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Determination of the X-Ray Diffraction Curve of Amorphous Phase

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The method for determination of diffraction pattern of amorphous phase existing in a multiphase system has been described. In the course of analysis several samples containing different amounts of amorphous as well as crystalline phases have been involved according to the general theory for phase analysis. The method is based on the difference in convergence of Fourier series by which diffraction patterns of multiphase samples and of individual phases of these samples are defined, since diffraction pattern of amorphous phase exhibits stronger convergent Fourier series than diffraction pattern of crystalline phase. The method is illustrated by three-phase model system containing one amorphous phase.

The solution of multiphase systems with unknown or less known compounds by x-ray diffraction is complicated because an exact distribution of the x-ray intensity diffracted by these compounds is not known. An amorphous phase of multiphase samples usually produces a diffuse x-ray pattern in Bragg-angle intervals, in which crystalline phases of samples yield sharp maxima. Therefore the determination of a correct shape of a diffuse x-ray pattern, corresponding to a pure amorphous phase, from x-ray patterns of polyphase samples is difficult. The determination of an amorphous phase diffraction curve required for quantitative phase-analysis can be performed by applying a general method for phase analysis (GMPA)[1]. In the present work a procedure for such determination is developed. The method is based on the main relations of the GMPA and the fact that the Fourier series of more smooth curves converge more rapidly than those of less smooth curves[2].

THEORY

According to the GMPA[1], the x-ray diffraction curve of a multiphase sample can be represented as a sum function $\Phi(x)$, i. e. as a sum of products of component functions $\varphi_i(x)$, characteristic of individual phases, with the corresponding weight fractions w_i:

$$\Phi(x) = \sum_{i=1}^{r} \varphi_i(x)\, w_i \tag{1}$$

where r is the number of phases. The sum function $\Phi(x)$ and the individual function $\varphi_i(x)$ are defined by a row of n elements $F(n)$ and $f_i(n)$, respectively. Therefore equation (1) can be written in a form that is more convenient for quantitative phase analysis:

$$F(n) = \sum_{i=1}^{r} f_i(n)\, w_i \tag{2}$$

The number of phases r in a sample can be determined on the basis of the following considerations. For r-phase samples which differ with regard to the weight fractions of individual phases, the sum functions $\Phi_j(x)$ ($j = 1, \ldots, r + 1$) satisfy the equation

$$\sum_{i=1}^{r} \alpha_i \Phi_i(x) = \Phi_{r+1}(x) \tag{3}$$

where α_i are proportionality coefficients.

To determine r, sufficiently wide intervals of the x-ray diffraction curve of r + 1 samples should be developed into Fourier series. Each Fourier series is represented by the coefficients $A_j(n)$ and $B_j(n)$. By substituting the Fourier coefficients for the row $F_j(n)$ into equation (3), one obtains the expressions

$$\sum_{i=1}^{r} \alpha_i A_i(n) = A_{r+1}(n) + \Delta_A(n) \tag{4}$$

$$\sum_{i=1}^{r} \alpha_i B_i(n) = B_{r+1}(n) + \Delta_B(n) \tag{5}$$

in which $\Delta_A(n)$ and $\Delta_B(n)$ are elemental deviations.

The deviation factor including deviations of all 2n Fourier coefficients is equal to

$$R_f = \frac{\sum_{n} (|\Delta_A(n)| + |\Delta_B(n)|)}{\sum_{n} (|A_{r+1}(n)| + |B_{r+1}(n)|)} \tag{6}$$

The proportionality coefficients α_i and the corresponding statistics (deviation factor R_f, correlation factor R and t_i-values for the determination of significance whether $\alpha_i \neq 0$) can be calculated by the least-squares-method using a system of 2n equations ($n \gg r$).

If the amorphous phase is one of the constituents of a multiphase system, then in a criterial analysis of the number of phases in the system the conditions imposed on the value of the deviation factor R_f should be more rigorous than if the system analysed consists only of crystalline phases. The determination of the number of phases in a system made up only of crystalline constituents, with identical structural characteristics in all samples analysed, may be regarded as completed if, including the experimental error, the value of R_f is less than 0.1. However, if the analysed system contains an amorphous

phase, the value of R_f must be less than 0.05 for the assumed number of phases to be considered reliable. The reliability with which phase number is determined depends also on the difference between values of R_f obtained under a correct and an incorrect assumption of the number of phases. When this difference is larger the reliability of defining the number of phases is higher.

