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*Acta Cryst.* (1981). A**37**, 525–529

# Diffracted Intensities From Partially Ordered Layer Structures With Layer Shift: Two Dimensional

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(*Received* 30 *August* 1980; *accepted* 26 *January* 1981)

## Abstract

A general expression for the diffracted intensities from an aggregate of partially disordered layer structures consisting of plane lattice layers displaced randomly along **a** and **b** by arbitrary fractions $a/q_a$ and $b/q_b$ has been worked out. The approach is similar to that of Wilson [*X-ray Optics* (1962). London: Methuen] and has been followed by Ray, De & Bhattacherjee [*Clay Miner.* (1980), **15**, 393]. The expression is very general in nature and is suitable for studying the variation of intensities from such crystallites with any amount of displacements. Numerical computations for several cases have been carried out and results discussed. It is concluded that the peak will broaden and background increase as the magnitudes and probabilities of disorder increase.

## Introduction

In a previous publication (Ray, De & Bhattacherjee, 1980) a general expression for the diffracted intensities from a partially disordered layer structure with a displacement has been worked out. The displacement, as is commonly found in minerals, consists of a one-dimensional shift of a layer parallel to the adjacent layers by an arbitrary fraction $b/q$ along the $b$ axis, where $q$ is any integer. This expression is quite suitable for investigating the nature of the diffraction pattern from the layer structure when the displacement is gradually changed by any fraction of the axial length **b** in this direction. It would be more general and interesting to study the effect on the diffraction pattern when the layer is displaced in two directions simultaneously by $a/q_a$ and $b/q_b$ along **a** and **b**, where $q_a$ and $q_b$ are both integers. As mentioned in the previous paper (Ray *et al.*, 1980) such situations are closer to reality and are likely to occur in several minerals with a layer type structure, which are prone to this type of disorder because of their structural characteristics. Wilson (1962) has also made an attempt to study the diffraction from hexagonal cobalt with displacements **a**/3 and 2**b**/3. However, a more general expression of the diffracted intensity from a disordered structure of the above type is expected to be very useful in distinguishing between conglomerations of layer crystallites with different types of displacement and perhaps to estimate the magnitude of the displacements. The present work aims at fulfilling this objective.

## Theory

The present derivation is based primarily on the model of disordered crystals with plane lattice layers as described in the previous work (Ray *et al.*, 1980). Here too the layers are taken to be parallel to the **ab** plane with **c** perpendicular to the layer. The disorder consists of shifts of the layer parallel to itself by $a/q_a$ and $b/q_b$ along **a** and **b** respectively, where $q_a$ and $q_b$ are integers. All symbols used carry the usual meaning as in the previous publication (Ray *et al.*, 1980).

Let the shift of a layer be $a/q_a$ along the $a$ axis and the probability of such shift be $\alpha$. Corresponding quantities in the $b$ direction for a layer are taken to be

0567-7394/81/040525-05$01.00 

$b/q_b$ and $\beta$. Then, as in Ray *et al.* (1980), here too we can write

$$^aR_m = \frac{1}{q_a}\left[1 + (q_a - 1)\left(1 - \frac{q_a}{q_a - 1}\alpha\right)^m\right] \quad (1a)$$

$$^aW_m = \frac{1}{q_a}\left[1 - \left(1 - \frac{q_a}{q_a - 1}\alpha\right)^m\right] \quad (1b)$$

and

$$^aR_m + (q_a - 1)\,^aW_m = 1. \quad (1c)$$

Likewise,

$$^bR_m = \frac{1}{q_b}\left[1 + (q_b - 1)\left(1 - \frac{q_b}{q_b - 1}\beta\right)^m\right] \quad (2a)$$

$$^bW_m = \frac{1}{q_b}\left[1 - \left(1 - \frac{q_b}{q_b - 1}\beta\right)^m\right] \quad (2b)$$

