

which is known as the “dielectric loss.” This relation holds exactly for light absorption in a material and is used later to relate optical transitions and light absorption. In the case of semiconductors where free carriers exist, the real part of the complex dielectric constant  $\kappa_1$  is related to the imaginary part of the complex conductivity by

$$\kappa_1 = \kappa_l - \frac{\sigma_i}{\omega\epsilon_0}, \quad (4.27)$$

where  $\kappa_l$  is the real part of the dielectric constant due to the crystal lattices and we may expect  $\kappa_1$  to become zero at a specific frequency (plasma frequency). This relation is often used to discuss the classical theory of plasma oscillation (see Sects. 5.4.1 and 5.5).

## 4.2 Direct Transition and Absorption Coefficient

In this Section we will consider the band-to-band direct transition of an electron from the valence band to the conduction band induced by the incident light. To do this we consider the electron motion induced by the incident light in a perfect crystal. The Hamiltonian of the electron is given by

$$H = \frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 + V(\mathbf{r}), \quad (4.28)$$

where  $\mathbf{A}$  is the vector potential of the electromagnetic field and  $V(\mathbf{r})$  is the periodic potential of the crystal. The vector potential is expressed by the plane wave:

$$\mathbf{A} = \frac{1}{2}A_0\mathbf{e} \left[ e^{i(\mathbf{k}_p \cdot \mathbf{r} - \omega t)} + e^{-i(\mathbf{k}_p \cdot \mathbf{r} - \omega t)} \right], \quad (4.29)$$

where  $\mathbf{k}_p$  and  $\mathbf{e}$  are the wave vector of the electromagnetic field and its unit vector (polarization vector), respectively. In the above equation the vector potential is expressed as a real number by adding its complex conjugate. Using the relation  $\mathbf{A} \cdot \mathbf{p} = \mathbf{p} \cdot \mathbf{A}$  and neglecting the small term  $A^2$ , the Hamiltonian is rewritten as

$$H \simeq \frac{p^2}{2m} + V(\mathbf{r}) + \frac{e}{m}\mathbf{A} \cdot \mathbf{p} \equiv H_0 + H_1. \quad (4.30)$$

Assuming  $H_1 = (e/m)\mathbf{A} \cdot \mathbf{p}$  as the perturbation, the transition probability per unit time  $w_{cv}$  for the electron from the initial state  $|v\mathbf{k}\rangle$  to the final state  $|c\mathbf{k}'\rangle$  is calculated to be

$$\begin{aligned} w_{cv} &= \frac{2\pi}{\hbar} |\langle c\mathbf{k}' | \frac{e}{m}\mathbf{A} \cdot \mathbf{p} | v\mathbf{k} \rangle|^2 \delta[\mathcal{E}_c(\mathbf{k}') - \mathcal{E}_v(\mathbf{k}) - \hbar\omega] \\ &= \frac{\pi e^2}{2\hbar m^2} A_0^2 |\langle c\mathbf{k}' | \exp(i\mathbf{k}_p \cdot \mathbf{r}) \mathbf{e} \cdot \mathbf{p} | v\mathbf{k} \rangle|^2 \\ &\quad \times \delta[\mathcal{E}_c(\mathbf{k}') - \mathcal{E}_v(\mathbf{k}) - \hbar\omega]. \end{aligned} \quad (4.31)$$

The matrix element of the term which includes the momentum operator  $\mathbf{p}$  is called the matrix element of the transition and gives the selection rule and the strength of the transition. Let us consider the Bloch function to express the electron state:

$$|j\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}} u_{j\mathbf{k}}(\mathbf{r}), \quad (4.32)$$

where  $j = v$  and  $c$  represents the valence band and conduction band states, respectively. Then the matrix element of the transition is given by

$$\begin{aligned} \mathbf{e} \cdot \mathbf{p}_{cv} &= \frac{1}{V} \int_V e^{-i\mathbf{k}'\cdot\mathbf{r}} u_{c\mathbf{k}'}^*(\mathbf{r}) e^{i\mathbf{k}_p\cdot\mathbf{r}} \mathbf{e} \cdot \mathbf{p} e^{i\mathbf{k}\cdot\mathbf{r}} u_{v\mathbf{k}}(\mathbf{r}) d^3\mathbf{r} \\ &= \frac{1}{V} \int_V e^{i(\mathbf{k}_p + \mathbf{k} - \mathbf{k}')\cdot\mathbf{r}} u_{c\mathbf{k}'}^*(\mathbf{r}) \mathbf{e} \cdot (\mathbf{p} + \hbar\mathbf{k}) u_{v\mathbf{k}}(\mathbf{r}) d^3\mathbf{r}. \end{aligned} \quad (4.33)$$

From the property of the Bloch function,  $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{R}_l)$ , where  $\mathbf{R}_l$  is the translation vector, and the matrix element is rewritten as

$$\begin{aligned} \mathbf{e} \cdot \mathbf{p}_{cv} &= \frac{1}{V} \sum_l \exp\{i(\mathbf{k}_p + \mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_l\} \\ &\times \int_{\Omega} e^{i(\mathbf{k}_p + \mathbf{k} - \mathbf{k}')\cdot\mathbf{r}} u_{c\mathbf{k}'}^*(\mathbf{r}) \mathbf{e} \cdot (\mathbf{p} + \hbar\mathbf{k}) u_{v\mathbf{k}}(\mathbf{r}) d^3\mathbf{r}, \end{aligned} \quad (4.34)$$

where  $\Omega$  is the volume of the unit cell. Summation with respect to  $\mathbf{R}_l$  becomes 0 except for

$$\mathbf{k}_p + \mathbf{k} - \mathbf{k}' = \mathbf{G}_m (= m\mathbf{G}), \quad (4.35)$$

