Table 1. α_3/α_2 *for background corrected scan* ($\pm 1°$ *at* $\theta = 45°$) *for various crystals*

Resolution (full-width at half-height)	α_3/α_2		
	Lead	Iron	Nickel
4 meV	1·00	0·86	0·76
2 meV	0·93	0·50	0·39

It is clear from these results that, in general, extremely high resolution is required in order to make any appreciable reduction in the TDS correction, and for soft materials, such as the organic crystals referred to earlier, little improvement can be made. In any case, it will still be necessary to calculate the TDS correction for an 'elastic' diffraction measurement and the energy resolution function will have to be included in the integration. In addition, the use of an analyser will reduce the Bragg intensity and it is doubtful whether the reduction which can be achieved in the TDS correction will be sufficient, on its own, to make the use of the analyser worthwhile.

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Treatment of accidentally absent reflexions in least-squares refinement of crystal structures.

By A. J. DUNNING, *Unilever Research Laboratory, Port Sunlight, Cheshire, England* and V. VAND,* *Materials Research Laboratory and Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.*

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An improved method of including accidentally absent reflexions in the least-squares refinement of crystal structures, so as to accelerate the initial convergence of the procedure, is discussed. It is shown that when the calculated structure factors of these reflexions are less than the observed threshold value they determine nothing more about the structure, and should not be included in expressions for either the standard deviations or the shifts during refinement of atomic parameters.

In a least-squares refinement of a crystal structure, corrections Δx_i to variable parameters x_i (coordinates, temperature factors, *etc.*) are computed by expanding the formula for a structure factor, $F(hkl)$, into a Taylor series in x_i. After neglecting non-linear terms, a least-squares matrix is formed. If non-diagonal terms are neglected,

$$\Delta x_i = \Sigma\, w \Delta F(\delta F_c/\delta x_i) / \Sigma\, w(\delta F_c/\delta x_i)^2 , \qquad (1)$$

where the sums extend over all measured reflexions, and $\Delta F = |F_o| - |F_c|$, where F_o is the observed structure factor and F_c is the structure factor calculated from the initial parameters, x_i. Both F_o and F_c may differ from the true value F_t of the structure. The statistical weight of a structure factor is given by $w = 1/\sigma^2$, where σ is the standard deviation of F_o.

In general there are three classes of reflexion:

Class 1. Well-observed reflexions, to which a value of w can be assigned based on an error analysis of the system, and which can be incorporated into the least-squares procedure without further question.

Class 2. Accidentally absent reflexions which are smaller in magnitude than some instrumental threshold, $F_{\rm lim}$, in which case we know that $O \le |F_o| < F_{\rm lim}$ with uniform probability distribution in the interval.

Class 3. Totally unobserved reflexions, such as those outside the sphere of reflexion, or those which are known to be zero owing to symmetry requirements.

Class 3 reflexions should be given zero weight, which is equivalent to leaving them out of the calculation altogether.

The question of how to treat the class 2 reflexions arises. The knowledge of a limit obviously carries some useful information about the structure, and it therefore appears that such reflexions should be included in the refinement procedure. However, as they represent a probability distribution of errors which is no longer normal, the usual least-squares procedure breaks down. Previous authors, however, have incorporated these reflexions in the least-squares procedure as though their errors were normally distributed.

Hamilton (1955) discussed the treatment of unobserved reflexions, averaging over their intensities. Truter, Cruickshank & Jeffrey (1960) used, in principle, a similar procedure in the analysis of nitrogen perchlorate for a centro-

* Deceased 4 April 1968.

symmetric space group. By assuming the signs known, and averaging over the structure factors, they obtained for the expected average value of the observed structure factor,

$$|F_o| = 0{\cdot}5\ F_{\lim}\ , \qquad (2)$$

and for its weight

$$w = 12/(F_{\lim})^2\ . \qquad (3)$$

Cruickshank & Pilling (1961) remarked also on this scheme, and noted that it resulted in improvement of the estimated standard deviation of the coordinates by some 20%.

Arnott (1965) recently raised again the question of the treatment of accidentally absent reflexions in least-squares refinement of crystalline fibre structures, and arrived at similar results to those above.

We discovered that this scheme is incorrect when we attempted to use it in the refinement of n-hexatriacontane. In this structure, first described by Shearer & Vand (1956), all the thirty-five C–C aliphatic bond lengths should be the same. Their deviations from a mean can thus serve as a very good indication of the actual accuracy in coordinates when various refinement procedures are used. The structure has been refined to an R value of 10·7% by the use of 154 class 1 reflexions. By adding 210 class 2 reflexions, the R value of class 1 reflexions increased to 12·2%, and the standard deviations of the coordinates calculated from Cruickshank's formula,

$$\sigma^2(x) = 1/\ \Sigma\ w(\delta|F_c|/\delta x)^2\ , \qquad (4)$$

seemingly improved by more than 10%. However, the standard deviations in the bond lengths increased from 0·021 to 0·032 Å, indicating that the improvement in coordinates was illusory.

