Kramers-Kronig analysis of the optical constants of Zn_3As_2 and Zn_3P_2*

I. Review of calculation methods

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The present paper consists of five parts and is devoted mainly to the results of optical constants examination in Zn_3As_2 and Zn_3P_2 which are compounds of II_3-V_2 type with broad energy gap. The analysis of the up to now state-of-affairs, so far as the application of the Kramers-Kronig analysis method (KK) to the complex coefficient of reflection is concerned has indicated that it is necessary to develop the research in three additional directions described in the first three parts of this series.

In the part I a critical analysis of the calculation methods used till now and based on dispersion relations due to Kramers and Kronig has been presented. The general idea of the extrapolation methods has been discussed. Next, four methods of extrapolation of reflection coefficients have been considered, being followed by a discussion of two extrapolation methods for the phase angle and three original (elaborated lately) methods of calculations based on KK relations. Also, three other methods of optical constant calculations have been reported for which the KK relations are not exploited.

In the parts II and III some proposals of effective improvements of the calculation methods based on KK integral are given. Additionally, in both these parts the results of calculations for GaAs (a relatively well known semiconductor) are presented and used next for testing the methods of calculation improved by us. For these methods the analysis of errors and accuracies is very widely presented in the part IV. Finally, the part V contains the results of calculations of optical constants for Zn_3As_2 and Zn_3P_2, carried out by using the improved methods of calculation and basing on our own measurements of optical properties of those semiconductors.

1. Introduction

The dispersion relations, well-known in the theory of analytic functions, have been used in physics since twentieths of this century [1]. They may be applied when the physical system, described by a complex function, responses to the input signal in accordance with the principles of linearity and causality [2]. Hence, the application of dispersion relations in so many different fields like, for instance, analysis of electric circuits [3] and optics of solid state is so common. In the last field the dispersion relations are known, among others, for the complex electric permittivity and complex refractive index [4], as well as for the complex reflection coefficient [5, 6]. It turned out, that the knowledge of reflection spectrum for

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given substance allowed to obtain the spectra of the remaining optical constant of this substance.

This way of determining the optical constants has been first suggested by Robinson in 1952 [7]. Next works were published by Jahoda in 1957 [8], and by Philipp and Taft in 1959 [9]. Phillip and Taft in their paper on optical constants of Ge within the range of 1−10 eV have initiated the application of the method proposed by Robinson to semiconductor physics. In the next years there appeared further articles devoted to the optical constants of Ge [10, 11] as well as to these of Si [12], InSb, InAs, and GaAs [13] and PbS, PbSe, PbTe and SnTe [14]. In all these works the most simple method of calculation, called the Philipp-Taft method was used. This method will be considered in Section 3.2 and its detailed analysis may be found in part III of this work. Unfortunately, the application of this method led to nonphysical results in many cases, especially, when the results of the reflection spectrum were available solely in relatively narrow spectral range. Hence, the necessity of looking for other methods became evident. The methods, due to Roessler (1965), Ahrenkiel (1971) and Leveque (1977), belonging to the most important technique will be shortly considered in Sections 3.1, 5.1 and 5.3. Besides, the part III of this work will be devoted to the methods by Ahrenkiel and Leveque. The procedures suggested by Mac Rae (1976), Tulvinski and Terentev (1970), and Spitzer and Kleinman (1961) are mentioned in Sections 5.2, 3.4, and 4 of the present review of the methods. The Section 6 is devoted to the methods of determining the optical constants from the reflection spectrum, in which the Kramers-Kronig (KK) integral is not employed. These are the dispersion analysis method (Section 6.1), the method based on the measurement of dependence of the reflection spectrum upon the incidence angle (Section 6.2) and the algorithm employing the Fourier series (Section 6.3) proposed by King in 1977. In spite of so great number of the existing methods often very subtle and complicated that the Philipp-Taft method is still most widely used in practice (see, for instance, [15–20]). An attempt to make a detailed causal analysis of this fact may be also found in this work.

2. General idea of extrapolation method

The Kramers-Kronig (KK) relations allow to calculate the real or imaginary part of the complex function, if the other part of this function is known within the whole range of variability. This function must fulfil some conditions described in *Appendix A*. It turns out that the KK relation may be applied to the calculations of one (real or imaginary) part of the complex function of real variable, which may be, for instance, the logarithm of the complex coefficient of reflection

$$\hat{r} = \frac{E_R}{E_I} = |\hat{r}| e^{i\theta}, \tag{1}$$

where E_I, E_R — intensity of the electric field for the incident and reflected waves, respectively.

Since one of the quantities easiest to measure in the range of the basic light absorption is the coefficient of reflection $R = |\hat{r}|^2$, and since it suffices to know one of the quantities:

$\hat{r}$, $\hat{n}$ or $\hat{\varepsilon}$ to determine the other ones, the KK relation was used to calculation of the phase angle $\Theta(E)$ on the base of the measured reflection spectrum $R(E)$ [5]:

$$\Theta(E) = \frac{E}{\pi} P \int\limits_0^\infty \frac{\ln R(x)}{E^2 - x^2} dx, \tag{2}$$

where P denotes the principal value of the integral.

For obvious reasons the measurements of reflection are restricted to some finite interval of energy (E_a, E_b), while the calculations of the phase $\Theta(E)$ of the light reflected require the knowledge of the whole reflection spectrum $(0, \infty)$. The issue from this situation is the extrapolation from both sides of the interval (E_a, E_b).

In order to simplify the considerations the integral given by the eq. (2) may be divided into three parts

$$\Theta(E) = \frac{E}{\pi} \left[P \int\limits_0^{E_a} \frac{\ln R(x)}{E^2 - x^2} dx + P \int\limits_{E_a}^{E_b} \frac{\ln R(x)}{E^2 - x^2} dx + P \int\limits_{E_b}^\infty \frac{\ln R(x)}{E^2 - x^2} dx \right]$$

$$= \Theta_1(E) + \Theta_2(E) + \Theta_3(E). \tag{3}$$

On the other hand, in order to describe the optical properties of the semiconductors it is convenient to specify four spectral regions [21]:

    (i) region of semiconductor transparency,
    (ii) region of interband transitions,
    (iii) region of plasma vibrations of valence electrons,
    (iv) region of transitions from internal levels, lying below the valence band, to the condition band.

The interval (E_a, E_b) covers, as a rule, the whole second region, sometimes the third region and partly the first and the fourth ones. The contribution from the unmeasured third and fourth parts, lying usually within the region of vacuum ultraviolet, is described by $\Theta_3(E)$, while that from the unmeasured part of the first region (usually infrared) to the whole phase is described by $\Theta_1(E)$. Before we start to estimate this contribution it should be noticed that the region of sharp structure of $R(E)$ occurs both in the second and fourth parts, but the absolute value of $R(E)$ in the fourth region is usually less than in the second one. In the first region, apart from the lattice vibration spectrum, the energy of which is far from the interval (E_a, E_b), the coefficient of reflection depends weakly upon the energy. Finally, the third region is the interval of quick decay of the $R(E)$ value.

By performing the integration by parts, the KK integral (2) may by transformed into the following form [8]:

$$\Theta(E) = \frac{1}{2\pi} P \int\limits_0^\infty \frac{1}{R(x)} \frac{dR(x)}{dx} \ln \left| \frac{x+E}{x-E} \right| dx. \tag{4}$$

This vary form of this integral allows already to forsee to some extent the contributions of the regions $(0, E_a)$ and (E_b, ∞) to $\Theta(E)$: Firstly, under previous assumptions, the contribution of the structure of $R(E)$ to the phase of the reflected wave is the greater the closer

are x and E due to the presence of the expression $\ln(|x+E|/|x-E|)$ in the integrand. The contribution to the total phase of the reflected wave from the parts positioned very far from the region (E_a, E_b) is strongly damped by this logarithm, provided that E belongs to, the region comparable with (E_a, E_b). This fact allows to neglect the lattice vibration spectrum of the semiconductor. Secondly, since the region of smooth changes of $R(E)$ (small dR/dE) gives small contribution to the total phase and dR/dE in the region of semiconductor transparence is small, it is clear that the contribution of $\Theta_1(E)$ to $\Theta(E)$ is small.

In the region (E_b, ∞) the term $\dfrac{1}{R}\dfrac{dR}{dE}$ may take the values comparable with the values within the region (E_a, E_b) coming from this term. Therefore, if the singularity in $R(E)$ is close to the measuring region, its contribution in the vicinity of the point E_b may be significant. Thus, inclusion of the whole sharp structure $R(E)$ into the interval would be the best issue (E_a, E_b). Unfortunately, however, this is not always possible.

Now, we shall present different methods of the estimation of the contributions of $\Theta_1(E)$ and $\Theta_3(E)$ to the total phase of the light reflected.