and

$$^bR_m + (q_b - 1)\,^bW_m = 1. \quad (2c)$$

Here $^aR_m$ and $^aW_m$ are the probabilities of the $m$th added layer being in the right and wrong place respectively when the displacements are $a/q_a$ in the $a$ direction only. Similarly, $^bR_m$ and $^bW_m$ denote corresponding probabilities when the displacements consist of only $b/q_b$ along **b**. Considering all possible right and wrong places that the $m$th layer may occupy, we get

$$[^aR_m + (q_a - 1)\,^aW_m][^bR_m + (q_b - 1)\,^bW_m] = 1. \quad (3)$$

Following a similar procedure and using the same symbol as in Ray *et al.* (1980), we can write the average value of the structure factor for two layers separated by $m$ interlayer distances as

$$\begin{aligned} J_m = {} & F^2\,^aR_m\,^bR_m + F^2\,^aR_m\,^bW_m\left\{\exp\left(2\pi i\frac{k}{q_b}\right) + \exp\left(2\times 2\pi i\frac{k}{q_b}\right) + \cdots + \exp\left[(q_b - 1)\,2\pi i\frac{k}{q_b}\right]\right\} + F^2\,^aW_m\,^bR_m \\ & \times\left\{\exp\left(2\pi i\frac{h}{q_a}\right) + \exp\left(2\times 2\pi i\frac{h}{q_a}\right) + \cdots + \exp\left[(q_a - 1)2\pi i\frac{h}{q_a}\right]\right\} + F^2\,^aW_m\,^bW_m \\ & \times\left\{\exp\left(2\pi i\frac{h}{q_a}\right) + \exp\left(2\times 2\pi i\frac{h}{q_a}\right) + \cdots + \exp\left[(q_a - 1)2\pi i\frac{h}{q_a}\right]\right\} \\ & \times \exp\left(2\pi i\frac{k}{q_b}\right) + \exp\left(2\times 2\pi i\frac{k}{q_b}\right) + \cdots + \exp\left[(q_b - 1)2\pi i\frac{k}{q_b}\right]\Big\}, \end{aligned} \quad (4)$$

where $h$ and $k$ are the indices of reflections and $F$ is the structure factor of a normal layer. With (1) and (2) the above expression can be simplified to

$$\begin{aligned} J_m = F^2 & \left\{[1 - (q_a - 1)\,^aW_m] + {}^aW_m\frac{\sin[(q_a - 1)\pi h/q_a]}{\sin(\pi h/q_a)}\exp(\pi ih)\right\} \\ & \times\left\{[1 - (q_b - 1)\,^bW_m] + {}^bW_m\frac{\sin[(q_b - 1)\pi k/q_b]}{\sin(\pi k/q_b)}\exp(\pi ik)\right\}. \end{aligned} \quad (5)$$

From (1$b$) we get

$$\begin{aligned} & [1 - (q_a - 1)\,^aW_m] + {}^aW_m\frac{\sin[(q_a - 1)\pi h/q_a]}{\sin(\pi h/q_a)}\exp(\pi ih) \\ & = A(h,q_a) - (1 - \gamma)^m[A(h,q_a) - 1], \end{aligned} \quad (6)$$

where

$$A(h,q_a) = \left\{1 + \frac{\sin[(q_a - 1)\pi h/q_a]}{\sin(h/q_a)}\exp(\pi ih)\right\}\frac{1}{q_a}$$

and

$$\gamma = \frac{q_a}{q_a - 1}\alpha.$$

Similarly, with (2$b$) we obtain

$$\begin{aligned} & [1 - (q_b - 1)\,^bW_m] + {}^bW_m\frac{\sin[(q_b - 1)\pi k/q_b]}{\sin(\pi k/q_b)}\exp(\pi ik) \\ & = A(k,q_b) - (1 - \delta)^m[A(k,q_b) - 1], \end{aligned} \quad (7)$$

where

$$\delta = \frac{q_b}{q_b - 1}\beta.$$

From (6) and (7), (5) transforms to

$$J_m = F^2\{A(h,q_a) - (1-\gamma)^m[A(h,q_a) - 1]\} \times \{A(k,q_b) - (1-\delta)^m[A(k,q_b) - 1]\}. \quad (8)$$

