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Interpretation of Diffractometer Line Profiles Distortion due to the Diffraction Process*

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On the basis of the kinematic theory of powder diffraction it is shown that the angle factor

$$J(\theta) \propto \sin^2 \theta \cos \theta / (1 + \cos^2 2\theta)$$

describes the distortion of the line profile due to the diffraction process when the incident radiation consists of a spectral distribution $h_1(\lambda)$ (the angle scale equivalent of which is $h(\epsilon)$). The distortion includes the effects of the Lorentz and polarization factors, trigonometric factors associated with the experimental powder method and the effects of physical absorption.

In the absence of other aberrations the angle scale spectral distribution $h(\epsilon)$ is (to the first order) recovered from the observed distribution $f(\epsilon)$ from the equation

$$f(\epsilon)J(\theta) = h(\epsilon).$$

A_{LPU} the correction to be applied to counterbalance the shift in the observed profile due to the distortion of the profile caused by the diffraction process, is inferred from $J(\theta)$ and is applicable to crystal powders encountered in precision lattice parameter determinations.

1. Introduction

In three earlier papers (Ladell, Parrish & Taylor, 1959*a, b*; Ladell, Mack, Parrish & Taylor, 1959; hereinafter abbreviated as *LPTa, b*, *LMPT*), the interpretation of diffractometer line profiles by the method of centroids was discussed. In these papers attention was primarily focussed on operational procedures required in precision lattice parameter determinations. It was shown that it was necessary to correct the centroids of observed profiles for the effect of dispersion and the distortion due to the angle factor (Lorentz, polarization and geometric powder factors) which arises from the diffraction process.

In this paper the role of the diffraction process in the generation of diffractometer line profiles of polycrystalline specimens will be considered in greater detail. Using less restrictive assumptions than those which were used in the classical derivation of the integrated intensity formula for powder diffraction, it will be shown that the angle factor

$$J(\theta) \propto \sin^2 \theta \cos \theta / (1 + \cos^2 2\theta) \quad (1)$$

arises inherently from the diffraction process (when absorption is included) and describes the distortion of the angle scale spectral distribution in the absence of other aberrations.

In an earlier treatment Pike (1959) considered the effects of the Lorentz and polarization factors for two extreme limiting cases, but did not consider the effect of absorption. In an accompanying note (Pike & Ladell,

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1961) it is shown that Pike's treatment can be extended to include the correction for absorption. In the derivation given here, the more general case is considered and results are obtained which cover the intermediate cases in addition to the limiting cases cited by Pike.

The results obtained by Pike for the limiting case cited, namely,

$$\beta(\psi) \propto (1 + \cos^2 \psi) \tan \frac{1}{2}\psi \quad (2)$$

(Pike, 1959, equations (13), (16)) is recovered in this analysis when the effects of absorption are not considered.

Although some aspects of the role of absorption in the centroid method have been considered by Wilson (1958), the treatment given here considers specifically the effect of physical absorption in distorting the shape of the line profile and a quantitative correction is derived to account for this effect in the centroid method of precision lattice parameter determination.

The philosophy of the centroid method of precision lattice parameter determination, as well as the treatment of more complex problems arising in the interpretation of diffractometer line profiles, is to make the proper allowances for all the spectral, instrumental, geometrical and specimen factors which contribute to the line profile. In principle the verification of the proper treatment of the experimental data is the recovery of $h_1(\lambda)$, the spectral distribution of the incident beam, from $f(\epsilon)$, the observed profile, although this is not often realized in practice. To accomplish this recovery it is necessary to account for the following factors which distort the observed line profile:

- (i) Dispersion.
- (ii) Lorentz and polarization factors.
- (iii) Physical absorption.
- (iv) Powder method angle factor.
- (v) Instrumental aberrations.
- (vi) Perfection of crystals in the specimen.

Factors (i) through (iv) are called the geometrical factors. Since the angle factor (1) has been previously (*LPTa*, *LMPT*) used to account specifically for Lorentz and polarization effects in apparent contradiction (Pike & Ladell, 1961) to (2), factors (ii) and (iii) will be derived in this paper. Factors (i) and (iv) will be discussed only briefly.

The instrumental factors (v) have been discussed in detail (Parrish & Wilson, 1959). The effect of the crystal perfection (vi) on the corrections implied by the angle factor will also be described.

