hundred atoms in the asymmetric unit one may need to use triple-phase invariants with a standard deviation of $\pi/3$ or so. Again, in order to introduce enough magic-integer defined phases, it will be necessary to use long magic-integer sequences with up to eight integers. If a maximum integer of 100 can be tolerated then a root-mean-square error of slightly more than $\pi/4$ will result. If three variables, x, y and z, are used then there will be 24 primary reflexions and, our experience suggests, 70 to 100 secondary reflexions. This will be a large base from which a complete structure solution should be possible. The time requirement for the whole process would be dominated by that to calculate a Fourier map at intervals of 1/400 in each of three directions. While this is a formidable task it is by no means an impossible one and it would be worth while to put this amount of effort into an operation which offered real hope of success with a major structural problem.

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Relations between Integrated Intensities in Crystal Diffraction Methods for X-rays and Neutrons

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In addition to the classical experimental methods of crystal diffraction a number of new methods have become available using the time-of-flight technique for neutrons and energy-dispersive detectors for X-rays. It is shown that there are simple relations between the formulae for the integrated intensities of the different methods, and that the intensity formulae for all the methods can be simply generated, provided that one of them is derived in the usual way. Formulae are given for the powdered crystal and the ideally imperfect crystal in the kinematical approximation as well as for the large perfect crystal in the framework of the dynamical theory.

1. Introduction

The integrated intensity is an important quantity in all diffraction methods used for structure analysis. If a monochromatic beam is used the integration is performed over the scattering angle while in the case of a polychromatic beam the integration is over wavelength. Table 1 summarizes the possible experimental methods and presents the formulae for the integrated intensities in the kinematical approximation. In the

case of a powdered crystal the formulae apply to the whole Debye–Scherrer ring (cone) and in the case of a rotating single crystal a full (2π) rotation is assumed. We shall refer to the methods in Table 1 as $A1$, $A2$ etc. and discuss them below. The notation used is explained in §§ 2 and 3.

The classical methods are the powder method ($A1$), the Laue method ($B2$) and the monochromatic rotating-crystal method ($A3$). However, in the last few years the time-of-flight (TOF) methods for neutrons and the energy-dispersive spectroscopic (EDS) methods for X-rays have made the remaining methods listed in

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Table 1 experimentally interesting. In the latter methods a fixed scattering angle, $2\theta_0$, and a polychromatic incident beam are used. The wavelength distribution of the scattered beam is measured by means of the time-of-flight technique in the neutron case and using semiconductor detectors in the X-ray case.

In the standard textbooks [e.g. Zachariasen (1945), von Laue (1960)] the formula for the integrated intensity of each of the classical methods is derived separately and the calculations are rather lengthy. We shall show that there are simple relations between the formulae for the integrated intensities of all the methods listed in Table 1. The relations are closely related to the diffraction geometries and to the Lorentz factors of the methods considered. As will be demonstrated, they enable a quick derivation of the integrated intensity formula for any of the methods in Table 1, provided that one of them is derived in the usual way.

The formulae given in Table 1 are derived with the assumption of neglible absorption and extinction (ideally imperfect crystal). Several materials can nowadays be grown in the form of large single crystals of high perfection. For these crystals the dynamical theory of diffraction is used. Integrated intensity formulae for the relevant diffraction methods are given in § 4.

2. Relations between the intensity formulae

All the integrated intensities are proportional to the intensity of the incident beam, $i_0(\lambda)\Delta\lambda$, where $i_0(\lambda)$ is the intensity per unit wavelength range and $\Delta\lambda$ is the spectral width. In the monochromatic methods (column A in Table 1) the wavelength is fixed ($\lambda=\lambda_0$). The spectral width, $\Delta\lambda_0$, is a constant determined by the experimental conditions.