The incorrectness of this weighting scheme can be demonstrated by the following consideration.

Suppose that we have a good set of reflexions of class 1 and that the refinement yielded parameters x_i very near their true values. Then all the F_c will be nearly correct, and if the problem is overdetermined, the differences $||F_c|-|F_t||$ will be generally smaller than $||F_o|-|F_c||$, and also smaller than $F_{\lim}$, provided that there are no systematic errors, and that $F_{\lim}$ is of the order of the typical $||F_o|-|F_c||$. If we now add a large group of class 2 reflexions, then, by the use of equation (2) we shall be adding comparatively large values of ΔF into terms for the sums of Δx_i. These terms will introduce random 'noise' into equation (1), so that appreciable shifts away from nearly true values of x_i will result. In fact we are forcing the values of $|F_c|$ to move towards $\frac{1}{2}F_{\lim}$, instead of leaving them to be statistically uniformly distributed throughout the interval $(0, F_{\lim})$, as theoretically they should be for a centrosymmetrical structure.

From a general consideration of the combination of two independent observations, one with a uniform error distribution in the range (a, b) and the other with a Gaussian error distribution with mean m and second central moment σ^2, we have found that the least-squares weighting procedure (namely the use of the reciprocal of the second central moment of the error distribution for the weight of each observation) leads to some anomalous predictions for the variable being estimated. An example of the unsatisfactory nature of the minimum variance (least-squares) estimate of two such independent observations is that when $\sigma < [(m-b)\,(b-a)/6]^{1/2}$ it lies outside the uniform error distribution, which immediately contravenes one of the observations.

To overcome these shortcomings we have combined independent observations by taking the product of the relevant error distribution functions to construct a likelihood function which is then used to obtain estimates of the observed variables. At this stage the idea of least-squares estimates has been abandoned in favour of estimates based on the likelihood function. After some straightforward analysis of the likelihood function it is apparent that the 'best' estimates for the 'observed' variables when $|F_c| > F_{\lim}$ are given when the weights are:

$$w = c(F_c - F_{\lim})^2 \qquad (5)$$

and c is a constant whose value is somewhat arbitrary, although when this weighting scheme is used in a least-squares refinement the initial rate of convergence is affected by the value of c. When $|F_c| < F_{\lim}$, $w = 0$ is the 'best' weight for a class 2 reflexion for reasons given below, although there are provisos connected with this statement.

When these weights are used in a least-squares refinement there are two chief objections: (*a*) they are not 'minimum-variance' weights; (*b*) the weights depend implicitly through F_c on the parameters being estimated. But, despite this lack of rigour and the problems associated with (*b*), the weighting scheme has worked extremely well in the refinement of n-hexatriacontane and lithium laurate. It would seem, therefore, to be a worthwhile method of including accidentally absent reflexions in the least-squares refinement of crystal structures.

Usually, in a Fourier synthesis, class 2 reflexions are left out. Suppose that we include them, using equation (2). This is equivalent to adding to a Fourier synthesis from class 1 reflexions an additional variation in electron density, which has coefficients of magnitude $\frac{1}{2}F_{\lim}$ and signs the same as F_c. As an electron density map depends more on the signs than on the magnitudes of its terms, the additional map would have positive peaks near the assumed atomic positions. However, as its terms would differ from F_c, it would contain a large component of random 'noise', the slope of which would spoil the accuracy of the peak positions obtained from the class 1 reflexions.

It appears that when $F_{\lim}$ is known with certainty the correct procedure, both for centrosymmetric and non-centrosymmetric space groups, is as follows: when $|F_c| < F_{\lim}$, no additional information can be obtained for x_i except that the set of x_i is consistent with $F_{\lim}$, and therefore one should take $w = 0$ (*i.e.* leave the reflexion out of the refinement). Thus, Δx_i is unaffected by this information. Note that by using $F_o = F_c$, *i.e.* $\Delta F = 0$, $w \neq 0$, Δx_i will be decreased so that during the refinement the rate of change of x_i will be reduced. However, this procedure would lower the $\sigma(x_i)$ given by equation (4) by adding a term to the denominator. This would obviously be incorrect, as mere knowledge that a set of x_i satisfied a certain limit should not bring any increase in accuracy to x_i.

