

Dependence of Integral Intensity on Line Broadening in Powder Diffraction Pattern

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Abstract Relation of integral intensity in powder diffraction pattern to volume integration of intensity in reciprocal space is presented. The integral intensity in powder diffraction pattern is different quantity from the volume integration of intensity in reciprocal space. Though the volume integrations of intensity are constant in reciprocal space, the integral intensities in powder diffraction pattern are different if line broadenings are different. The smaller integral intensity is obtained from the greater broadening. It is called as dependence of integral intensity on the line broadening. The volume integration of intensity in reciprocal space is proportional to the product of the integral intensity and the variance of line profile in powder diffraction pattern, not to integral intensity only. It implies that size-profile, Fourier transform, integral intensity, maximum intensity, integral breadth and variance have new meanings. Size distribution data of CeO_2 powder sample obtained from integral breadth and variance of new meanings shows a good agreement with TEM data.

Key words dependency on broadening, integral intensity, powder diffraction pattern

Introduction

Line profile (LP) is given by intensity versus reciprocal space variable s , $I(s)$, in powder diffraction pattern (PDP) and integral intensity (II) is defined as

$$I = \int_{-\infty}^{\infty} I(s) ds \quad (1)$$

When intensity versus vector s is $J(s)$ in reciprocal space, volume integral intensity (VII) is obtained by

$$J = \int J(s) dv^* \quad (2)$$

where dv^* is the volume element in reciprocal space.

In the previous research[12, 13] relation between I and J is known as

$$I = J \quad (3)$$

From this we obtained $I(s)$ as dJ/ds and its Fourier transform (FT) as the common volume between crystallite and its “ghost”. The common volume model of FT is continually used ever in the previous research[10, 11].

It is known that II is constant if the total volumes of crystallites in powder samples are constant and it is independent of average size of crystallites.

Experimental examination, whether it is right or not, has not been reported because nobody

has doubted about it. However, we have observed several times the fact that the smaller II is obtained from the greater line broadening (LB) though volume compositions of crystalline phase are constant. It makes for us to doubt about accuracy of equation (3).

In this paper, we consider the relation between I and J in a new viewpoint. It depends on relation between $I(s)$ and $J(s)$. We confine here to the ideal condition in which powder sample is not oriented and LP is obtained as physical profile without instrumental broadening. Starting from the new relation between I and J , physical meanings of size-profile, FT, II, maximum intensity (MI), integral breadth (IB) and variance [16] will be considered again. The result is evaluated by size distribution analysis of the powder sample CeO₂ data [3].

1. LB-Dependence of II

1.1. Relation between I and J

If $I(s)$ is LP of a single particle, $I(s)$ is given by [4].

$$I(s) = J(se) \quad (4)$$

where se is direction vector fixed in reciprocal space.

It is important that $I(s)$ is LP of the single particle, not of powder sample. Someone may doubt equation (4) if $I(s)$ is LP of powder sample, but equation (4) is satisfied for single particle. Even in the previous research[8], who pointed out that Bragg's equation was not exact, introduced equation (4) for single particle.

By using equation (4) in equation (1), II is obtained as

$$I = \int_{-\infty}^{\infty} J(se) ds = \int_{s=se} J(s) dl^* \quad (5)$$

where dl^* is the length element on the line $s = se$ in reciprocal space.

I is the line integration, not the volume integration in reciprocal space.

I has different meaning from J in reciprocal space. If $J(s)$ is spherical symmetry

$$I(s) = J(s)$$

and VII is obtained as

$$J = 4\pi \int_{-\infty}^{\infty} s^2 I(s) ds = 2\pi\sigma^2 I \quad (6)$$

where

$$\sigma^2 = \frac{\int_{-\infty}^{\infty} s^2 I(s) ds}{I} \quad (7)$$

is the variance as measure of LB [14–16] in PDP.

J is proportional to the product of II and the variance, not to only II. I and J are different quantities for the single particle. II and VII of powder sample are obtained by summation of particles, respectively.

If $J(s)$ is spherical symmetry, equation (6) is also satisfied for powder sample, because IIs

of all the particles are the same and VIIs, too. Furthermore, equation (5) must be also satisfied for $J(s)$ of powder sample. It is important that $J(s)$ is for powder sample, not for single particle. Mapping from $J(s)$ to $I(s)$ must be fixed for the given diffraction system and it is independent of what the sample is. For $I(s)$ and $J(s)$ of the same sample, equation (5) holds always true.

