Acta Cryst. (1978). A**34**, 652–655

Crystal Powder Statistics.
I. Lorentzian Line Profiles in Diffraction Spectra of Bernoullian Samples

By G. Allegra

Istituto di Chimica del Politecnico, Piazza Leonardo da Vinci 32, 20133 *Milano, Italy*

I. W. Bassi

Istituto di Ricerche 'G. Donegani', Soc. Montedison, Novara, Italy

and V. S. Meille

Istituto di Chimica del Politecnico, Piazza Leonardo da Vinci 32, 20133 *Milano, Italy*

(*Received* 30 *January* 1978; *accepted* 16 *March* 1978)

A Bernoullian powder sample is defined as an ensemble of parallelepiped crystals where the probability of any layer being on the surface is independent of its size as well as of the number of its predecessors, although being different for the three types of layers parallel to the crystal faces. It is shown that the line profile of any reflection is given by the Lorentzian, or Cauchy, distribution $I(\varepsilon) = A/(1 + K^2\varepsilon^2)$, where ε is the reciprocal coordinate measured from the peak with intensity A, and $2/K$ is the half-peak width, provided the average size of the crystals is at least of the order of 10 unit cells along each of the three edges.

Introduction

Most of the current work on line profiles of crystal powder diffraction spectra is based upon their Fourier analysis, which may lead to the probability distributions of unit-cell rows along different directions, as well as to the effect of the strains affecting the polycrystalline specimens (see, for example, Stokes & Wilson, 1942; Warren, 1969).

In this as well as in subsequent papers, we have deemed it useful to reverse somehow the above approach; namely, to hypothesize given probability distributions of crystal dimensions from which to derive the corresponding line profiles. The presence of strains has been ignored in view of the fact that their separate effect may be experimentally evaluated, at least in principle (Warren, 1969).

The Cauchy, or Lorentzian, distribution $I(\varepsilon) = A/(1 + K^2\varepsilon^2)$ is sometimes considered as a satisfactory representation of the diffraction line shapes of polycrystalline specimens; $I(\varepsilon)$ is the intensity at the reciprocal coordinate ε measured from the peak with intensity A, and $2/K$ is the full width at half-peak height. It will be shown in this paper that, if the effect of particle strain is neglected, such a line shape is characteristic of samples where the statistical ensemble of the crystals is described by the following simple rule. Each perfect crystal is a parallelepiped with edges parallel to the unit-cell vectors **a**, **b** and **c**; it may therefore be considered as constituted of three different classes of layers, of single unit-cell thickness, parallel to (**b**,**c**), (**a**,**c**) and (**a**,**b**). Any layer belonging to the first class within the crystalline ensemble has a probability α ($\ll 1$) of being a terminal layer, regardless both of its lateral dimensions and of the number of its predecessors; the same applies to layers of the other two classes, their respective probabilities being β and γ ($\ll 1$). In this, as well as in a following paper (Allegra & Ronca, 1978), the parameters α, β and γ will be used with the same meaning; no confusion with the direct cell angles should arise, since they will never enter the resulting mathematical expressions. In practice, the validity of the following results should be sufficiently guaranteed for most purposes by keeping each of the probabilities $<0{\cdot}1$, which means that the average crystal size corresponds to more than 10 unit cells along each direction. In general, the probability for a crystal to have edge lengths $N_1 a$, $N_2 b$, $N_3 c$ along **a**, **b** and **c** is given by

$$P(N_1,N_2,N_3) = \alpha\beta\gamma(1-\alpha)^{N_1-1}(1-\beta)^{N_2-1}(1-\gamma)^{N_3-1} \simeq \alpha\beta\gamma\exp(-N_1\alpha - N_2\beta - N_3\gamma), \quad (1)$$

where (N_1,N_2,N_3) are any three integral numbers. Since the resulting statistics correspond to a Bernoullian distribution of edge lengths along any of the three directions, we shall designate the crystalline ensemble as a Bernoullian powder sample.

