

TO THE PROBLEM OF DECOMPOSITION OF COMPLEX OPTICAL SPECTRA INTO INDIVIDUAL CONTRIBUTIONS

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Assuming that the complex spectral curves measured under different experimental conditions can be expressed as a sum of arbitrary contributions with identical spectral shapes in all curves, we developed computational methods to find the shapes of these contributions and their amplitudes. One of these methods exploits the minimization program MINUIT, the second is based on alternating iterations. Both methods were checked using simulated complex curves.

1. INTRODUCTION

When studying optical absorption, photoconductivity or luminescence spectra in extrinsic region in semiconductors we often face the situation that the obtained spectral curves are composed of several overlapping bands. Such situation occurs both in relatively pure undoped or slightly doped semiconductors where the presence of background impurities and native defects or their complexes determined the form of optical spectra and in intermediate or heavily doped semiconductors, where complexes are formed. To decompose complex spectra into the individual contributions is a comparatively easy task if the shapes and positions of elementary contributions are known either from other experiments or from theoretical calculations. This approach is frequently used when the necessary information is at hand, agreement of calculations with experiments being ensured by fitting parameters.

Another method of decomposition was suggested by Fock and Alentzev [1]. This method assumes that a set of composed spectra formed by overlapping individual bands of different amplitudes and identical shapes in every curve is at our disposal. If the number of different spectral curves for decomposition is sufficiently high, we can – in some cases – obtain the simple bands by subtracting one spectrum from another after it was multiplied by a properly chosen constant factor. This method works well if we can unambiguously choose this multiplication factor, e.g. if at the edges of the spectra the regions could be found where overlapping can be neglected; then from the ratio of intensities in this region the multiplication factor can be determined [1]. We used this method for decomposition of complex photoconductivity curves of SI GaAs samples and found that it works well only with comparatively simple, only slightly overlapping spectra. We failed to find a simple algorithm for simplification of spectra in a more complicated case, when we could not establish with certainty the regions with no overlap, needed for reliable application of this method.

The approach we shall describe in what follows is based on the assumptions identical with those of the method of Fock and Alentzev. The geometrical insight

into the problem is used to determine the first approximation of amplitudes of contributions for the minimization or iteration procedure. The test calculations were performed on simulated spectra.

In the first part the formulation of the problem is given and the method of its solution is suggested. Then a possible way how to decrease drastically the number of unknowns is discussed. However, the cost for it is rather high. The equations became more complicated and not easy to solve. The experience with the minimization program MINUIT in solving this problem creates the body of this paper.

2. THEORY

Let the spectral curves we want to use for calculations be known in a set of points and expressed in the form

$$(1) \quad FE_i(\lambda_j) = \sum_{k=1}^N A_{ik} \varphi_k(\lambda_j)$$

where $FE_i(\lambda_j)$ are the measured experimental values of the i -th spectral curve (photoconductivity or absorption) for the wavelength λ_j . We suppose that these curves are composed of N elementary curves $\varphi_k(\lambda_j)$, $k = 1, 2, \dots, N$. Equation (1) can also be written in a matrix form $\mathcal{F} = \mathcal{A}\varphi$, where \mathcal{F} is the $M \times P$ matrix, \mathcal{A} is the $M \times N$ matrix and φ is the $N \times P$ matrix. The conditions under which we can write the spectral curves as a linear combination of elementary contributions has been discussed elsewhere [2]. These elementary spectral curves are supposed to be identical for all M experimental curves. The amplitude of the k -th elementary contribution to the i -th experimental curve is denoted by A_{ik} , we suppose, for the sake of simplicity, that A_{ik} are not negative. The number of wavelengths at which the measurements were performed is P . Hence we have $M \times N$ unknown amplitudes A_{ik} and $N \times P$ unknown values of elementary curves $\varphi_k(\lambda_j)$. The number of equations equal to the number of measurements is $M \times P$. Consequently, if the condition