3. Extrapolation of methods for reflection coefficient

3.1. Roessler method

This is the simplest of the methods being in common use, though it was not the one first applied. Roessler employed the average value theorem to the Stielties integral and calculated [22], for $E \in (E_a, E_b)$

$$\Theta_1(E) = \frac{1}{2\pi}\int_0^{E_a} \ln R(x)\frac{d}{dx}\ln\left|\frac{x+E}{x-E}\right|dx = A\ln\left|\frac{E_a+E}{E_a-E}\right|, \tag{5}$$

$$\Theta_3(E) = \frac{1}{2\pi}\int_{E_b}^{\infty} \ln R(x)\frac{d}{dx}\ln\left|\frac{x+E}{x-E}\right|dx = B\ln\left|\frac{E_b+E}{E_b-E}\right|, \tag{6}$$

where

$$A = -\frac{\ln R(\xi)}{2\pi}, \quad \xi \in (0, E_a),$$

$$B = \frac{\ln R(\eta)}{2\pi}, \quad \eta \in (E_b, \infty)$$

The quantities A and B were calculated from the system of equations for two energies (for instance, $E = E_c$ and $E = E_d$), which belong to the transparence region of semiconductor, $\Theta(E) = 0$,

$$A\ln\left|\frac{E_a+E_c}{E_a-E_c}\right| + \Theta_2(E) + B\ln\left|\frac{E_b+E_c}{E_b-E_c}\right| = 0, \tag{7}$$

$$A\ln\left|\frac{E_a+E_d}{E_a-E_d}\right| + \Theta_2(E) + B\ln\left|\frac{E_b+E_d}{E_b-E_d}\right| = 0. \tag{8}$$

The calculations were carried out as follows: $R(E)$ was determined experimentally in the region (E_a, E_b), while A and B were found from formulae (7) and (8) by determining $\Theta_2(E_c)$ and $\Theta_2(E_d)$, for $\Theta(E_c) = \Theta(E_d) = 0$. Next, $\Theta(E)$ was calculated for all E (clearly, except for E_a and E_b, because of singularities occurring at these points).

Thus, though Roessler does not call his procedure explicite the extrapolation, he approximates the coefficient of reflection in the regions $(0, E_a)$ and (E_b, ∞) by the straight lines $R(E) = R(\xi) = \text{const}$, ignoring the continuity of the curve $R(E)$ at the points E_a and E_b. The same method was next applied by him to the case of perpendicular reflection in the work [23].

Roessler suggested also an improved variant of his method in the work [24], which is hardly mentioned in the literature, but in which he took into considerations also the case of rapid changes of the reflection coefficient at the immediate vicinity of the measurement limits E_a and E_b. When the dependence of ξ and η upon E may be neglected, $\Theta(E)$ may be calculated in the previous way, but, if it is not the case, another approach to the problem becomes necessary. For $\Theta_1(E)$ the logarithmic term in the formula (5) suggests that only the close vicinity of the point E_a should be encountered, provided that E is close to E_a. The expression describing $\Theta_1(E)$ in the relation (3) may be integrated by parts, to obtain

$$\Theta_1(E) = \frac{1}{2\pi} \ln \left| \frac{E+E_a}{E-E_a} \right| \left\{ \ln R(E_a) - \int\limits_0^{E_a} \frac{\ln[(E+x)/|E-x|]}{\ln[(E+E_a)/|E-E_a|]} \frac{d\ln R(x)}{dx} dx \right\} \tag{9}$$

This is a quite general expression. Similar procedure may be applied to $\Theta_3(E)$. The integral in the above expression does not introduce any great change to $\Theta_1(E)$ if there is no strong structure of the reflection coefficient in the vicinity of E_a. The said integral may be approximated by a simple function of energy. Roessler has estimated the above integral for a concrete case of sodium iodide by assuming an exponential change of $R(E)$ below E_a.

The method due to Roessler – ignoring the non-physical discontinuity of the curve $R(E)$ at the points E_a and E_b, as being insignificant for calculation of optical constants with in the measurements limits of $R(E)$ – should give some good results in the case when the structure of the reflection coefficient disappears at the vicinity of the measuring limits of E_a and E_b. In the opposite case a strong influence of the dependence of ξ and η upon E may be observed. The method discussed would be mathematically rigorous, if the energies ξ and η (or rather the constants A and B) were determined separately for each energy E for which the change of phase $\Theta(E)$ is calculated.

3.2. Philipp-Taft extrapolation

Philipp and Taft have assumed in [9] that the reflection coefficient in the region $(0, E_a)$ has a constant value $R(E) = R(E_a)$, i.e.

$$\Theta_1(E) = \frac{E}{\pi} P \int\limits_0^{E_a} \frac{\ln R(E_a)}{E^2 - x^2} dx = \frac{\ln R(E_a)}{2\pi} \ln \left| \frac{E+E_a}{E-E_a} \right|, \tag{10}$$

while in the region (E_b, ∞) it changes and takes the following form:

$$\ln R(E) = A\ln E + \ln B, \tag{11}$$

or, equivalently, that $R(E) = BE^A$. For the first time Philipp and Taft calculated in this way the optical constants of germanium at $E_b = 11.3$ eV [9]. The constants A and B have been estimated from the conditions that the phase is equal to zero at one point of the transparency region, $\Theta(0.6\,eV) = 0$, and the condition that the calculations are consistent with the transmission measurements in the region 0.6–1.7 eV, The extrapolation according to the formula (1) has been carried out up to the energy of 30 eV (where the calculation was broken) by using the expression

$$\Theta_3(E) = \frac{E}{\pi} P \int\limits_{E_b}^{30eV} \frac{A\ln x + \ln B}{E^2 - x^2}\, dx. \tag{12}$$

In the paper [9] it has not been explained why the calculations have been broken just at 30 eV if the integral (12) may be easily calculated until infinity.

In the paper [26] the integral (12) has been calculated for diamond by assuming that above 35 eV, $d(\ln R)/d(\ln E) = -4 = A$.

Philipp and Taft assumed generally that the region between E_b and the energy, above which the approximation $d(\ln R)/d(\ln E) = -4$ may be applied, contains no fundamental transitions. The only structure element in this region should come from the plasma vibration at E_p. The reflection should be great below E_p, while above E_p it should quickly fall down tending to the function given in (12) for $A = -4$. In the opinion of Philipp and Taft, in order to perform an extrapolation in this region the value of $\Theta(E)$ should be known at least, at one point of this region. This value may be determined from the condition $\Theta(E) = 0$, $E < E_g$.

The said method was also employed by other authors. Rimmer and Dexter [10] used an analogical extrapolation, $\ln R(E) = AE + B$, for germanium truncating the calculations at 30 eV. This was necessary, since for such extrapolation the integral (2) is divergent. Zivitz and Stevenson [27] fixed the upper limit of calculations on the base of the condition of disappearing of $\Theta(E)$ in the transparency region. Cardona and Greenaway [14] assumed $A = -4$, which gave satisfactory results for semiconductors belonging to groups IV–VI and V. The parameter B was found from continuity condition for the curve $R(E)$ at the point E_b, while the integral $\Theta_3(E)$ was calculated to infinity.

The authors of the work [28] write that they used the Philipp-Taft method for GaAs, but they also say that the values of $R(E)$ outside the measurement interval were almost constant. Hence, it should be concluded that the parameter A was there close to zero, which is not consistent with the anticipated decrease of the reflection coefficient like $R(E) \sim E^{-4}$. $\Theta_3(E)$ was probably calculated to infinity.

According to the authors of the work [29] the analytical form of $\Theta_3(E)$ calculated by using extrapolation of (11) to infinity is the following

$$\Theta_3(E) = \frac{E}{\pi} P \int\limits_{E_b}^{\infty} \frac{A\ln x + \ln B}{E^2 - x^2}\, dx = -\frac{\ln R(E_b)}{2\pi} \ln\left|\frac{E_b + E}{E_b - E}\right|$$

$$-\frac{A}{\pi} \sum_{m=1}^{\infty} \frac{1}{(2m-1)^2}\left(\frac{E}{E_b}\right)^{2m-1}, \tag{13}$$

where the fact is encountered that

$$\ln \left| \frac{x+E}{x-E} \right| = 2 \sum_{m=1}^{\infty} \frac{1}{(2m-1)^2} \left(\frac{E}{x} \right)^{2m-1}, \tag{14}$$

and

$$\ln B + A \ln E_b = \ln R(E_b).$$

In the formulae (13) and (14) m denotes natural numbers.

Somewhat later (in seventieths) in the calculations methods due to Philipp and Taft the parameter B was written down in the region (E_b, ∞) as

$$R(E) = R(E_b) \left(\frac{E}{E_b} \right)^{-A}, \ E > E_b \tag{15}$$

In this form this method was applied by ELLIS and STEVENSON [30] to Cd_3As_2, Zn_3As_2 Cd_3P_2 and the three-component mixed crystal to determine the parameter A from the continuity condition for dR/dE at E_b, since – according to them – the choice of A such that $\Theta(E)$ is zero for $E < E_g^*$, may result in discontinuity of dR/dE at the point E_b. The upper limit of integration (E_f) has been determined by taking advantage of the sum rule

$$\int_0^{\infty} (n-1)kE dE = 0, \tag{16}$$

so that

$$\int_0^{E_f} (n-1)kE dE < 0.01, \tag{17}$$

Another form of KK integral (slightly different from that given by formula (2) which was used in papers [14, 30–33]) should be mentioned in order to complete this review. Considering that

$$\int_0^{\infty} \frac{\ln R(E)}{E^2 - x^2} \, dx = 0, \tag{18}$$

he formula (2) may be transformed to the form

$$\Theta(E) = \frac{E}{\pi} \int_0^{\infty} \frac{\ln R(x) - \ln R(E)}{E^2 - x^2} \, dx. \tag{19}$$

The transformation (2) → (19) is valid for all physically possible spectra of reflection [14]. This allows to avoid singularities of the integrand which is now finite for $x \to E$, since the reflection spectrum has no infinite maximum at E. Such infinite jumps have never been observed experimentally.

