

center of $d(2L)$ is part of $t(\phi L)$. The three-pyramid formed by the same three points and the corresponding vertex of $d(2L)$ forms the second part of

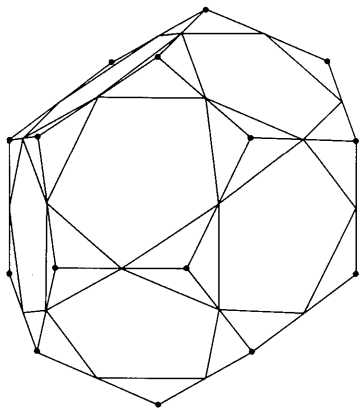


Fig. 12. Composition of the dodecahedron from *skene* and *tristomos*. When the midpoints of the edges of $d(2L)$ are connected with the center, these lines and the edge lines of the dodecahedron yield a decomposition of $d(2L)$ into 20 $t(\phi l)$ with axes along the C_3 axes of $d(2L)$, and 12 $s(\phi l)$ with axes along the C_2 axes of $d(2L)$. This composite cell falls outside the generations defined in § 4 but yields an alternative form of space filling.

$t(\phi L)$. Hence $d(2L)$ is composed of 20 $t(\phi L)$ and 12 $s(\phi L)$.

This dodecahedron, because of the scaling factor 2, belongs to a new branch of possible generations. It was shown in proposition 5.1 that the cells s and t can be extended in periods of three generations. It follows that the composition according to proposition 6.4 can be used to yield an alternative way of space filling with icosahedral symmetry, based on the same set of elementary cells.

The author is indebted to the referee of the first version of this paper for pointing out some mistakes in relation to the icosahedral group, for suggestions on the title and introduction, and for comments on the references.

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Acta Cryst. (1982). **A38**, 264–269

The Analysis of Powder Diffraction Data

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(Received 26 June 1981; accepted 5 November 1981)

Abstract

A comparison has been carried out between the results of analyses of several sets of neutron powder diffraction data using three different methods: the Rietveld method [Rietveld (1967). *Acta Cryst.* **22**, 151–152; (1969) *J. Appl. Cryst.* **2**, 65–71], a modification of the Rietveld method to include off-diagonal terms in the weight matrix [Clarke & Rollett (1982). *Acta Cryst.* Submitted] and the SCRAP method, which involves the estimation of observed Bragg intensities [Cooper, Rouse & Sakata (1981). *Z. Kristallogr.* **157**, 101–117]. Two simulations have also been carried out to demonstrate the way in which the results can differ in more extreme cases. This study has confirmed that the values of the estimated standard deviations given by the Rietveld method are not reliable and that, of the methods considered, only the SCRAP method will in

general give reliable values for the estimated standard deviations of the structural parameters.

Introduction

An analysis of the Rietveld profile refinement method (Rietveld, 1967, 1969) by Sakata & Cooper (1979) showed how the results obtained by this method differ from those given by a conventional integrated intensity method and indicated that the values given for the e.s.d.'s (estimated standard deviations) of the refined parameters are unreliable. New methods for the refinement of powder diffraction data have subsequently been developed which will give more reliable values using two quite different approaches to the problem.

In a recent paper Clarke & Rollett (1982) have described a modification of the Rietveld method which allows for correlation between neighbouring residuals, whilst an alternative approach (SCRAP), which involves the estimation of the Bragg intensities, has been developed by Cooper, Rouse & Sakata (1981). It is the purpose of this paper to present a comparison of results obtained from the same experimental data using both of these methods of analysis and to compare their effectiveness in overcoming the limitations of the unmodified Rietveld method.

The modification of the Rietveld method was suggested initially by Rollett (1979) and we shall therefore refer to the two new methods as the Rollett method and the SCRAP method.

Weighting schemes

The Rollett method involves the introduction of two additional terms in the expression for the diagonal elements of the variance matrix (V_{jj}): (i) a constant A_R and (ii) a constant B_R multiplied by the fourth power of the structure factors for the reflections which contribute to the intensity at the profile point.* The SCRAP method allows for the introduction of a constant A_S in exactly the same way and this provides an estimate of the variance contributions which are independent of position on the profile. However, the second term, which provides an estimate of variance contributions which are dependent on the Bragg intensity, is added in the SCRAP method to the matrix for the least-squares fitting of the Bragg intensities and has the form $B_S I_k^2$. We would therefore expect the value of A_S to correspond to the variance of the background and the value of B_S to reflect the level of relative precision associated with the strongest Bragg intensities, *i.e.* in the range 10^{-4} to 10^{-2} , which corresponds to a precision of a few percent.