$$(2) \quad M \times P \geq N \times P + N \times M$$

is fulfilled, where the equality sign holds for the case when all $M \times P$ equations are independent, the set of equations can be solved for unknowns A_{ik} and $\varphi_k(\lambda_j)$. That means that for the number of measurements we must have

$$(3) \quad P \geq \frac{M \times N}{(M - N)}.$$

Under this condition the number of unknowns is equal to or smaller than the number of equations at our disposal and we can search for the solution of the system of equations (1). However, the number of measurements for each curve is usually much larger than the minimum value of (3), so that we have an overdetermined

problem and using the least squares methods the spectral shapes of elementary curves might be determined with sufficient accuracy.

From the form of the system of nonlinear equations (1) we can infer immediately that it has two annoying properties. If $\varphi_k(\lambda_j)$ are solutions of the system, then also $C_k \varphi_k(\lambda_j)$ are solutions if simultaneously A_{ik} are replaced by A_{ik}/C_k . That means that the system (1) has to be completed by normalization equations. Moreover, also the linear combination

$$\bar{\varphi}_l(\lambda_j) = \sum_{k=1}^N \alpha_{kl} \varphi_k(\lambda_j),$$

where α is a nonsingular matrix, is a solution if the matrix of amplitudes \mathcal{A} is replaced by $\mathcal{A}\alpha^{-1}$. We shall return later to the problem how to cope with this property.

To prove the existence of roots and the convergence of the Newton's process of iteration for the system (1) we can use the theorem of Kantorovitch [3] if we limit ourselves to the P linearly independent equations. The Jacobian of the system (1) completed by normalization equations is of the form of a sparse matrix consisting mostly of zero elements. The matrix has the inverse and also the sum of second order partial derivatives is limited. That means that the assumptions of the theorem are fulfilled and hence it follows, that the iteration process will converge if we choose the initial approximation sufficiently close to the roots of the system. The range of convergence depends on the constraints imposed on the solutions.

This approach using, e.g., Newton's iteration method is obviously unpractical as the order of the Jacobian matrix is too high and special programs to deal with sparse matrices are needed. Instead of solving system (1) we could, in principle, eliminate first $\varphi_k(\lambda_j)$ and solve instead of (1) the new system for A_{ik} only and calculate $\varphi_k(\lambda_j)$ as a second step. We shall demonstrate this approach for the simple case of $M = 3$ and $N = 2$.

We eliminate the unknowns $\varphi_1(\lambda_j)$ and $\varphi_2(\lambda_j)$ for each wavelength using, e.g., the Kramer's method. If we explore the linearly independent combinations of equations FE_i, FE_k , we come, after some calculations, to one equation for A_{ik}

$$(4) \quad FE_1(\lambda_j) D_{23} - FE_2(\lambda_j) D_{13} + FE_3(\lambda_j) D_{12} = 0$$

where we denoted

$$D_{k1} = \begin{vmatrix} A_{k1} & A_{k2} \\ A_{11} & A_{12} \end{vmatrix}.$$

To obtain the solution for six unknowns A_{ik} we have to use six independent sets of $FE_i(\lambda_j)$ values in this case, i.e., $j = 1, 2, \dots, P$, and $P = 6$ in accordance with the relation (3).

The existence of solutions of the system (4) and the convergence of the corresponding Newton's procedure can be again proved by the Kantorovitch' theorem [3], after verifying the existence of the inverse of the Jacobi matrix as well as the other necessary conditions (the existence of the norm of the matrices involved in calculations [3]). The normalization conditions can be included in the system (4) in some

way convenient for calculations, e.g.,

$$\sum_{j=1}^P FE_i(\lambda_j) = \sum_{k=1}^N A_{ik}$$

for each curve $i = 1, 2, \dots, M$.

A similar set of equations can be derived for all possible M , N and P satisfying the relation (3) and also the existence of roots can be proved. In this procedure the number of unknowns is only $M \times N$ instead of $M \times N + N \times P$ as in the previous case. But the equations for A_{ik} are much more complicated and of higher order so that this approach cannot be recommended either.

