The next approximation $2\alpha \rightarrow 0$ leads to the final result for ΔV:

$$\lim_{\beta,\alpha\rightarrow 0} \Delta V \propto |\mathbf{h}|^3 6 \sin\alpha[\cos\theta - \cos(3\theta)]/\sin^6\theta$$
$$\propto |\mathbf{h}|^3 6\alpha[\cos\theta - \cos(3\theta)]/\sin^6\theta$$
$$\propto |\mathbf{h}|^3 [\cos\theta/\sin^4\theta]$$
$$\propto 1/(\lambda^3 \tan\theta). \quad (29)$$

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Statistical Descriptors in Crystallography. II.
Report of a Working Group* on Expression of Uncertainty in Measurement

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(*Received* 18 *August* 1994; *accepted* 15 *December* 1994)

Abstract

The Working Group has examined recent recommendations for evaluating and expressing uncertainty in measurement [*Guide to the Expression of Uncertainty in Measurement*, International Organization for Standardization (ISO, 1993)]. The present publication updates an earlier report of the IUCr Subcommittee on Statistical Descriptors [Schwarzenbach, Abrahams, Flack, Gonschorek, Hahn, Huml, Marsh, Prince, Robertson, Rollett & Wilson (1989). *Acta Cryst.* A**45**, 63–75]. This new report presents the concepts of standard uncertainty, of combined standard uncertainty, and of Type A and Type B evaluations of standard uncertainties. It expands the earlier dictionary of statistical terms, recommends replacement of the term *estimated standard deviation* (e.s.d.) by *standard uncertainty* (s.u.) or by *combined standard uncertainty* (c.s.u.) in statements of the statistical uncertainties of data and results, and requests a complete description of the experimental and computational procedures used to obtain all results submitted to IUCr publications.

Introduction

The International Organization for Standardization (ISO) has issued a document (ISO, 1993), hereafter referred to as *Guide*, with the purpose of establishing general rules for evaluating and expressing the uncertainty of the result of a measurement. Based on a recommendation of the Comité International des Poids et Mesures, the rules are intended to be applicable to a broad spectrum of measurements. A recent NIST Technical Note (Taylor

* Appointed 4 March 1993 as a Working Group of the International Union of Crystallography Commission on Crystallographic Nomenclature. The final report of the Working Group was accepted on 20 September 1994 by the Commission and 15 December 1994 by the Executive Committee.

& Kuyatt, 1993, hereafter referred to as *Note*) presents a succinct account of the *Guide* that is useful for the general reader.*

The urgent need for such generally applicable rules derives from the fact that a measurement result is now considered complete only when accompanied by a quantitative statement of its uncertainty (see, for example, *Guide* page 4 or *Note* page 13). This new policy concerning measurement results was foreshadowed in *Notes for Authors* [*Acta Cryst.* (1983), **A39**, 174–176, Section 10, paragraph 2]. Therefore, the procedures and nomenclature adopted in the *Guide* and the *Note* are likely to have an impact on IUCr publication practice since it is Union policy to maintain consistency in its publications with internationally recommended nomenclature standards. Accordingly, the IUCr Commission on Crystallographic Nomenclature established a Working Group, drawn from the membership of the Subcommittee on Statistical Descriptors (Schwarzenbach *et al.*, 1989), which was charged with undertaking an examination of the *Guide* and the preparation of such recommendations as may be appropriate for presentation to the crystallographic community.

Following examination of the above documents, the Working Group has concluded that the *Guide* represents a major step towards a rational and unified treatment of the expression of uncertainty in measurement, applicable to an extremely wide range of situations and problems. It notes with satisfaction that the 1989 report of the Subcommittee on Statistical Descriptors, hereafter referred to as *Report* I, is generally in very good agreement with the recommendations of the *Guide*. In this paper, one definition in the section *Definition of statistical terms* of *Report* I is modified and seven new definitions are added; one recommendation is expanded and four additional recommendations are proposed for use in all IUCr publications.† The most important concept introduced by the *Guide*, expressed by the term *uncertainty*, is presented first.

Uncertainty of measurement

The uncertainty of the result of a measurement, or the uncertainty of the measured value of the specific quantity subject to measurement (*i.e.* the *measurand*), expresses doubt about how well the result represents the value of the measurand. The measurement *only* provides an *estimate* of the value of the measurand. Since the value of a measurand is an unknowable quantity, its deviation from the measurement result (*error*) is also unknowable. The uncertainty reflects the lack of exact knowledge of the value of the measurand owing to random and systematic effects, including deficiencies in the model that relates the observations to the measurand. Uncertainty is itself an estimate based on recognized, *i.e. known*, sources of uncertainty consistent with presently available knowledge; unrecognized, *i.e. unknown*, sources of uncertainty cannot be taken into account.