We have therefore carried out a series of analyses using the SCRAP method for the data sets referred to by Clarke & Rollett (1982), varying the values of A_S and B_S in order to determine their most appropriate values. In order to do so we have considered the relevant criterion to be that the most suitable weighting

* The suffix *R* has been added here to clarify the distinction between A_R , A_S and A (equation 1) and between B_R and B_S .

scheme should lead to a value of the agreement factor, as defined by Sakata & Cooper (1979), as close to unity as possible.

The agreement factor has the form

$$A = \left\{ \left(\sum_j w_j \Delta_j^2 \right) / (N - P) \right\}^{1/2}, \quad (1)$$

where Δ_j is the residual difference between observed and calculated values of the appropriate quantity, w_j is the weight associated with that difference and N and P are the numbers of observations and refined parameters, respectively. The proximity of A to unity is thus a measure of the statistical goodness-of-fit of the weighted observed and calculated quantities. Two agreement factors are considered in the SCRAP analysis, one for the profile fitting, which reflects the goodness-of-fit of the peak shapes, and one for the fitting of the Bragg intensities.

The values obtained for A_S and B_S are compared in Table 1 with the corresponding quantities ($250 \times A_R$ and $250 \times B_R$) obtained from the Clarke & Rollett analyses. The approximate background level is also given. Although the values of the parameters and their e.s.d.'s given by the two methods are in reasonable agreement it is clear from Table 1 that the weighting schemes do not correspond sufficiently well for a detailed comparison to be worth while. However, a number of interesting facts do emerge from these analyses, as discussed below.

Firstly, in the SCRAP analysis the agreement factor for the Bragg intensities was independent of the value used for A_S , and the values of the structural parameters and their e.s.d.'s were also insensitive to changes in its value. This result is somewhat unexpected, since it implies that the uncertainty in the background level has little effect on the structural parameters. However, it is probable that the importance of this uncertainty is related to the magnitude of the Bragg intensities in such a way that its effect is taken into account by the value of B_S .

It is also interesting to note that the optimum value for A_S is in most cases about four or five times the approximate value of the background, whereas one might expect this factor to be about unity. The one exception is the Al_2O_3 analysis for which it is indeed unity. However, it would seem to be significant that this set of data was collected with an analyser and this

Table 1. Comparison of weighting factors

	Rollett		SCRAP		Background (approx)
	$250 \times A_R$	$250 \times B_R$	A_S	B_S	
UO_2 (r.t.)	2500	0.0015	1032	0.0004	200
Al_2O_3	5000	0.0015	38	0.0004	38
Formic acid	40000	0.0030	3800	0.0100	900
Acetic acid	40000	0.0100	4000	0.0100	1000

result is therefore consistent with the observation that the peak shape approximates more closely to a Gaussian function when an analyser is used. The need to increase the value of A_S in the other cases therefore probably reflects an inadequacy of the Gaussian function as a model of the peak shape.

The magnitude of the values for B_S implies that even for the simpler diffraction patterns for UO_2 and Al_2O_3 the Bragg intensities are determined with a precision which does not exceed 2% of the integrated intensity, even if counting statistics alone would indicate otherwise. This limit to the precision is in accordance with previous experience (see Sakata & Cooper, 1979). For the more complicated diffraction patterns for formic acid and acetic acid an uncertainty of 10% in the integrated intensities is insufficient to reduce the agreement factor below 1.5, indicating that this simple form for the variance is unable to account adequately for all the sources of error in these cases.

Direct comparison

Since the additional weighting factors cannot be introduced in the same way in the two methods we have carried out a set of analyses with $A_R = A_S = B_R = B_S = 0$. Although these may not lead to the most physically reasonable results they will enable a direct comparison to be made under identical conditions. Moreover, the weighting scheme used is then identical to that used in the original Rietveld analyses, so that the results of these can also be included in the comparison. Results of such analyses are given in Tables 2 to 5 for three of the data sets referred to above, namely those for UO_2 , Al_2O_3 and acetic acid.