where  $\mathbf{G}_m$  is the reciprocal lattice vector ( $\mathbf{G}$  is the smallest reciprocal lattice vector and  $m$  is an integer). The wave vector of light (electromagnetic waves) with a wavelength of  $1\mu\text{m}$  is  $|\mathbf{k}_p| = 6.28 \times 10^4 \text{ cm}^{-1}$  and the magnitude of the reciprocal lattice vector for a crystal with a lattice constant of  $5\text{\AA}$  is  $|\mathbf{G}| = 1.06 \times 10^8 \text{ cm}^{-1}$ , and thus the inequality  $k_p \ll G$  is fulfilled in general. Therefore, the largest contribution to the integral in (4.34) is due to the term for  $\mathbf{G}_m = 0$  ( $m = 0$ ). This condition may be understood to be equivalent to the conservation of momentum. From these considerations (4.35) leads to the important relation

$$\mathbf{k}' = \mathbf{k} \quad (4.36)$$

for the optical transition. That is, electron transitions are allowed between states with the same wave vector  $\mathbf{k}$  in  $\mathbf{k}$  space. In other words, when a photon of energy greater than the band gap is incident on a semiconductor, an electron with wave vector  $\mathbf{k}$  in the valence band is excited into a state with the same wave vector in the conduction band. From this fact the transition is referred to as a **direct transition**.

Since the integral with respect to  $\hbar\mathbf{k}$  in (4.35) vanishes because of the orthogonality of the Bloch functions, we obtain



$$\mathbf{e} \cdot \mathbf{p}_{cv} = \frac{1}{\Omega} \int_{\Omega} u_{c\mathbf{k}'}^*(\mathbf{r}) \mathbf{e} \cdot \mathbf{p} u_{v\mathbf{k}}(\mathbf{r}) d^3\mathbf{r} \delta_{\mathbf{k},\mathbf{k}'} . \quad (4.37)$$

Using the above results, the photon energy absorbed in the material per unit time and unit volume is given by  $\hbar\omega w_{cv}$ , which is equivalent to the power dissipation of the electromagnetic waves per unit time and unit volume given by (4.26):

$$\hbar\omega w_{cv} = \frac{1}{2} \omega \kappa_2 \epsilon_0 E_0^2 . \quad (4.38)$$

From the relation between the electric field and the vector potential,  $\mathbf{E} = -\partial\mathbf{A}/\partial t$ , we may put  $E_0 = \omega A_0$ ; thus the imaginary part of the dielectric constant is given by the equation

$$\begin{aligned} \kappa_2 &= \frac{2\hbar}{\epsilon_0 \omega^2 A_0^2} \omega_{cv} \\ &= \frac{\pi e^2}{\epsilon_0 m^2 \omega^2} \sum_{\mathbf{k}, \mathbf{k}'} |\mathbf{e} \cdot \mathbf{p}_{cv}|^2 \delta[\mathcal{E}_c(\mathbf{k}') - \mathcal{E}_v(\mathbf{k}) - \hbar\omega] \delta_{\mathbf{k}\mathbf{k}'} . \end{aligned} \quad (4.39)$$

It is evident that the absorption coefficient is obtained by inserting  $\kappa_2$  into (4.21).

### 4.3 Joint Density of States

In the previous section we derived the dielectric function for the direct transition, which is given by (4.39). When we assume that the matrix element  $\mathbf{e} \cdot \mathbf{p}_{cv}$  varies very slowly as  $\mathbf{k}$  or is independent of  $\mathbf{k}$  (this is a good approximation), the term  $|\mathbf{e} \cdot \mathbf{p}_{cv}|^2$  in (4.39) may be moved out of the summation. The imaginary part of the dielectric constant can then be rewritten as

$$\kappa_2(\omega) = \frac{\pi e^2}{\epsilon_0 m^2 \omega^2} |\mathbf{e} \cdot \mathbf{p}_{cv}|^2 \sum_{\mathbf{k}} \delta[\mathcal{E}_{cv}(\mathbf{k}) - \hbar\omega], \quad (4.40)$$

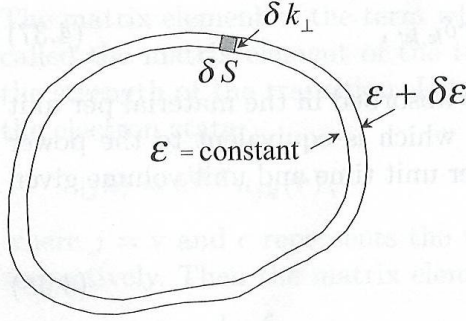
$$\mathcal{E}_{cv}(\mathbf{k}) = \mathcal{E}_c(\mathbf{k}) - \mathcal{E}_v(\mathbf{k}) . \quad (4.41)$$

The summation with respect to  $\mathbf{k}$  in (4.40) may be understood as the summation of the pair states of  $|\mathbf{v}\mathbf{k}\rangle$  and  $|\mathbf{c}\mathbf{k}\rangle$  due to the delta function and called the **joint density of states**. Replacing the summation  $\sum$  by an integral in  $\mathbf{k}$  space, the joint density of states  $J_{cv}(\hbar\omega)$  is written as

$$J_{cv}(\hbar\omega) = \sum_{\mathbf{k}} \delta[\mathcal{E}_{cv}(\mathbf{k}) - \hbar\omega] = \frac{2}{(2\pi)^3} \int d^3\mathbf{k} \cdot \delta[\mathcal{E}_{cv}(\mathbf{k}) - \hbar\omega], \quad (4.42)$$

where the spin degeneracy factor 2 is taken into account. Integration of the above equation is carried out by the following general method.

Consider two constant energy surfaces in  $\mathbf{k}$  space,  $\mathcal{E} = \hbar\omega$  and  $\hbar\omega + d(\hbar\omega)$ . The density of states in  $d(\hbar\omega)$  is then obtained as follows.



