CALCULATED POWDER X-RAY DIFFRACTION LINE PROFILES

VIA ABSORPTION

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ABSTRACT

We have calculated powder X-ray diffraction (PXRD) line profiles based on the absorption of X-rays in passing through materials. The results showed that the line profile function depends on the absorption coefficient of the sample. The observed aluminum PXRD patterns are in excellent agreement with the calculated line profile functions derived from absorption. This work also demonstrated that both Cauchy and Gauss profile fitting functions are the approximation of the calculated line profile obtained in this paper.

INTRODUCTION

PXRD pattern provides a lot of information of a crystalline sample. It is well known that, if the crystal structure is known, the interplanar spacing, \( d \), of a crystalline sample can be calculated via the Bragg’s equation and the peak intensity can be calculated by the intensity theory. However, the line profile, or the line shape, cannot be predicted by any theory even for an ideal case. This is probably due to the XRD theory that the line profile of an ideal sample, collected on an ideal instrument, does not have a defined shape, but the Dirac delta function, i.e., the intensity line would have an infinitely small angle distribution and very strong intensity at exact Bragg angle.

However, so far, there is no experimental evidence showing the delta-function line profile. In other words, all observed diffraction peaks have the non-zero width; usually, for most common XRD instruments, an observed peak has the width of 0.1 degree in full width at half maximum (FWHM). Up to our knowledge, the observed delta-function-like peak has not been reported.

About one hundred years ago, Scherrer (Scherrer, 1918) discussed line profile mediated by the finite size of the powder sample, and the famous Scherrer formula provides the relationship between the observed FWHM and the crystallite size of the crystalline sample. Shortly after Scherrer’s work, Laue (Laue, 1926) considered the case of crystallites having the form of a parallelepiped and introduced the general form of the integral breadth, and also used Cauchy and Gaussian functions to model line profiles for the first time.
In the real cases, the PXRD line profile will be broadened by the imperfect experiment and sample conditions. These conditions can be the imperfection of a crystalline sample, such as its small size (less than 25 microns, for example) and the dislocations in the crystals; the sample residual stress has been shown to cause the broadened as well (Guinier, 1963). It is well known that the imperfectly designed diffractometer is another source for PXRD line broadening. However, in principal, all imperfections can be eliminated; therefore, the delta function PXRD line profile would had been observed. We propose that, in reality, some “hidden effects” may prevent any PXRD line profile forms in the shape of a delta function even in the ideal case, and these “hidden effects” lead the formation of the characteristic line profile of real PXRD peaks. We define this profile the *intrinsic profile* in this paper.

We assume, in this work, that the PXRD peak always has its particular profile, caused by the absorption of X-rays in passing through the materials. As all materials absorb the X-rays, the absorption generated profile is of course the intrinsic profile. To the author’s knowledge, there is no such study correlating PXRD line profile to X-ray absorption. Some works on line profile analysis (Mittemeijer, 2004) has been done. However, they discussed the broadening of the line and how to fitting the profile, not related to the intrinsic profile as we proposed in this paper.

In this paper, we will calculate the non-trivial PXRD line profile which is generated by the absorption of X-rays, and then compare the calculated line profile with that of observed. The deviation of calculated and observed PXRD line profiles is estimated to demonstrate the agreement also. At the end of this paper, some comparisons between our calculated line profile and some common profile fitting functions, such as Cauchy fitting and Gaussian function fitting, will be discussed.

**THE INTENSITY CALCULATION FOR THE ABSORBED XRD BEAM**

The intensity of a diffraction line can be obtained by superposing of the amplitude of the wave beams. Assume a sample has \(N+1\) crystalline planes with \(d\) as its interplanar spacing, which reflects the incidence X-ray, as shown in Fig.1. By setting \(A_n\) as the reflecting amplitude of the X-ray by the \(n\)'th plane, which may be the function of the absorption coefficient \(\mu\). Letting \(\delta l_n\) be the path difference between two close beams, and \(\exp(i\phi_n)\) be the reflecting phase factor, where \(\phi\) is the phase angle, which can be obtained by \(\delta l\) as

\[
\phi = 2\pi \delta l / \lambda = 2\pi 2d(\sin \theta) / \lambda,
\]

where \(\lambda\) is the wave length.

