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The Treatment of Data Collected with a Single-Crystal Diffractometer

BY T. A. HAMOR

Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England

H. STEINFINK

Materials Science and Engineering, ETC 9.104, University of Texas, Austin TX 78712, USA

AND B. T. M. WILLIS

Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, England

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Abstract

Published crystal structure determinations, obtained using a single-crystal diffractometer, are occasionally based on an incorrect space group or on data of poor quality. This paper recommends ways of avoiding some obvious pitfalls.

Introduction

The Commission on Journals at its meeting in Hamburg, Germany, 8 August 1984, appointed a subcommittee for the purpose of raising the common standards for crystal structure papers. This paper presents the recommendations of the subcommittee.

Once a crystal is mounted and centred on a fully-automated diffractometer a number of decisions must be made in order to derive the best set of structure amplitudes in a given interval of time. For example, is it necessary to measure symmetry-related reflections? How can one ensure that the correct unit cell and space group have been determined? Should weak reflections be examined separately? These and other related points are discussed below.

Determination of unit cell and space group

The unit cell must be chosen to represent the correct symmetry of the lattice. A unique lattice can be defined by an infinite number of unit cells, although the converse is not true, for a specific cell defines only one lattice. The crystal system, determined by the presence of a minimum set of symmetry operators, imposes restrictions on the unit cell which then describes one of the 14 Bravais lattices. The choice of such a unit cell is not always obvious, especially from data obtained by automated single-crystal diffractometers. After the refined unit-cell parameters are obtained, authors should determine the 'reduced' cell parameters. These are based on the three shortest non-coplanar translations of the lattice. The Niggli matrix of the reduced cell will indicate the true crystal system and Bravais lattice. Buerger (1957) and Azaroff & Buerger (1958) have described the processes of cell reduction, calculation of the Niggli matrix and transformation of a reduced cell to the appropriate true cell, which correctly represents the crystal symmetry* (see also *International Tables for Crystallography*, 1983, §9.3).

In cases where there is an ambiguity, statistical analysis of the intensities is the usual determining factor for the choice of a centrosymmetric or non-centrosymmetric space group. The statistical evidence may be ambiguous and very useful and sensitive techniques for detecting the absence of an inversion centre in crystals have been described by Kurtz & Perry (1968), Abrahams (1972) and Woolfson (1970). If the chirality of a structure is reported, authors must support their choice by presenting a suitable number of F_o and F_c values for Bijvoet pairs exhibiting the largest differences between their F_c values. If the crystal has a polar axis, then the atomic arrangements at opposite ends of the axis are not related by any symmetry element of the point group (see also *International Tables for Crystallography*, 1983, §10.5). The proper orientation of this axis should always be confirmed by structure-factor calculations.

Data collection

A minimum data set would consist of reflections collected as close to the limit of the copper sphere as is

* The reduced cell may correspond to the true cell, in which case no further transformation is required.

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feasible. For example, using copper radiation, θ_{max} should not be less than 70° ($\sin\theta/\lambda = 0{\cdot}6$ Å^{-1}) unless the nature of the crystal is such that there are very few reflections at high angles. Measurements should extend to at least 1 Å^{-1} if the data permit. The increase in resolution with high-angle data is well worth the effort.

It is recommended that a data set be obtained by merging the intensities from *at least* two sets of symmetry-equivalent reflections other than Friedel pairs. (A Friedel pair consists of the reflections hkl and $\bar{h}\bar{k}\bar{l}$.) In the triclinic system it is impossible to choose symmetry-equivalent reflections which are not Friedel pairs, but for the remaining systems there is no such difficulty. The measure of agreement between symmetry-equivalent reflections should be reported as R_{int}, where $R_{int} = \sum|F - \langle F\rangle|/\sum F$ or $R_{int} = \sum|F^2 - \langle F^2\rangle|/\sum F^2$. Authors should state whether R_{int} is based on F or F^2.