The development will be based on the kinematic theory of X-ray diffraction. Although all the mechanisms which cause the distortion of line profiles are important, we will be concerned here with the distortions due to the diffraction process. Because of its importance in the technique of precision lattice parameter determination by the method of centroids, the

correction factor, Δ_{LPU} (the shift of the centroid of the distorted line profile from the centroid which would be manifest in the absence of the distortion due to the diffraction process) will be determined. It will be assumed in the following discussion that the specimen consists of crystallites whose average dimensions are of the order of 10^{-4} cm., i.e., there is no line broadening caused by small particle size. The analysis applies to the common radiations normally used in powder diffractometry, e.g., the *K* lines of Mo, Cu, Co, Fe and Cr, and assumes that anomalous dispersion does not make a significant contribution.

In the following discussion, equations from Zachariasen (1945) and James (1950) will be indicated by prefixing the numerical designation of the equations given by these authors with *Z* and *J*, respectively.

2. Dispersion

The effect of dispersion has been discussed and the correction Δ_D has been derived (*LPTa*, eq. (5)) and calculated (*LMPT*, Fig. 1) for various radiations on the basis of an assumed spectral distribution (*LPTa*, eqs. (25), (26)). It should be noted that the correction factor Δ_D can be eliminated in the experimental arrangement (Ladell & Lowitzsch, 1960) by moving the counter tube in such a manner that the time rate of change of $\sin \theta$ is kept constant, rather than in the usual manner of scanning at a constant angular velocity. The feasibility of such a mechanism for precision diffractometry is being explored. Since the correction Δ_D may eventually be eliminated in the experimental procedures, it will be kept separate from the other factors.

3. Line profile distortions related to the diffraction process

The distortions due to (ii), (iii) and (iv) give rise to a composite angle factor given by (1). It should be noted that the classical theory (*Z*, 3.86) (as has been pointed out by Pike (1959)) is based on the restrictive assumptions that λ is strictly monochromatic and the specimen has perfect crystallites with a unique *d*-spacing associated with each reflection. The corrections for distortions (ii), (iii) and (iv) are lumped together and called† Δ_{LPU} , which has been calculated for various wavelengths using (1) (*LMPT*, Fig. 2). In this section the composite angle factor will be derived with the less restrictive assumption that the incident X-ray beam is not strictly monochromatic and consists of a spectral distribution $h_1(\lambda)$. In Section 4 the question

† Δ_{LPU} , as defined here, replaces the quantity Δ_{LP} which has been used earlier (*LPTa*, *LMPT*). The revised notation is used to indicate that the correction factor also accounts for absorption. Although the numerical values of Δ_{LPU} and Δ_{LP} are the same, the earlier notation Δ_{LP} is semantically incorrect as is explained in the accompanying note (Pike & Ladell, 1961).

of a distribution of d -spacings (Lang, 1956), such as would be manifest in a strained specimen, will be considered.

An observed line profile results from the convolution (*LPTa*, 4)

$$f(\varepsilon) = h \star (j \star k(\varepsilon)). \quad (3)$$

The argument ε , is the angular deviation from a given fiducial angle which shall be designated $2\theta_B$, i.e., $\varepsilon = 2\theta - 2\theta_B$; $h(\varepsilon)$ is the spectral profile on the angle scale, $j(\varepsilon)$ is the multiple convolution of all the instrumental aberrational distributions (v), and $k(\varepsilon)$ is the intrinsic diffraction profile of the powder. Since $h(\varepsilon)d\varepsilon = h_1(\lambda)d\lambda$, $h(\varepsilon)$ can be determined from the known spectral distribution $h_1(\lambda)$. We have

$$\begin{aligned} h(\varepsilon) &= d \cos(\theta_B + \frac{1}{2}\varepsilon)h_1(\lambda) \\ &= d \cos(\theta_B + \frac{1}{2}\varepsilon)h_1[2d \sin(\theta_B + \frac{1}{2}\varepsilon)], \quad (4) \end{aligned}$$

where d is the interplanar spacing for a specific set of parallel diffracting planes common to all the diffracting crystals in the powder specimen. θ_B defines† a fiducial wavelength λ_B ; by Bragg's law

$$\lambda_B = 2d \sin \theta_B = \psi(\theta_B). \quad (5)$$

3.1. Distortions due to diffraction

In order to separate the instrumental from the other distortions, it shall be assumed that the instrumental aberrations are negligible. Alternatively the 'observed' profile may be construed as the actual profile unfolded by $j(\varepsilon)$. This assumption creates no difficulty when applied to the centroid method of precision lattice parameter determination because this is the normal procedure, i.e., the unfolding is accomplished simply by subtracting the known centroid of $j(\varepsilon)$ from the centroid of the actual line profile (*LPTa*, *b*). Thus (3) is written

