Acta Cryst. (1997). A**53** 673–675

Comparing Independently Determined Structures

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(*Received 14 February 1997; accepted 13 May 1997*)

Abstract

Ordered weighted differences between matching parameters in independently determined structures, the experimental deviates, follow a Gaussian distribution only if both determinations are effectively subject solely to the influence of random effects and all uncertainties in the parameters are reliably evaluated and propagated. Departures from Gaussian are readily detectable by plotting experimental deviates against corresponding normal probability deviates; a normal distribution produces a linear array of unit slope and zero intercept. Application of this procedure to the results of an X-ray and a neutron diffraction determination of the structure of $Ni(ND_3)_4(NO_2)_2$ at ~11 K [Iversen, Larsen, Figgis, Reynolds & Schultz (1996). *Acta Cryst.* B**52**, 923–931] reveals uncertainties in both experiments to be underestimated by a factor of 2 for the atomic coordinates and 1.5 for the atomic displacement parameters (ADPs). In addition, two ADP deviates depart significantly from the remaining twenty that are normally distributed; the difference between X-ray and neutron values for one N-atom ADP is highly significant. Uncorrected parameter problems introduced into further modeling may lead to false inferences.

1. Introduction

Crystal structure redetermination at the same temperature and pressure as the original determination, possibly performed with different radiation or wavelength, is becoming more frequent. The reasons for undertaking such studies may include doubts about one or more aspects of the original determination, requirements for greater accuracy in measuring deformation or valence-charge densities, increased interest in the relatively lighter atoms in the structure or possible presence of disorder, and the availability of higher-quality crystals. Although matching parameter magnitudes are often compared in course of such studies, differences between them are not always examined rigorously enough to detect potential problems with the data. The purpose of this communication is to demonstrate the capability of the method described by Hamilton (1974), based on the use of normal probability distributions (Abrahams & Keve, 1971), in identifying such problems. This method is applied hereunder to the results of two determinations of the crystal structure of $Ni(ND_3)_4(NO_2)_2$ at ~11 K by Iversen, Larsen, Figgis, Reynolds & Schultz (1996), hereafter ILFRS; one of the determinations was based on X-ray measurement, the other on neutron diffraction. Use of the normal probability distribution, in the form of quantile–quantile plots, is noted in *International Tables for Crystallography*, Vol. C (Prince & Spiegelman, 1992). The tabulated values of normal and half-normal probability deviates that make the procedure rather easy to apply were omitted to conserve space; they may, however, be found in *International Tables for X-ray Crystallography*, Vol. IV (Hamilton, 1974) and may also be derived from *Tables of Normal Probability Functions* (National Bureau of Standards, 1953).

2. Outline of method

The results of any two independent sets of measurement or the quantities derived therefrom, including independently determined structures, may be readily compared by normal probability methods. Taking the value of the ith refined structural parameter from the first determination as $\xi(1)_i$ and its associated combined standard uncertainty as $u_c[\xi(1)_i]$, with matching values from the second determination denoted by $\xi(2)_i$ and $u_c[\xi(2)_i]$, the weighted difference $\Delta\xi_i$ between the two is defined as

$$\Delta\xi_i = [\xi(1)_i - \xi(2)_i]/\{u_c^2[\xi(1)_i] + u_c^2[\xi(2)_i]\}^{1/2}. \quad (1)$$

The ordered distribution of the experimental deviates is Gaussian if each is subject only to random effects and, in addition, is correctly weighted, *i.e.* if the corrections applied to the experimental $|F(hkl)|^2$ magnitudes from which the structural parameters are derived compensate for all systematic influences, the uncertainties in the measurements are reliably evaluated and all necessary variables are entered correctly in the refinement model. Recommended procedures for evaluating both Type A and Type B sources of uncertainty and their possible covariances are found in Schwarzenbach, Abrahams, Flack, Prince & Wilson (1995) or ISO (1993).

In case the sign of $\Delta\xi_i$ is consequential as, for example, if the comparison being made is between $|F_1(hkl)|^2$ and $|F_2(hkl)|^2$, where absolute amplitude magnitudes in the two sets of measurement contain significant information content, then the expected distribution is normal or two-tailed. If the sign is redundant, as for atomic coordinates in centrosymmetric structures, then

the expected distribution is half-normal or single-tailed. Normally distributed $\Delta\xi_i$ form a linear array with zero intercept and slope of unity on being plotted against the corresponding normal or half-normal probability deviates. The presence of uncorrected error in any component of $\Delta\xi_i$ causes a departure from Gaussian that is thereby immediately recognizable (see Abrahams & Keve, 1971, for a full discussion).

