

Two-Photon Interband Transitions at Critical Points in Semiconductors.

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Summary. — The two-photon transition probability between electronic energy bands in crystals is obtained in correspondence to all types of critical points. Expressions are given for the discontinuities in the absorption rate of one of the two photons as a function of its frequency when the sum of the energies of the two photons is equal to the energy difference of the conduction and of the valence band at that particular critical point. The results indicate sharp peaks in correspondence to saddle points M_1 , besides the sharp edge at M_0 already found by Braunstein. For noncubic materials the anisotropy is shown to influence the shape of the edge M_0 and of the peak M_1 . In the limiting case of a two-dimensional crystal the two-photon transition probability gives a sharp logarithmic singularity at M_1 . The results are analogous to those for one-photon processes, but all the singularities and the peaks are sharper in this case and their intensities depend on the position of the virtual states. The possibility of studying other critical points besides the edge by two-photon spectroscopy is discussed and substances such as hexagonal BN, cubic ZnS, and AlSb and GaAs seem to be good candidates for detecting two-photon transition to higher-lying critical points of the conduction band.

1. - Introduction.

The theory of the two-photon absorption has been developed first at the fundamental band gap by BRAUNSTEIN ⁽¹⁾, from the general theory given by GÖPPERT-MAYER ⁽²⁾, in the case in which the surfaces of constant energy

⁽¹⁾ R. BRAUNSTEIN: *Phys. Rev.*, **125**, 475 (1962).

⁽²⁾ M. GÖPPERT-MAYER: *Ann. der Phys.*, **9**, 273 (1931).

around the critical point (of type M_0) are of spherical shape. The absorption coefficient has been shown to have a very simple form which depends on the band parameters obtainable from the single-photon absorption ⁽³⁾.

The theory depends upon the excitation of an electron from the valence band to the conduction band by the simultaneous absorption of two general photons which may be of different frequency. This is a nonlinear optical phenomenon ⁽⁴⁾ that takes place through a number of intermediate states as specified by time-dependent second-order perturbation theory. The approximation in the theory is that the intermediate states connect both initial and final states by electric-dipole transition having a total oscillator strength nearly equal to one.

HOPFIELD *et al.* have first observed the two-photon absorption in KI ^(5,6). Recently experiments have been done on a number of semiconductors such as CdS ^(7,8), PbTe ⁽⁹⁾, and GaAs ⁽¹⁰⁾, and ZnS ⁽¹¹⁾.

The purpose of this paper is to compute the transition probability rate for two-photon processes at the point (M_0), also for anisotropic materials and in the two-dimensional case and at the saddle point M_1 in the three-dimensional and two-dimensional cases.

Partial results on the saddle point have already been given in a previous publication ⁽¹²⁾. The behaviour of the absorption coefficient of the first photon K_1 as a function of the frequency ω_1 is here given for all cases as in ref. ⁽¹³⁾ for one-photon processes. Some numerical examples are also reported relative to a number of semiconductors, such as hexagonal BN in two dimensions, cubic ZnS, and AlSb and GaAs in three dimensions. They show that a structure in the absorption coefficient of the photon $\hbar\omega_1$ should be observed in correspondence to a saddle point when the density of the second photon is $\sim 10^{18}$ ph/cm³.

⁽³⁾ R. BRAUNSTEIN and E. O. KANE: *Journ. Phys. Chem. Solids*, **23**, 1423 (1962).

⁽⁴⁾ See, for instance, N. BLOEMBERGEN: *Nonlinear Optics* (New York, Amsterdam, 1965).

⁽⁵⁾ J. J. HOPFIELD, J. M. WORLOCK and K. PARK: *Phys. Rev. Lett.*, **11**, 414 (1963).

⁽⁶⁾ J. J. HOPFIELD and J. M. WORLOCK: *Phys. Rev.*, **137**, A 1455 (1956).

⁽⁷⁾ P. J. REGENSBURGER and E. PANIZZA: *Phys. Rev. Lett.*, **18**, 113 (1967).

⁽⁸⁾ R. BRAUNSTEIN and N. OCKMAN: *Phys. Rev.*, **134**, A 499 (1964).

⁽⁹⁾ C. K. PATEL, P. A. FLEURY, R. E. SLUSHER and H. L. FRISCH: *Phys. Rev. Lett.*, **16**, 971 (1966).

⁽¹⁰⁾ N. G. BASOV, A. Z. GRASYUK, I. G. ZUBAREV and V. A. KATULIN: *Žurn. Ėksp. Teor. Fiz. Pis'ma Redakt.*, **1**, 29 (1965) (English translation: *JETP Lett.*, **1**, 118 (1965)).

⁽¹¹⁾ E. PANIZZA: *Appl. Phys. Lett.*, **10**, 265 (1967).

⁽¹²⁾ F. BASSANI and A.-R. HASSAN: *Opt. Comm.*, **1**, 371 (1970).

⁽¹³⁾ F. BASSANI: *Rend. S.I.F.*, Course XXXIV (New York, 1966), p. 33; J. C. PHILLIPS: *Phys. Rev.*, **104**, 1263 (1956); in *Solid-State Physics*, Vol. **18**, edited by F. SEITZ and D. TURNBULL (1966).

In Sect. 2 we give a general expression for the absorption coefficient of one of the two photons obtained from second-order time-dependent perturbation theory.

In Sect. 3 we discuss the shape of the absorption coefficient in correspondence to critical points in the two-dimensional approximation.

In Sect. 4 we discuss the shape of the absorption coefficient in correspondence to critical points in the three-dimensional approximation.

In Sect. 5 we give numerical examples for BN, ZnS and GaAs and AlSb.

2. - General formulation of the problem.

In second-order time-dependent perturbation theory, the probability amplitude for an electron to make a transition from state v of the valence band to state c of the conduction band can be written in the form

$$(1) \quad a_{cv} = \left(-\frac{i}{\hbar}\right)^2 \sum_n \int_0^t dt' H'_{cn}(t') \int_0^{t'} dt'' H'_{nv}(t''),$$

where H'_{cn} and H'_{nv} are the matrix elements between states v or c and the intermediate state n due to the perturbation Hamiltonian of the photons

$$H' = \frac{e}{mc} (\mathbf{A}_1 \cdot \mathbf{p} + \mathbf{A}_2 \cdot \mathbf{p}),$$

where the vector potentials of the electromagnetic fields are

$$\mathbf{A}_1 = A_{01} \boldsymbol{\epsilon}_1 \exp [i(\boldsymbol{\eta}_1 \cdot \mathbf{r} - \omega_1 t)] + \text{c.c.}$$

and

$$\mathbf{A}_2 = A_{02} \boldsymbol{\epsilon}_2 \exp [i(\boldsymbol{\eta}_2 \cdot \mathbf{r} - \omega_2 t)] + \text{c.c.},$$

$\boldsymbol{\eta}_1$ and $\boldsymbol{\eta}_2$ being the wave vectors of the two photons, ω_1 and ω_2 their angular frequencies, and $\boldsymbol{\epsilon}_1$ and $\boldsymbol{\epsilon}_2$ their polarizations. We do not consider the nonlinear effect due to the term \mathbf{A}^2 ⁽¹⁴⁾ in first order because it contributes much less at the wavelength of interest here.

