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Interner Bericht

DESY F41-70/6

Juli 1970

DESY-~~1110/1111~~

15. SEP. 1970

Optical Absorption of Semiconductors from

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Paper to be presented at the "Tenth International Conference on the
Physics of Semiconductors" Aug. 17 - 21, 1970, Cambridge, Massachusetts

Optical Absorption of Semiconductors from 15 to 170 eV

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The absorption spectrum caused by transitions from outermost core d and p electrons of several semiconductors has been investigated with synchrotron radiation. The d-electron absorption shows, in crystalline materials, considerable structure associated with the density of conduction states. This structure is usually broadened in amorphous materials. No density of states structure is observed for the p-electron transitions. Both p and d transitions, however, show the spin-orbit splitting of the corresponding core levels. Delayed d transitions have also been observed.

INTRODUCTION

The optical constants of Ge, Se, and the III-V compounds have been studied for photon energies up to 25 eV.^{1,2} Below 8 eV these constants show considerable structure which can be correlated with critical points in the optical density of states. The failure to observe sharp structure above 8 eV could be the result of the use, in previous work, of line sources with a typical separation of 1 eV between adjacent lines. For this reason we have studied the absorption spectra of germanium, selenium, and several III-V compounds in the 15 - 170 eV photon energy region with the continuous radiation emitted by the DESY synchrotron.^{3,4} For transitions originating at the outermost core d-electrons of the III-V compounds and of Se we have found structure due to the density of final (conduction) states and also to the spin-orbit split-

ting of the core level. Transitions from the outermost p-levels of the core have been seen; they do exhibit spin-orbit splitting but no evidence of splitting due to the density of conduction states. The sharp d and p peaks are followed by broad continua in a manner similar to the delayed onset of thresholds described by Fano and Cooper.⁵ An analogous effect has already been observed for the II-VI compounds.⁶

EXPERIMENTAL TECHNIQUE

We used as samples either unsupported films or films deposited onto thin carbon foils. In both cases the samples were backed during evaporation by a microscopic slide which has been coated with KCl. They were subsequently floated on water and picked up with a copper mesh. The samples on carbon substrates are not good for work at photon energies $\hbar\omega \lesssim 40$ eV. Both amorphous and crystalline samples were prepared by varying the substrate temperature T_s . The III-V compounds were all found to be crystalline when deposited at $T_s \gtrsim 250^\circ$ C. GaAs, GaP, InAs, and InP were amorphous when deposited on a room temperature substrate. Amorphous films of InSb and GaSb were obtained by evaporation on to substrates cooled to below -20° C. We did not prepare unsupported films of AlSb: The hygroscopic nature of this material precluded floatation on water. Flash evaporation was used in order to insure stoichiometry. High purity crushed single crystals were used as source material.

Crystalline Ge was obtained with $T_s \simeq 300^\circ$ C and amorphous at room temperature. For the deposition of crystalline Se ($T_s \gtrsim 150^\circ$ C) it was found necessary to coat the substrate with a very thin evaporated layer of Te ($\sim 50 \text{ \AA}$).⁷

The procedure for spectroscopic work with synchrotron radiation has been described elsewhere.^{3,4,6} We used a normal incidence monochromator (1440 lines/mm grating) for the 15 - 35 eV region and a grazing incidence Rowland mount (2400 and 3600 lines/mm) from 30 to 170 eV. In no case was the width of the structure observed determined by instrumental resolution. Some measurements were also performed with a sliding mirror monochromator.⁸ All work was performed at room temperature. An empty substrate was introduced in the light path when measuring the reference beam for samples deposited on carbon (or Te-coated carbon) substrates. The film thickness was determined both, with the Tolansky method and with a quartz crystal monitor. The accuracy of the thickness determined and thus of the absolute values of the absorption coefficient α , was better than $\pm 20\%$.

