HOSSFELD, F. (1967). Thesis, Technische Hochschule Aachen.
HOSSFELD, F. & MAIER, G. (1967). *Z. angew. Phys.* **22**, 145.
KRATKY, O., POROD, G. & KAHOVEC, L. (1951). *Z. Elektrochem.* **55**, 53.
LAKE, J. A. (1967). *Acta Cryst.* **23**, 191.
LINNIK, J. W. (1961). *Die Methode der Kleinsten Quadrate in moderner Darstellung.* Berlin: VEB Deutscher Verlag der Wissenschaften.
LUZZATI, V. (1957). *Acta Cryst.* **10**, 33.
MAZUR, J. & WIMS, A. M. (1966). *J. Res. Nat. Bur. Stand.* **70**A, 467.
MONAHAN, J. E. & LANGSDORF, JR., A. (1965). *Ann. Phys. N.Y.* **34**, 238.
MORSE, P. M. & FESHBACH, H. (1953). *Methods of Mathematical Physics,* Vol. I. New York: McGraw-Hill.
PORTEUS, J. O. (1962). *J. Appl. Phys.* **33**, 700.
SAUDER, W. C. (1966). *J. Appl. Phys.* **37**, 1495.
SZEGÖ, G. (1959). *Orthogonal Polynomials.* New York: American Mathematical Society.
TAYLOR, T. R. & SCHMIDT, P. W. (1967). *Acta Phys. Austr.* **25**, 293.
TITCHMARSH, E. C. (1948). *Introduction to the Theory of Fourier Integrals.* Oxford: Clarendon Press.

Acta Cryst. (1968). A**24**, 650

Correction for Preferred Orientation of Plate-like Particles in Diffractometric Powder Analysis

BY EDWARD STURM
Department of Geology, Brooklyn College of the City University of New York

AND WILLIAM LODDING
Department of Geology, Rutgers University, New Brunswick, New Jersey

(*Received* 16 *February* 1968)

A major problem of quantitative powder diffraction analysis is the tendency of many samples to be preferentially oriented. The approach proposed here is to work with easily prepared, preferentially oriented flat samples, whose orientation can be characterized in quantitative terms. Once the orientation is known, the observed intensities may be corrected for the effects of orientation. Although the approach is general, correction factors are developed and experimental results are presented only for the most common mode of preferred orientation, as exhibited by plate-like particles.

Introduction

Any sample assemblage of morphologically anisotropic powder-sized particles tends to be preferentially oriented. To overcome the effects of preferred orientation, several techniques of sample preparation have been worked out which are supposed to result in randomly oriented samples (Byström-Asklund, 1966; Niskanen, 1964). No technique can guarantee ideally random orientation, and it is the uncertainty regarding the degree of randomness achieved which lowers the value of these techniques. Other techniques are attempts to derive the intensity of an equivalent, randomly oriented sample from the diffraction data of the preferentially oriented sample. Randomizing diffraction data from polymers showing certain types of preferred orientation has been attempted by employing specialized sample holders that spin the specimen, by weighting each quantum of the line profile by a certain function, and by integrating over the total angle intercepted (Desper & Stein, 1967). The tedium of the computational work can be almost eliminated by the use of an electronic device which combines the output of a pulse height analyzer with that of a function generator before integrating the modified signal (Ruland & Dewaelheyns, 1967). The aim of these techniques is to obtain meaningful intensity readings by averaging the diffraction data. The approach suggested here is to prepare preferentially oriented specimens and to determine the specific distribution function which characterizes the orientation. The effects of preferred orientation may then be cancelled out by correcting the observed intensities for the various reflections.