Mathematical treatment

It is convenient to assume that all the crystals are parallel to each other within the sample, with the obvious assumption that the amplitudes diffracted by any two of them have no phase coherence. Although the overall intensity diffracted for any reciprocal-vector length $S(=2\sin\theta/\lambda)$ is the same as for the completely disordered sample, the above artifice allows both the real and the reciprocal axes to be considered coincident for all the crystals. Indicating with (x^*,y^*,z^*) the components of $\mathbf{S}$ along the reciprocal unit-cell vectors ($\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ respectively), the average diffracted intensity may be expressed as

$$\langle I(x^*,y^*,z^*)\rangle = \mathscr{N}|F^2(x^*,y^*,z^*)| \times \sum\sum\sum_{r,s,t=-\infty}^{+\infty} \left\langle \exp\left[2\pi i\left(\frac{rx^*}{a^*}+\frac{sy^*}{b^*}+\frac{tz^*}{c^*}\right)\right]\right\rangle \tag{2}$$

where $F(x^*,y^*,z^*)$ is the structure factor expressed in electrons per unit cell, $\mathscr{N}$ is the total number of unit cells, while a^*, b^* and c^* are the lengths of $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$. The exponential in the right-hand side is the phase factor relative to a pair of unit cells belonging to two rth-neighbor layers of class 1, two sth-neighbor layers of class 2, two tth-neighbor layers of class 3. The average of each phase factor must be evaluated after assigning a unit weight whenever a unit cell has an (r,s,t) neighbor within the same crystal, zero otherwise. Since the probability of having two rth neighbors among the layers of the first class [*i.e.* parallel to $(\mathbf{b},\mathbf{c})$] is $(1-\alpha)^r$ and is independent of the corresponding probabilities pertaining to the other two layer classes, we have

$$\left\langle \exp\left[2\pi i\left(\frac{rx^*}{a^*}+\frac{sy^*}{b^*}+\frac{tz^*}{c^*}\right)\right]\right\rangle = (1-\alpha)^r(1-\beta)^s(1-\gamma)^t \times \exp\left[2\pi i\left(\frac{rx^*}{a^*}+\frac{sy^*}{b^*}+\frac{tz^*}{c^*}\right)\right], \tag{3}$$

and

$$\begin{aligned}\sum\sum\sum_{r,s,t=-\infty}^{+\infty} &\left\langle \exp\left[2\pi i\left(\frac{rx^*}{a^*}+\frac{sy^*}{b^*}+\frac{tz^*}{c^*}\right)\right]\right\rangle \\ &= \left[\sum_{r=-\infty}^{+\infty}(1-\alpha)^r\exp\left(\frac{2\pi irx^*}{a^*}\right)\right] \times \left[\sum_{s=-\infty}^{+\infty}(1-\beta)^s\exp\left(\frac{2\pi isy^*}{b^*}\right)\right] \times \left[\sum_{t=-\infty}^{+\infty}(1-\gamma)^t\exp\left(\frac{2\pi itz^*}{c^*}\right)\right] \\ &= \left[-1+\frac{1}{1-(1-\alpha)\exp\left(\frac{2\pi ix^*}{a^*}\right)}+\text{c.c.}\right] \times \left[-1+\frac{1}{1-(1-\beta)\exp\left(\frac{2\pi iy^*}{b^*}\right)}+\text{c.c.}\right] \\ &\quad \times \left[-1+\frac{1}{1-(1-\gamma)\exp\left(\frac{2\pi iz^*}{c^*}\right)}+\text{c.c.}\right],\end{aligned} \tag{3'}$$

where c.c. stands for 'complex conjugate' of each preceding term. Since (α,β,γ) are $\ll 1$ by assumption, the value of the above expression is negligibly small except when x^*/a^*, y^*/b^* and z^*/c^* are very close to integral values. Putting