RESULTS

The absorption spectrum of selenium is shown in Fig. 1. The same results were obtained for amorphous and crystalline selenium. The sharp peak around 56 eV, due to transitions originating at the $3d$ core levels, shows a spin-orbit splitting of 1.0 eV (D^1 and $D^1 + \Delta_d$). A slight wing (D^2) is seen on the high energy side of the peak, followed by a minor peak (D^3) at 63 eV. This sharp structure is followed by a broad continuum. Sharp peaks (P , $P + \Delta_p$), related to the $3p$ core levels and their spin-orbit splitting, appear again at 162 and 168.5 eV. The energy of all sharp structure observed in this work is shown in Table I. The absorption spectra of crystalline InSb, GaSb, and AlSb are shown in Fig. 2, those of GaAs, GaP, and Ge in Fig. 3, and those of InAs and InP in Fig. 4.

These figures show sharp structures related to transitions from p and d levels of the outermost core shell of the constituent atoms. For the crystalline III-V compounds, considerable fine structure (D_{III}^1 , $D_{III+\Delta_d}^1$, D_{III}^2 , $D_{III+\Delta_d}^2$, Δ_{III}^3 , Δ_{III}^4) appears in connection with the d core levels of the cation; it is replaced by a broad hump in the amorphous materials. All other sharp peaks (D_V , from the d levels of the anion, and P_{III} , P_V , from p core levels) show at most only the spin-orbit splitting of the core levels, no difference is observed for these structures between amorphous and crystalline material.

DISCUSSION

The dashed curve in the insert of Fig. 1 represents the shape of the absorption spectrum of Se expected on the basis of the calculated density of conduction states⁹ assuming constant matrix elements and including the spin-orbit splitting of the d core levels. If this spectrum is broadened, a good approximation to the measured curve is obtained, thus ruling out exciton and other many-body effects. The D^2 structure is also seen in the density of conduction states and thus is not related to spin-orbit interaction. The observed D^1 , $D^{1+\Delta_d}$ doublet is not only of spin-orbit origin: a splitting of about 1 eV is seen also in the calculated density of conduction states. The D^3 peak corresponds in the calculated curve to the second group of mostly s-like conduction bands: inclusion of matrix elements should decrease the calculated strength of this peak with respect to the predominantly $d \rightarrow p$ D^1 peak. The fact that the essential features of the density of conduction states of the crystal are preserved in amorphous Se suggests the preservation of a considerable degree of the trigonal crystalline order.

The D_{III}^1 , D_{III}^2 structure of Figs. 2, 3 and 4 can also be associated with a double peak in the calculated density of conduction states.¹⁰ This double structure corresponds essentially to the two lowest conduction bands: These bands are very flat near X (the lowest) and near L (the second lowest), thus giving rise to a double peak in the density of states. The D_{III}^1 and D_{III}^2 peaks show the spin-orbit splitting of the d level in the indium compounds (~ 1 eV). This splitting is too small (0.5 eV) to be seen in the gallium compounds, with the exception of the D_{III}^1 peak of GaP. The $D_{\text{III}}^1 - D_{\text{III}}^2$ orbital structure also appears in recent electron energy loss data.¹¹

The continua above the sharp d transitions are very strong for the antimonides and the indium compounds (Figs. 2, 3): this is a general feature of all materials containing elements of the 5-th and lower rows of the periodic table.^{5,6} Sharp structure which should occur in the region of the continuum (such as P peaks) is not observed in this case. These continua are considerably weaker in Fig. 3 which involves only atoms of the 3-rd and 4-th row of the periodic table.

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Figure Captions

1. Absorption spectrum of Se between 40 and 170 eV. The same results were found for amorphous and crystalline Se. The insert shows a detail of the sharp structure between 50 and 70 eV and the spectrum calculation on the basis of the density of conduction states.
2. Absorption spectra of crystalline AlSb, GaSb, and InSb.
3. Absorption spectra of crystalline GaP, GaAs, and Ge.
4. Absorption spectra of crystalline InP and InAs.