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* E_g denotes the energy gap of semiconductor.

It should be noticed that the Philipp-Taft method is used very widely because of its simplicity. However, in many cases its application leads to nonphysical results taking the form of negative values of the absorption coefficient in the region of transparency, or – for high energies – to violation of the boundary conditions by the optical constants. The detailed analysis of the above method and its modification will be discussed in the part III of this work [41].

3.3. Velicky method

This method, described in [34], does not propose any concrete form of extrapolation, but seems rather to suggest a mathematical trick allowing to generalize the extrapolation procedure.

If it is assumed that in the region $(0, E_a)$ the coefficient of reflection has the form $R(E) = R(E_a)$, it may be believed that the spectrum of reflection is known within the interval $(0, E_b)$. Let $\Psi = \ln R(E)$ and

$$
\Psi_1(E) := \begin{cases} \Psi(E), & E \in (0, E_b), \\ 0, & E \in (E_b, \infty), \end{cases}
$$

$$
\Psi_2(E) := \Psi(E) - \Psi_1(E). \tag{20}
$$

The KK integral takes the form

$$
\Theta(E) = \frac{E}{\pi} P \int_0^{E_b} \frac{\Psi_1(x)}{E^2 - x^2} dx + \frac{E}{\pi} P \int_{E_b}^{\infty} \frac{\Psi_2(x)}{E^2 - x^2} dx. \tag{21}
$$

The first integral may be easily calculated, while the second is equal to

$$
\frac{E}{\pi} \sum_{m=1}^{\infty} \int_{E_b}^{\infty} \left(\frac{E}{x}\right)^{2m-2} \frac{\Psi_2(x)}{x^2} dx = \sum_{m=1}^{\infty} a_m E^{2m-1}, \tag{22}
$$

where $a_m = \dfrac{1}{\pi} \displaystyle\int_{E_b}^{\infty} \dfrac{\Psi_2(x)}{x^{2m}} dx$.

Hence

$$
\Theta(E) = \frac{\ln R(E_a)}{2\pi} \ln \left| \frac{E + E_a}{E - E_a} \right| + \Theta_2(E) + \sum_{m=1}^{\infty} b_m \left(\frac{E}{E_b}\right)^{2m-1} \tag{23}
$$

where $b_m = a_m E_b^{2m-1}$.

The series in the formula (23) is convergent for $E/E_b < 1$ being the slower convergent the closer is the ratio E/E_b to unity. This may lead to the errors when the calculation of the successive terms is truncated too soon. No concrete form of $R(E)$ in the interval (E_b, ∞)

was postulated by Velicky. If this is done, the number of series terms (23) may be determined to achieve the required accuracy.

If the description by Velicky was applied to the method of Roessler or to the extrapolation of Philipp-Taft type, the coefficient b_m would take the forms

$$b_m = - \frac{\ln R(\eta)}{\pi(2m-1)} \tag{24}$$

and

$$b_m = - \frac{\ln R(E_b)}{\pi(2m-1)} - \frac{A}{\pi} \frac{1}{(2m-1)^2}, \tag{25}$$

respectively. However, the method of $R(E)$ extrapolation by using a power series is the first to offer a possibility of full exploitation of the fact that a part of KK integral may be represented in the form of a series (see formula (22)).

3.4. Extrapolation by using a power series

This extrapolation proposed by TULVINSKY and TERENTEV [35] was based on the assumption that even if outside the point E_b the coefficient of reflection does not behave like E^{-4}, the character of its decay in the X-ray part of the spectrum is asymptotic and may be approximated with the power series of the form

$$R(E) = \sum_{m=1}^{N} c_m E^{-2m}, \ E \geqslant E_b. \tag{26}$$

In practice, the number of coefficients c_m, which may be determined from the condition $\Theta(E) = 0, E \in (0, E_g)$ depends upon the value of the measurement error $\Delta R/R$.

The advantage of the extrapolation of the power series for the method due to Velicky is that the concrete form of the coefficients b_m allows to sum the series with respect to E/E_b for given accuracy of calculation, independently of the number of determined coefficients c_m. If c_m is defined by the following relation [29]:

$$\frac{d\ln R(E)}{dE} = \sum_{m=1}^{N} \frac{c_m}{E_b} \left(\frac{E}{E_b}\right)^{-2m-1}, \tag{27}$$

the Velicky coefficients b_m in eq. (23) take the form

$$b_m = - \frac{\ln R(E_b)}{\pi(2m-1)} + \frac{1}{\pi} \sum_{l=1}^{N} c_l \frac{1}{(2m-1)(2m+2l-1)}. \tag{28}$$

As may be seen, the Philipp-Taft method is a version of the above method. The latter, having the same shortcomings as the Philip–Taft method improves, after all, only the accuracy of the results. Apart from some subtleties, the Roessler method may be also considered as a particular case of the extrapolation by power series.

4. Extrapolation of the phase angle $\Theta(E)$

The methods of the refractive index extrapolation, described earlier, consisted in selection of suitable functions and their parameters. The phase shift $\Theta(E)$ or its part may be treated in an analogous way [36, 37].

Spitzer and Kleinman [36] calculated the integral (2) for quartz within the limits defined by the measurement range of reflection coefficient, and next added a corrective term

$$\Delta\Theta(E) = A + BE + CE^2, \tag{29}$$

the constants A, B, C being obtained from the condition of disappearence of $\Theta(E)$ at three chosen energies, where it was known that the extinction coefficient k was small ($k \leqslant 0.003$).

Miloslavski [37] also calculated the integral (2) within the limits of measurements, and next added a corrective term, which had been determined by expanding $\Theta_1(E) + \Theta_2(E)$ into series with respect to x/E assuming that $E \in (E_a, E_b)$:

$$\Delta\Theta(E) = \frac{\ln R(E)}{2\pi} \ln \frac{(E_b - E)(E + E_a)}{(E_b + E)(E - E_a)} - \frac{E}{\pi} \sum_{l=0}^{\infty} (E^{-2l-2} a_l - E^{2l} b_l), \tag{30}$$

where $a_l = \int\limits_0^{E_a} \ln R(x)\, x^{2l}\, dx$, $b_l = \int\limits_{E_b}^{\infty} \ln R(x)\, x^{-2l-2} dx$.

The method of the phase angle extrapolation seems to have more shortcomings than the methods of $\Theta(E)$ extrapolation. The most serious argument against the extrapolation of $\Theta(E)$ (note that this extrapolation is rarely used), is the fact that the run of the curve $R(E)$ in the range of both the low and high energies can be predicted easier than that of $\Theta(E)$, under the condition that within the range of semiconductor transparency $\Theta(E)$ is close to zero due to small absorption in this region. This property is successfully employed in both extrapolation procedures. Moreover, the values of $\Theta(E)$ considered in this method are loaded with a measurement error of $R(E)$ magnified by the calculations, which diminishes the reliability of the results obtained.

5. Other methods of calculation

The next three methods are so much different that it will be convenient to present them separately. In the first of them, elaborated by Ahrenkiel [38] (instead of choosing the suitable extrapolation methods) the convergence of the KK integral is improved, the second one [39] is based on interpolation of a part of the phase angle $\Theta(E)$, while the third one [40] is based on cyclic computations performed with the help of the KK relation to which the available measurements of absorption or the Drude-Lorentz equation are used to complete to the reflection measurements.

5.1. SKK method

This is the so-called substractive Kramers-Kronig method given by Ahrenkiel [38] and based on the transformation of the ordinary KK relation (2), to the form in which the inte-

grand is convergent with E^{-4} instead of E^{-2}, as it was the case in the integral (2):

$$\Theta(E) = E\left[\frac{1}{\pi}P\int\limits_0^\infty \frac{(E_0^2-E^2)\ln R(x)}{(E_0^2-x^2)(E^2-x^2)}\,dx + \frac{\Theta(E_0)}{E_0}\right]. \tag{31}$$

Transformation (2) → (31) is possible when the value of the phase shift of the wave reflected at one point of energy scale $E_0 \in (E_a, E_b)$ is known. This condition, however, may be fulfilled also when no suitable measurements in E_0 are available, then, however, the existence of the semiconductor transparency region must be taken into account provided that the measurements of reflection cover, at least, a part of this region.

Because of quick convergence of the KK integral (31), in order to obtain the correct values of optical constants within the interval (E_a, E_b) the extrapolation of the coefficient of reflection outside the measurement region is no more needed. It is only to avoid the discontinuities of the curve $R(E)$ that the values of $R(E)$ are assumed to be $R(E) = R(E_a)$ and $R(E) = R(E_b)$ in the regions of lower and high energy, respectively.

The SKK method is especially suitable in calculations of optical constants (on the base of the measured spectrum of reflection) if the energy interval available to measurements is relatively narrow. The predominance of this method over the traditional KK method has been shown with the help of numerous different tests (see, for instance, [29, 38]). The detailed SKK method will be discussed in the part III of this work [25].

