

A PEAKS ANALYSIS METHOD IN X-RAY POWDER DIFFRACTOMETRY

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ABSTRACT. — In order to enhance the mineralogical-crystallographic information available from an X-ray powder diffraction pattern, it is important to develop some methods which allow to reconstruct the experimental peak profile. As a contribute to this problem, in this paper we have tried to represent the maximum diffraction outline by suitable overlapping gaussian and exponential functions. This method is applied to some peaks belonging to different crystalline materials as quartz, silicon and fluorite. The parameters of the used functions appear to be related to the Bragg angle and the chemical-physical characteristics of the powder sample.

RIASSUNTO. — Per aumentare il numero di informazioni di natura mineralogico-cristallografica ottenibili da un diffrattogramma di polveri a raggi X, e per migliorare la loro qualità, si è cercato di rappresentare il profilo dei picchi di diffrazione mediante la sovrapposizione di gaussiane ed esponenziali. I valori dei parametri delle funzioni usate appaiono correlati con l'angolo di Bragg e con le caratteristiche chimico-fisiche del campione di polvere.

Introduction

In the last few years several researchers have tried to improve the quality of the information obtainable from an X-ray powder diffraction pattern. ALBERTI A. (1970), CROCHE R., GATINAU L. (1977), HALL M.M. (1977), KATTAK C.P., COX D.E. (1977), MORAWECK B. et al. (1977), YOUNG R.A. et al. (1977), DEHEZ R. et al. (1980), IMIRZI A. (1980), YOUNG R.A. (1980), COOPER M.J. et al. (1981), DE COURVILLE-BRENASIN et al. (1981), ALBINATI A., WILLIS B.T.M. (1982), ALLEGRA G. (1982), IMMIRZI A., PORZIO W. (1982), NAIDU

S.V.N., HOUSKA C.R. (1982). In this study it results of fundamental importance to develop some methods that allow to take account of instrumental effects, deriving mainly from the apparatus geometry, in order to enhance resolution as well as to better quantify some physical and crystallographic properties of crystalline powdered sample (size of the crystalline coherent domains, distribution of crystallite size, nature and extent of lattice imperfections).

The instrumental factors cause a pure profile to be more or less asymmetrical, broadened and displaced from its theoretical 2θ angle.

A complete and exhaustive discussion of the role of the geometry to produce aberrations in a pure diffraction profile is given by KLUG H.P. and ALEXANDER L.E. (1974) who also treat the influence of several instrumental factors in a quantitative way. However a rigorous mathematical approach to take account of specific instrumental and physical aberrations results generally rather difficult to apply in routine X-ray powder diffraction analysis. Such a difficulty is evident from the lack of sufficient experimental data from literature relative to peak profile analysis performed on crystalline phases of different nature.

From a practical point of view, to overcome such a problem, various attempts have been made to represent the peak profile of a powder diffraction pattern through analytical functions (gaussian, cauchy, modified lorentian with variable coefficient, used

separately or combined among them in different way; IMMIRZI A. (1980), ALBINATI A. e WILLIS B.T.M. (1982). Nevertheless owing to the asymmetrical broadening of the peak caused by some instrumental function, chiefly at low 2θ angles, at present, no adequate solution have been given to the problem. In this paper we report the experimental results of a study concerning the line profile analysis of peaks belonging to some crystalline phases as silicon, fluorite and quartz. The aim of this work is to show that the experimental line profile of a peak may be performed by a suitable overlapping gaussian and exponential functions, in a high resolution powder diffractometry.

Methods

The utilized function to describe the line profile of a powder diffraction peak is:

$$Y(x) = k e^{-b|x-h|} + I_{G\max} e^{-d(x-c)^2} + B \quad (1)$$

where: $b > 0$, $d > 0$,

$$d = \frac{1}{2\sigma^2}, \quad c = 2\theta_{\max}$$

and:

$$\text{for } x < a_r \quad \begin{cases} b = b_l \\ h = h_l \\ k = k_l \end{cases}$$

$$\text{for } x > a_r \quad \begin{cases} b = b_r \\ h = h_r \\ k = k_r \end{cases}$$

$$\text{for } a_l \leq x \leq a_r \quad k = 0$$

a_l and a_r are the x values within which the gauss function is sufficient to fit by itself the peak profile; σ represents the parameter which describes the breadth of the gaussian. The peak function is the overlapping of two exponentials (taken at right and left from the maximum of the peak) and a gaussian. Being each analytical function fully defined by knowing three parameters, as whole nine ones are necessary to describe the peak. The parameter B may be independently determined from intensity measurements and its value must be confirmed by goodness of the least square method used to fit the experimental data.