For practical solution we used the minimization program MINUIT [4]. We estimated the zero approximation for the amplitudes A_{ik} from the shape of the experimental curves $FE_i(\lambda_j)$ as parameters of the minimization procedure. With their help we calculated $\varphi_k(\lambda_j)$ using the set of equations (1) which we treated as a set of linear equations for an overdetermined problem. We minimize the χ -square function defined as the sum of squared differences of the experimental points $FE_i(\lambda_j)$ and calculated values according to (1). The correct values of A_{ik} and consequently the correct values of $\varphi_k(\lambda_j)$ were then searched for by the MINUIT program. The details of the minimization procedure are described in the paper by F. James and M. Roos [4].

To solve the system (1) for $\varphi_k(\lambda_j)$ we used either the subroutine DECOMPSOLVE [5], or, more favourably, the subroutine NNLS (nonnegative least squares [6]), in which the constraint that the solutions $\varphi_k(\lambda_j)$ should be nonnegative could be used directly (but more machine time was needed in this case).

To avoid the ambiguity in decomposition of the complex spectral curves we took care to ensure that the number of curves to decompose M be sufficiently higher than the number of elementary curves N so that the constraints imposed on the problem limit sufficiently the number of possible solutions. The knowledge of the shape of at least some of the elementary curves was also of great help. In more complicated cases with several elementary contributions the computer time was saved if the curves were decomposed by parts, starting at lower energy side where with certainty only two or three elementary curves participated in the measured spectra. Then the values of their parameters were fixed and next part of curves and parameters was added. In some cases, if there were some physical grounds for it, we also used additional demand that the chosen elementary curves be the shortest ones.

In addition to the minimization procedure MINUIT we used for decomposition also the method of alternating iterations. After estimation of the zeroth approximation of the A_{ik} and introducing it into (1) we solved this system taken now as a system of linear equations for the unknowns $\varphi_k(\lambda_j)$. The standard subroutine (nonnegative least squares method [6]) was again used for solution so that the constraints that $\varphi_k(\lambda_j)$ should be nonnegative was respected. The obtained $\varphi_k(\lambda_j)$ values were then used and system (1) was now solved again as an overdetermined linear system for

next approximation of A_{ik} using the same method. This procedure was repeated and the error was calculated in each step: The convergence of the process was very good if we succeeded at the beginning in assessing correctly (within $\sim 30\%$ accuracy) the zeroth approximation of A_{ik} values.

The results were in agreement with the minimization procedure MINUIT and were obtained in much less machine time needed for the MINUIT. As a rule we used both of the procedures for each set of curves to check the reliability of the decomposition.

3. GEOMETRICAL INSIGHT INTO THE PROBLEM OF UNIQUENESS OF THE DECOMPOSITION

We shall consider now the experimental curves F_i and elementary contributions φ_j as vectors formed by p -tuples of nonnegative numbers, Let the rank of the matrix \mathcal{F} of all experimental curves F_i be N , then we can choose the basis ψ_i , $i = 1, \dots, N$, of the subspace F of all linear combinations of elementary vectors φ_j , $j = 1, 2, \dots, N$ which also form the basis of this space. The condition that all experimental curves are linear combinations of φ_j vectors with nonnegative coefficients implies that all F_i vectors are contained in one polyhedral of the total space.