5.2. Mac Rae method

MAC RAE [39] had at his disposal a wide range of his own measurements as well as the measurements of other authors for thin layers of white tin, i.e. the measurements of the index of refraction $n(E)$ and extinction coefficient $k(E)$ within the intervals 0.1–1.3 eV and 14.5 –20.5 eV as well as the measurements of the coefficient of reflection $R(E)$ in the interval 2.1–14.5 eV. For the cases where $n(E)$ and $k(E)$ were known, $R(E)$ and $\Theta(E)$ were calculated from the relations

$$R(E) = \frac{(n-1)^2+k^2}{(n+1)^2+k^2}, \tag{32}$$

$$\Theta(E) = \arctan\frac{2k}{n^2+k^2-1}. \tag{33}$$

The change of phase may be splitted into two parts

$$\Theta(E) = \frac{E}{\pi}P\int\limits_0^{20.5\,\text{eV}} \frac{\ln R(x)}{E^2-x^2}\,dx + \frac{E}{\pi}P\int\limits_{20.5\,\text{eV}}^\infty \frac{\ln R(x)}{E^2-x^2}\,dx. \tag{34}$$

The first integral in formula (34) may be easily calculated from the measurement results, while the other integral, denoted by $\Delta\Theta$, may be determined in the regions in which $\Theta(E)$ is known. Having determined the values of $\Delta\Theta(E)$ in the intervals 0.1–1.3 eV and 14.5–20.5 eV, $\Delta\Theta(E)$ was interpolated by a smooth function in the interval 1.3–14.5 eV. Then, by substitution of $\Delta\Theta(E)$ to the eq. (34) $\Theta(E)$ may be obtained within the interval 2.1–14.5 eV, which, together with the knowledge of $R(E)$ allowed to calculate $n(E)$ and $k(E)$ in this interval.

Additionally, in order to complete the spectrum of the already known $n(E)$ and $k(E)$, Mac Rae exploited the results from literature and extrapolated the coefficient of refraction basing on the points $n = 0.88$, $E = 20.5$ eV and $n = 0.965$, $E = 27.5$ eV. The above method gives, perhaps, the most reliable estimations of the optical constants, however, only in the extraordinary cases such a combination of the measurements completing so well one another is possible.

5.3. Leveque method

In the region of low energies, LEVEQUE [40] exploited the absorption measurements restricted, in principle, to the absorption edge in order to complete the measurements of reflection. For this purpose he carried out the cyclic calculations by employing the KK relations between $\theta(E)$ and $R(E)$, respectively, beginning with the measurements of the reflection coefficient, completed with the help of an arbitrary extrapolation; the scheme of calculations is presented in fig. 1, where $[T]$ and $[T]^{-1}$ are operators defined as follows:

$$a(E) = [T] R(E),$$
$$R(E) = [T]^{-1} a(E),$$
(35)

and $[P]$ denotes the operation of fitting the results obtained from the measurements to the experimental results obtained in the respective measurement intervals for $R(E)$ and $a(E)$.
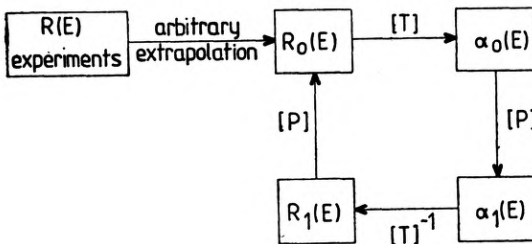

Fig. 1. Scheme of calculations according to the simples Leveque method (for explanation see text)

According to Leveque, the convergence of this method depends upon the accuracy of measurements and, the experimental data being loaded in reality with an experimental error, the convergence is assumed only for reduced overlaps of the measurement intervals for R and a. Sometimes, even the separation of both the domains becomes necessary.

Leveques suggested two methods of completing the measurements of the reflection coefficient from the high energy side. In the first of them he applied the cyclic self-consistent calculations, as it was the case for the low energy side, exploiting the approximate expression for the cross-section of the atoms of two-component compounds AB for those energies in which the optical absorption results from the purely atomic phenomena (for instance, above 30 eV for GaTe, according to [40]), ie.

$$\sigma_{AB} \cong \sigma_A + \sigma_B,$$
(36)

Hence

$$a_{AB} \cong N_{AB} \left(\frac{a_A}{N_A} + \frac{a_B}{N_B} \right),$$
(37)

where N_A, N_B and N_{AB} — concentrations of the respective atoms and molecules, a — absorption coefficient. The applicability of this method depends on the knowledge of the absorption coefficients of both the components in the energy interval in question.

The second method is based on the Drude-Lorentz equation and consists in assumption that the deep level electrons behave like dependent oscillators of eigenfrequency ω_0 and damping coefficient γ. In such a case the complex electric susceptibility $\hat{\chi}$ is:

$$\hat{\chi} = \sum_j \frac{\omega_{pj}^2}{\omega_{0j}^2 - \omega^2 - i\omega\gamma_j}, \tag{38}$$

where ω_{pj} is the plasma frequency

$$\omega_{pj} = \frac{N_j e^2}{m\varepsilon_0}, \tag{39}$$

and N_j denotes the number of electrons in the volume unit on the j-th level. In the single-electron approximation the complex dielectric permittivity $\hat{\varepsilon}(E)$ describes the probability of transition between two states distant by energy E. In $\hat{\varepsilon}(E)$ one may distinguish the parts corresponding to valence electrons and to electrons from deep levels. The boundary between these two groups of electrons is, of course, arbitrary and may be chosen suitably to assure the consistence. Thus, it may be written that

$$\hat{\varepsilon}(E) = 1 + \hat{\chi}(E) = 1 + [\hat{\chi}^v(E) + \hat{\chi}^p(E)] = \hat{\varepsilon}^v(E) + \hat{\chi}^p(E). \tag{40}$$

By applying the Kramers-Kronig relations and making the respective calculations

$$\hat{\varepsilon}(E) \rightleftarrows \hat{r}(E) = \sqrt{R}\exp(i\Theta), \tag{41}$$

$$\varepsilon^v(E) \rightleftarrows r^v(E) = \sqrt{R^v}\exp(i\Theta^v), \tag{42}$$

where R is a coefficient of reflection for the real solid and R^v is the coefficient of reflection for the virtual solid without deep electron levels, and applying the relation

$$\hat{\varepsilon} - \hat{\varepsilon}^v = \sum_l \frac{E_{pl}^2}{E_{0l}^2 - E^2 - iE\Gamma}, \tag{43}$$

in which the summing is carried out only with respect to deep electron levels numbered by l, Leveque suggested the cyclic calculations according to the scheme shown in fig. 2. The complex operators used in these calculations have been defined as

$$\begin{aligned} \tilde{r} &= [\Delta]\hat{r}^v, \\ \hat{r}^v &= [-\Delta]\hat{r}. \end{aligned} \tag{44}$$

The [KK] operator is equivalent to calculation of $\Theta(E)$ from the curve $R(E)$, i.e. to the rotation $\hat{r}(E)$ in the complex plane. The curves $R(E)$ and $R^v(E)$ are invariant with respect to this operator. The operator [EXP] acts, in turn, only on the real part of $\hat{r}(E)$ giving its real value in the measurement range. In the complex plane it is equivalent to a shift $\hat{r}$ along the circle of radius R_{exp}.

For the said virtual solid there exists an energy threshold behind which all the possibilities of optical transitions are exhausted and the extrapolation of E^{-4} type may by applied to the coefficient of reflection $R^{v}(E)$; consequently, it is possible to calculate accurately the KK relation.
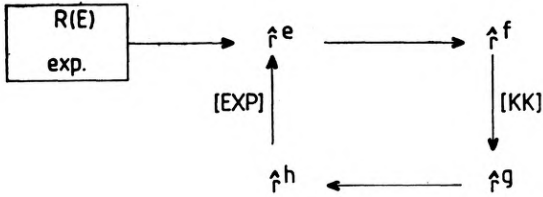

Fig. 2. Scheme of calculations according to the Leveque method taking account of both valence and core electrons (for explanation, see text)

Let us return to the calculation scheme shown in fig. 2. If the calculations are convergent, different functions r^{v} tend to $\hat{r}^{v}$ and $\hat{r}$, which are invariant with respect to [EXP] and [KK] operators, i.e.

$$\lim \hat{r}^{h} = \lim \hat{r}^{e} = \hat{r}, \tag{45}$$

$$\lim \hat{r}^{f} = \lim \hat{r}^{g} = \hat{r}^{v}. \tag{46}$$

Leveque received for GaTe the rapid convergence of this method; two or three cycles suffice to obtain the constant values. The parameters E_{0l} and Γ_{l} for the levels $3d$ and $4d$ of galium and tellurium, respectively, have been chosen to assure the consistence with the absorption curves for Ga and Te in the range of 40–120 eV. The operation denoted by [EXP] was performed by Leveque by hand which significantly complicated the calculations. The next objection raised to this method is the necessity of making measurements in wide range. In the part II of this work [25] an attempt to modify the Leveque method will be presented.