The parameter values which define the peaks line profile function were determined by a least square fitting method minimizing the following function.

$$\chi^2 = \sum_i W_i [Y(x_i)_{\text{obs.}} - Y(x_i)_{\text{calc.}}]^2 \quad (2)$$

where x_i is the 2θ angle, $Y(x_i)$ the measured intensity N_i at $2\theta_i$ and $W_i = 1/N_i$ is the statistical weight associated with the observed value.

Experiment

The intensities of the peak profiles for silicon, fluorite and quartz were measured with a PW1730 Philips automatic X-ray diffractometer on line with an Olivetti P6066 personal computer. The geometry of the apparatus is the usual one employed in the conventional X-ray diffractometers; the ours was equipped with a graphite AMR3-202

TABLE 1
Instrumentals conditions (*)

Phase	index	d	2θ	I_{\max}	Div.slite	Foc.slite mm
Silicon	111	3.135	25.67	13104	1°	0.2
Silicon	311	1.637	50.30	6826	1°	0.2
Silicon	531	0.918	98.56	4988	4°	0.2
Quartz	110	2.457	32.90	3344	1°	0.2
Fluorite	111	3.153	25.52	10501	1°	0.2
Fluorite	311	1.647	49.98	3035	1°	0.2

(*) The X-ray diffractometer was equipped with two series of Soller slits.

GVW7038 focusing monochromator. Measurements were performed with the instrumental conditions reported in tab. 1.

Each reflection was collected by using the $\text{CuK}\alpha$ radiation (40 KV, 20 ma) and sampling 1.28° 2θ wide range ($\pm 0.64^\circ$ from the maximum of the peak) with a scanning step of 0.02° . A broad focus X-ray tube was used and its projected focal spot dimension was 0.2×12 mm (take off angle = 6°).

The counting time was chosen in such a way to make acceptable the statistical counting error. The figures from 1 to 5 show for each analyzed reflection the pure functions utilized to reconstruct the peak profile (gaussian and exponential) together with the observed and calculated line profiles. Owing

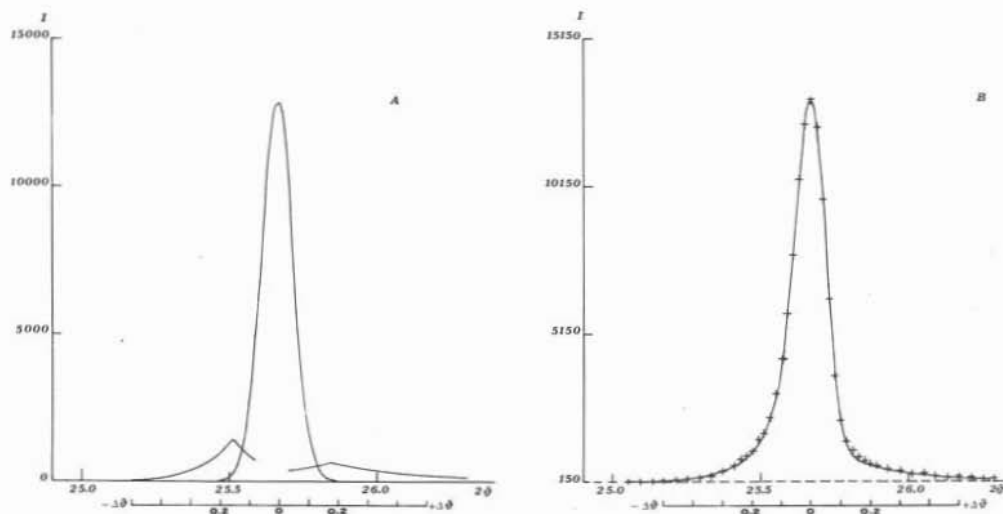


Fig. 1. — Silicon 111 peak profile. A: pure functions utilized to perform the peak; B: observed (crosses) and calculated (continue lines) peak profiles.

to a greater clearness of drawing, the tails of each peak have been represented only with half of experimental data with the exception of the fluorite line profile (fig. 5).