In addition there would be a resulting improvement in the disagreement function R' given by

$$R' = \Sigma\ w||F_o|-|F_c||/\ \Sigma\ w|F_o|\ . \qquad (6)$$

This improvement would be in some sense artificial, however, since in cases with many class 2 reflexions, a large number of small terms would be omitted from the numerator of equation (6). Nevertheless, the fact that a class 2 reflexion has $|F_c| < F_{\lim}$, particularly when $F_{\lim}$ is very small, should diminish R' to some extent, although no knowledge of the true discrepancies exists in this situation.

It would seem to be better, therefore, under these circumstances to quote the number of class 2 reflexions for which $|F_c| < F_{\text{lim}}$ as a percentage of the total number of class 2 reflexions, and to use this as a measure of agreement between the actual and the postulated structures as far as these reflexions are concerned.

If, however, $|F_c| \geq F_{\text{lim}}$, useful information for the refinement of the x_i is conveyed, namely that the initial set of x_i is impossible, and should be adjusted so as to satisfy the limit on F_c. Therefore a comparatively large weight can be assigned to such a reflexion. In practice in this case, for the calculation of ΔF, either $F_o = 0$ or $|F_o| = F_{\text{lim}}$ can be taken, and it should be possible to improve the rate of convergence of the refinement by applying the weighting scheme of equation (5). Particular choice of these weights should not affect the final result of the refinement because in the last stages of refinement all $|F_c|$ should become smaller than F_{lim} anyhow, and so *all* class 2 reflexions are finally weighted zero and may just as well be left out. They are of value only in the initial stages of refinement, where they may help to accelerate convergence. There is, however, a proviso here, namely that once a class 2 reflexion satisfies $|F_c| < F_{\text{lim}}$, if it is given $w = 0$, thereafter in the refinement there is a distinct possibility that it will not continue to satisfy this constraint. It might, therefore, be appropriate, particularly when there is a large number of reflexions involved, to use the weighting scheme of equation (3) for class 2 reflexions when $|F_c| < F_{\text{lim}}$. They should be omitted from the calculation of errors in parameters.

A more rigorous treatment of non-normal distributions of errors is in progress.

In the final stages of the refinement of n-hexatriacontane, most $|F_c|$ did in fact lie below the limit F_{lim}.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the General Secretary of the International Union of Crystallography (G. Boom, Laboratorium voor Fysische Metaalkunde der Rijksuniversiteit, Universiteitscomplex Paddepoel, Groningen, The Netherlands). Publication of an item in a particular issue cannot be guaranteed unless the draft is received 8 weeks before the date of publication.

Bragg *Festschrift*

In March 1970 the Union journals (Sections A and B of *Acta Crystallographica*, and the *Journal of Applied Crystallography*) will form a *Festschrift* in honour of the eightieth birthday of Professor Sir Lawrence Bragg, F.R.S. Contributions are invited, which may be either strictly scientific or of an informal or biographical nature. Scientific papers should be submitted in the ordinary way to the appropriate Co-editor; other contributions should be submitted to the Editor. In order to allow sufficient time for refereeing and printing the closing date for receipt of contributions is 31 July 1969.

New Co-editors of *Acta Crystallographica*

The Executive Committee of the International Union of Crystallography has approved of the appointment of two new Co-editors of *Acta Crystallographica:* W. C. Hamilton (U.S.A.) and P. J. Wheatley (U.K.). Their addresses are printed on the inner front cover, along with those of the other Co-editors. Dr Wheatley will be active as Co-editor immediately, while Dr Hamilton will take up the actual work on 1 September 1969 as he is now engaged in the preparations for the Eighth Congress of Crystallography which takes place in August this year.

International Union of Crystallography

Prices of publications to customers in the Netherlands

Owing to the recent introduction of the turnover tax in the Netherlands, it is necessary to increase the prices of some Union publications to customers in the Netherlands. The increases apply to the publications handled by A. Oosthoek's Uitgevers Mij N.V. and are: *Structure Reports* Dfl. 5·00 per volume (Dfl. 2·50 for personal subscribers), *Fifty Years of X-ray Diffraction* Dfl. 2·00, and *Symmetry Aspects of M. C. Escher's Periodic Drawings* Dfl. 1·00. The prices of the small incidental publications remain unaltered. *These increases do not apply to orders placed with Messrs Oosthoek from countries outside the Netherlands.*

Safe Use of X-ray Equipment

The following notice has been received from the Commission on Crystallographic Apparatus:

With X-ray equipment, there is continual need to remind oneself of the potential dangers from radiation as well as those associated with high voltage. Use of equipment of this type involves a responsibility for the safety and health of one's colleagues and any other person who approaches the apparatus as well as for one's own protection. The dan-