6. Calculation methods not based on KK relation

6.1. The dispersion analysis

In this case, it is assumed that the medium examined behaves like a set of independent harmonic oscillators, i.e. that the complex dielectric function describing this medium has a well known form

$$\hat{\varepsilon}(E) = 1 + \sum_{i} \frac{\varrho_i}{E_{0i}^2 - E^2 - iE\Gamma_i} \tag{47}$$

We assume some hypothetical values E_{0i}, Γ_i, ϱ_i, i.e. we determine $\hat{\varepsilon}(E)$, and next, by applying the relation

$$R(E) = \left| \frac{\hat{\varepsilon}(E)^{1/2} - 1}{\hat{\varepsilon}(E)^{1/2} + 1} \right|^2 \tag{48}$$

we determine the hypothetical spectrum of reflection, which is compared with the measured spectrum of reflection. By varying ϱ_i, Γ_i, E_{0i} the calculated spectrum may be fitted to the dependence obtained by measurements.

The approach presented being used most frequently to determine the optical constants in the infrared gives good results in the analysis of reflection spectrum, provided that its course is not too flat, as then a great number of oscillators must be taken into account and the whole method becomes of low effectiveness [15].

In order to improve the dispersion analysis the latter is completed sometimes by [KK] analysis [46]. The change of phase during reflection Θ, is calculated as follows:

$$\Theta(E) = \Theta_{DA}(E) + \frac{E}{\pi} P \int_0^\infty \frac{\ln[R(x)/R_{DA}(x)]}{E^2 - x^2} \, dx, \tag{49}$$

where R_{DA} and Θ_{DA} are the quantities obtained from the dispersion analysis of the measured spectrum of reflection $R(E)$.

6.2. Angular dependence of reflection spectrum

The Fresnel formulae describing the dependence of the complex coefficients of reflection, $\hat{r}_p$ and $\hat{r}_s$, depending upon the state of polarization and the incidence angle Φ have the well known forms

$$\hat{r}_p = \frac{\hat{n}^2 \cos\Phi - (\hat{n}^2 - \sin^2\Phi)^{1/2}}{n^2 \cos\Phi + (\hat{n}^2 - \sin^2\Phi)^{1/2}},$$

$$\hat{r}_s = \frac{\cos\Phi - (\hat{n}^2 - \sin^2\Phi)^{1/2}}{\cos\Phi + (\hat{n}^2 - \sin^2\Phi)^{1/2}}, \tag{50}$$

and show that when, for instance, the relation $R_p(\Phi) = |r_p(\Phi)|^2$, is known the refractive index $\hat{n}$ may be determined by the method of numerical fitting. It may be seen that the minimum condition is that the reflection spectrum is known for two different angles of incidence or for two states of polarization.

The advantage offered by this method is that it reduces the errors of calculated optical constants caused by the state of the examined sample [23]. This is particularly useful in examination of strongly anisotropic substances, like graphite [47]. The difficulties connected with the measurements of the reflection in the light polarized at different temperatures and in wide range of energy for different angles of incidence are probably the reason that the method mentioned above is rarely quoted in the literature.

6.3. Fourier-series algorithm

KING [48] suggested in 1977 a new method for calculation of phase change Θ, which occurs during reflection, basing on the coefficient of reflection R, measured within some energy range. In the method suggested by King the fact is exploited that the function $\hat{r}(\omega)$ is analytic and the derivative $d\omega \ln r(\omega)$ is bounded. Then the relations hold

$$\left[\frac{1}{2R(\omega)} \frac{dR(\omega)}{d\omega}\right]_{\omega = -\cot\frac{\Omega}{2}} = \sum_{m=1}^\infty a_m \sin\Omega m \tag{51}$$

and

$$\Theta(\omega) = \sum_{m=1}^{\infty} a_m \left[\omega - 2^{m-1} I_m(\omega) - \sum_{l=1}^{m/2} \binom{m-l-1}{l-1} (-1)^l \frac{m}{l} 2^{m-2l-1} I_{m-2l}(\omega), \right. \tag{52}$$

where

$$I_m(\omega) = \omega - \sum_{j=0}^{m-1} \frac{(-1)^j}{2^{j+1}} \binom{m}{j+1} \left[\binom{2i}{j} \mathrm{tg}^{-1}\omega + \sum_{l=0}^{j-1} \frac{1}{j-l} \binom{2j}{l} \sin(2j-2l)\tan^{-1}\omega \right].$$

Thus, the measured spectrum of reflection may be used to find the Fourier coefficients a_m (see formula (51)). Next, $\Theta(\omega)$ is obtained on the base of eq. (52).

This method is, in principle, equivalent to the methods based on Kramers-Kronig relation. If compared with the latters this method – according to conclusions of the work [48] – is characterized by a shorter computer time and lower sensitivity to the error made by the extrapolation of $R(\omega)$ outside the computed interval.

7. Conclusions and remarks

The KK relations have been used for the first time in reflection spectroscopy by ROBINSON [7] in 1952, who based his work on the paper by BODE [9]. The calculations made by Robinson concerned the infrared part of the reflection coefficient spectrum. His method has been summarized by JAHODA [8], who used it to calculate the optical constants of BaO close to the absorption edge. He mentioned the extrapolation of $R(E)$ in the high energy region by saying that it may be based on known values of n and k in the transparency region (n — known, $k = 0$). Since the year 1959, after the works by PHILIPP and TAFT [9] broadening the calculations to cover also the ultraviolet part of the spectrum, the KK relations have been commonly used in the methods of determination of optical properties in solids.

The optical constants in semiconductor are determined in order to recognize its structure as well as possible. For this purpose the knowledge of the spectrum structure, for instance, the virtual part of the electric permitivity or the coefficient of absorption is mainly needed. The values of optical constants begin to play a part in the more subtle examinations, when, for instance, some concrete model should be fitted to the obtained spectra. Thus, the basic requirement addressed to the methods of determining the optical constants is the demand that they give the spectrum a structure consistent with the real one.

In the case of KK analysis of the reflection spectrum this requirement is restricted, in a natural way, to the interval in which the measurements have been made. The statement, that all the presented methods satisfy this basic condition, though not ideally, is quite obvious. For instance, the usage of the Philipp-Taft method may result in some deformation of the structure, which precludes the correct read-out of the position of the characteristic points in the spectrum $\varepsilon_2(E)$. It happens often that this method is very good for one type of reflection spectrum, while in some other case it gives worse results than other methods. Therefore, so many versions of the Philipp-Taft method are used in practice.

The simplest, already mentioned, method of calculation of the KK integral is the method due to ROESSLER [22] based on the approximation of the reflection coefficient by the straight line from both the sides of measurement interval, by applying the average value theorem for the Stielties integral.

The widely used extrapolations employing the PHILIPP-TAFT method [9] (see also [10, 12, 14–21, 24, 26–33, 42–44]) and the second version of the ROESSLER [24] or RIMMER-DEXTER [10], take account also of the simple behaviour of the coefficient of reflection, for instance, of the type

$$R(E) = BE^A \text{ or } R(E) = B\exp(EA). \tag{53}$$

These methods suffer from two shortcomings. Firstly, the constants (for instance A, B) are usually chosen from the conditions describing the behaviour of the phase in low energies. Small error in the constant value may be negligible in the low energies, but may lead to great discrepancies in the region of high energies. Secondly, there exists an infinite number of extrapolations which fulfil one or two of the conditions usually taken into considerations. The choice of the unsuitable extrapolation even if undetectable in low energies, may cause incorrect results in the vicinity of high energy limit of the measurements.

Thus, from the theoretical viewpoint all the methods described above are insufficiently justified, apart from the fact that after all the optical transitions in the region of X-rays are exhausted, a decay of reflection coefficient of the form $R(E) \sim E^{-4}$ is expected. Nevertheless, such procedures render, as a rule, good results in the region of low energies, though $\Theta(E)$, and hence also the absorption, may take negative (and by the same means – nonphysical) values (see [45], for instance) below E_g due to the way in which the extrapolation parameters are determined. Analogical shortcomings are attributed to the extrapolation methods used to determine the phase angle $\Theta(E)$ as well as to the extrapolation by power series, though the latter way is exploited to a slightly less degree.

Almost ideal issue from this situation is the procedure presented by MAC RAE [39]; unfortunately a broad range of measurements remains rarely at the disposal. Being still possible for the thin films it becomes very difficult for solids, if possible at all.

The LEVEQUE method [40] gives (under the condition of the convergence of calculations) the values of $\Theta(E)$ consistent with the absorption measurements from the low energy side and the value of $\hat{\varepsilon}(E)$ – from the high energy side – consistent with the measurements of absorption or with Drude-Lorentz equation applied to the deep electron levels. On the other hand, however, this method is difficult to use as it requires some manual corrections of [EXP] in the cyclic calculations and, moreover, it has not been checked yet for other materials, except for GaTe. Wide range of measurements of $R(E)$ and $\alpha(E)$ is also necessary for its verification.

The SKK method [38], due to its high convergence and the low demands concering the extrapolation, gives the results better than the other methods in the case when the values $R(E)$ are available only in a narrow range of energy. On the other hand, this method suffers from additional computational error depending on the distance of energy E for which the calculation are being performed from the point of expansion E_0, which becomes visible at the distances between E and E_0 greater than several eV.

The Philipp-Taft and Roessler methods give the better results the broader the measurement range. In the case, when the measurements of the reflection coefficient are available only in a relatively narrow energy range the Ahrenkiel methods seems to be the best one. Much more accurate algorithms, like those of Mac Rae or Leveque, require the measurement data which are difficult to achieve if possible at all. In order to recognize the behaviour of the optical constants outside the measurement range the method due to Leveque or the algorithm proposed by TULVINSKY and TERENTEV [35] may be used. Also some versions of the Philipp-Taft method will be useful in this case. As far as the values of the optical constants are concerned, there is no method based on KK relation which would give the reliable results in the case, when the measurements of reflection coefficient are available within narrow interval of few to several electronovolts.