In tab. 2, for each peak, the parameters values of the gauss and exponential functions are reported; in this table are also reported the χ^2 values as they result from equation (2). To evaluate the agreement between observed and calculated line profile the χ^2 values must be compared with 64 or 256 resulting from the following relation:

$$\chi^2 = \sum_{i=1}^{64} \frac{a_i^2}{N_i}$$

according as we assume the statistical counting error a_i equal to $\sqrt{N_i}$ or $2\sqrt{N_i}$ respectively; 64 is the number of experimental data and N_i the measured intensity at ($2\theta_i$).

Discussion and conclusion

From the experimental data it results that the line profile of an X-ray powder diffraction peak may be performed by using two exponentials and one gaussian. Thence nine parameters have to be determined to define such functions. However as far as the gaussian is concerned, the experimental data suggest that such a function may be represented by knowing only one parameter. In fact the $2\theta_{max}$ and the I_{max} values of the gaussian coincide with the $2\theta_{max}$ and the I_{max} of the peak respectively within the experimental errors. Thus it seems sufficient to define the gauss function through the σ parameter alone. From the collected data, it emerges that such a parameter increases with the increasing of diffraction angle for a specific crystalline phase (table 2). When the three reflections of silicon are considered over a range of 25° - 100° the breadth of the

TABLE 2

Y Function's parameters (fit on 64 points)

	Si1. (111)	Si1. (311)	Si1. (531)	Qz (110)	Fl. (111)	Fl. (311)
I_{Gmax}	13057	6561	4988	3318	10501	3036
	5.4	6.16	8.05	5.11	5.88	6.51
$2\theta_{max}$	25.66	50.30	98.56	3290	25.50	49.97
b_1	0.09	0.05	0.07	0.07	0.09	0.06
I_1	1510	720	711	391	1477	517
h_1	25.52	50.15	98.38	3278	25.35	49.81
b_r	0.033	0.042	0.055	0.033	0.040	0.055
I_r	644	559	637	276	843	565
h_r	2.85	50.47	98.74	33.02	25.68	50.14
bkg	149	154	320	120	100	130
χ^2	218	133	162	118	256	103

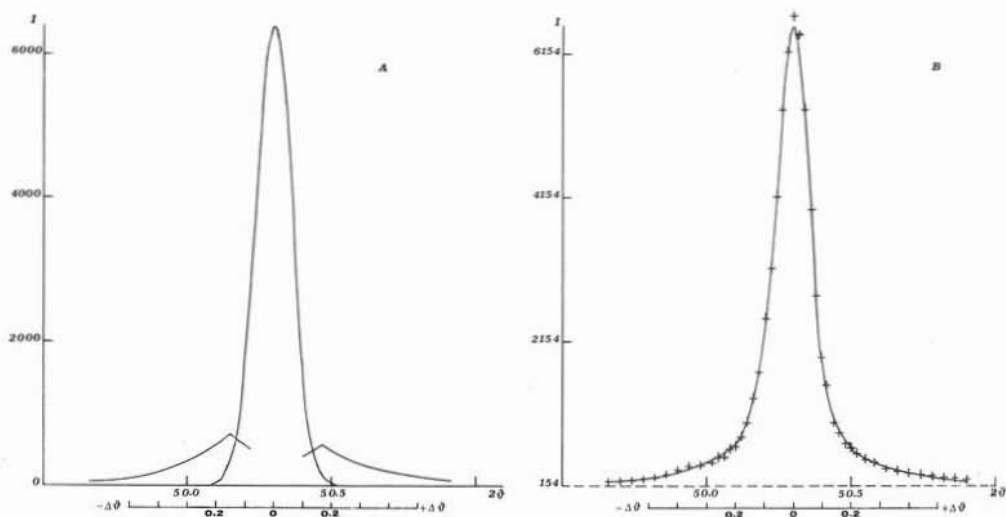


Fig. 2. — Silicon 311 peak profile. *A*: pure functions utilized to perform the peak; *B*: observed (crosses) and calculated (continue lines) peak profiles.

