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Laboratory of Surface and Interface Physics, Eötvös University, Budapest¹⁾

On the Evaluation of X-Ray Diffraction Experiments by the Regularization Method

By

V. A. TRUBIN and A. SZASZ

The characteristic property of diffractometers as the presence of occasional and systematic errors in measured patterns requires such an evaluation which is as informative as possible. This circumstance gives rise to the problem of optimal planning of the experiment. The X-ray diffraction optimization problem with application of the regularization method is studied. The proposal permits to determine more accurately the unknown true characteristics of the X-ray diffraction experiment.

Die charakteristischen Eigenschaften von Diffraktometern, wie zufällige und systematische Fehler in den gemessenen Diagrammen, erfordern eine Auswertung, die so informativ wie möglich ist. Diese Umstände geben Anlaß zu dem Problem der optimalen Planung des Experiments. Es wird das Röntgenbeugungs-Optimierungsproblem unter Anwendung der Regelungsmethode untersucht. Die vorgeschlagene Methode erlaubt, die unbekannten wahren Charakteristiken des Röntgenbeugungsexperiments genauer zu bestimmen.

1. Introduction

The standard modifying effects caused by the diffractometer can be considered in the course of evaluation by the so-called instrumental function [1].

The search for instrument response is an inverse task of the X-ray diffraction measurements, and the accuracy of its solution is determined by two main factors:

- the relative random noise,
- the systematic deviations caused by the instrument.

We consider now the linear system of equations for X-ray diffraction as follows:

$$I_0(s) = \int_{s/2}^{s/2} I_g(s - s') P(s') ds' + \zeta(s)$$

or

$$I_0 = KP + \zeta, \quad (1)$$

where K is the total X-ray diffraction matrix, I_0 the X-ray diffraction measurement vector, P the vector of the unknown pattern, ζ the vector of statistical disturbances having zero time average. Moreover let ζ and P have a-priori Gaussian densities: $N(0, \zeta)$ and $N\{M[P(0)], P(0)\}$ [5].

The use of constraints in solving the Fredholm internal equations of the first kind like (1) has been investigated recently by several authors [2 to 6].

It has become apparent that the need for constraint information depends on the degree of ill-posedness of the problem, as characterized by the decay rate of the kernel spectrum and also the smoothness of the solution.

¹⁾ Muzeum krt. 6–8, H-1088 Budapest, Hungary.

The optimal smoothing methods are often sufficient to give satisfactory numerical solutions for several ill-posed problems, but on the other hand, the ineffectiveness of the unconstrained regularization and the improvement introduced by the constraints have been clearly demonstrated [10].

It is usually accepted that an instrumental function $I_g(s)$ from the convolution equation (1) is assigned to the summarized systematic deviations caused by the instrument.

The half-width β of X-ray diffraction line controls the effects. However, in practice the value β and the relative noise level are almost always interconnected. This relation is usually displayed in the fact that with increase of β the X-ray signal intensity $I_0(s)$ is becoming higher, i.e. the signal/noise ratio is increased. This fact can be accounted for as a decrease of the relative noise level. It is reasonable to speak about the existence of some optimal mode for the diffractometric measurements.

2. Investigation of Optimal Mode of X-Ray Diffraction Measuring

In diffractometric experiments two modes of measurements are existing for the purpose of signal restoration: with or without monochromators.

The monochromator instrument function with consideration of only slot distortions can be described as [7]

$$I_g(s) = \begin{cases} 1/2\beta_1, & \beta_1 > \beta_2; & |s| \leq \beta_1 - \beta_2, \\ 4/\beta_1\beta_2(\beta_2 + \beta_1 - |s|); & \beta_1 - \beta_2 \leq |s| \leq \beta_1 + \beta_2, \\ 0; & \beta_2 + \beta_1 \leq |s|, \end{cases} \quad (2)$$

where β_2 is the half-width of output slot, and β_1 the half-width of the input slot geometric image. In the special but practically important case $\beta_1 = \beta_2 = \beta$ (2) becomes

$$I_g(s) = \begin{cases} 1/2\beta(1 - |s|/2\beta) & \text{at } |s| \leq 2\beta, \\ 0 & \text{at } |s| > 2\beta, \end{cases} \quad (3)$$

i.e. $I_g(s)$ has a triangular shape (Fig. 1). For this triangular instrumental function we have (Fig. 2)

$$\tilde{I}_g(\omega) = (\sin \beta\omega/\beta\omega)^2. \quad (4)$$

To reveal the relation of signal level $I_0(s)$ and noise level to the half-width β of the instrumental function, a numeric calculation was made by substitution of (3) into (1) at different values. The function $P(s) = \exp(-s^2/2c^2)$ is selected with half-width c . The

