ON THE PHOTOCONDUCTIVITY OF GaP CRYSTALS

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(Received November 30, 1966)

The anomalous photoconductivity response of very high-ohmic GaP crystals was investigated. On base of the experiments it can be concluded that the effect is connected with the different mobilities in the corresponding minima of the conduction band. Based on calculations it is shown that the presence of the effect is connected with very short lifetimes.

Investigation of the photoconductivity response curves (PCR) of GaP brought some interesting new effects: first the anomalous photoconductivity response (APC)[1], observed firstly by D. F. NELSON, L. F. JOHNSON and M. GERSHENZON [1], and successively investigated by the authors [2], [3], and furthermore, an interesting oscillation effect, attributed to interactions between excess carriers and longitudinal optical phonons [4]. The present article gives some more details on our work concerning the problem of APC, the conclusions having been published in [2], [3].

Experimental methods

The GaP crystals investigated were vapour-grown whiskers (very high-ohmic, dark conductivity $\sigma_d(296°K) \approx 3 \cdot 10^{-12} \Omega^{-1}\,cm^{-1}$; dimensions $0{,}6 \times 0{,}6 \times 0{,}05\,cm^3$) and platelets (dark conductance $\Sigma_d(296°K) \approx 3 \cdot 10^{-10} \Omega^{-1}$; dimensions $0{,}8 \times 0{,}1 \times 0{,}1\,cm^3$). The whiskers were triangular in cross-section. Contacts were soldered Sn contacts with suitable impurities.

The PCR measurements were carried out at either 296°K or 77°K, with and without additional steady illumination. PCR curves were taken by two independent Xe-lamp—monochromator systems, one for d. c. measurements and an other for measurements using mechanically chopped light (chopping frequency $\approx$ 1350 c/s). In d. c. measurements a Zeiss SPM1 monochromator and a megohmmeter JUPITER, (type JM 242) were used, while under a. c. conditions the monochromatic light was produced by a 3MP—2 monochromator, and the signals in this latter case were detected by a calibrated selective amplifier system (ME3, type У2—6 amplifier, ME3, type СД—1 phase-sensitive detector coupled with an automatic potentiometer). In the experiments performed at 77°K, we have used a finger type Dewar. In both arrangements it was, of course, possible to measure the incident light intensity.

[1] The APC is an effect involving a second, and sometimes big rise in PCR spectral curves far beyond the absorption edge.

As in d. c. measurements PCR was taken point by point, the light energy was measured at every wave-length by a movable mirror rendering possible to focus the light energy onto a thermocouple. In a. c. measurements, the exciting light passed through an inclined quartz plate, which reflected a fraction of it onto a PbS-cell, coupled with a selective measuring amplifier system. The apparatus was previously calibrated against a thermocouple having been set in the place of the sample.

For the additional steady illumination a stabilized tungsten lamp was used, followed by suitable filters to produce various wave-lengths: glass filters, a continuouly adjustable Zeiss-interference filter, Ge or Si filters.

If not mentioned otherwise, PCR curves were taken by regulating the slits of the monochromator so as to keep the incident light energy approximately constant over the investigated spectral range. (The incident photon flux (Q) was calculated on basis of this constant energy, and changes in conductivity ($\Delta\sigma$) were related to these values, *i. e.* $\Delta\sigma/Q$ was calculated.) In a. c. measurements $\Delta\sigma$ was calculated according to the formula $\Delta\sigma = v/V_0 R_L$ [5], where v is the measured a. c. voltage, V_0 the voltage applied to the crystal (in our case 750 V), R_L the input resistance of the amplifier, while in d. c. measurements changes in conductance ($\Delta\Sigma$) were used instead of $\Delta\sigma$.

Experimental results

In order to get new informations about APC, first of all we have systematically investigated the effect of double injection. Steady illumination of wave-lengths ranging from 2,5 ev to 0,35 ev, was employed. On Fig. 1 the effect of long wavelength illumination (Si-filter) is to be seen (temperature 296°K). At room temperature strengthening the intensity of steady illumination, we generally obtained the following effect: first PCR rose both in the range of indirect and direct transitions. Then from a certain intensity, PCR in the indirect region remained almost constant, while APC gradually disappeared approaching this constant level of PCR in the region of indirect transitions. This feature of PCR curves was also found when using steady light of shorter wave-lengths (Fig. 2. red filter, Fig. 3. blue filter). This fact, *i. e.* the disappearing of APC with increasing intensity of steady illumination, seemed to be in contradiction with the explanation suggested in [1], according to which the level of APC ought to mean some level of saturation with increasing intensity of steady illumination.

At this point there still remained two possible ways of explanation which determined the means of our further experiments. According to the first

i) APR would be an effect simply correlated with the decrease of penetration depth in the region of direct transitions.

The values of the absorption coefficient, k, of GaP available for us [6] did not contradict such an effect, though less in magnitude. According to the second

ii) APR would be due to the fact that in the region of direct transitions, electrons are excited into the [000] minimum of the conduction band (Fig. 4a.), where the mobility (provided a scattering by acoustic modes) is about 15 times larger than in the [100] minimum.

