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Photoelectric Yield Near Threshold from Clean Surfaces of InP; Observation of Excitation out of Valence, Surface and Impurity States

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(15. V. 68)

Abstract. It is argued that the photoelectric yield from clean semiconductor surfaces usually observed and described by a cubic and linear spectrum is due to direct transitions of valence electrons. Experimental results are presented that show an emission due to surface states and/or imperfections in the bulk. A distinction between the two possibilities is not feasible with the available knowledge and would require very pure semiconductors.

Introduction

The photoelectric yield spectra from clean surfaces of semiconductors are very similar in the vicinity of the threshold. They can be described by [1-6]

$$Y = C_n(h\nu - E_n)^n \quad E_n < h\nu \leq E_t \quad (1)$$

$$Y = C(h\nu - E) \quad h\nu > E_t \quad (2)$$

where $n = 3 \pm 0.5$ and E_t is the photon energy where transition occurs between (1) and (2).

It was shown that in the case of InAs [4] the emitted electrons are due to direct transitions out of valence states for both the linear and the cubic parts of the yield described by (1). It is to be expected that the same holds true for all semiconductors where the cubic and linear parts of the yield are tangential as discussed in Reference [5]. In this case, photoemission from surface states, if it exists, should be observed as an *addition* to the yield spectrum described by (1) and (2). The yield from such an emission is expected to be small and therefore to be observable as a departure from (1) at photon energies below and not more than a few tenths of an eV above the cubic threshold E_3 of (1). With most semiconductors one does not expect a measurable photoemission from surface states because the Fermi level lies in the lower part of the band gap at the surface. In the case of InP however, the Fermi level lies close to the conduction band [5] so that surface states, if present, are occupied.

This paper represents a re-interpretation of the measurements presented in Reference [5] with the method described in Reference [7].

II. Experimental Results

Figure 1 shows a logarithmic plot of the yield spectra obtained from two cleavages (marked *A* and *B*) of the same crystal. Curve *B* is the one shown in Figure 2 of

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Reference [5]; the dashed part obeys Equation (1) and is due to direct transitions from the bulk. The solid line curve *B* represents a departure from Equation (1). Curve *A* was obtained from another cleavage of the same crystal and shows an extended low-energy branch of the yield spectrum. The curves shown in Figure 1 suggest that the yield spectrum be described as the sum of two spectra; one with low threshold ($h\nu < 4.7$ eV in Curve *A* 1) and the other with higher threshold and represented by (1) and (2). If the yield spectrum for $h\nu < 5.5$ eV of curve *A* is extrapolated to higher photon energies and subtracted from the measured yield (dashed curve), the difference coincides with curve *B*. Notice that the transition from 'cubic' to 'linear' yield, which occurs [5] at $h\nu = 6.06$ eV is smooth and is incompatible with the addition of a new group of electrons. It is reasonable to assume then that the dashed line *B* in Figure 1 represents emission from the valence band while the long wavelength branch is due to electrons emitted from higher lying levels. A more positive answer is given by the energy distributions Figures 2 and 3.