Whereas uncertainty designates a general concept, its quantitative measure is called *standard uncertainty*. The standard uncertainty is an estimate of the *standard deviation*, *i.e.* the positive square root of the variance, of the probability distribution of the possible values of the measurand. The standard uncertainty may consist of several components corresponding to different sources of uncertainty. The term *standard uncertainty* (s.u.) is synonymous with, and replaces, the familiar term *estimated standard deviation* (e.s.d.) in statements of the statistical uncertainties of data and measurement results. Uncertainty components may be classified into two categories based on their method of evaluation, known as Type A and Type B, see below. The purpose of this classification is to indicate the two fundamentally different *methods* of evaluating uncertainty components. This contrasts with the traditional classification of uncertainty as arising from a combination of random and systematic effects. Categorizing the methods of evaluating uncertainty components rather than the components themselves avoids the traditional ambiguities associated with attempts at distinguishing between random and systematic effects. The result of a Type A evaluation of an uncertainty component may be referred to as a *Type A standard uncertainty*, that of a Type B evaluation as a *Type B standard uncertainty*. Both types represent standard deviations.

In crystallography as elsewhere, the measurands Y are usually derived from a number of other observed quantities $X_1, X_2, \ldots, X_N$, each of which is also a source of uncertainty:

$$Y = f(X_1, X_2, \ldots, X_N). \quad (1)$$

The functional relationship f is generally non-linear. Measurands of interest to structural crystallographers include atomic coordinates, bond lengths and displacement tensors; the quantities X_n include diffraction intensities. The standard uncertainty of a derived quantity Y is called the *combined standard uncertainty* (c.s.u.). This term should be used only where it is essential to distinguish it from the component standard uncertainties of the quantities X_n. The combined standard uncertainty of the estimate y of Y is calculated according to (2) from the individual uncertainty components $u(x_n)$ of the estimates x_n of X_n, obtained from both Type A and Type B

* Copies of NIST Technical Note 1297 may be obtained from the NIST Calibration Program or from Dr B. N. Taylor or Dr C. E. Kuyatt, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.

† By special arrangement with the IUCr, the combined reports I and II can be found on the World Wide Web at URL http://www.unige.ch/crystal/astat/preface.html. A text version is available by anonymous ftp from ftp.unige.ch in subdirectory /pub/soft/difrac/astat. Consult the README.1ST file instructions.

evaluations. The coefficients of the estimated variances $u^2(x_n)$ and covariances $u(x_m)u(x_n)r(x_m, x_n)$ are obtained by linearizing $f(X_1, \ldots, X_N)$ in the vicinity of the x_n $(1 \leq n \leq N)$ with a first-order Taylor series, leading to the usual approximation:

$$u_c^2(y) = \sum_{n=1}^{N} (\partial f/\partial X_n)^2 u^2(x_n) + 2\sum_{m=1}^{N-1}\sum_{n=m+1}^{N} (\partial f/\partial X_m)(\partial f/\partial X_n) \times u(x_m)u(x_n)r(x_m, x_n), \quad (2)$$

where $r(x_m, x_n)$ is the correlation coefficient of x_m and x_n. Equation (2) is the *law of propagation of uncertainty*. It shows how the combined standard uncertainty of the measurement result is obtained from the standard uncertainties of the quantities upon which it depends. The calculation of standard uncertainties of measurands refined by least squares is described in *Report* I.

In the simplest case, a *Type A standard uncertainty* is calculated from a series of N observations; it is the familiar standard deviation of the mean of the N observations, *i.e.* $N^{-1/2}$ times the positive square root of the sample estimate of the population variance. More generally, any estimate of uncertainty based on a statistical analysis of experimental data is of Type A. If the probability density function (p.d.f.) of the measurand is sufficiently well known, as is the case for counting statistics represented by the Poisson distribution, the standard uncertainty may be derived from very few or even one single observation and is also classified as Type A. Even though net diffraction intensities do not obey Poisson statistics (Wilson, 1992), their (combined) standard uncertainties from counting statistics are calculated from those of the peak and background counts which in turn are estimated from Poisson statistics. It is good practice to derive scaling factors of intensities correcting for crystal decay as well as additional contributions to the uncertainty from the variations of periodically measured check reflections, *i.e.* of additional series of repeated observations. Corrections for anisotropic radiation damage have been described by Abrahams & Marsh (1987). Uncertainties of diffraction intensities derived by such widely applied procedures are thus of Type A. Uncertainties of the results of a structure determination derived by proper statistical procedures, usually from a least-squares refinement on intensities, are also of Type A.