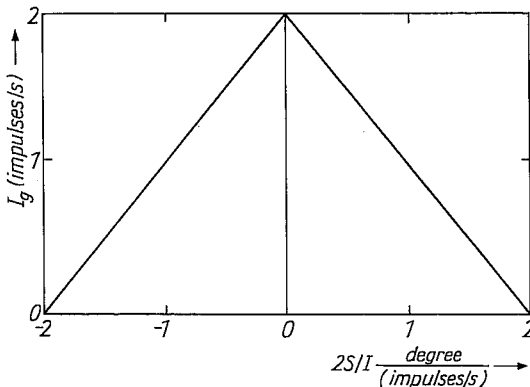


Fig. 1. Instrumental function of monochromator

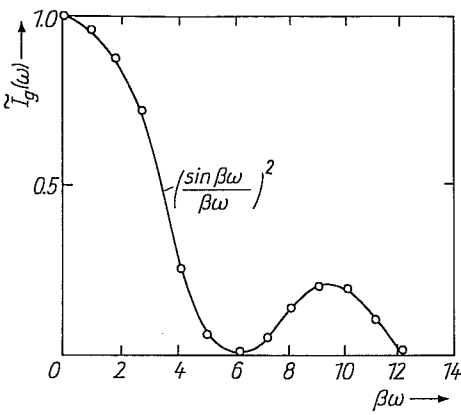


Fig. 2. Fourier transformation of the instrumental function of the monochromator

relations are given on Fig. 3. $I_{0\max} = \max [I_0(s)]$ (in arb. units) and $\sigma'_{I_0} = \sigma_{I_0}/I_{0\max}$; the standard deviation of $I_{0\max}$ is about 1% at $\beta' = \beta/c = 0.6$ (its absolute value does not depend upon β). It is known [4, 6] that the explicit form of the solution of (1) for $P(s)$ is difficult, associated with the instability of the solution due to the noisy signal $I_0(s)$. The level of the instability is different for various β . The maximal stability of the solution takes place at β where the relative noise is minimal. Let us demonstrate it on an example using $I_g(s)$ [from (3)] as an instrumental function.

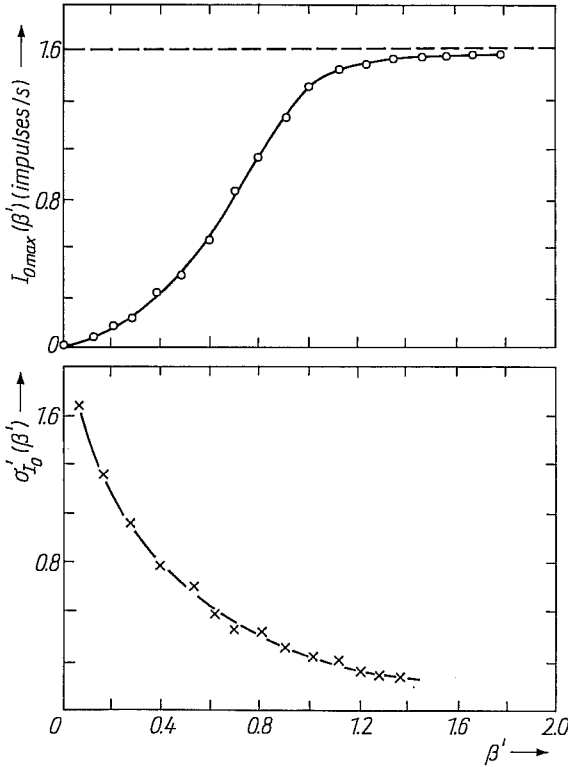


Fig. 3. The dependence of maximum signal value $I_{0\max}(\beta')$ and the relative signal value $\sigma'_{I_0}(\beta')$ on relative half-width of the instrumental function β'

