culated by JB from Hartree wave functions without exchange, fits our curve from sin θ/λ = 0·5 onwards.)

Finally, Fig. 3 gives a comparison between the scattering factor of Cu^+, calculated by us from wave functions with exchange, and that for Cu calculated by Viervoll & Ögrim without exchange. The discrepancies are appreciable throughout the Cu K range. Likewise, Viervoll & Ögrim's values for Ca and Cr are considerably smaller than ours at low sin θ/λ values. It appears, therefore, that more calculations for moderately heavy elements are very desirable.

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A Generalized Treatment of Cold Work in Powder Patterns*

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Calculations of the effect of particle-size and cold-work distortion in the broadening of powder-pattern lines have been simplified in several previous treatments by considering the reflections as 00*l* for orthorhombic axes. By a suitable transformation of variables and axes, it is possible to carry through the calculation for the general *hkl* reflection for a crystal of any system. The general result obtained is identical to that previously obtained with the simplifying assumptions. The result is expressed in terms of particle-size and distortion Fourier coefficients which are obtained from the experimental peak shapes.

1. Introduction

To develop a Fourier treatment of the broadening of X-ray powder pattern lines by cold-work distortion, Stokes & Wilson (1942, 1949) and Warren & Averbach (1950) have assumed a transformation of axes such that the reflection could be considered as 00*l* for orthorhombic axes. This simplifies considerably the mathematical treatment, but for the general *hkl* reflection from crystals of low symmetry such a transformation is not possible. Nevertheless, the result obtained by this simplified treatment appears to be quite general, suggesting that the transformation to orthorhombic axes is not really necessary. It is the purpose of this paper to give a generalized treatment for any

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hkl reflection and to show that the previous results are indeed quite general.

2. Generalized theory

We consider the *hkl* reflection from any crystal with axes $\mathbf{a}_1\mathbf{a}_2\mathbf{a}_3$ and corresponding reciprocal axes $\mathbf{b}_1\mathbf{b}_2\mathbf{b}_3$. Owing to the distortion, the position of cell $m_1m_2m_3$ is given by

$$\mathbf{R}_m = m_1\mathbf{a}_1+m_2\mathbf{a}_2+m_3\mathbf{a}_3+\boldsymbol{\delta}(m_1m_2m_3)\,.$$

In terms of unit vectors $\mathbf{s}_0$ and $\mathbf{s}$ for the directions of the primary and diffracted beams, the intensity from one crystal is given by

$$I = I_eF^2\sum_m\sum_{m'}\exp\left[\frac{2\pi i}{\lambda}(\mathbf{s}-\mathbf{s}_0).(\mathbf{R}_m-\mathbf{R}_{m'})\right].$$

Represent the diffraction vector in terms of continuous variables

$$(\mathbf{s}-\mathbf{s}_0)/\lambda = h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3\,.$$

The intensity is then given in terms of $h_1h_2h_3$ by

$$I = I_eF^2\sum_m\sum_{m'} \times\exp\left[2\pi i\{(m_1-m_1')h_1+(m_2-m_2')h_2+(m_3-m_3')h_3\}\right] \times\exp\left[2\pi i\{h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3\}.\{\boldsymbol{\delta}(m_1m_2m_3)-\boldsymbol{\delta}(m_1'm_2'm_3')\}\right].$$

Let

$$n_1 = m_1-m_1',\; n_2 = m_2-m_2',\; n_3 = m_3-m_3'\,,$$

$$\boldsymbol{\delta}(n_1n_2n_3) = \boldsymbol{\delta}(m_1m_2m_3)-\boldsymbol{\delta}(m_1'm_2'm_3')\,,$$

and let $N(n_1n_2n_3)$ be the number of cells in the crystal with an $n_1n_2n_3$ neighbor. Using an average of the distortion terms for all pairs of cells with the same $n_1n_2n_3$, the intensity reduces to the triple sum

$$I = I_eF^2\sum_{n_1}\sum_{n_2}\sum_{n_3}N(n_1n_2n_3) \times\langle\exp\left[2\pi i\{h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3\}.\boldsymbol{\delta}(n_1n_2n_3)\right]\rangle \times\exp\left[2\pi i(n_1h_1+n_2h_2+n_3h_3)\right].\qquad(1)$$