**Fig. 4.2.** Derivation of the general form of the joint density of states. Consider two constant energy surfaces  $\mathcal{E}$  and  $\mathcal{E} + \delta\mathcal{E}$  displaced by  $\delta\mathcal{E}$ . The small element of volume in  $\mathbf{k}$  space is then defined by the product of the bottom area  $\delta S$  and the distance  $\delta k_{\perp}$  perpendicular to the constant energy surface

$$J_{cv}(\hbar\omega) \cdot d(\hbar\omega) = \frac{2}{(2\pi)^3} \int_{\hbar\omega=\mathcal{E}_{cv}} \frac{dS}{|\nabla_{\mathbf{k}}\mathcal{E}_{cv}(\mathbf{k})|} \cdot d(\hbar\omega). \quad (4.43)$$

Therefore, the joint density of states  $J_{cv}(\hbar\omega)$  is rewritten as

$$J_{cv}(\hbar\omega) = \frac{2}{(2\pi)^3} \int_{\hbar\omega=\mathcal{E}_{cv}} \frac{dS}{|\nabla_{\mathbf{k}}\mathcal{E}_{cv}(\mathbf{k})|}, \quad (4.44)$$

where we have to note that the integral is carried out over the constant energy surface,  $\hbar\omega = \mathcal{E}_{cv}(\mathbf{k})$ , because of the delta function. This general form of the density of states is derived as follows. Referring to Fig. 4.2, let us consider constant energy surfaces displaced by a small amount of energy  $\delta\mathcal{E}$  in  $\mathbf{k}$  space,  $\mathcal{E}$  and  $\mathcal{E} + \delta\mathcal{E}$ . The small element of the volume  $\delta V(\mathbf{k})$  in  $\mathbf{k}$  space is defined by the volume contained in the bottom area  $\delta S$  and its height  $\delta k_{\perp}$  between the two constant energy surfaces. The states allowed in a volume element  $d^3\mathbf{k}$  in  $\mathbf{k}$  space per unit volume is given by

$$\frac{2}{(2\pi)^3} d^3\mathbf{k} = \frac{2}{(2\pi)^3} \delta V(\mathbf{k}). \quad (4.45)$$

The distance between the constant energy surfaces is given by  $(\partial k_{\perp}/\partial \mathcal{E})\delta\mathcal{E} = (\partial \mathcal{E}/\partial k_{\perp})^{-1}\delta\mathcal{E}$ , where  $\partial \mathcal{E}/\partial k_{\perp}$  is the gradient of  $\mathcal{E}$  in the direction normal to the energy surfaces and we find

$$\frac{\partial \mathcal{E}}{\partial k_{\perp}} = |\nabla_{\mathbf{k}}\mathcal{E}| = \sqrt{\left(\frac{\partial \mathcal{E}}{\partial k_x}\right)^2 + \left(\frac{\partial \mathcal{E}}{\partial k_y}\right)^2 + \left(\frac{\partial \mathcal{E}}{\partial k_z}\right)^2}, \quad (4.46)$$

or

$$\delta k_{\perp} = \frac{\delta \mathcal{E}}{|\nabla_{\mathbf{k}}\mathcal{E}|}. \quad (4.47)$$

From the definition of the volume element  $\delta V(\mathbf{k}) = \delta S \cdot \delta k_{\perp}$ , the density of states in energy space between  $\mathcal{E}$  and  $\mathcal{E} + \delta\mathcal{E}$  is given by

$$\rho(\mathcal{E})d\mathcal{E} = \frac{2}{(2\pi)^3} \int_S \frac{dS}{|\nabla_{\mathbf{k}}\mathcal{E}|} d\mathcal{E}. \quad (4.48)$$



It is evident from the above derivation that the joint density of states is obtained by replacing  $\mathcal{E}(\mathbf{k})$  by  $\mathcal{E}_{cv}(\mathbf{k})$  in the above equation and thus that the derivation of (4.44) is straightforward.

The joint density of states  $J_{cv}(\hbar\omega)$  given by (4.44) diverges when  $\nabla_{\mathbf{k}}\mathcal{E}_{cv}(\mathbf{k}) = 0$  is satisfied. This leads to a maximum probability for the optical transition. We may expect such behavior at various points in the Brillouin zone. Such a point in the Brillouin zone is called a **critical point** or **singularity** of the joint density of states. The behavior may be expected to occur under the following two conditions:

$$\nabla_{\mathbf{k}}\mathcal{E}_c(\mathbf{k}) = \nabla_{\mathbf{k}}\mathcal{E}_v(\mathbf{k}) = 0, \quad (4.49)$$

$$\nabla_{\mathbf{k}}\mathcal{E}_c(\mathbf{k}) = \nabla_{\mathbf{k}}\mathcal{E}_v(\mathbf{k}) \neq 0. \quad (4.50)$$

These equations reflect the conditions that the slopes of the two bands are parallel. The former condition means that the slopes are horizontal and will be satisfied at points of Brillouin zone with high symmetry. For example, this condition is satisfied at the  $\Gamma$  point. The second condition is satisfied at various points of Brillouin zone. The critical points behave differently depending on the type of critical point. The properties of the critical points were first investigated by van Hove [4.5] and thus are called **van Hove singularities**.

In order to discuss the singularities in more detail we expand  $\mathcal{E}_{cv}(\mathbf{k})$  at the point  $\nabla_{\mathbf{k}}(\mathbf{k}) = 0$  ( $\mathbf{k} = \mathbf{k}_0$ ,  $\mathcal{E}_{cv} = \mathcal{E}_G$ ) in a Taylor series and keep terms up to the second order:

$$\mathcal{E}_{cv} = \mathcal{E}_G + \sum_{i=1}^3 \frac{\hbar^2}{2\mu_i} (k_i - k_{i0})^2, \quad (4.51)$$

where the first-order term of  $\mathbf{k}$  disappears due to the singularity condition  $\nabla_{\mathbf{k}}\mathcal{E}_{cv} = 0$ . The constant  $\mu_i$  has the dimension of mass and is given by the following equation with the effective mass  $m_e^*$  of the conduction band and  $m_h^*$  of the valence band.

