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W. Gudat, E.E. Koch, and P.Y. Yu
Deutsches Elektronen-Synchrotron DESY, Hamburg

Manuel Cardona and Claude M. Penchina
Max-Planck-Institut für Festkörperforschung, Stuttgart

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W. Gudat, E.E. Koch[+], and P.Y. Yu,[x]
Deutsches Elektronen-Synchrotron,
Hamburg
Manuel Cardona and Claude M. Penchina,[*]
Max-Planck-Institut für Festkörperforschung,
Stuttgart

ABSTRACT

The absorption and reflection spectra of GaP, GaAs, GaSb, InP, InAs, and InSb in the region from 15 to 40 eV are presented and compared with those obtained from characteristic electron energy losses. From these data, information about the density of conduction states, the matrix elements for transitions from the outermost core levels to the conduction bands, and the energy and spin-orbit splittings of those core levels is obtained. X-ray photoemission data (ESCA) in the region from 10 to 1487 eV are also presented and compared with the results of absorption and emission spectroscopy.

[+] Permanent address: Sektion Physik der Universität München,
German Federal Republic.

[x] Present address : University of California, Berkeley, California.

[*] Permanent address: Dept. of Physics & Astronomy, University of
Massachusetts, Amherst, Massachusetts, 01002.

I. INTRODUCTION

The optical properties of the III-V semiconductors have received considerable attention, especially in the region of interband transitions.[1,2] Computer calculations of the dielectric constant from the band structures have yielded assignments of the observed optical structure to transitions at definite regions of the Brillouin zone.[3] Most of the optical transitions between the valence and conduction bands occur below 7 eV, a region in which continuous conventional vacuum uv spectroscopical sources are available. Above 7 eV the usual gas discharge sources yield discrete spectra and poor resolution ensues.

The most appropriate source for spectroscopical work in this region has proven to be the radiation emitted by the electron synchrotrons.[4] Brief reports on absorption measurements in III-V compounds, performed with synchrotron radiation for photon energies between 15 and 160 eV, have recently appeared.[5,6] This work yields information about the energies of core levels, including their spin-orbit splittings, the density of conduction states, and the matrix elements for core to conduction band transitions. We present in this paper absorption and reflection measurements in the 15-40 eV region for amorphous and crystalline GaP, GaAs, GaSb, InP, InAs, and InSb and reflection measurements for crystalline CdTe. Our results are compared with the optical constants obtained from earlier reflectance measurements and those obtained in characteristic electron energy loss experiments. A comparison is also made with theoretical calculations of densities of conduction states.

The optical measurements mentioned above yield energy differences between the ground state and excited states. Under the usual assumptions, Koopmans' theorem yields for this difference the difference between the energies of two corresponding one-electron states. Information about the energy of the initial one-electron core states referred to the Fermi energy can be obtained with X-ray photoemission spectroscopy (ESCA). We present here ESCA measurements for the III-V compounds mentioned. By comparing these results with the optical absorption data and the density of conduction states we conclude that the energy of the optical transitions is, within the scatter of available data, equal to the difference between the final and initial one electron energies. Similar conclusions also seem to apply to other materials of the germanium-zincblende family.[7,8]

II. EXPERIMENT

a. Optical measurements

The experiments were performed with the radiation of the DESY electron synchrotron, monochromatized with a normal-incidence grating instrument. The typical resolution was 2 Å over the whole energy range (15 - 40 eV), i.e., 0.1 eV at 25 eV. Measurements for the materials under consideration above 40 eV have been published elsewhere.[5] A Bendix open magnetic multiplier was used as a detector. The samples for the transmission measurements were obtained by flash evaporation. They were found to be amorphous by electron microscopy when evaporated on substrates at room temperature (GaP, GaAs, InP, InAs) or at -30°C (InSb, GaSb). Crystalline samples were obtained for substrate temperatures between 200 and 300°C. The films were deposited on a KCl-coated microscope slide and mounted on a copper mesh after removing them from the substrate by floatation on water. Those used for the transmission measurements had thicknesses between 500 and 1400 Å, as determined with a Tolansky interferometer with an accuracy of about 10%. Samples of at least three different thicknesses were measured for each material. The thickness was also determined during evaporation with a calibrated quartz-crystal thickness monitor. This determination agreed usually within 10% with the Tolansky value, although sometimes deviations as high as 20% were found. We therefore believe that the absolute values determined for the absorption coefficient are affected by an error of less than 20%, which stems mainly from uncertainties in the sample thicknesses.

For the reflection measurements we used polished bulk samples. They were etched either in methanol + Br_2 (GaAs, InAs, InP, GaP) or in methanol + I_2 (InSb, GaSb). Measurements were performed under nearly-normal incidence (15°) with the reflectometer described elsewhere.[9]

b) ESCA Measurements

The ESCA measurements were performed with the ESCA-3 system manufactured by Vacuum Generators at a pressure lower than 10^{-8} torr. The samples used were cut, polished, and etched (see etchants above) n-type crystals with carrier concentrations sufficiently high to place the Fermi energy at less than 0.1 eV from the bottom of the conduction band. The K (1s) line of carbon, in lampblack or graphite form (283.8 ev[10]), was used for the calibration of the spectrometer. The measurements were performed with the 1486.6 eV x-rays line of an Al anode and the 1253.6 eV line of a Mg anode.

All samples measured were fairly conducting and, with the exception of GaAs and GaP, no charging effects[7] were observed. This was checked by performing experiments with different x-ray tube emission currents: charging of the sample produces a shift of the ESCA lines roughly proportional to the emission current. Such shifts were observed for GaAs and GaP probably due to the poor electrical contact between sample and sample holder. This poor contact can be attributed, at least in GaAs, to the presence of an oxide surface layer since it is also associated with the presence of the characteristic chemicaly shifted lines of As in As_2O_3 in the ESCA spectrum.[10] Bombardment of the sample with Ar -ions produces a disappearance of both, the As_2O_3 lines and the charging effects. At the same time, an increase in the Ga and As lines and a decrease in the strength of the omnipresent K_I line of oxygen after ion bombardment was observed. While no charging effect was observed for GaSb and InSb, a disappearance of the Sb_2O_3 lines after ion bombardment was also noted. All measurements were performed at room temperature.

III. RESULTS

a. Optical Measurements

The absorption spectra of crystalline and amorphous GaP, GaAs, GaSb, InP, and InSb, obtained in the manner described above in the 15-40 eV region, are shown in Fig. 1. The spectra for InAs have already appeared elsewhere.[6] Superimposed on the tail of the valence to conduction band transitions one sees structure which can easily be identified with transitions originating at the outermost d core levels of the cations (D_{III}) and of the anions (D_V, antimonides only). The D_V structures of the arsenides occur above 40 eV.[5] No such structures exist for the phosphides since P does not have d-levels in the core. The D_{III} transitions show considerable fine structure in the crystalline materials (especially in the antimonides) which appears broadened in the corresponding amorphous compounds.

In Fig. 2, we compare the crystalline spectra of Fig. 1 and Ref. 6 with those obtained from characteristic electron energy losses[12] (CEL) and from the Kramers-Kronig processing of early reflectivity data.[13] Such comparison is not possible for InP because of the unavailability of CEL and previous reflectivity data. The agreement between the coarse features of the three absorption spectra for each material of Fig. 2 (only two are available for GaSb) is quite reasonable. This is particularly so when one considers the amount of processing the experimental data of Ref. 12 and 13 have to undergo before the absorption spectra are obtained. The reflectivity spectra of Ref. 13 are limited to energies smaller than 26 eV and thus, a Kramers-Kronig analysis is bound to give inaccurate data in the region above 15 eV. Also, the discrete line source used in Ref. 13 does not permit resolution of the fine structure of the D_{III} transitions. This fine structure appears more prominently in the CEL data which are obtained continuously as a function of frequency. A doublet D_{III} structure is recognised for GaAs, GaSb, and InAs and less clearly for GaP and InSb. The superiority of the resolution obtained with synchrotron radiation is clearly manifested in the quadruplet structure observed for InAs and InSb. The largest discrepancies are observed for GaP. It is, however, gratifying that our data lie half-way between the CEL data and those of Ref. 13.