$$f(\varepsilon) = h \star k(\varepsilon). \quad (6)$$

The intrinsic diffraction profile of the powder, $k(\varepsilon)$, which would be observed for the monochromatic wavelength λ_B is given by

$$k(\varepsilon) = E(\theta_B)U(\mu_0)I_0SR_1(\varepsilon). \quad (7)$$

The factor $E(\theta_B)$, the 'powder method' angle factor, is given by

$$E(\theta_B) = (\frac{1}{2} \cos \theta_B)(1/(2\pi R \sin 2\theta_B)) = 1/(8\pi R \sin \theta_B), \quad (8)$$

where R is the distance from the goniometer axis of rotation to the detector. The term $(\frac{1}{2} \cos \theta_B)$ is the probability of finding a crystal at the correct glancing angle of incidence (*Z* 3.80) and $1/(2\pi R \sin 2\theta_B)$, the factor required to measure the intensity *per unit length* of the diffraction cone (of radius $R \sin 2\theta_B$) instead of the intensity in the entire cone.

The absorption factor

† This notation is not the same as that used in *LPTa*, where θ_B was designated as the angle equivalent of $\tilde{\lambda}$.

$$U(\mu_0) = 1/(2\mu_0), \quad (9)$$

where μ_0 is the (true) linear absorption coefficient of the crystal, and results from a derivation analogous to that given for reflection from a crystal face (*J* 2.41*a*, also Fig. 20).

I_0 is the strength of the incident beam and S is the beam cross-section.

$R_1(\varepsilon)$ is the single crystal interference function for unpolarized radiation given by

$$R_1(\varepsilon) = R(\varepsilon)(1 + \cos^2 2\theta_B)/2, \quad (10)$$

where $R(\varepsilon)$ is the single crystal interference function for polarized radiation (electric vector normal to the plane of incidence). The polarization factor appearing in (10) arises from considerations shown in the literature (*Z* 3.11, 3.12 and Fig. 3.3).

$R(\varepsilon)$ is derived by James (1950) by considering reflection from a crystal slab of infinite lateral extent composed of p planes with interplanar spacing d (*J* pages 36–38, replace a with d , θ_0 with θ_B , and λ with λ_B). James (*J* 2.23 and 2.20) gives

$$R(\varepsilon) = |q|^2 \sin^2(pB\varepsilon)/\sin^2(B\varepsilon), \quad (11)$$

where

$$B = 2\pi d (\cos \theta_B)/\lambda_B \quad (12)$$

and

$$-iq = i(Nd\lambda_B/\sin \theta_B)F(e^2/mc^2). \quad (13)$$

(In (13) F is the structure factor, e and m the electronic charge and mass respectively, c is the velocity of light, and N the number of scattering unit cells.)

Substituting $k(\varepsilon)$ given by (7) into (6) we have

$$\begin{aligned} f(\varepsilon) &= I_0Sh \star E(\theta)U(\mu_0)R_1(\varepsilon) \\ &= I_0S \int_{-\infty}^{\infty} R_1(\sigma)h(\varepsilon - \sigma)E_1(\varepsilon - \sigma)U_1(\varepsilon - \sigma)d\sigma. \quad (14) \end{aligned}$$

Since $R_1(\varepsilon)$ is an extremely sharp distribution we can write‡

‡ The arguments which substantiate this statement are the following.

$R_1(\varepsilon)$ is approximated by the Gaussian distribution $R_2(\varepsilon)$ where

$$R_2(\varepsilon) = ((1 + \cos^2 2\theta_B)/2)|q|^2(2p^2) \exp(-p^2B^2\varepsilon^2/\pi).$$

The approximation is such that

$$\begin{aligned} \int_{-\infty}^{\infty} R_1(\varepsilon)d\varepsilon &= \int_{-\infty}^{\infty} R_2(\varepsilon)d\varepsilon, \\ R_1(0) &= R_2(0), \end{aligned}$$

and the width at half maximum of both distributions, R_1 and R_2 , is the same.