In the polychromatic methods (column B in Table 1) the Bragg angle is fixed ($\theta=\theta_0$) and the angular width, $\Delta\theta_0$, is a constant determined by the experimental conditions. The wavelength range of the diffracted beam is then given by

$$\Delta\lambda=\lambda\cot\theta_0\Delta\theta_0 . \quad (1)$$

Thus, given the integrated intensity of any method in the A column, the integrated intensity of the corresponding B method (on the same horizontal line in the table) is obtained by substituting $\Delta\lambda_0$ for $\Delta\lambda$ given by equation (1).

The integrated intensity of B1 is obtained by multiplying that of B2 by the factor

$$j'\tfrac{1}{2}\cos\theta_0\Delta\theta_0 , \quad (2)$$

where j' is the multiplicity factor for the powder method and $\frac{1}{2}\cos\theta_0\Delta\theta_0$ is the probability that a crystallite in the powder is oriented for Bragg reflexion.

The integrated intensity of B3* is obtained by multiplying that of B2 with the factor

$$j''\frac{\Delta\theta_0}{2\pi} , \quad (3)$$

where j'' is the multiplicity factor for the rotating-crystal method and $\Delta\theta_0/(2\pi)$ is the fraction of time during which the crystal is oriented for Bragg reflection.

In the A column there are only two methods because no integration is possible in method A2. The integrated intensity of A1 is obtained by multiplying that of A3 with the factor

$$\pi\cos\theta , \quad (4)$$

and by substituting j'' with j'. The physical significance of equation (4) is seen by rewriting it as follows:

$$\tfrac{1}{2}\cos\theta\Delta\theta\frac{2\pi}{\Delta\theta} . \quad (5)$$

Like equation (2) the factor contains the probability that a crystallite in the powder is oriented for Bragg reflexion. In addition one has to take into account that the crystallite is diffracting continuously whereas the rotating crystal is oriented for reflexion only a fraction of time.

3. Formulae for the ideally imperfect crystal

Using the relations derived above, one can begin with the theoretical expression for the integrated intensity of an arbitrary method and then work through a closed loop. As an example we will begin with the well known formula for the total diffracted power in a Debye–Scherrer ring (method A1):

$$P_{A1}=j'i_0(\lambda_0)\Delta\lambda_0 VN^2|F|^2\lambda_0^3\frac{p}{4\sin\theta} , \quad (6)$$

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* For simplicity only zero-layer reflexions are considered here. The treatment can easily be extended to reflexions in arbitrary layers.

Table 1. *Integrated-intensity formulae for diffraction methods (kinematical approximation)*

Beam Sample	A. Monochromatic $\lambda=\lambda_0$	B. Polychromatic $\theta=\theta_0$
1. Powdered crystal	$j'i_0(\lambda_0)\Delta\lambda_0 VN^2|F|^2\lambda_0^3\dfrac{p}{4\sin\theta}$ *	$j'i_0(\lambda)VN^2|F|^2\lambda^4\dfrac{p\cos\theta_0\Delta\theta_0}{4\sin^2\theta_0}$ †
2. Fixed single crystal	No integrated intensity measurements possible	$i_0(\lambda)VN^2|F|^2\lambda^4\dfrac{p}{2\sin^2\theta_0}$ *
3. Rotating single crystal	$j''i_0(\lambda_0)\Delta\lambda_0 VN^2|F|^2\lambda_0^3\dfrac{p}{2\pi\sin 2\theta}$ *	$j''i_0(\lambda)VN^2|F|^2\lambda^4\dfrac{p\Delta\theta_0}{4\pi\sin^2\theta_0}$ ‡

* Zachariasen (1945).   † Buras (1963).   ‡ Buras, Giebultowicz, Minor & Rajca (1970).

where V = crystal volume, N = number of crystal unit cells per unit volume, F = structure factor and p = polarization factor.