$$\frac{1}{\mu_i} = \frac{1}{m_{e,i}^*} + \frac{1}{m_{h,i}^*}. \quad (4.52)$$

**Table 4.1.** Joint density of states  $J_{cv}(\hbar\omega)$  for 3-dimensional critical points

types of critical points				$J_{cv}(\hbar\omega)$	
types	$\mu_1$	$\mu_2$	$\mu_3$	$\hbar\omega \leq \mathcal{E}_G$	$\hbar\omega \geq \mathcal{E}_G$
$M_0$	+	+	+	0	$C_1(\hbar\omega - \mathcal{E}_G)^{1/2}$
$M_1$	-	+	+	$C_2 - C_1(\mathcal{E}_G - \hbar\omega)^{1/2}$	$C_2$
$M_2$	-	-	+	$C_2$	$C_2 - C_1(\hbar\omega - \mathcal{E}_G)^{1/2}$
$M_3$	-	-	-	$C_1(\mathcal{E}_G - \hbar\omega)^{1/2}$	0

$$C_1 = \frac{4\pi}{(2\pi)^3} \left( \frac{8\mu_1\mu_2\mu_3}{\hbar^6} \right)^{1/2}$$

The mass  $\mu_i$  is called the reduced mass of the electron and hole. Using this result, the joint density of states  $J_{cv}$  at the critical point is then calculated in the following way. Defining the new variable

$$s_i = \frac{\hbar(k_i - k_{i0})}{\sqrt{2|\mu_i|}}, \quad (4.53)$$

equation (4.51) is rewritten as

$$\mathcal{E}_{cv}(s) = \mathcal{E}_G + \sum_{i=1}^3 \alpha_i s_i^2, \quad (4.54)$$

where  $\alpha_i = \pm 1$  is the sign of  $\mu_i$ , and  $\alpha_i = +1$  for  $\mu_i > 0$  and  $\alpha_i = -1$  for  $\mu_i < 0$ . Using the definition of the variable we may calculate the joint density of states given by (4.44) (for the  $M_0$  critical point:  $\alpha_i > 0$  for all  $\alpha_i$ ) as

$$\begin{aligned} J_{cv}(\omega) &= \frac{2}{(2\pi)^3} \left( \frac{8|\mu_1\mu_2\mu_3|}{\hbar^6} \right)^{1/2} \int_{\mathcal{E}_{cv}=\hbar\omega} \frac{dS}{|\nabla_S \mathcal{E}_{cv}(s)|} \\ &= \frac{2}{(2\pi)^3} \left( \frac{8|\mu_1\mu_2\mu_3|}{\hbar^6} \right)^{1/2} \int_{\mathcal{E}_{cv}=\hbar\omega} \frac{dS}{2s}, \end{aligned} \quad (4.55)$$

where  $s = (s_1^2 + s_2^2 + s_3^2)^{1/2}$ . It is straightforward to obtain the density of states for the  $M_0$  critical point. In this case we have  $\mathcal{E}_{cv} - \mathcal{E}_G = s_1^2 + s_2^2 + s_3^2 = s^2$  and then we obtain  $\int dS = 4\pi s^2$  for  $\hbar\omega > \mathcal{E}_G$ , which leads to the following result for the joint density of states  $J_{cv}(\omega)$ :

$$J_{cv}(\hbar\omega) = \begin{cases} 0 & ; \hbar\omega \leq \mathcal{E}_G \\ \frac{4\pi}{(2\pi)^3} \left( \frac{8\mu_1\mu_2\mu_3}{\hbar^6} \right)^{1/2} \sqrt{\hbar\omega - \mathcal{E}_G} & ; \hbar\omega \geq \mathcal{E}_G. \end{cases} \quad (4.56)$$

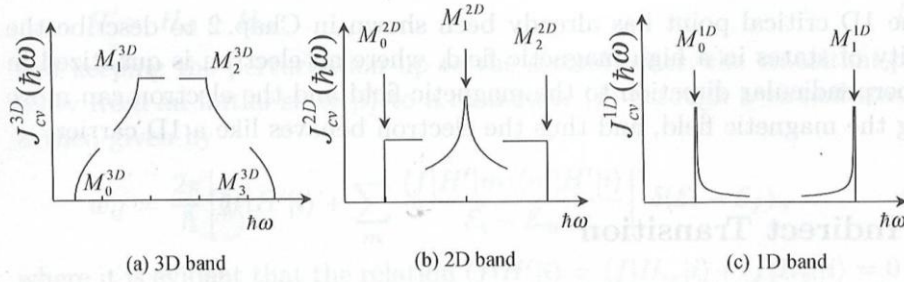
It is evident from (4.51) or (4.54) that the singularities or critical points are classified in four categories depending on the combination of the signs of

**Table 4.2.** Joint density of states  $J_{cv}(\hbar\omega)$  for 1-dimensional and 2-dimensional critical points

types of critical points		$J_{cv}(\hbar\omega)$	
dimension	types	$\hbar\omega \leq \mathcal{E}_G$	$\hbar\omega \geq \mathcal{E}_G$
1D	$M_0$	0	$A(\hbar\omega - \mathcal{E}_G)^{-1/2}$
1D	$M_1$	$A(\mathcal{E}_G - \hbar\omega)^{-1/2}$	0
2D	$M_0$	0	$B_1$
2D	$M_1$	$(B_1/\pi)(B_2 - \ln \mathcal{E}_G - \hbar\omega )$	$(B_1/\pi)(B_2 - \ln \mathcal{E}_G - \hbar\omega )$
2D	$M_2$	$B_1$	0

$$\begin{aligned} A &= \frac{2}{4\pi} \cdot \left( \frac{2|\mu|}{\hbar^2} \right)^{1/2}, \quad B_1 = \frac{2}{4\pi} \cdot \left( \frac{4|\mu_1\mu_2|}{\hbar^4} \right)^{1/2}, \\ B_2 &= \ln|2B_3 - (\mathcal{E}_G - \hbar\omega) + 2\sqrt{B_3^2 - (\mathcal{E}_G - \hbar\omega)B_3}| \end{aligned}$$





**Fig. 4.3.** Joint density of states  $J_{cv}(\hbar\omega)$  for (a) 3D, (b) 2D and (c) 1D bands

the reduced masses, or in other words we define the critical point  $M_j$  ( $j = 0, 1, 2$  and  $3$ ) by  $j$ , the number of negative  $\mu_i$ . The critical point  $M_0$  has 3 positive reduced masses ( $j = 0$ : zero negative reduced mass):  $\mu_1 > 0$ ,  $\mu_2 > 0$  and  $\mu_3 > 0$ . The critical points  $M_1$ ,  $M_2$  and  $M_3$  are for 1, 2, and 3 negative reduced masses, any of  $\mu_1$ ,  $\mu_2$  and  $\mu_3$ . The joint density of states  $J_{cv}(\omega)$  for the critical points  $M_1$ ,  $M_2$  and  $M_3$  have been calculated and the results are summarized in Table 4.1 (see for example [4.6, 4.7]).