By performing the integration, considering only one intermediate state which gives the dominant contribution to the probability amplitude—this is justified by the energy denominator which could decrease the contribution of

⁽¹⁴⁾ M. IANNUZZI and E. POLACCO: *Phys. Rev. Lett.*, **13**, 371 (1964); *Phys. Rev.*, **138**, A 806 (1965); G. FORNACA, M. IANNUZZI and E. POLACCO: *Nuovo Cimento*, **36**, 1231 (1965); A. GOLD and J. P. HERNANDEZ: *Phys. Rev.*, **139**, A 2002 (1965).

the higher bands—we get

$$(2) \quad a_{cv} = -\frac{i e^2 A_{01} A_{02}}{\hbar m^2 c^2} \left[\frac{P_{cn}^{(1)} P_{nv}^{(2)}}{E_n - E_v - \hbar\omega_1} + \frac{P_{cn}^{(2)} P_{nv}^{(1)}}{E_n - E_v - \hbar\omega_2} \right] \cdot \left(\exp \left[\frac{i}{\hbar} (E_c - E_v - \hbar\omega_1 - \hbar\omega_2) t \right] - 1 \right) / \frac{i}{\hbar} (E_c - E_v - \hbar\omega_1 - \hbar\omega_2),$$

where P_{cn} and P_{nv} are the momentum matrix elements, with the normal condition, $P_{ij}^{(1)} = \delta(k_i - k_j - \eta_1) P_{ij}^{(1)}$, which justifies the dipole approximation with

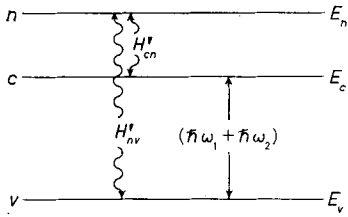


Fig. 1. — Schematic diagram of the two-photon transition process with one intermediate state (n) above the conduction state (c) and a valence band (v).

$\eta_1 = \eta_2 = 0$, since η is negligible with respect to the extent of the B.Z. For a study of the magnitude of the effect of including the photon momentum one can see the paper by PIACENTINI⁽¹⁵⁾, who finds an effect below the possible present experimental detection. The superscripts (1) and (2) indicate the polarization components of the two photons, E_c , E_v and E_n are the energies in the conduction, valence and intermediate bands respectively. The situation is shown schematically in Fig. 1.

The number of transitions per unit time in the unit volume is obtained in the usual way from the probability amplitude as

$$(3) \quad W = \frac{8\pi^3 \hbar e^4 c^4 N_1 N_2}{n^4 m^4 c^4 \omega_1 \omega_2} \int d\mathbf{k} \left[\frac{P_{cn}^{(1)} P_{nv}^{(2)}}{E_n - E_v - \hbar\omega_1} + \frac{P_{cn}^{(2)} P_{nv}^{(1)}}{E_n - E_v - \hbar\omega_2} \right]^2 \cdot \delta(E_c - E_v - \hbar\omega_1 - \hbar\omega_2),$$

where N_1 and N_2 are the density of the two photon beams and n is the index of refraction of the medium.

The absorption coefficient K_1 for photon $\hbar\omega_1$ when the two photons are simultaneously absorbed is

$$K_1 = \frac{2W}{\text{flux}} = \frac{2W}{N_1(c/n)},$$

the factor 2 being due to the spin.

For direct allowed transitions, P_{cn} and P_{nv} can be taken as constants near the band edges and are given in terms of the oscillator strength f for the transition by

$$|P_{cn}|^2 = \frac{1}{2} m \hbar \omega_{cn} f_{cn}$$

(15) M. PIACENTINI: *Nuovo Cimento*, **63 B**, 458 (1969).

and

$$|P_{nv}|^2 = \frac{1}{2} m \hbar \omega_{nv} f_{nv}.$$

Considering incoherent radiation and neglecting the cross-term in the quadratic expansion in eq. (3), we see that this is justified by the large energy denominator in (3) when $\hbar\omega_1$ is very different from $\hbar\omega_2$. When $\hbar\omega_1 \simeq \hbar\omega_2$ the neglect of the cross-term is a good approximation only for incoherent radiation as shown by BRAUNSTEIN^(1,8).

Finally we obtain

$$(4) \quad K_1 = \frac{\hbar^3 e^4 \omega_{cn} \omega_{nv} N_2}{2cn^3 m^2 \omega_1 \omega_2} \int d\mathbf{k} \left[\frac{f_{cn}^{(1)} f_{nv}^{(2)}}{(E_n - E_v - \hbar\omega_1)^2} + \frac{f_{cn}^{(2)} f_{nv}^{(1)}}{(E_n - E_v - \hbar\omega_2)^2} \right] \cdot \delta(E_c - E_v - \hbar\omega_1 - \hbar\omega_2).$$

The shape of the absorption coefficient near the critical points is a function of the \mathbf{k} dependence of E_c , E_v and E_n . In general near a critical point we can give a quadratic expansion of the energy as a function of \mathbf{k} ⁽¹³⁾ and the sign of the coefficients of this expansion defines the nature of the critical point and the peculiar shape of $K_1(\omega_1, \omega_2)$. We will consider critical points of the type M_0 (all coefficients of the expansion of $(E_c - E_v)$ are positive) and of the type M_1 (saddle point with one coefficient of the expansion of $(E_c - E_v)$ negative) and will compute the absorption coefficient in the two-dimensional and three-dimensional cases.

3. - Two-dimensional case.

We consider first the case of layer compounds where it is a good approximation to assume that the energy bands depend only on two components of the vector \mathbf{k} and are flat in the third direction. This amounts to neglecting the interaction between different layers, an approximation which has given reasonable results on the optical properties of graphite⁽¹⁶⁾. We will consider the two cases of a point M_0 and a point M_1 , which are the ones of physical interest in two-photon absorption.