Figure 3 shows the reflection spectra of crystalline GaP, GaAs, GaSb, InP, InAs, and InSb directly measured with synchrotron radiation. For the sake of comparison, we have added to this figure the early data of Ref. 13 for GaAs, InAs, GaP, and InSb, and the spectra calculated from the data of Fig. 1 and from the CEL data of Ref. 12. In order to calculate the reflection spectra from the data of Fig. 1, we must obtain the real part of the refractive index n by performing the appropriate Kramers-Kronig inversion. For this purpose, the data of Fig. 1 in the 15-40 eV interval were extended to lower energies with the data of Ref. 13 and to higher energies with those of Ref. 5. The obtained spectral dependences of n are shown in Fig. 4.

Since the incoming and reflected intensities were not determined simultaneously, no accurate absolute values of the reflectivity were obtained. We have therefore, scaled the measured reflectivities so as to coincide with the ones calculated from Fig. 1 around the first D_{III} maximum. The agreement between the two sets of available reflectivity spectra is particularly good for InP and GaAs. In all cases the largest discrepancies appear for the data of Philipp and Ehrenreich,[13] a fact which can be attributed to the inadequacy of the conventional gas discharge spectroscopic source available to these authors. The quadruplet structure of the D_{III} transitions, discussed in connection with Fig. 1, can also be seen in our measured reflectivity spectra (Fig. 3) of InAs and InP but not for InSb. Remaining discrepancies between the solid and the dashed curves of Fig. 3, may be due to structural differences between the thin films used for the transmission work and the bulk samples used to measure reflection spectra. There may be in this last case, some influence of the surface treatment (polish and etch). Also, scattered light should affect reflectivity more strongly than transmission measurements especially because of the small reflectivities above 15 eV as compared with the values below 15 eV. We point out in this respect that the CEL data were taken for evaporated thin films with the exception of GaP, for which an etched bulk crystal was used.[12]

The energies of the various structures observed in the 15-40 eV region with the three methods discussed above (reflection, transmission, CEL) are given in Table I.

b) ESCA Measurements

Figure 5 shows the ESCA spectra of the outermost d levels of GaP ($M_{IV,V}$ of Ga), GaAs, ($M_{IV,V}$ of Ga and of As), GaSb ($M_{IV,V}$ of Ga and $N_{IV,V}$ of Sb), InP ($N_{IV,V}$ of In), InAs ($N_{IV,V}$ of In, $M_{IV,V}$ of As) and InSb ($N_{IV,V}$ of In, $N_{IV,V}$ of Sb). The resolution is essentially determined by the width of the x-ray source ($K\alpha_{1,2}$ line of Al, 1.2 eV width). It suffices to resolve the $N_{IV,V}$ spin-orbit doublet of Sb and to give an indication of this splitting for In in InP. The structures observed are tabulated in Table II.

It is interesting to point out that all the Sb lines of InSb and GaSb and the As lines of InAs measured after etching appeared split. They had the low-energy component of Table II accompanied by a second component with 3 eV higher binding energy. Similar doublet structures were also observed for crystalline Sb. The high energy component of these doublets can be attributed to antimony and arsenic oxides.[11] These components disappear after bombardment with Ar-ions (1μA for one hour). Such disappearance is accompanied by a decrease in the intensity of the oxygen 532 eV line. This line is present in all our samples although in the antimonides it is mashed by the M_{IV} line of Sb_2O_3. Also, charging effects,[7] which were observed for GaP and GaAs due to poor contact with the sample holder, disappeared after ion bombardment.

IV DISCUSSION

We present in Fig. 6, the effective number of electrons per molecule $N_{eff}(\omega)$ which have contributed to the transitions in the range of Fig. 1 at energies lower than ω. This number is obtained with the expression:

$$N_{eff}(\omega) = 2.28 \times 10^{15} a_o^3 \int_{\omega_o}^{\omega} \mu(\omega) n(\omega) d\omega \quad (1)$$

where a_o is the lattice constant in cm, μ the absorption coefficient in cm^{-1}, n the real part of the refractive index, (Fig. 4), and the photon energy ω must be given in electron volts. As initial energy ω_o we have taken 13 eV. We notice in Fig. 6 that up to 40 eV only a small fraction of the outermost core d electrons have exhausted their oscillator strength. One must actually go to 100 eV in InSb and to about 250 eV in GaP if one wants to get N_{eff} to be the total number of outermost core d electrons (20 in InSb, 10 in InP).[14] The large energy spread of these transitions, as compared with the typical 10 eV spread of the valence transitions,[14] is essentially the atomic centrifugal barrier effect of Fano and Cooper.[15]

Figures 1 and 2 contain contributions of the core electrons superimposed on the tail of the valence band transitions. In order to study quantitatively the core electrons contribution, we fit the tail of the valence transitions before the onset of D_{III} to a power law of the form ω^{-r}: r turns out to lie between 2 and 3. We then subtract this extrapolation from the total absorption coefficient in the D_{III} region and obtain the experimental curves of Fig. 7. These curves can be interpreted with the standard expression for the imaginary part of the dielectric constant of a cubic material (in atomic units)[14]

$$\varepsilon_i(\omega) = \frac{nc\mu}{\omega} = \frac{4\pi^2}{3\omega^2} < P^2 > N_d(\omega) \qquad (2)$$

where $<P^2>$ is a square average matrix element of the linear momentum, which we shall treat as nearly independent of energy, and $N_d(\omega)$ the combined density of states. Because of the flatness of core levels, N_d is essentially determined by the density of conduction states. Since n is only weakly frequency-dependent in the region of interest (see Fig. 4), we conclude from Eq. (2) that the absorption coefficient μ should be proportional to N_d/ω. We must, however, allow for the contribution of two sets of core D_{III} levels, because of the spin-orbit splitting of the cation (0.9 eV for In, 0.5 eV for Ge[16]) and we must also take into account the multiplicity of these levels. We thus find:

$$\frac{nc\mu}{\omega} = \varepsilon_i(\omega) = \frac{4\pi^2}{3\omega^2} - < P^2 > 3N_c(\omega-\omega_d) + 2N_c(\omega-\omega_d-\Delta_d) \qquad (3)$$

where N_c represents the density of conduction states, ω_d the onset of the D_{III} transitions and Δ_d the spin-orbit splitting of the core states. We show in Fig. 7 the fit to the experimental data with Eq. (3) using the calculated N_c.[17,18] From these fits we obtain the average matrix elements $< P^2 >$ listed in Table III. These matrix elements are nearly an order of magnitude smaller than the typical valence-conduction matrix elements (0.6 Bohr radii^{-1}, see Ref. 14).

In Figs. 1, 2, and 7 the strength of the D_{III} structure decreases with increasing atomic number of the anion (GaP > GaAs > GaSb) and it increases with increasing atomic number of the cation. This trend can be qualitatively explained in terms of Phillips' ionicity scale[19] (the Phillips' ionicities f_i for the compounds under consideration are listed in Table IV). The D_{III} structures correspond to transitions from the d core levels of the cation to the cation-like lowest conduction bands. An increase in ionicity shifts the electron density of the lowest conduction bands towards the cation. The core wave functions contributing to D_{III} are rather strongly localized around the cation and therefore a shift of the conduction wave function towards the cation should produce an increase in the strength of the D_{III} structures. According to Table IV the ionicity increases when the atomic number of the cation increases and viceversa for the anion. Thus the strengths of D_{III} is expected to increase when the atomic number of the cation increases and decrease when that of the anion increases, in agreement with the observations.