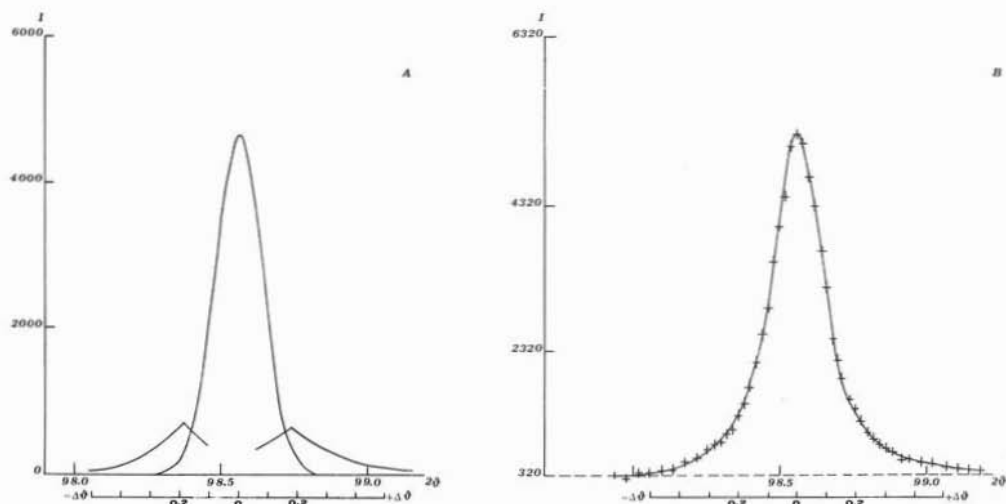


Fig. 3. — Silicon 531 peak profile. *A*: pure functions utilized to perform the peak; *B*: observed (crosses) and calculated (continue lines) peak profiles.

gauss function was found to be related to the 2ϑ angle by the following relation:

$$\sigma(2\vartheta) = K + K_1 \operatorname{tg} \vartheta \quad (4)$$

where K and K_1 are two constants and ϑ the Bragg's angle. The values of these constants, as determined by a least square regression are 0.0477 and 0.0283 respectively. The experimental values of $\sigma(2\vartheta)$ and those calculated from the equation (4)

are reported.

$2\vartheta^\circ$	$\sigma(2\vartheta) \times 10^{-2}$	
	<i>obs.</i>	<i>calc.</i>
25.67	5.4	5.42
50.30	6.16	6.11
98.56	8.05	8.07

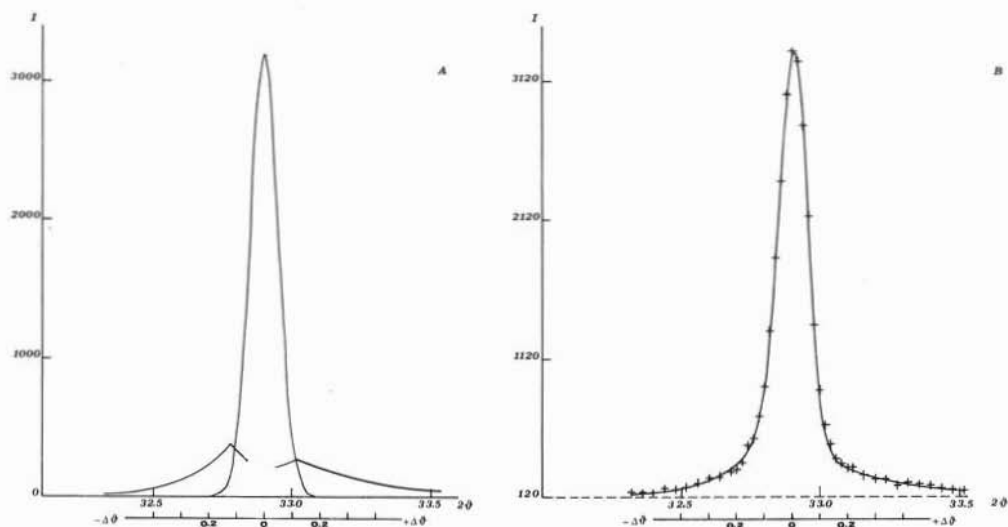


Fig. 4. — Quartz 110 peak profile. A: pure functions utilized to perform the peak; B: observed (crosses) and calculated (continue lines) peak profiles.