In the part I of this work also some other methods are mentioned in which the KK analysis is not employed. These methods are not more accurate or simpler in application which is evidenced, among others, by the fact that they are very rarely applied to determine the optical constants in semiconductors.

Thus, the present situation is characterized by a lack of a reliable method of calculations of optical constants from the measured spectrum of reflection coefficient. In the further parts of this work the discussion of difficulties, which appear when attempting to elaborate an ideal method of its solution, will be presented.

Appendix A

Derivation of the dispersion relations

There exist two main groups of proofs of dispersion relations, called also the Kramers-Kronig relations. In one case the properties of Fourier transform [1] are employed, while in the other, some properties of complex functions of complex variables are used [2]. In this Appendix the second way of prooving will be presented, since it is both more general and interesting.

The proof of the KK relation will be based on the Cauchy theorem [2]: If $f(z): C \to C$ is holomorphic in one connected region D, then

$$\oint_\gamma \frac{f(z)}{z-a}\, dz = 2\pi i f(a),\tag{A.1}$$

holds for an arbitrary closed curve γ lying in the region D, where a — arbitrary point inside the integration curve. On the other hand, the function $f(z): C \to C$ is holomorphic in the region D, when for each $z \in D$ there exists a limit

$$\lim_{\Delta z \to 0} \frac{f(z+\Delta z)-f(z)}{\Delta z} = f'(z).\tag{A.2}$$

If $a \in R$, and the integral (A.1) is calculated only along the real axis, except for the point a which may be surrounded by an infinitely small half-circle to omit the singularity in (A.1), the imaginary part of the given function at the point a will be determined by the real part of the same function at all the points on the real axis. And similarly, in order to determine the real part at one point it suffices to know the behaviour of the imaginary part of the function examined along the real axis.

Let $f(z): C \to C$ be holomorphic and $|f(z)| \to 0$ when $|z| \to \infty$ and $Im\, z \geqslant 0$. The function $\dfrac{f(z)}{z-a}$ will be integrated along the closed curve γ shown in fig. A.1. The circulation of the curve is accepted by a respective convention. In order to perform the further calculations the integral along the path γ is splitted into the integrals along its particular parts, i.e.
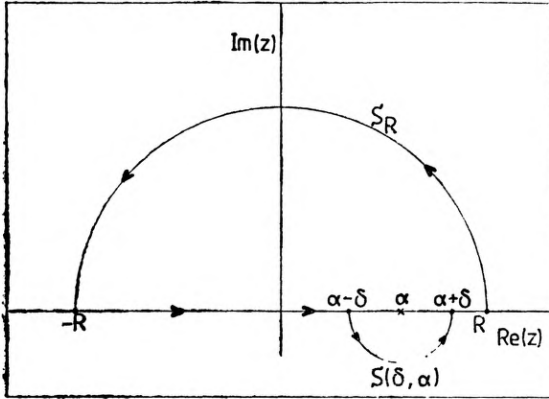
$$\oint_\gamma \frac{f(z)}{z-a}\ dz = I_1 + I_2 + I_3, \tag{A.3}$$

Fig. A.1. The path of integration γ for the function $\dfrac{f(z)}{z-a}$ (see formula (A.1)) presented in the Gaussian plane

where I_1 denotes the integral from $-R$ to R with the exception of straight line segment $(a-\delta,\ a+\delta)$, I_2 — the integral along the semi-circle $S(\delta, a)$, I_3 — integral along the semi-circle S_R. Here the integrals are calculated at the limits $R \to \infty$ and $\delta \to 0$. Now, the above components will be calculated consecutively

$$I_1 = \lim_{\substack{R \to \infty \\ \delta \to 0}} \left\{ \int_{-R}^{a-\beta} \frac{f(z)}{z-a}\ dz + \int_{a-\delta}^{R} \frac{f(z)}{z-a}\ dz \right\}, \tag{A.4}$$

but

$$\lim_{\delta \to 0} \left\{ \int_a^{a-\delta} g(x)dx + \int_{a+\delta}^{b} g(x)dx \right\} =: P \int_a^b g(x)dx. \tag{A.5}$$

The symbol $\int P$ denotes here the integral in the sense of principal value of Cauchy and the eq. (A.5) give its definition [2]. The integral in the sense of Cauchy principal value is used only when the integrand exhibits some singularities and the Riemann integral for it does not exist. If the function $g(x)$ has no singularities along the (a, b) segment, then

$$P \int_a^b g(x)dx = \int_a^b g(x)dx. \tag{A.6}$$

Taking account of the above notation we obtain

$$I_1 = \lim_{R \to \infty} P \int_{-R}^{R} \frac{f(x)}{x-a}\ dx = P \int_{-\infty}^{\infty} \frac{f(x)}{x-a}\ dx. \tag{A.7}$$

In the above equation "z" was replaced by "x", since the integral (A.7) runs only along the real axis. The existence of I_1 is guaranteed, among others, by the assumption that $|f(x)| \xrightarrow{|z| \to \infty} 0$. The consecutive

component of the integral (A.3) is I_2:

$$I_2 = \lim_{\delta \to 0} \int_{S(\delta,a)} \frac{f(z)}{z-a}\, dz = \lim_{\delta \to 0} \int_{S(\delta,a)} dz\, \frac{f(z)-f(a)}{z-a} + \lim_{\delta \to 0} \int_{S(\delta,a)} dz\, \frac{f(a)}{z-a}\,. \tag{A.8}$$

From the holomorphism of $f(z)$ it follows that the function $\dfrac{f(z)-f(a)}{z-a}$ is also holomorphic. Hence, the first component of the formula (A.2) being the integral from the holomorphic function along the path, which is reducable to a single point, is equal to zero. On the other hand,

$$\int_{S(\delta,a)} \frac{f(a)}{z-a}\, dz = f(a) \int_{\pi}^{2\pi} \frac{re^{i\theta}id\theta}{re^{i\theta}} = i\pi f(a), \tag{A.9}$$

where the substitution $z-a = re^{i\theta}$ has been made. Finally,

$$I_2 = i\pi f(a). \tag{A.10}$$

The integral I_3 in (A.3) remains still to be calculated

$$I_3 = \lim_{R \to \infty} \int_{S_R} \frac{f(z)}{z-a}\, dz = \lim_{R \to \infty} \int_0^\pi \frac{f(Re^{i\theta})}{Re^{i\theta}-a}\, iRe^{i\theta}\, d\Theta, \tag{A.11}$$

where the substitution $z = Re^{i\theta}$. When $R \to \infty$, then $|f(Re^{i\theta})| \to 0$. and $|Re^{i\theta}-a| \to R$. Therefore, the integral (A.11) is equal to zero at the limit $R \to \infty$. The final result of considerations is the following:

$$\oint_\gamma \frac{f(z)}{z-a}\, dz = I_2 + I_2 + I_3 = i\pi f(a) + P \int_{-\infty}^\infty \frac{f(x)}{x-a}\, dx. \tag{A.12}$$

But from the fact that $f(z)$ is a holomorphic function, it follows that the equation (A.1) is valid. From (A.1), and (A.12) it is obtained that

$$P \int_{-\infty}^\infty \frac{f(x)}{x-a}\, dx = i\pi f(a). \tag{A.13}$$

The above dependence is called the dispersion relation or the Kramers-Kronig integral (KK integral). Thus, when requiring that $f(z): C \to C$ be holomorphic and disappear at infinity in the upper half-plane and on the real axis, the dependence (A.13) is obtained for an arbitrary $a \in R$.

The dispersion relation (A.13) may be written with the help of a pair of equations:

$$P \int_{-\infty}^\infty \frac{f_R(x)}{x-a}\, dx = -\pi f_I(a), \tag{A.14}$$

$$P \int_{-\infty}^\infty \frac{f_I(x)}{x-a}\, dx = \pi f_R(a), \tag{A.15}$$

where $f(x) = f_R(x) + if_I(x)$. These equations interrelate two real functions of real variable. Each two real functions fulfilling the relations (A.19) and (A.20) form a pair of Hilbert transforms. Thus, instead of exploiting the dispersion relations, the theory of Hilbert transforms may be employed [1].

Detailed description of the dispersion relations for optical constants of the semiconductor crystal is given in Appendix B.

Appendix B

The dispersion relations for optical constants

In order to describe the interaction of the electromagnetic wave (EM) with the semiconductor a number of complex functions are introduced the argument of which is the frequency of the EM-wave incident on the sample. Most frequently these are: complex refractive index, $\hat{n} = n+ik$, complex coefficient of reflection $\hat{r} = re^{i\theta}$, and complex coefficients of electrical permittivity $\hat{\varepsilon} = \varepsilon_1+i\varepsilon_2$ and polarizability $\hat{\chi} = \chi_R+i\chi_I$. These quantities are connected with each other and for each of them the KK integral may be written.