We assume that the intensity is spread out in reciprocal space about the point *hkl* through distances which are small compared to $|\mathbf{H}| = |h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_2|$. On this basis we can make the approximation

$$(h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3).\boldsymbol{\delta}(n_1n_2n_3)\rightarrow\mathbf{H}.\boldsymbol{\delta}(n_1n_2n_3) = |\mathbf{H}|\varepsilon(n_1n_2n_3)\,,$$

where $\varepsilon(n_1n_2n_3)$ is the component of $\boldsymbol{\delta}(n_1n_2n_3)$ along $\mathbf{H}$ (normal to the plane *hkl*). Let $h_1 = h+p_1$, $h_2 = k+p_2$, $h_3 = l+p_3$. Since we are interested only in small values of $p_1p_2p_3$, the sum in (1) can be replaced by integrals:

$$I = I_eF^2\iiint^{+} N(n_1n_2n_3)\,\langle\exp\left[2\pi i|\mathbf{H}|\varepsilon(n_1n_2n_3)\right]\rangle \times\exp\left[2\pi i(n_1p_1+n_2p_2+n_3p_3)\right]dn_1dn_2dn_3\,.\qquad(2)$$

For a powder pattern, the total diffracted power in a reflection is given by the general relation

$$P = \frac{MjR^2\lambda^3}{4v_a}\iiint\frac{I(p_1p_2p_3)}{\sin\theta}dp_1dp_2dp_3\,,\qquad(3)$$

where $I(p_1p_2p_3)$ is the intensity per crystal, M is the number of crystals, j is the multiplicity, R is the sample to receiver distance, and v_a is the volume of the unit cell. Since $(\mathbf{a}_1.\mathbf{a}_2\times\mathbf{a}_3)(\mathbf{b}_1.\mathbf{b}_2\times\mathbf{b}_3) = 1$,

$$dn_1dn_2dn_3dp_1dp_2dp_3 = (\mathbf{a}_1.\mathbf{a}_2\times\mathbf{a}_3)dn_1dn_2dn_3(\mathbf{b}_1.\mathbf{b}_2\times\mathbf{b}_3)dp_1dp_2dp_3 = dV_adV_b\,.$$

Let $K = (I_eF^2jR^2\lambda^3)/(4v_a\sin\theta)$. Combining (2) and (3), we have

$$P = K\iint M(n_1n_2n_3)\,\langle\exp\left[2\pi i|\mathbf{H}|\varepsilon(n_1n_2n_3)\right]\rangle \times\exp\left[2\pi i(n_1p_1+n_2p_2+n_3p_3)\right]dV_adV_b\,,\qquad(4)$$

where $M(n_1n_2n_3)$ is the number of $n_1n_2n_3$ pairs summed over all the crystals in the sample, and

$$\langle\exp\left[2\pi i|\mathbf{H}|\varepsilon(n_1n_2n_3)\right]\rangle$$

is now an average over all $n_1n_2n_3$ pairs in the sample. As seen from (4), the total diffracted power in a reflection involves two volume integrals, one in crystal space and the other in reciprocal space.

We now transform the axes and variables with a matrix for orthogonal transformations

$$\alpha_{ij} = \begin{matrix}\alpha_{11} & \alpha_{12} & \alpha_{13}\\ \alpha_{21} & \alpha_{22} & \alpha_{23}\\ \alpha_{31} & \alpha_{32} & \alpha_{33}\end{matrix}$$

where $\sum_i\alpha_{ij}^2 = 1$, $\sum_i\alpha_{ij}\alpha_{ik} = 0\;(j \neq k)$ and the determinant $|\alpha_{ij}| = 1$. In terms of the matrix α_{ij} and the transposed matrix α_{ji}, we introduce the four new sets of quantities p_i', n_i', $\mathbf{a}_i'$ and $\mathbf{b}_i'$:

$$\left.\begin{aligned} p_i &= \sum_j\alpha_{ij}p_j'\,, & p_i' &= \sum_j\alpha_{ji}p_j\,,\\ n_i &= \sum_j\alpha_{ij}n_j'\,, & n_i' &= \sum_j\alpha_{ji}n_j\,,\\ \mathbf{a}_i &= \sum_j\alpha_{ij}\mathbf{a}_j'\,, & \mathbf{a}_i' &= \sum_j\alpha_{ji}\mathbf{a}_j\,,\\ \mathbf{b}_i &= \sum_j\alpha_{ij}\mathbf{b}_j'\,, & \mathbf{b}_i' &= \sum_j\alpha_{ji}\mathbf{b}_j\,.\end{aligned}\right\}\qquad(5)$$

