YOUNG: Many people have avoided step-scans in the past because of the large amount of numerical output. However, a step-scan with an individual dead-time correction on each step gives us the only accurate way of making counting-loss corrections.

LADELL: There are electronic circuits which are capable of making counting corrections automatically up to 10^6 c.p.s. I do not know if these are commercially available.

HOSOYA: They are from JOEL.

WEISS: All these devices introduce an error of perhaps 10% in the correction. So you must make sure that the correction itself is small.

ROGERS: Dr Hughes at Cardiff found that when the peak counting rates with an unattenuated beam were such as to lead to 25–30% counting losses, he could avoid these losses by suitable attenuation at a cost of only an extra 10% in the total time taken for his experiment.

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Assessment of Accuracy in Powder Intensity Measurement

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The assessment of the overall accuracy in powder intensity measurement involves the estimation of the error of virtually every term in the intensity equation. Problems related to the accuracy of those quantities which are needed for the determination of relative structure factors are discussed. An example of the consideration of errors in an absolute measurement is given.

Introduction

The attainment of experimental structure factors F of high precision and the assessment of their absolute accuracy are current problems of considerable consequence to crystallography and its applications. Many possible sources of error exist in the individual techniques used in X-ray intensity measurements and in the transformation of the measurements to F values. Investigation of these factors is therefore of prime importance in defining the accuracy to be associated with different levels of experimental sophistication. The purpose of this paper is to discuss the assessment of accuracy in powder intensity measurement. Consideration will be limited to measurements made using the symmetrical Bragg method, counter technique and monochromatized radiation, on centrosymmetric crystals of known structure.

The square of the absolute F value of a Bragg reflexion from a powder specimen can be expressed as (James, 1962)

$$F^2 = \left[\frac{16\pi\omega\mu R^2 V^2}{r_0^2\lambda^3 A P_0}\right]\left[\frac{\sin\theta\sin 2\theta}{p(\theta,\theta_M)}\ \frac{E}{j}\right], \quad (1)$$

where ω is the angular velocity of the detector, μ the linear absorption coefficient, R the distance from the specimen to the receiving slit, V the volume of the unit cell, $r_0 = e^2/mc^2$ the classical electron radius, λ the X-ray wavelength, A the area of the receiving slit, P_0 the total power in the primary beam, θ the Bragg angle, θ_M that of the monochromator crystal, $p(\theta, \theta_M)$ the polarization factor, j the multiplicity, and E the total diffracted energy for a reflexion.

The mosaic crystal formula (1), which assumes symmetrical geometry, proper focusing and correct diffractometer alignment, is valid for a specimen free of preferred orientation, extinction, surface roughness and porosity. It is essential that the effects of deviations from these conditions be considered in accurate measurements. In addition, virtually every term in equation (1) requires careful consideration. We shall discuss mainly the problems related to the accuracy of the quantities in the second term of equation (1); the measurement of the quantities in the first term – the scale factor – has been the subject of the contribution by Chipman (1969).

Measuring geometry and diffractometer alignment

The effects of deviations from idealized diffraction conditions are important for low-angle reflexions, particularly if the receiving slit is very narrow, as is necessary when a diffracted-beam monochromator is used. Horizontal divergence and an asymmetrical intensity distribution in the primary beam cause systematic effects on E values, which added up can be of the order of 1% at $\theta \simeq 10°$ (Suortti & Paakkari, 1966). However, the most serious errors are caused by maladjustment of the specimen. For instance, an inaccuracy of 0·2° (in 2θ) in the zero alignment of the X-ray focus, the centre of the goniometer, the specimen surface and the receiving slit may result in an error of $\simeq 5\%$ in E at $\theta = 10°$, if the receiving slit is very narrow. To attain

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* Read by K. Kurki-Suonio.

an accuracy of about 0·4% in E at this Bragg angle, the zero alignment must be correct to within 0·02° in 2θ.