3'1. *Edge point M_0 .* - Let us take the zero of energy of the top of the valence band and expand the energies as follows:

$$\begin{aligned} E_v &= -\alpha v k_x^2 - \beta_v k_y^2, \\ E_c &= E_g + \alpha_c k_x^2 + \beta_c k_y^2, \\ E_n &= \Delta E + \alpha_n k_x^2 + \beta_n k_y^2, \end{aligned}$$

⁽¹⁶⁾ F. BASSANI and G. PASTORI-PARRAVICINI: *Nuovo Cimento*, **50 B**, 95 (1967).

with α and β defined as positive quantities, where E_g and ΔE are the separation of the valence band from both the lower conduction and intermediate bands respectively.

When $\hbar\omega_1 + \hbar\omega_2 < E_g$, K_1 vanishes because the δ -function condition of formula (4) cannot be satisfied.

When $\hbar\omega_1 + \hbar\omega_2 > E_g$, we have

$$|k_x| = (\hbar\omega_1 + \hbar\omega_2 - E_g - (\beta_c + \beta_v) k_y^2)^{\frac{1}{2}} / (\alpha_c + \alpha_v)^{\frac{1}{2}};$$

the first integral in (4) becomes

$$(5) \quad I_1 = \frac{2\pi}{L(\alpha_c + \alpha_v)^{\frac{1}{2}}} \frac{1}{N^{\frac{1}{2}} M_1^2} \int_0^{((\hbar\omega_1 + \hbar\omega_2 - E_g) / (\beta_c + \beta_v))^{\frac{1}{2}}} \frac{dk_y}{\sqrt{1 - A k_y^2 (1 + B_1 k_y^2)^2}},$$

where L is the interlayer separation and

$$\begin{aligned} N &= \hbar\omega_1 + \hbar\omega_2 - E_g, \\ M_1 &= \Delta E - \hbar\omega_1 + \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\hbar\omega_1 + \hbar\omega_2 - E_g), \\ B &= \left| (\beta_n + \beta_v) - \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\beta_c + \beta_v) \right|, \\ A &= \frac{\beta_c + \beta_v}{N}, \quad B_1 = \frac{|B|}{M_1}. \end{aligned}$$

By performing the integration we obtain, for B positive or negative ($|B| \neq 0$),

$$I_1 = \frac{\pi}{L(\alpha_c + \alpha_v)^{\frac{1}{2}}} \frac{1}{N^{\frac{1}{2}} M_1^2 A^{\frac{1}{2}}} \left[\frac{1}{(B_1/A + 1)^{\frac{1}{2}}} \frac{\pi}{2} + \frac{1}{(B_1/A - 1)^{\frac{1}{2}}} \frac{\pi}{2} \right];$$

for $\hbar\omega_1 + \hbar\omega_2$ not too different from E_g we can expand the above expression with respect to B_1/A to obtain

$$I_1 = \frac{\pi^2}{L(\alpha_c + \alpha_v)^{\frac{1}{2}} (\beta_c + \beta_v)^{\frac{1}{2}}} \frac{1}{M_1^2} \left(1 - \frac{B_1}{A} \right).$$

Similarly the second integral in (4) becomes

$$I_2 = \frac{\pi^2}{L(\alpha_c + \alpha_v)^{\frac{1}{2}} (\beta_c + \beta_v)^{\frac{1}{2}}} \frac{1}{M_2^2} \left(1 - \frac{B_2}{A} \right),$$

where

$$M_2 = \Delta E - \hbar\omega_2 + \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\hbar\omega_1 + \hbar\omega_2 - E_g),$$

$$B_2 = B/M_2.$$

Then

$$(6) \quad K_1 = \frac{\pi^2 \hbar^3 e^4 \omega_{cn} \omega_{nv} N_2}{2Lcn^3 m^2 \omega_2 (\alpha_c + \alpha_v)^{\frac{1}{2}} (\beta_c + \beta_v)^{\frac{1}{2}}} \cdot \frac{1}{\omega_1} \left[\frac{f_{cn}^{(1)} f_{nv}^{(2)}}{M_1^2} \left(1 - \frac{B_1}{A}\right) + \frac{f_{cn}^{(2)} f_{nv}^{(1)}}{M_2^2} \left(1 - \frac{B_2}{A}\right) \right].$$

At the edge point, where $\hbar\omega_1 + \hbar\omega_2 = E_g$, the above expression gives

$$(7) \quad K_1 = \frac{\pi^2 \hbar^3 e^4 \omega_{cn} \omega_{nv} N_2}{2Lcn^3 m^2 \omega_2 (\alpha_c + \alpha_v)^{\frac{1}{2}} (\beta_c + \beta_v)^{\frac{1}{2}}} \frac{1}{\omega_1} \left[\frac{f_{cn}^{(1)} f_{nv}^{(2)}}{(\Delta E - \hbar\omega_1)^2} + \frac{f_{cn}^{(2)} f_{nv}^{(1)}}{(\Delta E - \hbar\omega_2)^2} \right].$$

The behaviour of K_1 as a function of ω_1 is shown in Fig. 2. If we put $\alpha_c = \beta_c$, $\alpha_v = \beta_v$ and $\alpha_n = \beta_n$, then $B = 0$ and the form (6) gives the absorption coefficient for one edge point with spherical symmetry in k -space.

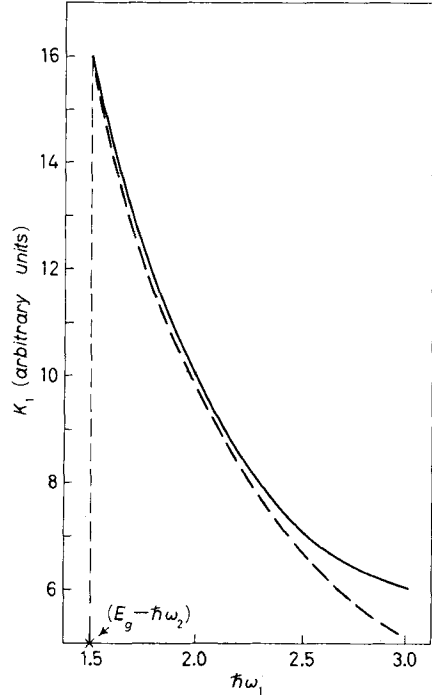


Fig. 2. - Absorption coefficient for the first photon K_1 at the point M_0 in the two-dimensional case. The frequency ω_2 of the second photon is a fixed quantity. The dashed curve ($|B| \neq 0$) indicates the effects of anisotropy with respect to the isotropic case (solid curve, $B = 0$). $\Delta E = 5$, $E_g = 4$, $\hbar\omega_2 = 2.5$, $(\alpha_n + \alpha_v)/(\alpha_c + \alpha_v) = 0.8$, $\beta_c + \beta_v = 0.03$, $\beta_n + \beta_v = 0.04$.

