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Profile Analysis Application in the Modelling of Multiwave Diffraction

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Abstract

The results of intensity profile analysis of Bragg reflections are used for the calculation of the reflectivity $Q(\Delta\theta_{ij}, \sigma_{ij}) = W(\Delta\theta_{ij}, \sigma_{ij})(|F|^2\mathrm{Lp})_{ij}$ in the energy transfer equation for multiwave X-ray diffraction in crystals. The diffraction profiles in the profile analysis are fitted by different analytical functions and the fitting results are used for modelling the multiwave diffraction. The results of modelling multiwave diffraction in Si and V_3Si crystals with different grades of perfection demonstrate that the method suggested here is sensitive to the content of defects in crystals and can be used not only for simultaneous reflection correction in X-ray structure analysis but also for estimation of single-crystal perfection.

Theory of the method

The account of the simultaneous reflection effect is a very important problem in precise X-ray structure analysis of single crystals (Coppens, 1968; Lehmann, 1980) and numerous methods and computer programs based on modelling of multiwave diffraction in crystals have been suggested for its solution (*e.g.* Chernyshev, Nesterenko, Zhukov, Fetisov & Aslanov, 1988; Tanaka & Saito, 1975; Soejima, Okazaki & Matsumoto, 1985). The majority of existing theoretical models for multiwave X-ray diffraction in crystals are based on the approximate solution of the intensity transfer equation within the framework of kinematical diffraction theory (Caticha-Ellis, 1969; Chang, 1984). In the second-order approximation this equation for diffraction of N beams is written in the form

$$\Delta P = r\sum_{i=1}^{N}(-Q_{0i}Q_{0i} - Q_{0i}Q_{1i} + Q_{0i}Q_{i1}), \qquad (1)$$

where, following Chang (1984), ΔP is the change of the intensity flow of the primary reflection due to secondary reflections i, r is a factor describing the efficiency of scattering by a crystal and Q_{ij} is the reflectivity of the jth crystallographic plane for the ith beam (the $i-j$ reflection), which can be determined as

$$Q(\Delta\theta_{ij}) = W(\Delta\theta_{ij}, \sigma_{ij})(|F|^2\mathrm{Lp})_{ij}. \qquad (2)$$

$\Delta\theta_{ij}$ is the $i-j$-reflection deviation from the Bragg angle, $\sigma_{ij} = S\sigma_{ij-1} = S\sigma_{1-ij}$ is the peak-width parameter of the $i-j$ reflection and S is the parameter responsible for the width change in successive reflections; $(\mathrm{Lp})_{ij}$ is the Lorentz–polarization factor of the $(i-j)$th reflection and $|F_{ij}|$ is the structure factor of the reflection.

The function $W(\Delta\theta_{ij}, \sigma_{ij})$ depends on the mosaicity distribution in the crystal, which is usually unknown, and on the experimental conditions. For ideal crystals the distribution of mosaic blocks is described by the δ function and for ideal mosaic crystals by the Gaussian function (Post, 1976). But the situation is more complicated for real crystals with crystal lattice defects (Krivoglaz, 1983) where the mosaicity distribution can be described by different probability functions.

To find the $W(\Delta\theta_{ij}, \sigma_{ij})$ function in real crystals, considered in X-ray structure analysis, we have used mathematical modelling and fitting of the model to experimental reflection intensity profiles. The Bragg reflections with different *hkl* indices having rather high intensity were used for fitting. The fitting quality was estimated by the following values of the descrepancy factors:

$$R = \left(\sum_{l,m}^{K,N}||\xi_{lm}| - |I_{lm}||\right)/\sum_{l,m}^{K,N}|\xi_{lm}|, \qquad (3)$$

$$wR = \left[\sum_{l,m}^{K,N}w(|\xi_{lm}| - |I_{lm}|)^2/\sum_{l,m}^{K,N}w|\xi_{lm}|\right]^{1/2}, \qquad (4)$$

$$\mathrm{GOF} = \left[\sum_{l,m}^{K,N}w(|\xi_{lm}| - |I_{lm}|)^2/(NK-P)\right]^{1/2}, \qquad (5)$$

where ξ_{lm} and I_{lm} are the experimental and modelled reflection intensities on the mth step of the lth Bragg reflection intensity profile, respectively, $w_{lm} = 1/\sigma^2(\xi_{lm})$ is the statistical weight and P is the number of refined parameters. Possible anisotropy of the $W(\Delta\theta_{ij}, \sigma_{ij})$ function was taken into account in the intensity profile analysis by allowance for the σ_{ij} dependence on the *hkl* direction.

The profile analysis procedure used here is, in general, similar to that described in our book (Aslanov *et al.*, 1989).