The spectra shown in Fig. 7 for the Ga compounds represent essentially the density of conduction states (the small spin-orbit splitting of the core levels is not resolved in the experimental spectra). This density of states has two peaks (D_{III}^1, D_{III}^2) as the most prominent features.[17,18] The D_{III}^1 peaks originate at the rather flat two lowest conduction bands near X and D_{III}^2 at the second lowest (L_3) band near L. We have also observed the equivalent of the D_{III}^1-D_{III}^2 structures in the reflection spectrum of CdTe (see D_{II}^1,D_{II}^2 Fig. 8). We did not see the spin-orbit splitting of the D_{II}^1-D_{II}^2 structures in this spectrum: this splitting was also missing in the reflection spectrum of InSb (Fig. 3). The D_{III}^3 and D_{III}^4 structures, observed for a number of III-V compounds (Table 1) also appears for CdTe. (For the divalent Cd these lines are labeled D_{II}). In the absence of density of states calculations we believe that these structures are associated with the $\Gamma_{12}(D_{II}^3)$ and the upper $\Gamma_{15}(D_{II}^4)$ conduction bands. These bands are typically 8 eV and 11 eV above the bottom of the conduction band.[20] There are indeed rather flat portions of the bands at energies near that of Γ_{12}.

Concerning the spectra of the amorphous materials, (Fig. 1) we note a complete disappearance of the fine structure of the D_{III} transitions (exception: InSb which may have some slight crystallinity). Reference 21 reported a similar lack of fine structure for the valence transitions and also a shift towards lower energies in the position of their maximum of the order of 1 eV. Such a shift is analogous to that observed in Fig. 1. We note that the D_V-D_V+ Δ structure is essentially the same for amorphous and for crystalline material (InSb, Fig. 1). These peaks do not show any fine structure related to the density of conduction states.

In Table II it is easy to see that the chemical shifts of the core levels of a compound (with respect to the pure element[22]) are nearly the same for all levels of a given atom in a given compound. We have therefore listed in Table IV the average chemical shifts determined for the III-V compounds. We observe in general, positive shifts δ_{III} for the cations and negative shifts δ_V for the anions, corresponding to a transfer of electrons from cation to anion in the partially ionic bonding. Similar effects have been reported for the II-VI compounds.[7] The difference $\delta = \delta_{III} - \delta_V$ should therefore be related to some effective charge. As shown in Table IV, the chemical shift for a given atom usually increases with increasing ionicity of the compound (exception: GaAs→ GaSb) however a simple relationship between δ and f_i was not found. This may be due in part, to uncertainties in δ which stem from the uncertainties in the measurements of core levels of the compound (typically ±0.2 eV) and the pure element (typically ±0.3 eV)[22]. Also the role of the Fermi energy as the reference in ESCA measurements introduces considerable uncertainties: due to surface states (surface charge layers) all bands, including the core levels, may be bent near the surface. It is at present, not clear whether the observed core levels are those at the surface, at the bulk, or somewhere in between. The answer to this question should be determined by the penetration depth of the X-rays and the escape length of the photo-electrons. We are presently performing ESCA measurements in semiconductors as a function of doping in order to clarify this problem.

We note that the core shift of the anions rapidly goes to zero through the sequence P-As-Sb. A similar effect was also found by Vesely and Langer [7] for the II-VI compounds through the sequence S-Se-Te. This effect is, to some extent, related to the decrease of the gap of the material through these sequences. The core levels of the anion are actually tied more closely to the valence band than to the conduction band since the top of the valence band is largely anion-like. The reference energy for the ESCA measurements, i.e. the Fermi energy is very close to the bottom of the conduction band in the bulk. A decrease in the k=0 gap should have as a result a decrease in the "binding energies" of the anion without a corresponding change in the binding energies of the cation which are tied to the conduction band.

Following our assumption that the Fermi level (ESCA reference level) coincides with the bottom of the conduction band, and using the calculated densities of conduction states, it is possible to estimate from the ESCA data the energies of the main peaks ($D_{III}{}^{1}$, D_V) seen in absorption spectroscopy. These energies should be equal to the corresponding ESCA binding energy plus the energy $\delta\omega_c$ of the X_1-X_3 conduction states (first peak in the density of states) measured from the bottom of the conduction band. We list in Table V the difference between the energy of several peaks in the absorption spectra of III-V compounds and the corresponding ESCA binding energies. In most cases this difference is close to the calculated value of $\delta\omega_c$, also listed in Table V. The few existing discrepancies are probably due to experimental uncertainties. We thus conclude that the optical excitation energies, are within the accuracy of available information equal to the difference in the one-electron energies of the final and initial states.

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FIGURE CAPTIONS

1. Absorption spectra of several crystalline (solid line) and amorphous (dashed line) III-V compounds in the 15-40 eV region at room temperature.

2. Comparison of the crystalline spectra of Fig. 1 (solid line) with those obtained from characteristic electron energy losses[12] (- -) and from reflection measurements with conventional vacuum uv sources.[13] (.— .— .— .) The vertical flags indicate estimated errors. (InP not included in Refs. 12 and 13).

3. Reflection spectra of six crystalline III-V semiconductors obtained with synchrotron radiation (- -) at room temperature compared with earlier reflectivity data[13] (—··—··InP and GaSb not available), with Kramers-Kronig calculations from the data of Fig. 1 (————) and with calculations from characteristic energy loss data[12] (—·—·— InP not available).

4. Real part of the refractive index of several III-V semiconductors obtained as discussed in the text from the data of Fig. 1.

5. ESCA spectra of the outermost d core levels of GaP, GaAs, GaSb, InP, InAs and InSb, as observed with the K_α line of Al.

6. Number of effective electrons which corresponds to the crystalline spectra of Fig. 1, as obtained with Eq. (1).

7. Contribution of the D_{III} transitions to the absorption spectrum of GaAs, GaSb, InAs and InSb (————) compared with the density of conduction states[17,18] appropriately modified so as to take into account the $N_{IV,V}$ splitting of In and Ga(- - - - - -) This splitting is too small to be resolved experimentally in the Ga compounds. (0.5 eV[16]).

8. Reflection spectrum of CdTe between 11 and 25 eV measured at room temperature with synchrotron radiation.

	GaP	GaAs	GaSb	InP	InAs	InSb	CdTe(D_{II})
D^1_{111}	20,6[a] 20,9[b] 21,3[c]	20,9[a] 20,6[b] 21,0[c]	20,8[a] 20,4[b] 20,8[c]	18,8[a] 18,8[b]	18,5[a] 18,5[b]	18,3[a]	13,1[a]
$D^1_{111}+\Delta_d$	21,2[a]			19,7[a] 19,7[b]	19,5[a] 19,4[b] 19,6[c]	19,2[a] 18,9[b] 19,1[c]	
$D^{1\,\prime}_{111}$						20,0[a]	
D^2_{111}	23.1[a] 23,2[b] 23,3[c]	23.0[a] 22,9[b] 23,2[c]	22,3[a] 22,2[b] 22,5[c]	21,6[a] 21,6[b]	21,5[a] 21,3[b] 21,6[c]	20,8[a] 20,9[b] 21,0[c]	15,6[a]
$D^2_{111}+\Delta_d$				22,4[a] 22,5[b]	22,3[a] 22,1[b]	21,5[a]	
D^3_{III}	25[b]		24,4[b]	24,4[b]	26,0[a] 24,7[b]	25[a] 25[c]	18,9[b]
D^4_{III}			28,4[a] 28,3[b] 28,5[c]	28,5[a] 29,8[b]	29,2[a] 27,5[b] 27,5[c]	28,1[a]	21,8[a]
D_V		43,1[d]	33,2[a]		43,0[d]	32,9[a]	
$D_V+\Delta_d$			34,5[a]			34,3[a]	

a - From transmission in thin films

b - From reflection in single crystals

c - From characteristic energy losses (Ref. 12)

d - From transmission in thin films(Ref. 5)

TABLE I Compilation of the energies of the experimental structures observed for several III-V compounds and for CdTe.

