award of a Senior Research Fellowship. He would also like to thank Professor Dr O. W. Flörke, Institut für Mineralogie, Ruhr Universität, F.R.G. for providing facilities for part of the work and the Heinrich-Hertz-Stiftung, for financial support.

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Acta Cryst. (1975). A**31**, 245

Statistics of Derived Intensities

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(*Received* 12 *August* 1974; *accepted* 1 *November* 1974)

The variance of diffractometer-collected diffraction intensities is discussed in terms of instrumental instability and uncertainties in the parameter used to bring the intensities to a common scale. It is shown that the inconsistent and/or divergent behavior of the reflections used as standards contributes in a major way to the uncertainty in the scaling parameter and can often account for the largest portion of the variance in excess of the Poisson contribution for reflections with large intensities.

Introduction

Intensity data from counter techniques are expected on theoretical grounds to follow the Poisson distribution. They should therefore have variances equal to the total counts in each measurement. It has been found, however, that the variances of the measurements within a crystallographic data set are larger than the measured counts. At least three observations exist which support this statement:

(1) Multiple measurements of intense reflections in a data set agree with each other less well than predicted, if considerable time elapses between measurements;

(2) At convergence of least-squares refinement the observed and calculated data for the more intense reflections disagree more strongly than one might predict using Poisson statistics, and;

(3) the standard error of fit determined from least-squares refinement is usually greater than 1·0 if Poisson statistics variances are used.

Observation 3 is, of course, model dependent while observation 2 is at least potentially model dependent. The largest discrepancies, however, are commonly found among the more intense data. This distribution would seem to have sources other than the model. Many workers (*e.g.*, Busing & Levy, 1957; Peterson & Levy, 1957; Stout & Jensen, 1968, p. 456) have included in the calculation of the variances, S^2, of the intensity data, a term proportional to the square of total counts, T, or net counts, I:

$$e.g., \; S^2(I)=T+P^2I^2. \tag{1}$$

The factor P has been termed the 'instability constant' by some workers and the 'ignorance factor' (Corfield, Doedens & Ibers, 1967) by others. It is common practice to use 0·01 to 0·05 for the value of P. The larger values are usually chosen for crystals which show marked decomposition.

Several rationalizations have been advanced for the use of equation (1):

(1) It reduces the weights used for intense reflections in least-squares refinement (but any factor which is an

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increasing function of intensity would have a similar effect);

(2) It 'accounts for uncorrected effects' such as absorption (Peterson & Levy, 1957; McGinnety, Doedens & Ibers, 1967) (but there is no guarantee that these will affect predominantly the intense reflections, and, of course, no weighting scheme can compensate for any systematic error such as absorption) and;

(3) It can be used to reduce the standard error of fit to 1·0 (Corfield *et al.*, 1967) (but there are an infinity of functions which would have this effect).

Three justifications for the form of (1) can be advanced, if the total counts are an underestimation of the variance:

(1) The P^2I^2 term is the correct form for the contribution to the variance due to instrumental instability* (Busing & Levy, 1957; Peterson & Levy, 1957).

(2) The P^2I^2 term is the correct form for some neglected contribution or contributions to the variance, or;

(3) The P^2I^2 term is the second term in a Taylor series approximation to the variance.

It will be demonstrated below that uncertainties in the scaling parameter used to put a data set on a single scale contribute a term to the variance which, like the instrumental instability term, involves the square of the net intensity. In many cases these two terms when added together account for the commonly used magnitudes of P.

I. The instability constant

The multiple measurements of standard reflections throughout the time span of data collection provide a convenient way of estimating the instability constant, P.

The measurements of the intensities, J_i, of standard i at various times during the irradiation of a crystal may be used to estimate a function or composite function, f_i, which approximates J_i as a function of time. This function yields an estimate of the intensity at time zero, J_i^0, and a scaling function, $k_i \equiv J_i^0/f_i$. The observed scatter in the J_i about the functions f_i are now used to estimate P. The total χ^2 is calculated for each standard with the assumption that the functions f_i give the correct values of the intensities, and the contribution from Poisson statistics is subtracted to leave the residual variance. Of course, for this procedure to be valid it is necessary that the number of observations J_i be large compared to the number of degrees of freedom lost in determining f_i.