Material	D_{III}^1	$D_{III}^1 + \Delta_d$	D_{III}^2	$D_{III}^2 + \Delta_d$	D_{III}^3	D_{III}^4	D_V	$D_V + \Delta_d$	P_{III}	$P_{III} + \Delta_d$	P_V	$P_V + \Delta_p$
GaP	20.6	21.2 ^a	23.1	-	-	-	-	-	106.1 ^a	109.4 ^a	131.2 ^a	-
GaAs	20.9	-	23.0	-	-	-	43.1	-	106.2	109.8	143	-
GaSb	20.8	-	22.3	-	-	28.4	33.2	34.5	-	-	-	-
InP	18.8	19.7	21.6	22.4	-	28.5	-	-	-	-	129.9	130.8
InAs	18.5	19.5	21.5	22.3	26	29.2	43	-	-	-	142	-
InSb	18.3	19.2	20.8	21.5	25	28.1	32.9	34.3	-	-	-	-

	D^1	$D^1 + \Delta_d$	D^2	D^3			P	$P + \Delta_p$				
Se	55.2	56.2	58	63	-	-	-	-	162.0	168.5	-	-
Ge	32.2	-	-	-	-	-	-	-	123.2	127.0	-	-

a) ESCA work gives for the energies of the corresponding core states referred to the Fermi energy values which are about 2.5 eV lower than those listed here. Hence the maximum in the density of conduction states is about 2.5 eV above the Fermi energy of the material used in the ESCA work. See D.W. Langer, Z. Naturf. 24a, 1555 (1969)

Table I. Energies (in eV) of the absorption peaks due to transitions from outermost d and p core levels to conduction states for several semiconductors.