When a physical system (a semiconductor crystal in our case) is under an external electromagnetic field, then the electric compound of the latter $E(t)$ produces a respective polarization $P(t)$. By assuming that the system is linear and stationary in time we may write [2]:

$$P(t) = \int_{-\infty}^{\infty} G(t-t')E(t')dt'. \tag{B.1}$$

Since the effect may not be preceded in time by its cause, the upper limit of integration in the integral (B.1) is t, or it should be assumed that for $t-t' = \tau < 0$, $G(\tau) = 0$. The integral (B.1) expresses the low of causality which allows to define a set of holomorphic functions, for which the KK relations occur (see *Appendix A*). The function $G(\tau)$ must be restricted for all τ and absolutely integrable, i.e.

$$\int_{0}^{\infty} |G(\tau)|d < \infty. \tag{B.2}$$

Let the perturbation be a monochromatic EM-wave of frequency

$$E(t) = E_0 e^{i-\omega t}. \tag{B.3}$$

Then the formula (B.1) takes the form

$$P(t) = \int_{-\infty}^{t} G(t-t')E_0\exp(-i\omega t')dt' = \Big[\int_{-\infty}^{t} G(t-t')\exp(i\omega(t-t'))dt' \Big] E_0\exp(-i\omega t), \tag{B.4}$$

and after substitution of $t-t' = \tau$, we obtain

$$P(t) = \Big[\int_{0}^{t} G(\tau)\exp(i\omega\tau)d\tau\Big] E_0\exp(-i\omega t). \tag{B.5}$$

Let

$$\varepsilon_0\hat{\chi}(\omega): = \int_{0}^{\infty} G(\tau)\exp(i\omega\tau)d\tau, \tag{B.6}$$

hence

$$P(t) = \varepsilon_0\hat{\chi}(\omega)E(t). \tag{B.7}$$

The quality $\chi(\omega)$ defined by the formula (B.6) is called polarizability. It is a complex function of real variable. The further step is to define this function in the Gaussian plane to make it holomorphic. In view of (B.6) $\hat{\chi}(z)$ is defined for any $z \in C$:

$$\varepsilon_0\hat{\chi}(z): = \int_{0}^{\tau 0} G(\tau)\exp(iz\tau)d\tau. \tag{B.8}$$

The parameter τ_0 in the integral (B.8) has been introduced to assure the existence of $\hat{\chi}(z)$ also for z lying in the lower half-plane, $Im(z) < 0$, which is needed to carry out the proof of the KK integral given in *Appendix A*. In order to make it consistent with eq. (B.6) having a physical meaning it is assumed that $\tau_0 = \infty$

on the real axis and in the upper half-plane $Im(z) > 0$. From the relation (B.8) it follows that $\chi(z)$ is holomorphic, since there exist $\dfrac{\partial \hat{\chi}(z)}{\partial z}$ and $\dfrac{\partial \hat{\chi}(z)}{\partial z^*} = 0$, in other words, the conditions of Cauchy-Riemann are fulfilled. For z such that $Im(z) > 0$ it holds

$$|\hat{\chi}(z)| = \frac{1}{\varepsilon_0} \left| \int\limits_0^\infty G(\tau)\exp(i\tau z)d\tau \right| < \frac{1}{\varepsilon_0} \frac{\sup |G(\tau)|}{|z|}. \tag{B.9}$$

From the above relation it follows that when $|z| \to \infty$, then $|\hat{\chi}(z)| \to 0$. To prove it the fact is exploited that $|G(\tau)|$ is restricted for each τ. When $Im(z) = 0$ the Fourier transform (B.6) is obtained. From its existence for every ω it follows that the inverse Fourier transform

$$G(\tau) = \frac{1}{2\pi} \int\limits_{-\infty}^\infty \varepsilon_0 \hat{\chi}(\omega)\exp(-i\omega\tau)d\omega. \tag{B.10}$$

also exists. Hence we obtain $|\hat{\chi}(\omega)| \to 0$, when $|\omega| \to \infty$. Thus the holomorphic function $\hat{\chi}(z)$ which fulfils the assumption of KK relation given by the formula (A.13) has been defined.

It the causality law was not satisfied, $\hat{\chi}(z)$ would be defined as follows

$$\varepsilon_0 \hat{\chi}(z) := \int\limits_{\tau_1}^{\tau_2} G(\tau)\exp(i\tau z)d\tau, \tag{B.11}$$

where $\tau_1 < 0$, and $\tau_2 > 0$. It may be easily seen that when $|z| \to \infty$, then $|\hat{\chi}(z)| \to \infty$. Here $|\hat{\chi}(z)|$ increases so quickly that the function $\hat{\chi}(z)$ may not be transformed, even to such form that the condition of disappearence of $|\hat{\chi}(z)|$ at infinity be fulfilled. Thus, if the function described by the formula (B.6) disobeys the causality law the KK relation may not be written for it since it does not satisfy the respective assumption. Hence, it may be said that the KK relation reflects the physical law of causality.

On the other hand, the polarization vector is connected with the charge and polarization current in the following way

$$\varrho_{\text{pol}} = -\nabla P, \quad j_{\text{pol}} = \frac{dP}{dt}. \tag{B.12}$$

When considering the crystal as a uniform and isotropic medium in which the EM-wave is connected with the macroscopic fields B and E the Maxwell equations take the form

$$\nabla \times E = -\frac{\partial B}{\partial t}, \quad \nabla E = \frac{\varrho_{\text{pol}}}{\varepsilon_0},$$

$$\varepsilon_0 c^2 \nabla \times B = j_{\text{pol}} + \varepsilon_0 \frac{\partial E}{\partial t}, \quad \nabla B = 0. \tag{B.13}$$

By taking advantage of the connection (B.12) of ϱ_{pol} and j_{pol} with P, and after simple rearrangements the following relation may be obtained from eqs. (B.13)

$$\nabla^2 E - \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2} = -\frac{1}{\varepsilon_0}\nabla(\nabla P) + \frac{1}{\varepsilon_0 c^2}\frac{\partial^2 P}{\partial t^2}. \tag{B.14}$$

Assuming the solution of the eq. (B.14) in the form

$$E = E_0 \exp\left[-i\omega\left(t - \frac{r}{c}\hat{n}\right) \right], \tag{B.15}$$

and employing the formulae: $P = \varepsilon_0 \hat{\chi} E$ and $\varrho_{\text{pol}} = 0$ (due to assumed homogeneity of the medium) the following relations is obtained

$$\hat{n}^2 := 1 + \hat{\chi}. \tag{B.1 6}$$

Let it be a definition of the complex index of refraction $\hat{n}$. The physical meaning of this quantity follows from the formula for the EM-wave (B.15):

$$E = E_0 \exp\left[-i\omega\left(t - \frac{r}{c}\,\hat{n}\right)\right] = E_0 \exp\left[-i\omega\left(t - \frac{r}{c}\,n\right)\right]\exp\left(-\frac{\omega k}{c}\,r\right), \tag{B.17}$$

where $\hat{n} = n + ik$. The real part of $\hat{n}$ has the meaning of an ordinary index of refraction describing the phase velocity of light $v_{phase} = c/n$, while the imaginary part of $\hat{n}$ describes the damping $k > 0$, of the EM-wave amplitude. Since the energy carried by the EM-wave is proportional do the squared modulus of the amplitude, k describes the absorption of energy by the medium. If I denotes the radiation intensity, then

$$I = I_0 \exp\left(-2\,\frac{\omega k}{c}\,r\right) = I_0 \exp(-ar) \tag{B.18}$$

defined by the above equation is called the absorption coefficient. By introducing the vector of electric induction

$$D: = \varepsilon_0 E + P = \varepsilon_0(1 + \hat{\chi})E, \tag{B.19}$$

the complex dielectric permittivity $\hat{\varepsilon}$ may be defined as

$$\hat{\varepsilon}: = 1 + \hat{\chi}. \tag{B.20}$$

Now, the complex coefficient of reflection $\hat{r}$ is to be derived. Here, the well-known Fresnel formulae for the case of reflection from the surface described by the complex coefficient of reflection are employed. Let a_0 denote the incidence angle, n_0 — refractive index of medium, from which the EM-wave is reflected, $\hat{r}_\perp$, $\hat{r}_\parallel$ — complex coefficients of reflection for the light polarized perpendicularly and parallelly to the incident plane, respectively. Then

$$\hat{r}_\perp = \frac{x - n_0 \cos a_0}{n_0 \cos a_0 + x},$$
$$\hat{r}_\parallel = \frac{\hat{n}^2 \cos a_0 - n_0 x}{n_0 x + \hat{n}^2 \cos a_0}, \tag{B.21}$$

where $x^2 = \hat{n}^2 - n_0^2 \sin^2 a_0$. In the particularly simple case, when $a_0 = 0$ and $n_0 = 1$ we obtain

$$\hat{r} = \hat{r}_\parallel = \hat{r}_\perp = \frac{1 - \hat{n}}{1 + \hat{n}}. \tag{B.22}$$

Generally we may write

$$\hat{r} = r \exp(i\Theta), \tag{B.23}$$

where r denotes the amplitude reflection coefficient and Θ denotes the phase change during reflection.