$$\frac{x^*}{a^*}=h+\frac{\Delta x^*}{a^*};\quad \frac{y^*}{b^*}=k+\frac{\Delta y^*}{b^*};\quad \frac{z^*}{c^*}=l+\frac{\Delta z^*}{c^*}, \tag{4}$$

where h, k, l are integers and $\Delta x^*/a^*$, $\Delta y^*/b^*$, $\Delta z^*/c^*$ are $\ll 1$, we may expand the exponentials in (3) up to first-order terms, neglecting -1 inside each parenthesis and (α,β,γ) in comparison with unity, so that (2) transforms to

$$\begin{aligned}&\left\langle I\left(h+\frac{\Delta x^*}{a^*},k+\frac{\Delta y^*}{b^*},l+\frac{\Delta z^*}{c^*}\right)\right\rangle \\ &= \mathscr{N}|F^2(hkl)|\,.\left(\frac{1}{\alpha-\frac{2\pi i\Delta x^*}{a^*}}+\text{c.c.}\right) \\ &\times\left(\frac{1}{\beta-\frac{2\pi i\Delta y^*}{b^*}}+\text{c.c.}\right).\left(\frac{1}{\gamma-\frac{2\pi i\Delta z^*}{c^*}}+\text{c.c.}\right),\end{aligned} \tag{5}$$

where the small variation of the structure factor around (hkl) is neglected.

Our purpose is to obtain the integrated intensity for any value of S in the vicinity of the (hkl) Bragg point. If α^*, β^*, γ^* are the angles between $(\mathbf{b}^*,\mathbf{c}^*)$, $(\mathbf{a}^*,\mathbf{c}^*)$, $(\mathbf{a}^*,\mathbf{b}^*)$, respectively, let us recall that

$$S^2 = x^{*2}+y^{*2}+z^{*2}+2x^*y^*\cos\gamma^*+2x^*z^*\cos\beta^* + 2y^*z^*\cos\alpha^*, \tag{6}$$

wherefrom we may obtain the increments for both sides of the equation, *i.e.*

$$\begin{aligned}S\Delta S &= \Delta x^*(x^*+y^*\cos\gamma^*+z^*\cos\beta^*) \\ &+\Delta y^*(x^*\cos\gamma^*+y^*+z^*\cos\alpha^*) \\ &+\Delta z^*(x^*\cos\beta^*+y^*\cos\alpha^*+z^*),\end{aligned} \tag{7}$$

neglecting higher-order terms in the increments. From (7) we obtain Δx^* as a function of $(\Delta S,\Delta y^*,\Delta z^*)$, taking $x^*\simeq ha^*$, $y^*\simeq kb^*$, $z^*\simeq lc^*$ and $S\simeq S(hkl)\equiv S_0$,

$$\Delta x^* = A\Delta S - B\Delta y^* - C\Delta z^*, \tag{8}$$

with

$$\begin{aligned}&A=S_0/q_1;\quad B=q_2/q_1;\quad C=q_3/q_1; \\ &q_1 = ha^*+kb^*\cos\gamma^*+lc^*\cos\beta^*; \\ &q_2 = ha^*\cos\gamma^*+kb^*+lc^*\cos\alpha^*; \\ &q_3 = ha^*\cos\beta^*+kb^*\cos\alpha^*+lc^*.\end{aligned} \tag{8'}$$

With the above substitution, (5) may be written as

$$\langle \mathscr{I}^{0}_{hkl}(\Delta S,\Delta y^*,\Delta z^*)\rangle = \frac{\left\langle I\left(h+\dfrac{\Delta x^*}{a^*},\,k+\dfrac{\Delta y^*}{b^*},\,l+\dfrac{\Delta z^*}{c^*}\right)\right\rangle}{|F^2(hkl)|}$$