The total reflecting amplitude of reflecting beam, denoted by \(A_{Tot}\), is the superposition of all wave amplitudes, thus
\[ A_{\text{Tot}} = \sum_{n=0}^{N} A_n \exp(i\phi_n), \quad (1) \]

Fig.1. Schematic diagram of X-ray reflection by crystalline planes

and the diffracting intensity is

\[ I = (A_{\text{Tot}})^* A_{\text{Tot}} = |A_{\text{Tot}}|^2. \quad (2) \]

By considering that the absorption happens in the media where the beam passing through, we have \( I = I_0 \exp(-\mu s) \) (Guinier, 1963), where \( s \) is the minimum unit of the beam length passing from the media, i.e., from zeroth plane to the first plane, and then reflecting from first plane to the zeroth plane (see Fig. 1), we thus obtain

\[ A_n = \sqrt{I_0} \exp(-f(\mu s)n), \quad (3) \]

where \( I_0 \) is the reflected intensity, and \( f(\mu s) \) is a function of \( s \) and \( \mu \) to be determined. We can calculate \( s \) (see Fig.1) by \( d \) as

\[ s = 2(d/\sin \theta). \]

Note that \( s \) is of the order of \( d \), i.e., \( \sim 10^{-10} \text{m} \) (or \( 10^{-8} \text{cm} \)), except for the small angle (\( \theta \ll 0.1 \text{rad} \)) diffraction.

It can be seen from Eq.(1) that the series is a geometric progression with the proportional factor \( \exp(-f(\mu s)) \exp(i\phi) \), thus,

\[ A_{\text{Tot}} = \sum_{n=0}^{N} A_n \exp(i\phi_n) = A_0 \left( 1 - e^{-f(\mu s)N} \exp(iN\phi) \right) \left( 1 - e^{-f(\mu s)} \exp(i\phi) \right). \]

We therefore obtain the diffraction intensity with the absorption considered

\[ I_a = A_{\text{Tot}}^* A_{\text{Tot}} = I_0 \frac{1 + e^{-2f(\mu s)N} - 2e^{-f(\mu s)N} \cos(N\phi)}{1 + e^{-2f(\mu s)} - 2e^{-f(\mu s)} \cos(\phi)}. \quad (4) \]

When the sample is very big, i.e., \( N \to \infty \), Eq.(4) can be simplified as
\[ I_a = \frac{I_0}{1 + e^{-2f(\mu s)}} \left( 1 - 2e^{-f(\mu s)} \cos(\phi) \right) \quad \text{(for } N \gg 1). \] (5)

The simplest case of Eq.(5) is that \( f(\mu s) = 0 \), i.e., the intensity is independent of the absorption. In this case the intensity is just the distribution function of a diffracting grating,

\[ I = I_0 \frac{\sin^2(N\phi/2)}{\sin^2(\phi/2)} \quad \text{(for } f(\mu s) = 0). \]

This formula implies that the intensity of a large perfect crystal (\( N \to \infty \)) will be a delta function. Therefore, the distribution function of the diffracting grating is just the non-absorption case of Eq.(4).

**EXPERIMENTAL DEMONSTRATION AND APPLICATION**

In order to obtain the line profile concretely, we firstly determine the form of the function \( f(\mu s) \) as following. Assuming \( \mu s \ll 1 \), and by expanding the function \( \exp(f(\mu s)) \) to a Taylor series at the Bragg angle (i.e., \( \phi = 2\pi \) in Eq.(5)) i.e., \( \exp(-f(\mu s)) = 1 - f(\mu s) + (f(\mu s))^2/2! + O(\mu s) \), one has

\[ I_a = \frac{1}{1 - 1 + f(\mu s) - f(\mu s) + 2f(\mu s)^2/2! + \cdots} \approx \frac{1}{(f(\mu s))^2} \] (6)

On the other hand, the X-ray absorption theory of PXRD shows that the diffraction intensity is inversely proportional to the absorption coefficient, i.e.,

\[ I_a \propto \frac{1}{\mu}, \] (7)

by comparing Eq.(6) and (7), the following relationship is obtained,

\[ f(\mu s) = (\mu s)^{1/2}. \] (8)

In order to estimate the order of \( \mu s \), one can consider a copper (Cu) sample with Cu \( K_\alpha \) radiation. The massive absorption coefficient of Cu is \( \mu_{\text{m}} = 52.7 \text{ (cm}^2/\text{g}) \), and the density is 8.90(g/cm\(^3\)). As \( s \) is the order of \( 10^{-10} \text{ m} \), we have \( \mu s = \mu_{\text{m}} \rho s \) is of the order of \( 10^{-6} \), so that the higher order of \( \mu s \) could be omitted. We therefore obtain the peak of the line profile at the exactly Bragg’s angle (\( \theta = \theta_0 \)):

\[ I_{\text{max}} = \frac{I_0}{\left( 1 - e^{-\sqrt{\mu s}} \right)^2} \approx \frac{I_0}{\mu s} . \]

As the quantity of \( \mu s \) is of the order of \( 10^{-6} \), we can estimate that \( I_{\text{max}} \) is of the order of \( 10^6 I_0 \).