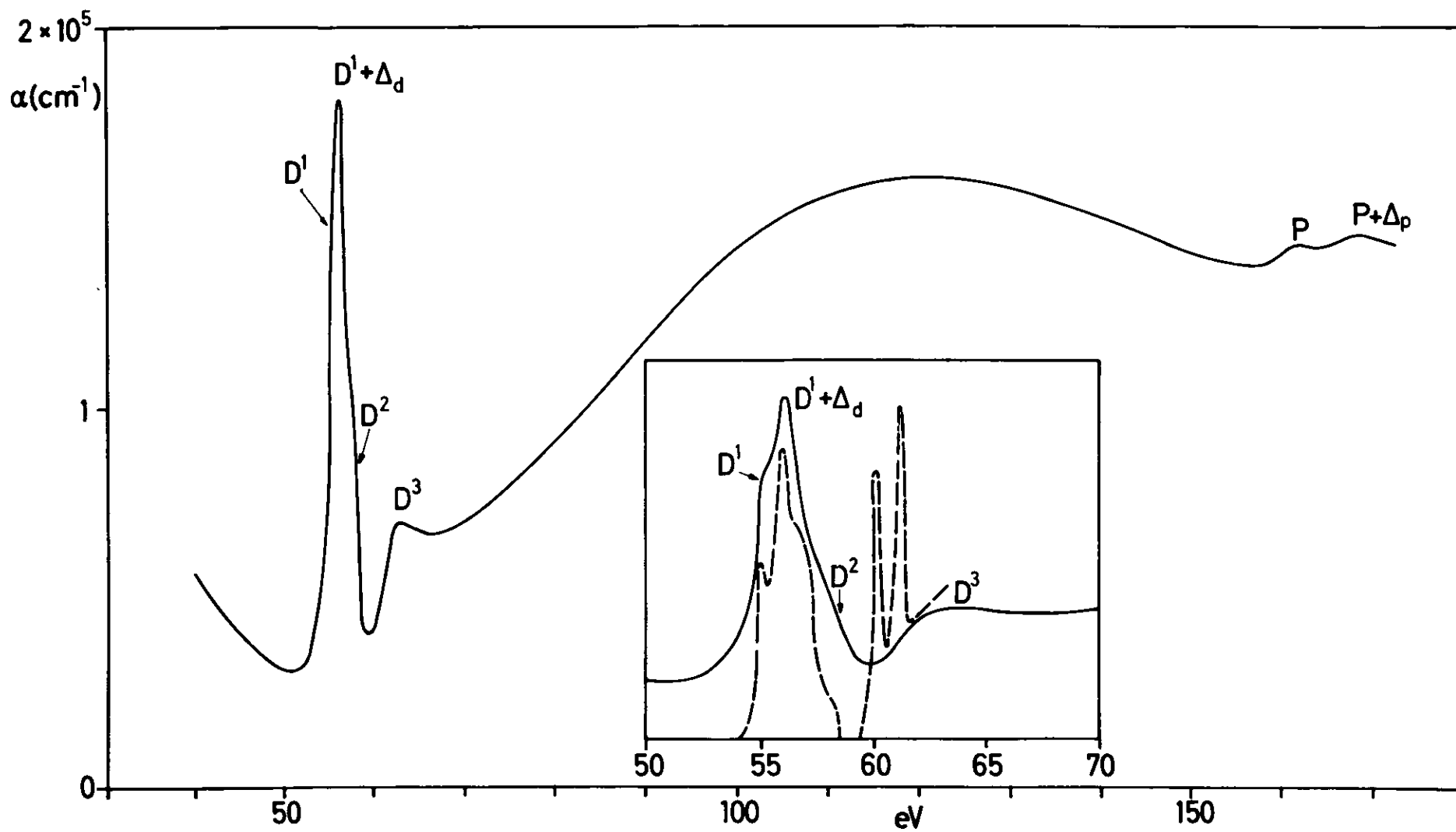


Fig.1

