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Data Smoothing and Distortion of X-ray Diffraction Peak. II: Application

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Appendix A: comparison of the change amplitudes of peak parameters by smoothing

In order to handle the smoothing changes of peak parameters we hope to find out the highest amplitude among these changes by which the criterion of smoothing can be set.

The procedure is, firstly, to set a criterion for evaluating the larger amplitude of two factors in the form of *A*'*B*'=*D*' then to find out the highest change one from each two peak parameters after smoothing.

1. Criterion of evaluating the larger amplitude from two factors in the form of *A'B'=D'*

Generally equation *AB*=*D* describes the reversed relationship between factor *A* and factor *B*. With increasing *A*, *B* decreases or *vice versa* if *D* is constant. The relative change of *A* and *B* in *AB*=*D* is given as

$$(A \pm \Delta A)(B \pm \Delta B) = D \quad . \qquad \text{(A1)}$$

It can be reduced, if *A*>0 and *B*>0, as

$$[(A \pm \Delta A) / A][(B \pm \Delta B) / B] = 1 \quad , \qquad \text{(A2)}$$

where $(A \pm \Delta A) / A$ is the relative change of *A* (*A*') and $(B \pm \Delta B) / B$ the relative change of *B* (*B*').

So eq. (A2) can be written as

$$A'B'=1 \quad . \qquad (A3)$$

From eq. (A3), A' (or B') increases when A' (or B') >1 and decreases if A' (or B')<1 and no change when A' (or B')=1.

If D varies, $AB=D$ gets the form

$$A'B'=D' \quad . \qquad (A4)$$

That is, A' (or B' or D') increases when A' (or B' or D') >1 and decreases when A' (or B' or D')<1 and no change if A' (or B' or D')=1. Given D', from eq. (A4) there still exists the reversed relationship between factor A' and factor B'. Numerically creating, if

Case I $D'=1$ (D is fixed), then $A'=B'=1$ (no change),

or $A'>1$ and $B'<1$, $\Delta A/A>\Delta B/B$, also $A'>B'$,

or $A'<1$ and $B'>1$, $\Delta B/B>\Delta A/A$, also $B'>A'$;

Case II $D'>1$ (D increases), $A'>1$ and $B'>1$, $A'=(D')^{0.5}$ and $B'=(D')^{0.5}$, $\Delta B/B=\Delta A/A$,

or $A'>(D')^{0.5}$ and $B'<(D')^{0.5}$, $\Delta A/A>\Delta B/B$,

or $A'<(D')^{0.5}$ and $B'>(D')^{0.5}$, $\Delta B/B>\Delta A/A$,

or $B'<1$ and $A'>(D')^{0.5}$, $\Delta A/A>\Delta B/B$,

or $A'<1$ and $B'>(D')^{0.5}$, $\Delta B/B>\Delta A/A$;

Case III $D'<1$ (D decreases), $A'<1$ and $B'<1$, $A'=(D')^{0.5}$ and $B'=(D')^{0.5}$, $\Delta B/B=\Delta A/A$,

or $A'>(D')^{0.5}$ and $B'<(D')^{0.5}$, $\Delta A/A>\Delta B/B$,

or $A'<(D')^{0.5}$ and $B'>(D')^{0.5}$, $\Delta B/B>\Delta A/A$,

or $A'<(D')^{0.5}$ and $B'>1$, $\Delta B/B>\Delta A/A$,

or $A'>1$ and $B'<(D')^{0.5}$, $\Delta A/A>\Delta B/B$.

From the above consideration, it is derived that $(D')^{0.5}$ is the sole criterion to distinguish the larger amplitude ($>(D')^{0.5}$) from A' and B' for all cases I, II and III.

2. Symmetric case

The integral width is defined as the multiplying FWHM by shape coefficient (*SC*) then there exists

$$IW = HW \times SC \quad . \qquad (A5)$$

Given *IW*, *HW* is reversed to *SC*. Since FWHM increases in the course of smoothing, *SC* must be decreasing. From eq. (A5) it gets

$$IW^s / IW = (HW^s / HW)(SC^s / SC) \quad . \qquad (A6)$$

Let $D' = IW^s/IW$, $A' = HW^s/HW$ and $B' = SC^s/SC$ then eq. (A6) becomes the form of $D' = A'B'$. From the increasing of FWHM ($A'>1$), the decreasing of shape coefficient ($B'<1$) and the increasing of integral width in the course of smoothing ($D'>1$) it derives that the amplitude of FWHM change of smoothing is higher than that of shape coefficient (see case II). Since $B' = SC^s/SC$ is less than unity, $A'>1$ and $D'>1$, from eq. (A6), it also derives that $D'/A' <1$ or $A'>D'$, that is, the amplitude of smooth change (increasing) of FWHM is higher than that of integral width.

From the section 3.*B)* of former paper it is deducted that

$$SC / SC^s = (I^s_{\max} / I_{\max})(HW^s / HW) \quad . \qquad (A7)$$

Let $D = SC / SC^s$, $A = I^s_{\max} / I_{\max}$ and $B = HW^s / HW$ then eq. (A7) takes the form of $D'=A'B'$. Since shape coefficient decreases ($SC^s/SC<1$ or $SC/SC^s >1$), maximum decreases ($I^s_{\max} / I_{\max} <1$) and FWHM increases ($HW^s/HW >1$) after smoothing, that is, $D'>1$, $A'<1$ and $B'>1$, according to case II, the amplitude of B' (HW^s/HW) is higher than that of A' ($I^s_{\max} / I_{\max}$).