Following Wilson (1962), we may write the intensity of reflection $G^2(0)$ for $\omega = 0$, where $\omega$ is a variable in reciprocal space denoting distance from an exact reciprocal-lattice point, as

$$G^2(0) = NJ_0 + 2(N-1)J_1 + 2(N-2)J_2 + \cdots + 2J_{N-1}, \quad (9)$$

which is similar to (9) of our previous paper (Ray *et al.*, 1980). Substitution of values of $J_m$ from (8) transforms $G^2(0)$ or intensity $I(0)$ to

$$\begin{aligned} G^2(0) = {} & F^2A(h,q_a)A(k,q_b)\{2[N + (N-1) + (N-2) \\ & + \cdots + 1] - N\} - F^2A(k,q_b) \\ & \times \{A(h,q_a) - 1\}\{2N[1 + (1-\gamma) \\ & + (1-\gamma)^2 + \cdots + (1-\gamma)^{N-1}] - N\} \\ & - F^2A(h,q_a)\{A(k,q_b) - 1\} \\ & \times \{2N[1 + (1-\delta) + (1-\delta)^2 \\ & + \cdots + (1-\delta)^{N-1}] - N\} \\ & + F^2\{A(h,q_a) - 1\}\{A(k,q_a) - 1\} \\ & \times \{2N[1 + (1-\gamma)(1-\delta) \\ & + (1-\gamma)^2(1-\delta)^2 \\ & + \cdots + (1-\gamma)^N(1-\delta)^N] - N\}. \quad (10) \end{aligned}$$

Assuming

$$N \gtrsim \frac{1}{\gamma} \gtrsim \frac{1}{\delta} \gtrsim \frac{1}{\gamma+\delta} \quad (11)$$

and $0 < \gamma < 1$, $0 < \delta < 1$, such that $\gamma + \delta \gg \gamma\delta$, we can further simplify the intensity expression to

$$\begin{aligned} G^2(0) = {} & F^2N^2A(h,q_a)A(k,q_b) \\ & - F^2A(k,q_b)\{A(h,q_a) - 1\}\frac{N(2-\gamma)}{\gamma} \\ & - F^2A(h,q_a)\{A(k,q_b) - 1\}\frac{N(2-\delta)}{\delta} \\ & + F^2\{A(h,q_q) - 1\}\{A(k,q_b) - 1\} \\ & \times \frac{N(2-\overline{\gamma+\delta})}{\gamma+\delta}. \quad (12) \end{aligned}$$

We now try to evaluate the intensity $G^2(\omega) = I(\omega)$ for any arbitrary value of the reciprocal-space variable $\omega$ ($\omega \neq 0$). Proceeding as in the previous work (Ray *et al.*, 1980), we can write the intensity as

$$\begin{aligned} I(\omega) = {} & G(\omega)\,G^*(\omega) \\ = {} & F_1^2 + F_2^2 + F_3^2 + \cdots + F_N^2 \\ & + 2\cos 2\pi\omega(F_1F_2 + F_2F_3 + F_3F_4 \\ & + \cdots + F_{N-1}F_N) \\ & + 2\cos 4\pi\omega(F_1F_3 + F_2F_4 + F_3F_5 \\ & + \cdots + F_{N-2}F_N) \\ & + 2\cos 6\pi\omega(F_1F_4 + F_2F_5 + F_3F_6 \\ & + \cdots + F_{N-3}F_N) + \cdots \\ & + 2\cos 2(N-1)\,\pi\omega F_1F_N \\ = {} & NJ_0 + 2(N-1)J_1\cos 2\pi\omega \\ & + 2(N-2)J_2\cos 4\pi\omega \\ & + 2(N-3)J_3\cos 6\pi\omega \\ & + \cdots + 2\times 1\times J_{N-1}\cos 2(N-1)\pi\omega. \quad (13) \end{aligned}$$