Wherever there is a finite probability that particles will assume a certain position, a normal distribution must result. In practice, the conditions for normal distributions are met by any aggregate of morphologically anisotropic particles whose tendency toward preferred orientation has not been interfered with. Therefore, the preferred orientation of powdered samples is best dealt with in terms of the normal distribution of radii of probability. We may characterize the orientation of a crystallite by the position of the perpendicular to a given crystallographic plane. The lengths of the radii of probability, drawn from a common origin, are proportional to the number of particles in the given direction, and therefore are also related to the observed intensities. The spatial distribution of intensities representing preferred orientation of platelets, for example, is cylindrically symmetrical and has a plane of symmetry perpendicular to the major direction or the longest radius. In this case, the distribution function

of the radii of probability is periodic, the period being 180°; in other words, the distribution is hemispherically normal. This type of orientation is known to polymer scientists as *uniplanar* (Heffelfinger & Burton, 1960) or *selective uniplanar* (Sisson, 1936). Because of the cylindrical symmetry, a section through the hemispherical normal distribution which includes the principal radius is sufficient to characterize the distribution. Such a section represents a semicircular normal probability density distribution. It is this section that one scans in the common procedures of powder diffraction analysis when using flat samples prepared in the usual fashion. The following discussion is confined to this distribution, because it is the most common probability density function encountered in powder diffractometric work. The expression for the semicircular normal density distribution may be written as follows:

$$\Psi(\varphi,k,\gamma)=C_0 \exp\left[k \cos 2(\varphi-\gamma)\right] \quad (1)$$

where Ψ is the radius of probability which, as will be pointed out below, is related to the observed intensity, φ is the angle variate, and γ is the angle of the principal radius or the center of gravity of the distribution. The constant k characterizes the dispersion of the radii of probability about the center of gravity of the distribution. C_0 and k are related so that the area under the given curve equals unity, that is, for the semicircular normal distribution:

$$\int_{\gamma-(\pi/2)}^{\gamma+(\pi/2)} \Psi(\varphi,k,\gamma)d\varphi=1$$

and

$$C_0=\frac{1}{4\pi J_0(k)}, \quad (2)$$

where $J_0(k)$ is a Bessel function of the first kind of pure imaginary argument (Gumbel, Greenwood & Durand, 1953; Vistelius, 1966; von Mises, 1918). The role of k in circular and semicircular normal distributions remotely resembles that of the standard deviation in linear normal distributions, in that both are measures of concentration or central tendency. For randomly oriented samples, k equals zero and, in that case, C_0 is proportional to the intensity of a given crystallographic plane observed at any angle. For practical purposes, C_0 and k may be determined from observed intensities, and therefore the function specifying the preferred orientation of the sample may be found. As will be pointed out below, this may be done in several ways.

The semicircular normal distribution

The orientation of the plane of preferred orientation is known for flat samples prepared for X-ray work. By choosing the perpendicular to the plane of preferred orientation to be the origin, the angle γ vanishes. When working with ratios of intensities of a given crystallographic plane observed on several sample sections, that is, surfaces cut at various angles (φ) to the plane of preferred orientation, factors affecting the observed intensities, other than those due to preferred orientation, cancel out. In that case, Ψ of equation (1) is proportional to the observed intensity. Thus, replacing Ψ by the observed intensity I and using the ratio of intensities collected from two sample sections, the dispersion constant, k, may be found. That is,

$$k=\frac{\ln I_{\varphi(hkl)}-\ln I_{\varphi'(hkl)}}{\cos 2\varphi-\cos 2\varphi'}, \quad (3)$$

where I_φ and $I_{\varphi'}$ are the intensities of a given crystallographic plane observed on sample sections φ and φ'. A simplification results if one of the sample sections is the plane of preferred orientation and the other the 45° sample section, *i.e.* φ equals zero and φ' equals 45°. For this case, equation (1) becomes:

$$I_{\varphi(hkl)}=I_{45^\circ(hkl)} \exp\left[(\ln I_{0^\circ}-\ln I_{45^\circ})\cos 2\varphi\right]. \quad (4)$$

For the sake of clarity, it is believed desirable to consider the following practical aspects and an example before discussing further theoretical details. The material used in this study was kaolinite, a silicate forming plate-like particles. The powdered sample was pressed into approximately one half inch thick pellets at 20,000 p.s.i. The data used for the examples given below were collected from two surfaces or sample sections on each of three pressed pellets of the sample material. The intensities were measured by the usual counting techniques or by measuring the area under the peaks. Data were obtained with a standard X-ray diffractometer. No specialized equipment was used. The procedure followed for finding the dispersion constant k is indicated in the following array:

	(00l)	(060), (3$\bar{3}\bar{1}$), (33$\bar{1}$)
0° section	A	C
45° section	B	D

A, B, C, and D represent sets of diffraction data. The constant k was determined from sets of data (AB) as well as (CD), (AC) or (BD). One example will suffice to illustrate the procedure for finding the value of the dispersion constant by the use of data from two sample sections. The intensities of the 002 reflection collected from the sample section parallel to the plane of preferred orientation ($\varphi=0°$) and a 45° section ($\varphi=45°$) were used (Table 1). Then, by equation (3), $k=\ln 760 - \ln 218=1{\cdot}2$. The value of 1·2 characterizes the preferred orientation of the sample in terms of the semicircular normal distribution. In other words, knowing the particular value of k, the radius of probability at any angle φ of the sample, and thus the expected intensity, may be computed by use of equation (4). Other procedures for the determination of k are given below.

Preferred orientation determined from a single sample section

The ratio of intensities of reflections from two or more crystallographic planes, obtained from a single sample

section, has been used as a sensitive index for preferred orientation (Martin, 1966; Brindley & Kurtosy, 1961). In all cases where the distribution of intensities is normal and cylindrically symmetrical, and the angle φ of the sample section is known, the value of k and thus the distribution function may be found. Further, the intensity distributions of the reflections from crystallographic planes of a sample are identical in shape, though not in size. The general case where the angle between the normal to the principal plane and the normal to a particular crystallographic plane is other than 90° is illustrated in Fig. 1. The assemblage of radii of probability is still cylindrically symmetrical, and the plane of symmetry perpendicular to the principal radius is preserved, but the distribution of radii for the subsidiary crystallographic plane is bi-modal, with lobes on either side of the plane of symmetry. Although the concept of the normal distribution of the perpendiculars to the crystallographic planes is general, it may aid the intuitive approach if we picture the (00l) planes to lie in the plane of preferred orientation, as is the case with many platelets, and a general plane (hkl) making an angle δ, other than 90°, with the (00l) planes (Fig. 1). When working with intensities of two, or more, crystallographic planes, observed on a single sample section, one must take into account not only the symmetry of the assemblage of probability functions but also the structure factors and various pertinent geometric factors. It will be recalled here that this was not necessary in the case where ratios of intensities of reflections from a crystallographic plane observed on two or more sample sections were used. In that case, the various factors which are independent of preferred orientation cancel out. Generally, for any sample section of a preferentially oriented powdered specimen the intensity of a reflection is:

$$I_{\varphi(1)} = V_{\varphi(1)}(k)\mu_{(1)}F^2_{(1)}f(\theta)_{(1)} \qquad (5)$$

where $f(\theta) = (1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)$, and F is the structure factor (Klug & Alexander, 1954). The subscript (1) refers to a given crystallographic plane (hkl). μ is a multiplicity factor which, for the type of distribution discussed here, can have values of 1 or $\frac{1}{2}$, depending on whether or not the principal radius of the distribution of a given crystallographic plane coincides with the symmetry elements of the assemblage (Fig. 1). $V_\varphi(k)$ refers to the magnitude of the radius of probability at the given angle φ for the unit distribution function. For the subsidiary planes

$$V_\varphi(k) = \frac{1}{N}\sum^{N} \tfrac{1}{2}\,\{\exp\,[(k\cos 2(\delta-\varphi)] + \exp\,[k\cos 2\,(180°-\delta-\varphi)]\}\,, \qquad (6)$$

where δ is the inter-row angle $[hkl]^*\wedge[h'k'l']^*$ and N is the number of planes contributing to the intensity observed; that is, N will be more than unity for cases where reflections from several planes cannot be resolved. When working with ratios of intensities, *i.e.* $I_{\varphi(1)}/I_{\varphi(2)}$, where (1) and (2) refer to (hkl) and ($h'k'l'$) respectively, $V_\varphi(k)$ is computed for each of the planes whose reflections are used. Knowing the inter-row angles, one may find k from the following ratios:

$$R_I = R_\mu R_V R_{F^2 f(\theta)}$$

or

$$\frac{R_I}{R_\mu R_{F^2 f(\theta)}} = R_V\,. \qquad (7)$$

where the subscripts refer to the quantities of equation (5) and each R represents the ratios of the computed or observed quantities. We use the data of Table 1 to illustrate procedures for the application of the equations developed above. The dispersion constant k for the sample pellets used was previously found to be 1·2. The inter-row angles were computed for $[00l]^*\wedge[060]^*$, $[00l]^*\wedge[\bar{3}\bar{3}\bar{1}]^*$, $[00l]^*\wedge[33\bar{1}]^*$. Because the value for k is known, we may compute the ratio of the structure factors from the observed intensities, that is:

$$\frac{\mu_{(2)}}{\mu_{(1)}}\,\frac{R_I}{R_V} = R_{F^2 f(\theta)}\,. \qquad (8)$$

For the 0° sample section the multiplicity factor $\mu_{(002)}/\mu_{(060,\,\bar{3}\bar{3}\bar{1},\,33\bar{1})}$ equals unity. N of equation (6) is unity for the (00l) planes and 3 for the sum of the radii of probability of (060), ($\bar{3}\bar{3}\bar{1}$) and ($33\bar{1}$). Then, using the observed values of 760/33 for R_I we find $R_{F^2 f(\theta)}$ equals 2·17. This compares well with the theoretical value of 2·12 (Table 1).

For practical reasons one may think of the plane of preferred orientation as the ideal sample section.

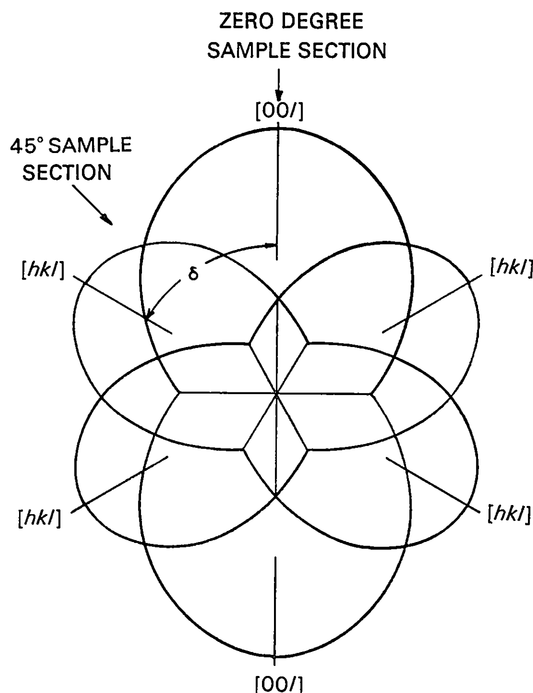

Fig. 1. Semicircular normal distribution function for two crystallographic planes with $\delta \neq 90°$.

Table 1. *Summary of data*

hkl	I* $F^2f(\theta)\cdot 10^{-3}$	II* R_F	III* Sample 1 0° Section	III* Sample 1 45° Section	IV* Sample 2 45° Section	IV* Sample 3 45° Section
001	488	3·90	760	218	431	547
002	265	2·12			253	
003	50	0·40				59
060	41·5 } 125·4					
$33\bar{1}$	42·5 } 125·4		33	58·5	67	83
$33\bar{1}$	41·4 } 125·4					

* I Data from Brindley & Robinson (1946).
II The theoretical ratio $F^2{}_{(1)}f(\theta)_{(1)}/F^2{}_{(2)}f(\theta)_{(2)}$ where (1) is (00*l*) and (2) is (060,3 $\bar{3}\bar{1}$, $33\bar{1}$).
III Intensity by counting techniques.
IV Intensity is the product of peak height and width at half-height.

