Inter-Band Transition Probabilities and Photon Momentum.

M. PIACENTINI

Istituto di Fisica dell'Università - Roma
Gruppo Nazionale di Struttura della Materia del CNR - Sezione di Roma

(ricevuto il 18 Marzo 1969)

Summary. — The theory of inter-band transitions is re-examined in the case of finite photon momentum q. New expressions for the joint density of states near critical points are derived. They give Van Hove's expressions in both the limits of long and short wavelengths. The dispersion relation for the transverse dielectric function ε_{2T} due to inter-band processes is given explicitly and it is compared to that of the longitudinal dielectric function ε_{2L}. It is shown that in the limit $q=0$ ε_{2T} equals ε_{2L} even for anisotropic media. The possibility of an experimental evidence of the effects caused by a finite photon momentum on the shape of the optical absorption is discussed.

1. – Introduction.

In 1962 TAUC (1) proposed to extend the study of optical processes in solids taking into account the photon momentum, and summarized the progress made in this way in explaining some peculiar behaviour of excitons and excitonic lines. In the preceding year ELLIOTT (2) had taken into account the photon momentum in showing that the $n=1$ line of the yellow series of Cu_2O had to be ascribed to a quadrupole transition (3).

The effect of a finite photon momentum on inter-band transitions has not been considered yet and the problem has grown of importance in these last years. The use of synchrotron radiation has practically opened to spectroscopists

(1) J. TAUC: *Proc. Int. Conf. Phys. Semicond.* (Exeter, 1962), p. 333.
(2) R. J. ELLIOTT: *Phys. Rev.*, **124**, 340 (1961).
(3) E. F. GROSS and A. A. KAPLYANSKII: *Sov. Phys. Solid State*, **2**, 353 (1960); **2**, 2637 (1961).

the regions of soft X-rays and vacuum ultra-violet (4); in these regions the photon momentum $q = 2\pi n/\lambda$ may be significant, even if still smaller than the Brillouin zone dimensions.

In this paper we attempt to study the finite photon momentum inter-band transitions, neglecting any electron-hole interaction or lifetime broadening.

In Sect. **2** we generalize the theory of interband processes and obtain the behaviour of the joint density of states near critical points. The dependence of the imaginary part of the dielectric function on the photon momentum is also discussed.

In Sect. **3** the limiting cases of vertical transitions and of transitions from deep bands are considered and selection rules are examined. It is shown also that, using the proper perturbation operators in the matrix element, the longitudinal as well as the transverse dielectric function can be obtained from the theory of Sect. **2**.

In Sect. **4** the possibility of an experimental evidence of the obtained results is discussed. While for dipole allowed transitions such evidence does not seem possible, the case of dipole forbidden transitions is open to discussion.

2. – Theory.

2·1. *General considerations.* – The theory of optical inter-band transitions gives the following expression for the imaginary part of the dielectric function (5):

$$\varepsilon_2(q\boldsymbol{\epsilon}, \omega) = 2\left(\frac{2\pi e}{m\omega}\right)^2 \sum_{v,c} \sum_{\boldsymbol{k},\boldsymbol{k}'} |P_{vc}(\boldsymbol{k}, \boldsymbol{k}', q\boldsymbol{\epsilon})|^2 \delta[E_c(\boldsymbol{k}') - E_v(\boldsymbol{k}) - \hbar\omega]\,, \tag{1}$$

where v indicates an occupied band and c an unoccupied one, $P_{vc}(\boldsymbol{k}, \boldsymbol{k}', q\boldsymbol{\epsilon})$ is the transition probability matrix element

$$P_{vc}(\boldsymbol{k}, \boldsymbol{k}', q\boldsymbol{\epsilon}) = \int_{\text{crystal}} \psi_c^*(\boldsymbol{k}', \boldsymbol{r}) \exp[iq\boldsymbol{\epsilon}\cdot\boldsymbol{r}]\, \boldsymbol{e}\cdot\boldsymbol{p}\,\psi_v(\boldsymbol{k}, \boldsymbol{r})\, \mathrm{d}^3\boldsymbol{r} = \tag{2a}$$

$$= \delta(\boldsymbol{k}' - \boldsymbol{k} - q\boldsymbol{\epsilon})(\boldsymbol{k} + q\boldsymbol{\epsilon}, c|\boldsymbol{e}\cdot(\boldsymbol{p} + \hbar\boldsymbol{k})|\boldsymbol{k}, v)\,. \tag{2b}$$

An electromagnetic wave propagating through the crystal along $\boldsymbol{\epsilon}$ with momentum $q = n(\omega)\cdot\omega/c$ and polarized along $\boldsymbol{e}$ has been considered. Moreover

(4) T. Sagawa, Y. Iguchi, M. Sasanuma, T. Nasu, S. Yamaguchi, S. Fujiwara, M. Nakamura, A. Ejiri, T. Masuoka, T. Sasaki and T. Oshio: *Journ. Phys. Soc. Japan*, **21**, 2587 (1966); P. Jaegle and G. Missoni: *Phys. Rev. Lett.*, **18**, 887 (1967); P. Jaegle, F. Combet Farnoux, P. Dhez, M. Cremonese and G. Onori: *Phys. Lett.*, **26** A, 364 (1968); B. Feuerbacher, M. Skibowski, W. Steinmann and R. P. Godwin: *Journ. Opt. Soc. Am.*, **58**, 137 (1968); R. Haensel, C. Kunz, T. Sasaki and B. Sonntag: *Phys. Rev. Lett.*, **20**, 1436 (1968).

the abbreviation

$$(\boldsymbol{k}', c|f(\boldsymbol{r}, \boldsymbol{p})|\boldsymbol{k}, v) = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} u_c^*(\boldsymbol{k}', \boldsymbol{r}) f(\boldsymbol{r}, -i\hbar\boldsymbol{\nabla}) u_v(\boldsymbol{k}, \boldsymbol{r})\, \mathrm{d}^3\boldsymbol{r}$$

has been introduced, where u indicates the periodic part of Bloch functions.