Substitution of the value of $J_m$ from (8) transforms (13) to

$$\begin{aligned} I(\omega) = {} & F^2A(h,q_a)A(k,q_b) \\ & \times [N + 2(N-1)\cos 2\pi\omega \\ & + 2(N-2)\cos 4\pi\omega + \cdots \\ & + 2\times 1\times\cos 2\pi(N-1)\omega] \\ & - F^2A(k,q_b)\{A(h,q_a) - 1\} \\ & \times [N + 2(N-1)(1-\gamma)\cos 2\pi\omega \\ & + 2(N-2)(1-\gamma)^2\cos 4\pi\omega \\ & + \cdots + 2\times 1\times(1-\gamma)^{N-1}\cos 2(N-1)\pi\omega] \\ & - F^2A(h,q_a)\{A(k,q_b) - 1\} \\ & \times [N + 2(N-1)(1-\delta)\cos 2\pi\omega \\ & + 2(N-2)(1-\delta)^2\cos 4\pi\omega \\ & + \cdots + 2\times 1\times(1-\delta)^{N-1}\cos 2(N-1)\pi\omega] \\ & + F^2\{A(h,q_a) - 1\}\{A(k,q_b) - 1\} \\ & \times [N + 2(N-1)(1-\gamma+\delta)\cos 2\pi\omega \\ & + 2(N-2)(1-\overline{\gamma+\delta})^2\cos 4\pi\omega \\ & + \cdots + 2\times 1\times(1-\overline{\gamma+\delta})^{N-1} \\ & \times \cos 2(N-1)\pi\omega]. \quad (14) \end{aligned}$$

Applying the assumptions of (11) we can write (14) as

$$
\begin{aligned}
I(\omega) = {} & F^2 A(h,q_a)\, a(k,q_b) \\
& \times \left\{ 2\left[ N \frac{\sin N\pi\omega}{\sin \pi\omega} \cos(N-1)\pi\omega \right.\right. \\
& + \frac{1}{2} \frac{\sin^2 (N-1)\pi\omega}{\sin^2 \pi\omega} \\
& \left.\left. - \frac{N-1}{2} \frac{\sin(2N-1)\pi\omega}{\sin \pi\omega} \right] - N \right\} \\
& - F^2 A(k,q_b)\{A(h,q_a)-1\} \\
& \times \left[ 2N \frac{1-(1-\gamma)\cos 2\pi\omega}{1-2(1-\gamma)\cos 2\pi\omega + (1-\gamma)^2} - N \right] \\
& - F^2 A(h,q_a)\{A(k,q_b)-1\} \\
& \times \left[ 2N \frac{1-(1-\delta)\cos 2\pi\omega}{1-2(1-\delta)\cos 2\pi\omega + (1-\delta)^2} - N \right] \\
& + F^2\{A(h,q_a)-1\}\{A(k,q_b)-1\} \\
& \times \left[ 2N \frac{1-(1-\overline{\gamma+\delta})\cos 2\pi\omega}{1-2(1-\overline{\gamma+\delta})\cos^2 \pi\omega + (1-\overline{\gamma+\delta})^2} \right. \\
& \left. - N \right]. \qquad (15)
\end{aligned}
$$

Equation (15), which is very similar to equation (16) of Ray *et al.* (1980) gives the intensity variation with $\omega$ from a disordered crystallite with displacements $a/q_a$ and $b/q_b$ along the $a$ and $b$ axes. However, this expression contains two more terms–one giving the contribution of one additional displacement ($a/q_a$ or $b/q_b$) and the other, the last term, the joint contribution of both the displacements.

### Special cases

Let us now consider some special cases of the general equation (15) in order to understand the significance of the different terms more comprehensively.