3. Application to the structural results reported for $Ni(ND_3)_4(NO_2)_2$

Following independent structural refinement based first on X-ray then on neutron diffraction measurement, ILFRS compared matching ith atomic coordinates or 'thermal parameters'* $\xi(1)_i$ and $\xi(2)_i$ by means of the term $\delta\xi_i/\sigma$, where $\delta\xi_i = \xi(1)_i - \xi(2)_i$ and $\sigma_i = [\sigma_1^2 + \sigma_2^2]_i^{1/2}$. It may be noted that $\delta\xi_i$ is a simple parameter difference, not a weighted deviate as in (1). The r.m.s. value $\langle(\delta\xi_i/\sigma)^2\rangle^{1/2}$ for the nine positional parameters common to the two determinations (values for the D atoms were obtained only in the neutron determination) was 1.73 and, for the 22 atomic displacement parameters (ADPs) in common, was 1.92. The former r.m.s. value was regarded as indicating 'excellent' agreement, similar to the results of the IUCr oxalic acid dihydrate project (Coppens *et al.*, 1984); the latter as 'very good' agreement. Average or r.m.s. values, however, are necessarily less informative than the individual data in Figs. 1 and 2, as seen below.

ILFRS emphasized that 'care should be taken with every step of the process of data collection, data reduction and nuclear and electronic structure refinement' in order to obtain accurate structural parameters but provided no details of the method used for evaluating the uncertainties in $\xi(1)_i$. However, the use of σ as an 'estimated standard deviation' changes the form of (1) for the present application to

$$\Delta\xi_i = [\xi(1)_i - \xi(2)_i]/\{\sigma^2[\xi(1)_i] + \sigma^2[\xi(2)_i]\}^{1/2}, \quad (2)$$

where $\sigma^2[\xi(1)_i]$ is defined only as the reciprocal of the least-squares weight.

The resulting ordered $\Delta\xi_i$ experimental deviates for the nine common positional parameters, based on (2), are plotted in Fig. 1 against the half-normal probability deviates. They give a good fit to a straight line demonstrating that both sets of measurement and their subsequent refinements are influenced primarily by random, not systematic, effects. However, the slope of 1.94 (12), intercept of −0.16 (14) and correlation coefficient (r) of 0.99 (19) derived by linear regression shows that the denominator in (2) has most likely been underestimated by a factor of 1.94, assuming the error in the numerator to be negligible. While the figure does not reveal how this joint underestimation is partitioned between the two independent experiments, an unbiassed estimate apportions the underestimation equally. The standard uncertainties in atomic positional parameters derived by either structural refinement may hence be taken as too small by a factor of 1.94 although matching parameters agree well. The denominator in the r.m.s. value of $\langle(\delta\xi_i/\sigma)^2\rangle^{1/2}$ for the nine positional parameters should also be doubled.

The ordered $\Delta\xi_i$ experimental deviates for the 22 ADPs common to the two refinements are plotted in Fig. 2 against the half-normal probability deviates. The fit obtained by linear regression to all 22 points is poor, with slope of 2.31 (23), intercept of −0.55 (22) and r = 0.92 (60). Omitting the two largest experimental deviates [corresponding to $\delta(U^{33}N1)/\sigma$ = 3.48, $\delta(U^{22}N2)/\sigma$ = 6.61] from the fitting process results in the rather good linear fit shown in the figure, with slope of 1.50 (5), intercept of −0.10 (4) and r = 0.99 (10). All ADP