The contribution given to $\varepsilon_2(q\boldsymbol{\epsilon}, \omega)$ by each pair of bands is

$$\text{(3)} \qquad \varepsilon_{2vc}(q\boldsymbol{\epsilon}, \omega) = \\ = 2\left(\frac{2\pi e}{m\omega}\right)^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3} \left|(\boldsymbol{k} + q\boldsymbol{\epsilon}, c|\boldsymbol{e}\cdot(\boldsymbol{p} + \hbar\boldsymbol{k})|\boldsymbol{k}, v)\right|^2 \cdot \delta[E_c(\boldsymbol{k} + q\boldsymbol{\epsilon}) - E_v(\boldsymbol{k}) - \hbar\omega],$$

and this is the expression we are concentrating on.

2·2. *Joint density of states.* – The argument of the δ-function of eq. (3) indicates the conservation of energy and gives an implicit equation for the transition energy $\hbar\omega$ since the final state depends on $\hbar\omega$ also through q. Let us introduce the function

$$\text{(4)} \qquad f(\boldsymbol{k}, \omega) = E_c(\boldsymbol{k} + q\boldsymbol{\epsilon}) - E_v(\boldsymbol{k}) - \hbar\omega$$

and the set of surfaces $f(\boldsymbol{k}, \omega) = \text{const}$, defined in the reciprocal space taking ω as a parameter. Each of these surfaces represents a measure of the difference between the photon energy $\hbar\omega$ and the energy gap existing between the states represented by $\psi_c(\boldsymbol{k} + q\boldsymbol{\epsilon}, \boldsymbol{r})$ and $\psi_v(\boldsymbol{k}, \boldsymbol{r})$. Obviously the energy conservation is fulfilled only on the surface $f(\boldsymbol{k}, \omega) = 0$. Using this set of surfaces as new variables, eq. (3) transforms into

$$\text{(5)} \qquad \varepsilon_{2vc}(q\boldsymbol{\epsilon}, \omega) = 2\left(\frac{2\pi e}{m\omega}\right)^2 \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} \left[\int_{f=\text{const}} \frac{\left|(\boldsymbol{k}+q\boldsymbol{\epsilon}, c|\boldsymbol{e}\cdot(\boldsymbol{p}+\hbar\boldsymbol{k})|\boldsymbol{k}, v)\right|^2}{|\boldsymbol{\nabla}_{\boldsymbol{k}} f(\boldsymbol{k}, \omega)|_{f=\text{const}}}\, \mathrm{d}\sigma \right] \delta(f)\mathrm{d}f = \\ = 2\left(\frac{2\pi e}{m\omega}\right)^2 \frac{1}{(2\pi)^3} \int_{f=0} \frac{\left|(\boldsymbol{k} + q\boldsymbol{\epsilon}, c|\boldsymbol{e}\cdot(\boldsymbol{p} + \hbar\boldsymbol{k})|\boldsymbol{k}, v)\right|^2}{|\boldsymbol{\nabla}_{\boldsymbol{k}} f(\boldsymbol{k}, \omega)|_{f=0}}\, \mathrm{d}\sigma\,.$$

If the matrix element is almost constant through the Brillouin zone, the main contribution to the shape of $\varepsilon_{2vc}(q\boldsymbol{\epsilon}, \omega)$ is given by the generalized joint density of states

$$\text{(6)} \qquad J_{vc}(q\boldsymbol{\epsilon}, \omega) = \frac{1}{(2\pi)^3} \int_{f=0} \frac{\mathrm{d}\sigma}{|\boldsymbol{\nabla}_{\boldsymbol{k}} f(\boldsymbol{k}, \omega)|_{f=0}}\,.$$

Analogously to the case of vertical transitions, characteristic variations in $J_{vc}(q\boldsymbol{\epsilon}, \omega)$ are expected near points for which

$$\nabla_{\boldsymbol{k}} f(\boldsymbol{k}, \omega) = \boldsymbol{0} \tag{7a}$$

on the surface

$$f(\boldsymbol{k}, \omega) = 0 \,. \tag{7b}$$

From eq. (7a) the discontinuities in the shape of ε_{2vc} occur at general critical points [6], defined by

$$\nabla_{\boldsymbol{k}} E_c(\boldsymbol{k} + q\boldsymbol{\epsilon}) = \nabla_{\boldsymbol{k}} E_v(\boldsymbol{k}) \,. \tag{8}$$

The symmetry critical points, defined by

$$\nabla_{\boldsymbol{k}} E_c(\boldsymbol{k} + q\boldsymbol{\epsilon}) = \nabla_{\boldsymbol{k}} E_v(\boldsymbol{k}) = \boldsymbol{0} \,, \tag{9}$$

occur very exceptionally. Since symmetry states occur either at the centre of the zone or on the surface of it or along some particular direction, eq. (9) can be satisfied only for photon momenta of the same order of magnitude as the Brillouin zone dimensions, that is to say in the X-ray range.

The analytic behaviour of the joint density of states near a singularity occurring at $(\boldsymbol{k}_0, \omega_0)$ can be obtained expanding $f(\boldsymbol{k}, \omega)$ in a Taylor series about

TABLE I. – *Coefficients used in the expansion of $f(\boldsymbol{k}, \omega)$ near a critical point.* Column 1 gives their mathematical definition; column 2 their general expression; column 3 their expression in the case of nearly vertical transitions.