*Case* I. Let us first consider the case when $h = nq_a$ and $k = n'\, q_b$, $n$ and $n'$ both being integers. Under these conditions (15) can be shown to become

$$
\begin{aligned}
I(\omega) = F^2 & \left\{ 2\left[ N \frac{\sin N\pi\omega}{\sin \pi\omega} \cos(N-1)\pi\omega \right.\right. \\
& + \frac{1}{2} \frac{\sin^2 (N-1)\pi\omega}{\sin^2 \pi\omega} \\
& \left.\left. - \frac{N-1}{2} \frac{\sin(2N-1)\pi\omega}{\sin \pi\omega} \right] - N \right\}. \qquad (16)
\end{aligned}
$$

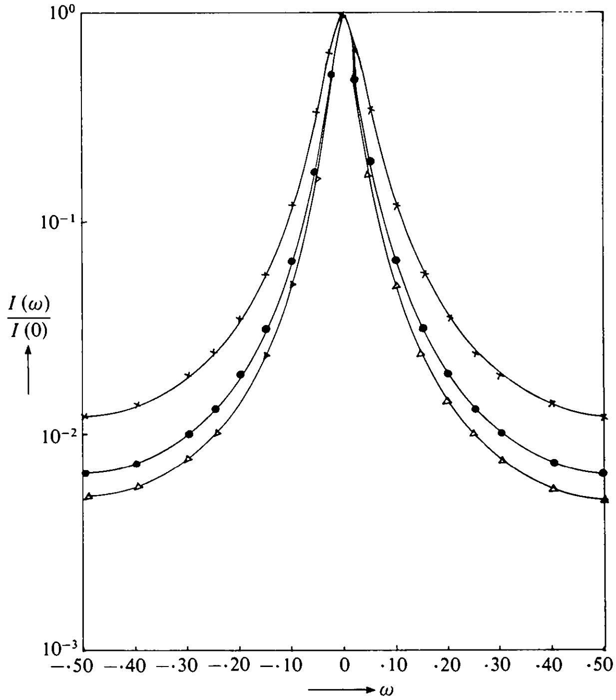


Fig. 1. $I(\omega)/I(0)$ *versus* $\omega$ for different values of $q_a$, $q_b$. $\alpha = \beta = 0{\cdot}05$. × $q_a = 2$, $q_b = 2$; ● $q_a = 3$, $q_b = 3$; △ $q_a = 4$, $q_b = 4$.

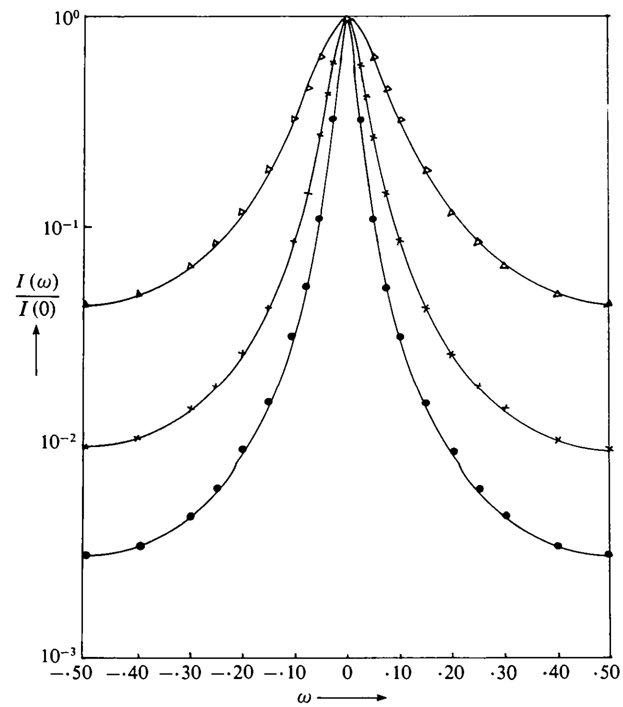


Fig. 2. $I(\omega)/I(0)$ *versus* $\omega$ for different values of $\alpha$, $\beta$. $q_a = 2$, $q_b = 3$. △ $\alpha = 0{\cdot}1$, $\beta = 0{\cdot}1$; × $\alpha = 0{\cdot}05$, $\beta = 0{\cdot}05$; ● $\alpha = 0{\cdot}03$, $\beta = 0{\cdot}03$.