From equation (1), for all N observations of the ith standard, we predict the total squared scatter expected for the observed intensities about any trend:

$$\sum_{j=1}^{N} S_{ij}^2 = \sum_{j=1}^{N} T_{ij} + P_i^2 \sum_{j=1}^{N} J_{ij}^2 \, .$$

The observed scatter is given by

$$\chi_i^2 = \sum_{j=1}^{N} (J_{ij} - f_{ij})^2 .$$

Assuming now that (1) is the correct form for the sample variance $S^2(I)$

$$\chi_i^2 = \sum_j T_{ij} + P_i^2 \sum_j J_{ij}^2$$

or

$$P_i^2 = \frac{\chi_i^2 - \sum_j T_{ij}}{\sum_j J_{ij}^2} \, . \tag{2}$$

The values of the P_i will have components due to any fluctuations in I which arise in the experimental chain: source, crystal, detector. In addition, the P_i contain any differences due to discrepancies between the fitting function f_i and the parent function. For stable crystals the P_i tend to be characteristic of the diffractometer. At the University of Washington the values are usually in the range $P_i = 0{\cdot}004$ to $0{\cdot}008$ (card-controlled Picker diffractometer).

II. Uncertainty of the scaling parameter

In general, there are different f_i for each of the i standard reflections leading to different scaling functions k_i. In the absence of other information (the usual case), the best approximation to the correct scaling parameter for a general reflection in the data set is an appropriate average of the f_i evaluated at the time the general reflection was collected (*e.g.*, see McGinnety, Doedens & Ibers, 1967; Stout & Jensen, 1968, p. 194; Ibers, 1969). Although the failure of the f_i to agree may be highly systematic (the intensities of the standard reflections frequently change according to different functions), it seems reasonable to accept this lack of agreement as a measure of the uncertainty of the overall scaling factor at some particular time. Restated in a statistical jargon: the variance of the measured standard reflections, taken as a group, is our best estimate of the behavior of all the data.

If the assumption just stated is valid, the contribution of the several standard reflections, considered as a group, to the variance in the intensity data may now be calculated. Taking K to be some average function representing the population k_i, then for any particular reflection, collected at time t, we have

$$I^0 = K I_{\text{obs}} \tag{3}$$

and

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* The I^2 dependence of the instrumental instability factor has been observed experimentally. It can be justified in terms of the expectation that variations in instrumental parameters will be normally distributed about their mean values (central-limit theorem) and give rise to constant relative errors in the observed intensities, *i.e.* $\langle \sigma(I)/I \rangle = \text{constant}$.

$$\sigma^2(I^0)=I^{02}\left\{\left(\frac{\sigma(K)}{K}\right)^2+\left(\frac{\sigma(I_{\text{obs}})}{I_{\text{obs}}}\right)^2\right\}, \tag{4}$$

where K is evaluated at time t and covariance terms are neglected.

We examine now the sources of error. $K(t)$ contains J_i^0 and $f_i(t)$. The J_i^0 and $f_i(t)$ are calculated quantities and their uncertainties arise from the errors in the J_i and from the procedure for determining the function f_i. The J_i and I_{obs} are measured quantities and their errors derive from counting statistics and experimental instabilities.

The term $\sigma(I_{\text{obs}})$ may be estimated from equation (1). The sample variance of the k_i at time t may be calculated by

$$S^2(K)=\frac{1}{M-1}\left[\sum_i^M (K-k_i)^2\right] \tag{5}$$

where i runs over the M scaling functions determined from the M standards.

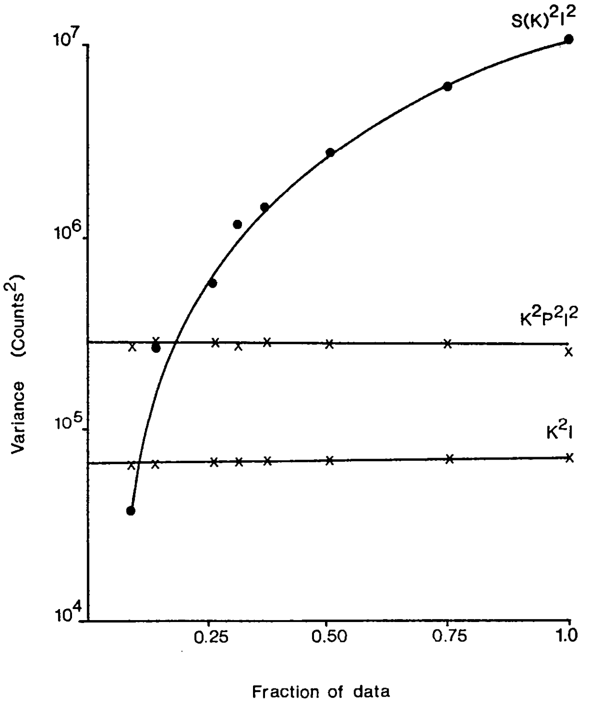

Fig. 1. Contributions to the variance of I^0.