The UO_2 data exhibit very little peak overlap and the agreement factor for the profile fitting is essentially the same for all methods, although its value is somewhat larger than that for the Bragg intensity fitting in the SCRAP analysis. In these circumstances the values of the e.s.d.'s are slightly larger from the Rollett analysis than those from the SCRAP analysis, with only one exception.

For Al_2O_3 the agreement factor for the profile fitting is again similar in magnitude for all these methods of

Table 2. Results for UO_2 (r.t.)

	Rietveld	Rollett	SCRAP
u	8680 (313)	8347 (359)	8735 (342)
v	-5969 (298)	-5664 (325)	-5999 (328)
w	1869 (64)	1782 (68)	1865 (71)
λ (Å)	1.00332 (4)	1.00334 (5)	1.00332 (4)
$\Delta 2\theta$	32.88 (22)	32.44 (27)	32.18 (22)
B_U (Å ²)	0.262 (24)	0.265 (38)	0.263 (34)
B_O (Å ²)	0.530 (26)	0.511 (41)	0.527 (37)
A_p	1.60	1.60	1.59
A_B			1.28

Table 3. Results for Al_2O_3

	Rietveld	Rollett	SCRAP
u	14196 (106)	14115 (143)	14183 (109)
v	-16165 (137)	-16071 (178)	-16156 (140)
w	5502 (44)	5471 (54)	5499 (44)
λ (Å)	1.42362 (3)	1.42361 (2)	1.42362 (2)
$\Delta 2\theta$	5.23 (11)	5.10 (15)	5.17 (12)
x_{Al}	0.35221 (8)	0.35217 (12)	0.35230 (13)
x_O	0.55636 (9)	0.55640 (15)	0.55632 (17)
B_{Al} (Å ²)	0.182 (17)	0.178 (26)	0.174 (27)
B_O (Å ²)	0.195 (10)	0.197 (15)	0.188 (16)
A_p	1.16	1.19	1.14
A_B			1.49

Table 4. Results for acetic acid: profile parameters

	Rietveld	Rollett	SCRAP
u	3768 (339)	3181 (317)	3664 (306)
v	-4021 (366)	-3452 (329)	-3978 (322)
w	1979 (83)	1794 (75)	1983 (70)
$\Delta 2\theta$	402.5 (3)	402.8 (3)	401.4 (3)
a (Å)	13.2126 (10)	13.2126 (12)	13.2106 (10)
b (Å)	3.8947 (3)	3.8946 (3)	3.8941 (4)
c (Å)	5.7613 (5)	5.7612 (5)	5.7589 (6)
A_p	1.71	1.39	1.89
A_B			2.35

Table 5. Results for acetic acid: structural parameters

	Rietveld	Rollett	SCRAP
C(1) x	0.1626 (7)	0.1644 (11)	0.1614 (14)
y	0.3024 (21)	0.3043 (32)	0.3008 (41)
z	0.1592 (32)	0.1611 (48)	0.1539 (64)
C(2) x	0.0891 (7)	0.0891 (12)	0.0888 (15)
y	0.3941 (26)	0.3876 (43)	0.3872 (52)
z	0.3483 (25)	0.3495 (38)	0.3462 (53)
O(1) x	0.1225 (8)	0.1246 (13)	0.1248 (17)
y	0.1182 (24)	0.1157 (37)	0.1120 (45)
O(2) x	0.2524 (7)	0.2538 (11)	0.2522 (14)
y	0.3876 (20)	0.3932 (36)	0.3916 (48)
z	0.1694 (20)	0.1682 (32)	0.1658 (48)
D(1) x	0.1284 (9)	0.1286 (13)	0.1297 (17)
y	0.5159 (29)	0.5195 (43)	0.5164 (53)
z	0.4853 (27)	0.4864 (42)	0.4838 (60)
D(2) x	0.0523 (8)	0.0519 (13)	0.0506 (15)
y	0.1570 (27)	0.1566 (44)	0.1532 (52)
z	0.4088 (25)	0.4115 (40)	0.4095 (56)
D(3) x	0.0257 (10)	0.0284 (16)	0.0277 (22)
y	0.5349 (30)	0.5348 (50)	0.5382 (65)
z	0.2794 (26)	0.2790 (41)	0.2768 (52)
D(4) x	0.3231 (8)	0.3217 (13)	0.3209 (15)
y	0.5504 (22)	0.5527 (38)	0.5499 (50)
z	0.3843 (23)	0.3801 (37)	0.3793 (47)
C(1) B (Å ²)	0.81 (19)	0.57 (30)	0.87 (35)
C(2) B (Å ²)	0.79 (19)	0.88 (30)	0.28 (49)
O(1) B (Å ²)	0.60 (22)	0.28 (34)	0.84 (48)
O(2) B (Å ²)	-0.69 (20)	0.07 (36)	0.17 (54)
D(1) B (Å ²)	2.86 (28)	2.41 (40)	2.40 (53)
D(2) B (Å ²)	1.91 (25)	2.37 (43)	2.95 (42)
D(3) B (Å ²)	2.57 (26)	2.61 (42)	2.27 (53)
D(4) B (Å ²)	1.21 (22)	1.60 (39)	2.24 (51)