The first idea was that if APC were simply a „geometric" effect, it could have been provoked using an inclined light ray in PCR measurements, producting thus the diminution of penetration depth even at energies corresponding to indirect transitions. Unfortunately, the refraction index of GaP ($n = 3{,}1$) is rather large so as to make this effect hardly observable. Using a light inclined by 60° to normal incidence, its deviation within the substance did not exceed 15°, corresponding to an effective diminution of penetration depth only by a factor 1,06. It was surprising and pointed at the sensitivity of the measuring circuitry that some resulting change of about 1,1 times could be observed at all. Of course, it was not possible to draw quantitative conclusions from this effect.

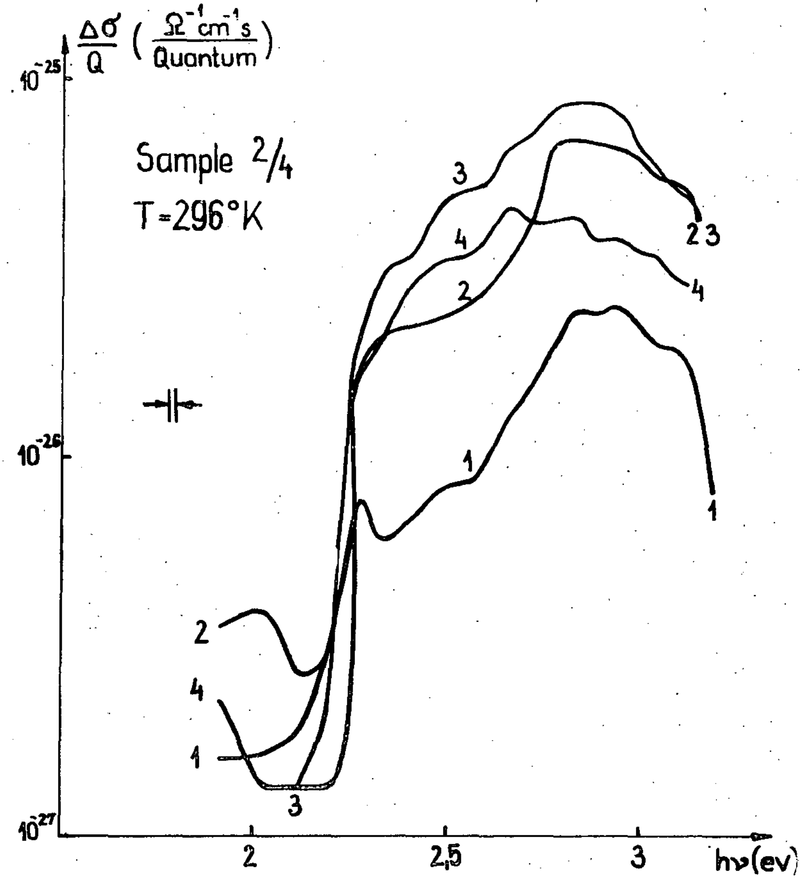

Fig. 1. PCR spectral curves. $Q \approx 5 \cdot 10^{12}$ quantum/s. Secondary illumination through Si filter ($\lambda > 1{,}1\mu$) of various intensities (curve *1*: 0 quantum/s; *2*: $9 \cdot 10^{12}$ quantum/s; *3*: $3{,}5 \cdot 10^{13}$ quantum/s; *4*: $2 \cdot 10^{14}$ quantum/s)

The experiment which seemed of great importance, and at last led to the most probable interpretation of APC was the following. We have measured PCR under special conditions, namely, choosing the incident intensity of exciting light so as to produce an approximately constant near-surface density of generation. This constant generation rate can be approximated by keeping $Qk = const.$ over the whole experimental range. (The least value of Q, for large k depends on the energy reserves of the illumination system.)

Condition $Qk = const.$ ensures the uniform density of generation on the surface and, at other points of the sample, a decreasing generation density with increasing $h\nu$.