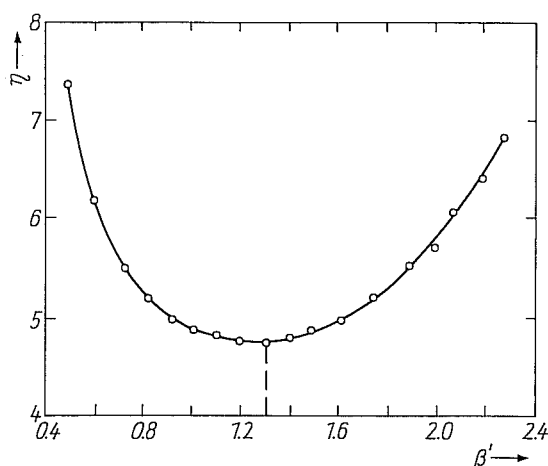


Fig. 4. The amplification coefficient dependence of irregularized error of solution η on parameter β' (for monochromator)

The square root of the standard deviation of the irregularized solution of (1) can be expressed with (3) as

$$\sigma_p = \sigma_{I_0} \left[\frac{1}{N} \sum_{j=N_1}^{N_2} \frac{1}{[\tilde{I}(\omega_j)]^2} \right]^{1/2}, \quad (5)$$

where N is the discrete number of the variable $S = 2\theta$ (θ is the Bragg angle) (for Fourier terms it is numbered by the frequencies ω): $N_1 = -N/2 + 1$; $N_2 = N/2 + 1$; $I_g(\omega_j)$ is the Fourier term which is the image of the instrument function $I_g(s)$ of the monochromator per Fourier frequency. The curve of the ratio $\eta = \sigma_p/\sigma_{I_0}$ versus the relative value of parameter β' is given in Fig. 4. The function has a minimum at some β' characterizing the most informative measuring mode.

There is a relatively large error for the irregularized solution to determine $P(s)$ from (1), so for better evaluation it is necessary to use a more convergent (stable) so-called regularization method [6]. Using the regularization method for the determination of $P(s)$, in addition of the above-mentioned factors other problems arise, too: to choose the type of stabilizing functional; to determine the value of the regularization parameter; the unknown solution of the distributive noise level; etc. [8 to 13]. However, the instability minimum can be obtained by the regularized solution. Let us measure the error of the regularized solution by $q(\beta)$ [6]

$$q(\beta) = \left\{ \sup_s [\gamma(s, \beta)]^2 + \sigma_p^2 \right\}^{1/2}, \quad (6)$$

where

$$\sigma_p^2 = - \int_{-\infty}^{\infty} \frac{\alpha M(\omega) \tilde{P}_T(\omega)}{[\tilde{I}_g(\omega)]^2 + \alpha M(\omega)} \exp(i\omega s) d\omega, \quad (7)$$

$$\sigma_p^2 = \int_{-\infty}^{\infty} \frac{[\tilde{I}_g(\omega)]^2 S(\omega)}{[\tilde{I}_g(\omega)]^2 + \alpha M(\omega)^2} d\omega, \quad (8)$$

where $\tilde{I}_g(\omega)$ and $\tilde{P}_T(\omega)$ are Fourier function images of $I_g(s)$ and of the accurate solution $P_T(s)$. $S(\omega)$ is the noise spectral density of the experimental curve, α the regularization parameter, $M(\omega)$ the stabilizing function [6, 12].

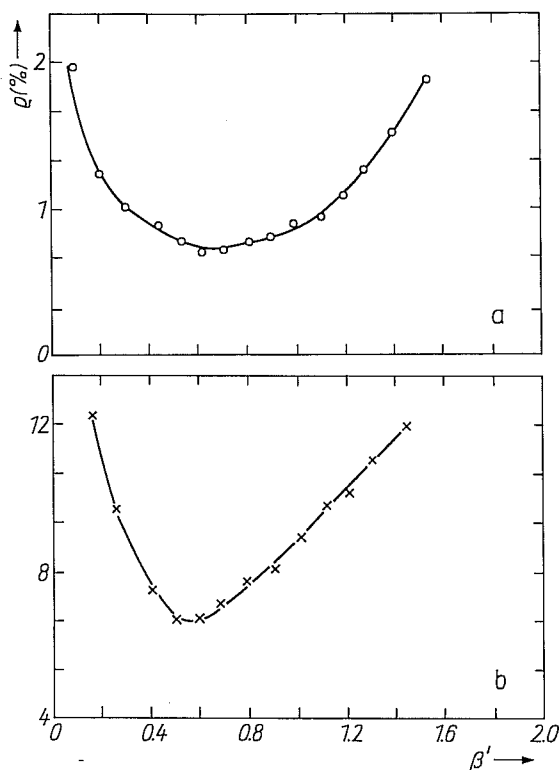


Fig. 5. The dependence of the measured error of the regularized solution on parameter β' from a) low and b) high noise level