3'2. *Saddle point.* - Let us expand the energy in the case of a saddle point:

$$E_v = -\alpha_v k_x^2 - \beta_v k_y^2,$$

$$E_c = E_0 + \alpha_c k_x^2 - \beta_c k_y^2,$$

$$E_n = E_{n_0} + \alpha_n k_x^2 + \beta_n k_y^2$$

with $(\beta_c - \beta_v) > 0$, where E_0 and E_{n_0} are the separation of the valence band from both the lower conduction and intermediate bands respectively.

Substituting in (4) and performing the δ -function integral, we get for the first integral

$$I_1 = \frac{2\pi}{L(\alpha_c + \alpha_v)^{\frac{1}{2}}} \frac{1}{N^{\frac{1}{2}} M_1^2} \int \frac{dk_y}{(Ak_y^2 - 1)^{\frac{1}{2}} (1 + B_1 k_y^2)^2}$$

with

$$|k_x| = \left(\frac{\hbar\omega_1 + \hbar\omega_2 - E_0 + (\beta_c - \beta_v)k_y^2}{\alpha_c + \alpha_v} \right)^{\frac{1}{2}},$$

where

$$N = |E_0 - \hbar\omega_1 - \hbar\omega_2|,$$

$$M_1 = E_{n_0} - \hbar\omega_1 - \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} |E_0 - \hbar\omega_1 - \hbar\omega_2|,$$

$$B_1 = \left\{ (\beta_n + \beta_c) + \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\beta_c - \beta_v) \right\} |M_1|,$$

$$A = (\beta_c - \beta_v) |N|.$$

After integration we obtain

$$I_1 = \frac{\pi}{L(\alpha_c + \alpha_v)^{\frac{1}{2}}} \frac{1}{N^{\frac{1}{2}} M_1^2 A^{\frac{1}{2}}} \left[-\frac{A}{B_1} + \frac{1}{2(1 + B_1/A)} \log \frac{|1 + (1 + B_1/A)^{\frac{1}{2}}|}{|1 - (1 + B_1/A)^{\frac{1}{2}}|} + \frac{A}{B_1(1 + B_1/A)} + \frac{1}{2(1 + B_1/A)^{\frac{3}{2}}} \log \frac{|1 + (1 + B_1/A)^{\frac{1}{2}}|}{|1 - (1 + B_1/A)^{\frac{1}{2}}|} \right];$$

for $\hbar\omega_1 + \hbar\omega_2$ not too different from E_0 we can expand the above expression with respect to B_1/A and obtain

$$I_1 = \frac{\pi}{L(\alpha_c + \alpha_v)^{\frac{1}{2}}} \frac{1}{N^{\frac{1}{2}} M_1^2 A^{\frac{1}{2}}} \left[\left(1 - \frac{5B_1}{4A} \right) \log \frac{4A}{B_1} + \frac{B_1}{4A} - 1 \right].$$

Similarly the second integral in (4) becomes

$$I_2 = \frac{\pi}{L(\alpha_c + \alpha_v)^{\frac{1}{2}}} \frac{1}{N^{\frac{1}{2}} M_2^2 A^{\frac{1}{2}}} \left[\left(1 - \frac{5B_2}{4A} \right) \log \frac{4A}{B_2} + \frac{B_2}{4A} - 1 \right],$$

where

$$M_2 = E_{n_0} - \hbar\omega_2 - \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} |E_0 - \hbar\omega_1 - \hbar\omega_2|,$$

$$B_2 = \left\{ (\beta_n + \beta_v) + \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\beta_c - \beta_v) \right\} |M_2|;$$

then

$$(8) \quad K_1 = \frac{\pi \hbar^3 e^4 \omega_{cn} \omega_{nv} N_2}{2 L c n^3 m^2 \omega_2 (\alpha_c + \alpha_v)^{\frac{1}{2}} (\beta_c - \beta_v)^{\frac{1}{2}} \omega_1} \cdot \left[\frac{f_{cn}^{(1)} f_{nv}^{(2)}}{M_1^2} \left\{ \left(1 - \frac{5B_1}{4A} \right) \log \frac{4A}{B_1} + \frac{B_1}{4A} - 1 \right\} + \frac{f_{cn}^{(1)} f_{nv}^{(2)}}{M_2^2} \left\{ \left(1 - \frac{5B_2}{4A} \right) \log \frac{4A}{B_2} + \frac{B_2}{4A} - 1 \right\} \right].$$

So we have a logarithmic behaviour around the saddle point just as in the one-photon processes (13). The behaviour of the absorption coefficient as a function of ω_1 for a given value of ω_2 is reported in Fig. 3.

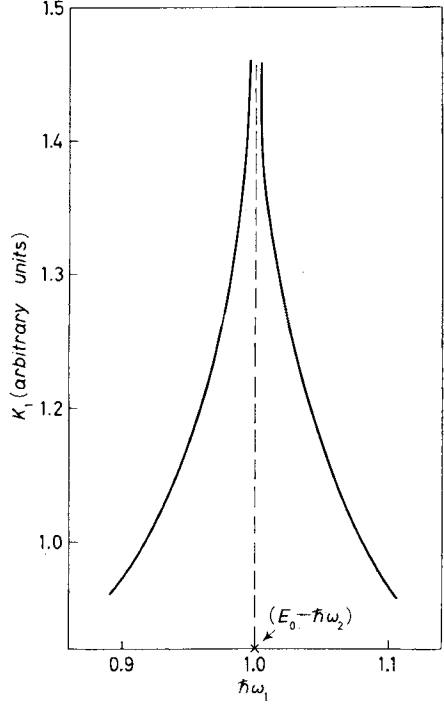


Fig. 3. - Absorption coefficient K_1 at the saddle point M_1 , in the two-dimensional case. The frequency ω_2 of the second photon is a fixed quantity. $E_0 = 3$, $E_{n0} = 4.5$, $\hbar\omega_2 = 2$, $(\alpha_n + \alpha_v)/(\alpha_c + \alpha_v) = 0.5$, $\beta_c - \beta_v = 0.01$, $\beta_n + \beta_v = 0.03$.

4. - Three-dimensional case.