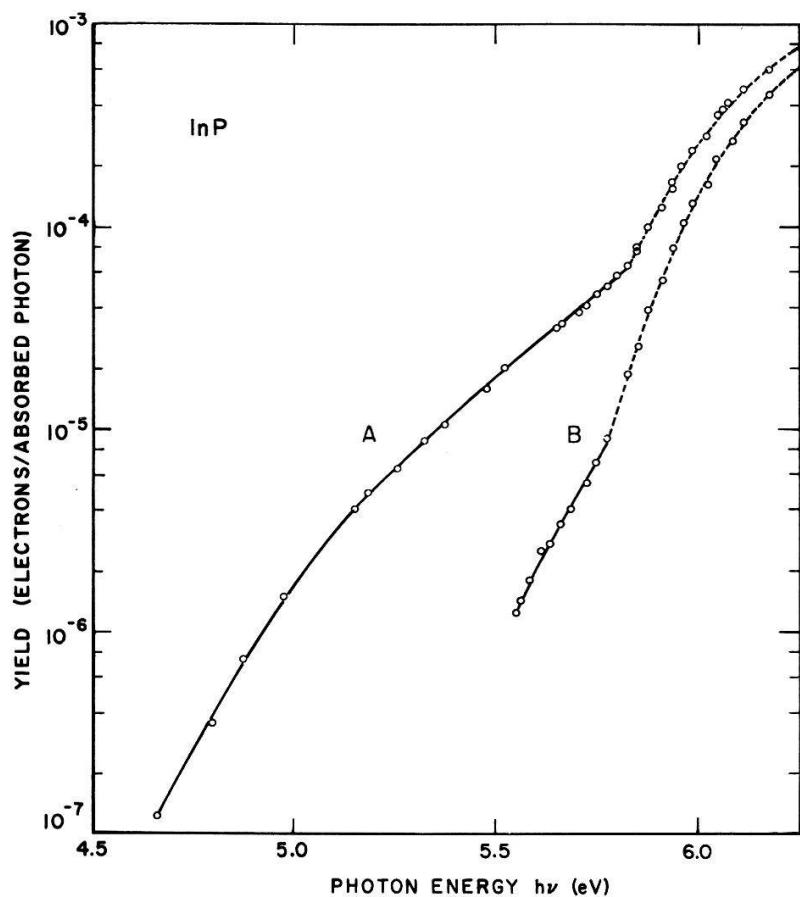


Figure 1

Logarithmic plot of the photoelectric yield spectrum from two cleaved 110 surfaces of InP. The dashed part of curve *B* is the one described by Equation (1) and (2) of the text. It represents emission out of the valence band. The solid lines represent an additional emission from surface states and/or imperfections in the bulk.

Figure 2 shows energy distributions of electrons from surfaces *A* and *B*. The dashed curve shows the distribution of electrons from surface *B* at $h\nu = 6.17$ eV; the solid curves are distributions obtained from surface *A*. The distributions from the

2 surfaces are displaced by 0.22 ± 0.02 eV. Contact potential measurements (Kelvin method) gave the work functions $\Phi_A = 4.45$ eV for surface *A* and $\Phi_B = 4.65$ eV for surface *B*. Thus the displacement of the distributions in Figure 2 indicates a difference in work function which is due to different position of the Fermi level in the gap at the surface, the electron affinity remaining the same [7]. Notice the high-energy tails indicating emission of electrons with initial states higher than the valence band.

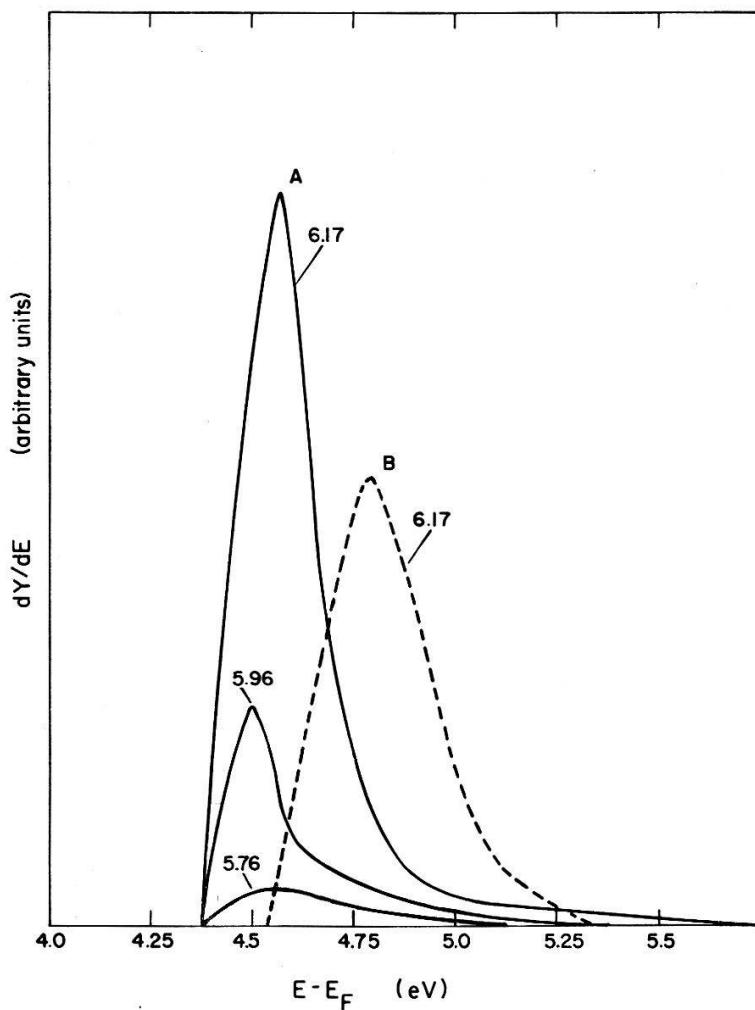


Figure 2

Energy distributions of photoelectrons from 2 surfaces of InP. The dashed line was obtained from surface *B*. Notice the high-energy tails due to emission of electrons from surface states and/or imperfections in the bulk.