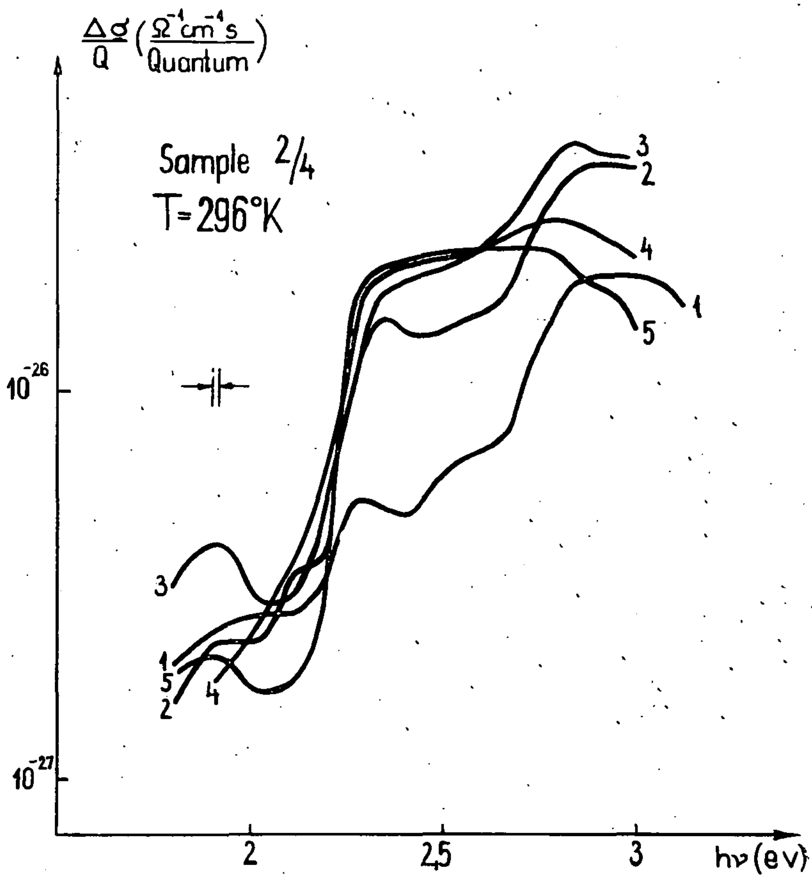

Fig. 2: PCR spectral curves. $Q \approx 3 \cdot 10^{12}$ quantum/s. Secondary illumination through red filter (type KC-10, $\lambda > 0{,}6\mu$) of various intensities (curve *1*: 0 quantum/s; *2*: $3 \cdot 10^{13}$ quantum/s; *3*: $1{,}8 \cdot 10^{14}$ quantum/s; *4*: $4{,}8 \cdot 10^{14}$ quantum/s; *5*: $1 \cdot 10^{15}$ quantum/s)

The result of this experiment is to be seen in Fig. 5. For comparison, the PCR of sample 1/1, of relatively low resistance, which does not show APC, is also to be seen in the figure.

It is also to be mentioned that at the highest employed injection rates ($Q > 10^{15}$ quantum/s), a strong peak appeared in PCR at 296°K, coinciding with the beginning of indirect band gap [4]. In this case APR was less expressed (Fig. 6.). At lower levels of illumination or at reduced temperatures this peak was inobservable.

Investigation of PCR at reduced temperatures also presented some interesting features. Obviously, the thermal ionization of the centres in crystals 2/4 and 2/6 was such that at 77°K a strong impurity PCR was observed (Figs. 7., 8.). The steady illumination, even at the least intensities employed, ionized these centres and APC appeared in a more expressive form compared with room temperature measurements.

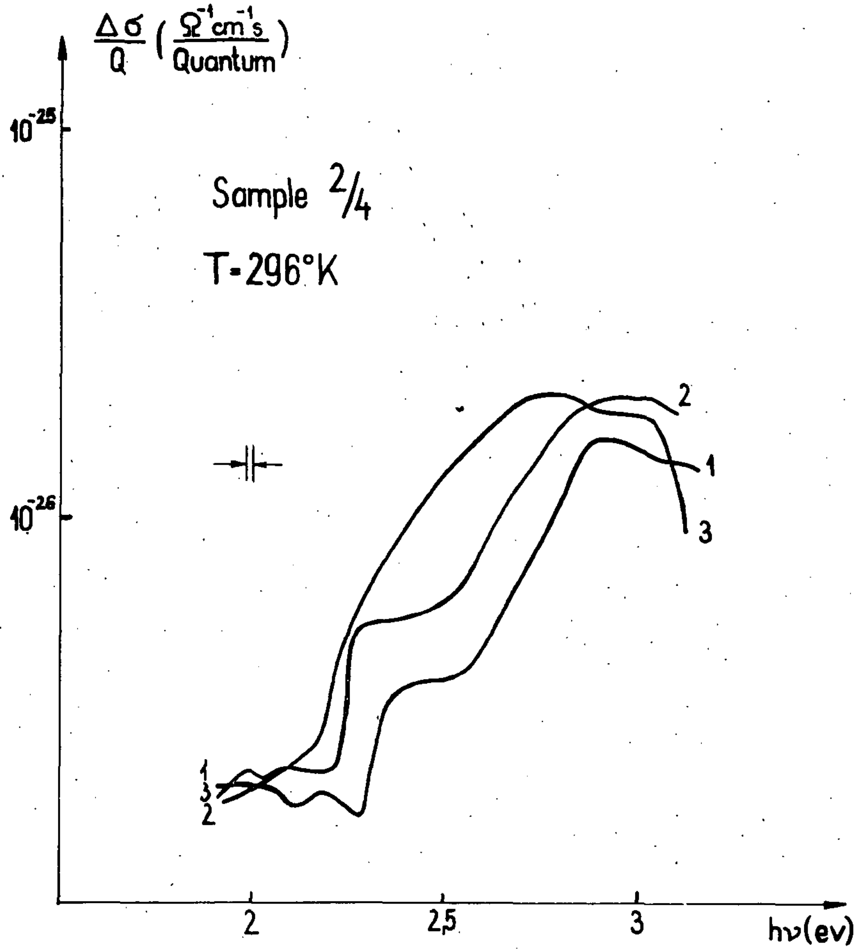

Fig. 3. PCR spectral curves. $Q \approx 8 \cdot 10^{12}$ quantum/s. Secondary illumination through blue filter (type CC5+C3C14, $0{,}38\mu < \lambda < 0{,}48\mu$) of various intensities (curve *1*: 0 quantum/s; *2*: $1{,}5 \cdot 10^{14}$ quantum/s; *3*: $9 \cdot 10^{14}$ quantum/s)

The PCR *versus* incident photon flux curves taken at two characteristic wavelengths show linear PCR at room temperature, even in the range of APC, *i. e.* in the region of direct transitions, though some superlinearity was observed at

