Considerations about the variability of the Bragg's law fulfilment

L. Pérez-Arrieta and C. Tabares-Muñoz
Instituto de Física "Luis Rivera Terrazas", Universidad Autónoma de Puebla,
Apartado postal J-48, 72570 Puebla, Pue., México,
e-mail: tabares@sirio.ifuap.buap.mx

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On working with an X-ray powder diffractometer, due to practical difficulties, the surface of the specimen some times is not accurately placed on the working plane of the goniometer. This disagreement produces an asymmetric broadening of the diffraction line profile, and also a shift in the peaks positions. In this work we expose some considerations about the way each diffracted beam fulfils the Bragg's law, addressed to its possible application for correcting the 2θ shifts caused by the specimen-displacement error of polycrystalline samples.

Keywords: X-ray diffraction; polycrystals.

Al trabajar con un difractómetro de rayos X para polvos, algunas veces, debido a dificultades prácticas, la superficie de la muestra no queda colocada con precisión en el círculo focalizador del goniómetro. Este error produce un ensanchamiento asimétrico del perfil del pico difractado, así como un desplazamiento de las posiciones de los picos. En este trabajo exponemos algunas consideraciones acerca de la manera característica con que cada haz difractado cumple la ley de Bragg, para su posible aplicación en la corrección, en difractogramas de muestras policristalinas, de los desplazamientos angulares causados por el desplazamiento de la muestra.

Descriptores: Difracción de rayos X; policristales.

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1. Introduction

The quality of X-ray measurements depends on several factors; among them we can find:

a) the specimen quality [1,2],

b) the specimen preparation [3],

c) the specimen holder [4], and

d) the geometry deviations [5].

In connection with the last factor, we find the flat-specimen error and the specimen-displacement error; these two errors cause asymmetric broadening of the diffraction line profile towards low 2θ angles.

The specimen-displacement error additionally causes a shift in the peaks positions, which can significatively complicate the symmetry determination process, particularly in the cases of low symmetry specimens. Generally, these 2θ shifts are corrected by displacing the diffraction pattern as a whole to the most convenient position, which is determined by using an internal standard; but displacing the diffraction pattern in this way, one can not bring the complete set of the standard's peaks into coincidence with the reported 2θ positions for it; only one experimental peak can be brought into very good agreement, while the rest of them come only into an approximate agreement.

The specimen-displacement error occurs because the surface of the sample is not co-concentric with the goniometer focusing circle, due to practical difficulties in accurately placing the sample at this level. According to Ron Jenkins [5], the flat-specimen error and the specimen-displacement error have respectively the following forms:

a) $\Delta 2\theta$ = - $(1/6)\alpha^2 \cot\theta$, in which α is the angular aperture of the divergence slit, and

b) $\Delta 2\theta$ = - $2s\,(\cos\theta/R)$, where s is the displacement of the specimen from the focusing circle, and R is the goniometer radius.

This error gives an absolute shift in 2θ peak position, which amounts approximately 0.01^o 2θ per each 15 μm displacement.

2. Development

The Bragg equation

$$n\lambda = 2d\sin\theta \tag{1}$$

can be used to obtain a wide set of related angular values by using a specific value of the wavelength (λ_1) and a series of values $N\lambda_1$ where N = 0.1, 0.2, 0.3, ... 0.9, 1.0, 1.1, 1.2.... On doing so, the Bragg equation takes the form

$$nN\lambda_1 = 2d\sin\theta, \tag{2}$$

whence we can calculate the 2θ angles for the first order (n=1) maxima by means of the following expression:

$$2\theta = 2\arcsin\left(\frac{1*N\lambda_1}{2d}\right). \tag{3}$$

By applying Eq. (3) to the (111) Silicon planes ($d_{(111)}$ = 3.1354 Å), using λ_1 = 1.541783 Å, we obtain the set of values shown in Table I.

TABLE I. Calculated angular values 2θ for beams diffracted by Si (111) planes as function of λ.

N	Nλ_1	2θ	2θ /N
0.2	0.308356	5.637	28.185
0.4	0.616713	11.288	28.220
0.6	0.925070	16.966	28.277
0.8	1.233426	22.687	28.359
1.0	1.541783	28.466	28.466
1.2	1.850139	34.320	28.600
1.4	2.158496	40.267	28.763
1.6	2.466853	46.331	28.957
1.8	2.775209	52.535	29.286
2.0	3.083566	58.909	29.454
3.0	4.625349	95.055	31.685

The third column shows that, in principle, we can direct the beams diffracted by one family of planes, along a direction having the angular value of our choice, if we can modify accordingly the wavelength value. Figure 1 shows this idea, applied to various Silicon planes families; here, we can see that each one of these curves has its own slope, in other words, we can say that: each curve has its own way of obeying the Bragg's law and it is for this reason that one cannot correct properly the diffraction pattern just by displacing it in the 2θ direction in one movement.

From this, it turns out, that to correct a diffraction pattern, we must perform the process one peak at a time.

The last column of Table I, corresponding to the "normalized" angular values $(2\theta)/N$, shows also that there is not a linear dependence between 2θ and λ. Figure 2 illustrates the behavior of these "normalized" angular values, which in the case of the beams diffracted by the (111) family planes present a small deviation that suggests a small angular error on displacing the diffraction pattern in the 2θ direction, but this same displacement will correspond to a bigger error in the cases of beams diffracted by other planes families, even in this "normalized" situation.