$R_2(\varepsilon)$ has no appreciable value except in the small range $(-\Delta, \Delta)$ where we have let

$$\Delta = 3.5 \text{ (standard deviation of } R_2) = \frac{3.5 (\log 2)^{\frac{1}{2}}/\pi^{\frac{1}{2}}}{p^2\pi d (\cos \theta_B)/\lambda_B}.$$

Accordingly one obtains

$$\int_{-\infty}^{\infty} R_1(\sigma)h(\varepsilon - \sigma)d\sigma = \int_{-\Delta}^{\Delta} R_2(\sigma)h(\varepsilon - \sigma)d\sigma.$$

Since $h(\varepsilon) \approx h(\varepsilon \pm \Delta)$, we have

$$f(\varepsilon) = EU I_0 S \left[\int_{-\infty}^{\infty} R_1(\sigma) d\sigma h(\varepsilon) \right] \\ = EU \tau h(\varepsilon), \quad (15)$$

where

$$\tau = I_0((1 + \cos^2 2\theta_B)/2)(e^2/mc^2 V)(\lambda_B^3/\sin 2\theta_B) F^2 \delta v. \quad (16)$$

In (16), V is the volume of the unit cell of the crystal and δv the volume of the diffracting aggregate of crystals. τ is the integrated intensity for a small crystal (*J* 2·30, 2·31). Eq. (15) is the basic relationship which specifies how $h(\varepsilon)$, the angle scale spectral distribution, is distorted by the diffraction process in producing $f(\varepsilon)$. Each ordinate $h(\varepsilon)$ is attenuated by the factors $EU\tau$ to produce the corresponding ordinate $f(\varepsilon)$.

Since $E = E(\theta_B)$, $U = U(\mu_0) = U(\lambda_B)$, $\tau = \tau(\theta_B, \lambda_B)$ and $\lambda_B = \psi(\theta_B)$, we can rewrite (15) as

$$f(\varepsilon) = E(\theta_B) U(\theta_B) \tau(\theta_B) h(\varepsilon) \quad (17)$$

or

$$f(\theta) = E(\theta) U(\theta) \tau(\theta) h(\theta) = h(\theta)/J(\theta), \quad (18)$$

where we have defined $J(\theta)$ by

$$E(\theta) U(\theta) \tau(\theta) = 1/J(\theta). \quad (19)$$

3·2. Definition of Δ_{LPV}

Before proceeding to evaluate the angle factor given by (19) we will find the correction Δ_{LPV} , (*LPTa*, *LMPT*) from its definition

$$\tilde{\theta}_f + \Delta_{LPV} = \tilde{\theta}_h, \quad (20)$$

where $\tilde{\theta}_f$ and $\tilde{\theta}_h$ are the centroids (*LPTb*) of $f(\theta)$ and $h(\theta)$. We have

$$\Delta_{LPV} = \left[\int_{\theta_1}^{\theta_2} \theta h(\theta) d\theta / \int_{\theta_1}^{\theta_2} h(\theta) d\theta \right] \\ - \left[\int_{\theta_1}^{\theta_2} \theta (h(\theta)/J(\theta)) d\theta / \int_{\theta_1}^{\theta_2} (h(\theta)/J(\theta)) d\theta \right]. \quad (21)$$

In order to find the explicit angle dependence $J(\theta)$, we must first determine $E(\theta)$, $\tau(\theta)$ and $U(\theta)$.

$$\int_{-\Delta}^{\Delta} R_2(\sigma) h(\varepsilon - \sigma) d\sigma \approx h(\varepsilon) \int_{-\Delta}^{\Delta} R_2(\sigma) d\sigma \approx h(\varepsilon) \int_{-\Delta}^{\Delta} R_1(\sigma) d\sigma.$$

In a typical example for diffraction at $\theta_B = 70^\circ$, with Cu radiation $\lambda_B = 1.54 \text{ \AA}$, with crystallites 10^{-4} cm . thick,

$$\Delta = 3.5 \sqrt{(\log 2)/\pi} (1.54) \times 10^8 / (2\pi \times 10^4 \cos 70^\circ) \\ = 1.18 \times 10^{-4} \text{ radians.}$$

The approximation $h(\varepsilon) \approx h(\varepsilon \pm \Delta)$ is equivalent to the approximation

$$h_1(\lambda) \approx h_1(\lambda \pm \Delta\lambda),$$

where

$$\Delta\lambda = \lambda_B \cot \theta_B (\Delta/2) = 0.000034 \text{ \AA}.$$

In terms of the example, we would need to be able to distinguish between the ordinates $h_1(\lambda)$ and $h_1(\lambda \pm 0.000034)$ before the approximation is invalidated.

