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# A Mathematical Treatment of X-Ray Line Broadening due to Doublet Separation

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A mathematical treatment of the broadening of X-ray diffraction lines due to the separation of the $K\,\alpha_1\alpha_2$ doublet is described. The presented method consists of compounding two profiles of the same shape and breadth $B$, but differing in height by a factor of two, and separated by some angular increment $\delta$. The calculations are given for the functions $\exp(-k^2\,\varepsilon^2)$ and $(1 + k^2\,\varepsilon^2)^{-1}$. The following results are obtained for various ratios of $\delta$ and the resultant line breadth $B_0$: 1) integral breadth and the breadth at half-maximum intensity of the resultant profile, 2) the height of the resultant profile, 3) the deviation of the peak of the resultant profile from the position of the peak of the stronger component, $K\,\alpha_1$, and 4) the limiting value of $\delta/B_0$ for which occurs the transformation of the resultant profile with one peak into the profile with two peaks. All these values strongly depend on the analytical function which is assumed for the profile of the components.

## INTRODUCTION

The broadening of the X-ray diffraction lines due to the angular separation $\delta$ of the $K\,\alpha_1\alpha_2$ doublet is small at low Bragg angles $\Theta$. It becomes progressively important as $\Theta$ increases. Sometimes it is possible to avoid this problem by measuring the separate profile of either the $\alpha_1$ or $\alpha_2$ component at angles sufficiently large to resolve clearly the doublet. However, this possibility fails if the pure diffraction broadening is too great to permit the complete resolution of the two lines. Therefore, one must take into account the $K\,\alpha$-doublet broadening in the majority of the cases of crystallite size and lattice distortion measurements (Klug and Alexander[1]).

When the line profile is known, the correction curve can be derived according to Jones[2]. He considered the experimental profile of a line at $\Theta = 80^0$, where the components were completely resolved. The method consists of compounding two such profiles of the same shape and integral breadth $B_i$, which differ in height by a factor of two and are separated by some angular increment $\delta$. Dividing the area of the resultant profile (calculated by Simpson's formula) by its height (determined graphically), Jones obtained the integral breadth $B_{0i}$ of the resultant profile.

Rachinger[3] proposed the solution by a graphic procedure where the distance $\delta$ between $\alpha_1$ and $\alpha_2$ must be calculated.

This paper presents a mathematical solution of the problem. Assuming the functions $\exp(-k^2\varepsilon^2)$ or $(1 + k^2\varepsilon^2)^{-1}$ for the profiles of the components, the following results are obtained:

$B_{oi}$, the integral breadth;

$B_{o½}$ the breadth at the half maximum intensity;

$I(\varepsilon_0)$, the height of the resultant profile;

$\varepsilon_0$, the deviation of the peak of the resultant line from the position of the peak of the component $\alpha_1$ and

$\delta_t/B_o$, the limiting value of $\delta/B_o$, where occurs the transformation of the resultant profile with one peak into the profile with two peaks.

## MATHEMATICAL TREATMENT

For describing the profile of the components we consider first the function exp $(-k^2\varepsilon^2)$. One can write

$$I_1(\varepsilon) = \exp(-k^2\varepsilon^2)$$

and

$$I_2(\varepsilon) = \frac{1}{2} \exp[-k^2(\varepsilon - \delta)^2]$$

where $I_1(\varepsilon)$ is the profile of the stronger component, $\alpha_1$; $I_2(\varepsilon)$ the profile of the weaker component, $\alpha_2$, $\delta$ is the angular distance between the components, and $\varepsilon$ is an angular variable with the origin at the peak of the $\alpha_1$ line. For simplicity let us take the parameter $k$ to be equal to unity. In this case the integral breadth of the components $B_i = \sqrt{\pi}$, and the half-maximum breadth $B_{½} = 2\sqrt{\ln 2}$. For the resultant profile we can write

$$I(\varepsilon) = \exp(-\varepsilon^2) + \frac{1}{2} \exp[-(\varepsilon - \delta)^2].$$

For $\delta < \delta_t$ the resultant profile has only one peak denoted by $\varepsilon_0$. The profile for $\delta = \delta_t$ has, besides the peak $(\varepsilon_0)$, also the inflection point $\varepsilon_t$ where $dI(\varepsilon)/d\varepsilon$ is equal to zero. The profile for $\delta > \delta_t$ has two peaks ($\varepsilon_{01}$ and $\varepsilon_{02}$) and one minimum (at the point $\varepsilon_{min}$). The limiting value $\delta_t$ where the transformation of the resultant profile with one peak into the profile with two peaks occurs will be calculated later.