From the orthogonal nature of the matrix and the relations (5) it follows that

$$\begin{aligned} &n_1p_1+n_2p_2+n_3p_3 = n_1'p_1'+n_2'p_2'+n_3'p_3'\,,\\ &p_1\mathbf{b}_1+p_2\mathbf{b}_2+p_3\mathbf{b}_3 = p_1'\mathbf{b}_1'+p_2'\mathbf{b}_2'+p_3'\mathbf{b}_3'\,,\\ &n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3 = n_1'\mathbf{a}_1'+n_2'\mathbf{a}_2'+n_3'\mathbf{a}_3'\,,\\ &\mathbf{a}_1'.\mathbf{a}_2'\times\mathbf{a}_3' = \mathbf{a}_1.\mathbf{a}_2\times\mathbf{a}_3,\; \mathbf{b}_1'.\mathbf{b}_2'\times\mathbf{b}_3' = \mathbf{b}_1.\mathbf{b}_2\times\mathbf{b}_3\,,\\ &\mathbf{a}_i'.\mathbf{b}_j' = \delta_{ij}\,,\\ &M(n_1n_2n_3) = M(n_1'n_2'n_3'),\; \varepsilon(n_1n_2n_3) = \varepsilon(n_1'n_2'n_3')\,,\\ &dV_adV_b = dn_1'dn_2'dn_3'dp_1'dp_2'dp_3'\,.\end{aligned}$$

In terms of the new variables,

$$P = K\iiiint\!\!\iint M(n_1'n_2'n_3')\langle\exp[2\pi i|\mathbf{H}|\varepsilon(n_1'n_2'n_3')]\rangle$$
$$\times\exp[2\pi i(n_1'p_1'+n_2'p_2'+n_3'p_3')]\,dn_1'dn_2'dn_3'dp_1'dp_2'dp_3'\,. \quad (6)$$

The orthogonal conditions imposed on the matrix leave it with three degrees of freedom. We now impose two additional conditions. The vector normal to the planes hkl was introduced as $\mathbf{H} = h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3$. We now require that

$$\mathbf{H}.\mathbf{b}_2' = 0,\ \mathbf{H}.\mathbf{b}_3' = 0\,. \quad (7)$$

This automatically makes $\mathbf{a}_1'$ parallel to $\mathbf{H}$, but $\mathbf{b}_1'$ is not necessarily parallel to $\mathbf{H}$.

Since $\mathbf{H} = (\mathbf{H}.\mathbf{b}_1')\mathbf{a}_1'+(\mathbf{H}.\mathbf{b}_2')\mathbf{a}_2'+(\mathbf{H}.\mathbf{b}_3')\mathbf{a}_3'$, we have

$$|\mathbf{a}_1'|\,|\mathbf{b}_1'|\cos(\mathbf{H},\mathbf{b}_1') = 1\,. \quad (8)$$

We now perform the integration with respect to p_2' and p_3' over a range $-w$ to $+w$ which is large enough to include everything belonging to the reflection hkl:

$$\int_{-w}^{+w}\exp[2\pi i n_2'p_2']\,dp_2' = \frac{\sin 2\pi n_2'w}{\pi n_2'}\,,$$

$$P = K\iiiint M(n_1'n_2'n_3')\langle\exp[2\pi i|\mathbf{H}|\varepsilon(n_1'n_2'n_3')]\rangle$$
$$\times\exp[2\pi i n_1'p_1']\frac{\sin 2\pi n_2'w}{\pi n_2'}\cdot\frac{\sin 2\pi n_3'w}{\pi n_3'}\,dn_1'dn_2'dn_3'dp_1'\,. \quad (9)$$

In carrying out the integration over n_2' and n_3',

$$\int_{-\infty}^{+\infty}\frac{\sin 2\pi n_2'w}{\pi n_2'}\,dn_2' = \frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{\sin x}{x}\,dx = 1\,,$$

the contribution is mainly from the vicinity of $n_2' = 0$ and we can set $n_2' = 0$, $n_3' = 0$ in the other terms under the integral.