We demand that among our set of F_i vectors we have vectors lying in $N - 1$ dimensional hyperplanes, $N - 1$ in each of all N hyperplanes. By the decomposition procedure we found a basis ψ of F subspace, the vectors of which can be expressed as

$$(5) \quad \psi_i = \alpha_{i1}\varphi_1 + \alpha_{i2}\varphi_2 + \dots + \alpha_{iN}\varphi_N.$$

As all vectors ψ_i in general are not of the same polyhedron as F , naturally not all α_{ik} have to be nonnegative. For F_i vectors lying in hyperplanes we can write (e.g., for the case of $N = 3$)

$$(6) \quad F_i = a_{i1}\psi_1 + a_{i2}\psi_2 + a_{i3}\psi_3 = (a_{i1}\alpha_{11} + a_{i2}\alpha_{21} + a_{i3}\alpha_{31})\varphi_1 + (a_{i1}\alpha_{12} + a_{i2}\alpha_{22} + a_{i3}\alpha_{32})\varphi_2 + (a_{i1}\alpha_{13} + a_{i2}\alpha_{23} + a_{i3}\alpha_{33})\varphi_3$$

where one of the coefficients of φ_i is equal to zero. Let, e.g.,

$$(7) \quad (a_{i1}\alpha_{13} + a_{i2}\alpha_{23} + a_{i3}\alpha_{33}) = 0.$$

Using all $N - 1$ vectors F_i from the i -th hyperplane we obtain $N - 1$ equations for unknown α_{ij} , which together with normalization equation determine in a unique way all α_{ij} , $i = 1, 2, 3$. Repeating the process for all hyperplanes, we obtain all elements of transformation matrix α which, according to our assumption, is not singular. With the help of its inverse we can obtain the elementary contribution φ_j (i.e. the "true" basis of F) in the unique way.

Let us suppose now that not $N - 1$ but at least one of F_i vectors lies in each of N hyperplanes. Then in the case of $N = 3$ we shall have

$$(8) \quad a_{i1}\alpha_{1k} + a_{i2}\alpha_{2k} + a_{i3}\alpha_{3k} = 0,$$

if φ_k is missing in a given hyperplane. As all a_{ij} are nonnegative, at least one of α_{jk} must be less than zero. Let, e.g., $\alpha_{3k} < 0$. We shall also suppose that the vectors φ_k are partly nonoverlapping. From the condition of nonnegativity of ψ_k we obtain

$$(9) \quad \alpha_{31}\varphi_1 + \dots + \alpha_{3k}\varphi_k + \dots = \psi_3 \geq 0$$

for all tuples of φ vectors. We can write for the $|\alpha_{3k}|$

$$(10) \quad |\alpha_{3k}| \leq \frac{\varphi_1}{\varphi_k} \alpha_{31} + \dots + \frac{\varphi_N}{\varphi_k} \alpha_{3N}.$$

After choosing such value of λ_j for which $\varphi_k(\lambda_j) > 0$ and simultaneously $\varphi_i(\lambda_j) = 0$, $i \neq k$, we obtain $|\alpha_{3k}| = 0$. The same procedure can be applied for other F_i vectors in the rest of hyperplanes. The conclusion is that under these conditions α can be only a permutation matrix, the basis vectors again can be chosen in a unique way.

If none of the above discussed conditions is met, the choice of the basis vectors ψ_i is, in general, not unique. However, the vectors ψ_i will be close enough to the vectors φ_i if vectors F_i lie close to the hyperplanes and/or if vectors φ_i are "almost" nonoverlapping. The procedure used above enables an estimation of the distance between corresponding ψ_i and φ_i vectors.