The integral breadth of the resultant profile will be

$$B_{oi} = \frac{\int_{-\infty}^{+\infty} I(\varepsilon)\, d\varepsilon}{I(\varepsilon_0)} = \frac{\frac{3}{2}\sqrt{\pi}}{I(\varepsilon_0)} \tag{1}$$

The position $\varepsilon_0$ of the resultant profile can be obtained from the following condition

$$\left.\frac{dI(\varepsilon)}{d\varepsilon}\right|_{\varepsilon = \varepsilon_0} = 0 \tag{2}$$

which leads to the equation:

$$\ln \frac{2\varepsilon_0}{\delta - \varepsilon_0} = 2\delta\varepsilon_0 - \delta^2. \tag{3}$$

For a given value of $\delta$ (*i. e.* $\delta/B_i$) it is possible to obtain graphically from the equation (3) the corresponding value $\varepsilon_0$. There is only one intersection ($\varepsilon_0$) of the functions

$$y_1 = \ln \frac{2\,\varepsilon_0}{\delta - \varepsilon_0} \qquad\qquad y_2 = 2\,\delta\varepsilon_0 - \delta^2$$

if $\delta < \delta_t$, and there are three intersections ($\varepsilon_{01}$, $\varepsilon_{02}$ and $\varepsilon_{min}$) for $\delta > \delta_t$. In the case when $\delta = \delta_t$, besides the intersection ($\varepsilon_0$), there is the point ($\varepsilon_t$) where the straight line $y_2$ is the tangent to the curve $y_1$. Using the obtained values $\varepsilon_0$ one can calculate the height of the maximum of the resultant profile

$$I(\varepsilon_0) = \exp(-\varepsilon_0^2) + \frac{1}{2}\exp[-(\varepsilon_0 - \delta)^2]$$

and then the resultant integral breadth $B_{oi}$ according to (1). The results are represented in Figures 1 and 2. It is obvious from Fig. 2 that the ratio $\varepsilon_0/\delta$ is approximately equal to $^1/_3$ only for small values of $\delta/B_{oi}$. When $\delta/B_{oi}$ increases, $\varepsilon_0/\delta$ decreases, and the peak of the resultant profile approaches the position of the peak of the component $\alpha_1$.

The resultant breadth at the half-maximum intensity, $B_{0\frac{1}{2}}$, can be determined as follows. If the points where the resultant profile has the value $\frac{1}{2} I(\varepsilon_0)$ are denoted by $\varepsilon'_{\frac{1}{2}}$ and $\varepsilon''_{\frac{1}{2}}$, one can write

$$B_{0\frac{1}{2}} = |\varepsilon_{\frac{1}{2}}'| + \varepsilon_{\frac{1}{2}}''. \tag{4}$$

The values $\varepsilon'_{\frac{1}{2}}$ and $\varepsilon''_{\frac{1}{2}}$ can be calculated for a given value $\delta/B_{0\frac{1}{2}}$ from

$$\frac{1}{2} I(\varepsilon_0) = \exp(-\varepsilon^2_{\frac{1}{2}}) + \frac{1}{2}\exp[-(\varepsilon_{\frac{1}{2}} - \delta)^2]$$

or

$$2\exp(-\varepsilon_{\frac{1}{2}}^2) = I(\varepsilon_0) - \exp[-(\varepsilon_{\frac{1}{2}} - \delta)^2]. \tag{5}$$

The expression (5) is more appropriate for a graphical solution. Fig. 3 represents the graphical finding of the values $\varepsilon_{\frac{1}{2}}'$ and $\varepsilon_{\frac{1}{2}}''$ for $\delta = 1$ $\left(i.\,e.\text{ for } \frac{\delta}{B_{\frac{1}{2}}} = \frac{1}{2\sqrt{\ln 2}}\right)$. The values of $B_{\frac{1}{2}}/B_{0\frac{1}{2}}$ and $\varepsilon_0/\delta$ as functions of $\delta/B_{0\frac{1}{2}}$ are represented in Figs. 1 and 2.