It remains to establish whether the electrons responsible for the high-energy parts in Figure 2 and the long wavelength yield in Figure 1 are emitted by the clean surface of InP or represent spurious emission. The answer to this question is given by Figure 3a, which is a logarithmic plot of the distributions shown in Figure 2 (the range of amplitudes is too large for a linear representation). The energy distributions are normalized, i.e. the total area under each curve (in a linear plot) is proportional to the yield. We observe that the low energy cutoff of the distributions corresponding to the long wavelength branch of yield *A*, Figure 1, is the same and is as sharp as that for the distributions at $h\nu = 5.76, 5.96$ and 6.17 eV. Therefore these electrons are emitted by

the clean InP surface. If they were coming from another surface, their low-energy cut off would be at a different value of $E - E_F$ because of differences in work function. Furthermore, the position of this spurious emitter in the energy analyzer would be less favorable than that of the InP surface and the energy resolution would be much poorer: the low-energy cut off would not be as sharp.

Figure 3b shows the same energy distributions but displaced in such a way that the abscissa shows the initial states of the electrons. This plot shows clearly that the electrons in the solid curve Figure 1 originate from states lying up to 1.1 ± 0.05 eV above the top of the valence band.

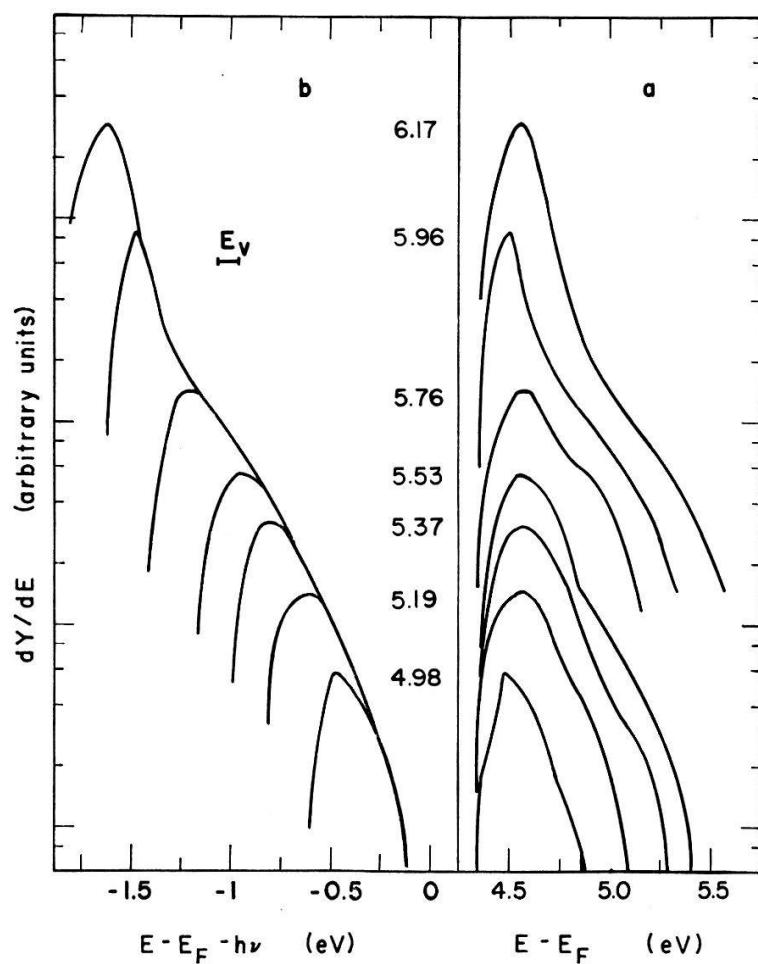


Figure 3

Logarithmic plot of energy distributions obtained from surface A. (a) Energy-distributions of electrons as emitted. (b) Displaced energy distributions with energy scale representing initial states of electrons. The high energy ends of the measured distributions do not overlap with the precision shown in (b); the discrepancies do not exceed 0.05 eV. An average was shown for the clarity of the figure. This procedure is justified by the large degree of noise (10–20% of signal) present, due to the small currents involved ($j_{\max} \approx 5 \times 10^{-13}$ amp.). E_v represents the top of the valence band.