The specimen

Consideration of errors arising from specimen effects requires that one is able to separate the different systematic effects from each other, in order to prove their absence or to define the accuracy of any necessary corrections. A review of the problems encountered in preparing a useful specimen is given by Weiss (1966), and the effects of preferred orientation have been discussed in the accompanying paper of de Wolff (1969). We shall consider the possibility of correcting diffracted intensities for the effects of specimen porosity and surface roughness. Since the intensity of fluorescent X-rays is not affected by preferred orientation, its measurement is a suitable means for independently studying granularity effects. (For light elements the fluorescent radiation cannot be observed but in such cases the effects are small.) DeMarco & Weiss (Weiss, 1966) have shown that the ratio r of the Bragg intensity from a powder specimen to a bulk specimen is

$$r \simeq 1 - \frac{\mu+\mu^*}{2\mu^*}(1-r^*), \tag{2}$$

where r^* is the ratio of the fluorescent intensity from the porous powder specimen to that from a polished bulk specimen, and μ, μ^* are the linear absorption coefficients for the incident and fluorescent radiations, respectively.

Fig. 1 gives the values of r^* measured by Inkinen, Paakkari & Suortti (1968) for two specimens of carbonyl process nickel (the particle size 3–5 μm) which were pressed with 2000 kg.cm^{-2}. The sample A was pressed against a well polished steel plate and measurements were made on this smooth surface. The surface of the specimen B was treated with emery papers. The exciting radiation was Mo $K\alpha$ and a pulse-height analyser was set to accept only Ni K components. The values of r^* for the specimen A do not show any angular dependence, whereas the results for the specimen B indicate that the effect due to rough surface is strongly dependent on scattering angle (*cf.* de Wolff, 1956; Paakkari & Suortti, 1968). By means of Fig. 1 and equation (2) the necessary corrections to the Bragg intensities can be determined to an accuracy of about 1%.

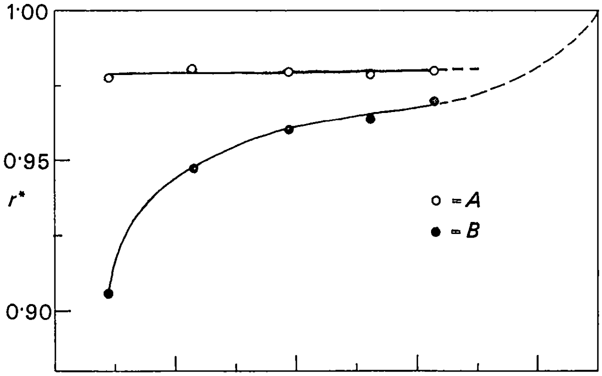

Fig. 1. The ratio r^* of the fluorescent intensity from powder specimens of carbonyl process nickel to that from a polished bulk specimen as a function of the scattering angle. The powder specimens were pressed with 2000 kg.cm^{-2}, A against a polished steel plate, and B like A but the surface was treated with emery papers.

Wavelength

A determination of the wavelength distribution in the monochromatized beam should be made with a good single crystal in a high order. Further, if the X-ray tube is operated at high potential, a study of the wavelength purity should also be made in order to observe the half-wavelength contamination in the monochromatized beam. The second order can usually be reduced to negligible proportions by the use of pulse-height discrimination; the absence of half-wavelength diffraction from a suitable single crystal confirms the result.

Measurement of E

The conditions under which the Bragg peaks are measured must be chosen with two points in mind: first, one must obtain a good estimate of the background under the Bragg peak, in order to make a valid background subtraction; secondly, the background must be as small as possible to enhance the peak-to-background ratio. If the fluorescence yield of the elements in the specimen is great for the incident radiation, it is preferable to use a diffracted-beam monochromator. By a proper monochromatizing technique and by energy discrimination, the background intensity can often be reduced to a level which is mainly due to the detector background.