Table 1

λ_j	Correct values of φ			Calculated by MINUIT			Calculated by iterations		
1000	0.0000	0.0183	0.0000	0.0000	0.0184	0.0000	0.0000	0.0181	0.0000
1100	0.0785	0.0392	0.0000	0.0786	0.0389	0.0022	0.0789	0.0385	0.0014
1200	0.1564	0.0773	0.0000	0.1566	0.0768	0.0044	0.1573	0.0760	0.0028
1300	0.2334	0.1409	0.0000	0.2338	0.1402	0.0064	0.2351	0.1391	0.0035
1400	0.3090	0.2369	0.0000	0.3096	0.2361	0.0080	0.3118	0.2349	0.0033
1500	0.3827	0.3679	0.0000	0.3836	0.3671	0.0091	0.3871	0.3659	0.0021
1600	0.4540	0.5273	0.0000	0.4553	0.5265	0.0100	0.4603	0.5255	0.0001
1700	0.5225	0.6977	0.0000	0.5242	0.6971	0.0106	0.5296	0.6947	0.0000
1800	0.5878	0.8521	0.0001	0.5899	0.8516	0.0114	0.5955	0.8482	0.0000
1900	0.6494	0.9608	0.0019	0.6517	0.9603	0.0142	0.6589	0.9576	0.0060
2000	0.7071	1.0000	0.0183	0.7090	1.0000	0.0317	0.7176	1.0000	0.0136
2100	0.7604	0.9608	0.1054	0.7595	0.9637	0.1188	0.7632	0.9684	0.1022
2200	0.8090	0.9521	0.2679	0.7998	0.8642	0.3775	0.7888	0.8840	0.3654
2300	0.8526	0.6977	0.7788	0.8304	0.7241	0.7815	0.7965	0.7678	0.7764
2400	0.8910	0.5273	1.0000	0.8616	0.5613	1.0000	0.8146	0.6176	1.0000
2500	0.9239	0.3679	0.7788	0.9009	0.3933	0.7868	0.8638	0.4354	0.7869
2600	0.9510	0.2369	0.3679	0.9341	0.2468	0.3881	0.9233	0.2635	0.3858
2700	0.9724	0.1409	0.1054	0.9665	0.1370	0.1471	0.9553	0.1407	0.1351
2800	0.9877	0.0743	0.0183	0.9903	0.0748	0.0461	0.9897	0.0687	0.0448
2900	0.9969	0.0392	0.0019	0.9989	0.0356	0.0320	0.9988	0.0286	0.0304
3000	1.0000	0.0183	0.0001	1.0000	0.0139	0.0330	1.0000	0.0073	0.0302

Until now we discussed the cases where the rank of the F matrix was equal to N . If it is less than N , then we can decompose F_i vectors only into $M < N$ ψ_i vectors that are linear combinations of φ_i vectors. In any case the new ψ_i vectors are simpler than the original F_i vectors and often the desired shape of the φ_i curves can be anticipated. If we can supplement the original set of F_i vectors in some way with new vectors and increase the rank of the F_i matrix, the process of decomposition can be repeated and full decomposition achieved.

4. DECOMPOSITION OF SIMULATED CURVES

A set of seven curves F_i for decomposition was obtained by summation of two gaussian curves and one curve of sinusoidal shape. Their amplitudes were chosen in such a way that the rank of matrix \mathcal{F} was 3. The number of points for each curve was $P = 21$. In table 1 the values of elementary curves at all points are given together with values obtained by decomposition procedure.

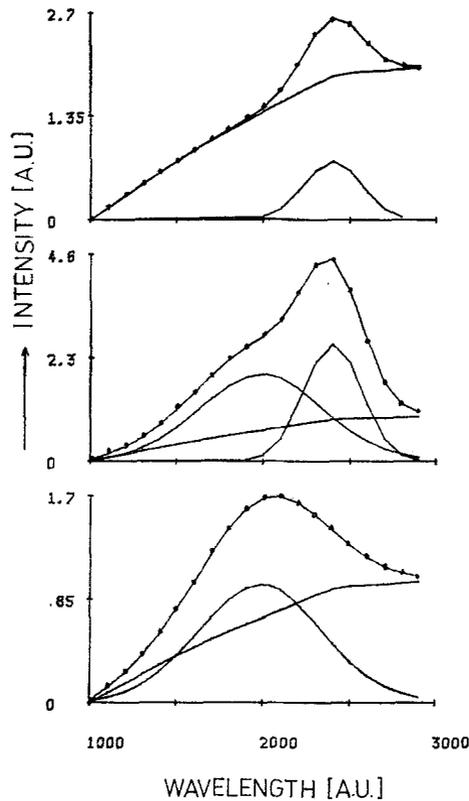


Fig. 1. Example of decomposition of simulated curves. Dots — simulated curves. Full lines — calculated curves and elementary contributions.