Now, the conditions may be considered which must be always fulfilled by the spectral characteristics of the optical constants of semiconductors. From the fact that k, as well as the absorption coefficient a, must be positive (since the sample material is a medium absorbing EM radiation) it follows that $\Theta(E) > 0$, for each energy $E = \hbar\omega$. This conclusion may be obtained by transforming the eq. (B.22) to the forms

$$n = \frac{1 - R}{1 - 2\sqrt{R}\cos\Theta + R,} \tag{B.24}$$

$$k = \frac{2\sqrt{R}\sin\Theta}{1 - 2\sqrt{R}\cos\Theta + R} \tag{B.25}$$

here $R = |\hat{r}|^2 = r^2$. When the vibration frequency increases the phase difference between the excitation and oscillator reaction increases until it reaches the maximal value equal to π. Thus, by applying the harmonic

oscillator model we get $\Theta(\infty) = \pi$. This condition, in face of the dependences (2) and (11) from [41], leads to the conclusion that with the increase of energy $R(E)$ must tend to zero like E^{-4}.

The fact that $R(\infty) = 0$ follows also from the lack of photon-electron interaction at high energies. If the contribution to the optical constants coming only from the interband transitions is taken into account, then for $E < E_g(E_g$ — energy gap in semiconductors)

$$k(E) = 0, \quad a(E) = 0, \quad \varepsilon_2(E) = 0, \quad \Theta(E) = 0 \tag{B.26}$$

should hold. Hence, if follows that in the region below the energy gap no interband transitions occur. Due to the lack of basic absorption this region is called the transparence region.

As it has been already shown, the function $\hat{\chi}(z)$ satisfies the assumptions of the KK relation (A.13) Thus it holds

$$P \int_{-\infty}^{\infty} \frac{\hat{\chi}(\omega)}{\omega - \omega_0} \, d\omega = i\pi\hat{\chi}(\omega_0). \tag{B.27}$$

After having exploited the relation $\hat{\chi}^*(z) = \hat{\chi}(-z^*)$ (following directly from the formula (B.8)), which for $\omega \in R$ takes the forms $\chi_R(\omega) = \chi_R(-\omega)$, $\chi_I(\omega) = -\chi_I(-\omega)$, we obtain

$$-\frac{2\omega_0}{\pi} P \int_0^{\infty} \frac{\chi_R(\omega)}{\omega^2 - \omega_0^2} \, d\omega = \chi_I(\omega_0),$$

$$\frac{2}{\pi} P \int_0^{\infty} \frac{\chi_I(\omega)\omega}{\omega^2 - \omega_0^2} \, d\omega = \chi_R(\omega_0). \tag{B.28}$$

The interval of both the complex dielectric permittivity $\hat{\varepsilon}(\omega)$ and complex refractive index $\hat{n}(\omega)$ are broadened to cover the Gaussian plane by using the results of such procedure carried out earlier for $\hat{\chi}(\omega)$, since the relations (B.16) and (B.20) hold. Moreover, the functions $\hat{n}(z)$ and $\hat{\varepsilon}(z)$ obtained in this way are holomorphic, since the function $\hat{\chi}(z)$ is holomorphic. But $|\hat{n}(z)|$ and $|\hat{\varepsilon}(z)|$ in the upper half-plane and on the real axis do not disappear at infinity as it is required by the KK relations. This requirement is fulfilled first by the functions

$$f_1(z) := \hat{n}(z) - 1, \quad f_2(z) := \hat{\varepsilon}(z) - 1. \tag{B.29}$$

The KK relations are written for just these functions, which after taking account of the conditions: $\hat{\varepsilon}(z) = \hat{\varepsilon}^*(-z^*)$ and $\hat{n}(z) = \hat{n}^*(-z^*)$, take the forms:

$$-\frac{2\omega_0}{\pi} P \int_0^{\infty} \frac{\varepsilon_1(\omega)}{\omega^2 - \omega_0^2} \, d\omega = \varepsilon_2(\omega_0),$$

$$\frac{2}{\pi} P \int_0^{\infty} \frac{\varepsilon_2(\omega)\omega}{\omega^2 - \omega_0^2} \, d\omega = \varepsilon_1(\omega_0) - 1, \tag{B.30}$$

and

$$-\frac{2\omega_0}{\pi} P \int_0^{\infty} \frac{n(\omega)}{\omega^2 - \omega_0^2} \, d\omega = k(\omega_0),$$

$$\frac{2}{\pi} P \int_0^{\infty} \frac{k(\omega)\omega}{\omega^2 - \omega_0^2} \, d\omega = n(\omega_0) - 1, \tag{B.31}$$

where the dependence $\int_0^{\infty} \frac{d\omega}{\omega^2 - \omega_0^2} = 0$

has ben employed. It is still the complex coefficient of reflection $\hat{r}$ to be determined. The KK formulae will be not written for $\hat{r}$, but for $\ln\hat{r}$, which is justified by the later practical application of these relations. There is no greater problem – as it was the case in the previous situations – connected with the satisfaction of the condition of holomorphism (see the formula (B.22)) by the function to which the dispersion relations are to be applied. On the other hand, the limiting condition is not fulfilled since $\hat{r}(\infty) = 0$. Thus, the function $|\ln\hat{r}(\infty)| = \infty$ must be transformed so as to obtain the holomorphic function disappearing at infinity. This is possible, for instance, by creating the function

$$\Phi(z) := \frac{\ln\hat{r}(z) - \ln\hat{r}(\omega')}{z - \omega'}, \tag{B.32}$$

where ω' is an arbitrary point on the real axis. The KK relation (A.13) written for the function $\Phi(z)$ from the eq. (B.32) will have the following form

$$i\pi\ln\hat{r}(\omega_0) = i\pi\ln\hat{r}(\omega') + (\omega_0 - \omega') P \int_{-\infty}^{\infty} \frac{\ln\hat{r}(\omega)}{(\omega - \omega_0)(\omega - \omega')} \, d\omega, \tag{B.33}$$

but $\ln\hat{r}(-\omega) = \ln\hat{r}^*(\omega)$ and $\ln\hat{r} = \ln r + i\Theta$, hence

$$\Theta(\omega_0) = \Theta(\omega') - \frac{2(\omega_0 - \omega')}{\pi} P \int_{0}^{\infty} \frac{\ln\hat{r}(\omega)(\omega^2 + \omega_0\omega')}{(\omega^2 - \omega_0^2)(\omega^2 - \omega'^2)} \, d\omega,$$

$$\ln\hat{r}(\omega_0) = \ln r(\omega') + \frac{2(\omega_0 - \omega')}{\pi} P \int_{0}^{\infty} \frac{\Theta(\omega)(\omega\omega_0 + \omega\omega')}{(\omega^2 - \omega_0^2)(\omega^2 - \omega'^2)} \, d\omega. \tag{B.34}$$

By taking advantage of the physically justified fact that for $\omega' \to 0$ and $\Theta(\omega') \to 0$ the eqs. (B.34) is simplified to the forms

$$\frac{2\omega_0}{\pi} \int_{0}^{\infty} \frac{\ln r(\omega)}{\omega^2 - \omega_0^2} \, d\omega = -\Theta(\omega_0), \tag{B.35}$$

$$\frac{2\omega_0^2}{\pi} \int_{0}^{\infty} \frac{\Theta(\omega)}{\omega(\omega^2 - \omega_0^2)} \, d\omega = \ln r(\omega_0) - \ln r(0), \tag{B.36}$$

respectively. When in the formula (B.35) the light frequency is replaced by the quantum energy $E = \hbar\omega$ and the modulus of the amplitude reflection coefficient by the energetic coefficient of reflection $R = r^2$ the most frequently used form of the KK integral is obtained which connects the modulus of the reflection coefficient with the change of phase during reflection

$$\frac{E_0}{\pi} \int_{0}^{\infty} \frac{\ln R(E)}{E_0^2 - E^2} \, dE = \Theta(E_0). \tag{B.37}$$

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Определение оптических констант полупроводников Zn₃As₂ и Zn₃P₂ с помощью соотношения Крамерса-Кронига.

Часть I. Обзор методов расчёта

Работа состоит из пяти частей и посвящена главным образом результатам исследований оптических констант Zn₃As₂ и Zn₃P₂ двух соединений типа II₃–V₂ с большой энергетической щелью. Результатом анализа существующего до настоящего времени состояния в области применения

метода анализа Крамерса-Кронига (КК) для комплексного коэффициента отражения оказалась необходимость развития работы в дополнительных направлениях, описанных в трёх первых частях.

В I части представлен критический анализ применяемых до настоящего времени методов расчёта, основанных на дисперсионных соотношения Крамерса-Кронига. Обсуждена общая идея методов экстраполяции, а затем описаны четыре метода экстраполяции коэффициента отражения, два метода экстраполяции фазового угла, а также три оригинальных (недавно разработанных) метода расчёта, использующих соотношения КК. Обсуждены также три метода расчёта оптических констант, в которых не используется интеграл КК. Показаны и обсуждены преимущества, а также недостатки применяемых до сих пор методов.

Во II и III частях описаны предложения эффективных улучшений методов расчёта, основанных на применении интеграла КК. Дополнительно в обеих этих частях представлены результаты расчётов для GaAs, который послужил (в качестве полупроводника со сравнительно хорошо известными оптическими свойствами) для проверки улучшенных нами методов расчёта. Анализ ошибок и точности этих методов очень подробно проводится в IV части. Пятая часть содержит результаты расчёта оптических констант Zn_3As_2 и Zn_3P_2, произведённых с помощью усовершенствованных методов расчёта, а также на основе наших результатов измерений оптических свойств этих полупроводников.