analysis, but in this case that for the fitting of the Bragg intensities in the SCRAP analysis is larger. The Rollett method now gives larger values for the e.s.d.'s than does the SCRAP method for the profile parameters, but slightly smaller values for those for the structural parameters.

The acetic acid data provide the poorest fit to the Bragg intensities and in this case the Rollett method gives a significantly lower value for the agreement for the profile fitting. The values for the e.s.d.'s of the profile parameters are again mostly higher than those given by the SCRAP method, but in this case there is a significant difference between the values given by the two methods for the e.s.d.'s of the structural parameters. The values from the Rollett analysis are on average 20% smaller than those given by the SCRAP method and 60% larger than those given by the Rietveld method.

It is clear from the results of this direct comparison that, whilst the SCRAP and Rollett analyses both indicate that the Rietveld values of the e.s.d.'s are unreliable, there is not necessarily agreement between the two methods on what the best estimates should be. It is therefore of interest to consider why the two methods should give different results.

In their analysis of the Rietveld method Sakata & Cooper (1979) showed that correlation between neighbouring residuals can arise from differences between the observed and calculated values of the Bragg intensities and also that the residuals depended on the profile parameters and the structural parameters in two distinct and separable ways. It is, however, important to note that correlation between neighbouring residuals can also arise from systematic differences between the observed and calculated peak shapes. For example, if the peak shape is assumed to be a Gaussian but in practice contains additional intensity in the tails of the peak, perhaps due to thermal diffuse scattering, then there will be some correlation between neighbouring residuals even if the observed and calculated Bragg intensities are identical. Thus there are two different factors which can lead to correlation between neighbouring residuals.

Whilst this correlation is fairly easy to visualize, it is important to realize that the nature of the model used, from the point of view of the separability of the factors depending on the two different types of parameters, can cause errors in the values of the e.s.d.'s, even when it causes no appreciable correlation. Such a situation would arise if the model provided an extremely good fit for the Bragg intensities. In order to demonstrate this we have carried out an analysis of the experimental data for UO_2 with the observed intensities scaled over the individual peaks so that the observed and calculated Bragg intensities are in very close agreement. Under these circumstances we would expect a reliable analysis of the data to give extremely small values for

the e.s.d.'s of the structural parameters. We have analysed these data (simulation 1) using both the Rietveld method with and without modification, and the SCRAP method, and the results are given in Table 6.

For this simple case the structural parameters comprise simply the temperature factors of the two types of atom. Comparing the e.s.d.'s of these parameters, as given by the different methods of analysis, we find that the SCRAP method does indeed provide values consistent with the near-perfect agreement between the observed and calculated Bragg intensities, whereas those given by the Rollett method are about eight times larger. The Rollett method also gives larger values for the e.s.d.'s of the profile parameters and fairly appreciable, though not statistically significant, differences in the values of all parameters compared with those given by the Rietveld method. In contrast the agreement between the parameter values given by the SCRAP and Rietveld methods is extremely good for these data.

Comparing these results with those given in Table 2, which are for the analysis of the original data before scaling, we see that the SCRAP method gives the same results in the two cases, apart from a decrease in the values of the e.s.d.'s for the structural parameters by a factor of about nine. This is entirely consistent with the better fitting of the Bragg intensities. In contrast, the Rietveld method gives only very small changes in the values of all the e.s.d.'s, whilst the Rollett method gives larger values for the e.s.d.'s of the profile parameters and e.s.d. values for the structural parameters which are smaller by only about 30%.