If powder sample is not oriented, $J(s)$ is spherical symmetry though individual particle is not, and then equation (6) is satisfied. In this case, we can also say that equation (4) holds true for the powder sample. It is not discussed here.

II and VII are different quantities for powder sample, too.

1.2. LB-dependence of II

J is proportional to the volumes of crystallites [5] and it is constant independent of average size of crystallites if the total volume is constant in powder sample. Therefore, constant quantity is not I but the product of I and σ^2 in PDP. The smaller II is obtained from the greater σ^2 . This implies that II is not constant. It is called as LB-dependence of II. It can not be obtained from the classical theories of powder diffraction.

2. Some Characteristic Parameters of Size Profile

2.1. Size profile

Size profile is represented by diffraction of particles with homogenous electron density [8].

Diffraction intensity of homogenous density particle is written as [5]

$$J(s) = \int V(t) e^{-2\pi i s t} dt \quad (8)$$

where $V(t)$ is the common volume between the particle and “ghost” shifted as t . $J(s)$ is spherical symmetry for the spherical particle and intensity of powder sample is proportional to $J(s)$ in reciprocal space.

Inserting equation (8) into equation (4) gives $I(s)$ as follows.

$$I(s) = \int V(t) e^{-2\pi i s t} dt = \int_{-\infty}^{\infty} \varphi(t) e^{-2\pi i s t} dt \quad (9)$$

where

$$\varphi(t) = \int_{et=t} V(t) da \quad (10)$$

is FT of $I(s)$ where da is the area element on the plane $et=t$ in real space.

FT is obtained by integration of $V(t)$ on the plane $et=t$, not only the common volume.

The common volume of sphere with diameter D is given by

$$V(t|D) = \frac{\pi}{6} D^3 \left(1 - \frac{3|t|}{2D} + \frac{1}{2} \frac{|t|^3}{D^3} \right), \quad (|t| < D) \quad [6, 10]. \quad (11)$$

Then FT of the sphere, $\varphi(t|D)$, is obtained as

$$\varphi(t|D) = \frac{\pi^2}{30} D^5 \left(1 - 5 \frac{|t|^2}{D^2} + 5 \frac{|t|^3}{D^3} - \frac{|t|^5}{D^5} \right), \quad (-D < t < D) \quad (12)$$

This is 5-dimensional polynomial and 1st coefficient is zero, i.e. “hook effect” is represented. For the powder sample with size distribution density, $p(D)$, FT is obtained as

$$\varphi(t) = \frac{\pi^2}{30} \int_{|t|}^{\infty} P(D)(D^5 - 5D^3|t|^2 + 5D^2|t|^3 - |t|^5)dD. \quad (13)$$

This is a new model of FT of size profile, $\varphi(0) \propto \langle D^5 \rangle$ and $\varphi'(0) = 0$. It is different from the known FTs [10, 13].

2.2. MI, II and VII

MI is given by $I(0)$ and it is obtained as

$$I(0) = \int_{-\infty}^{\infty} \varphi(t)dt = \frac{\pi^2}{36} \langle D^6 \rangle \quad (14)$$

from equation (13) where $\langle D^n \rangle$ is n th-order moment of D . $I(0)$ is mean-square of volumes. It equals to $J(0)$.

MI is intensity at original point in reciprocal space and it is proportional to $\langle D^6 \rangle$, not to $\langle D^4 \rangle$.

II is obtained as

$$I = \varphi(0) = \frac{\pi^2}{30} \langle D^5 \rangle \quad (15)$$

II is proportional to $\langle D^5 \rangle$, not to $\langle D^3 \rangle$. II depends on size though the total volume is constant. LB-dependence becomes to size-dependence in size profile.

VII is obtained as

$$J = \frac{\pi}{6} \langle D^3 \rangle \quad (16)$$

VII is proportional to the average volume.

Only VII has the same meaning with the previous, but it is not II in PDP.

2.3. IB and variance

From equation (14) and equation (15), IB is obtained as

$$\beta = \frac{I}{I(0)} = \frac{6 \langle D^5 \rangle}{5 \langle D^6 \rangle} \quad (17)$$

IB is determined by 5-dimensional average size $\langle D^6 \rangle / \langle D^5 \rangle$, not 3-dimensional average size $\langle D^4 \rangle / \langle D^3 \rangle$.