Inserting (4.56) into (4.39) the imaginary part of the dielectric constant for the  $M_0$  critical point is given by

$$\kappa_2(\omega) = \frac{e^2}{2\pi\epsilon_0 m^2 \omega^2} |\mathbf{e} \cdot \mathbf{p}_{cv}|^2 \left( \frac{8\mu_1\mu_2\mu_3}{\hbar^6} \right)^{1/2} \sqrt{\hbar\omega - \mathcal{E}_G}, \quad (4.57)$$

where  $\hbar\omega > \mathcal{E}_G$ . The absorption coefficient is obtained by inserting this equation for  $\kappa_2(\omega)$  into (4.21):

$$\alpha(\omega) = \frac{e^2 |\mathbf{e} \cdot \mathbf{p}_{cv}|^2}{2\pi\epsilon_0 m^2 c n_0 \omega} \left( \frac{8\mu_1\mu_2\mu_3}{\hbar^6} \right)^{1/2} \sqrt{\hbar\omega - \mathcal{E}_G} \quad \text{for } \hbar\omega > \mathcal{E}_G. \quad (4.58)$$

It is evident from (4.51) that  $\mathcal{E}_{cv}$  becomes a maximum at  $\mathbf{k}_0$  for the  $M_0$  critical point (all of  $\mu_i$  are positive) and that  $\mathcal{E}_{cv}$  becomes a minimum at  $\mathbf{k}_0$  for the  $M_3$  critical point (all of  $\mu_i$  are negative). On the other hand, the  $M_1$  ( $M_2$ ) critical point exhibits a saddle point at  $\mathbf{k}_0$ , where  $\mathcal{E}_{cv}$  shows a maximum (minimum) at  $\mathbf{k}_0$  in one direction and a minimum (maximum) in other directions. When we consider a pair of conduction and valence bands, the lowest energy critical point is  $M_0$  and the highest energy critical point is  $M_3$ . For example a simple treatment of the tight-binding method gives the following energy bands in the case of the simple cubic lattice:

$$\mathcal{E}_{cv}(\mathbf{k}) = (\mathcal{E}_G + 3\gamma) - \gamma(\cos k_x a + \cos k_y a + \cos k_z a), \quad (4.59)$$

which gives rise to the joint density of states shown in Fig. 4.3a. The joint densities of states  $J_{cv}$  for 2-dimensional (2D) and 1-dimensional (1D) bands are summarized in Table 4.2 and in Fig. 4.3b-c. It is very important to point out that in Fig. 4.3b-c the joint densities of states  $J_{cv}$  at the saddle point for the 2D critical point and at the 1D critical points diverge. The behavior



of the 1D critical point has already been shown in Chap. 2 to describe the density of states in a high magnetic field, where an electron is quantized in the perpendicular direction to the magnetic field and the electron can move along the magnetic field, and thus the electron behaves like a 1D carrier.

#### 4.4 Indirect Transition

In Sects. 4.1 and 4.2 we considered the process where an electron in the valence band absorbs one photon and makes a transition to the conduction band vertically in  $\mathbf{k}$  space, i.e. a direct transition. This process plays the most important role in direct gap semiconductors such as GaAs, InSb and so on. On the other hand, we have shown in Chaps. 1 and 2 that the conduction band minima in Ge and Si are located at the  $L$  point and  $\Delta$  point, respectively, whereas the top of the valence band at the  $\Gamma$  point. Therefore, the fundamental absorption edge (lowest optical transition) is not direct, and thus direct transitions of electrons from the top of the valence band to the lowest conduction band minima is not allowed. Experimental results in Ge and Si reveal a weak transition for the photon energy corresponding to the indirect band gap between the top of the valence band at  $\mathbf{k} = 0$  and the conduction minima at  $\mathbf{k} \neq 0$ . This process is interpreted as the indirect transition in which an electron in the valence band absorbs a photon and then absorbs or emits a phonon to make the transition to the conduction band minima. This process is caused by a higher-order interaction or second-order perturbation in quantum mechanics, as described below in detail. The higher-order perturbation produces a weaker transition probability compared with the direct transition, and thus the weak absorption is explained. In addition we have to note that the transition is validated through a virtual state for the transition from the initial to the final states, and for this reason the transition is called an indirect transition.

Let us define the Hamiltonian  $H_e$  for electrons,  $H_l$  for lattice vibrations,  $H_{el}$  for the electron-phonon interaction and  $H_{er}$  for the electron-radiation (photon) interaction. Then the total Hamiltonian is written as

$$H = H_e + H_l + H_{el} + H_{er}. \quad (4.60)$$

We will discuss the Hamiltonian of the lattice vibrations and the electron-phonon interaction in Chap. 6 and will not go into detail here. The Hamiltonian of electrons and phonons is written as  $H_0 = H_e + H_l$  and the eigenstates are expressed as

$$|j\rangle = \begin{cases} |c\mathbf{k}, n_{\mathbf{q}}^{\alpha}\rangle & (\text{for an electron in the conduction band}) \\ |v\mathbf{k}, n_{\mathbf{q}}^{\alpha}\rangle & (\text{for an electron in the valence band}) \end{cases}, \quad (4.61)$$

where  $\mathbf{k}$  is the wave vector of the electron and  $n_{\mathbf{q}}^{\alpha}$  is the phonon quantum number of mode  $\alpha$  and wave vector  $\mathbf{q}$ . Expressing the perturbation Hamiltonian as



$$H' = H_{\text{el}} + H_{\text{er}} \quad (4.62)$$

and keeping the perturbation up to the second order, the transition probability from an initial state  $|i\rangle$  to a final state  $|f\rangle$  through a virtual state  $|m\rangle$  is then given by