CATION LEVELS

	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V
GaP		1144.3	1117.45	160.0	108.5	104.65	19.2						
GaAs	1302	1143.8	1117.0	159.85	108.15	104.35	19.3						
GaSb	1303.6	1144.8	1117.95	160.65	109.15	105.2	20.05						
Ga$^{(a)}$	1297.7	1142.3	1115.4	158.1	106.8	102.9	17.4						
InP				826.7	703.5	665.3	451.5	444.0	123.05	79.4		18.1	17.4
InAs				826.55	703.20	665.20	451.35	443.80	122.55	78.3		17.2	
InSb				826.15	702.6	664.8	451.0	443.45	122.2	77		16.75	
In$^{(a)}$				825.6	702.2	664.3	450.8	443.1	121.9	77.4		16.2	

TABLE II

ANION LEVELS

	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V
GaP	128.8	129.7	186.6									
InP	128.3	129.1	186.1									
P(a)	132.2		189.3									
GaAs	1358	1322.3	203.9	144.95	139.95	40.8						
InAs		1322.35	203.80	144.25	139.65	40.65						
As(a)	1358.6	1323.1	203.5	146.4	140.5	41.2						
GaSb			945	811.9	765.9	536.8	527.4	152.0			32.6	31.45
InSb				811.4	765.05	536.3	527.0	151.6	97.1		32.20	31.05
Sb(a)			943.7	811.9	765.6	536.9	527.5	152.0	98.4		31.4	

(a) From Ref. 22

TABLE II (continued) Compilation of the binding energies of core levels with respect to the Fermi energy obtained with ESCA spectroscopy.

	GaAs	GaSb	InAs	InSb
$\langle P^2 \rangle$	0.11	0.085	0.14	0.10
photon energy	21.5 eV	21 eV	23 eV	19 eV

TABLE III   Average matrix element $\langle P^2 \rangle$ in (Bohr radii)$^{-1}$ - required to fit the experimental absorption with the density of states (Fig. 7) at the given photon energy.

	GaP	GaAs	GaSb	InP	InAs	InSb
δ_{III}	1.90	1.60	2.5	1.2	0.85	0.4
δ_V	-2.85	-0.55	0.0	-3.4	-0.6	-0.5
$\delta_{III}-\delta_V$	4.75	2.15	2.5	4.6	1.45	0.9
f_i	0.37	0.31	0.26	0.42	0.36	0.32

TABLE IV   Chemical shifts of cation (δ_{III}) and anion (δ_V) observed in the III-V compounds. Also, ionicity f_i according to Phillips.[19]

	$E_\alpha - E_{ESCA}$				$\delta\omega_c$
	D_{III}	D_V	P_{III}	P_V	Calculated (band theory)
GaP	1.6		1.45	2.1	
GaAs	1.6	2.3	1.7		1.8[a]
GaSb	0.8	1.8			1.5[b]
InP	1.4			1.6	
InAs	1.6	2.35		2.25	2.5[a]
InSb	1.85	1.85			1.75[b]

a - From Ref. 3

b - From Ref. 13

TABLE V Difference between the energy of absorption structure E_α due to transitions originating at outermost core d and p levels and the corresponding ESCA energies compared with the energy $\delta\omega_c$ of the first maximum in the calculated density of conduction states (origin = bottom of conduction band).

REFERENCES

1. H.R. Philipp and H. Ehrenreich, Phys. Rev. 129, 1550 (1963)

2 M. Cardona, K.L. Shaklee, and F.H. Pollak, Phys. Rev. 154, 696 (1967)

3. C.W. Higginbotham, F.H. Pollak and M. Cardona, Proceedings of the International Conference on the Physics of Semiconductors, Moscow 1968 (Nauka, Moscow, 1968) p. 57

4. R.P. Godwin, Springer Tracts in Modern Physics 51, 15 (1969)

5. M. Cardona, W. Gudat, B. Sonntag, and P.Y. Yu, Proceedings of the International Conference on the Physics of Semiconductors, Cambridge, Mass. 1970 (Publication of the U.S. Atomic Energy Commission, 1970) p.209

6. M. Cardona, W. Gudat, E.E. Koch, M. Skibowski, B. Sonntag, and P.Y. Yu, Phys. Rev. Letters 25, 659 (1970)

7. C.J. Vesely and D.W. Langer, Phys. Rev. 4, 451 (1971)

8. M. Cardona and R. Haensel, Phys. Rev. 131, 2605 (1970)

9. G. Rosenbam, B. Feuerbacher, R.P. Godwin, and M. Skibowski, Appl. Opt. 7, 1917 (1968)

10. S. Hagström and S.E. Karlsson, Arkiv Fysik 26, 451 (1964)

11. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johannson, T. Bergmark, S.E. Karlsson, J. Lindgren, and B. Lindberg, ESCA (Amquist and Wiksells, Uppsala, 1967).

12. C. v. Festenberg, Z. Physik 227, 453 (1969)

13. H. Ehrenreich and H.R. Philipp, Phys. Rev. 129, 1550 (1963) Data tabulated by B.O. Seraphin, in "Semiconductors and Semimetals", Vol. 3, edited by R.K. Willardson and A. Beer, (Academic Press Inc., N.Y., 1967)

14. M. Cardona, Proceedings of the Enrico Fermi Summer School, Varenna 1971 (to be published)

15. U. Fano and J.W. Cooper, Rev. Mod. Phys. 40, 441 (1968)

16. F. Herman and S. Skillman, Atomic Energy Levels (Prentice Hall Englewood Cliffs, N.J., 1963)

17. F.H. Pollak, C.W. Higginbotham, and M. Cardona, Proc. Phys. Soc. Japan Suppl. 21, 20 (1966)

18 D.J. Stukel, T.C. Collins, and R. W. Euwema, in "Electronic Density of States", National Bureau of Standards, special publication 323, Washington D.C., 1971, p. 93

19. J.C. Phillips, Rev. Mod. Phys. 42, 317 (1970)

20. F. Herman, R.L. Kortum, C.D. Kuglin, and J.L. Shay, in "II-VI Semiconducting Compounds", ed. by D.G. Thomas (Benjamin, N.Y., 1967) p. 503