There are several advantages in adopting the merging procedure in data collection. One is that the differences between symmetry-related F's give an indication of the errors (random and systematic) in measuring F. Another is that large differences (large value of R_{int}) could indicate the need to correct for systematic errors, such as absorption, or might indicate wrong assumptions regarding the symmetry. The final R value will usually be greater than R_{int} and any refinement leading to $R < R_{int}$ may be questioned. The time spent in collecting data consisting of at least two equivalent sets of reflections need not be significantly longer than that spent in collecting a unique set of data. A statistically more significant result is obtained from independent measurements of two equivalent reflections in a given time than from a single measurement of one reflection at twice that time. Any small increase in the total time of measurement would be caused only by the slewing speed of the instrument in accessing a larger volume of reciprocal space.

The most popular scans are the θ–2θ (or ω–2θ) and ω scans. The finite volume which is occupied by the reciprocal lattice point is fully illuminated in each of these scans, together with some of the surrounding background. The preferred scan is that which covers the smallest volume of background, as this gives the highest signal-to-background ratio. This criterion is usually satisfied better by the θ–2θ scan than by the ω scan, unless the mosaic spread of the crystal is exceptionally large.

For each reflection two intensity measurements are made: the intensity in scanning across the Bragg peak and that in the background on either side of the peak. If the background count is very small relative to the peak count, then the time spent on each reflection should be the same, irrespective of the strength of the reflection. This then ensures that each reflection is determined to the same absolute precision. However, for weak reflections, whose intensities are only two or three times the background intensity, longer times of counting are required to achieve the same precision as for the strong reflections. The appropriate counting times are readily determined from the tables given by Arndt & Willis (1966).

Reflections with intensities less than some chosen criterion are usually omitted in the refinement process. However, they should be part of the list of structure factors to be deposited.

Data analysis

The most important systematic error with X-rays is absorption. For a spherical crystal of radius R and linear absorption coefficient μ, the absorption correction is a function of μR and θ only. Let us suppose that data are collected from such a crystal in the range $\theta = 0$ to 70° (Cu radiation) or to 25° (Mo radiation). Then if $\mu R = 0{\cdot}55$ ($\theta_{max} = 70°$) or $1{\cdot}2$ ($\theta_{max} = 25°$), the intensities at high angles relative to those at low angles are reduced by 10% on applying the correction. In other words, unless μR is less than $0{\cdot}55$ ($\theta_{max} = 70°$) or $1{\cdot}2$ ($\theta_{max} = 25°$), it is necessary to correct the intensity data if the uncertainties, $\Delta I/I$, in the intensity measurements are to be no more than 10%. The need for a correction is even more urgent when the crystal is non-spherical. If the percentage difference between transmission factors for the largest and smallest dimensions of the crystal is large compared with the final value of R then absorption corrections should be applied.

The weighting scheme used in analysing the data may be based on counting statistics, on empirical considerations and on the spread of values of symmetry-equivalent intensities. The proper weight to be assigned to each observation i is the reciprocal of the variance of that observation:

$$w_i = 1/\sigma_i^2$$

where σ_i is the standard deviation.

The weights should be such that when average values of $\sum w(|F_o| - |F_c|)^2$ are calculated for subsets of the data grouped according to such variables as $\sin\theta$ or $|F_o|$, these averages are relatively constant and independent of the subset considered. Difficulty in achieving this criterion may indicate the presence of systematic errors in the data or in the postulated model. Alternatively the method of normal probability plots may be applied (see *International Tables for X-ray Crystallography*, 1974, §4.3.1). Plots of av. $\Delta F/\sigma$ *versus* $\sin\theta$ or $|F|$ may be helpful in establishing the nature of any systematic errors.

If it is found that for very intense reflections $|F_o|$ is systematically smaller than $|F_c|$ by an amount greater than would be expected from the overall discrepancy index, an extinction correction should be introduced in the data refinement.

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