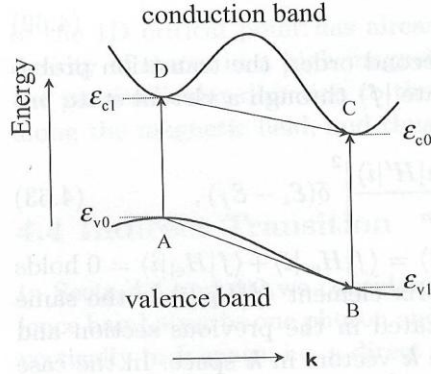
$$w_{if} = \frac{2\pi}{\hbar} \left| \langle f|H'|i\rangle + \sum_m \frac{\langle f|H'|m\rangle \langle m|H'|i\rangle}{\mathcal{E}_i - \mathcal{E}_m} \right|^2 \delta(\mathcal{E}_i - \mathcal{E}_f), \quad (4.63)$$

where it is evident that the relation  $\langle f|H'|i\rangle = \langle f|H_{\text{er}}|i\rangle + \langle f|H_{\text{el}}|i\rangle = 0$  holds because of the following reasons. The matrix element  $\langle f|H_{\text{er}}|i\rangle$  is the same as the element for the direct transition stated in the previous section and the transition is allowed between the same  $\mathbf{k}$  vectors in  $\mathbf{k}$  space. In the case of an indirect transition, however, the wave vectors  $\mathbf{k}$  are different between the initial state  $|i\rangle$  at the top of the valence band and the final state  $|f\rangle$  at the bottom of the conduction band, and thus we find that  $\langle f|H_{\text{er}}|i\rangle = 0$ . On the other hand, the matrix element  $\langle f|H_{\text{el}}|i\rangle$  ensures momentum conservation (wave vector conservation),  $\delta(\mathbf{k}_i \pm \mathbf{q} - \mathbf{k}_f)$ , but energy is not conserved because of the small value of the phonon energy compared with the band gap. Therefore, we find that  $\langle f|H_{\text{el}}|i\rangle = 0$ . From these considerations only the second term in (4.63) will contribute to the indirect transition and so finally we get

$$w_{if} = \frac{2\pi}{\hbar} \left| \sum_m \frac{\langle f|H'|m\rangle \langle m|H'|i\rangle}{\mathcal{E}_i - \mathcal{E}_m} \right|^2 \delta(\mathcal{E}_i - \mathcal{E}_f). \quad (4.64)$$

When we insert (4.62) into (4.64), such terms as  $\langle f|H_{\text{el}}|m\rangle \langle m|H_{\text{el}}|i\rangle$ ,  $\langle f|H_{\text{er}}|m\rangle \langle m|H_{\text{er}}|i\rangle$  and so on appear. However, these terms will not contribute to the indirect transition for the reason stated above. Finally, we find that the two processes shown in Fig. 4.4 will remain. The first process is: (1) an electron at the top of the valence band A interacts with radiation to absorb a photon and makes a transition to a virtual state D in the conduction band, followed by a transition by phonon absorption or emission to the final state C. The second process is: (2) an electron makes a transition from the top of the valence band A to a virtual state in the valence band B by absorbing or emitting a phonon and then absorbs a photon to end up at the final state C. The second process can be understood in a different way: an electron in the valence band B absorbs a photon, leaving a virtual state of a hole there and making a transition to the final state C, and an electron at the top of the valence band A is then transferred to this virtual state by absorbing or emitting a phonon. These processes are expressed by the following equation:

$$w_{if} = \frac{2\pi}{\hbar} \left| \frac{\langle C\mathbf{k}_f, n_{\mathbf{q}}^{\alpha} \pm 1 | H_{\text{el}} | D\mathbf{k}_i, n_{\mathbf{q}}^{\alpha} \rangle \langle D\mathbf{k}_i, n_{\mathbf{q}}^{\alpha} | H_{\text{er}} | A\mathbf{k}_i, n_{\mathbf{q}}^{\alpha} \rangle}{\mathcal{E}_i - \mathcal{E}_D} + \frac{\langle C\mathbf{k}_f, n_{\mathbf{q}}^{\alpha} \pm 1 | H_{\text{er}} | B\mathbf{k}_f, n_{\mathbf{q}}^{\alpha} \pm 1 \rangle \langle B\mathbf{k}_f, n_{\mathbf{q}}^{\alpha} \pm 1 | H_{\text{el}} | A\mathbf{k}_i, n_{\mathbf{q}}^{\alpha} \rangle}{\mathcal{E}_i - \mathcal{E}_B} \right|^2 \times \delta(\mathcal{E}_i - \mathcal{E}_f),$$



**Fig. 4.4.** Processes for the indirect transition. (1) An electron at the top of the valence band A interacts with radiation to absorb a photon and makes a transition to a virtual state D in the conduction band, followed by a transition by phonon absorption or emission to the final state C. (2) An electron makes a transition from the top of the valence band A to a virtual state in the valence band B by absorbing or emitting a phonon and then absorbs a photon to end up at the final state C

where the upper sign (+) of  $\pm$  represents phonon emission and the lower sign (−) of  $\pm$  corresponds to phonon absorption. When we neglect the phonon energy term  $\hbar\omega_q$  because of its smallness compared to the photon energy or the band gap, we find following relations:

$$\begin{aligned} k_f &= k_i \mp q, \\ \mathcal{E}_i - \mathcal{E}_f &= \mathcal{E}_v(k_i) + \hbar\omega \mp \hbar\omega_q^\alpha - \mathcal{E}_c(k_f), \\ \mathcal{E}_i - \mathcal{E}_D &= \mathcal{E}_v(k_i) + \hbar\omega - \mathcal{E}_D(k_i) \cong \mathcal{E}_c(k_f) - \mathcal{E}_D(k_i) \cong \mathcal{E}_{c0} - \mathcal{E}_{c1}, \\ \mathcal{E}_i - \mathcal{E}_B &= \mathcal{E}_v(k_i) \mp \hbar\omega_q^\alpha - \mathcal{E}_B(k_f) \cong \mathcal{E}_v(k_i) - \mathcal{E}_B(k_f) \cong \mathcal{E}_{v0} - \mathcal{E}_{v1}. \end{aligned}$$