As the first step the singular values of FE matrix were found (they were equal to 21.3724, 4.2442, 2.0574, 0.0283, 0.0000, 0.0006, and 0.0000) and in this way the dimensionality of the problem, i.e., the rank of \mathcal{F} was established. Then the zeroth approximation for amplitudes was chosen intentionally far enough from correct values using random numbers $A_{ik}^0 = A_{ik}^{\text{corr}} (0.5 + RND)$, where A_{ik}^{corr} is the correct amplitude and RND is the random number ranging from 0 to 1. Afterwards the calculations using MINUIT and the iteration procedure were performed. An example of curves decomposed into elementary contributions is shown in fig. 1.

If the errors in A_{ik}^0 were below $\sim 30\%$, then the average errors in calculated amplitudes were below $\sim 3.5\%$ after 5 steps of iteration and below $\sim 2.3\%$ if MINUIT was used. They decreased with increasing M and P . The largest errors in the shape determination of the elementary curves are apparent from table 1. The errors depend somewhat on the form of the elementary curves. The larger the halfwidth of the curve the less is the error in the determined amplitude and in the shape in the vicinity of its maximum. All calculations were performed in single precision.

5. DISCUSSION

The methods described above offer the possibility of decomposing even complicated spectra into the individual contributions without knowledge of their shapes. We assumed only that these shapes are identical for each elementary curve in all composed spectra of our set and that they do not depend on the experimental conditions. The validity of this assumption will be discussed in [2]. The values of A_{ik} for zero approximation were determined approximately from the shape of the complex curves, sometimes with the help of literature data. In more complicated cases several estimations were made and results then compared.

The total number of elementary curves needed for decomposition was determined using singular value decomposition of the F matrix, the rank of this matrix being equal to the number of basis vectors. If the determined number of elementary curves N was smaller than needed (in the case of large experimental errors), the fit remained poor. On the other hand, if it was larger, then the surplus curve showed to be either of small amplitude with scattered points or of the shape close to some of other elementary curves.

The number of experimental curves M used for decomposition was usually twice as large or more than the number of elementary curves N , so that the uniqueness of the decomposition was ensured with sufficient precision. The highest number of curves we simultaneously used for decomposition was 28, the largest N was 5. We used this method for the determination of the ionization and absorption cross sections of impurity centres in SI GaAs crystals, doped with Cr or V ions. Absorption or photoconductivity curves obtained either with samples with different impurity concentrations or with different population of impurity levels were used for de-

composition. The results are described in a separate paper [7]. Luminescence spectra were decomposed by this method, too.

As a result of calculations we obtained the spectral shapes of cross sections for the individual impurities and amplitudes of their contributions to the composed spectral curve and their confidence interval, which also enable us to estimate simultaneously the error in the determination of the spectral shapes of the elementary curves in a suitable form.

6. CONCLUSIONS

The decomposition of complex spectral curves into the individual contributions of arbitrary shapes can be achieved with the help of the minimization program MINUIT or by the alternating iterations. The uniqueness of the decomposition is ensured by the physical constraints on the values of elementary contributions and their amplitudes (non-negative values) and/or by additional demands on the properties of elementary contributions. The procedure was checked using simulated curves. Also the convergence range for zero approximation of the parameters of decomposition was investigated and was found to exceed 30 per cent of their value for the case where the number of curves for decomposition is at least twice as large as the number of elementary curves, provided that they behave well in the sense discussed above.

The described method of decomposition of complex spectra enables the study of the behaviour of deep impurities by optical methods in more complicated cases of compound semiconductors and has larger area of applicability.

The author is indebted to M. Lokajčiček and V. Kundrať who kindly shared their experience in using MINUIT and to M. Nekvinda for valuable discussions and comments.

Received 4. 4. 1986.

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