This expression is free from defect and the terms containing defects vanish. This is identical with the case for $k = qn$ in Ray *et al.* (1980) as expected.

*Case* II. For $h = nq_a$, $k = n' q_b \pm 1$, the situation is analogous to that of (16) of Ray *et al.* (1980) when $k = nq \pm 1$. Here too we get, under the above conditions,

$$I(\omega) = NF^2 \frac{\delta(2-\delta)}{1 - 2(1-\delta)\cos 2\pi\omega + (1-\delta)^2}, \quad (17)$$

which is, as expected, identical with (19) of Ray *et al.* (1980). This shows that for this type of reflection, the intensity will be unaffected by a displacement in the $a$ direction but will be affected by $b$-axis displacements.

*Case* III. When $h = nq_a \pm 1$, $k = n' q_b$, the situation becomes almost similar to that of case II except that the intensity is now affected by $a$ displacement and remains unaffected by $b$-axis disorder. Equation (15) reduces to

$$I(\omega) = NF^2 \frac{\gamma(2-\gamma)}{1 - 2(1-\gamma)\cos 2\pi\omega + (1-\gamma)^2}. \quad (18)$$

Both (17) and (18) will on simplification reduce to equation (6) of Wilson (1962).

*Case* IV. $h = nq_a \pm 1$ and $k = nq_b \pm 1$. This is the most general case when both the displacements will manifest themselves in the observed intensity which will be given by

$$I(\omega) = NF^2 \frac{(\gamma+\delta)(2-\overline{\gamma+\delta})}{1 - 2(1-\overline{\gamma+\delta})\cos 2\pi\omega + (1-\overline{\gamma+\delta})^2}. \quad (19)$$

## Numerical computations and discussion

Numerical computations for different values of $\alpha$, $\beta$ and $q_a$, $q_b$ have been carried out for reflections $h = nq_a \pm 1$ and $k = n' q_b \pm 1$ which correspond to case IV. Hence, (19) was used for these calculations. The results of the calculation for different cases have been shown in Figs. 1 and 2. Fig. 1 shows that all the curves are symmetrical and have the same general features. Only the sharpnesses of the relative intensity peaks increase as the magnitudes of the displacements, *i.e.* $a/q_a$ and $b/q_b$, both decrease–an observation similar to that of Ray *et al.* (1980). Similarly, Fig. 2 reveals that the peaks of the relative intensities corresponding to a fixed value of $q_a$, $q_b$ become broader and background more enhanced as the probabilities, *i.e.* $\alpha$ and $\beta$, increase. These are expected results, as an increase in the values of $\alpha$ and $\beta$ and a decrease in the values of $q_a$ and $q_b$ obviously mean that the magnitude and probability of shift both increase and hence the crystal becomes more defective.

Thus the general conclusion is that the magnitude and the probabilities of the defect will not only broaden the peak but increase the general background as well.

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*Acta Cryst.* (1981). A**37**, 529–535

# Intermolecular Energy, Structure and Stability of Regular Stacks of Tetrathiafulvalene (TTF) and Tetracyanoquinodimethane (TCNQ)


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(*Received* 9 *December* 1980; *accepted* 26 *January* 1981)

## Abstract


The lattice energy of isolated, regular tetrathiafulvalene ($C_6H_4S_4$) and tetracyanoquinodimethane ($C_{12}H_4N_4$) segregated and mixed stacks was minimized for four structural parameters; a longitudinal and transverse slip of neighbouring molecules relative to each other, a rotation of a neighbouring molecule perpendicular to the molecular planes and the perpendicular distance between two neighbouring molecules. The van der Waals and repulsive interactions only were calculated from atom–atom potentials. The absolute minima of the lattice energies were achieved at stack structures slipped longitudinally with all stack parameters deviating less than about 0·1 Å from their observed mid-range values. The mixed stack proved to


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