To define the shape of the individual function $\varphi_A(x)$ pertaining to the amorphous phase, it is sufficient to determine only $2k$ Fourier coefficients ($k \ll n$). This is because the Fourier series for the amorphous phase converges more rapidly than the Fourier series for crystalline phases. The individual function $\varphi_A(x)$ is defined by a row of elements, $f_A(n)$, that is, by a row of $a_A(n)$ and $b_A(n)$, the cosine and sine function coefficients of the Fourier series:

$$\varphi_A(x) = \frac{a_0}{2} + \sum_{n=1}^{k} a_A(n) \cos 2\pi nx + \sum_{n=1}^{k} b_A(n) \sin 2\pi nx \tag{7}$$

The remaining elements $a_A(m)$ and $b_A(m)$ vanish for all values of m such that $k < m \leqslant n$. Substitution of $\varphi_A(x)$ for $\Phi_r(x)$ into equation (3) and, correspondingly, replacing $A_r(n)$ and $B_r(n)$ in equations (4,5) by $a_A(n)$ and $b_A(n)$ will give a system of 2n equations. From this system $r-1$ coefficients α_i as well as k products $\alpha_A a_A(n)$ and k products $\alpha_A b_A(n)$ can be determined. All together, $r-1+2k$ unknown values can be determined. The system of 2n equations with $r-1+2k$ unknowns can be solved by the least-squares method provided that $2n \gg r-1+2k$.

This condition is not usually satisfied, because the number of Fourier coefficients n is limited due to the rapid convergence of the series. For this reason, the $2k$ coefficients are not calculated from a single system of equations, but successively, pair by pair. The coefficients calculated in this manner are used to set up the r-th Fourier series which represents the individual function of the amorphous phase. The first pair of coefficients a (1) and b (1) can be calculated from the equation:

$$\sum_{i=1}^{r-1} \alpha_i(1)\, \Phi_i(x) + a(1) \cos 2\pi x + b(1) \sin 2\pi x = \Phi_{r+1}(x) \tag{8a}$$

In this way, $r-1$ of all proportionality factors have been calculated as well as a (1) and b (1), so the total number of calculated unknowns is $r-1+2=r+1$. To solve the system of 2n equations of type (8a) with $r+1$ unknowns, the least-squares procedure is allowed when $2n \gg r+1$.

The next pair a (2) and b (2) is calculated from an expression similar to (8a),

$$\sum_{i=1}^{r-1} \alpha_i(2)\, \Phi_i(x) + \alpha_r(2)\, \varphi_{r,2}(x) + a(2) \cos 2\pi 2x + b(2) \sin 2\pi 2x = \Phi_{r+1}(x) \tag{8b}$$

where $\varphi_{r,2}(x)$ is a function represented by two terms with the coefficients a (1) and b (1), respectively:

$$\varphi_{r,2}(x) = a(1) \cos 2\pi x + b(1) \sin 2\pi x \tag{8c}$$

System (8b) permits the calculation of r of the coefficients α_i as well as the calculation of a (2) and b (2), which accounts for $r+2$ unknowns in all. The least-

-squares method can be applied, since 2n is still overwhelmingly larger than $r + 2$ when $2n \gg r + 1$.

In general, the k-th pair a (k) and b (k) can be calculated from the equation

$$\sum_{i=1}^{r-1} \alpha_i (k)\, \Phi_i (x) + \alpha_r (k)\, \varphi_{r,k} (x) + a(k) \cos 2\pi kx + b (k) \sin 2\pi kx = \Phi_{r+1} (x) \qquad (8d)$$

where $\varphi_{r,k} (x)$ is a function defined as

$$\varphi_{r,k} (x) = \alpha_r (k-1)\, \varphi_{r,k-1} (x) + a(k-1) \cos 2\pi (k-1)\, x + b (k-1) \sin 2\pi (k-1)\, x \qquad (8e)$$

Again, system (8d), containing $r + 2$ unknowns, can be solved by the least--squares method because $2n \gg r + 2$, as shown above.

DISCUSSION

To carry out a quantitative phase analysis of a multiphase system based on the GMP procedure, two preliminary steps must be taken: (1) determination of the total number of phases in the system and (2) determination of the shape of individual phase functions.