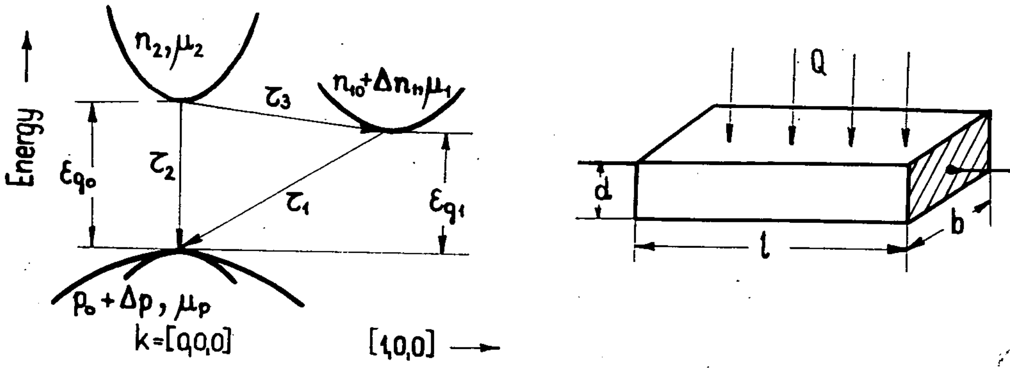

Fig. 4a. Energy band model for GaP. *4b.* Schematic diagram for calculation of APC

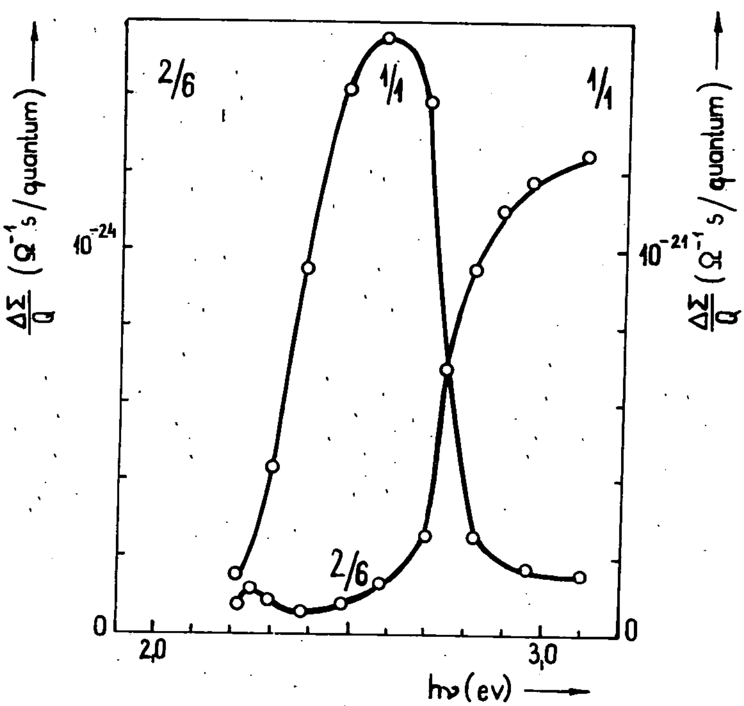

Fig. 5. PCR spectral curves (d. c. method) taken at uniform near-surface densities of generation