21. J. Stuke and G. Zimmerer, Phys. Stat. Sol. (b) 49, 513 (1972)

22. J.A. Bearden and A.F. Burr, Rev. Mod. Physics 39, 125 (1967)

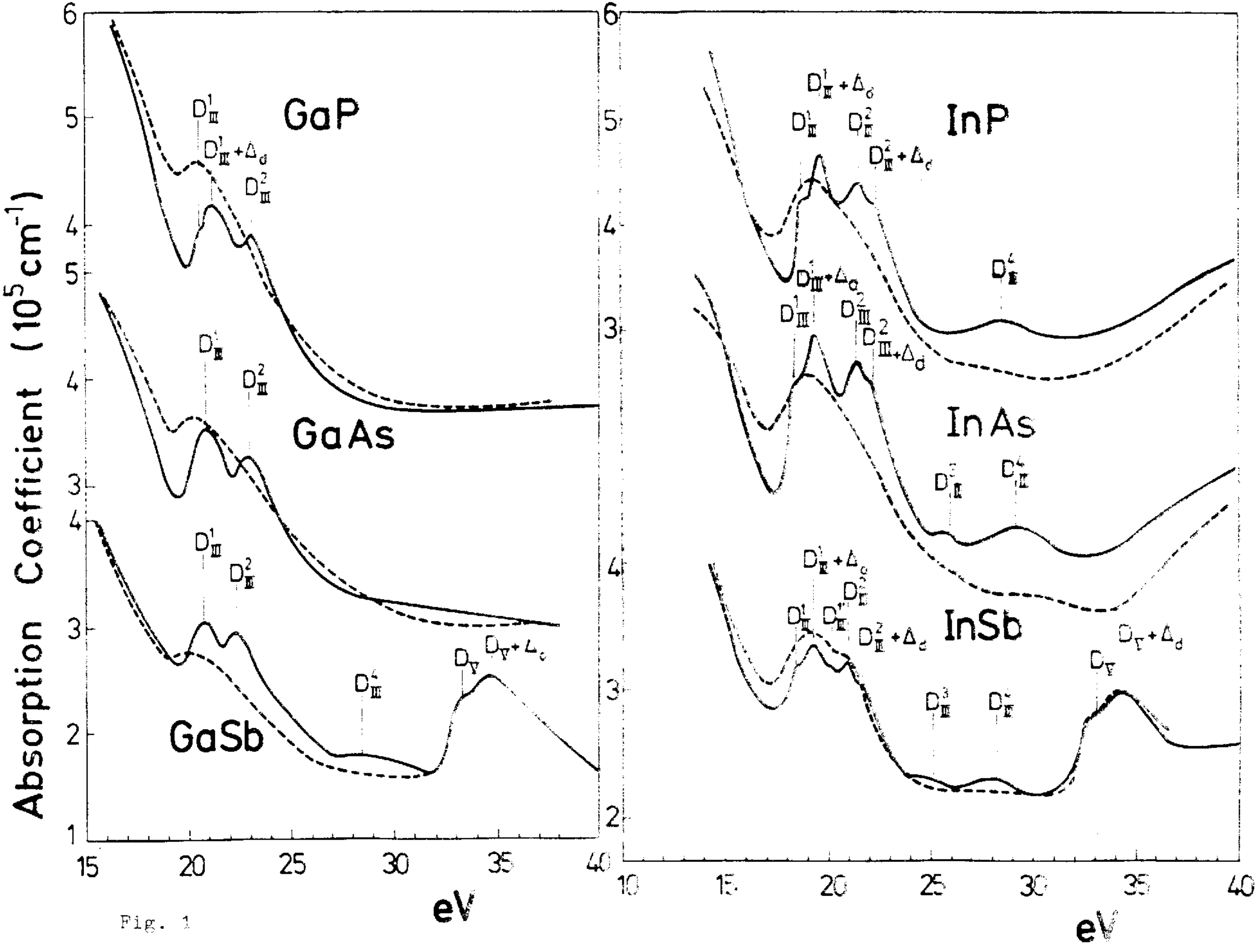

Absorption Coefficient (10⁵ cm⁻¹)
eV
GaP
GaAs
GaSb
InP
InAs
InSb
D¹_III
D¹_III + Δ_d
D²_III
D²_III + Δ_d
D³_III
D⁴_III
D_V
D_V + Δ_d
15
20
25
30
35
40
10
1
2
3
4
5
6

Fig. 1

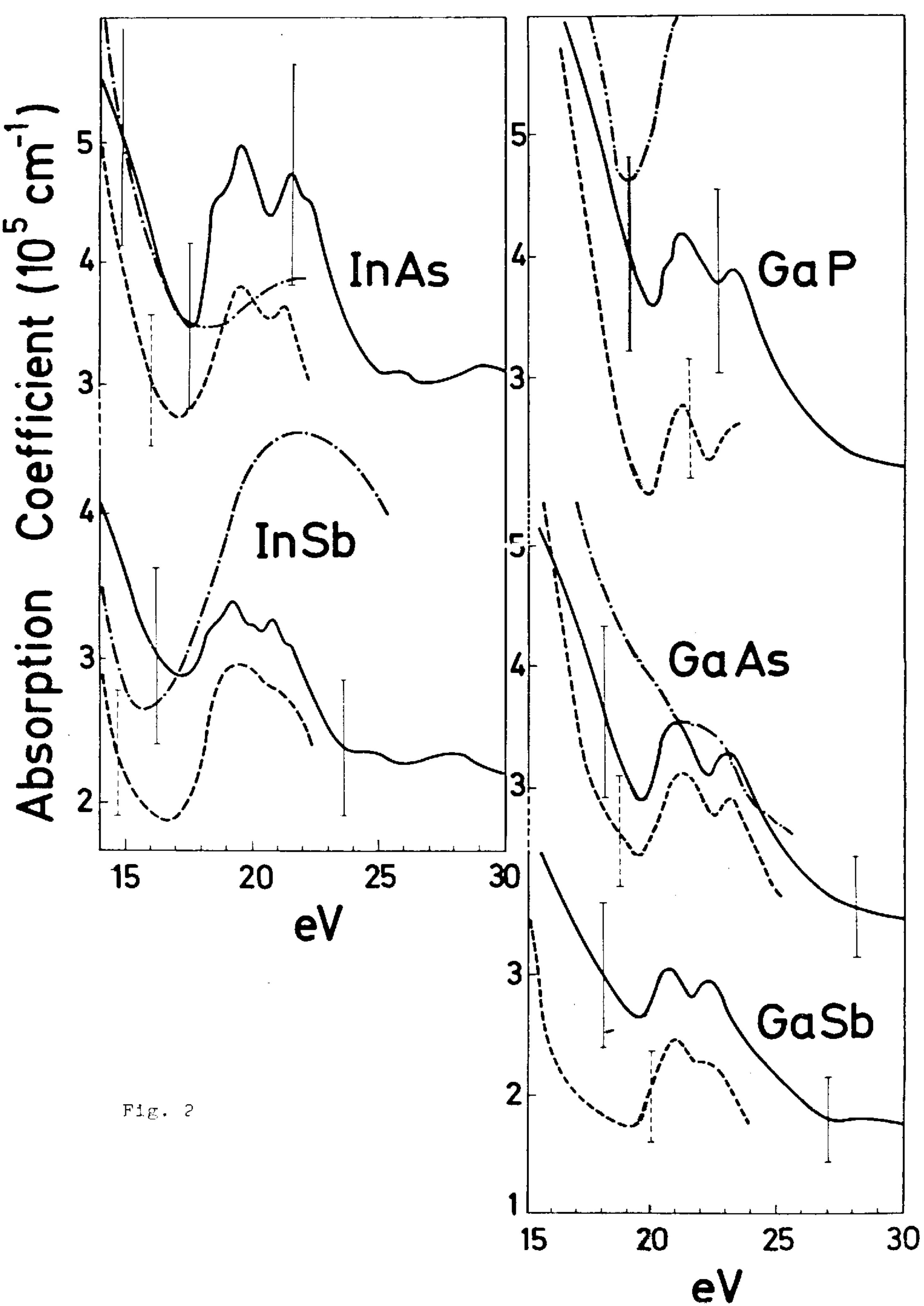

Absorption Coefficient (10^5 cm^{-1})
InAs
InSb
GaP
GaAs
GaSb
5
4
3
2
1
15
20
25
30
eV