$a_i = \dfrac{1}{2}\dfrac{\partial^2 f(\boldsymbol{k}, \omega)}{\partial k_i^2}$	$\dfrac{\hbar^2}{2\mu_i}$	$\dfrac{\hbar^2}{2\mu_i}$
$c_i = \dfrac{\partial^2 f(\boldsymbol{k}, \omega)}{\partial k_i \partial\omega}$	$\dfrac{\hbar^2 \varepsilon_i}{m^*_{c_i}}\dfrac{dq}{d\omega}$	$\dfrac{\hbar^2 \varepsilon_i}{m^*_{c_i}}\dfrac{dq}{d\omega}$
$a_4 = \dfrac{1}{2}\dfrac{\partial^2 f(\boldsymbol{k}, \omega)}{\partial\omega^2}$	$\dfrac{1}{2}\left[\nabla_{\boldsymbol{k}} E_c \cdot \boldsymbol{\epsilon}\dfrac{d^2q}{d\omega^2} + \sum_i \dfrac{\hbar^2\varepsilon_i^2}{m^*_{c_i}}\left(\dfrac{dq}{d\omega}\right)^2\right]$	$\dfrac{\hbar^2}{2}\left[\sum_i \dfrac{\varepsilon_i^2}{2(m^*_{c_i} - m^*_{v_i})}\dfrac{d^2(q^2)}{d\omega^2} + \sum_i \dfrac{\varepsilon_i^2\mu_i}{m^*_{c_i}}\left(\dfrac{dq}{d\omega}\right)^2\right]$
$c_4 = -\dfrac{\partial f(\boldsymbol{k}, \omega)}{\partial\omega}$	$\hbar - \nabla_{\boldsymbol{k}} E_c \cdot \boldsymbol{\epsilon}\dfrac{dq}{d\omega}$	$\hbar\left[1 - \hbar\sum_i \dfrac{\varepsilon_i^2 q}{m^*_{c_i} - m^*_{v_i}}\dfrac{dq}{d\omega}\right]$
$\dfrac{1}{\mu_i}$	$\dfrac{1}{m^*_{c_i}(\boldsymbol{k}_0 + q_0\boldsymbol{\epsilon})} - \dfrac{1}{m^*_{v_i}(\boldsymbol{k}_0)}$	$\dfrac{1}{m^*_{c_i}(\boldsymbol{K}_0)} - \dfrac{1}{m^*_{v_i}(\boldsymbol{K}_0)}$

(6) J. C. PHILLIPS: *Solid-State Physics*, vol. **18** (New York, 1966).

the singularity. With the condition that $(\boldsymbol{k}_0, \omega_0)$ must be a solution of the system of eqs. (7*a*) and (7*b*), we have

$$(10)\quad f(\boldsymbol{k}, \omega) = \sum_{i=1}^{3} a_i (k_i - k_{0i})^2 + \left[\sum_{i=1}^{3} c_i (k_i - k_{0i}) - c_4\right](\omega - \omega_0) + a_4 (\omega - \omega_0)^2 + \dots .$$

The coefficients of the expansion are displayed in Table I. Following VAN

TABLE II. – *Joint density of states in the case of finite photon momentum.* The coefficients α, β, γ are displayed in the case of nearly vertical transitions in the second column.

	$E < 0$	$E > 0$
Three-dimensional lattice		
M_0	0	$\dfrac{\pi\sqrt{c_4' E - \alpha E^2}}{\sqrt{a_x a_y a_z}}$
M_1	$\dfrac{\pi(R - \sqrt{\alpha E^2 - c_4' E})}{\sqrt{\lvert a_x\rvert a_y a_z}}$	$\dfrac{\pi R}{\sqrt{\lvert a_x\rvert a_y a_z}}$
Two-dimensional lattice		
M_0	0	$\dfrac{\pi}{2\sqrt{a_x a_y}}$
M_1	$\dfrac{\ln 2R - \ln(\sqrt{\beta E^2 - c_4' E} - \gamma E)}{2\sqrt{\lvert a_x\rvert a_y}}$	$\dfrac{\ln 2R - \ln\sqrt{c_4' E - \alpha E^2}}{2\sqrt{\lvert a_x\rvert a_y}}$

$E = \hbar(\omega - \omega_0)$	
$c_4' = \dfrac{c_4}{\hbar}$	
$\alpha = \dfrac{1}{\hbar^2}\left[a_4 - \sum_i \dfrac{c_i^2}{4a_i}\right]$	$\approx \dfrac{1}{2}\left(\dfrac{\mathrm{d}q}{\mathrm{d}\omega}\right)^2 \sum_i \dfrac{\varepsilon_i^2}{m_{c_i}^* - m_{v_i}^*}$
$\beta = \dfrac{1}{\hbar^2}\left[\dfrac{c_x^2}{4\lvert a_x\rvert} - a_4\right]$	$\approx \dfrac{1}{2}\left(\dfrac{\mathrm{d}q}{\mathrm{d}\omega}\right)^2 \left[\dfrac{\varepsilon_x^2}{m_{c_x}^* - m_{v_x}^*} + \dfrac{\varepsilon_y^2}{m_{c_y}^*}\right]$
$\gamma = \dfrac{1}{\hbar}\dfrac{c_y}{2\sqrt{a_y}}$	$\approx \dfrac{\varepsilon_y\sqrt{\mu_y}}{2m_{c_y}^*}\dfrac{\mathrm{d}q}{\mathrm{d}\omega}$

HOVE (7), the singularities are classified as M_0, M_1, M_2 and M_3 critical points according to the signs of the coefficients a_i ($i = 1, 2, 3$). Performing the integration of eq. (6) in a similar way as that explained by BASSANI (5), one obtains the explicit expressions for the joint density of states. They are given in Table II in the cases of two- and three-dimensional M_0 and M_1 singularities (8). While for M_0 critical points the surface $f(\boldsymbol{k}, \omega) = 0$ is a closed one and therefore the field of integration is limited, in the case of M_1 critical points the corresponding surface $f(\boldsymbol{k}, \omega) = 0$ is open. In order to avoid this difficulty, it has been necessary to introduce an upper limit of integration R, large compared with $\hbar(\omega - \omega_0)$. The final expressions depend on R, as shown in Table II, but this constant can be considered as a reference term.

2·3. *Nearly vertical transitions.* – Since inter-band transitions in the optical region carry photon momenta much smaller than the Brillouin zone dimensions, they can be considered to be nearly vertical. This means that the energies and the states involved differ very little from those interested in the vertical case occurring at $\boldsymbol{K}$.