Table 6. *Results for simulation 1 (scaled UO_2 data)*

	Rietveld	Rollett	SCRAP
u	8720 (325)	8502 (414)	8716 (341)
v	-5985 (310)	-5793 (363)	-5979 (326)
w	1862 (67)	1805 (73)	1860 (70)
λ (Å)	1.00334 (4)	1.00339 (6)	1.00333 (4)
$\Delta 2\theta$	32.12 (21)	31.77 (29)	32.12 (22)
B_U (Å ²)	0.264 (25)	0.239 (30)	0.263 (4)
B_O (Å ²)	0.529 (27)	0.521 (32)	0.527 (4)
A_P	1.70	1.73	1.76
A_B			0.14

Table 7. *Results for simulation 2 (scaled UO_2 data)*

	Rietveld	Rollett	SCRAP
u	8587 (113)	8595 (54)	8735 (5)
v	-5837 (107)	-5839 (46)	-5998 (5)
w	1830 (23)	1828 (10)	1865 (1)
λ (Å)	1.00332 (2)	1.00332 (1)	1.0033178 (6)
$\Delta 2\theta$	32.187 (75)	32.207 (42)	32.187 (3)
B_U (Å ²)	0.258 (8)	0.281 (11)	0.263 (33)
B_O (Å ²)	0.527 (10)	0.547 (13)	0.527 (37)
A_P	0.59	0.46	0.03
A_B			89.5

The other extreme situation, which can easily be simulated, is one in which there is very good agreement between the observed and calculated peak shapes. In order to provide an indication of the full range of possibilities we have therefore carried out a second simulation in which the calculated intensity values have been scaled to provide values of the observed intensities which give an almost identical peak shape for the observed and calculated intensities without changing the values of the observed integrated intensities. The results of the analysis of these data (simulation 2) are given in Table 7.

In this case the SCRAP method gives the same results as for the original data (Table 2), except for a reduction in the e.s.d.'s of the profile parameters by a factor of almost 70. In contrast, the Rietveld method reduces the values of all the e.s.d.'s by a factor of about three, which is not reasonable. The Rollett method gave large values for the correlation factors and inclusion of these led to a non-positive weight matrix. It was therefore necessary to adjust the values of these factors to achieve a satisfactory analysis, with the nearest-neighbour correlation factor reduced to 0.90. Analyses with different values for this factor confirmed that the e.s.d.'s decrease in value systematically as the correlation factor is increased, and that the Rollett method also reduces the e.s.d.'s for the structural parameters by a factor of about three. Again, this result is not reasonable for these data.

Discussion

The results of the direct comparison of the Rietveld, Rollett and SCRAP analyses for a number of sets of experimental data clearly indicate that the values of the e.s.d.'s given by the Rietveld method are unreliable, but also show that the Rollett and SCRAP methods will not necessarily give similar results. In particular, it should be noted that the introduction of off-diagonal weights in the Rollett method always leads to an increase in the values of the e.s.d.'s for the structural parameters, whereas it is possible for the SCRAP method to give values which are appreciably smaller than those given by both the Rietveld and the Rollett methods. However, this will only occur if there is a considerably better fit to the Bragg intensities than there is to the peak shape functions, as defined by the appropriate agreement factors. Such a case is illustrated in simulation 1.

In practice there is usually poorer fitting of the Bragg intensities and in general the SCRAP method will then give larger values for the e.s.d.'s of the structural parameters than those given by both the Rietveld and the Rollett methods. A fairly extreme case is shown in simulation 2, where the SCRAP values are larger by factors of about four and three than those given by the Rietveld and Rollett methods, respectively. This

simulation also shows that the e.s.d.'s for the profile parameters may be significantly overestimated by the Rietveld and Rollett methods if the peak shapes are particularly well fitted.

These discrepancies between the e.s.d. values given by the different methods can readily be understood if we consider the analysis of the Rietveld method given by Sakata & Cooper (1979). In particular, it was shown in this analysis that the calculated intensity is derived from the product of two factors, one of which is a function of the structural parameters (p_c) only, and the other of which is a function of the profile parameters (p_p) only. In general this will have the form:

$$y'_i = K \sum_k I_k(k, p_c) G_{ik}(i, k, p_p), \quad (2)$$

where K is a scale factor and I_k is the Bragg intensity and G_{ik} the shape function for the k th peak.