Let us first consider the critical point M_0 with anisotropy in the k_x direction, taking the form of $E(\mathbf{k})$ as

$$E_v = -\alpha_v(k_x^2 + k_y^2) - \beta_v k_z^2,$$

$$E_c = E_g + \alpha_c(k_x^2 + k_y^2) + \beta_c k_z^2,$$

$$E_n = \Delta E + \alpha_n(k_x^2 + k_y^2) + \beta_n k_z^2.$$

By substituting in (4), the first integral becomes

$$I_1 = \int \frac{\delta(E_g - \hbar\omega_1 - \hbar\omega_2 + (\alpha_v + \alpha_c)(k_x^2 + k_y^2) + (\beta_v + \beta_c)) d\mathbf{k}}{[\Delta E - \hbar\omega_1 + (\alpha_n + \alpha_v)(k_x^2 + k_y^2) + (\beta_v + \beta_n)k_z^2]^2}.$$

When

$$\hbar\omega_1 + \hbar\omega_2 < E_g,$$

K_1 vanishes; when

$$\hbar\omega_1 + \hbar\omega_2 > E_g,$$

after integration over the δ -function, the preceding integral becomes

$$(9) \quad I_1 = \frac{2\pi}{\alpha_c + \alpha_v} \int_0^{(\hbar\omega_1 + \hbar\omega_2 - E_g)/(\beta + \beta_v)^{\frac{1}{2}}} \frac{dk_z}{\left[\Delta E - \hbar\omega_1 + \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\hbar\omega_1 + \hbar\omega_2 - E_g) + \left\{ (\beta_v + \beta_n) - \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\beta_c + \beta_v) k_z^2 \right\}^2 \right]^{\frac{1}{2}}},$$

which can be performed to give

$$\frac{\pi}{\alpha_c + \alpha_v} \left[\frac{k_z}{M_1(M_1 + Bk_z^2)} + \frac{1}{M_1^{\frac{3}{2}}\sqrt{B}} \operatorname{tg}^{-1} \frac{\sqrt{B}}{M_1^{\frac{1}{2}}} k_z \right]^{(\hbar\omega_1 + \hbar\omega_2 - E_g)/(\beta_c + \beta_v)^{\frac{1}{2}}},$$

where

$$B = \left| (\beta_v + \beta_n) - \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\beta_c + \beta_v) \right|,$$

$$M_1 = \Delta E - \hbar\omega_1 + \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\hbar\omega_1 + \hbar\omega_2 - E_g).$$

We obtain, by expanding for small $(\hbar\omega_1 + \hbar\omega_2 - E_g)$,

$$I_1 = \frac{\pi}{\alpha_c + \alpha_v} \left[\frac{1}{M_1^2} \left(\frac{\hbar\omega_1 + \hbar\omega_2 - E_g}{\beta_c + \beta_v} \right)^{\frac{1}{2}} \cdot \left\{ \left(1 - \frac{B}{M_1} \frac{\hbar\omega_1 + \hbar\omega_2 - E_g}{\beta_c + \beta_v} \right) + \left(1 - \frac{B}{3M_1} \frac{\hbar\omega_1 + \hbar\omega_2 - E_g}{\beta_c + \beta_v} \right) \right\} \right].$$

Similarly the second integral in (4) becomes

$$I_2 = \frac{\pi}{\alpha_c + \alpha_v} \left[\frac{1}{M_2^2} \left(\frac{\hbar\omega_1 + \hbar\omega_2 - E_g}{\beta_c + \beta_v} \right)^{\frac{1}{2}} \cdot \left\{ \left(1 - \frac{B}{M_2} \frac{\hbar\omega_1 + \hbar\omega_2 - E_g}{\beta_c + \beta_v} \right) + \left(1 - \frac{B}{3M_2} \frac{\hbar\omega_1 + \hbar\omega_2 - E_g}{\beta_c + \beta_v} \right) \right\} \right],$$

where

$$M_2 = \Delta E - \hbar\omega_2 + \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\hbar\omega_1 + \hbar\omega_2 - E_g).$$

Then

$$(10) \quad K_1 = \frac{\pi \hbar^3 \omega_{cn} \omega_{nv} e^4 N_2}{n^3 m^2 c \omega_2 (\alpha_c + \alpha_v) (\beta_c + \beta_v)^{\frac{1}{2}} \omega_1} \cdot \left[\frac{f_{en}^{(1)} f_{nv}^{(2)} \left(\frac{(\hbar\omega_1 + \hbar\omega_2 - E_g)^{\frac{1}{2}}}{[\Delta E - \hbar\omega_1 + ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(\hbar\omega_1 + \hbar\omega_2 - E_g)]^2} - \frac{2B}{3(\beta_c + \beta_v)} \frac{(\hbar\omega_1 + \hbar\omega_2 - E_g)^{\frac{1}{2}}}{[\Delta E - \hbar\omega_1 + ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(\hbar\omega_1 + \hbar\omega_2 - E_g)]^3} \right) + \frac{f_{en}^{(2)} f_{nv}^{(1)} \left(\frac{(\hbar\omega_1 + \hbar\omega_2 - E_g)^{\frac{1}{2}}}{[\Delta E - \hbar\omega_2 + ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(\hbar\omega_1 + \hbar\omega_2 - E_g)]^2} - \frac{2B}{3(\beta_c + \beta_v)} \frac{(\hbar\omega_1 + \hbar\omega_2 - E_g)^{\frac{1}{2}}}{[\Delta E - \hbar\omega_2 + ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(\hbar\omega_1 + \hbar\omega_2 - E_g)]^3} \right) \right].$$

As a consequence of expression (10) the curve of $K_1(\omega_1)$ starts from the edge and increases with increasing values of $(\hbar\omega_1 + \hbar\omega_2)$. If there is complete isotropy we have the limiting case $B = 0$ and the formula (10) reduces to the expression given by BRAUNSTEIN. The behaviour of the absorption coefficient as a function of $\hbar\omega_1$, for fixed ω_2 , is given in Fig. 4.