$$= \mathscr{N}\sum_{\pm}\left[\frac{1}{\alpha \pm \dfrac{2\pi i(A\Delta S - B\Delta y^* - C\Delta z^*)}{a^*}} \times \frac{1}{\beta \pm \dfrac{2\pi i\Delta y^*}{b^*}}\,\frac{1}{\gamma \pm \dfrac{2\pi i\Delta z^*}{c^*}}\right], \tag{9}$$

where the sum is to be extended to the eight terms containing the different combinations of + and − signs. The integrated intensity that produces the line profile in the powder spectrum is

$$\langle \mathscr{I}_{hkl}(\Delta S)\rangle = \int_{\mathscr{S}}\langle \mathscr{I}^{0}_{hkl}(\Delta S,\Delta y^*,\Delta z^*)\rangle\,\mathrm{d}^2\mathscr{S}, \tag{10}$$

where $\mathscr{S}$ is the surface of the sphere with radius $S_0 + \Delta S$, in reciprocal space. Obviously enough, the surface element $\mathrm{d}^2\mathscr{S}$ must be expressed in terms of a double differential containing $\mathrm{d}\Delta y^*\mathrm{d}\Delta z^*$ in order for the integration to be carried out. To this effect, it is useful first to refer to orthogonal coordinates (x^*_0,y^*_0,z^*_0) in reciprocal space, with the convention that x^*_0 coincides with x^*, while y^*_0 lies in the plane containing the x^* and y^* axes. In the orthogonal coordinates $\mathrm{d}^2\mathscr{S}$ may be simply expressed as

$$\mathrm{d}^2\mathscr{S} = \mathrm{d}\Delta x^*_0\,\mathrm{d}\Delta y^*_0/|\cos\sigma|, \tag{11}$$

where σ is the angle between the reciprocal vector $\mathbf{S}_0$ and the axis x^*_0; consequently, $\cos\sigma = x^*_0/S_0$ and

$$\mathrm{d}^2\mathscr{S} = (S_0/|x^*_0|)\,\mathrm{d}\Delta x^*_0\,\mathrm{d}\Delta y^*_0. \tag{12}$$

From the above, the linear transformation connecting (x^*,y^*,z^*) with (x^*_0,y^*_0,z^*_0) is given by the matrix product

$$(x^*_0,y^*_0,z^*_0) = (x^*,y^*z^*) \times \begin{pmatrix} 1 & 0 & 0 \\ \cos\gamma^* & \sin\gamma^* & 0 \\ \cos\beta^* & \dfrac{\cos\alpha^* - \cos\beta^*\cos\gamma^*}{\sin\gamma^*} & \dfrac{R^*}{\sin\gamma^*} \end{pmatrix} \tag{13}$$

where $R^* = (1 - \cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^* + 2\cos\alpha^*\cos\beta^*\cos\gamma^*)^{1/2}$.

Because of the special choice of axial orientation, (13) shows that the transformation leading from (y^*,z^*) to (y^*_0,z^*_0) is a subset of the general transformation, *i.e.*

$$(y^*_0,z^*_0) = (y^*,z^*) \times \begin{pmatrix} \sin\gamma^* & 0 \\ \dfrac{\cos\alpha^* - \cos\beta^*\cos\gamma^*}{\sin\gamma^*} & \dfrac{R^*}{\sin\gamma^*} \end{pmatrix}. \tag{14}$$

Equation (12) may now be expressed in terms of (x^*,y^*z^*), considering that S_0/x^*_0 coincides with A [compare (8′) and (13)]:

$$\mathrm{d}^2\mathscr{S} = |A|\,R^*\,\mathrm{d}\Delta y^*\,\mathrm{d}\Delta z^*, \tag{15}$$

since the Jacobian $J(y^*_0,z^*_0/y^*,z^*)$ is obviously the determinant of the 2 × 2 matrix reported in (14), *i.e.* R^*.