$$P = K\iint M(n_1'00)\langle\exp[2\pi i|\mathbf{H}|\varepsilon(n_1'00)]\rangle$$
$$\exp[2\pi i n_1'p_1']\,dn_1'dp_1'\,. \quad (10)$$

From the relation between the vectors in reciprocal space which is illustrated by Fig. 1, we have

$$\cos(\mathbf{H},\mathbf{b}_1')\,d|p_1'\mathbf{b}_1'| = d((2\sin\theta)/\lambda)\,.$$

Combining with (8), we obtain

$$dp_1' = |\mathbf{a}_1'|\cos\theta\, d(2\theta)/\lambda\,.$$

The observed distribution of power in a powder pattern $P_{2\theta}$ is related to the total power by

$$P = \int P_{2\theta}\,d(2\theta)\,.$$

Let M be the total number of cells in the sample, and let $K' = MK|\mathbf{a}_1'|\cos\theta/\lambda$. Expressing dp_1' in terms of $d(2\theta)$, and omitting the integration with respect to $d(2\theta)$, gives the observable distribution $P_{2\theta}$:

$$P_{2\theta} = K'\int[M(n_1'00)/M]\,\langle\exp[2\pi i|\mathbf{H}|\varepsilon(n_1'00)]\rangle$$
$$\times\exp[2\pi i n_1'p_1']\,dn_1'\,. \quad (11)$$

From Fig. 1, $\cos(\mathbf{H},\mathbf{b}_1')|p_1'\mathbf{b}_1'| = (\sin\theta-\sin\theta_0)2/\lambda$ where θ_0 is the Bragg-law angle corresponding to the center of the hkl peak. Combining with (8), $p_1' = (\sin\theta-\sin\theta_0)2|\mathbf{a}_1'|/\lambda$. If $L = n_1'|\mathbf{a}_1'|$ is the distance between a cell and its $(n_1'00)$ neighbor (a distance normal to the hkl planes), $\varepsilon(n_1'00) = \Delta L$, the change in this length due to the distortion.

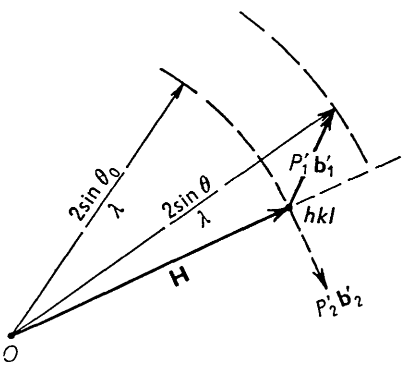

Fig. 1. Relation between the vectors in reciprocal space. The vector $\mathbf{b}_2'$ is perpendicular to $\mathbf{H}$ but not necessarily in the plane of $\mathbf{H}$ and $\mathbf{b}_1'$.

$$P_{2\theta} = K'\int[M(n_1'00)/M]\,\langle\exp[2\pi i|\mathbf{H}|(\Delta L)_L]\rangle$$
$$\times\exp[2\pi i n_1'|\mathbf{a}_1'|(\sin\theta-\sin\theta_0)2/\lambda]\,dn_1'\,. \quad (12)$$

For convenience in the final evaluation of the Fourier coefficients, we introduce the arbitrary quantities m and a such that $L = n_1'|\mathbf{a}_1'| = ma$. To compare multiple orders of a set of planes, let l represent the order, so that $|\mathbf{H}_l| = l/d_1$, where $|\mathbf{H}_1| = 1/d_1$. Finally we replace the integral by a sum and express $P_{2\theta}$ as a Fourier series.

$$P_{2\theta} = K''\sum_m A_L^P A_L^D(l)\exp[2\pi i m x]\,, \quad (13)$$

where

$$x = (\sin\theta-\sin\theta_0)2a/\lambda\,,$$
$$A_L^P = M(n_1'00)/M\,,$$
$$A_L^D(l) = \langle\exp[2\pi i l(\Delta L)_L/d_1]\rangle\,.$$

Expressing the shape of a powder-pattern reflection by the Fourier series represented by (13), we obtain the products of two coefficients, one relating to particle size and the other to distortion. The result expressed by (13) is perfectly general for any hkl reflection, for any crystal system. It is identical to the results previously obtained with the simplifying assumption of a $00l$ reflection for orthorhombic axes.