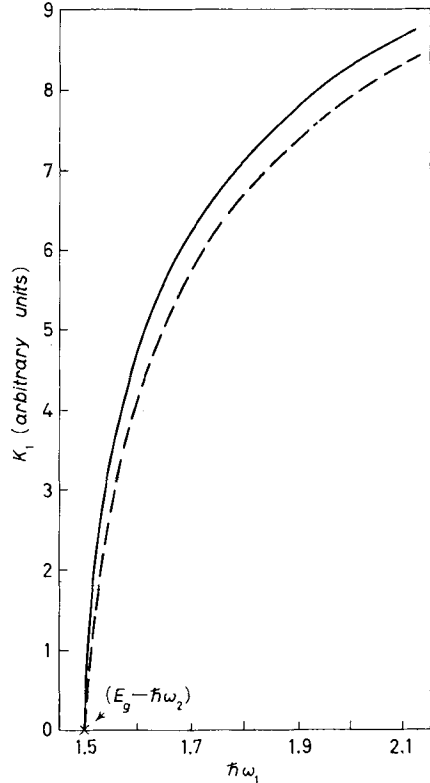


Fig. 4. - Absorption coefficient K_1 vs. $\hbar\omega_1$ for the point M_0 in the 3-dimensional case. The dashed curve ($|B| \neq 0$) indicates the effect of the anisotropy with respect to the isotropic case (solid curve, $B = 0$). $\Delta E = 5$, $E_g = 4$, $\hbar\omega_2 = 2.5$, $\beta_n + \beta_v = 0.06$, $\beta_c + \beta_v = 0.1$, $(\alpha_v + \alpha_n)/(\alpha_v + \alpha_c) = 0.4$.

4.1. *Saddle point.* — Let us now consider the case of a saddle point M_1 with a negative effective mass in one direction.

The form of $E(\mathbf{k})$ can be taken as

$$\begin{aligned} E_v &= -\alpha_v(k_x^2 + k_y^2) - \beta_v k_z^2, \\ E_c &= E_0 + \alpha_c(k_x^2 + k_y^2) - \beta_c k_z^2, \\ E_n &= E_{n0} + \alpha_n(k_x^2 + k_y^2) + \beta_n k_z^2, \end{aligned}$$

with $(\beta_c - \beta_v) > 0$.

By substituting in (4) the first integral becomes

$$I_1 = \int \frac{\delta(E_0 - \hbar\omega_1 - \hbar\omega_2 + (\alpha_c + \alpha_v)(k_x^2 + k_y^2) - (\beta_c - \beta_v)k_z^2) d\mathbf{k}}{[E_{n0} - \hbar\omega_1 + (\alpha_n + \alpha_v)(k_x^2 + k_y^2) + (\beta_n + \beta_v)k_z^2]^2}.$$

After integrating over the δ -function we get

$$(11) \quad I_1 = \frac{\pi}{\alpha_c + \alpha_v} \int \frac{dk_z}{(M_1 + Bk_z^2)^2},$$

where

$$\begin{aligned} M_1 &= E_{n0} - \hbar\omega_1 - \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (E_0 - \hbar\omega_1 - \hbar\omega_2), \\ B &= \beta_n + \beta_v + \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} (\beta_c - \beta_v), \end{aligned}$$

and the limits on k_z are defined by the condition

$$E_0 - \hbar\omega_1 - \hbar\omega_2 + (\alpha_c + \alpha_v)(k_x^2 + k_y^2) - (\beta_c - \beta_v)k_z^2 = 0$$

and by limiting the region of \mathbf{k} -space.

For $\hbar\omega_1 + \hbar\omega_2 < E_0$, the limits of k_z in eq. (11) are $((E_0 - \hbar\omega_1 - \hbar\omega_2)/(\beta_c - \beta_v))^{\frac{1}{2}}$ and $R/(\beta_c - \beta_v)^{\frac{1}{2}}$ ($R^2 \gg (E_0 - \hbar\omega_1 - \hbar\omega_2)$). By performing the integral and expanding to lowest order in $(E_0 - \hbar\omega_1 - \hbar\omega_2)$ we obtain

$$I_1 = \frac{2\pi}{\alpha_c + \alpha_v} \left[\frac{\pi}{4B^{\frac{1}{2}}} \frac{1}{[E_{n0} - \hbar\omega_1 - ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(E_0 - \hbar\omega_1 - \hbar\omega_2)]^{\frac{1}{2}}} - \frac{1}{\beta_c - \beta_v^{\frac{1}{2}}} \frac{(E_0 - \hbar\omega_1 - \hbar\omega_2)^{\frac{1}{2}}}{[E_{n0} - \hbar\omega_1 - ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(E_0 - \hbar\omega_1 - \hbar\omega_2)]^2} \right].$$

A similar equality holds for the second integration in (4) (by putting $\hbar\omega_1$ instead $\hbar\omega_2$ in the last expression).

Then K_1 becomes on one side of the saddle point

$$(12) \quad K_1 = \frac{\pi \hbar^3 \omega_c \omega_{n0} N_2 e^4}{m^2 c n^3 \omega_2 (\alpha_c + \alpha_v)} \frac{1}{\omega_1} \cdot \left[f_{cn}^{(1)} f_{nv}^{(2)} \left(\frac{\pi}{4B^{\frac{1}{2}}} \frac{1}{[E_{n0} - \hbar\omega_1 - ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(E_0 - \hbar\omega_1 - \hbar\omega_2)]^{\frac{1}{2}}} \right. \right. \\ \left. \left. - \frac{1}{(\beta_c - \beta_v)^{\frac{1}{2}}} \frac{(E_0 - \hbar\omega_1 - \hbar\omega_2)^{\frac{1}{2}}}{[E_{n0} - \hbar\omega_1 - ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(E_0 - \hbar\omega_1 - \hbar\omega_2)]^2} \right) + \right. \\ \left. + f_{cn}^{(2)} f_{nv}^{(1)} \left(\frac{\pi}{4B^{\frac{1}{2}}} \frac{1}{[E_{n0} - \hbar\omega_2 - ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(E_0 - \hbar\omega_1 - \hbar\omega_2)]^{\frac{1}{2}}} \right. \right. \\ \left. \left. - \frac{1}{(\beta_c - \beta_v)^{\frac{1}{2}}} \frac{(E_0 - \hbar\omega_1 - \hbar\omega_2)^{\frac{1}{2}}}{[E_{n0} - \hbar\omega_2 - ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(E_0 - \hbar\omega_1 - \hbar\omega_2)]^2} \right) \right].$$

For $\hbar\omega_1 + \hbar\omega_2 > E_0$ the limits of k_z in eq. (11) are 0 and $R/(\beta_c - \beta_v)^{\frac{1}{2}}$. The integral can be easily performed and expanded to lowest order in $(\hbar\omega_1 + \hbar\omega_2 - E_0)$.