Fig. 2

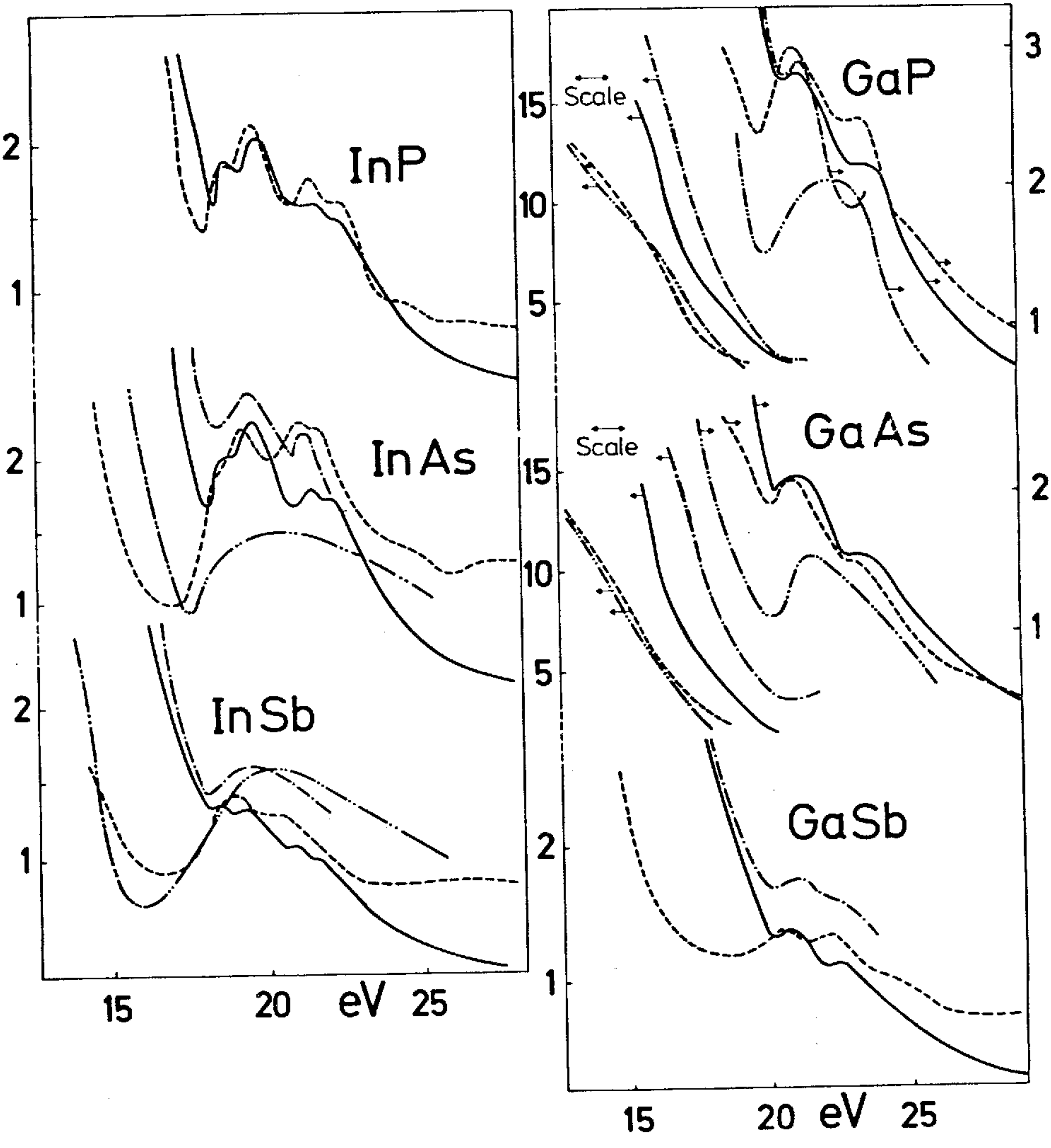


Fig. 3

Reflectivity (%)

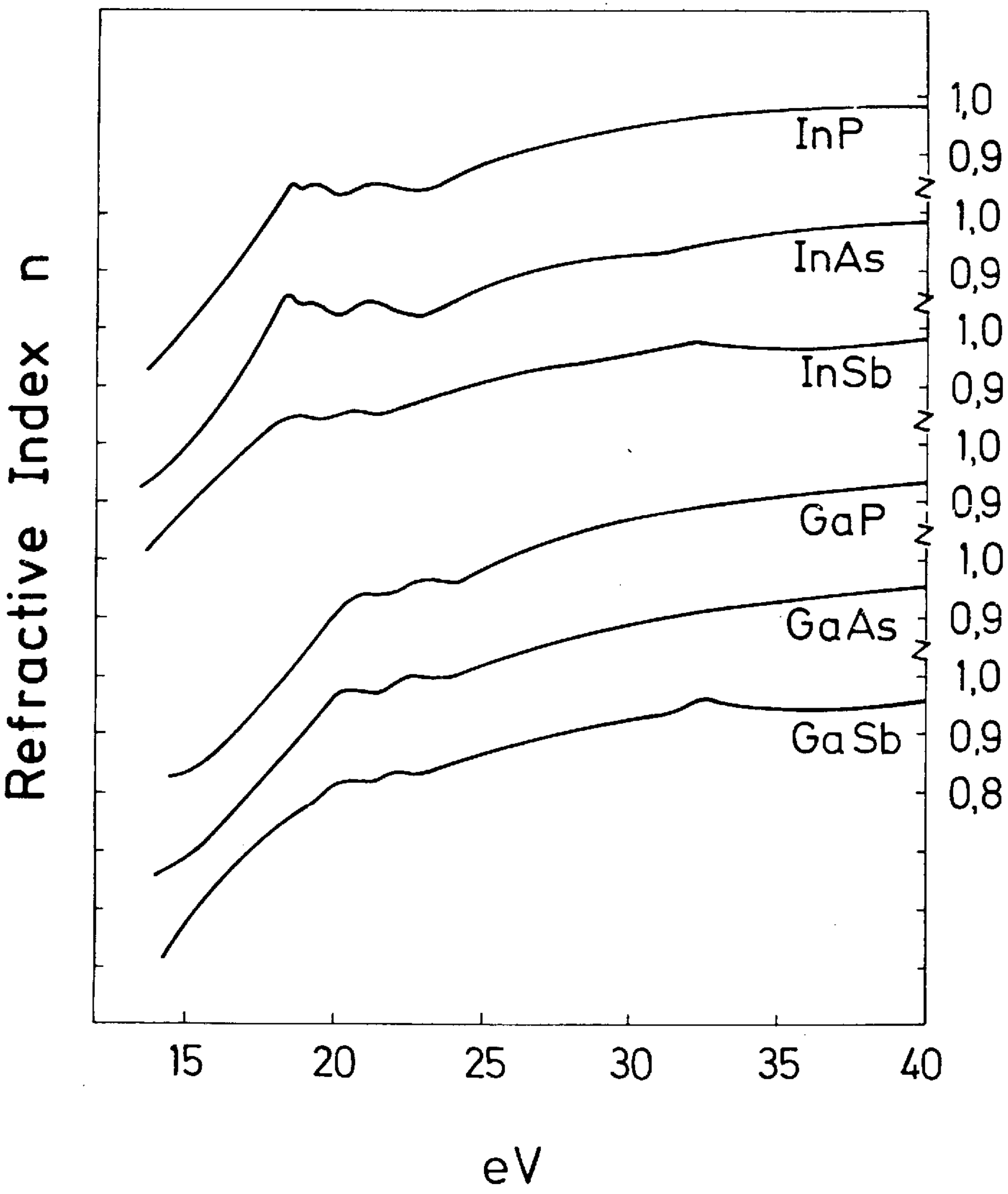

Refractive Index n
1,0
0,9
1,0
0,9
1,0
0,9
1,0
0,9
1,0
0,9
1,0
0,9
0,8
InP
InAs
InSb
GaP
GaAs
GaSb
15
20
25
30
35
40
eV