The condition that the straight line $y_2$ is the tangent to the curve $y_1$ leads to the equations

$$\ln \frac{2\,\varepsilon_t}{\delta_t - \varepsilon_t} = 2\,\delta_t\varepsilon_t - \delta_t^2 \tag{6}$$

$$2\,\varepsilon_t(\delta_t - \varepsilon_t) = 1. \tag{7}$$

Eliminating $\delta_t$ from (6) and (7) we obtain

$$\ln(4\,\varepsilon_t^2) = \varepsilon_t^2 - \frac{1}{4\,\varepsilon_t^2}. \tag{8}$$

A graphical solution of equation (8) gives

$$\varepsilon_t = 1.531$$

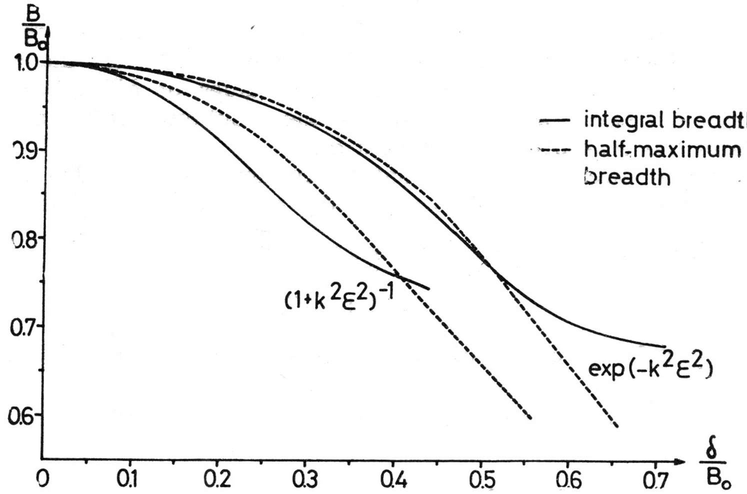
and from (7) it follows that

$$\delta_t = 1.858$$

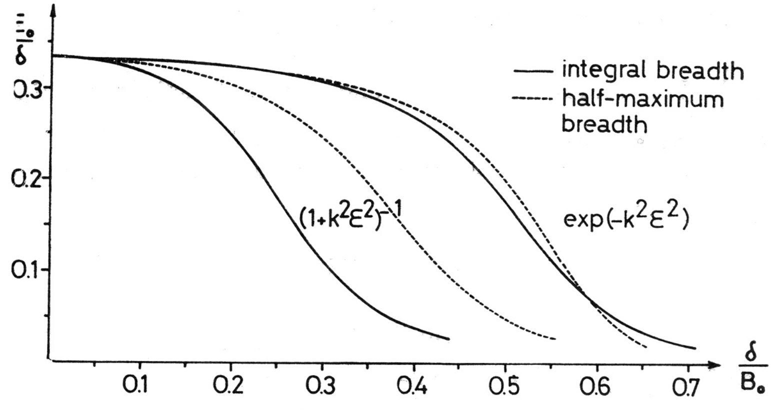
The following values correspond to $\delta_t$:

$$\delta_t/B_{oi} = 0.710 \qquad \delta_t/B_{o½} = 0.655 \qquad \varepsilon_o/\delta_t = 0.0175$$
$$B_i/B_{oi} = 0.677 \qquad B_{½}/B_{o½} = 0.587 \qquad I(\varepsilon_o)/I_1(0) = 1.017$$

The curves shown in Figs. 1 and 2 are plotted only to the above »limiting« values.




