip at 5 eV or whether the yield is made up of two peaks at 4.85 and 5.3 eV [curve B, Fig. 4(b)]. With the first interpretation, we would expect a peak in R around 5 eV, while in the latter case one should observe peaks in R near 5.3 and 4.85 eV, respectively. Figure 4a shows that R has a peak at 5.4 eV and that it does not drop off below 5 eV. We therefore interpret this structure as being due to two different peaks. The energy distributions given in Fig. 5 suggest that the final state of the transitions corresponding to these two peaks is the same. The reflectivity curves for the III-V compounds[38] exhibit a strong peak due to the transition L_{3v}-L_{3c} to the upper conduction bands at the [111] zone boundary. Since the two peaks observed in the yield are at about the right photon energy and are separated by approximately the same energy as the spin-orbit splitting discussed above at 2.82 and 3.25 eV, we suggest that they correspond to the L_{3v}'-L_{3c} transition. In the energy-distributions shown in Fig. 5 the final state of this transition lies 3.3 eV above the Fermi level. If the Fermi level at the surface lies at 0.6 eV above the valence band, the point L_{3c} will be 3.9 eV above $\Gamma_{15v}^{3/2}$: accordingly, the L_{3v} points will be located 1.05 and 1.45 eV below $\Gamma_{15v}^{3/2}$ and L_{1c} lies approximately 2.2 eV above the top of the valence band. As pointed out in Sec. IV.C, however, it is possible that the surface is degenerate n type, in which case no conclusions can be drawn from Fig. 5.

In Table I we also report a weak maximum observed in the reflectivity at 2.4 eV. It has been observed with the same reproducibility as the remainder of R and is temperature dependent. We do not have an interpretation for it; it may be due to an optical critical point off a point of high symmetry like the peak at 3.7 eV.

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[38] H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters 8, 59 (1962).