However, for the application of the equations developed here, other sample sections may provide more useful information. Pressed pellets of powdered samples or similar aggregates make it possible to work with other sections. As shown in Fig. 1, crystallographic planes which, because of preferred orientation, yield only weak reflections when observed on the plane of preferred orientation, may yield considerably stronger reflections when observed on other sections. Further, in cases where the angle between the two crystallographic planes, whose intensities are measured, equals 90°, the 45° sample section yields intensity data which are quantitatively equivalent to those obtainable from randomly oriented specimens only. In other words, in this case, the exponent in equation (1) vanishes and therefore the expression is mathematically equivalent to that for random orientation, where k equals zero.

Because of symmetry, certain simplifications of equation (6) are possible when working with data collected from the plane of preferred orientation, which are not possible for other sample section data. Otherwise, the procedures are identical. By the use of equation (6) the following values were found for the sample pellet (whose orientation, it will be recalled is characterized by $k=1{\cdot}2$): $V_{45°(00l)}=1{\cdot}00$, $V_{45°(060)}=1{\cdot}30$, $V_{45°(3\bar{3}\bar{1})}=1{\cdot}00$, $V_{45°(33\bar{1})}=1{\cdot}05$. Using these values $R_V=1{\cdot}79$ by equation (7). Table 2 contains a summary of the results obtained by the use of this value for R_V.

It is our contention that, for quantitative powder diffraction work, it is advantageous to work with oriented specimens whose orientation can be characterized in quantitative terms rather than with so-called randomly oriented samples which are rarely ideally random. No specialized equipment is required to carry out studies based on the relations developed here. The sample preparation, however, must be carried out with care. Small errors in the measurement of φ, for example, may affect the results significantly. Although this paper deals with preferred orientation of plate-like particles, which can be described in terms of the semicircular normal distribution, the approach is general, so that similar relations may be developed for other modes of preferred orientation that are based on a normal distribution.

Table 2. *Computed ratios of structure factors, based on 45° sample section data*

Ratio	I*	II*	III*
$I_{(001)}/I_{(060,\ etc.)}$	431/67	3·90	3·60
$I_{(001)}/I_{(060,\ etc.)}$	547/83	3·90	3·69
$I_{(002)}/I_{(060,\ etc.)}$	218/58·5	2·12	2·09
$I_{(002)}/I_{(060,\ etc.)}$	253/67	2·12	2·11
$I_{(003)}/I_{(060,\ etc.)}$	59/83	0·40	0·40

* I is the ratio of observed intensities, R_I
II is the ratio of theoretical structure factors
III is the ratio of the calculated structure factors, R_F. The value of R_V used in these computations was 1·79 (see text).

References

Brindley, G. W. & Kurtosy, S. S. (1961). *Amer. Min.* **46**, 1205.

Brindley, G. W. & Robinson, K. (1946). *Miner. Mag.* **27**, 242.

Byström-Asklund, A. M. (1966). *Amer. Min.* **51**, 1233.

Desper, C. R. & Stein, R. S. (1967). *Polymer Letters* (*J. Polym. Sci. B*), **5**, 893.

Gumbel, E. J., Greenwood, J. A. & Durand, D. (1953). *J. Amer. Statist. Ass.* **48**, 131.

Heffelfinger, C. J. & Burton, R. L. (1960). *J. Polym. Sci.* **47**, 289.

Klug, H. P. & Alexander, L. E. (1954). *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, p. 125. New York: John Wiley.

Martin, T. R. (1966). *Proc.* 14*th National Clay Conf.* p. 271. New York: Pergamon Press.

Mises, R. von (1918). *Phys. Z.* **19**, 490.

Niskanen, E. (1964). *Amer. Min.* **49**, 705.

Ruland, W. & Dewaelheyns, A. (1967). *J. Sci. Instrum.* **44**, 236.

Sisson, W. A. (1936). *J. Phys. Chem.* **40**, 343.

Vistelius, A. B. (1966). *Structural Diagrams*, p. 81. New York: Pergamon Press.