Let us split $q\boldsymbol{\epsilon}$ into two components $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ connecting $\boldsymbol{K}$ with $\boldsymbol{k} + q\boldsymbol{\epsilon}$ and $\boldsymbol{k}$ respectively:

$$\left\{\begin{aligned} &\boldsymbol{k} + q\boldsymbol{\epsilon} = \boldsymbol{K} + \boldsymbol{q}_1\,, \\ &\boldsymbol{k} = \boldsymbol{K} - \boldsymbol{q}_2\,, \\ &\boldsymbol{q}_1 + \boldsymbol{q}_2 = q\boldsymbol{\epsilon}\,. \end{aligned}\right. \tag{11}$$

If $(\boldsymbol{K}_0, \Omega_0)$ represents a vertical singularity, the corresponding one $(\boldsymbol{k}_0, \omega_0)$ for nearly vertical transitions differs very little from it; this difference, obtained expanding E_c, E_v and their gradients in a Taylor series about $(\boldsymbol{K}_0, \Omega_0)$, neglecting effective-mass variations and evaluating the expansions at $(\boldsymbol{k}_0, \omega_0)$, is given by

$$\hbar\omega_0 - \hbar\Omega_0 = \boldsymbol{\nabla}_{\boldsymbol{k}} E_v|_{\boldsymbol{K}_0} \cdot q\boldsymbol{\epsilon} + \frac{\hbar^2 q^2}{2} \sum_i \frac{\varepsilon_i^2}{m^*_{c_i} - m^*_{v_i}}\,, \tag{12}$$

$$\left\{\begin{aligned} &q_{1_i} = -\frac{\mu_i}{m^*_{v_i}}\, q\varepsilon_i\,, \\ &q_{2_i} = \frac{\mu_i}{m^*_{c_i}}\, q\varepsilon_i\,. \end{aligned}\right. \tag{13}$$

If the vertical transition occurs at a symmetry critical point, $\hbar\omega_0 - \hbar\Omega_0$ is quadratic in q. It can further be shown that in correspondence to symmetry

(7) L. VAN HOVE: *Phys. Rev.*, **89**, 1189 (1953).

(8) M. PIACENTINI: *Analisi delle transizioni interbanda nell'assorbimento di radiazione di sincrotrone*, Thesis, Rome.

critical points for vertical transitions, where eq. (9) holds with $q = 0$, there is a general critical point satisfying eq. (8) for which the results of Table II hold.

2'4. *Matrix element.* – In the limit of nearly vertical transitions the matrix element of eq. (2*b*) can be expanded in powers of q. Applying the $\boldsymbol{k}\cdot\boldsymbol{p}$ method, $u_v(\boldsymbol{k}, \boldsymbol{r})$ and $u_c(\boldsymbol{k} + q\boldsymbol{\epsilon}, \boldsymbol{r})$ can be expressed in terms of the orthonormal and complete set $\{u_m(\boldsymbol{K}, \boldsymbol{r})\}$ of periodic functions taken at $\boldsymbol{K}$ (9). In the case of two nondegenerate bands it gives

$$(14)\quad \begin{cases} u_c(\boldsymbol{k} + q\boldsymbol{\epsilon}, \boldsymbol{r}) = u_c(\boldsymbol{K} + \boldsymbol{q}_1, r) = u_c(\boldsymbol{K}, \boldsymbol{r}) + \sum\limits_{m\neq c} c_{cm}(\boldsymbol{q}_1) u_m(\boldsymbol{K}, \boldsymbol{r}) + \dots, \\ u_v(\boldsymbol{k}, \boldsymbol{r}) = u_v(\boldsymbol{K} - \boldsymbol{q}_2, \boldsymbol{r}) = u_v(\boldsymbol{K}, \boldsymbol{r}) + \sum\limits_{n\neq v} d_{vn}(\boldsymbol{q}_2) u_n(\boldsymbol{K}, \boldsymbol{r}) + \dots, \end{cases}$$

where c_{cm} and d_{vn} are given by ordinary perturbation theory:

$$(15)\quad \begin{cases} c_{cm} = \dfrac{\hbar}{m} \dfrac{(\boldsymbol{K}, m|\boldsymbol{q}_1\cdot\boldsymbol{p}|\boldsymbol{K}, c)}{E_c(\boldsymbol{K}) - E_m(\boldsymbol{K})} = -i(\boldsymbol{K}, m|\boldsymbol{q}_1\cdot\boldsymbol{r}|\boldsymbol{K}, c)\,, & m \neq c\,, \\ d_{vn} = -\dfrac{\hbar}{m} \dfrac{(\boldsymbol{K}, n|\boldsymbol{q}_2\cdot\boldsymbol{p}|\boldsymbol{K}, v)}{E_v(\boldsymbol{K}) - E_n(\boldsymbol{K})} = i(\boldsymbol{K}, n|\boldsymbol{q}_2\cdot\boldsymbol{r}|\boldsymbol{K}, v)\,, & n \neq v\,. \end{cases}$$

The right-hand side has been obtained using the commutation relations (10)

$$\boldsymbol{p} = \frac{-mi}{\hbar}[\boldsymbol{r}, H] = \frac{-mi}{\hbar}[\boldsymbol{r}, H(\boldsymbol{K})] - \hbar\boldsymbol{K}\,,$$

where $H(\boldsymbol{K})$ is the Hamiltonian operator in the $\boldsymbol{K}\cdot\boldsymbol{p}$ representation satisfying the Schrödinger equation $H(\boldsymbol{K}) u_n(\boldsymbol{K}, \boldsymbol{r}) = E_n(\boldsymbol{K}) u_n(\boldsymbol{K}, \boldsymbol{r})$.

Using eqs. (14) and (15) and considering only the linear terms in q, eq. (2*b*) becomes

$$(16)\quad \begin{aligned} P_{vc}(q\boldsymbol{\epsilon}, \boldsymbol{K}) = (\boldsymbol{K}, c|\boldsymbol{e}\cdot(\boldsymbol{p} + \hbar\boldsymbol{K})|\boldsymbol{K}, v) + i(\boldsymbol{K}, c|(q\boldsymbol{\epsilon}\cdot\boldsymbol{r})\boldsymbol{e}\cdot(\boldsymbol{p} + \hbar\boldsymbol{K})|\boldsymbol{K}, v) - \\ - i(\boldsymbol{K}, c|\boldsymbol{e}\cdot(\boldsymbol{p} + \hbar\boldsymbol{K})|\boldsymbol{K}, v)[(\boldsymbol{K}, c|\boldsymbol{q}_1\cdot\boldsymbol{r}|\boldsymbol{K}, c) + (\boldsymbol{K}, v|\boldsymbol{q}_2\cdot\boldsymbol{r}|\boldsymbol{K}, v)]\,. \end{aligned}$$

Elements of the form $(\boldsymbol{K}, n|\boldsymbol{r}|\boldsymbol{K}, n)$ are proportional to the dipole moment of an electron in state $\boldsymbol{K}$ and band n relative to the unit cell; they are null if the small group of $\boldsymbol{K}$ has inversion symmetry.