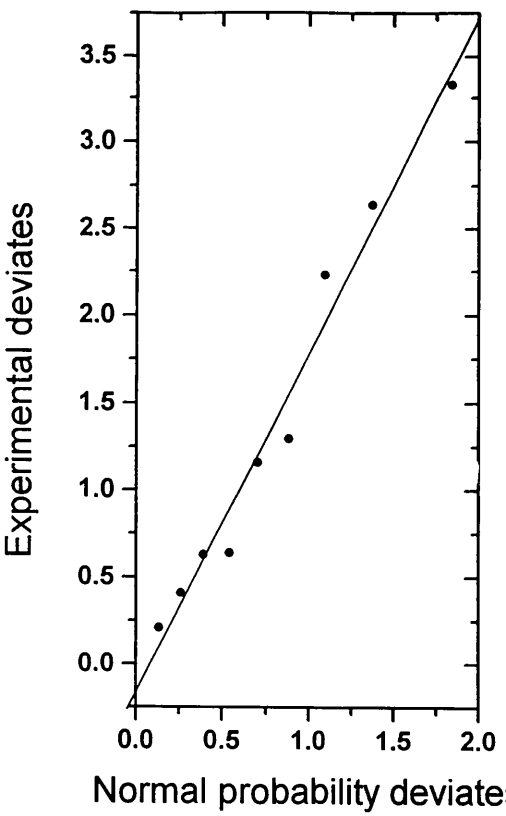

Fig. 1. Distribution of the nine atomic position experimental deviates, derived from the X-ray and neutron diffraction determination of the structure of $Ni(ND_3)_4(NO_2)_2$ at ~11 K and calculated as in equation (2), against the corresponding half-normal probability deviates. A Gaussian experimental deviate distribution would be linear with zero intercept and slope of unity; the line shown is derived by linear regression.

* The IUCr Subcommittee on Atomic Displacement Parameter Nomenclature recommends, *inter alia*, replacing terms such as 'temperature factor' or 'thermal parameter' by 'atomic displacement parameter' (Trueblood *et al.*, 1996).

experimental deviates hence conform closely to a normal distribution except for the two largest, which depart significantly. The joint value of all remaining $\sigma[\delta(U^{ij})]$'s has been underestimated by a factor of 1.5 and thus all individual $\sigma[(U^{ij})]$'s are most likely underestimated by the same factor. The 20 ADPs are hence in good agreement but the X-ray and neutron values for U^{22}N2 differ at the high-significance level of 4.4 'standard' uncertainties. The denominator in the r.m.s. value of $\langle(\delta\xi_i/\sigma)^2\rangle^{1/2}$ for the 22 ADPs should similarly be increased by the factor 1.5.

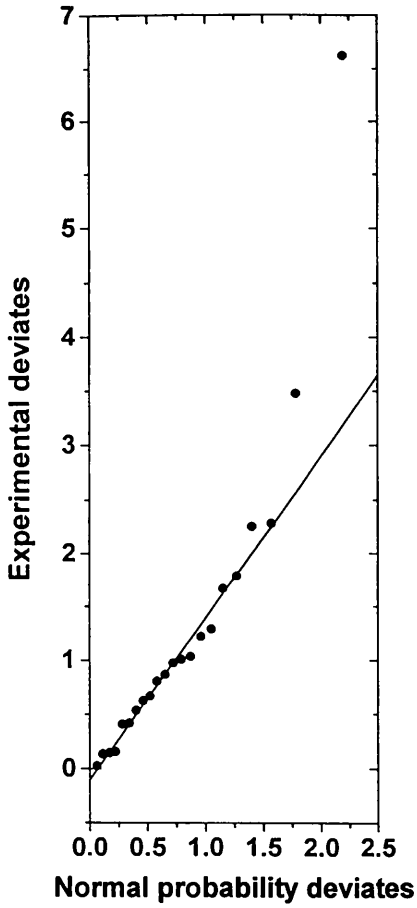

Fig. 2. Distribution of 20 atomic displacement parameter experimental deviates, derived from the X-ray and neutron diffraction determination of the structure of $Ni(ND_3)_4(NO_2)_2$ at ~11 K and calculated as in equation (2), against the corresponding half-normal probability deviates. The two remaining deviates [$\delta(U^{33}N1)/\sigma$ = 3.48 and $\delta(U^{22}N2)/\sigma$ = 6.61] are omitted from the fit to the line shown. Gaussian experimental deviate distributions are linear with zero intercept and slope of unity, that shown is derived by linear regression.

Examination of experimental deviate distributions can lead to the identification and possible solution of such problems as underestimated uncertainties and significant differences that otherwise may be overlooked in refinements such as ILFRSs, in which a major aim is the accurate measurement of ADPs from X-ray and neutron diffraction data prior to a study of the static electron-density distribution. The improved reliability of refinements using weights derived from the evaluation of Type A and Type B variances, as compared with those obtained from a popular empirical weighting scheme, has been discussed recently (Abrahams, Schmalle, Williams, Reller, Lichtenberg, Widmer, Bednorz, Spreiter, Bosshard & Günter, 1997). Full solution to problems with individual parameters revealed by normal probability analysis, following structural refinement, may however be possible only by additional experiment guided by further analysis.

It is a pleasure to thank the referees for comments leading to an improvement in the clarity of this communication and the National Science Foundation (DMR-9310461) for partial support of this work.

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