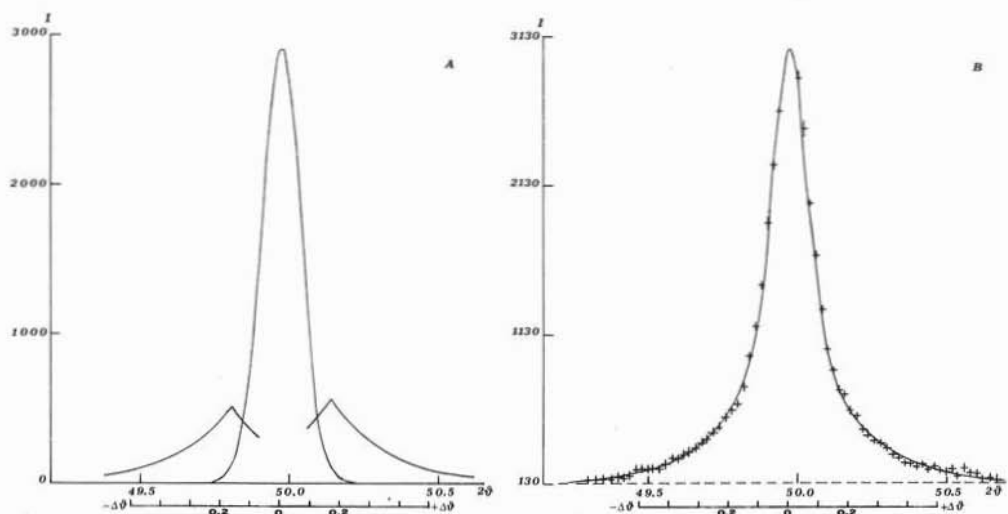


Fig. 5. — Fluorite 311 peak profile. A: pure functions utilized to perform the peak; B: observed (crosses) and calculated (continue lines) peak profiles.

The k constant depends on several instrumental factors and presumably on the physical and crystallographic characteristics of the powder sample. On other hand the K_1 constant depends on the wavelength and presumably on the dimension of the focal spot H . According to Bragg's relation it results infact that the broadening of the gaussian function is given by:

$$\Delta 2\vartheta = \frac{H}{\lambda} \operatorname{tg} \vartheta \quad \text{where:} \quad \frac{H}{\lambda} = K_1$$

In the diagram of fig. 6 the left and righth exponentials of the three reflections of the silicon are showed. In order to compare the contribute to the peak profile of the two exponentials, with respect to that given by

the gaussian, the intensity values of the exponentials were normalized to the maximum intensity of gaussian and then expressed as I_e/I_{Gmax} . Such normalized intensities have been plotted against $\Delta 2\theta$ values which were computed as differences with respect to the 2θ value of the maximum of the gauss function. From the data depicted in fig. 6 it results a low but not negligible contribute of the exponential to the peak profile. It also emerges that the peak profile may be represented in the range of $\pm 0.06 \div 0.10$ degree ($\Delta 2\theta$) with respect to its maximum by a gaussian alone.

As to the parameters values of exponentials, the diagram of fig. 6 reveals that those of the left exponential approach the ones of the right exponential as the Bragg angle increases. This behaviour, which contributes to render more symmetric the peak with the increasing of the 2θ value, is in a good agreement with the literature data (KLUG and ALEXANDER, 1974). In particular, among the various functions which contribute to form the peak profile, that one due to the axial divergence is certainly the most important; such an instrumental function, that seems to influence in a determinant way the peak shape in the tails of a maximum diffraction at low angles, shrinks with the increasing of 2θ until its influence is near zero in the range $90^\circ < 2\theta < 120^\circ$ (KLUG and ALEXANDER, 1974).

By using the same type of representation as in fig. 6 the left and right exponentials of silicon and fluorite are compared (fig. 7 and fig. 8). Such materials were chosen because their diffraction patterns contain a couple of reflections which fall approximately at the same Bragg angle ($2\theta = 25.67^\circ$ and $2\theta = 50.30^\circ$ for silicon and $2\theta = 25.52^\circ$ and $2\theta = 49.98^\circ$ for fluorite).

As regards to the two peaks of fluorite, fig. 7 and 8 show a relationship, between the parameters of the left and the right exponentials and the Bragg angle similar to that observed for silicon. Infact with the increasing of 2θ the parameter values of the left exponential approach closely those of the right one.