Fig. 4

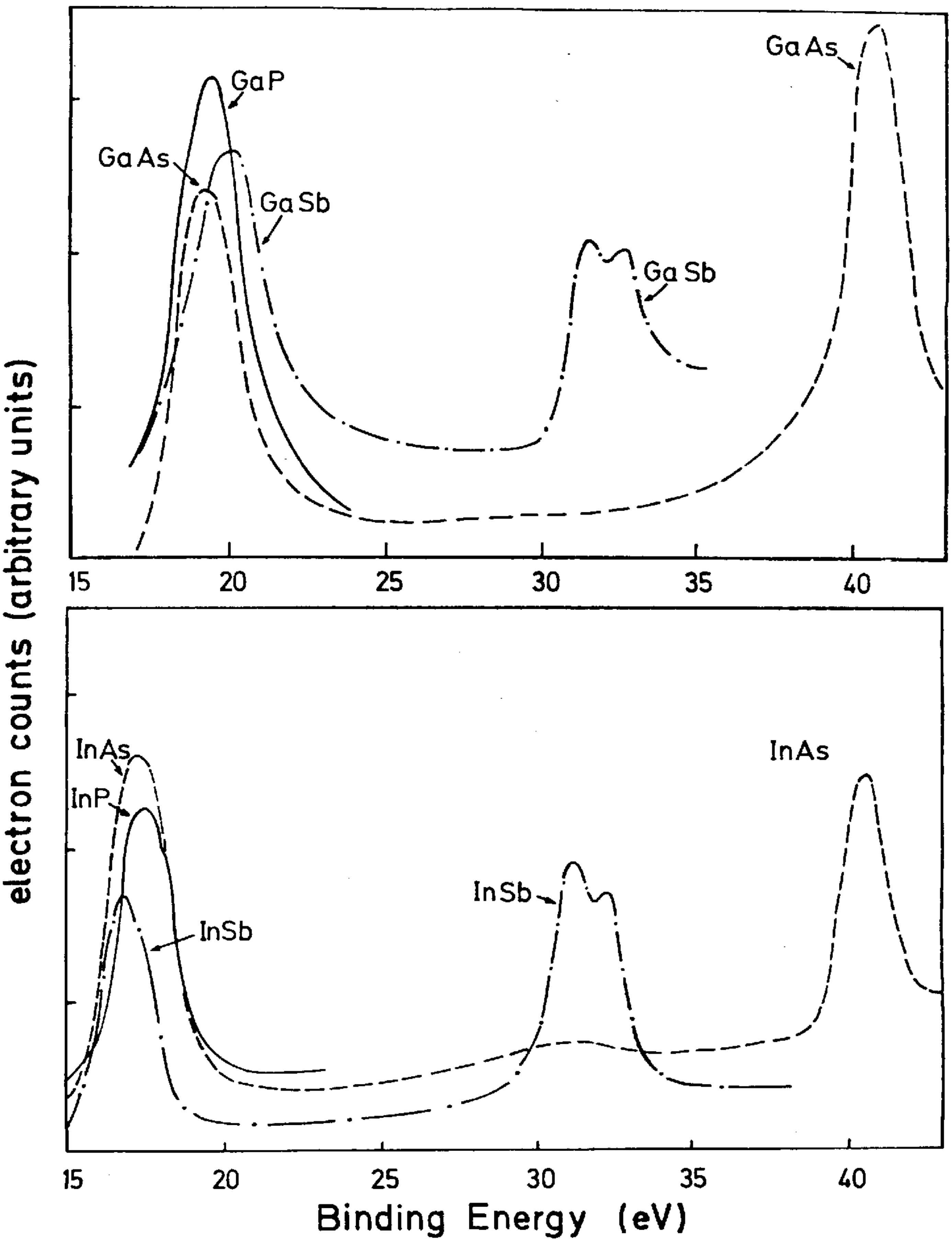

electron counts (arbitrary units)
GaP
GaAs
GaSb
Ga Sb
GaAs
15
20
25
30
35
40
InAs
InP
InSb
InSb
InAs
15
20
25
30
35
40
Binding Energy (eV)

Fig. 5

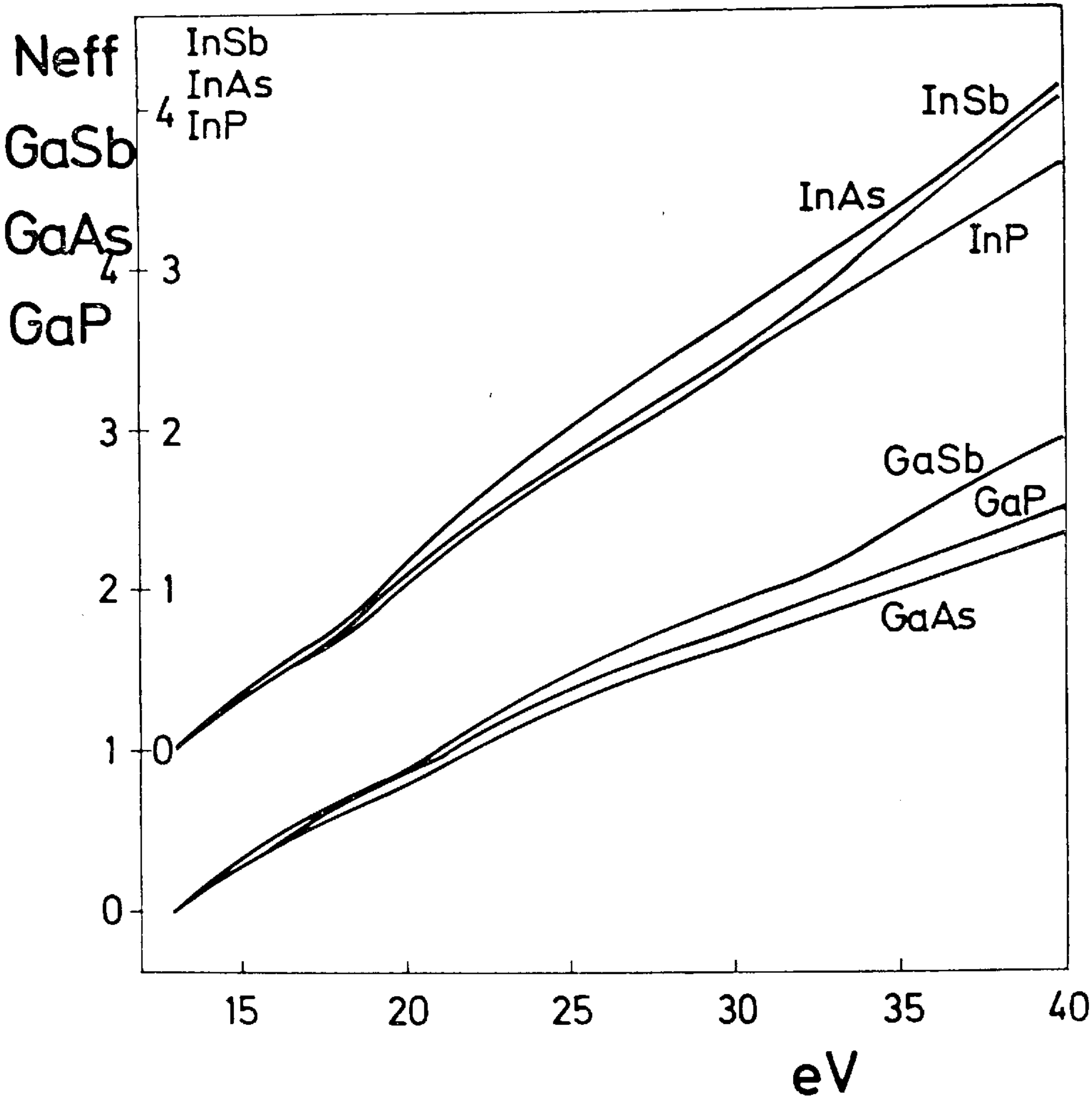
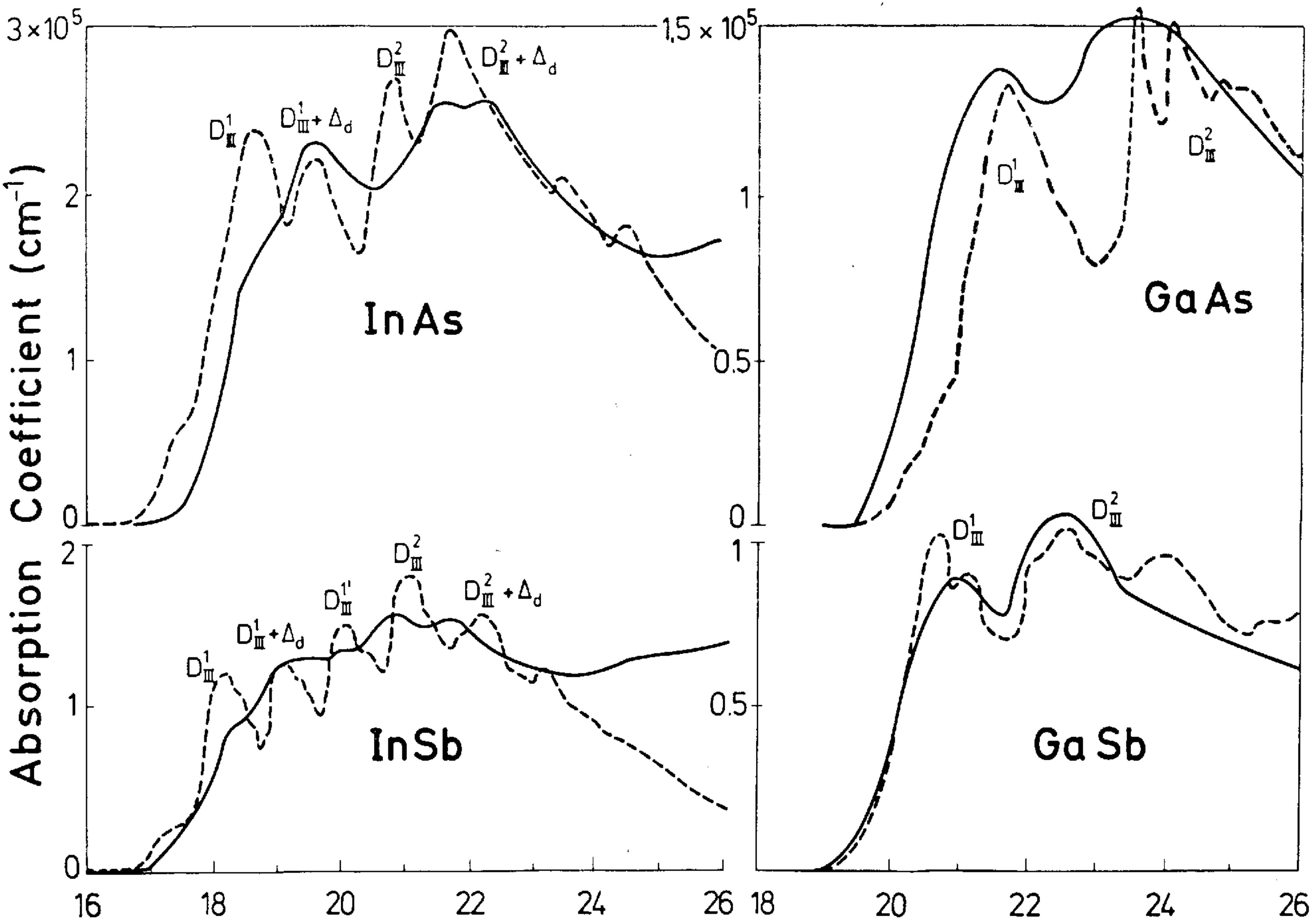