3·3. Wavelength and angle dependence of absorption factor

To find $U(\theta)$, the wavelength dependence of the linear absorption coefficient μ_0 will be determined; the angle dependence will then follow from (9) and (5). We will first determine μ_0 for the special case where absorption is virtually entirely due to the absorption by K electrons and then generalize the results to include L electron absorption as well.

For a crystal containing one element of atomic number Z we have:

$$(Z \text{ 3·100}) \quad \mu_0 = 2\pi K_0 \psi_0'', \quad (22)$$

where $K_0 = 1/\lambda$ and ψ_0'' is the imaginary part of the function ψ_0 given by

$$(Z \text{ 3·95}) \quad \psi_0 = -4\pi e^2 F_0 / (m\omega_0^2 V), \quad (23)$$

where

$$\omega_0 = (2\pi c/\lambda)^2.$$

If there are t atoms per unit cell

$$F_0 = t f = t \{ f_0 + \Delta f_K' + c \Delta f_K'' \}, \quad (24)$$

where f is the complex scattering factor, the real part of which is $f_0 + \Delta f_K' = (Z + \Delta f_K')$ and the imaginary part $\Delta f_K''$.

Thus

$$\psi_0'' = (-4\pi e^2 \lambda^2 / (m(2\pi c)^2 V)) t \Delta f_K''. \quad (25)$$

$\Delta f_K''$ is given by (*J* 4·61)

$$\Delta f_K'' = \frac{2^7 \exp(-4)}{9} \pi \left\{ \frac{4}{x^2(1-\delta_K)^2} - \frac{1}{x^3(1-\delta_K)^3} \right\} \quad (26)$$

$$\left. \begin{aligned} \delta_K &= \left(A - \frac{911}{\lambda_K} \right) / A \\ \text{where} \\ A &= (Z - 0.3)^2 + 1.33 + 10^{-5}(Z - 0.3)^4 \\ x &= \lambda_K / \lambda > 1 \end{aligned} \right\} \quad (27)$$

and λ_K is the wavelength of the K -absorption edge of the element (of atomic number Z).

Combining (22), (25), (26) and (27) we find

$$\mu_0 = \frac{t 2^8 e^2 \lambda^3 \exp(-4) \pi \{ 4\lambda_K(1-\delta_K) - \lambda \}}{9mc^2 V \left\{ \frac{\lambda_K^3(1-\delta_K)^3}{x^3} \right\}}. \quad (28)$$

Identifying the absorption with the element of atomic number Z , we can write (28) as

$$\mu_{0Z} = t K_3 \lambda^3 ((4A_Z - \lambda)/A_Z^3), \quad (29)$$

where

$$K_3 = 2^8 e^2 \exp(-4) \pi / (9mc^2 V) \quad (30)$$

and

$$A_Z = \lambda_K(1 - \delta_K). \quad (31)$$

The linear absorption of the crystal can be obtained from (29). We have

$$\mu_0 \text{ crystal} = K_3 \lambda^3 \left\{ \left[4 \sum_{Z=1}^g s_Z t_Z A_Z^{-2} \right] - \lambda \left[\sum_{Z=1}^g s_Z t_Z A_Z^{-3} \right] \right\}, \quad (32)$$

where g is the largest atomic number of the elements comprising the crystal matrix, s_Z is the fractional weight, and t_Z is the number of atoms of atomic number Z in the unit cell.

From (27) it is clear that

$$A_Z \approx 911/Z^2 > 1 \quad (33)$$

for atoms of atomic number Z which have absorption edges λ_K such that $\lambda_K > \lambda$ for wavelengths λ normally encountered in powder work. Thus where the absorption is due primarily to K electrons, the λ^3 term in (32) is the dominating term since

$$\left. \begin{array}{l} 4A_Z^{-2} \gg A_Z^{-3} \\ 4 \gg A_Z^{-1} \end{array} \right\}. \quad (34)$$

A complete specification of the λ dependence of μ_0 for absorption due to L electrons analogous to that given for K electrons will not be attempted. It suffices for our purposes, however, to conclude from empirical considerations that the absorption due to L electrons depends upon the wavelength in a manner similar to that determined for absorption due to K electrons. Thus, Victoreen (1948) has shown that the true atomic absorption coefficient, τ_a , is given within experimental error by the expressions:

$$\tau_a = \left\{ \left[3 - \frac{\lambda}{\lambda_3} \right] \lambda \frac{\lambda}{\lambda_1 \lambda_2} \right\} \pi \frac{e^2}{mc^2}, \quad (35)$$

where λ_1, λ_2 , and λ_3 are the critical wavelengths characteristic of a particular atom. From (35) and (32) we conclude that

$$\mu_0 = \lambda^3 (K_4 - K_5 \lambda), \quad (36)$$

where K_4 and K_5 are constants associated with the elements comprising the crystal matrix.