It is more or less standard practice to measure the diffracted intensities by using the following procedure: the general features of the background are investigated by step-scanning the detector in small increments over the entire angular range examined; the angular ranges for the integration of the Bragg peaks are selected so that all the Bragg intensity is included; with a receiving slit of proper area, each peak is scanned several times while integrated counts are accumulated; subtraction of the background, the dependence of which on scattering angle is assumed linear in the range of integration, yields the E values. It is desirable to keep the counting rate sufficiently low so that the dead-time correction is no greater than $\simeq 1\%$. It is always advisable to rotate the specimen in the plane of its surface to reduce statistical fluctuations from particle sampling. Variations in the primary beam intensity do not present a significant source of error since the stability of modern commercial X-ray sources in P_0 is better than 0·5% per day.

The random error and the error in the subtraction of the uniform background can be estimated on the basis of counting statistics. Systematic errors arise from half-wavelength diffraction (discussed above under wavelength) and from thermal diffuse scattering (TDS) which peaks at the Bragg reflexions. There are, in fact, no generally satisfactory experimental techniques which would lead to the elimination or correction of the TDS contribution to the Bragg reflexion. Therefore, the correction for TDS must be calculated by the application of a proper model for lattice vibrations. Several authors (*e.g.* Warren, 1953; Herbstein & Averbach, 1955; Chipman & Paskin, 1959; Borie, 1961) have studied this correction in mono-atomic cubic powders by making use of the Debye lattice model. Recently Suortti (1967) developed an improved method for calculation of the factor by which the observed E value is increased due to the inclusion of TDS. He concluded that first-order scattering by acoustic phonons is almost entirely responsible for variations in the TDS intensity, and that the actual profile of TDS intensity is a convolution of the Bragg intensity profile and the ideal or theoretical TDS profile. With present approximations the corrections for TDS are probably no more accurate than $\simeq 10\%$.

Polarization factor

With an incident-beam monochromator the polarization factor can be expressed as

$$p(\theta, \theta_M) = \frac{1 + K(\theta_M) \cos^2 2\theta}{1 + K(\theta_M)},$$

where K is the ratio of the reflecting power of the monochromator for the π polarization, to that for the σ component. For an ideally mosaic crystal, $K_m = \cos^2 2\theta_M$, and for a non-absorbing perfect crystal, $K_p = |\cos 2\theta_M|$. The use of an incorrect polarization factor causes serious errors in converting the intensity measurements to F values. The uncertainty in the correct form of K is reduced by selecting θ_M close to 0° (or 90°). Miyake, Togawa & Hosoya (1964) have shown, by comparison between filter and monochromator measurements, that with Cu $K\alpha$ radiation, reflected by a LiF(200) monochromator for which $2\theta_M = 45°$, the polarization factor with the generally accepted value K_m had a maximum error of 3·5%. For a more accurate determination of K, one can use polarized X-rays produced by anomalous transmission in a perfect Ge-crystal slab (Cole, Chambers & Wood, 1961). By utilizing the forward-diffracted beam, the plane of polarization can be rotated by rotating the crystal, while the beam itself stays almost fixed in space. By application of this method, K can be determined to an accuracy of about 1% (Suortti & Paakkari, 1968). Jennings (1968) measured K by examining the scattering from a large perfect crystal (Ge) face at 90° in two orthogonal planes. The value obtained for a LiF(200) monochromator and for Cu $K\alpha$ radiation was found not only to be far away from K_m, but not even to lie between K_p and K_m. In this case the use of K_m may lead to an error in the polarization factor of up to 15%.

