Considerations about the variability of the Bragg’s law fulfilment

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Recibido el 9 de mayo de 2002; aceptado el 25 de septiembre de 2003

On working with an X-ray powder diffractometer, due to practical difficulties, the surface of the specimen sometimes 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 $2\theta$ shifts caused by the specimen-displacement error of polycrystalline samples.

Keywords: X-ray diffraction; polycrystals.

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 $2\theta$ 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 $2\theta$ 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 $2\theta$ 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 $\alpha$ 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 $2\theta$ peak position, which amounts approximately 0.01° $2\theta$ per each 15 $\mu$m displacement.

2. Development

The Bragg equation

$$ n\lambda = 2d\sin \theta $$

(1)

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

$$ nN\lambda_1 = 2d\sin \theta, $$

(2)

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

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

(3)

By applying Eq. (3) to the (111) Silicon planes ($d_{(111)} = 3.1354$ Å), using $\lambda_1 = 1.541783$ Å, we obtain the set of values shown in Table I.
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 $2\theta$ 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 $2\theta$ and $\lambda$. 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 $2\theta$ 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.

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 $\lambda$. 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 ($\lambda$ and $d$), using the following system of equations:

\begin{equation}
\begin{array}{l}
n\lambda_1 = 2d\sin\theta_1,
\end{array}
\end{equation}

\begin{equation}
\begin{array}{l}
n\lambda_2 = 2d\sin\theta_2,
\end{array}
\end{equation}

in which we can express $\lambda_2$ as $Q$ times $\lambda_1$; doing so, we obtain

\begin{equation}
\begin{array}{l}
n\lambda_1 = 2d\sin\theta_1,
\end{array}
\end{equation}

\begin{equation}
\begin{array}{l}
nQ\lambda_1 = 2d\sin\theta_{Q\lambda_1}.
\end{array}
\end{equation}

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

\begin{equation}
Q = \frac{\sin\theta_{Q\lambda_1}}{\sin\theta_1}.
\end{equation}

Applying this equation to the internal standard, for which we have both, the set of experimental diffraction angles $\theta_1$ 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 $2\theta$; this expression is the correction function which allows us to find the correction factor $Q_1$ for a given $2\theta$ value, which can be the angular value of a specimen’s peak.

Rearranging Eq. (6), we obtain

\begin{equation}
2\theta_{Q\lambda_1} = 2\arcsin(Q \times \sin\theta_1).
\end{equation}

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.

\begin{table}
\centering
\caption{Calculated angular values $2\theta$ for beams diffracted by Si (111) planes as function of $\lambda$.}
\begin{tabular}{|c|c|c|c|}
\hline
$\lambda$ & $2\theta$ & $n\lambda_1$ & $N\lambda_1$ \\
\hline
0.2 & 5.637 & 0.308356 & \\
0.4 & 11.288 & 0.616713 & \\
0.6 & 16.966 & 0.925070 & \\
0.8 & 22.687 & 1.233426 & \\
1.0 & 28.466 & 1.541783 & \\
1.2 & 34.320 & 1.850139 & \\
1.4 & 40.267 & 2.158496 & \\
1.6 & 46.331 & 2.466853 & \\
1.8 & 52.535 & 2.775209 & \\
2.0 & 58.909 & 3.083566 & \\
3.0 & 95.055 & 4.625349 & \\
\hline
\end{tabular}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{Calculated angular values $2\theta$ for beams diffracted by various families of silicon planes, as function of $\lambda$.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{Normalized angular values $2\theta/N$, of a set of silicon family planes as function of $\lambda$.}
\end{figure}
TABLE II. This table shows the experimental values $2\theta_\lambda$, of a Silicon specimen (using $\lambda = 1.54056 \, \text{Å}$), the extended reported values $2\theta_{PDF}$, the correction factors $Q$ and the corrected values $2\theta_{Q\lambda}$.

<table>
<thead>
<tr>
<th>hkl</th>
<th>$2\theta_\lambda$</th>
<th>$2\theta_{PDF}$</th>
<th>$Q$</th>
<th>$2\theta_{Q\lambda}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>28.440</td>
<td>28.4421748058</td>
<td>1.00007489321</td>
<td>28.4421748056</td>
</tr>
<tr>
<td>220</td>
<td>47.275</td>
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<td>1.00054346388</td>
<td>47.3022578512</td>
</tr>
<tr>
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<td>56.083</td>
<td>56.1205290628</td>
<td>1.00061481484</td>
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<tr>
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<td>69.1301411514</td>
<td>1.00031857611</td>
<td>69.1301411516</td>
</tr>
<tr>
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<td>76.341</td>
<td>76.3771771120</td>
<td>1.00040156479</td>
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</tr>
<tr>
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<td>87.990</td>
<td>88.0261167604</td>
<td>1.00032638390</td>
<td>88.0261167602</td>
</tr>
</tbody>
</table>

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 $2\theta_\lambda$ of the specimen. These two values allows us to solve Eq. (7) to obtain the set of corrected values $2\theta_{Q\lambda}$ for the specimen.

Acknowledgments

We thank Dr. Raúl Brito Orta for his valuable suggestions. This work has been supported by CONACyT (Mexico). Grants: 3438E and E9212.