In calculating ΔP in (1) we have assumed that the factor r characterizing the scattering efficiency of X-rays in a crystal takes into account the extinction

and absorption effects, but, in addition, parameter S was refined for each sample. The $(\mathrm{Lp})_{ij}$ values were calculated according to formulae taken from papers by Zachariasen (1965) and by Unangst & Melle (1975). The parameters of (1) were determined by minimization of the functional

$$\Omega = \sum_{l=1}^{N\psi} |Y_l - P_l|^2, \qquad (6)$$

where $Y_l = (|F_m|^2 \mathrm{Lp})_l$, $P_l = (|F_c|^2 \mathrm{Lp})_l + \Delta P_l$ and $|F_m|$ and $|F_c|$ are the experimental and theoretical values of structure factors, respectively; N_ψ is the number of steps in the experimental ψ-scan profile used for refining the r and S parameters.

Examples of application

The method suggested was used for modelling multi-wave diffraction in Si and V_3Si single crystals of different perfection. Small cubes were cut from large crystals and then ground to spheres of about 0·3–0·33 mm diameter in an air-driven crystal grinder. As the grinding resulted in an increase in the amount of dislocation and point crystal-lattice defects in the sample surface layer, all ground samples were etched in a boiling mixture of HF and HNO_3 (in the proportion 1:2) to make the distribution of defects homogeneous over the sample.

The reflection intensity measurements were done by $\omega/2\theta$ scans on a CAD-4 diffractometer with Mo $K\alpha$ radiation (the incident X-ray beam was graphite monochromated). The measurements were carried out just after grinding and then repeated after etching, so there were two data sets for each sample. The type and parameters of the $W(\Delta\theta_{ij}, \sigma_{ij})$ functions were determined from the refinements on the set of 36 reflection profiles measured in the range $\sin\theta/\lambda \leq 1{\cdot}21$ Å^{-1} and uniformly distributed in reciprocal space. The reflections measured with relative intensity measurement error less than 2·0% were