A *Type B standard uncertainty* is obtained by means other than the statistical analysis of observations. Essentially, it reflects subjective opinion or *a priori* information on the uncertainty of the result of a measurement: it is evaluated by scientific judgement using all relevant information on the possible variability of an observation. The pool of information may include previous observations, experience with or general knowledge of the behaviour and properties of relevant materials and instruments, manufacturers' specifications, data provided in calibration and other certificates, and uncertainties assigned to reference data taken from handbooks. In a structure refinement, uncertainties assigned to restraints of distances, angles and vibrationally rigid bonds are of Type B unless they are derived from sample variances of relevant quantities observed in published structures. Most uncertainty components in the diffraction intensities are of Type A, although it may be possible on the basis of experience to recognize effects for which the associated uncertainties are obtained from Type B evaluations: thus, a Type B component may allow for doubts concerning, for example, the estimated shape and dimensions of the diffracting crystal and the subsequent corrections made for absorption, the reliability of an extinction correction *etc.*

Definition of statistical terms

The contents of this section supplement or replace the corresponding definitions published in *Report* I. The definitions given in *Report* I and not mentioned here remain valid.

Combined standard uncertainty (*c.s.u.*): *Standard uncertainty* of the result of a measurement when that result is obtained from the values of a number of other quantities through a functional relationship (1). It is calculated from the corresponding component uncertainties and is the positive square root of the combined variance $u_c^2(y)$ obtained from (2). The calculation of combined standard uncertainties of measurands refined by least squares is described in *Report* I. In mathematical formulae, the term is symbolized by u_c.

Error: The difference between the result of a *measurement* and the *true value* of a *measurand*. It is a measure of *accuracy*. Because the true value of the measurand is in principle unknowable, the error is also unknowable. In presenting a result it is implicitly assumed that the measurement model includes all known effects [see equation (1)], and that appropriate tests for the detection of unsuspected *systematic errors* have been performed [see the definitions or sections *Goodness of fit*, *Model*, *Systematic error* and *Defects in the model* in *Report* I and Prince & Spiegelman (1992)]. All contributions to the model are sources of uncertainty, which may be Type A or Type B according to the method used for their evaluation.

Measurand: Particular quantity subject to *measurement*. In most cases, a measurand Y is not measurable directly but depends on other measurable quantities, which themselves may be viewed as measurands, through some functional relationship (1). Measurands of interest to crystallographers include atomic coordinates, bond lengths and displacement tensors.

Measurement: Set of operations having the object of determining a value of a quantity.

Standard uncertainty (*s.u.*): *Uncertainty* of the result of a measurement expressed as a *standard deviation* (see *Report* I). In mathematical formulae, the term is symbolized by u.

Type A evaluation of uncertainty: Method of evaluation of uncertainty by the statistical analysis of a series of observations.

Type B evaluation of uncertainty: Method of evaluation of uncertainty by means other than the statistical analysis of a series of observations.

Uncertainty (*of measurement*): A parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand. It gives an indication of the lack of exact knowledge of the value of a *measurand*, not to be confused with the term *error*. Categorizing uncertainty into Type A and Type B components avoids possible ambiguity inherent in a categorization into random and systematic components.

Recommendations

Recommendation 8 below replaces the previous Recommendation 8 of *Report* I. Recommendations 10 to 13 are new.

8. Although multiplication of the elements of the variance–covariance matrix of the model parameters by the square of the goodness of fit, S^2, leads to conservative estimates of standard uncertainties, since S tends to be greater than 1.0, this practice is based on the questionable assumption that the variances of the observations by which the weights are assigned are *relatively* correct but uniformly underestimated. Should S lie outside the range expected at the given confidence level, then either the weights or the model or both are suspect. In particular, the uncertainties of the measurands I, $|F|^2$ or $|F|$ are usually not uniformly underestimated; all known Type A and Type B uncertainty components should be carefully estimated and included in (2). Publications should indicate whether standard uncertainties assigned to structural parameters refined by least squares have been multiplied by S. The value of S must be reported.

10. In IUCr publications, the term *estimated standard deviation* (e.s.d.) should be replaced, in all statements of the statistical uncertainties in data and in estimates of the values of the measurands, by the term *standard uncertainty* (s.u.), symbol u. When it is necessary to make it clear that the uncertainty estimate contains several components, the term *combined standard uncertainty* (c.s.u.), symbol u_c, should be used. In formulae concerned with statistics, the symbol σ shall be used to represent the positive square root of the variance of a usually unknown probability distribution, and the symbol s shall be used to represent the positive square root of a sample estimate of the variance σ^2 (s is also called the experimental standard deviation, and $s/n^{1/2}$ is called the experimental standard deviation of the mean of n sample estimates).

11. When reporting the result of a measurement and its uncertainty, the experiment must be thoroughly documented to include the following information:

(*a*) a clear description of the methods used to calculate the measurement result and its uncertainty from the experimental observations and other data;

(*b*) a list of all uncertainty components and their evaluation;

(*c*) a presentation of the data analysis in such a way that each of its important steps can be followed and the calculation of the reported result can be independently repeated; and

(*d*) a list of all factors and constants used in the analysis and their sources (*e.g.* atomic scattering factors, linear absorption factor, monochromator polarization ratio *etc.*).