The position of the latter was determined following the methods described in Reference [7]. The electrons with initial energy above the top of the valence band can be the result of excitation out of surface states, out of the conduction band or bulk donors or out of deep states in the band gap in the bulk. The experiment does not allow a distinction between the three possibilities.

Discussion

We have gathered the following information:

- a) the two surfaces have the same yield due to interband transitions, but the emission of electrons originating in the band gap differs: the latter is *not* due to intrinsic properties of InP.
- b) measurements on both surfaces were performed in vacuo ($\phi = 3 \times 10^{-10}$ Torr) within a few minutes following cleavage. The measurements were repeated during two hours and showed no time-dependence, which is in agreement with the low sticking probability of III-V compounds [8]. Therefore the yield at long wavelengths is not due to contamination of the surface.
- c) the work functions of the two surfaces differ by 0.2 eV; this difference is due to different positions of the Fermi level in the band gap at the surface. It is difficult to correlate these differences with bulk properties because of the difficulty in producing InP crystals. The material used was inhomogeneously doped and compensated. Conductivity measurements indicate a larger density of free electrons underneath surface *A* than near surface *B*. The positions of the Fermi levels at the surface shift in the same directions as in the bulk. Notice that the bulk was *n*-type in both cases and that the bands were very nearly flat. The shift in Fermi level at the surface suggests a low density of surface states.
- d) the electrical conductivity of the material below surfaces *A* and *B* vary only by a factor of 4, while the long wavelength branches Figure 1 vary by more than an order of magnitude. It is therefore unlikely that these electrons result from excitation of free electrons or out of donor states. However, the material may contain a much larger density of impurities deep in the gap that do not contribute to the conductivity.

The lack of detailed knowledge about the emitting material and the spectrum of surface states precludes an evaluation of the relative contributions of surface states or bulk impurities to the emission observable at long wavelengths. However, these show that emission from other than valence states can be observed in photoemission from semiconductors and that this emission is not included in the cubic or linear parts of the spectra ordinarily observed but represents an additional yield visible below the cubic threshold. They also show that the conclusive observation of photoemission out of surface states requires semiconductors of a very high purity.

Acknowledgments

This paper is dedicated to Professor BUSCH on the occasion of his sixtieth birthday. It is a pleasure to thank him for his inspiring teaching (his solid-state lectures are frequently interrupted by applause), for the high standards of excellence he sets by his example and above all for the very fine human relationship I enjoyed during my stay in his laboratory at ETH.

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The Magnetic Red Shift in Europium Chalcogenides

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Abstract. The comparison of optical absorption spectra of Eu^{2+} in Eu-chalcogenides, EuF_2 , KBr, and Sr-chalcogenides suggests the assignment of the absorption edge in Eu-chalcogenides to the $4f \rightarrow 5d$ transition instead of to an indirect transition between valence and conduction bands. The 'magnetic-exciton' model gives a suitable description of the magnetic red shift in this case. In solid solutions between ferromagnetic Eu-chalcogenides and isostructural Sr-chalcogenides the $4f \rightarrow 5d$ absorption band moves toward lower energies with increasing Eu concentration. This indicates the existence of a cation-cation interaction which decreases (as does the ferromagnetic Curie temperature) from EuO to EuTe and which is not observable in paramagnetic EuF_2 .

BUSCH and his collaborators [1-3] discovered the magnetic red shift of the optical absorption edge in Eu^{++} chalcogenide powders by measuring the diffuse reflectance as a function of temperature. Magnetic effects in the optical absorption spectrum of single crystals and evaporated thin films of Eu-chalcogenides have been investigated by several authors [4-6]. We report here additional experimental details which may help to characterize the mechanism of this interesting effect.

There are numerous known examples of magnetic ordering effects in optical spectra and their theoretical interpretations have many uncertainties [7, 8]. The magnetic red shift in the Eu-chalcogenides is of particular interest because the occurrence of a sharp absorption edge is combined with ferromagnetic ordering in a relatively simple crystal lattice.

Two different interpretations of the magnetic red shift have been evolved from different models of the band structure and the nature of magnetic interactions in these materials. BALTENSPERGER and his colleagues [9] relate the absorption edge to an indirect excitation from the valence into the conduction band in agreement with preliminary nonself-consistent APW-band-structure calculations by CHO [10, 11].