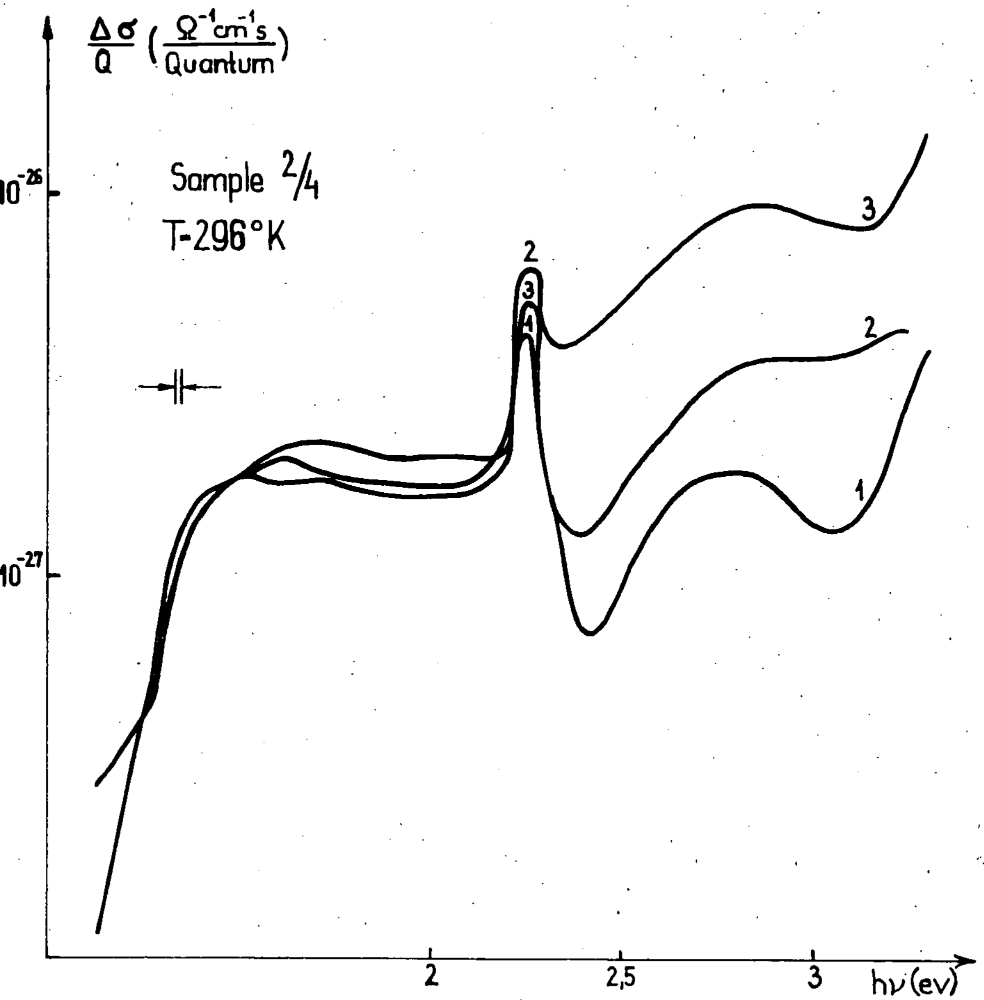

Fig. 6. PCR spectral curves. $Q > 10^{15}$ quantum/s. Secondary illumination through Si filter ($\lambda > 1{,}1\mu$) of various intensities (curve *1*: 0 quantum/s; *2*: $7 \cdot 10^{13}$ quantum/s; *3*: $1{,}8 \cdot 10^{14}$ quantum/s)

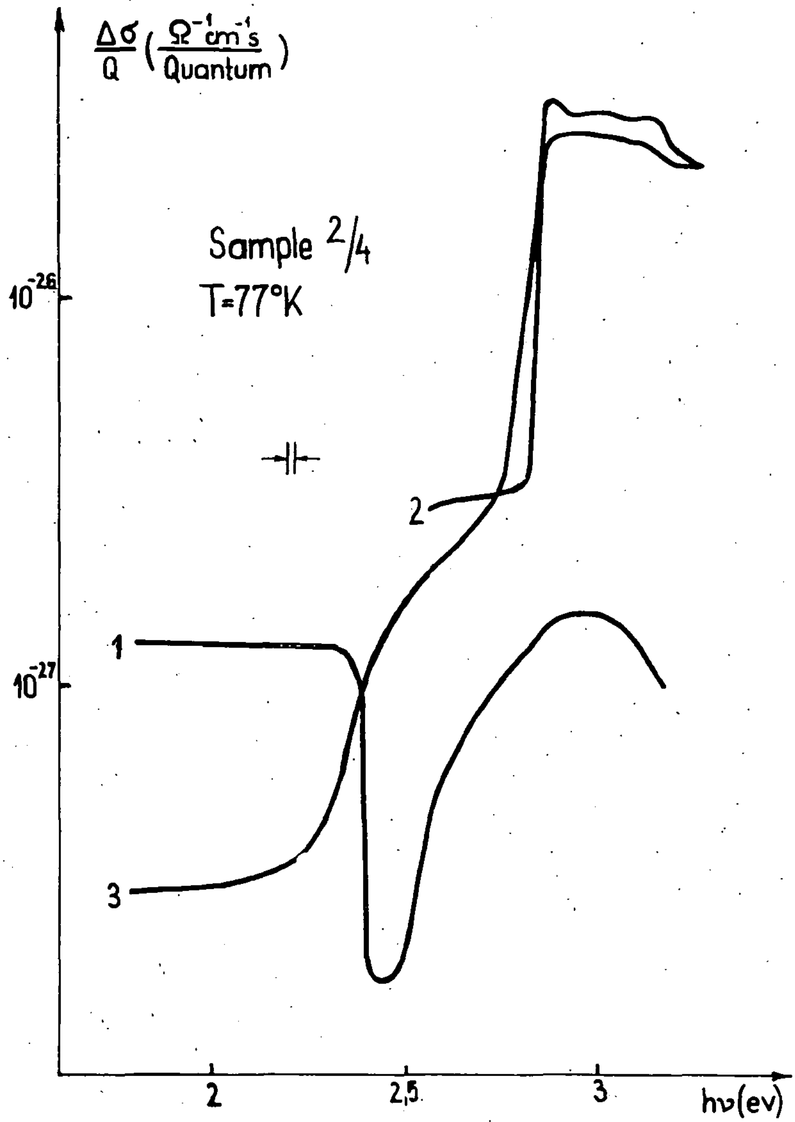

Fig. 7. PCR spectral curves. $Q \approx 10^{14} \div 10^{15}$ quantum/s. Secondary illumination through Si filter ($\lambda > 1{,}1\,\mu$) of various intensities (curve *1*: 0 quantum/s; *2*: $7 \cdot 10^{13}$ quantum/s; *3*: $1{,}8 \cdot 10^{14}$ quantum/s)