Neff
GaSb
GaAs
GaP
InSb
InAs
InP
4
4
3
3
2
2
1
1
0
0
InSb
InAs
InP
GaSb
GaP
GaAs
15
20
25
30
35
40
eV

Fig. 6



Absorption Coefficient (cm^{-1})
3×10^5
2
1
0
1,5 × 10^5
1
0.5
0
D_{III}^1
$D_{III}^1 + \Delta_d$
D_{III}^2
$D_{III}^2 + \Delta_d$
InAs
D_{III}^1
D_{III}^2
GaAs
2
1
0
D_{III}^1
$D_{III}^1 + \Delta_d$
$D_{III}^{1'}$
D_{III}^2
$D_{III}^2 + \Delta_d$
InSb
1
0.5
D_{III}^1
D_{III}^2
Ga Sb
16
18
20
22
24
26
18
20
22
24
26

Fig. 7

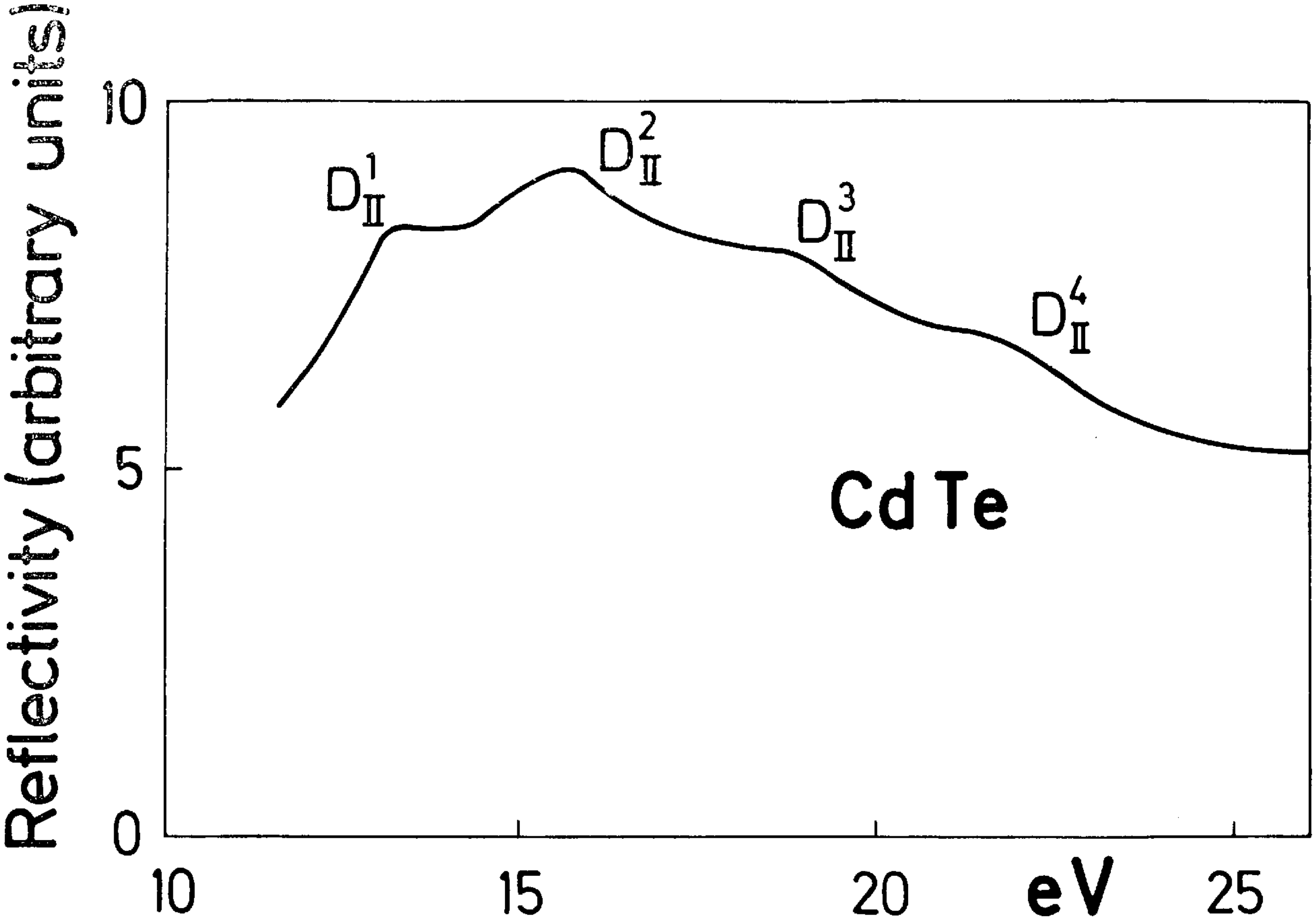

Reflectivity (arbitrary units)
10
5
0
10
15
20
eV
25
D_{II}^{1}
D_{II}^{2}
D_{II}^{3}
D_{II}^{4}
CdTe

Fig. 8