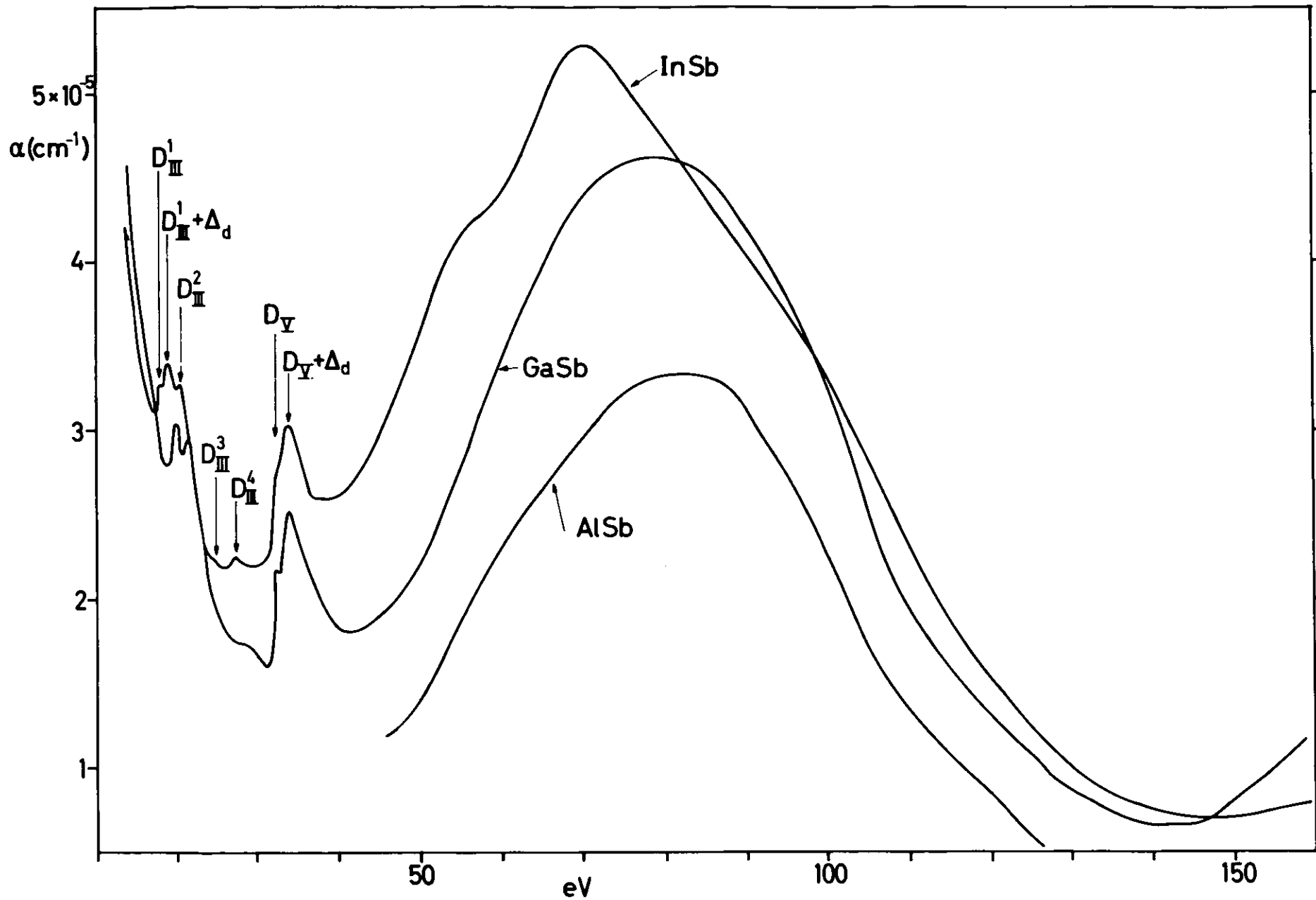


Fig.2

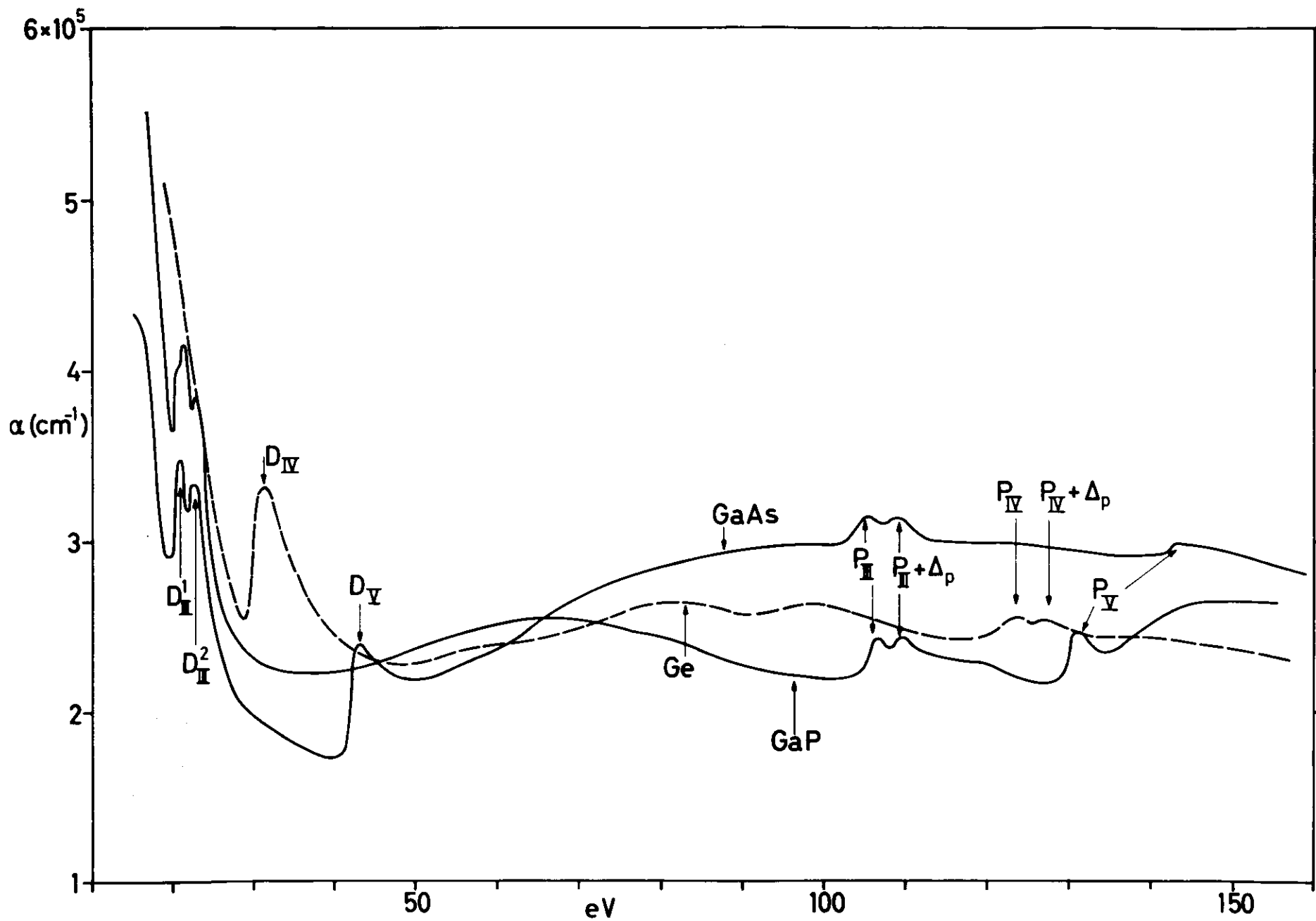