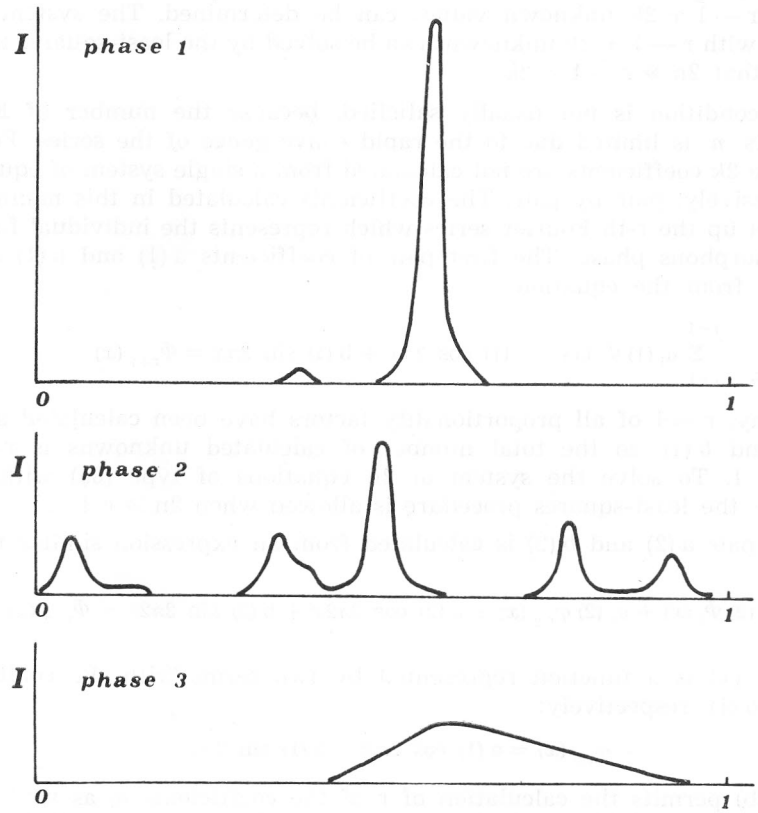

Figure 1. Idealized x-ray diffraction patterns of individual phases

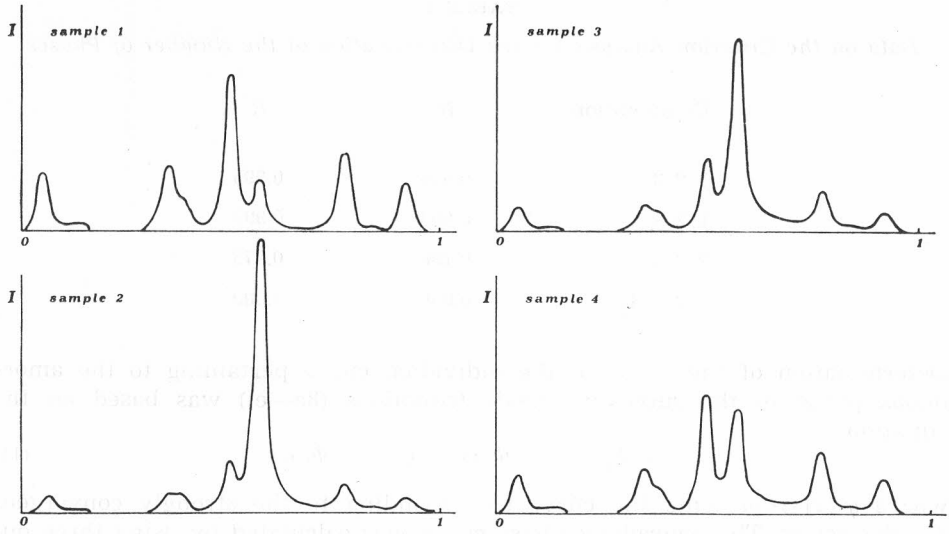

Figure 2. Sum functions belonging to samples 1—4

Let the first step be illustrated in a three-phase model-system consisting of four samples with different weight fractions of the three phases. One of the individual phase functions, corresponding to one of the idealized x-ray diffraction patterns is attributed to a pure amorphous phase (Figure 1). The four sum functions $\Phi_j(x)$ $(j = 1, \ldots, 4)$ corresponding to idealized x-ray diffraction patterns of the four samples, are shown separately in Figure 2. Each pattern is represented by 300 amplitudes used to calculate the coefficients of the four respective Fourier series. At first, a two-phase system was tentatively assumed, and the proportionality factors α_i, their deviation factor (R_f), correlation factors (R), and t_i-values were calculated by the least-squares procedure from a system of 100 equations:

$$\alpha_1 F_I(n) + \alpha_2 F_J(n) = F_L(n) \tag{9}$$

where $n = 1, \ldots, 50$ is the number of coefficients in each cosine and sine term. Various combinations of 3 out of the 4 equations were used. The same parameters were then calculated for a three-phase system, assumed in the model. Calculations were based on the following system containing 100 equations:

$$\alpha_1 F_I(n) + \alpha_2 F_J(n) + \alpha_3 F_K(n) = F_L(n) \tag{10}$$

where I, J, K and L are indices of samples included in the particular combinations.