On the other hand by comparing the parameter values of the exponentials relative to peak of silicon and fluorite occurring

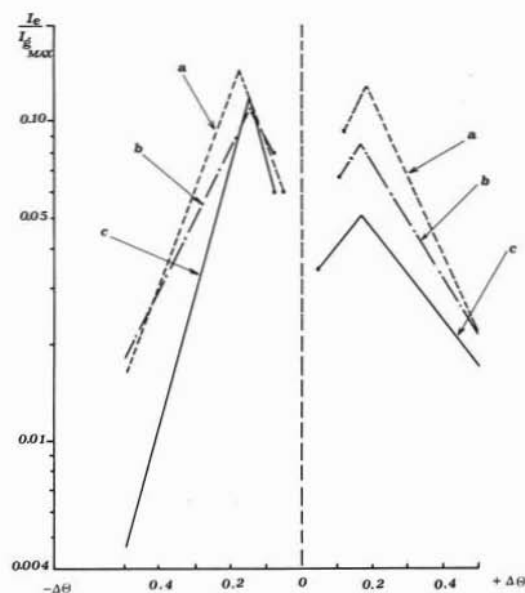


Fig. 6. — Diagram showing the right and left exponentials related to the silicon's peak profiles. a: 531 reflection ($2\theta = 98.56^\circ$); b: 311 reflection ($2\theta = 50.30^\circ$); c: 111 reflection ($2\theta = 25.67^\circ$).

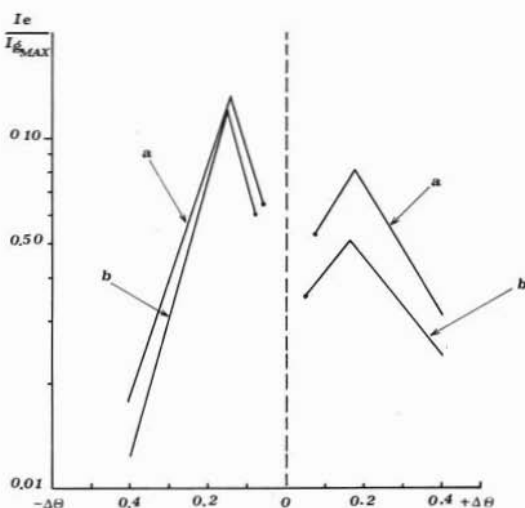


Fig. 7. — Diagram showing the right and left exponentials related to the reflections of fluorite (a) and silicon (b) at 2θ of about 50° .

approximately at same 2θ angle some substantial differences are evident.

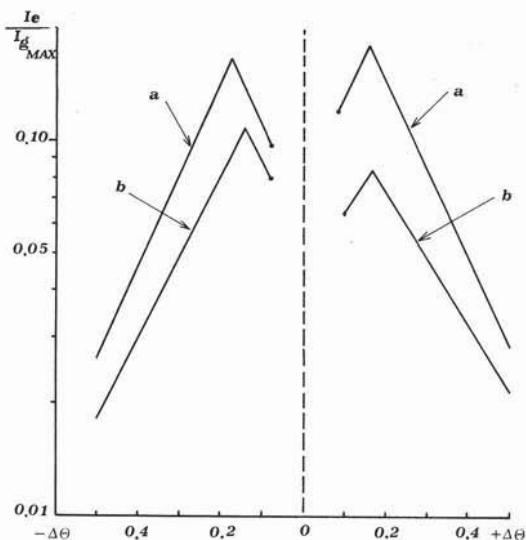


Fig. 8. — Diagram showing the right and left exponentials related to the reflections of fluorite (a) and silicon (b) at 2θ of about 50° .

In particular while the slope and $2\delta_{\max}$ of left and right exponentials for both the couples of peaks assume a similar values, the

intensity contribute given by exponentials to peaks profile, on the contrary, seems somewhat greater for fluorite than for silicon. Tentatively we may think to impute such a different behaviour to the lower absorption coefficient of silicon for the $\text{CuK}\beta$ radiation.

The experimental data collected in this preliminary study point out clearly that, within the measurements error, the line profile of an X-ray powder diffraction peak can be satisfactorily represented by unsophisticated analytical functions like gaussian and exponentials. Even if the number of parameters used seem to be high (nine parameters are required to define a peak profile on the whole) we think that this number may be lowered since some of them are presumably reciprocally related.

Furthermore, it seems to be of particular interest the existence of relationships between the parameters values of the employed functions and the Bragg angle. Some of them result well defined, while others have to be still defined quantitatively. Such considerations induce us to hope that the approach we have followed may be susceptible of improvements as well as of further developments.

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