2'5. *Momentum dependence of the dielectric function.* – The dielectric function of eq. (1) depends on both the frequency and the momentum of the absorbed

(9) E. O. Kane: *Semiconductors and Semimetals*, vol. **1** (New York, 1966).
(10) E. I. Blount: *Solid-State Physics*, vol. **13** (New York, 1962).

photons. So far we have been interested in the frequency; let us therefore examine briefly the dependence on q. At this purpose we remember that near a critical point $\boldsymbol{k}_0$ we have

$$\varepsilon_{2vc}(q\boldsymbol{\epsilon},\omega)=2\left(\frac{2\pi e}{m\omega}\right)^2\sum_{\text{star }\boldsymbol{k}_0}|P_{vc}(q\boldsymbol{\epsilon})|^2 J_{vc}(q\boldsymbol{\epsilon},\omega)\,. \tag{17}$$

$J_{vc}(q\boldsymbol{\epsilon},\omega)$ depends on the photon momentum through the energy at which the singularity occurs, as indicated in eq. (12). The matrix element is given by eq. (16). Combining these two results one has the general expression for the dielectric function near all critical points. In the case of an M_0 symmetry critical point, for instance, we have

$$\varepsilon_{2vc}(q\boldsymbol{\epsilon},\omega)\propto\frac{1}{\omega^2}\,(B_1+B_2q^2)\sqrt{(\hbar\omega-\hbar\Omega_0)-B_3q^2}\,, \tag{18}$$

where B_1 and B_2 are constants easily related to the matrix element and

$$B_3=\frac{\hbar^2}{2}\sum_i\frac{\varepsilon_i^2}{m^*_{c_i}-m^*_{v_i}}\,;$$

moreover we have neglected the term αE^2. It must be noted that for electromagnetic radiation, the momentum being a function of the frequency, only one of these two quantities is necessary to define ε_2.

3. – Discussion.

3·1. *Vertical transitions.* – The case of vertical transitions is immediately obtained from the results given in the preceding Section, if the limit q going to zero is performed. One has, for instance, for the M_0 singularity, $\lim_{q\to 0} c'_4=1$ and $\lim_{q\to 0}\alpha\approx 1/2mc^2$ so that αE^2 can be neglected in comparison with E, being $\approx 10^{-6}$ times smaller.

3·2. *Transitions from core states.* – At energies of some tens of eV and more one excites electrons from core states. Since the corresponding energy bands are nearly flat, one expects that the joint density of states depends on the conduction band only and that singularities occur in correspondence to its critical points. This can be verified performing the two limits $\nabla_{\boldsymbol{k}}E_v(\boldsymbol{k})\to 0$ and $m^*_v(\boldsymbol{k})\to\infty$ (that hold throughout the whole Brillouin zone for core states) in eq. (8) and the expressions of Table II. One obtains furthermore, by taking the above limits on eq. (12), that there is no shift of the critical-point energy due to photon momentum.

3·3. *Allowed and forbidden transitions.* – General selection rules can be obtained from the matrix element (2*a*) by using the method of LAX and HOPFIELD ([11]) on transitions connecting different points of the Brillouin zone.

In the case of nearly vertical transitions we have shown in Subsect. 2·4 that, if the group of $\boldsymbol{K}_0$ has inversion symmetry, $P_{vc} = E_1 + i(E_2 + M_1)$; transitions may be forbidden in the electrical dipole approximation (E_1) and allowed in the successive approximation ($E_2 + M_1$); it may also happen that the transition is forbidden in both approximations. An example of this case is given in graphite by the transition $\Gamma^+_{1g} \to \Gamma^-_{2u}$ for light polarized with the electric field perpendicular to the z-axis. SACHS has given tables of selection rules for multipole absorption of polarized light at different symmetry points of the Brillouin zone ([12]).

When the dipole transition is forbidden at the vertical critical point, we obtain from eq. (16) the following expansion in $(\boldsymbol{K} - \boldsymbol{K}_0)$ for the matrix element

$$(19) \qquad P_{vc} = \left[b_1|\boldsymbol{K} - \boldsymbol{K}_0| + \dots\right] + iq(\boldsymbol{K}, c|(\boldsymbol{\epsilon}\cdot\boldsymbol{r})\boldsymbol{e}\cdot(\boldsymbol{p} + \hbar\boldsymbol{K})|\boldsymbol{K}, v) \,.$$

Substituting into eq. (3) we obtain, in the case of an M_0 critical point,

$$(20) \quad \varepsilon_{2vc}(q\boldsymbol{\epsilon}, \omega) = \left(\frac{e}{m\omega}\right)^2 \frac{1}{a_\perp\sqrt{a_\parallel}}\sqrt{c_4' E - \alpha E^2}\left[|E_2 + M_1|^2 + b_1\left\langle\frac{1}{a}\right\rangle (c_4' E - \alpha E^2)\right].$$

This equation has been obtained in the case of a rotational ellipsoidal energy band, with the light entering in the direction of the principal axis; $a_\perp$ and $a_\parallel$ are the inverses of the reduced effective masses in the directions respectively orthogonal and perpendicular to the principal axis and

$$\left\langle\frac{1}{a}\right\rangle = \frac{1}{3}\left(\frac{2}{a_\perp} + \frac{1}{a_\parallel}\right)$$

is their mean value. The first term of eq. (20) corresponds to the allowed electrical-quadrupole and magnetic-dipole transition, the second term originates from the electrical-dipole forbidden transition.