We finally obtain,
\[ I_a = A_{tot}^* A_{tot} = I_0 \frac{1 + e^{-\sqrt{\mu_s}N} - 2e^{-\sqrt{\mu_s}N} \cos(N\phi)}{1 + e^{-\sqrt{\mu_s}N} - 2e^{-\sqrt{\mu_s}N} \cos(\phi)}. \] (9)

For \( N \to \infty \), we have the approximation

\[ I_a = \frac{I_0}{\mu_s + 4e^{-\sqrt{\mu_s}N} \sin^2\left(\frac{\phi}{2}\right)} = \frac{I_{max}}{1 + 4e^{-\sqrt{\mu_s}N} \sin^2\left(\frac{\phi}{2}\right) I\left(\mu_s\right)}. \] (10)

Eq.(9) is the main results of this work.

The experimental verification for the XRD line profile of Eq.(9) was carried out with of annealed Aluminum (Al) powder sample. The selected reflection plane is (200) with \( \mu_m = 48.7 \) (cm\(^2\)/g), and the density is \( \rho = 2.699 \) (g/cm\(^3\)). The radiation wavelengths are doublet \( K_\alpha \) lines, \( \lambda_{\alpha 1} = 1.54051 \) Å and \( \lambda_{\alpha 2} = 1.54433 \) Å, with the intensity ratio 1:0.45. The diffractometer used is the Rigaku D/max 2200PC. The experimental curve is not smoothed. One can see in Fig.2, that the difference between the calculated intensity and the experimental intensity \( (I_{cal} - I_{exp}) \) is less than 10%. Therefore, the calculated result is in a good agreement with the experimental results. We therefore conclude that the line profile is mainly shaped by the X-ray absorption, rather than broadening caused by instrumental or by the imperfection of a sample.

Fig.2. X-ray diffraction line-profiles of the experiment (red) and the theoretical (black) one for Aluminum powder (200) plane, with Copper (Cu) radiation of \( K_{\alpha 1} \) and \( K_{\alpha 2} \).

In order to compare our results with the other line profile fittings, we expand Eq(10) in the vicinity of \( \theta_B \). For \( \Delta \theta \ll 1 \), one has \( \sin(\theta_B + \Delta \theta) \approx \sin \theta_B + \Delta \theta \cos \theta_B \), such that Eq.(10)
can be re-written as
\[
I_a \approx \frac{I_{\text{max}}}{1 + \alpha \times (\Delta \theta)^2}, \tag{11}
\]
where \( \alpha = 4(2\pi d/\lambda)^2 \exp(-\mu s^{1/2}) \cos^2(\theta_0). \) By comparing Eq.(11) with the Cauchy fitting function,
\[
I_a \approx \frac{I_{\text{max}}}{1 + C(\Delta \theta)^2},
\]
We can see that the Cauchy fitting function is just an approximation of Eq.(10) with \( \Delta \theta \ll 1. \) Moreover, we can also theoretically obtain that the fitting coefficient \( C = \alpha. \)

Fig.3. the line profile for Al (200) with \( K_d/K_{\text{al}} = 0.45, \) (a) the calculated curve by Eq.(9); (b) the Cauchy fitting function with \( C = 10.56 \) and (c) the Gaussian fitting with \( \alpha = 583.0. \)

Another fitting function, the Gaussian one, can also be obtained by the approximation of Eq.(9). With the Taylor expansion \( \exp(-u^2) = 1 - u^2 + O(u^4), \) Eq.(11) can be written as the Gaussian fitting function \( I_a = I_{\text{max}} \exp(-\alpha (\Delta \theta)^2). \) Therefore, both the Cauchy fitting function and the Gaussian function are included in our calculated line profile. Although the difference between our calculated results and the Cauchy fitting one is not disparate by Fig.3, the physical meaning is totally different. Eq.(9) comes from the theoretical derivation which depends on the absorption of the sample, while the Cauchy fitting is only a fitting and the coefficient is chosen to fit the curve which has no physical meaning at all.

REFERENCES