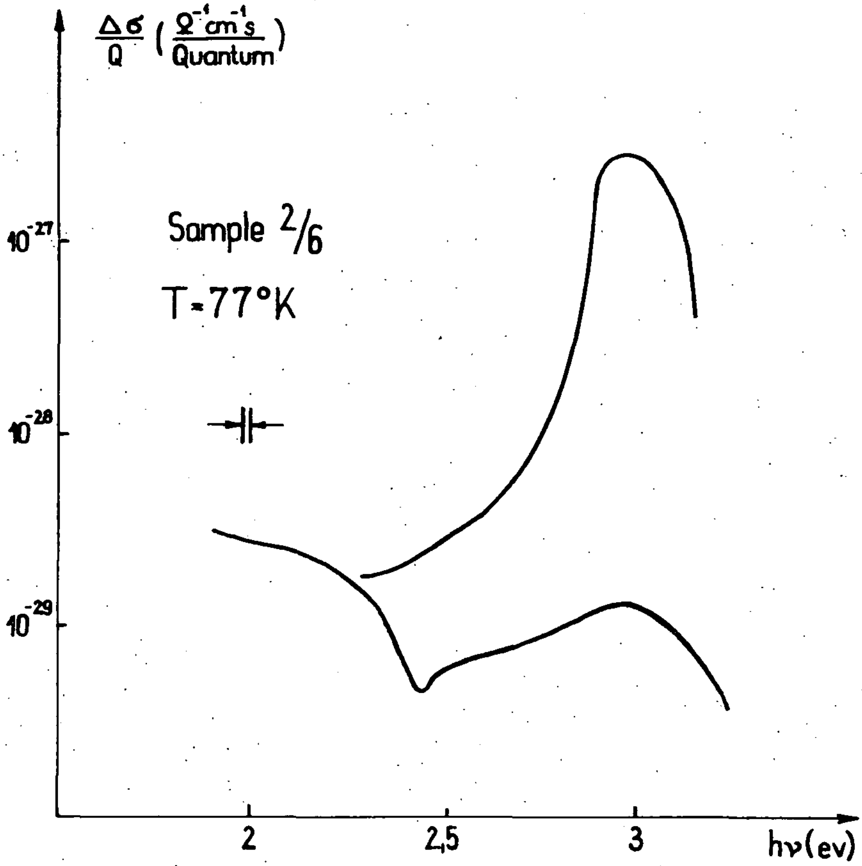

Fig. 8. PCR spectral curves. $Q \approx 10^{13}$ quantum/s. Secondary illumination through Si filter ($\lambda > 1{,}1\mu$) of various intensities (curve *1*: 0 quantum/s; *2*: $1 \cdot 10^{14}$ quantum/s)

$\lambda = 478$ nm and at $T = 77$°K (Figs. 9., 10.). This superlinearity can be interpreted as in CdS [7] by the actual relative position of the Fermi level at 77°K and the recombination centres involved.

Discussion

The PCR curves taken with double illumination, as pointed out, are in contradiction with the explanation suggested in [1]. The experiment involving constant near-surface density of generation enabled us to decide between the explanations i) and ii). Namely, the existence of APC under this special condition would be in contradiction with explanation i), while it is consistent with explanation ii). Inversely, explanation ii) does not lead to any contradiction with known experimental facts, therefore it is to be considered as the most probable explanation of APC.