1. Curves for correcting line breadths for $K\alpha$ — doublet broadening.




2 Changes in the peak position $\varepsilon_o$ of the resultant profile with the ratio of the doublet separation $\delta$, and resultant breadth $B_o$.

An analogous treatment can be realized by assuming another bell-shaped function for the components of the doublet. Let us consider the function $(1 + k^2\varepsilon^2)^{-1}$. For $k = 1$ we have $B_i = \pi$, $B_{1/2} = 2$. The resultant profile is

$$I(\varepsilon) = \frac{1}{1+\varepsilon^2} + \frac{1}{2} \cdot \frac{1}{1+(\varepsilon - \delta)^2}$$

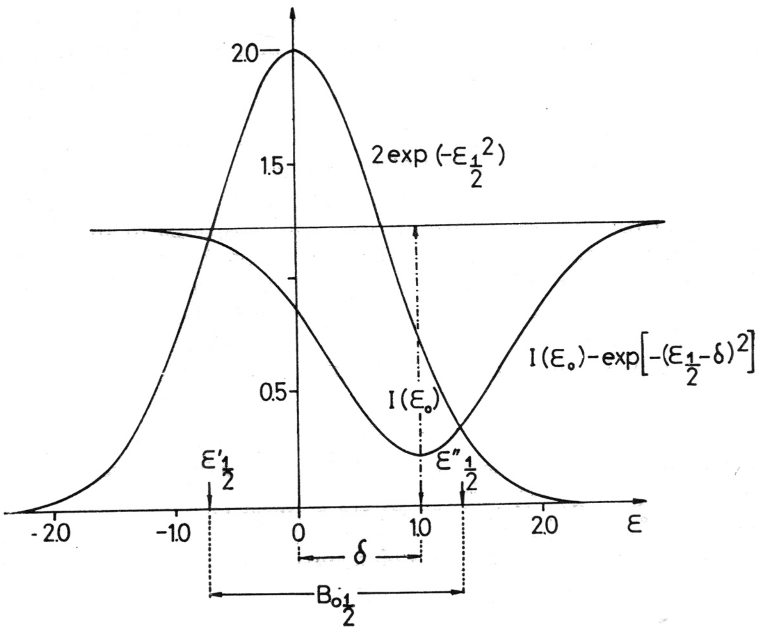
and its integral breadth is

$$B_{oi} = \frac{\frac{3}{2}\pi}{I(\varepsilon_0)} \tag{9}$$

Equation (2) leads to the expression

$$\frac{1+(\delta - \varepsilon_0)^2}{\sqrt{\delta - \varepsilon_0}} = \frac{1+\varepsilon_0{}^2}{\sqrt{2\varepsilon_0}} . \tag{10}$$

The value $\varepsilon_0$ for a given $\delta$ (*i. e.* for a given $\delta/B_i$) can be obtained graphically from (10). Using the obtained values $\varepsilon_0$ we can calculate the heights of the peaks of the resultant profiles $I(\varepsilon_0)$ and then the corresponding values $B_{oi}$ according to (9).




3. Graphical finding of the half-maximum breadth of the resultant profile $I(\varepsilon) = \exp(-\varepsilon) + {}^1/_2 \exp[-(\varepsilon - \delta)^2]$ for $\delta = 1$.

Half-maximum breadths $B_{0 1/2}$ can be found graphically in an analogous manner as for the function $\exp(-k^2\varepsilon^2)$ (see equation (4) and Fig. 3) using the expression

$$\frac{2}{1+\varepsilon_{1/2}{}^2} = I(\varepsilon_0) - \frac{1}{1+(\varepsilon_{1/2} - \delta)^2} \tag{11}$$