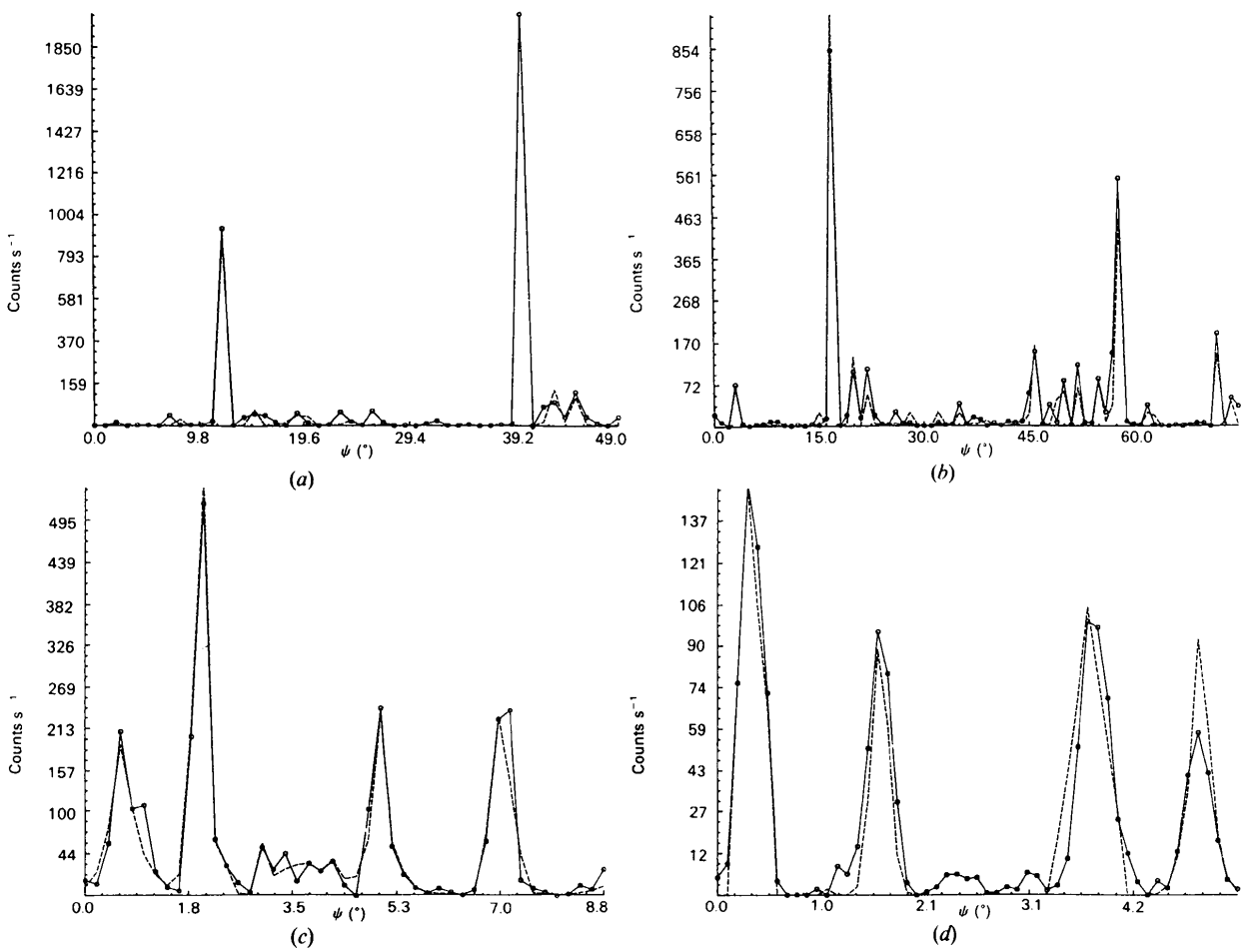

Fig. 1. The modelled and experimental profiles of azimuthal scanning of forbidden reflections. (*a*) The ground Si sample, reflection 402 (step of scan $\Delta\psi = 1°$); (*b*) the etched Si sample, reflection 402 ($\Delta\psi = 1°$); (*c*) the ground V_3Si sample, reflection $2\bar{1}2$ ($\Delta\psi = 0{\cdot}2°$); (*d*) the etched Si sample, reflection 212 ($\Delta\psi = 0{\cdot}1°$). Hollow circles indicate the measured intensity values, solid curves refer to the values interpolated over the experimental points and the dashed lines plot the corresponding modelled curves.

Table 1. *The values of statistical descriptors for reflection profile fitting of ground samples* (1) *and etched samples* (2)

The quantities underlined correspond to the 'best' model. The number of reflections in the refinement is 36 and the number of steps in the measured reflection profile is 96.

Sample	Function*	R (%)	wR (%)	GOF
Si (1)	G	11·24	18·18	3·66
	M	9·55	14·89	2·98
	I	12·22	16·91	3·41
	L	16·31	26·88	6·85
Si (2)	G	9·27	17·84	2·85
	M	12·86	17·61	3·11
	I	16·23	21·92	3·88
	L	19·73	27·72	5·18
V_3Si (1)	G	10·68	18·83	3·55
	M	9·21	12·70	2·64
	I	8·63	11·87	2·44
	L	15·39	15·91	3·91
V_3Si (2)	G	11·93	16·95	3·12
	M	18·53	24·79	4·56
	I	21·38	28·61	5·26
	L	26·83	36·06	6·63

* G = Gaussian, L = Lorentzian, M = modified Lorentzian and I = intermediate Lorentzian.

Table 2. *The values of statistical descriptors for modelling the ψ-scanning intensity profiles of forbidden reflections from the ground samples* (1) *and the etched samples* (2)

The quantities underlined correspond to the 'best' model. The number of reflections in the refinement is 36 and the number of steps in the measured reflection profile is 96.

Sample	hkl	N_ψ	Function	R (%)	wR (%)	GOF
Si (1)	402	50	G	25·61	27·23	7·48
			M	23·56	25·76	6·95
			I	20·67	22·67	6·47
			L	22·06	23·65	6·55
Si (2)	402	215	G	31·69	28·05	5·03
			M	33·08	29·01	5·21
			I	33·66	29·47	5·28
			L	35·09	30·53	5·48
V_3Si (1)	212	45	G	22·34	24·00	3·42
			M	20·98	22·69	2·86
			I	20·34	22·55	2·84
			L	19·54	22·67	2·86
V_3Si (2)	212	53	G	30·86	30·03	4·47
			M	32·29	30·79	4·86
			I	32·36	31·02	4·98
			L	33·07	31·82	5·02

* G = Gaussian, L = Lorentzian, M = modified Lorentzian and I = intermediate Lorentzian.

included in the data sets. The parameters of (1) were refined from 45 to 215 experimental points of ψ scanning. The reflection intensity profiles could be approximated by analytical functions, such as the Gaussian function (G), the Lorentzian function (L), the modified Lorentzian (M) and the intermediate Lorentzian (I) functions.

The results of the profile analysis for reflections from Si and V_3Si are presented in Table 1 for each case of surface preparation. Table 2 contains the values of the R factors and goodness of fit for modelling the ψ-scan profiles of forbidden reflections. The experimental and calculated profiles of ψ scans of forbidden reflections are shown in Fig. 1 and demonstrate a good coincidence of model and observation.

It follows from the tables that the models describing multiwave diffraction are different for crystals with and without a damaged surface layer. The crystals just after grinding are best fitted by Lorenzian functions, whereas for the etched crystal the $W(\Delta\theta_{ij}, \sigma_{ij})$ function is better described by the Gaussian function having a narrower spread. Ignorance of this fact can result in an error of 25% in the calculated ΔP quantities with the relative integrated intensity measurement error not exceeding 5%.

The sensitivity of the method described to crystal perfection allows the method to be used not only for simultaneous reflection correction in X-ray structure analysis but also for estimation of single-crystal perfection.

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