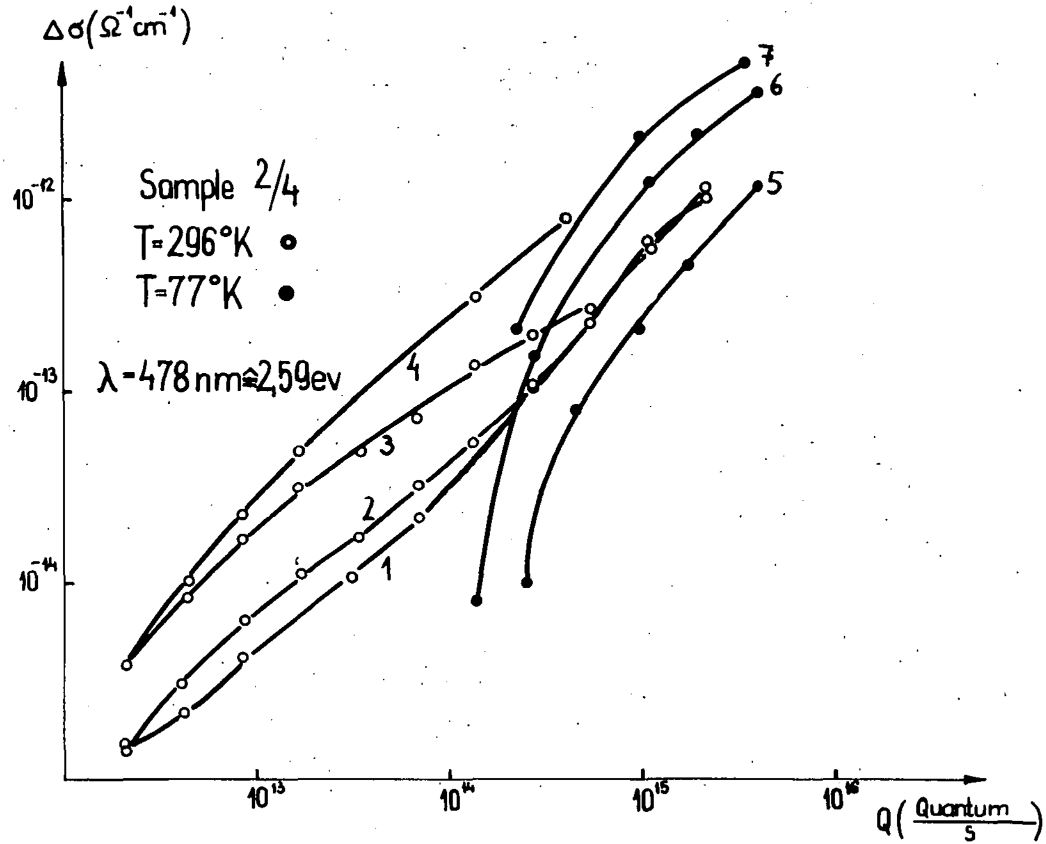

Fig. 9. Dependence of $\Delta\sigma$ on illumination intensity (Q) in the region of indirect transitions. Secondary illumination through glass filter (type ИКС-2, $\lambda > 0{,}95\mu$) of various intensities (curve *1*: 0 quantum/s; *2*: $6{,}3 \cdot 10^{13}$ quantum/s; *3*: $3 \cdot 10^{14}$ quantum/s; *4*: $7 \cdot 10^{14}$ quantum/s; curve *5*: 0 quantum/s; *6*: $7 \cdot 10^{13}$ quantum/s; *7*: $1{,}8 \cdot 10^{14}$ quantum/s)

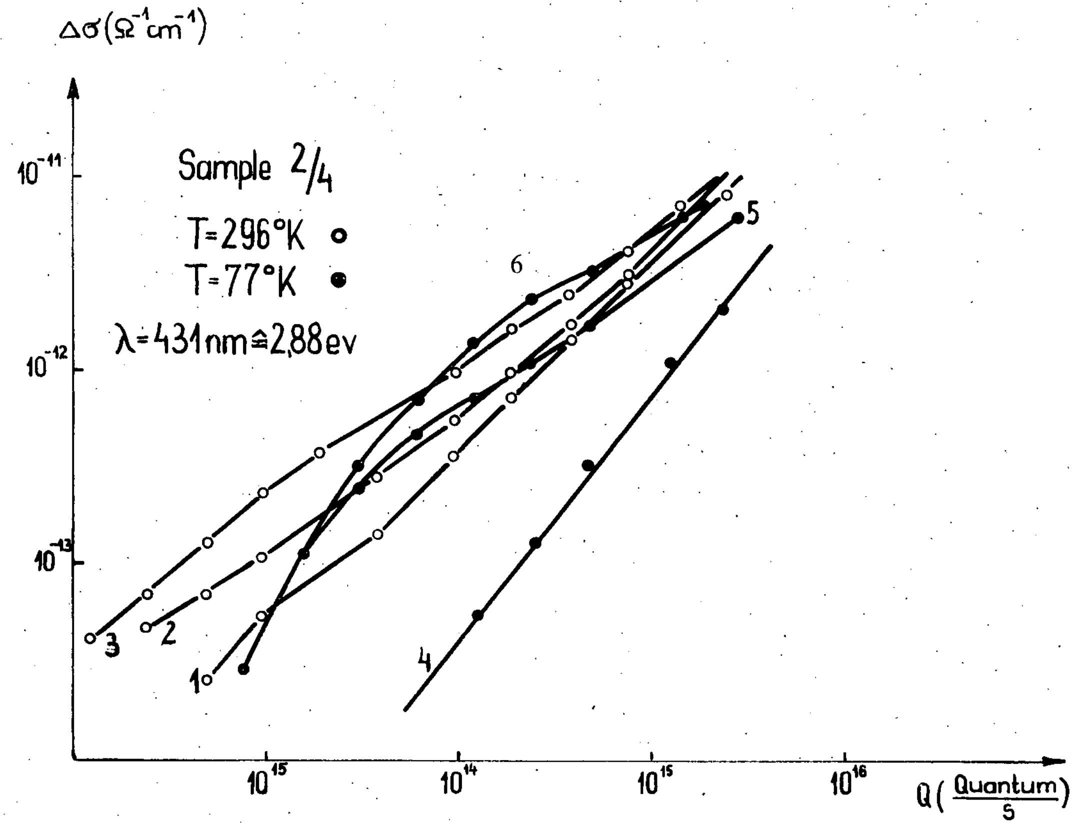

Fig. 10. Dependence of $\Delta\sigma$ on illumination intensity (Q) in the region of direct transitions. Secondary illumination through glass filter (type ИКС-2, $\lambda > 0{,}95\mu$) of various intensities (curves *1* and *4*: 0 quantum/s; *2* and *5*: $6{,}6 \cdot 10^{13}$ quantum/s; *3* and *6*: $1{,}8 \cdot 10^{14}$ quantum/s)

On Fig. 4a. the band scheme of GaP is to be seen. Using the notations of the figure and those of Fig. 4b., the conductivity change by illumination ($\Delta\sigma = \sigma_l - \sigma_d$) can be expressed as

$$\Delta\sigma = \frac{b}{l} q \int_0^d (\mu_1 \Delta n_1 + \mu_2 n_2 + \mu_p \Delta p)\, dx \qquad \text{(steady state)},$$

(q charge on the electron).