Assuming that the matrix element is independent of the wave vector  $\mathbf{k}$ , we may approximate

$$w_{if} = \frac{2\pi}{\hbar} \sum_{m,\alpha,\pm} |M_{cv}^{m,\alpha,\pm}|^2 \delta(\mathcal{E}_i - \mathcal{E}_f) \quad (4.65)$$

for the transition probability and

$$\begin{aligned} \kappa_2(\omega) &= \frac{\pi e^2}{\epsilon_0 m^2 \omega^2} \sum_{m,\alpha,\pm} |M_{cv}^{m,\alpha,\pm}|^2 \\ &\times \sum_{\mathbf{k},\mathbf{k}'} \delta[\mathcal{E}_c(\mathbf{k}') - \mathcal{E}_v(\mathbf{k}) - \hbar\omega \pm \hbar\omega_q^\alpha] \end{aligned} \quad (4.66)$$

for the imaginary part of the dielectric constant. The first summation is carried out for the virtual state ( $|m\rangle$ ), the phonon mode, and its emission (+) and absorption (−). The probability of phonon emission and absorption is proportional to  $n_q^\alpha + 1$  and  $n_q^\alpha$ , respectively, and the average excited phonon number is given by Bose–Einstein statistics as



$$n_q^\alpha = \frac{1}{\exp(\hbar\omega_q^\alpha/k_B T) - 1}. \quad (4.67)$$

Using these results (4.65) may be written as

$$w_{if} = \frac{2\pi}{\hbar} \sum_{m,\alpha,\pm} \left[ |A_{cv}^{m,\pm}|^2 \left( n_q^\alpha + \frac{1}{2} \pm \frac{1}{2} \right) \right] \times \sum_{\mathbf{k},\mathbf{k}'} \delta [\mathcal{E}_c(\mathbf{k}') - \mathcal{E}_v(\mathbf{k}) - \hbar\omega \pm \hbar\omega_q^\alpha]. \quad (4.68)$$

The second summation with respect to  $\mathbf{k}$  and  $\mathbf{k}'$  represents the density of states for the indirect transition, which is calculated as follows.

$$J_{cv}^{\text{ind}} = \sum_{\mathbf{k},\mathbf{k}'} \delta [\mathcal{E}_c(\mathbf{k}') - \mathcal{E}_v(\mathbf{k}) - \hbar\omega \pm \hbar\omega_q^\alpha] \sum_{\mathbf{k},\mathbf{k}'} \delta \left[ \mathcal{E}_{c0} - \mathcal{E}_{v0} + \frac{\hbar^2}{2} \left( \frac{k_x^2}{m_{hx}} + \frac{k_y^2}{m_{hy}} + \frac{k_z^2}{m_{hz}} + \frac{k_x'^2}{m_{ex}} + \frac{k_y'^2}{m_{ey}} + \frac{k_z'^2}{m_{ez}} \right) - \hbar\omega \pm \hbar\omega_q^\alpha \right], \quad (4.69)$$

where the conduction band near the bottom is approximated by  $\mathcal{E}_c(\mathbf{k}') = \hbar^2 k'^2/2m_e + \mathcal{E}_{c0}$  with the electron effective mass  $m_e$  and the valence band near the top by  $\mathcal{E}_v(\mathbf{k}) = -\hbar^2 k^2/2m_h + \mathcal{E}_{v0}$  with the hole effective mass  $m_h$ . The summation  $\sum_{\mathbf{k}}$  is replaced by  $2/(2\pi)^3 \int d^3\mathbf{k}$  and transformations such as  $x = \hbar k_x/\sqrt{2m_{hx}}$ ,  $x' = \hbar k'_x/\sqrt{2m_{ex}}$  etc. are used. Then the density of states is given by

$$J_{cv}^{\text{ind}} = \frac{2K}{(2\pi)^6} \int dx dy dz dx' dy' dz' \times \delta \left( x^2 + y^2 + z^2 + x'^2 + y'^2 + z'^2 + \mathcal{E}_G - \hbar\omega \pm \hbar\omega_q^\alpha \right), \quad (4.70)$$

where we have assumed that the spin of the electron is not changed in the transition (no spin-flip transition) and that the spin degeneracy is used for one of the bands. In addition we have used  $K$  and  $\mathcal{E}_G$  given by

$$K = \sqrt{\frac{2^6 m_{hx} m_{hy} m_{hz} m_{ex} m_{ey} m_{ez}}{\hbar^{12}}},$$

$$\mathcal{E}_G = \mathcal{E}_{c0} - \mathcal{E}_{v0}.$$

In order to carry out the integral of  $J_{cv}^{\text{ind}}$  we use polar coordinates  $(x, y, z) = (r, \theta, \phi)$  with  $r^2 = s$  and  $r'^2 = s'$  ( $\int \sin\theta d\theta d\phi = 4\pi$ ), which leads to

$$J_{cv}^{\text{ind}} = \frac{2K}{(2\pi)^6} \int (4\pi)^2 \frac{ds ds'}{4} \sqrt{ss'} \delta(s + s' + \mathcal{E}_G - \hbar\omega \pm \hbar\omega_q^\alpha).$$

The integral of the above equation is easily carried out by using the  $\delta$  function, and we obtain

$$\begin{aligned} J_{cv}^{\text{ind}} &= \frac{4\pi^2}{(2\pi)^6} 2K \int_0^{\hbar\omega \mp \hbar\omega_q^\alpha - \mathcal{E}_G} \sqrt{s} \sqrt{\hbar\omega \mp \hbar\omega_q^\alpha - \mathcal{E}_G - s} \, ds \\ &= \frac{2K}{(2\pi)^4} \cdot \frac{\pi}{8} (\hbar\omega \mp \hbar\omega_q^\alpha - \mathcal{E}_G)^2. \end{aligned} \quad (4.71)$$