As a consequence the residuals Δ_i can be considered as two separate terms, $\Delta_i - \sum_k G_{ik} \Delta_k$ and $\sum_k G_{ik} \Delta_k$ (see Fig. 1 of Sakata & Cooper, 1979), where Δ_k is the difference between the observed and calculated Bragg intensities. Since the value of the observed Bragg intensity will be insensitive to the values of the profile parameters we can, to a first approximation, assume that the first term depends only on the profile parameters and the second term depends only on the structural parameter. It therefore follows that the e.s.d.'s for the two types of parameters should be derived from the appropriate terms of the residuals and not from the total residuals.

Neither the Rietveld method nor the Rollett method distinguishes between the two types of parameters in this way, so that the values of the e.s.d.'s will necessarily be unreliable unless there is a comparable goodness-of-fit for the peak shapes and the Bragg intensities. In contrast the SCRAP method removes the terms dependent on Δ_k from the profile fitting procedure, so that the residuals depend only on the profile parameters. The terms dependent on Δ_k contribute to the residuals in the least-squares fitting of the resultant Bragg intensities and thus influence the standard deviations of the structural parameters only.

Moreover, correlation arising from deficiencies in the peak shape function will not necessarily influence the precision of the estimated observed Bragg intensities and hence the structural parameters. This again is illustrated by the results of simulation 1, in which the SCRAP method is capable of giving very precise values for the structural parameters, in spite of correlation between residuals associated with the peak shapes. In these circumstances similar precision would be obtained using an integrated intensity method. However, by introducing off-diagonal weights the Rollett method always reduces the precision of the structural param-

eters, even for cases where the Rietveld method already underestimates it.

Conclusions

The conclusions which can be drawn from this study are as follows.

1. The values of the e.s.d.'s given by the Rietveld method are not reliable.
2. Introduction of off-diagonal terms in the weight matrix may give better values for the e.s.d.'s, but will in general be insufficient to ensure their reliability.
3. Reliable values of the e.s.d.'s can only be determined if the form of the dependence of the calculated intensities on the two different types of parameters is taken into account.
4. Of the methods considered in this paper only the SCRAP method will in general give reliable values for the e.s.d.'s of the structural parameters.

Postscript

Since the present paper was written a further paper discussing the Rietveld method has been published by Prince (1981). However, Prince's paper is misleading because, although he also shows that the model must be adequate on the basis of statistical tests, he assumes that this conflicts with the conclusions of Sakata & Cooper (1979). [The introduction also contains a misquotation from the paper by Sakata & Cooper (1979). These authors do not assert that the profile method (always) 'leads to a systematic underestimate of the uncertainties of the crystallographic parameters'. Indeed, the present paper shows that these uncertainties may also be overestimated in certain circumstances.]

Acta Cryst. (1982). **A38**, 269–274

One-Dimensional Antiphase Structure of $\text{Au}_{22}\text{Mn}_6$ Studied by High-Voltage, High-Resolution Electron Microscopy

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(Received 29 July 1981; accepted 30 October 1981)

Abstract

Au–Mn alloys near the composition of 20% Mn have been investigated by the superstructure imaging technique using a 1 MV electron microscope. A new

superstructure, $\text{Au}_{22}\text{Mn}_6$, was proposed directly from the high-resolution images. The structure is based on the Au_4Mn structure of Ni_4Mo ($D1a$) type and consists of parallel columns with a width of three Mn-atom rows, and the columns are separated by one-

In fact the majority of the discussion presented by Prince is in very close agreement with the analysis of Sakata & Cooper. The three statistics S_P^2 , S_L^2 and S_R^2 defined by Prince's equations (9) to (11) are directly related to the quantities A_P^2 , A_B^2 and A_S^2 defined by Sakata & Cooper. Thus the conclusion that the model is only correct if S_L^2/S_R^2 is unity is very similar to the relationship between A_B^2 and A_S^2 for which the e.s.d. values are reliable, as derived by Sakata & Cooper. However, it is also misleading to call S_R^2 the 'replication mean square', since measurement at different 2θ values cannot be considered as replication in the sense used by Draper & Smith (1966).

The papers by Prince and by Sakata & Cooper are thus in agreement that the Rietveld method cannot calculate the standard deviations correctly if the model does not fit adequately. However, examination of published results indicates that in general the model does not fit adequately on the basis of these statistical criteria, so that the Rietveld method will consequently give unreliable values for the e.s.d.'s.

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