We are ready now to perform the integration (10) after the substitution (15). Since the average intensity [see equation (9)] virtually vanishes unless both Δy^* and Δz^* are very small, the double integral may be computed from $-\infty$ to $+\infty$ over both variables, while (x^*,y^*,z^*) and $S = S_0 \equiv S(hkl)$ may be considered as constant quantities, *i.e.*

$$\langle \mathscr{I}_{hkl}(\Delta S)\rangle = \mathscr{N}|A|R^* \times \sum_{\pm}\int\int_{-\infty}^{+\infty}\left\{\left[\alpha \pm \frac{2\pi i(A\Delta S - B\Delta y^* - C\Delta z^*)}{a^*}\right] \times \left(\beta \pm \frac{2\pi i\Delta y^*}{b^*}\right)\left(\gamma \pm \frac{2\pi i\Delta z^*}{c^*}\right)\right\}^{-1}\mathrm{d}\Delta y^*\mathrm{d}\Delta z^*. \tag{16}$$

Let us first consider the integral over Δy^*. Although the variable of integration is real, we may use the theorem of residues, since the absolute value of the integrand behaves as $1/|\Delta y^*|^2$ for $\Delta y^* \to \infty$. In order for any of the eight integrals to be non-zero, the two poles must be located on opposite sides with respect to the real axis. We have the following choices for the ± signs within brackets, depending on the actual sign of B, in order to obtain a non-zero result:

Sign within first brackets	Sign within second brackets	Sign of B
+	+	+
+	−	−
−	+	−
−	−	+

It is possible to verify that the above selection rules lead to the following result for the sum of integrals in (16):

$$\sum_{\pm}\int_{-\infty}^{+\infty} a^*b^*c^*\,\mathrm{d}\Delta z^*/\{[\alpha a^* + |B|\beta b^* \pm 2\pi i(A\Delta S - C\Delta z^*)][\gamma c^* + 2\pi i\Delta z]\}. \tag{17}$$

The eight integrals in (16) are thus reduced to four. With a similar argument, integration over Δz^* leads to

$$a^*b^*x^*\left[\frac{1}{\alpha a^* + \beta|B|b^* + \gamma|C|c^* + 2\pi i A\Delta S} + \mathrm{c.c.}\right]. \tag{18}$$

Now, substitution into (16) gives the following result, remembering that $R^*a^*b^*c^* = V^* = V^{-1}$ ($V =$ volume of the unit cell) and (8′),

$$\langle \mathscr{I}_{hkl}(\Delta S)\rangle = \mathscr{N}\,\frac{S(hkl)}{V}\cdot\frac{2Q(hkl)}{Q^2(hkl) + 4\pi^2S^2(hkl)\Delta^2S}. \qquad (19)$$

where

$$Q(hkl) = \alpha a^*|ha^* + kb^*\cos\gamma^* + lc^*\cos\beta^*| + \beta b^*|ha^*\cos\gamma^* + kb^* + lc^*\cos\alpha^*| + \gamma c^*|ha^*\cos\beta^* + kb^*\cos\alpha^* + lc^*|. \qquad (19')$$

It is apparent that the intensity given by (19) corresponds to a Lorentzian function, the peak height and the full width at half height being

$$\begin{cases} \langle \mathscr{I}_{hkl}(0)\rangle = \mathscr{N}\,\dfrac{2S(hkl)}{VQ(hkl)}; \\ W_{1/2,hkl} = Q(hkl)/[\pi S(hkl)] \text{ (in units } S\text{)}, \end{cases} \qquad (20)$$

while the intensity profile integrated over ΔS is

$$\mathscr{I} = \int_{-\infty}^{+\infty} \langle \mathscr{I}_{hkl}(\Delta S)\rangle\, d\Delta S = \mathscr{N}/V, \qquad (21)$$

as it is easy to obtain from (19). This is the well known general result characteristic of any crystalline system, irrespective of its actual morphological state (see, for example, Warren, 1969).