3. Evaluation of the Fourier coefficients

For the practical evaluation of the Fourier coefficients from (13), let Fig. 2 represent the experimental peak

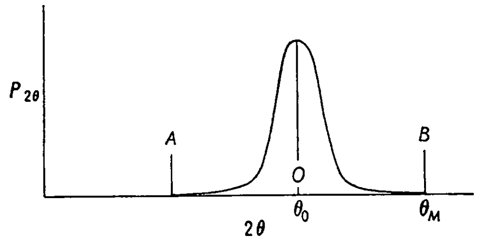

Fig. 2. Relation between the experimental diffraction peak and the interval *AOB* within which it is expressed as a Fourier series.

profile which we assume has been corrected for instrumental broadening by the method of Stokes (1948). We select a Fourier interval *AOB* which is large enough to include the measurable tails of the peak. If θ_M is the value at *B*

$$x_M = (\sin\theta_M - \sin\theta_0)2a/\lambda = \tfrac{1}{2}\,.$$

This determines the value of the arbitrary constant a. In terms of this interval *AOB*, Fourier coefficients for each m have already been determined in connection with the Stokes's correction. Each m is multiplied by the value of a, and the coefficient designated by the true length $L = ma$. By having retained the arbitrary constant a in (13), we are able to select a suitable interval to utilize efficiently the Lipson & Beevers strips for the evaluation of the Fourier coefficients.

The particle-size coefficient $A_L^P = M(n_1'00)/M$ is best interpreted in terms of columns of cells parallel to **H**. If n_D is the number of columns of length D, we have

$$A_L^P = \sum_{D=L}^{\infty}(D-L)n_D/\sum_{0}^{\infty}Dn_D\,.$$

As shown by Bertaut (1949), for small L, $A_L^P = 1-L/\langle D\rangle$ and

$$(dA_L^P/dL)_{L\to 0} = -1/\langle D\rangle\,,$$

giving directly the mean column length. The significance of the distortion coefficient $A_L^D(l)$ has been illustrated in connection with measurements on cold-worked tungsten (McKeehan & Warren, 1953).

Both the particle-size coefficient A_L^P and the distortion coefficient $A_L^D(l)$ are equal to unity for $L=0$. The distortion coefficient $A_L^D(l)$ is equal to unity for $l = 0$, so that if measurements are available for three or more orders, an extrapolation of the measured products $A_L^P A_L^D(l)$ to $l = 0$ gives the value of A_L^P. For metals, where there is no appreciable peak shift as a result of cold work, $A_L^D(l) = \langle\cos 2\pi l(\Delta L)_L/d_1\rangle$, and for very small l, $A_L^D(l) = \exp\,[-2\pi^2 l^2\langle(\Delta L)_L^2\rangle/d_1^2]$ regardless of the nature of the strains, providing only that they remain finite. A plot of $\ln A_L^P A_L^D(l)$ versus l^2 is therefore linear at small values of l. Williamson & Smallman (1954) have pointed out that if the strain distribution in the sample were a true Cauchy distribution, $\ln A_L^P A_L^D(l)$ would be linearly proportional to l. The apparent contradiction arises from the fact that the mean-square strain is infinite for a true Cauchy strain distribution. Since infinite mean-square strains are physically unrealistic, the safest extrapolation to $l = 0$ is given by plotting $\ln A_L^P A_L^D(l)$ versus l^2. The plot will not necessarily be linear in l^2, but it becomes more nearly linear the smaller l, and this is the really important condition for determining the intercept $\ln A_L^P$. When only two orders are available, the data do not suffice to show the curvature in the $\ln A_L^P A_L^D(l)$ versus l^2 plot, and the intercept $\ln A_L^P$ is not uniquely determined. Three or more orders are highly desirable. For cubic powder patterns third orders always coincide with another reflection, so that the third order can be obtained only if there is a strong preferred orientation which can be utilized.

Note added in proof.—It has been brought to my attention that part of this problem has been treated by Stokes & Wilson (1943).

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