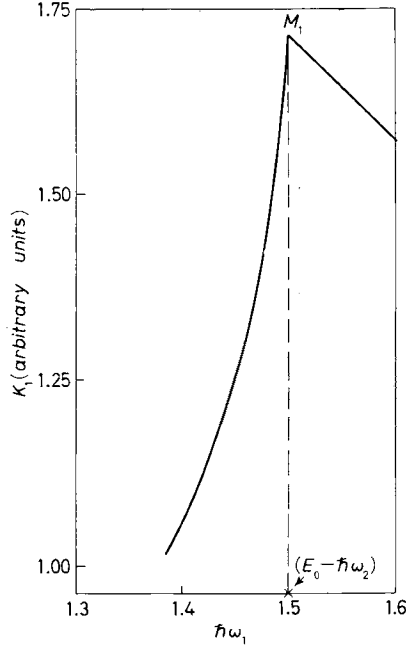


Fig. 5. - Absorption coefficient K_1 vs. $\hbar\omega_1$ near a saddle point M_1 in the three-dimensional case. As usual $\hbar\omega_2$ is a fixed quantity. $E_0 = 3$, $E_{nc} = 4.5$, $\hbar\omega_2 = 1.5$, $\beta_c - \beta_v = 0.01$, $\beta_n + \beta_v = 0.03$, $\alpha_n + \alpha_v = 0.3$, $\alpha_c + \alpha_v = 0.5$.

We obtain on the other side of the saddle point

$$(13) \quad K_1 = \frac{\pi^2 \hbar^3 e^4 \omega_{cn} \omega_{nv} N_2}{4cn^3 m^2 \omega_2 (\alpha_c + \alpha_v)^{\frac{1}{2}} B^{\frac{1}{2}} \omega_1} \cdot \left[\frac{f_{cn}^{(1)} f_{nv}^{(2)}}{[E_{n0} - \hbar\omega_1 - ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(\hbar\omega_1 + \hbar\omega_2 - E_0)]^{\frac{3}{2}}} + \frac{f_{cn}^{(2)} f_{nv}^{(1)}}{[E_{n0} - \hbar\omega_2 - ((\alpha_n + \alpha_v)/(\alpha_c + \alpha_v))(\hbar\omega_1 + \hbar\omega_2 - E_0)]^{\frac{3}{2}}} \right].$$

At the saddle point, $\hbar\omega_1 + \hbar\omega_2 = E_0$ and both (12) and (13) give

$$K_1 = \frac{\pi^2 \hbar^3 e^4 \omega_{cn} \omega_{nv} N_2}{4cm^2 n^3 \omega_2 (\alpha_c + \alpha_v) B^{\frac{1}{2}} \omega_1} \left[\frac{f_{cn}^{(1)} f_{nv}^{(2)}}{(E_{n0} - \hbar\omega_1)^{\frac{3}{2}}} + \frac{f_{cn}^{(2)} f_{nv}^{(1)}}{(E_{n0} - \hbar\omega_2)^{\frac{3}{2}}} \right].$$

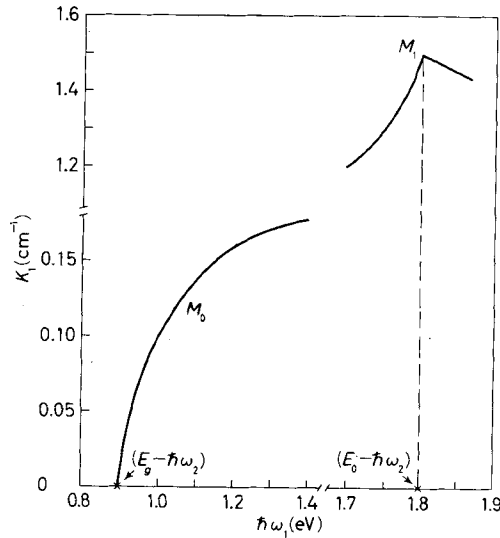


Fig. 6. - Absorption coefficient K_1 for AlSb at M_0 (Γ -point) and M_1 (L -point) in the same scale. The values of the parameters used are those of Tables I, II and III.

The behaviour of K_1 as function of the frequency ω_1 is shown in Fig. 5. It gives a peak which is similar to that obtained for the one-photon transition, but it is sharper because of the frequency dependence of the energy denominators, formulae (12) and (13). To the right of the saddle point E_0 , for instance the energy decreases in this case, while in the one-photon transitions it remained constant in lowest order.

5. - Applications.

To observe the absorption coefficient at the saddle point with a two-photon experiment one has to choose materials in which the gap at the saddle point is smaller than twice the fundamental gap because only in this way one can avoid one-photon transitions. We have considered four compounds: GaAs, ZnS, AlSb and BN which satisfy this condition. The effective masses m_v^* and m_c^* and the refractive index (n) for these compounds except BN are available from the single-photon absorption, for BN in the two-dimensional case the effective masses have been estimated from the available energy-band calculation⁽¹⁷⁾. Their gaps have been taken from their band structures; for GaAs, ZnS and AlSb the saddle point is at the L -point (Q -point for BN), the fundamental gap is at the Γ -point (P -point for BN).

In these semiconductors (except BN), the band structure calculations indicate an intermediate valence state which lies at nearly the same relative distance as that of the intermediate conduction state from the conduction band saddle point. So we can write the probability amplitude as the sum of two terms corresponding to these two intermediate states, then

$$a_{cv} = a_1 + a_2.$$

Therefore, the transition probability becomes

$$W = |a_1 + a_2|^2,$$

the two terms being of the same order of magnitude. Since the cross-product cancels we get

$$W = 2|a|^2,$$

and consequently we obtain twice the absorption coefficient at the saddle point.

In Table I we give the band parameters used in the calculation for the above-considered materials; some of them are rough guesses used for the purpose of exemplification. In Table II we give value of the absorption coefficient just above the edge (at the edge for BN) for $N_2 = 10^{18}$ ph/cm³. This value is in reasonable agreement with those observed experimentally⁽⁷⁻¹¹⁾. In Table III we report the expected absorption coefficient at the saddle point; for the case of BN we report the value of $\hbar\omega_1 + \hbar\omega_2 - E_0 = 0.3$ to give an idea of the magnitude of the singularity. Comparing the results of Table III and Table II

(17) E. DONI and G. PASTORI-PARRAVICINI: *Nuovo Cimento*, to be published.

TABLE I. - Inverse effective masses in units of $\hbar^2/2m$, taking the effective mass of the intermediate states as the free-electron mass; n is the refractive index.