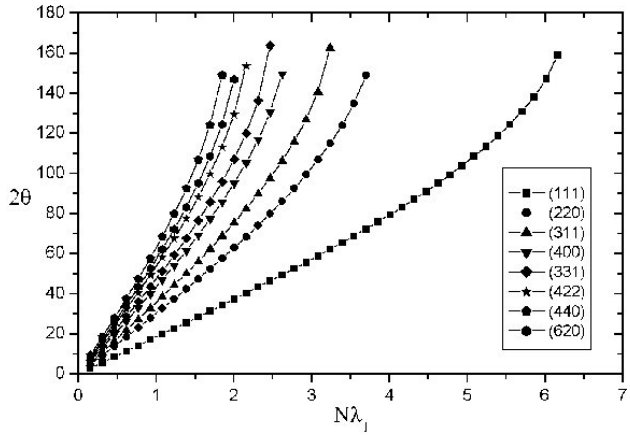

FIGURE 1. Calculated angular values 2θ for beams diffracted by various families of silicon planes, as function of λ.

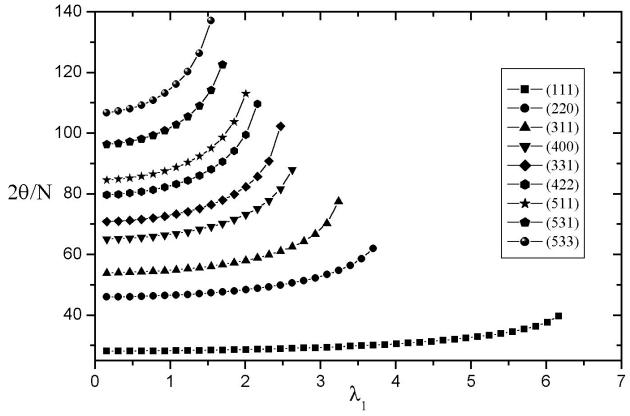

FIGURE 2. Normalized angular values $2\theta/N$, of a set of silicon family planes as function of λ_1.

In practice, to correct the diffraction pattern line by line, we encounter two main difficulties to find out the behavior of each diffracted beam as function of λ. The first one is the difficulty of changing the wavelength value, the second one is that we need to know the values of the specimen's interplanar spacings.

However, we can avoid these two problems (λ and d), using the following system of equations:

$$(a) \quad n\lambda_1 = 2d\sin\theta_1,$$
$$(b) \quad n\lambda_2 = 2d\sin\theta_2, \tag{4}$$

in which we can express λ_2 as Q times λ_1; doing so, we obtain

$$(a) \quad n\lambda_1 = 2d\sin\theta_{\lambda_1},$$
$$(b) \quad nQ\lambda_1 = 2d\sin\theta_{Q\lambda_1}. \tag{5}$$

The solution of the system of Eqs. (5) is

$$Q = \frac{\sin\theta_{Q\lambda_1}}{\sin\theta_{\lambda_1}} \tag{6}$$

Applying this equation to the internal standard, for which we have both, the set of experimental diffraction angles θ_{λ_1} and the reported (PDF) $\theta_{Q\lambda_1}$, we obtain a set of correction factors $\sum Q_{std}$, for which we can find a mathematical expression as a function of 2θ; this expression is the correction function wich allows us to find the correction factor Q_s for a given 2θ value, which can be the angular value of a specimen's peak.

Rearranging Eq. (6), we obtain

$$2\theta_{Q\lambda_1} = 2\arcsin(Q * \sin\theta_{\lambda_1}). \tag{7}$$

By means of this equation we can find the corrected angular position $2\theta_{Q\lambda_1}$ of the specimen's diffracted beams. Let us evaluate Eq. (7), with a known specimen like Silicon, which is widely used as internal standard for correcting experimental diffraction patterns, for this it is useful to build up Table II.

TABLE II. This table shows the experimental values 2 θ_{λ_1} of a Silicon specimen (using λ = 1.54056 Å), the extended reported values $2\theta_{PDF}$, the correction factors Q and the corrected values 2 $\theta_{Q\lambda_1}$.

hkl	$2\theta_{\lambda_1}$	$2\theta_{PDF}$	Q	$2\theta_{Q\lambda_1}$
111	28.440	28.4421748058	1.00007489321	28.4421748056
220	47.275	47.3022578510	1.00054346388	47.3022578512
311	56.083	56.1205290628	1.00061481484	56.1205290628
400	69.105	69.1301411514	1.00031857611	69.1301411516
331	76.341	76.3771771120	1.00040156479	76.3771771120
422	87.990	88.0261167604	1.00032638390	88.0261167602

In Table II, we can see that the corrected values given in the fifth column coincide with high accuracy with the extended values in the third column obtained from data reported in the PDF for Silicon.

3. Conclusion

From an experiment for which we mix carefully the specimen with a standard material, we obtain the angular positions of the beams diffracted by the standard. Using these values in equation (6), together with the reported values for the standard, we obtain a set of correction factors Q_{std}. These are used to obtain an equation or correction function which is solved to get the correction factors Q_{spec} for each experimental value $2\theta_{\lambda_1}$ of the specimen. These two values allows us to solve Eq. (7) to obtain the set of corrected values $2\theta_{Q\lambda_1}$ for the specimen.

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