The results are summarized in Table I. The three combinations to which equation (9) was applied gave R_f factors above 0.05 (range 0.076—0.188) and correlation factors below unity. This shows that the two-phase assumption is unacceptable. In contrast, the use of all samples in equation (10) gave $R_f = 0.00$, $R = 1.00$ and infinite t_i-values (not shown in Table I.). This shows that the model requires to be treated as a three-phase system.

TABLE I

Data on the Criterion Analysis for the Determination of the Number of Phases

Combination	R_f	R
1 2 3	0.076	0.995
1 2 4	0.093	0.993
2 3 4	0.188	0.975
1 2 3 4	0.000	1.000

Determination of the shape of the individual curve pertaining to the amorphous phase in the successive mode (equations (8a—e)) was based on the equation

$$\alpha_1 \Phi_I(x) + \alpha_2 \Phi_J(x) + \varphi(x) = \Phi_L(x) \tag{11}$$

where $\varphi(x)$ represents the curve corresponding to the strongly convergent Fourier series. The amorphous-phase curve was calculated by using three out of the four samples, as symbolized by the indices I, J, L. According to the results from Table I, any three samples may be used in combination, as for them $|\alpha_i| > 0$.

The required number of Fourier coefficients for best representation of the individual curve $\varphi(x)$ was determined by correlation of the sum functions of three samples. The correlation was performed by subsequent multiple repetition. For the first correlation, zero-values were assumed for the first two pairs of the coefficients of every sample, $A_j(p) = B_j(p) = 0$, $(p = 1, 2)$; for the second to fourteenth correlation, the assumptions were expanded to $p = 1, 2, 3$; $p = 1, \ldots, 4$; $\ldots$ $p = 1, \ldots, 15$. Figure 3 shows the dependence of R_f and R on the number of Fourier coefficients set zero for samples 1, 2 and 4. For Fourier coefficients from the eighth term onwards, R_f and R were constant ($R_f = 0.05$ and $R = 1.00$). Hence the correlations of these series, $F_j(n)$, where $n > 7$ are consistent with a system of only two phases, and $\varphi(x)$ is sufficiently characterized by seven Fourier coefficients ($k = 7$).

These coefficients were calculated pair by pair by the least-squares method from the 2n equations $(n = 1, \ldots, 50)$ based on the correlation of the sum functions of samples. The normalized curve represented by $\varphi(x)$ differed from the theoretically constructed curve in Figure 4a, and its R_f factor was still above zero ($R_f = 0.005$). This result required a recalculation, taking into account $\varphi(x)$. This was carried out according to the equation

$$\alpha_1 \Phi_I(x) + \alpha_2 \Phi_J(x) + \alpha_3 \varphi(x) + \Delta_1 \varphi(x) = \Phi_L(x) \tag{12}$$

where $\Delta_1 \varphi(x)$ is the recalculated function. If R_f remains above zero, the procedure is iterated until R_f falls below a fixed limit ($|R_f| < \varepsilon$), and the shape of the curve changes no longer from one iteration to another. We set $\varepsilon = 0.001$, which was attained by R_f at the second iteration. Finally, using this $\Delta_1 \varphi(x)$, we calculated the function