3·4. *Transverse and longitudinal dielectric functions.* – So far we have given a microscopic derivation of the transverse dielectric function $\varepsilon_{2T}(q\boldsymbol{\epsilon}, \omega)$. The theory developed in Sect. **2** can be used to obtain the longitudinal dielectric function $\varepsilon_{2L}(q\boldsymbol{\epsilon}, \omega)$ as well provided that the proper operator $\boldsymbol{\epsilon}\cdot(\boldsymbol{p} + \hbar\boldsymbol{k}) + \hbar q/2$ is used into eq. (2*b*) instead of $\boldsymbol{e}\cdot(\boldsymbol{p} + \hbar\boldsymbol{k})$. The joint density of states $J_{vc}(q\boldsymbol{\epsilon}, \omega)$

([11]) M. LAX and J. J. HOPFIELD: *Phys. Rev.*, **124**, 115 (1961).

([12]) M. SACHS: *Phys. Rev.*, **107**, 437 (1957).

is the same, depending only on the geometrical structure of the bands. The matrix element, on the contrary, is different. In the approximation of two nondegenerate bands and going to second-order terms in eqs. (14) and (15), in correspondence to a vertical critical point $\boldsymbol{K}_0$ with inversion symmetry we obtain the following general expression for the square of the matrix element modulus:

$$|P_{vc}(q\boldsymbol{\epsilon})|^2 = |(\boldsymbol{K}_0, c|\boldsymbol{e}\cdot(\boldsymbol{p}+\hbar\boldsymbol{K}_0)|\boldsymbol{K}_0, v)|^2 - 2A_{(L,T)}q^2 , \tag{21}$$

where

$$A_{(L,T)} = \left|(\boldsymbol{K}_0, c|\boldsymbol{e}\cdot(\boldsymbol{p}+\hbar\boldsymbol{K}_0)|\boldsymbol{K}_0, v)\right|^2 \operatorname{Re}\left[\frac{(\boldsymbol{K}_0, c|(\boldsymbol{q}_1/q\cdot\boldsymbol{r})^2|\boldsymbol{K}_0, c)}{2} + \frac{(\boldsymbol{K}_0, v|(\boldsymbol{q}_2/q\cdot\boldsymbol{r})^2|\boldsymbol{K}_0, v)}{2} + \frac{(\boldsymbol{K}_0, c|(\boldsymbol{q}_1/q\cdot\boldsymbol{r})\,\boldsymbol{e}\cdot(\boldsymbol{p}+\hbar\boldsymbol{K}_0)(\boldsymbol{q}_2/q\cdot\boldsymbol{r})|\boldsymbol{K}_0, v)}{(\boldsymbol{K}_0, c|\boldsymbol{e}\cdot(\boldsymbol{p}+\hbar\boldsymbol{K}_0)|\boldsymbol{K}_0, v)}\right] - \hbar s_{(L,T)} \operatorname{Im}\left[(\boldsymbol{K}_0, c|\boldsymbol{\epsilon}\cdot\boldsymbol{r}|\boldsymbol{K}_0, v)(\boldsymbol{K}_0, v|\boldsymbol{e}\cdot(\boldsymbol{p}+\hbar\boldsymbol{K}_0)|\boldsymbol{K}_0, c)\right];$$

Re and Im indicate the real and imaginary part of a complex quantity. In the case of longitudinal fields $\boldsymbol{e}\parallel\boldsymbol{\epsilon}$ and $s_L = -\boldsymbol{e}\cdot\boldsymbol{q}_2/q + \hbar/2$; in the case of transverse fields $\boldsymbol{e}\perp\boldsymbol{\epsilon}$ and $s_T = -\boldsymbol{e}\cdot\boldsymbol{q}_2/q$.

We can now give the difference between the longitudinal and the transverse dielectric functions corresponding to the same direction of polarization of the electric field up to terms of order q^2:

$$\varepsilon_{2T} - \varepsilon_{2L} = 4\left(\frac{2\pi e}{m\omega}\right)^2 J_{vc}(q\boldsymbol{\epsilon}, \omega)(A_L - A_T)q^2 . \tag{22}$$

Equation (22) shows that in the limit q going to zero longitudinal and transverse dielectric functions coincide also for anisotropic materials. Such result can be considered as a generalization of that previously obtained by ADLER for cubic substances ([13]). The difference between the longitudinal and the transverse dielectric functions appears in the q^2 coefficient and depends on both the kind of perturbation and the isotropic character of the material. We finally could relate eq. (22) with Lindhard's relation ([14]) $\varepsilon_T - \varepsilon_L = (q^2c^2/\omega^2)(1-1/\mu)$ and obtain the value of the magnetic permeability of the medium.

4. – Possibility for experimental evidence.

4·1. *Dipole allowed transitions.* – The new expressions given in Table II for the joint density of states differ from the old ones mainly by the term $\alpha\hbar^2(\omega-\omega_0)^2$ appearing under the square root. Let us analyse how large is the

([13]) S. L. ADLER: *Phys. Rev.*, **126**, 413 (1962).

([14]) J. LINDHARD: *Kgl. Danske Videnskab. Selskab., Mat.-Fys. Medd.*, **28**, 8 (1954).

contribution given by this term and if there is any possibility to have experimental evidence of it. Firstly let us consider the variation of the transition energy brought about by the finite photon momentum. In order to give the order of magnitude of this difference, eq. (12) can be rewritten as follows:

$$\frac{\omega_0 - \Omega_0}{\Omega_0} \approx \frac{n^2 \hbar \Omega_0}{2mc^2} \left(\frac{m_c^*}{m} - \frac{m_v^*}{m}\right)^{-1}.$$

For a small-gap semiconductor, such as Ge, $(\omega_0 - \Omega_0)/\Omega_0$ is of the order of $3 \cdot 10^{-5}$; it is much smaller than one can hope to detect by optical experiments.