Considering only the case, when $S(\omega) = \text{const}$ (white noise) and $M(\omega) = \omega^4$ (second-order stabilizer), a relation can be obtained for $q(\beta')$ (Fig. 5). The solution was expected as $P(s) = \exp(-s^2/2c^2)$ with half-width c . The noise level was selected from the following condition: at $\beta' = 0.5$ the experimental standard deviation should be a) 1% of $I_{0\text{max}}$ or b) 10% of $I_{0\text{max}}$. The regularization parameter α is characterized by the maximum of the a-posteriori density of the probability distribution α [8, 9]. The minimal error at the optimal $\beta' = \beta'_m$ value is presented in Fig. 5.

However, plotting such curves under real conditions is complicated by an unknown function $P_T(\omega)$

entering (7), but its determination is possible from (4).

The relation of error evaluation $\hat{q}(\beta)$ obtained from (4) as a result of such a substitution (for the instrumental function of the monochromator) is given in Fig. 6.

The iterative procedure was used for the search of the optimum β . It is concluded in the K -th step as

$$q^{(K)}(\beta) = \left\{ \sup_s [\gamma^{(K)}(s, \beta)]^2 + \sigma_p^2 \right\}^{1/2}, \quad (9)$$

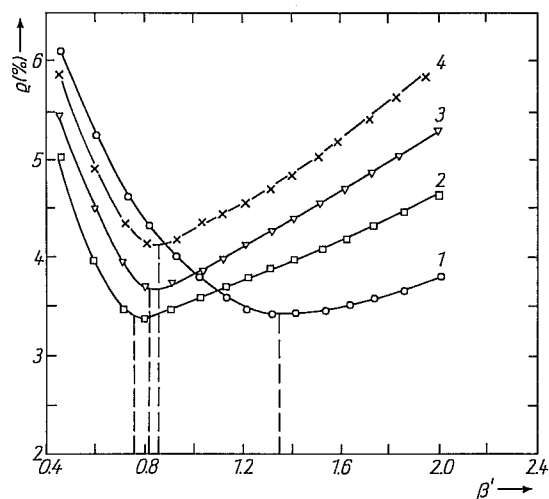


Fig. 6. The dependence of error evaluation (β') on different iteration steps ($K = 1, 2, 3, 4$)

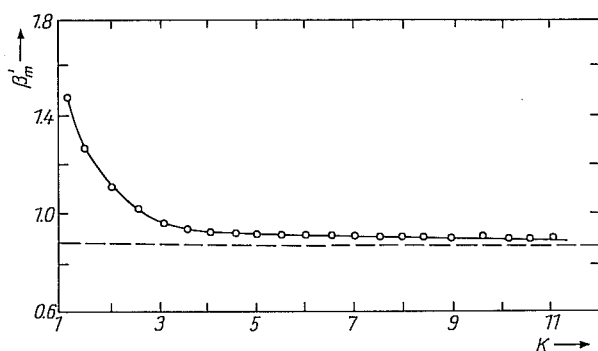


Fig. 7. The dependence of the minimum position $\beta'_m = \beta'$ on the iteration number K

where

$$\gamma^{(K)}(s, \beta) = - \int_{-\infty}^{\infty} \frac{\alpha M(\omega) [\tilde{P}_{\alpha}(\omega)_{\beta=\beta_m}^{(K-1)}]}{[\tilde{I}(\omega)]^2 + \alpha M(\omega)} \exp(i\omega s) d\omega \quad (10)$$

and $\beta_m^{(K-1)}$ is the minimum position of the curve $q^{(K-1)}(\beta)$ obtained in the $(K - 1)$ -st step. On Fig. 7 it is shown how $\beta^{(K)}$ is approaching the optimum value β_{mopt} (dashed line shows the changes caused by the increase of iteration step number K).

3. Conclusion

The optimal value of β_{mopt} for which the restoration error is minimum is investigated in this paper. The investigations testify the fact that a characteristic feature for diffractometers like the presence of occasional and systematic distortion factors is most informative in comparison to the majority of evaluation technics in X-ray investigations.

There is a possibility to determine by this method more accurately the unknown, true characteristics of X-ray diffraction patterns.

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