Eq. (A7) posseses another form as $(SC / SC^s)/(HW^s / HW) = I^s_{\max} / I_{\max}$. This is the equation of the form of $A'/B'=D'$ with $D'<1$, $A'>1$ and $B'>1$. It is deducted that $A'/B'<1$ and $B'>A'$ or the amplitude of FWHM change of smoothing is higher than that of reversed shape coefficient (SC/SC^s).

It is summarised that the amplitude of FWHM change of smoothing is higher than other six peak parameters (smoothing changes of peak position, integral intensity and asymmetric degree are zero).

3. Asymmetric case

The smoothing range of asymmetric peak is classified as the normal and abnormal two regions. The normal smoothing region is in the range larger than the conjunction point of $I_{\max}$ and *IW*. The abnormal region is in the range less than the conjunction point (marked by arrow in Fig. 4).

For the normal smoothing region

For the asymmetric case, let As=HW_l/HW_h (discussions for the case of As=HW_h/HW_l are omitted since the same procedures) so there exists

$$As^s / As = (HW_l^s / HW_l)/(HW_h^s / HW_h) \quad , \qquad \text{(A8)}$$

$$(HW_h^s / HW_h)(As^s / As) = HW_l^s / HW_l \quad , \qquad \text{(A8*)}$$

$$HW_h^s / HW_h = (HW_l^s / HW_l)/(As^s / As) \quad . \qquad \text{(A8**)}$$

From equation (A8*), $A'= HW_h^s / HW_h$, $B'= As^s / As$, $D'= HW_l^s / HW_l$. It is derived, from the decreasing of *As* (*B*'<1, getting less asymmetric) and the incrasings of HW_l and HW_h (*D*'>1, *A*'>1, broadening), that the amplitude of asymmetric change of smoothing is lower than that of FWHM in the higher angle side.

From eq. (A8**) (a form in *D*'=*A*'/*B*', *D*'>1, *A*'>1 and *B*'<1) it deduces that the amplitude of FWHM in the lower diffraction angle side is higher than that of asymmetric change.

From eq. (A8) (a form in *D*'=*A*'/*B*', *D*'<1, *A*'>1 and *B*'>1) it derives that the amplitude of FWHM in the lower diffraction angle side is lower than that of FWHM in the higher angle side.

Let prove that $HW_h^s / HW_h > HW_t^s / HW_t > HW_l^s / HW_l$ and then discuss the relationship between HW_t^s / HW_t and As^s / As . Subscript *t* means the total.

Since HW_t=HW_l+HW_h then $HW_t^s / HW_t = (HW_l^s + HW_h^s)/(HW_l + HW_h)$

$= (HW_h^s / HW_h)[(As^s + 1)]/[(As + 1)]$ and because *As*^{s}<*As*, (*As*^{s}+1)/(*As*+1)<1, hence $HW_t^s / HW_t < HW_h^s / HW_h$.

Similarly there is $HW_t^s / HW_t = (HW_l^s / HW_l)[(1/As^s + 1)]/[(1/As + 1)]$. As the *As*^{s}<*As*, (1/*As*^{s}+1)/(1/*As*+1)>1 hence $HW_t^s / HW_t > HW_l^s / HW_l$.

Because both amplitudes of the FWHM variations of smoothing in lower and higher angle sides are higher than that of asymmetric change and $HW_h^s / HW_h > HW_t^s / HW_t > HW_l^s / HW_l$, it is derived that the amplitude of asymmetric change (*As*^{s}/*As*) of smoothing is lower than that of general FWHM (HW_t^s / HW_t).

It is important to point out that this regulation of amplitude of asymmetric change is only valid for the case of no peak shifting or peak position keeping in the same place. Once shifting takes place the asymmetric value (*As*^{s}) is jumping down to lower value or to closer unity and hence its amplitude is out of this control described here.

For the abnormal smoothing region

Similarly, forget the term of As^s / As, it can be proved that the amplitude of $I_{\max}^s / I_{\max}$ is the maximum one among these smoothing distortions of peak parameters in the abnormal smoothing region.

Comparison of the amplitude of HW^s/HW with that of position shifting

Position shifting will take place in the course of smoothing when the peak is asymmetric. This shifting amplitude is controlled by asymmetric degree, smooth range and shape perfect coefficient (*SS*/*HW*). Since the amplitude of position shifting is calculated by the ratio of shifting step to the d spacing of the reflection (peak) and that of FWHM by the *HW*^{s}/*HW*, they could not compare each other in the form of *A'B'=D'*. However the numeric solution reveals that for a weak asymmetric peak (*As*<1.5) the amplitude of *HW*^{s}/*HW* is higher than that of position shifting in the smoothing range from 5 to 51 points with *SS*/*HW* >4%. This regulation is upset when *As*>1.5 and *SS*/*HW*<4%.