EXPERIMENT VERIFICATION FOR THE DEPENDENCE OF THE X-RAY DIFFRACTION LINE PROFILE WITH THE ABSORPTION OF SAMPLE

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ABSTRACT: X-ray diffraction (XRD) provides a lot of information of the micro-structure of the specimen by line profile analysis. It was supposed that the line profile is broadened by the size of the crystalline, and also broadened by instrument. We proposed recently, (Kejia Liu et al, Adv. in X-ray analysis, 54, 17 (2010)) that there is still another effect which broadening the line profile, that is, the absorption of the sample. In this work, we shall discuss the dependence of the line profile with the absorption coefficient in detail. We demonstrate the absorption broadening by two crystals with different absorptions, we find that the line profile is strongly affected by the absorption, and the observed XRD patterns are in excellent agreement with the calculated line profile functions. This concrete experimental evidence strongly supports the existence of the absorption broadening in the powder XRD.

1. Introduction

X-ray diffraction (XRD) provides both the structure information of a crystalline sample and the microstructure information. One can obtain a lot of micro-structure of the specimen by XRD line profile analysis [1].

XRD intensity function, \( I \), can be derived from the optical diffraction grating [2], the function called the interference function in optics,

\[
I = I_0 \sin^2 \left( \frac{2\pi Nd \sin(\theta)}{\lambda} \right) \sin^2 \left( \frac{2\pi d \sin(\theta)}{\lambda} \right),
\]

The width of the peak profile is measured by the full width at half maximum (FWHM) from the experiment peak profile. The first investigation for the line broadening was did by Sherrer[3], who found that the finite size of the sample causes the line profile broadening, by measuring the FWHM of profile, denoted by \( B_f \), one can calculate the grain size, \( L \), of a sample via the Scherrer formula[3],

\[
L = \frac{K\lambda}{B_f \cos(\theta)}.
\]

This formula could be derived from Eq.(1)[2]. We called this kind of broadening as the size broadening (SB) in this paper. However, one can not use this formula directly. If the grain size of the sample is big, e.g. a single crystal, i.e., \( N >> 1 \), \( L=Nd >> 1 \), then Eq.(1) expresses a delta function, and \( B_f \) must be so small that cannot be measured in
practice. Therefore, the Eq.(1) and (2) should be modified, for practical usage. 

The second broadening of line profile was proposed in the 1930’s by Jones.[4] It was supposed that the line profile is broadened by some effects included as the instrument broadening (IB), e.g., improperly designed instrument could affect the widths of the line profile, and the specimen transparency of the X-ray could do so also. By following the size broadening, IB is thought as a supplement the total broadening, so that \( B_f \) in Eq.(2) satisfying,

\[
B_h = B_f + B_g,
\]

where \( B_h \) is the measured FWHM; \( B_f \) is the size broadening and \( B_g \) is the instrument broadening (IB). In spite of that the instrument broadening was introduced by Jones[4] more than 50 years ago, however, as it caused by so many effects, the quantity of IB is obtained by measuring the FWHM of coarse crystals, hardly to be derived theoretically.

We proposed recently, that there is another broadening effect caused by the absorption of the sample [5], we called it the absorption broadening (AB). By taking the absorption into account, we finally obtained that the intensity of the XRD peak profile,[5]

\[
I = I_0 \frac{1 + e^{-\sqrt{\mu/s}} - 2e^{-\sqrt{\mu/s}} \cos(4\pi d N \sin(\theta)/\lambda)}{1 + e^{-\sqrt{\mu/s}} - 2e^{-\sqrt{\mu/s}} \cos(4\pi d \sin(\theta)/\lambda)},
\]

where \( N \) is the total number of the layers, \( \mu \) is the absorption of a sample, \( s \) is the path difference between two nearby X-ray beams which immerged in the material, \( \theta \) is the Bragg’s angle, \( d \) is the interplanar spacing and \( \lambda \) is the wave length. One can verify that by setting \( \mu = 0 \), Eq.(3) will be the interference function of Eq.(1), Therefore, Eq.(3) is the more general intensity function than Eq.(1).

If the sample is composed by the coarse grains, i.e. \( N >> 1 \), then Eq.(3) can be simplified as

\[
I = I_0 \frac{1}{1 + e^{-\sqrt{\mu/s}} - 2e^{-\sqrt{\mu/s}} \cos(4\pi d \sin(\theta)/\lambda)} .
\]

This formula gives the fundamental intensity function, i.e., it is intensity with neither SB nor IB but only AB being included.

We shall give some experimental demonstration in next section to verify the theoretical prediction.

2. Experiment demonstration

The main idea of the work is that the absorption does cause the peak broadening. The experiment shall demonstrate this prediction.

Experiment was conducted with Rigaku D/MAX 2200PC diffractometer and monochromatic Cu \( K_\alpha \) was used. Peak profiles for coarse powders with mess 200 of aluminum (Al) and iron (Fe) are shown in Fig.1. The size of the powder of mess 200 is about 10 \( \mu m \) in diameter, we therefore treat \( N >> 1 \), The powders were well-annealed so that there will be no micro-strain in it, so that one can use Eq.(4) to calculate their
intensities. The main difference for the two samples is the absorption coefficient, which are $\mu_{\text{Al}} = 131.5 \text{ cm}^{-1}$ for Al, and $\mu_{\text{Fe}} = 2527 \text{ cm}^{-1}$ for Fe. Note that $\mu_{\text{Fe}}$ is about 19 times bigger than $\mu_{\text{Al}}$. The line profiles for these two samples are shown in Fig.1. By comparing the two experiment curves, one can see the differences clearly. The smaller absorbing sample, Al, has the narrower peaks, and the doublet peaks ($K_{\alpha 1}$ and $K_{\alpha 2}$) are separated clearly, while the bigger absorbing sample Fe, has only one flattened peak, that means that the two peaks ($K_{\alpha 1}$ and $K_{\alpha 2}$) are merged into one, hardly to be separated. One therefore obtains that it is absorption that affects the profile, rather than the instrument.

One can also compare the experimental curve with the calculated ones, the difference between them are also shown in the figures (in black), the maximum difference is less than 16%. Therefore, the theoretical prediction is in excellent agreement with the experimental results.

We have thus demonstrated that the main broadening effect for the peak profile is the absorption broadening, under our experimental condition. Other broadening effects may have less influence, in our experiment results.

3. Conclusion

We have proposed a new broadening effect of the line profile, i.e., the absorption broadening. Experiment demonstration shows that absorption broadening is the main part of the whole line profile. Our theoretical predictions are strongly supported by experimental demonstration of the two crystals line profiles with different absorptions. We therefore conclude that the absorption broadening should be a very important broadening effect for XRD.

References