Substituting (36) into (9) and applying (5) we find

$$U(\theta) = 1/(16d^3 \sin^3 \theta (K_4 - 2dK_5 \sin \theta)). \quad (37)$$

Since λ^3 is the dominating term in μ_0 we can (within the limits of present experimental requirements) neglect the term $2dK_5 \sin \theta$ and obtain

$$U(\theta) \approx K_6 d^{-3} \cos^3 \theta, \quad (38)$$

where K_6 is a constant.

3.4. Angle dependence of τ and E

From (16) and (5) assuming negligible anomalous dispersion† we find

$$\tau(\theta) = K_1 d^3 (1 + \cos^2 2\theta) \sin^2 \theta \sec \theta, \quad (39)$$

where

$$K_1 = 4(e^2/(mc^2 V)) |F|^2. \quad (40)$$

† Where anomalous dispersion is not negligible, the structure factor is also a function of θ and λ ; $F = F(\theta, \lambda)$.

From (8) we have

$$E(\theta) = K_2 \operatorname{cosec} \theta, \quad (41)$$

where

$$K_2 = (8\pi R)^{-1}. \quad (42)$$

3.5. Combined angle factor

Combining (41), (40) and (38) and (19) we find

$$J(\theta) = K_1 K_2 K_6 \sin^2 \theta \cos \theta / (1 + \cos^2 2\theta). \quad (43)$$

Although this combined angle factor (43) is the same as that used by Ladell, Parrish & Taylor (*LPTa*), the origin of the factor was not discussed in their paper. The component of this factor excluding absorption, i.e., the component due exclusively to the Lorentz, polarization and trigonometric factor associated with the experimental powder method, can be obtained by multiplying (43) by (38):

$$U(\theta)J(\theta) = E\tau = K_1 K_2 d^3 \tan \theta (1 + \cos^2 2\theta). \quad (44)$$

Eq. (44) is in agreement with a result obtained by Pike.

The correction† Δ_{LPU} is found by substituting (43) in (21).

4. Crystal imperfection

Our considerations thus far have been concerned with a powder of perfect crystals (where the effects of extinction and refraction were assumed minimal). Real crystals, however, are known to have mosaic (imperfect) structure. Accordingly this case will now be considered.

In the mosaic structure model (Darwin, 1922) of a real crystal, there are two disorders: 1) atoms are arranged in layers which deviate from planarity, and 2) the crystal is composed of an assemblage of smaller ideal crystal blocks, each block slightly misoriented with respect to its neighboring blocks. Disorder of the second type plays a significant role in causing the enhancement and broadening of the diffraction pattern of large single crystals, changing the character of the diffraction pattern from that which would be observed for a large perfect crystal. This disorder, however, plays no role in powder diffractometry. For the powder case it is immaterial whether each individual crystal is an ideal block or an assemblage of diversely oriented ideal blocks since the crystal particles themselves are diversely (randomly) oriented. The first type of disorder, however, is of significance in powder work. In this disorder we can include such anomalies as strain and lattice distortion. The disorder can be treated by a crystal model in which a set of parallel diffracting planes (giving rise to a specific reflection) is characterized as follows: The distance between successive planes is not constant but varies (statistically) through-

† (21) is a more rigorous expression than that given earlier (*LPTa*, 7). The earlier expression becomes identical with (21) if $f(\theta)$ as defined in this paper is there substituted for $h(\theta)$.

out the crystal; the diffracting angle is determined by some 'average' value of the variable d -spacings. For the following it is more convenient to use r^* the reciprocal spacing ($r^* = 1/d$).

Let $P(r^*)dr^*$ be the frequency (of occurrence) of parallel diffracting planes (giving rise to a specific reflection (hkl)) for which the reciprocal spacing lies between r^* and $r^* + dr^*$.