$$\varphi_A(x) = \alpha_3 \varphi(x) + \Delta_1 \varphi(x) \tag{13}$$

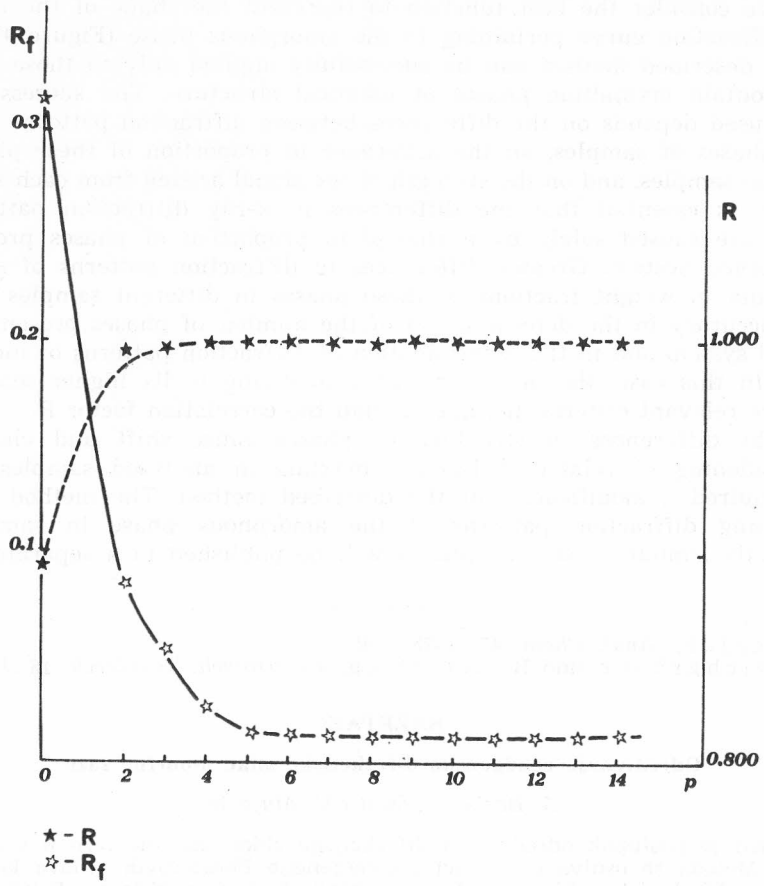

Figure 3. The dependence of the R_f-factor and R upon the number of Fourier coefficients p which were assumed to be zero

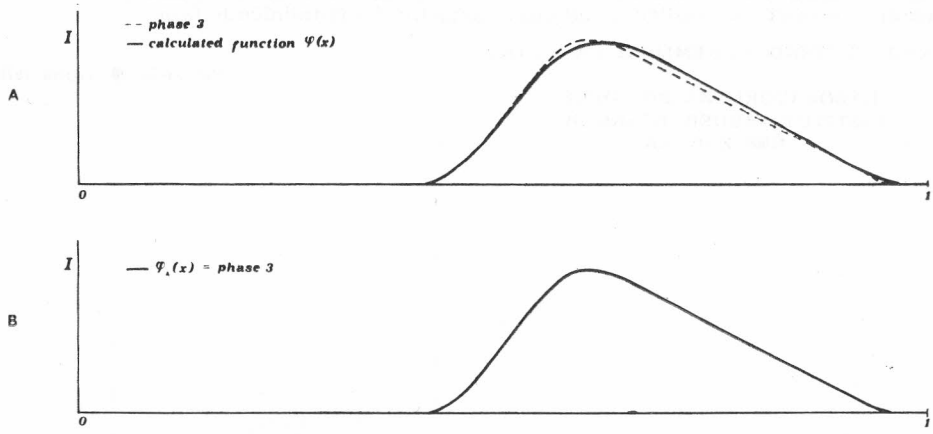

Figure 4. The difference between presumed and calculated curves of amorphous phase

which we consider the best function to represent the shape of the required x-ray diffraction curve pertaining to the amorphous phase (Figure 4b).

The described method can be successfully applied only to those systems which contain crystalline phases of identical structure. The success of the method used depends on the differences between diffraction patterns of individual phases of samples, on the difference in proportion of these phases in individual samples, and on the strength of the signal arising from each separate phase. It is essential that the differences in x-ray diffraction patterns of samples are caused solely by a change in proportion of phases present in the observed system. Greater differences in diffraction patterns of separate phases and in weight fractions of these phases in different samples lead to higher accuracy in the determination of the number of phases present in the observed system and in the determination of diffraction patterns of individual phases. In this case, the deviation factor R_f owing to its higher sensitivity, is a more relevant criterial parameter than the correlation factor R.

Slight differences in structure of phases cause shift and change in the broadening of related diffraction maxima in analyzed samples. These facts required a modification of the described method. The method for the determining diffraction patterns of the amorphous phase in samples of structurally similar crystalline phases will be published in a separate paper.

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SAŽETAK

Određivanje rendgensko-difrakcijske slike amorfne faze

A. Bezjak, I. Šmit i V. Alujević

Opisan je postupak određivanja difrakcijske slike amorfne faze u višefaznom sistemu. Metoda se osniva na razlici konvergencije Fourierovih redova kojima su definirane difrakcijske slike amorfne i kristaliničnih faza sistema. Fourierov red difrakcijske slike amorfne faze konvergentniji je od redova difrakcijskih slika kristaliničnih faza. Postupak je prikazan na trofaznom model sistemu koji sadrži jednu amorfnu fazu, a u skladu sa Općom teorijom fazne analize u analizu je uključeno nekoliko uzoraka sa različitim udjelima amorfne i kristaliničnih faza.

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