In order to make the equations valid for neutrons as well as for X-rays we have included the classical electron radius $e^2/mc^2 = 2\cdot82 \times 10^{-13}$ cm in the structure factor for X-rays. In case of X-rays the polarization factor, p, depends on the state of polarization of the incident beam and the scattering angle (Zachariasen, 1945). For nuclear scattering of unpolarized neutrons p equals 1. In case of neutron magnetic scattering the integrated intensity depends on the polarization state of the neutron beam, the state of alignment of the magnetic moments within the sample and the scattering angle (Bacon, 1962). A detailed discussion of this case is beyond the scope of this note.

Using the procedures described by the equations (1), (2) and (3) one has

$$P_{B1} = j'i_0(\lambda)VN^2|F|^2\lambda^4 \frac{p\cos\theta_0\Delta\theta_0}{4\sin^2\theta_0} , \tag{8}$$

$$P_{B2} = i_0(\lambda)VN^2|F|^2\lambda^4 \frac{p}{2\sin^2\theta_0} , \tag{9}$$

$$P_{B3} = j''i_0(\lambda)VN^2|F|^2\lambda^4 \frac{p\Delta\theta_0}{4\pi\sin^2\theta_0} , \tag{10}$$

$$P_{A3} = j''i_0(\lambda_0)\Delta\lambda_0 VN^2|F|^2\lambda_0^3 \frac{p}{2\pi\sin 2\theta} . \tag{11}$$

Finally it is seen that the procedure described by equation (4) transforms equation (11) into an expression identical with equation (5) which was the starting point.

4. Formulae for the large perfect crystal

The relations given in § 2 are slightly modified when dealing with a large perfect crystal. The integrated quantity recorded in the rotating-crystal methods ($A3$ and $B3$) is conveniently defined as the total amount of energy, E, which is diffracted as the crystal is turned with angular velocity, ω, through the reflexion range. The multiplicity factor is, of course, unity.

The powder methods are, for obvious reasons, excluded in this section. One therefore cannot work through a closed loop of intensity formulae as in § 3. However, as shown below, one can begin with a well-known formula of a classical method and end with another well known formula.

Beginning with method $A3$ the integrated energy is given by (Zachariasen, 1945)

$$E_{A3} = R^y i_0(\lambda_0)\Delta\lambda_0 S_0|b|^{-1/2}N|F|\lambda^2 \frac{K}{\pi\omega\sin 2\theta} , \tag{12}$$

where R^y is the reflexion power integrated on the y scale,* S_0 is the cross section of the incident beam, b is the ratio of the direction cosines of the incident and reflected beams relative to normal to surface, and K is a polarization factor which in the X-ray case is unity for normal polarization and $|\cos 2\theta|$ for parallel polarization of the incident beam.

The diffracted energy of method $B3$ is obtained by the substitution described in connexion with equation (1):

$$E_{B3} = R^y i_0(\lambda)S_0|b|^{-1/2}N|F|\lambda^3 \frac{K\Delta\theta_0}{2\pi\omega\sin^2\theta_0} . \tag{13}$$

Equation (13) is, to the best knowledge of the authors, derived for the first time in this note.

Finally, the integrated power of the classical Laue method (method $B2$) is obtained by using a slight modification of equation (3):

$$P_{B2} = \frac{\omega}{\Delta\theta} E_{B3} = R^y i_0(\lambda)S_0|b|^{-1/2}N|F|\lambda^3 \frac{K}{2\pi\sin^2\theta_0} . \tag{14}$$

5. Conclusion

We have shown that (a) in the framework of both the kinematical and the dynamical theories of diffraction there are relations of simple physical significance between the intensity formulae of the different experimental methods for integrated intensity measurements, and (b) in the framework of each of the two theories of diffraction the formulae for the integrated intensities of all methods can be simply generated using the above mentioned relations, provided that one of them is derived in the usual way.

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* R^y generally has to be calculated by numerical integration. However, in the Bragg case for a crystal with a negligibly small absorption coefficient one has the simple solutions $R^y = \frac{8}{3}$ (Darwin solution) or $R^y = \pi$ (Ewald solution). The Darwin solution is generally preferred for X-rays whereas the Ewald solution is more relevant for neutrons.

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