Let $\bar{r}_{P_1}^*$ be the centroid of $P_1(r^*)$ that is

$$\bar{r}_{P_1}^* = \int_{-\infty}^{\infty} r^* P_1(r^*) dr^*. \quad (45)$$

Let λ_B and θ_B be the fiducial wavelength and Bragg angle for which

$$\lambda_B \bar{r}_{P_1}^* = 2 \sin \theta_B. \quad (46)$$

From (46) and the definition $\theta = \theta_B + \frac{1}{2}\varepsilon$ it follows that

$$r^* - \bar{r}_{P_1}^* = \Delta r^* = 2/\lambda_B [\sin(\theta_B + \frac{1}{2}\varepsilon) - \sin \theta_B]. \quad (47)$$

Substituting Δr^* in (45) we find that

$$\int_{-\infty}^{\infty} r^* P_1(\Delta r^*) d\Delta r^* = \overline{\Delta r_{P_1}^*} = 0. \quad (48)$$

The distribution of d -spacings can be expressed in terms of the angle variable ε if we write

$$P(\theta, \varepsilon) = P_1(\Delta r^*) (d\Delta r^*/d\varepsilon) = P_1(\Delta r^*) \cos(\theta_B + \frac{1}{2}\varepsilon)/\lambda_B,$$

and in general we have

$$\bar{\varepsilon}_P = \int_{-\infty}^{\infty} \varepsilon P(\theta_B, \varepsilon) d\varepsilon = \Delta_P(\theta_B). \quad (49)$$

If the distribution $P(\varepsilon)$ is sufficiently narrow, such that $P(\varepsilon) \approx 0$ for values of ε larger than those for which the approximations $\varepsilon = \sin \varepsilon$ and $\cos \varepsilon = 1$ are valid, we have

$$\left. \begin{aligned} \Delta r^* &= \varepsilon \cos \theta_B / (2\lambda_B) \\ \bar{\varepsilon}_P &= (\cos^2 \theta_B / (4\lambda_B^2)) \overline{\Delta r_{P_1}^*} = 0, \end{aligned} \right\} \quad (50)$$

and for this case

$$\Delta_P(\theta_B) = 0. \quad (51)$$

Let $f(\varepsilon)$ given by (20) be regarded as the observed distribution (about $2\theta_B$) for diffraction from only those planes for which the reciprocal spacing is uniquely $\bar{r}_{P_1}^*$. If $\hat{f}(\varepsilon)$ is the observed distribution from *all* the planes, the reciprocal spacings of which are given by $P_1(r^*)$, we have

$$\hat{f}(\varepsilon) = f * P(\varepsilon). \quad (52)$$

By a well known theorem it follows from (50) that

$$\bar{\varepsilon}_f = \bar{\varepsilon}_f + \bar{\varepsilon}_P \quad (53)$$

or

$$\bar{\varepsilon}_f = \bar{\varepsilon}_f + \Delta_P.$$

In view of (50) and (51) Δ_P , defined by (49), need be

applied as a correction† to account for distortion only when $P(\varepsilon)$ is an excessively broad distribution-in- d -spacings.

If we assume that $P(\varepsilon)$ is a Gaussian distribution with variance V_P , it can be shown‡ that Δ_P is effectively nil for values of $\sqrt{V_P} < 1^\circ$. (The width at half maximum for $\sqrt{V_P} = 1^\circ$ is of the order of 1.2° .) Thus it can be assumed that Δ_P can be ignored for all cases where the observed profile is not broadened by more than about 1° in excess of the breadth expected from the spectral distribution and instrumental aberrations. Since broadening factors due to distributions of the type $P(\varepsilon)$ encountered in precision diffractometer lattice parameter determinations (where relatively unstrained crystals are used) are usually less than 1° , the correction Δ_P is usually ignorable. Thus, in general we have

$$\bar{\varepsilon}_f = \bar{\varepsilon}_f. \quad (54)$$

From (54) and (52) it is clear that the lattice parameter determined by the method of centroids represents the centroid of the distribution-in- d . We can also conclude from the results obtained in this section that the use of the correction Δ_{LPV} (defined by 21), is valid even when the observed distribution $f(\varepsilon)$ is significantly (but not excessively) broader than the spectral distribution $h(\varepsilon)$. This result is in agreement with Pike's conclusion (Pike, 1959, eq. (15)) for the limiting case of a strictly monochromatic incident beam. No contradiction arises for this limiting case as would be supposed from the fact that the same angle factor is found whether or not absorption is taken into account, since for this limiting case the wavelength dependence of the Lorentz factor is *a priori* eliminated.

Conclusion

On the basis of the kinematic theory of diffraction, it has been shown that the angle factor

$$J(\theta) = K_1 K_2 K_6 \sin^2 \theta \cos \theta / (1 + \cos^2 2\theta)$$

correctly describes the distortion of the line profile due to the diffraction process when physical absorption effects are included.