	α_v	α_c	α_n	$\beta_v^{(a)}$	$\beta_c^{(a)}$	$\beta_n^{(a)}$	n
BN	0.67 ^(b)	1.33 ^(b)	1	0.13	0.27	0.2	1.61
ZnS	0.72 ⁽¹⁸⁾	3.67 ⁽¹⁸⁾	1	0.15	0.73	0.2	3 ⁽¹⁹⁾
GaAs	10 ⁽²⁰⁾	12.5 ⁽²¹⁾	1	2.0	2.5	0.17	3.7 ⁽²²⁾
AlSb	1 ⁽²³⁾	3.33 ⁽²¹⁾	1	0.2	0.67	0.2	3.18 ⁽²⁴⁾

(a) Rough guesses from the curvature of the energy bands.

(b) From a rough estimate of the energy curvature around the point $P=2\pi/a$ ($\frac{2}{3}, 0, 0$) from ref. (17). The value of the inter-layer separation has been taken as 6.66 Å as in ref. (17).

TABLE II. - Band parameters in eV and the absorption coefficient K_1 in cm^{-1} at M_0 (Γ -point, P -point for BN). All the oscillator strengths f are taken to be ~ 1 and the density of the second photon beam $N_2 = 10^{18}$ ph/cm³.

	E_e	ΔE	$\hbar\omega_1$	$\hbar\omega_2$	K_1
BN	5.7 ⁽¹⁷⁾	8.2 ⁽¹⁷⁾	2.9 ^(a)	2.8	6
ZnS	3.7 ⁽²⁵⁾	8.9 ⁽²⁵⁾	3.44	1.9	0.1
GaAs	1.4 ⁽²⁵⁾	4.6 ⁽²⁵⁾	0.8	1.0	0.02
AlSb	1.9 ⁽²⁵⁾	4.1 ⁽²⁵⁾	1.6	1.0	0.19

(a) The energy value at the edge.

TABLE III. - Band parameters in eV and absorption coefficient K_1 in cm^{-1} at the saddle point (L -point, Q -point for BN). Also in this case $f \sim 1$ and $N_2 = 10^{18}$ ph/cm³.

	E_0	E_{n0}	$\hbar\omega_1$	$\hbar\omega_2$	K_1
BN	6.5 ⁽¹⁷⁾	8.7 ⁽¹⁷⁾	4	2.8	0.6
ZnS	5.8 ⁽²⁵⁾	9.2 ⁽²⁵⁾	3	2.8	0.45
GaAs	2.6 ⁽²⁵⁾	6.0 ⁽²⁵⁾	1.3	1.3	0.82
AlSb	2.8 ⁽²⁵⁾	5.3 ⁽²⁵⁾	1.8	1	1.5

(18) J. C. MIKLOSZ and R. G. WHEELER: *Phys. Rev.*, **153**, 913 (1967).

(19) F. HERMAN, R. L. KORTUM, C. D. KUGLIN and J. L. SHAY: in *II-VI Semiconducting Compounds*, edited by D. G. THOMAS (1967).

(20) H. EHRENREICH: *Journ. Appl. Phys.*, **32**, 2155 (1961).

(21) M. CARDONA: in *Semiconductors and Semimetals*, Vol. 3, edited by A. BEER (1967).

(22) O. MADELUNG: *Physics of III-V Compounds* (New York, London, 1964).

(23) D. N. NASKDOV and S. V. SLOBODCHIKOV: *Žurn. Tekhn. Fiz.*, **28**, 715 (1958),

(24) F. OSWALD and R. SCHADE: *Zeits. Naturforsch.*, **9a**, 611 (1954).

(25) D. L. GREENAWAY and G. HARBEKE: *Optical Properties and Band Structure of Semiconductors* (New York, London, 1968).

we can remark that at the saddle points the absorption coefficients are one order of magnitude larger than near the edge and consequently we think that two-photon transition can be detected in correspondence to saddle points.

* * *

The author is indebted to Prof. F. BASSANI for suggesting this problem and for useful discussions.

RIASSUNTO (*)

Si ottiene, in corrispondenza a tutti i tipi di punti critici, la probabilità delle transizioni a due fotoni fra le bande di energia elettronica nei cristalli. Si riportano le espressioni per le discontinuità nel rapporto di assorbimento di uno dei due fotoni in funzione della sua frequenza quando la somma delle energie dei due fotoni è uguale alla differenza di energia tra la banda di conduzione e quella di valenza in quel particolare punto critico. I risultati indicano picchi netti in corrispondenza ai punti di sella M_1 , oltre lo spigolo netto M_0 già trovato da Braunstein. Si dimostra che nei materiali non cubici l'anisotropia influenza la forma dello spigolo M_0 e del picco M_1 . Nel caso limite del cristallo bidimensionale la probabilità di transizione a due fotoni dà una netta singolarità logaritmica ad M_1 . I risultati sono analoghi a quelli dei processi ad un solo fotone, ma tutte le singolarità e tutti i picchi sono più netti in questo caso e le loro intensità dipendono dalla posizione degli stati virtuali. Si discute la possibilità di studiare altri punti critici oltre lo spigolo con la spettroscopia a due fotoni e sostanze come il BN esagonale, il ZnS cubico e AlSb e GaAs sembrano essere buoni candidati per ricercare transizioni a due fotoni verso più alti punti critici della banda di conduzione.

(*) Traduzione a cura della Redazione.

Двух-фотонные междузонные переходы в критических точках в полупроводниках.

Резюме (*). — Получается выражение вероятности двух-фотонных переходов между электронными энергетическими зонами в кристаллах в соответствии со всеми типами критических точек. Приводятся выражения для разрывов в интенсивности поглощения одного из двух фотонов, как функция его частоты, когда сумма энергий двух фотонов равна энергетической разности между зоной проводимости и валентной

(*) Переведено редакцией.

зоны в этой специальной критической точке. Результаты обнаруживают острые пики в соответствии с седловыми точками M_1 , помимо острого края при M_0 , полученного ранее Браунштейном. Показывается, что для некубических материалов анизотропия влияет на форму края M_0 и пика M_1 . В предельном случае двумерного кристалла вероятность двух-фотонного перехода имеет острую логарифмическую сингулярность при M_1 . Полученные результаты аналогичны результатам для одно-фотонных процессов, но все сингулярности и пики являются более острыми в этом случае и их интенсивности зависят от положения виртуальных состояний. Обсуждается возможность исследования других критических точек, помимо края, посредством двух-фотонной спектроскопии. Вещества, такие как гексагональный VN, кубический ZnS, AlSb и GaAs, по-видимому, представляют хорошие кандидаты для детектирования двух-фотонного перехода в более высоко лежащие критические точки зоны проводимости.