Inserting equation (15) and equation (16) to equation (6), variance is obtained as

$$\sigma^2 = \frac{5 \langle D^3 \rangle}{2\pi^2 \langle D^5 \rangle} \quad (18)$$

Variance is determined by $\langle D^5 \rangle / \langle D^3 \rangle$.

In the previous research[13] the variance has been introduced as the measure of LB before long, but it has not been widely used in size analysis [7]. We think that the reason is in its wrong meaning. It can be used as well as IB in LB analysis by using equation (18).

2.4. “Hook effect”

From equation (13) if derivative of $\varphi(t)$ in $t=0$

$$\varphi'(0) = 0 \quad (19)$$

is obtained. It is known as “hook effect” [2, 13]. In the previous research[15] “hook effect” was in principle impossible and only should be due to wrong data. But, “hook effect” is essential from the definition of FT. It means there is something problem in Fourier analysis of size profile based on $\varphi'(0) \neq 0$ [13].

Thus, the new consideration obtained from the broadening-dependence of II shows that LB analysis must be reexamined.

3. Size Distribution Analysis by IB and Variance

3.1. Principle

From IB and variance, $\langle D^6 \rangle / \langle D^5 \rangle$ and $\langle D^5 \rangle / \langle D^3 \rangle$ are obtained and size distribution can be obtained. For example, $\langle D^n \rangle$ is given by

$$\langle D^n \rangle = \langle D \rangle^n (1+c)^{(n^2-n)/2} [9]. \quad (20)$$

when size distribution $P(D)$ is lognormal distribution, where $\langle D \rangle$ is the mean-size and c is ratio of size variance and square of $\langle D \rangle$.

$\langle D \rangle$ and $(1+c)$ are obtained from following equations

$$\langle D^6 \rangle / \langle D^5 \rangle = \langle D \rangle (1+c)^5, \quad \langle D^5 \rangle / \langle D^3 \rangle = \langle D \rangle^2 (1+c)^7$$

And $P(D)$ can be obtained by

$$P(D) = \frac{1}{D [2\pi \ln(1+c)]^{1/2}} e^{-\frac{\ln^2 \left[\frac{D}{\langle D \rangle} (1+c)^{1/2} \right]}{2 \ln(1+c)}} \quad (21)$$

By this method, size distribution, $P(D)$, is directly obtained at once without assumption of initial distribution and repeating calculations.

3.2. Size distribution analysis of CeO₂

The presented method has been examined by size distribution analysis of CeO₂ data[3]. The result shows in Fig. with TEM data[1].

Though $P(D)$ has been obtained directly from IB and variance without repeating calculation, the result shows a good agreement with TEM data.

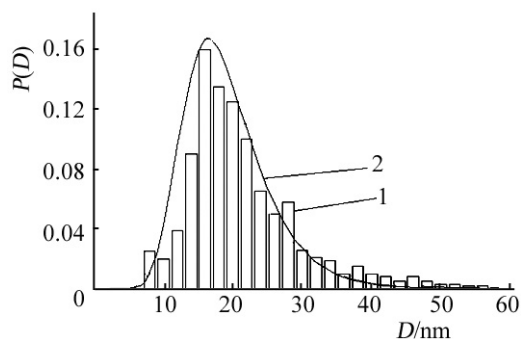


Fig. Size distribution of CeO₂
1—TEM data 2—IB+Variance

Conclusion

II and VII are not same quantities: I is the line integration in reciprocal space and J is proportional to the product of II and variance in PDP. It is obtained from the relation between LP and intensity distribution in reciprocal space. It is obvious that $I(s)$ is intensity at a point in reciprocal space, when $I(s)$ is physical profile of the sample with intensity distribution as $J(s)$.

Classical theories, which assert $I = J$, must be reexamined.

In the previous research[8] size profiles of a single spherical crystallite and powder sample of spherical crystallites with same size were different. However, if spherical particles have really homogenous density of electron, powder sample has the same LP with a single particle. According to the previous research[8], size profile of crystalline powder sample is not obtained from the homogenous density particles.

We proved that size profile of powder sample of spherical crystallites with same diameters equals to LP of a single particle with the same diameter and homogenous density of electron. It will be shown in another paper.

II depends on LB though VII is constant. Exact theory of powder diffraction must explain LB-dependence of II, “hook effect” and other new properties. Details will be discussed in following papers.

FT of size profile has other form than classical. Then intensity and broadening parameters have the new physical meanings.

All the results contradict to the classical concepts but exactness of the new results can be proved perfectly.

Good agreement of our analytical data and TEM data means that our viewpoint is not wrong.

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