A) In the region of indirect transitions ($\varepsilon_{g1} \leqq h\nu \leqq \varepsilon_{g0}$) we have $n_2 = 0$, $\Delta n_1/\tau_1 = \Delta p/\tau_p$. Using $\Delta n_1/\tau_1 = G = (Q/lb)k \exp(-kx)$, for very low values of diffusion coefficient

$$\Delta\sigma_{\text{indir.}} = \frac{b}{l} q \int_0^d (\mu_1 \tau_1 + \mu_p \tau_p) G\, dx.$$

B) For direct transitions ($h\nu \geqq \varepsilon_{g0}$), where $\Delta n_1/\tau_1 + n_2/\tau_2 = \Delta p/\tau_p$, $n_2/\tau_2 + n_2/\tau_2 = G$ and $n_2/\tau_3 = \Delta n_1/\tau_1$, we have

$$\Delta\sigma_{\text{dir.}} = \frac{b}{l} q \left[\int_0^d \left(\mu_1 + \mu_p \frac{\tau_p}{\tau_1} \right) \Delta n_1\, dx + \int_0^d \frac{G\tau_3}{\tau_1 + \tau_3} (\mu_2 \tau_2 + \mu_p \tau_p)\, dx \right],$$

or, by $\Delta p/\tau_p = G$, $n_2 = G\tau_2\tau_3/(\tau_2 + \tau_3)$ and $\Delta n_1/\tau_1 = G\tau_2/(\tau_2 + \tau_3)$,

$$\Delta\sigma_{\text{dir.}} = \frac{b}{l} q \int_0^d \left[\mu_1 \tau_1 + \mu_p \tau_p + \frac{\mu_2 \tau_2 - \mu_1 \tau_1}{\tau_2 + \tau_3} \tau_3 \right] G\, dx.$$

The *amount of APC* can thus be calculated using the ratio

$$\frac{\Delta\sigma_{\text{dir.}}}{\Delta\sigma_{\text{indir.}}} = \frac{\int_0^d \left[\mu_1 \tau_1 + \mu_p \tau_p + \frac{\mu_2 \tau_2 - \mu_1 \tau_1}{\tau_2 + \tau_3} \tau_3 \right] G\, dx}{\int_0^d [\mu_1 \tau_1 + \mu_p \tau_p] G\, dx}.$$

Supposing τ_1, τ_2 and τ_3 to be independent of generation density and thus of x, we have

$$\frac{\Delta\sigma_{\text{dir.}}}{\Delta\sigma_{\text{indir.}}} = 1 + \frac{\mu_2 \tau_2 - \mu_1 \tau_1}{\mu_1 \tau_1 + \mu_2 \tau_2} \frac{\tau_3}{\tau_2 + \tau_3} \equiv a.$$

Taking $a \approx 10$ for APC, this value can be explained by *e. g.* $\mu_2 = 15\mu_1$, $\tau_2 \approx \tau_1 \approx \tau_3$ and $\mu_p \tau_p \ll \mu_1 \tau_1$. This explanation is in good agreement with the fact that APC takes place only in crystals of very low PCR, *i. e.* of very short lifetimes.

The lifetime *e. g.* in sample 2/4 can also be calculated approximately by the relation

$$\tau = \frac{h\nu}{q} \frac{l}{b} v / V_0 R_L I_A \mu,$$

where I_A the absorbed light energy and μ the drift mobility of majority carriers (supposing $\mu = 10^2$ cm^2 volt^{-1} s^{-1}). Using the signal at 431 nm, the formula yielded $\tau \approx 5 \cdot 10^{-9}$ s, in a very good agreement with [1].

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Thanks are due to Prof. A. Budó, member of the Hungarian Academy of Sciences for rendering possible to perform some experiments in this institute, furthermore, to A. A. Volfson (Leningrad) for allowing to use his apparatus in a. c. measurements. One of the authors (J. Gy.) is indebted to the Hungarian Academy of Sciences for a scholarship.

References

[1] *Nelson, D. F., L. F. Johnson, M. Gershenzon:* Phys. Rev. **135**, A 1399 (1964).
[2] *Subashiev, V. K., J. Gyulai, G. A. Chalikyan:* Report on the Photoconductivity Conference, Odessa, 1965.
[3] *Gyulai, J., V. K. Subashiev, G. A. Chalikyan:* Phys. stat. sol. **17**, K49 (1966).
[4] *Наследов, Д. Н., В. В. Негрескул, С. И. Рагауцан, С. В. Слободчиков:* Ф. Т. Т. **7**, 3671 (1965).
[5] *Рывкин, С. М.:* Фотоэлектрические явления в полупроводниках (Физматгиз, Москва, 1963), p. 40.
[6] *Subashiev, V. K., S. A. Abagyan:* Proc. Intern. Conf. Phys. Semicond. (Dunod, Paris, 1964) p. 225.
[7] *Bube, R. H.:* Photoconductivity of Solids (J. Wiley, New York, 1960) p. 288.

О ФОТОПРОВОДИМОСТИ ФОСФИДА ГАЛЛИЯ

Й. Гьюлаи, В. К. Субашиев, Г. А. Чаликян

Была исследована аномальная фотопроводимость очень высокоомных кристаллов фосфида галлия. Из экспериментальных результатов получается, что аномальная фотопроводимость связана разными подвижностями в разных минимумах зоны проводимости. По расчетам было показано, что наличие эффекта самое вероятно в кристаллах с очень маленькими величинами времени жизни носителей.