Of particular importance in crystallographic structure determination is a thorough and complete description of data-reduction procedures used to convert observed Bragg and background intensities into $|F|^2$ and $|F|$ values. It is preferable to provide too much information rather than too little. Recommendation 4 of *Report* I is emphasized.

12. The numerical value of an estimate y and its standard uncertainty $u(y)$ should not be reported with an excessive number of digits. However, y should be quoted with sufficient accuracy to minimize the effect of round-off error* in subsequent calculations. In order to limit the round-off error of y (denoted by e) to 25% of $u(y)$, $u(y)$ should be quoted to two significant digits in the range 10 to 19, implying that corresponding digits also be quoted for y, and to one significant digit in the range 2 to 9. In general, uncertainties should be rounded up rather than to the nearest digit. For example, a bond distance of 1.542 49 Å with a s.u. of 0.015 32 Å should be reported as 1.542 (16) Å (e = 3%), and one of 2.163 52 Å with a s.u. of 0.004 81 Å should be reported as 2.164 (5) Å (e = 10%). Correlation coefficients should normally be quoted with two significant figures unless their absolute value is close to the value of 1.0, in which case three significant figures should be used.

13. Restraints, *e.g.* on distances, angles and displacement parameters, are observations supplementary to the diffraction data with uncertainties that may be of Type B. They affect the goodness of fit S and the uncertainties

* If $u(y)$ is reported by a one- or two-digit number, denoted by s, that corresponds to the final digits in the value of y, then the largest round-off error of y is $e = (50/s)\%$ of $u(y)$. Thus, for $s = 1$, $e = 50\%$. In some fields of science (*e.g.* high-energy physics), it is common practice to limit the maximum round-off error to 5%, which amounts to quoting $u(y)$ always as a two-digit number ($10 \leq s \leq 99$). In addition to recommendation 12, the IUCr admits this practice as an option.

of the refined parameters. They must be reported in as much detail as the diffraction data.

Suggested translations of the English terms uncertainty and standard uncertainty are

Unbestimmtheit, Standardunbestimmtheit in German;

incertitude, incertitude-type in French;

Неопределённость, стандартная неопределённость in Russian.

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Acta Cryst. (1995). A51, 569–585

Dynamical Theories of Dark-Field Imaging Using Diffusely Scattered Electrons in STEM and TEM

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(*Received* 26 *September* 1994; *accepted* 13 *February* 1995)

Abstract

Dynamical theories of atomic number sensitive image (or Z-contrast image) formed by thermal diffusely scattered (TDS) electrons are proposed based on first-principles considerations. 'Exact' theories are derived for simulating images obtained either in scanning transmission electron microscopy (STEM) using an annular dark-field detector or in transmission electron microscopy (TEM) using an on-axis objective aperture under hollow-cone beam illumination. The atom thermal vibrations are described using lattice dynamics with consideration of phase correlations. The effects that are comprehensively covered in the theory include: dynamical diffraction of the beam before and after TDS, thickness-dependent beam broadening or channelling, Huang scattering from defect regions, coherence of the thermal diffusely scattered electrons generated from the atomic layers packed within the coherent length, multiphonon and multiple phonon excitations, and the detector geometry. Simplified theories have been derived from this unified approach under various approximations. It has been shown that the incoherent imaging theory is a much simplified case of the practical imaging condition, and can be applied only for qualitative image interpretation. The coherent length in the z direction varies with the change of atomic mass in the column. It is thus possible that the z coherence may disappear for heavy elements. Finally, the theory of Huang scattering in high-angle dark-field TEM imaging has been illustrated, and the theoretically expected results have been observed experimentally.

1. Introduction

Atomic number (or projected mass thickness) sensitive high-angle dark-field (HADF) images of crystalline materials have been performed in transmission electron microscopy (TEM) (Bentley, Alexander & Wang, 1990; Treacy, 1993; Otten, 1991) and scanning transmission electron microscopy (STEM) (Pennycook & Jesson, 1990; Xu, Kirkland, Silcox & Keyse, 1990; Liu & Cowley, 1991). In STEM, the image is formed by collecting high-angle diffusely scattered electrons using a high-angle annular dark-field (HAADF) detector when a small electron probe, of diameter smaller than about 2 Å, is scanned across the specimen. The image is thus called a HAADF-STEM image, or 'Z-contrast' image because of the strong dependence of its contrast on atomic number. Based on the reciprocity theorem (Cowley, 1969), an analogous image can be formed in TEM using an on-axis objective aperture under hollow-cone beam illumination. Z-contrast imaging has attracted great attention because of its potential for providing chemical-sensitive structural information at atomic resolution.

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