Absolute measurement

In assessing the accuracy of an absolute measurement, attention must also be paid to the problems discussed by Chipman (1969). We shall give an example of the consideration of errors in an absolute experiment. In connection with the I.U.Cr. Powder Intensity Project, the group at the University of Helsinki (Inkinen, Paakkari & Suortti) have measured the absolute F value of the 111 reflexion from a standard powder specimen of nickel. The primary X-ray beam was attenuated by means of multiple foils. An estimate of the error in $F(111)$ due to the various experimental factors (other than the presence of specimen effects) is shown in Table 1. This measurement together with some other absolute experiments (Batterman, Chipman & DeMarco, 1961; Cooper, 1962; Togawa, 1965; Hosoya & Yamagishi, 1966; Paakkari & Suortti, 1967) demonstrates that if one is able to prepare powder specimens so that equation (1) is valid to $\simeq 0·5\%$ then it is possible, by the exercise of a great deal of care, to measure absolute structure factors to an accuracy of about 1%.

Table 1. *An estimate of the error in* $F(111)$ *of nickel, in per cent, due to the various experimental factors listed below*

Statistical accuracy	0·1
Background subtraction	0·3
Absorption coefficient (Cooper, 1965)	0·4
Dead-time correction	0·1
TDS correction	0·1
Polarization correction	0·1
Receiving slit	0·2
Attenuation factor	0·4
Total error (square root of sum of squares)	0·7%

My illness prevented me from attending the Cambridge Meeting, and I would like to thank Professor K. Kurki-Suonio for reading this paper.

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DISCUSSION

Chairman (Herbstein): Professor Kurki-Suonio should be congratulated on the way in which he presented this paper.

Post: When you rotate the Borrmann crystal, the anomalously transmitted beam will rotate in a circle of radius $t \sin \theta$.

Kurki-Suonio: This comes to about 0·2 mm, which is insignificant.

Weiss: Inkinen used an expression which I suggested to correct for porosity. I would not use this expression myself! The expression attempts to eliminate effects by comparing the fluorescence with that of a smooth sample.

Furnas: The energy discriminating properties of a Li-drifted Si radiation detector are such that if it is used with a multi-channel pulse-height analyser, one can record simultaneously all diffraction effects due to the subharmonics of the monochromatic wavelength which are reflected by the monochromator crystal.

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Current Status of the I.U.Cr.Powder Intensity Project

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The eventual objective of powder intensity measurements, in the present context, is to obtain absolute integrated Bragg intensities from specimens which are ideal with respect to all parameters such as extinction, preferred orientation, *etc.* At present, the Project has been limited to a comparison of X-ray techniques on a number of samples of carbonyl process nickel which are known to be non-ideal, but which were determined by actual measurement to yield identical integrated intensities using Cu $K\alpha$ radiation. Eleven samples have been measured in ten laboratories and six of these have been standardized by measurement of the incident beam. The results show that integrated intensities may not be relied on to better than 5%, even on a relative basis. It appears that, at the present time, the techniques for making an accurate measurement of the incident beam may be more reliable than those for measuring relative intensities.

Background

The study of electron density in crystals through the measurement of X-ray structure factors may be broadly classified into the study (*a*) of the positions of atoms within the unit cell and (*b*) of the details of the electron distribution once the position of the atoms is known. This latter case may be subdivided into effects arising from the thermal motion of the atoms and into those arising from the actual electronic distribution within the atom. It is well established that this distribution differs by only a few per cent from a distribution obtained by superposing free atoms having electron distributions calculated by modern approximation schemes. Thus, it is clear that a study of the influence of crystalline environment on such atoms will require an accuracy of better than, say, 1%. Furthermore, it is the outermost electrons which are most influenced by this environment and it is likely to be the lowest order Bragg reflections which are of greatest interest. The primary motive for making measurements of such reflexions on powders is the possibility of varying preparation conditions over a wide range so as to be better able to assess the effects of extinction than is possible with single crystals.

If attention is restricted to simple materials for which the Bragg peaks are intense and widely separated, modern diffractometers are able to reproduce integrated intensities to a precision approaching 0·1%. It has become clear, however, that the actual accuracy with which structure factors could be measured is far less. Because of this situation, it appeared that it would be fruitful to conduct an international project under the auspices of the Commission on Crystallographic Apparatus of the IUC to assess the actual accuracy possible. From the outset, it was visualized that the