Fig.3

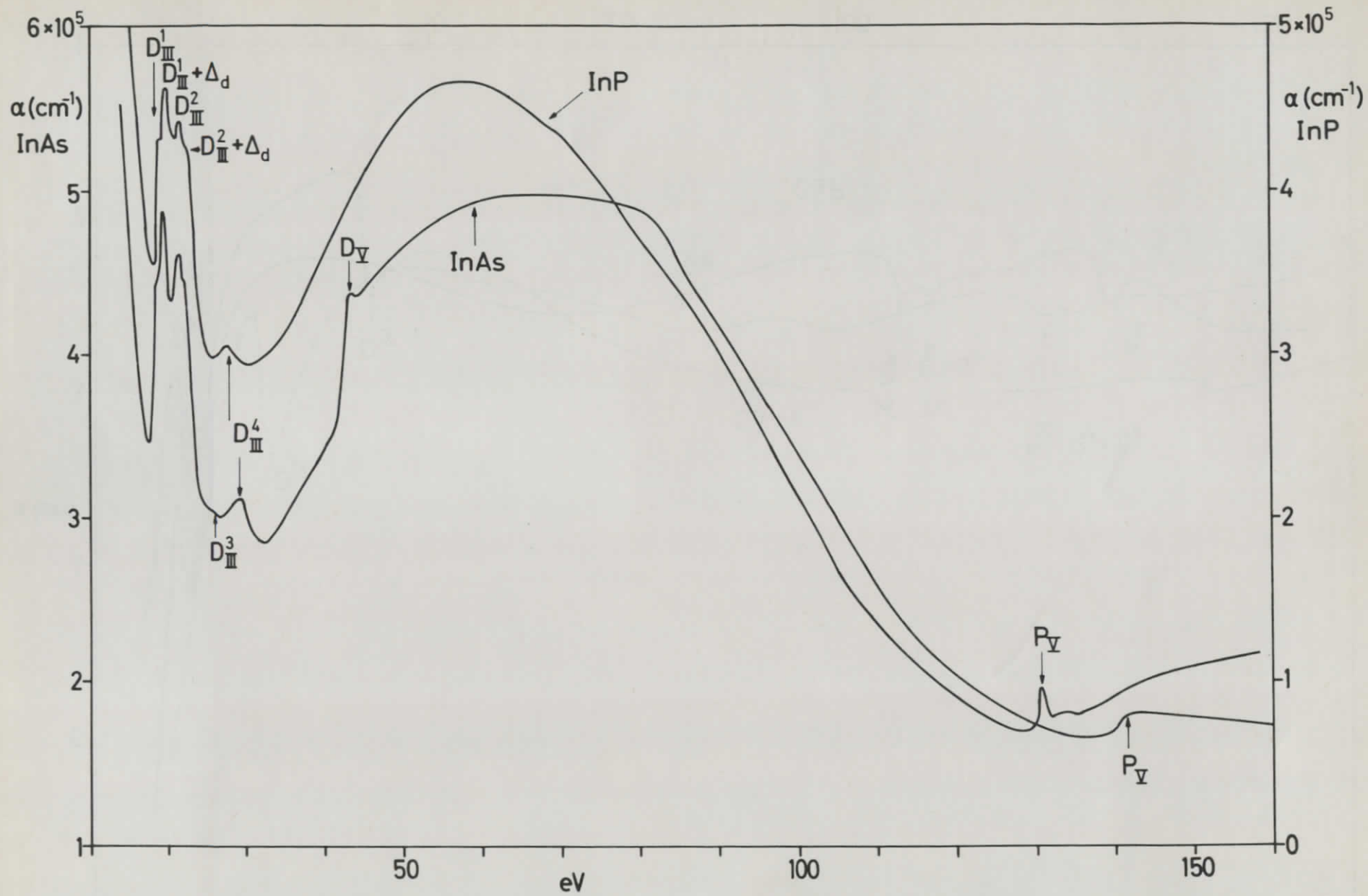


Fig.4