A related property is that the product of the peak height times the peak width is also independent of Q and S:

$$\langle \mathscr{I}_{hkl}(0)\rangle\, W_{1/2,hkl} = \mathscr{N}\,\frac{2}{\pi V}, \qquad (22)$$

i.e. the peak height is inversely proportional to its width, for a given value of the structure factor.

Although both the peak height and the half-peak width depend on the particular values of the Bragg indices (h,k,l), it may be easily seen from (19) and (20) that they are identical for reflections characterized by the same ratios between the indices, as expected (*i.e.* successive orders of one same reflection).

It may be useful to specialize the above result to the space groups for which $\cos\alpha^* = \cos\beta^* = \cos\gamma^* = 0$. We obtain from (19′):

$$\begin{cases} Q(hkl) = \alpha|h|a^{*2} + \beta|k|b^{*2} + \gamma|l|c^{*2}, \\ S(hkl) = (h^2a^{*2} + k^2b^{*2} + l^2c^{*2})^{1/2}. \end{cases} \qquad (23)$$

Consequently, [see equation (20)], the line profiles of the reflections along the diagonals tend to be broader than those along the axes of reciprocal space. For instance, in the simplest cubic case we have, for three typical choices (taking $\alpha = \beta = \gamma$; $a^* = b^* = c^* = 1/a$),

$$\langle \mathscr{I}_{hkl}(0)\rangle = \frac{2\mathscr{N}}{\alpha a^2}\,\frac{(h^2 + k^2 + l^2)^{1/2}}{|h| + |k| + |l|};$$

$$W_{1/2,hkl} = \frac{\alpha}{\pi a}\,\frac{|h| + |k| + |l|}{(h^2 + k^2 + l^2)^{1/2}}. \qquad (24)$$

As it may be seen, the peak width is largest for $|h| = |k| = |l|$ and smallest for $k = l = 0$, $h \neq 0$, the ratio between the corresponding values being $\sqrt{3}$; of course, the converse must be applied to the peak height.

Conclusions

It has been shown that, provided (i) all the perfect crystals belonging to the sample are parallelepipeds bounded by the same set of crystallographic planes, and (ii) the distribution of the three edge lengths is Bernoullian with an average value larger than 10 unit cells, all the diffraction line profiles have a Lorentzian shape. It appears quite reasonable to reverse the argument, *i.e.* if the vast majority of the crystals are parallelepipeds and their observed line profiles are (close to) Lorentzian, then the Bernoullian distribution for the three edge lengths should be approached. Under these conditions an appropriate choice for the parameters (α, β, γ) should allow a satisfactory interpretation of the observed line profiles in terms of (19). Once α, β and γ are known, several important statistics of the sample may be obtained. As examples, the average edge length along **a**, for example, is a/α, and the average volume of the crystals is $V/(\alpha\beta\gamma) = V\langle N\rangle$, $\langle N\rangle$ being the average number of units per crystal. A more detailed discussion of the statistical implications of the Bernoullian distribution will be given in a following paper (Allegra & Ronca, 1978).

More generally, it may be worth pointing out that the Lorentzian shape associated with any reflection of a general powder sample should always be related to a probability distribution $P(N) = \bar{\alpha}\exp(-N\bar{\alpha})(\alpha \ll 1)$ for the rows containing N unit cells, perpendicular to the diffracting planes. This proceeds directly from the general possibility of describing the diffracting domains in terms of the above mentioned unit-cell rows as independently diffracting entities (Bertaut, 1949; Warren, 1969).

This work was made possible by a Research Contract with Montedison SpA. The authors thank Dr G. Ronca for useful discussions.

References

Allegra, G. & Ronca, G. (1978). Submitted to *Acta Cryst.*
Bertaut, F. (1949). *C. R. Acad. Sci.* **228**, 187–189.
Stokes, A. R. & Wilson, A. J. C. (1942). *Proc. Cambridge Philos. Soc.* **38**, 313–322.
Warren, B. E. (1969). *X-ray Diffraction*, ch. 13. Reading, Mass.: Addison-Wesley.