In this case we have the following equations for $\delta_t$ and $\varepsilon_t$:

$$\frac{1+(\delta_t-\varepsilon_t)^2}{\sqrt{\delta_t-\varepsilon_t}}=\frac{1+\varepsilon_t^2}{\sqrt{2\,\varepsilon_t}} \tag{12}$$

$$\frac{1-3\,(\delta_t-\varepsilon_t)^2}{(\delta_t-\varepsilon_t)^{3/2}}=\frac{3\,\varepsilon_t^2-1}{\varepsilon_t^{3/2}\sqrt{2}} \tag{13}$$

A graphical solution of the equations (12) and (13) gives:

$$\varepsilon_t = 1.466 \qquad \delta_t = 1.860$$

The following values correspond to $\delta_t$:

$\delta_t/B_{oi} = 0.440$ $\quad$ $\delta_t/B_{o\frac{1}{2}} = 0.556$ $\quad$ $\varepsilon_o/\delta_t = 0.0268$

$B_i/B_{oi} = 0.743$ $\quad$ $B_{\frac{1}{2}}/B_{o\frac{1}{2}} = 0.598$ $\quad$ $I(\varepsilon_o)/I_1(o) = 1.114$

The curves shown in Fig. 1 and 2 are plotted only to the above »limiting« values.

## CONCLUSION

The results obtained mathematicaly and shown in Fig. 1 are in very good agreement with the correction curves obtained graphically by other authors. So, the curves $B_{\frac{1}{2}}/B_{o\frac{1}{2}}$ versus $\delta/B_{o\frac{1}{2}}$ in Fig. 1 are in complete agreement with the curves C and D presented by Klug and Alexander[1]. Our curves $B_i/B_{oi}$ versus $\delta/B_{oi}$ are the same as the curves obtained by Mirkin[4].

With respect to the dependence of $\varepsilon_o/\delta$ on $\delta/B_{oi}$ or $\delta/B_{o\frac{1}{2}}$ (shown in Fig. 2) it can be concluded that the use of the position of the centres of gravity has the advantage in relation to the use of the peak positions in the determination of the diffraction angles, when the mean wavelenght is used $\lambda_\alpha = (2\lambda_{\alpha_1} + \lambda_{\alpha_2})/3$. This conclusion in especially important when a callibrating substance is used, because the profile of a line of the standard is often different from the profile of the neighbour line of the specimen which is examined. Therefore the values $\varepsilon_o/\delta$ will be quite different for these two lines.

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## IZVOD

### Matematički tretman proširenja rendgenskih difrakcionih linija uslijed razdvajanja komponenata $K\alpha$ dubleta

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Opisano je matematičko rješenje korigiranja proširenja rendgenskih difrakcionih linija do kojeg dolazi uslijed razdvajanja komponenata $K\alpha$ dubleta. Metoda se sastoji u superpoziciji dvaju profila jednakog oblika i jednake širine $B$, razdvojenih međusobno kutnim razmakom $\delta$ i različitih u visini za faktor dva. Za razne omjere $\delta$

i rezultantne širine $B_0$ dobiveni su slijedeći rezultati za profile oblika $\exp(-k^2 \varepsilon^2)$ i $(1 + k^2 \varepsilon^2)^{-1}$: 1. integralna širina $B_{0i}$ i širina na polovici visine maksimuma intenziteta $B_{01/2}$ rezultatnog profila, 2. visina maksimuma $I(\varepsilon_0)$ rezultantnog profila, 3. kutna udaljenost $\varepsilon_0$ maksimuma rezultantnog profila od maksimuma jače komponente i 4. granična vrijednost omjera $\delta/B_0$ kad se rezultantni profil s jednim maksimumom transformira u profil s dva maksimuma. Sve te vrijednosti jako ovise o izboru analitičke funkcije kojom se opisuju profili komponenata. Omjer $\varepsilon_0/\delta$ približno je jednak $^1/_3$ samo za vrlo malene vrijednosti $\delta/B_0$. Može se zato zaključiti da upotreba položaja težišta ima prednost pred upotrebom položaja maksimuma rezultantnog profila kad komponente nisu potpuno razdvojene pa se koristi srednja vrijednost valne duljine $\lambda_a = (2\lambda_{a_1} + \lambda_{a_2})/3$.

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