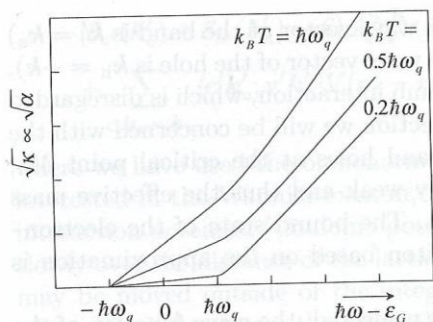
Finally, we obtain the dielectric function for the indirect transition given by

$$\begin{aligned} \kappa_2(\omega) &= \frac{\pi e^2}{\epsilon_0 m^2 \omega^2} \cdot \frac{K}{(4\pi)^3} \sum_{m, \alpha, \pm} |M_{cv}^{m, \alpha, \pm}|^2 (\hbar\omega \mp \hbar\omega_q^\alpha - \mathcal{E}_G)^2 \\ &= \frac{\pi e^2}{\epsilon_0 m^2 \omega^2} \cdot \frac{K}{(4\pi)^3} \sum_{m, \alpha} \left[ |A_{cv}^{m, \alpha, +}|^2 \cdot \frac{(\hbar\omega - \hbar\omega_q^\alpha - \mathcal{E}_G)^2}{1 - \exp(-\hbar\omega_q^\alpha/k_B T)} \right. \\ &\quad \left. + |A_{cv}^{m, \alpha, -}|^2 \cdot \frac{(\hbar\omega + \hbar\omega_q^\alpha - \mathcal{E}_G)^2}{\exp(\hbar\omega_q^\alpha/k_B T) - 1} \right], \end{aligned} \quad (4.72)$$

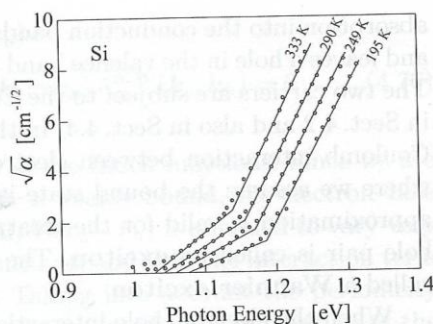
where the first and second terms on the right-hand side are associated with the transition followed by phonon emission and by phonon absorption, respectively.

The virtual state of the indirect transition is determined by the phonon mode and its deformation potential and also by the selection rule for the electron-radiation field interaction. As the simplest case we take into account a virtual state and a phonon mode and calculate the temperature dependence of the absorption coefficient. The denominator of the second term becomes large for the case  $k_B T \ll \hbar\omega_q^\alpha$  and the transition followed by phonon absorption disappears at low temperatures. On the other hand, the denominator of the first term becomes 1 at low temperatures. Therefore, the indirect transition will be governed by phonon emission at low temperatures. The feature is shown in Fig. 4.5, where  $\sqrt{\kappa_2}$  is plotted as a function of  $\hbar\omega - \mathcal{E}_G$  for different temperatures, by taking into account the fact that the square root of the imaginary part of the dielectric function and thus of the absorption coefficient is proportional to  $\hbar\omega \mp \hbar\omega_q - \mathcal{E}_G$  ( $\sqrt{\kappa_2} \propto \sqrt{\alpha} \propto (\hbar\omega \mp \hbar\omega_q - \mathcal{E}_G)$  ( $\alpha$ : absorption coefficient)). At lower temperatures the process of phonon absorption decreases and the absorption coefficient becomes very weak. We find that the phonon energy involved in the process is given by the half-width of the lower straight line and that the band gap  $\mathcal{E}_G$  lies in the middle of the line. The experimental results for Si are shown in Fig. 4.6, where the square root of the absorption coefficient  $\sqrt{\alpha}$  is plotted as a function of photon energy and find the feature of the indirect transition shown in Fig. 4.5 [4.8]. The turning point of the curve shifts to lower photon energy at higher temperatures, which is explained in terms of the temperature dependence of the band gap (the band gap decreases with increasing lattice temperature). The experimental results for Ge are shown in Fig. 4.7 [4.9], where turning points are observed in the

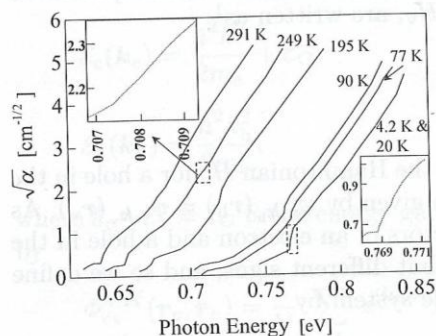




**Fig. 4.5.** Absorption coefficient at the indirect transition edge, where the square root of the absorption coefficient  $\sqrt{\alpha} \propto \sqrt{\kappa}$  is plotted as a function of photon energy minus the band gap  $\hbar\omega - \epsilon_G$  for different temperatures



**Fig. 4.6.** Square root of the absorption coefficient  $\sqrt{\alpha}$  plotted as a function of photon energy  $\hbar\omega$  for Si, where the transitions due to phonon absorption and emission are well resolved (from [4.8])



**Fig. 4.7.** The square root of the absorption coefficient  $\sqrt{\alpha}$  of Ge at the indirect transition edge is plotted as a function of photon energy  $\hbar\omega$  (from [4.9])

spectrum for  $T = 249\text{K}$  at about 0.65 eV and 0.71 eV. These turning points correspond to the transition due to the absorption and emission of one LO phonon, and the transition due to phonon emission disappears at low temperatures. A weak absorption is observed at  $T = 4.2\text{K}$  below the photon energy around 0.77 eV due to LA phonon emission process, which is believed to be due to a forbidden transition followed by TA phonon emission. It is most important to point out here that the square root of the absorption coefficient is not a straight line but exhibits a hump. This is caused by exciton effects as discussed in Sect. 4.5.

## 4.5 Exciton

### 4.5.1 Direct Exciton

In Sect. 4.2 we discussed optical absorption spectra due to direct transitions, where an electron in the valence band (wave vector  $\mathbf{k}$ ) is excited by photon