Let us now consider the joint density of states for an M_0 critical point, the expression of which can be put into the form:

$$J_{vc}(q\boldsymbol{\epsilon}, \omega) \propto \sqrt{E(1-\varrho B)},$$

where $\varrho = (\omega - \omega_0)/\omega_0$ measures how far from the singularity we are analysing $J_{vc}(q\boldsymbol{\epsilon}, \omega)$. The corrective term

$$B = \frac{\hbar\omega_0}{2mc^2} \left(\frac{m_c^*}{m} - \frac{m_v^*}{m}\right)^{-1} \left(\frac{c}{v_g}\right)^2$$

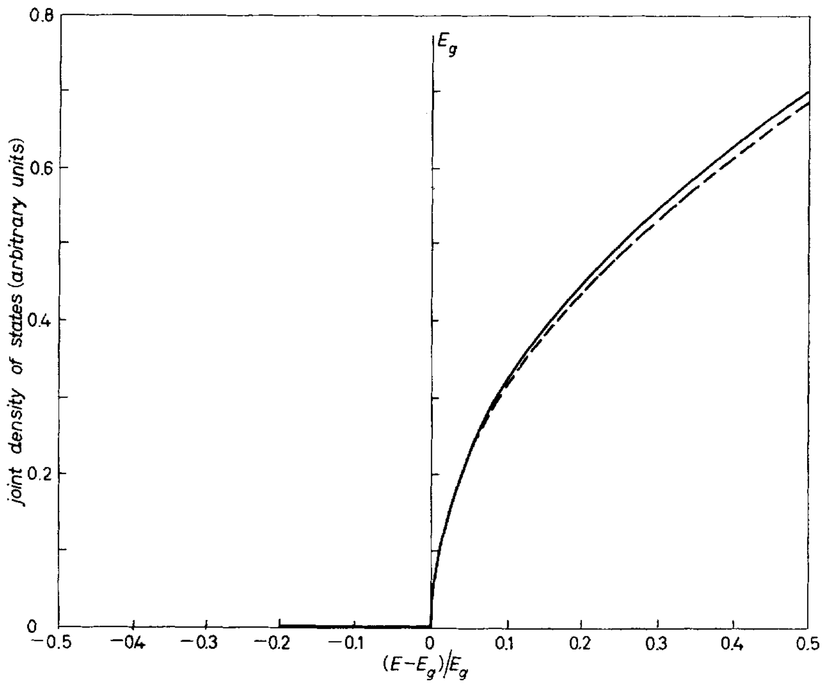

Fig. 1. – Joint density of states for an M_0 three-dimensional critical point. $E_g = 1$ eV; $(m_c^* - m_v^*)/m = 0.1$. Continuous line: $c/v_g = 1$ (corresponding to the vertical-transition approximation). Broken line: $c/v_g = 100$.

is of the order of $2\cdot10^{-6}$ times $(c/v_g)^2$ in the case of Ge. Here the group velocity $v_g = d\omega/dq$ of the light in the medium has been introduced. In correspondence to a resonance frequency of the medium, $q\approx 0$ and v_g is much smaller than c, being zero in the ideal limit of no broadening of the line. Even if no direct calculations have yet been performed, we expect that also in correspondence to a sharp absorption edge the index of refraction n varies rapidly and v_g is much smaller than c. But, since broadening effects are always present in solids, the variation of n will never be very large, as can be verified observing experimental data, so that the ratio c/v_g will be rather small. In Fig. 1 the joint density of states has been plotted *vs.* ϱ for two values of c/v_g, respectively 1 (solid line—it corresponds to the vertical transition) and 100 (broken line). An intermediate curve corresponding to $c/v_g = 10$ has been calculated, but

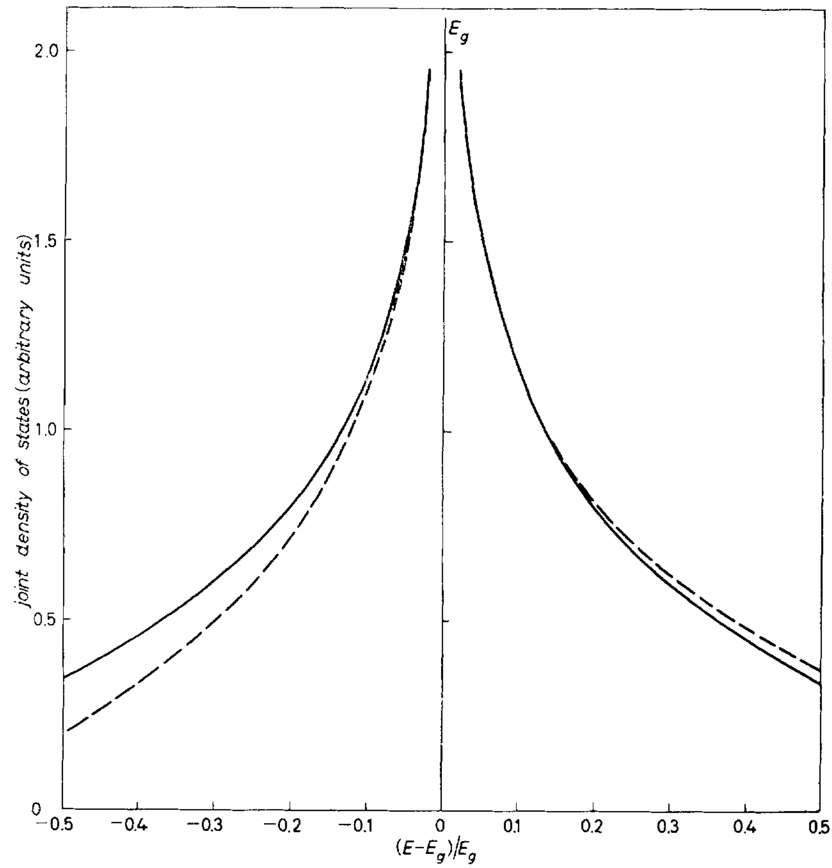

Fig. 2. – Joint density of states for an M_1 two-dimensional critical point with light propagating along the positive effective-mass direction. $E_g = 1$ eV. Continuous line: $c/v_g = 1$ (corresponding to the vertical transition approximation). Broken line: $c/v_g = 100$.

practically it coincides with the first one. The very small separation between the two curves shown in Fig. 1 can be somewhat increased by a larger energy transition than that considered (1 eV), but still the possibility of experimental evidence seems unlikely.