In the centroid method (*LPTa,b*, *LMPT*, Pike & Wilson, 1959; Pike & Ladell, 1961) of precision lattice parameter determination, the correction Δ_{LPV} derived here is used to account for the shift in the observed profile due to distortion of the line profile caused by the diffraction process. Δ_{LPV} (previously labeled Δ_{LP}

† Δ_P is generically the same as Δ_D of Section 3.1. As with the dispersion correction, Δ_P can be experimentally eliminated even for broad profiles if the counter is rotated such that $d/dt(\sin \theta) = \text{constant}$.

‡ We have

$$P(\varepsilon) = (2\pi V_P)^{-\frac{1}{2}} \exp(-\varepsilon^2/2V_P).$$

For values of $|\varepsilon| > 3.8\sqrt{V_P}$, $P(\varepsilon) < (0.001)P(0)$. Consider the case where $\sqrt{V_P} < 1^\circ$. In the range $(-3.8\sqrt{V_P} \leq \varepsilon \leq 3.8\sqrt{V_P})$, $|\varepsilon| \leq 3.8^\circ$, and $\sin \varepsilon \approx \varepsilon$ with an accuracy > 0.1 . For this case (50) is valid.

(*LPTa*) has been calculated for several radiations (*LMPT*, Fig. 2) and is used as prescribed in these earlier papers.

The similarity between the angle factor previously derived for the integrated intensity formula in the classical case (J (2.31, 2.50)) (strictly monochromatic X-rays) and the angle factor for the case discussed here (where there is a spectral distribution in the incident beam) is manifest because the λ^3 factor appearing in the integrated intensity formula is offset by the absorption factor (J 2.50), which to the first order is proportional to λ^3 . Thus the integrated intensity (J 2.50) is virtually independent of wavelength.

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Short Communications

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Acta Cryst. (1961). **14**, 53

The Lorentz factor in powder diffraction.* BY E. R. PIKE, *Department of Physics and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A.*, and JOSHUA LADELL, *Philips Laboratories, Irvington-on-Hudson, New York, U.S.A.*

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In a recent communication by Ladell, Parrish & Taylor (1959), a correction was suggested to be applied to the centroids of powder-diffraction lines for the purpose of counteracting the shift from true Bragg position caused by the effect of the Lorentz and polarization factors. More recently with M. Mack (Ladell, Mack, Parrish & Taylor, 1959) the same authors have published values of this correction calculated for various radiations. A similar correction was earlier reported by Pike (1959) in a theoretical study of the role of the Lorentz factor. There is a small discrepancy between the results of Pike and those suggested by Ladell *et al.*, and close inspection shows that the corrections are based upon different angular factors attributed to the Lorentz factor.

In restudying both papers to clarify the presumably divergent concepts of the Lorentz factor, an arithmetic error was discovered which has the effect of increasing the discrepancy. Although the discrepancy becomes smaller at higher angles, an apparent difference in lattice parameter of approximately one part in 10^5 is manifest if one of the corrections is preferred to the other.

In Pike (1959) the second-order terms in eq. (39) are

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in error by a factor of two; the correct expression should read

$$\psi - \psi_0 = -\frac{V}{\lambda^2} \tan^3 \theta \left\{ 3 + 2 \cot^2 \theta - \frac{16 \cos^2 \theta \cos 2\theta}{1 + \cos^2 2\theta} \right\}. \quad (1)$$

The asymptotic expressions quoted in the abstract are not affected by this error.

In Ladell, Parrish & Taylor (1959) and Ladell, Mack, Parrish & Taylor (1959) the suggested correction factor Δ_{LP} accounts not only for the Lorentz, polarization, and trigonometric factor associated with the powder method but also accounts for the effect of physical absorption, a wavelength-dependent factor (see Wilson, 1958). The theoretical basis for the suggested correction factor, Δ_{LP} , has been established in a later work (Ladell, 1961), but the role of absorption was not recognized in the earlier papers. To draw attention to this previously unrecognized property, the correction factor Δ_{LP} has been renamed Δ_{LPV} (Ladell, 1961).

In view of the foregoing it is now clear that the divergent angular factors previously reported take into account different effects. When the diffraction of powders is considered apart from absorption the angular factor is

$$B(2\theta) = \tan \theta (1 + \cos^2 2\theta) \quad (2)$$