In the case of a two-dimensional lattice the finite photon momentum does not affect at all the M_0 singularity and has an effect on the M_1 singularity only for incident radiation propagating on the plane perpendicular to the c-axis. If the light propagates along the positive effective-mass direction, the symmetric logarithmic divergence of the M_1 critical point turns into an asymmetric one, as Fig. 2 shows. It may be possible that in this case of an absorption peak the variation is significant and observable at least with differential techniques. On the contrary, practically no changes appear with light propagating along the negative effective-mass direction, as is shown in Fig. 3.

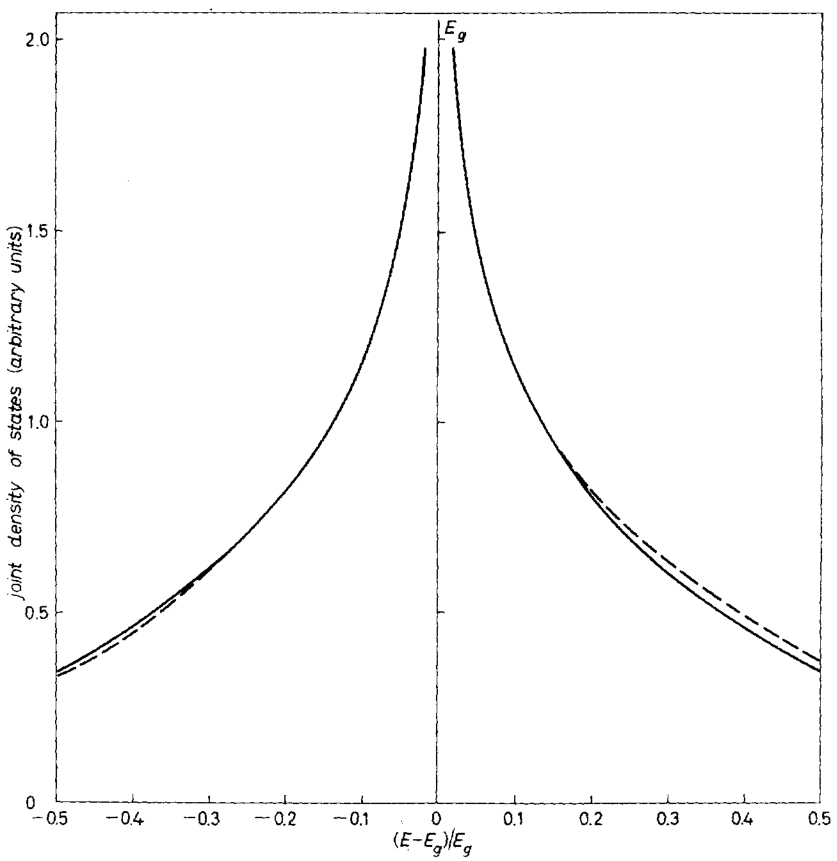

Fig. 3. – Joint density of states for an M_1 two-dimensional critical point with light propagating along the negative effective-mass direction. $E_g = 1$ eV. Continuous line: $c/v_g = 1$ (corresponding to the vertical transition approximation). Broken line: $c/v_g = 100$.

4·2. *Dipole forbidden transitions.* – The possibility of an experimental evidence of photon momentum effects may happen in the case of dipole forbidden transitions.

Since αE is much smaller than unity, as shown in the preceding Section, we can expand $(1-\alpha E)^{\frac{1}{2}}$ in a power series and rewrite eq. (20) in the following analytic form:

$$\varepsilon_{2vc}(q\boldsymbol{\epsilon}, \omega) \propto \sqrt{E}(p + qE + rE^2) , \tag{23}$$

where p, q, r here are a short-hand for the expressions

$$p = |E_2 + M_1|^2 , \qquad q = b_1 \left\langle \frac{1}{a} \right\rangle - \frac{p\alpha}{2} , \qquad r = -\frac{3}{2} b_1 \left\langle \frac{1}{a} \right\rangle \alpha$$

and must satisfy the condition

$$q^2 - \tfrac{4}{3} pr \geqslant 0 . \tag{24}$$

It must be observed at this point that a transition, which is forbidden in the dipole approximation, may be allowed at a higher order because of the spin-orbit interaction. If one tries to fit the experimental line shape of a dipole forbidden transition with eq. (23), the p-coefficient may be originated also from this spin-orbit effect. The r-coefficient corresponds really to a new term; if an absorption edge is fitted considering a finite r, fulfilling condition (24), one might think of it as the experimental evidence of photon momentum effects on interband transitions.

* * *

The author is very indebted to Prof. G. CHIAROTTI for suggesting the problem and to Prof. F. BASSANI for many helpful and stimulating discussions.

RIASSUNTO

Si estende la teoria delle transizioni interbanda al caso di fotoni dotati di impulso q non trascurabile. Le espressioni generali della densità congiunta degli stati sono calcolate nell'intorno dei punti critici; da queste espressioni, nei casi limite di lunghezza d'onda sia corte sia lunghe, si riottengono quelle di Van Hove. La relazione di dispersione della funzione dielettrica traversa ε_{2T} dovuta ai processi interbanda viene data esplicitamente e confrontata con la relazione di dispersione della funzione dielettrica longitudinale ε_{2L}. Si mostra che, nel caso limite $q=0$, ε_{2L} ed ε_{2T} coincidono anche per i mezzi anisotropi. Si discute infine la possibilità di osservare sperimentalmente l'effetto prodotto sulle curve di assorbimento ottico da fotoni il cui impulso non sia più trascurabile.

Вероятности междузонных переходов и импульс фотона.

Резюме (*). — Заново исследуется теория междузонных переходов в случае конечного импульса фотона q. Выводятся новые выражения для совместной плотности состояний вблизи критических точек. Они приводят к выражениям Ван Хова в обоих предельных случаях: длинноволновом и коротковолновом. В явной форме приводится дисперсионное соотношение для функции поперечной диэлектрической проницаемости ε_{2T}, обусловленной междузонными процессами, и это соотношение сравнивается с соотношением для функции продольной диэлектрической проницаемости ε_{2L}. Показывается, что в пределе $q=0$ ε_{2T} равно ε_{2L} даже для анизотропной среды. Обсуждается возможность экспериментального наблюдения влияния, обусловленного конечным импульсом фотоиа на форму оптического поглощения.

(*) *Переведено редакцией.*