III. Variance of the scaled intensity, I^0

Equation (4) may be rewritten as

$$\begin{aligned}\sigma^2(I^0)&=I_{\text{obs}}^2\sigma^2(K)+K^2\sigma^2(I_{\text{obs}})\\&=I_{\text{obs}}^2S^2(K)+K^2T+K^2P^2I_{\text{obs}}^2\end{aligned} \tag{6}$$

by substituting sample variance S^2 for the population variance σ^2. The last term of equation (6) is widely used (with inflated P values) in estimating the standard deviations of intensity data, but the first seems never to have been mentioned. Although there are occasional reports of standard deviations of scaling parameters (Ibers, 1969; Ammon, Watts & Stewart, 1970), we have found no reports of the propagation of these uncertainties into the estimated standard deviations of the reflections' intensities.

In the case of a highly stable crystal, the major sources of error are statistical errors in the measurements and the instrumental variation. One would expect a single function to fit *all* of the J_i simultaneously. For the case of an unstable crystal, however, the divergence in the f_i and hence in the k_i usually becomes increasingly important as the total irradiation time increases. It should be noted that crystals which do not show an overall decrease in intensity often exhibit some divergence of the various functions f_i. Even though the scaling parameter K may remain 1·0, it will still have non-zero and increasing variance. The general result is that a value of I^0 determined from measurements made near the end of a data set is more uncertain than if it were determined from measurements made near the beginning.

While for a moderately intense reflection the first term of (6) is initially small compared to the last term,

Table 1. *Fractional variance computed as a function of time for a medium intense reflection*

[Standard 2 Fe(TIM) (CO) (CH_3CN) $(PF_6)_2$]

Contributions to the variance are graphed in Fig. 1.

		Poisson		Instability		Scale factor		Total	
Fraction of data	t relative units	$\frac{K^2I_{\text{obs}}}{(I^0)^2}$ $\times 10^5$	$\frac{K\sqrt{I_{\text{obs}}}}{I^0}$ $\times 10^2$	$\frac{K^2P^2I_{\text{obs}}^2}{(I^0)^2}$ $\times 10^5$	$\frac{KPI_{\text{obs}}}{I^0}$ $\times 10^2$	$\frac{S^2I^2}{(I^0)^2}$ $\times 10^5$	$\frac{SI_{\text{obs}}}{I^0}$ $\times 10^2$	$\frac{S^2(I^0)}{(I^0)^2}$ $\times 10^5$	$\frac{S(I^0)}{I^0}$ $\times 10^2$
0	0	1·478	0·3845	6·400	0·8000	0	0	7·878	0·8876
0·09	1016	1·529	0·3910	6·400	0·8000	0·882	0·2970	8·811	0·9387
0·14	1516	1·526	0·3906	6·400	0·8000	6·188	0·7866	14·114	1·188
0·26	2809	1·554	0·3942	6·400	0·8000	13·57	1·165	21·52	1·467
0·31	3361	1·571	0·3964	6·400	0·8000	26·93	1·641	34·90	1·868
0·37	3975	1·554	0·3942	6·400	0·8000	33·31	1·825	41·26	2·031
0·50	5410	1·603	0·4003	6·400	0·8000	65·00	2·550	73·00	2·702
0·75	8135	1·631	0·4039	6·400	0·8000	141·2	3·758	149·2	3·863
1·00	10820	1·777	0·4216	6·400	0·8000	274·6	5·240	282·8	5·318

it can become one to two orders of magnitude larger than the last by the end of data collection (see Table 1).

Results

Table 2 shows the results of analyzing data collected from two crystals at the University of Washington. The multiple observations of each standard were fit by a linear function. Crystal 1 showed some decomposition with divergent behavior of the standards. The first data set for crystal 2 has large P and $S(K)$ resulting from a defective capacitor in the power supply of the counting circuitry. The capacitor was replaced and the second data set from crystal 2 was collected. Crystal 2 is judged to be a very stable crystal. In addition, the repaired diffractometer showed excellent instrumental stability.

Table 2. *Linear fit of counts as a function of time for standard reflections*: $C=A+Bt$

Crystal 1 Fe(TIM) (CO) (CH_3CN) $(PF_6)_2$
$t_{\max}=10821$ (233 h exposure) $\bar{P}=0·008$

Standard	Observations	A	B	k_t max
1	63	136820	−2·21	1·21
2	63	66920	−0·84	1·16
3	63	128669	−1·63	1·16
4	63	310420	−2·23	1·08
5	63	206117	−2·25	1·13
6	63	2147639	−26·33	1·15
7	63	569719	−4·03	1·08
8	63	1404810	−16·53	1·15
9	62	49103	−0·05	1·01

$K_{\max}=1·126$ $S(K_{\max})=0·059$ $S(K_{\max})/PK_{\max}=6·55$

Crystal 2 Fe(TIM) $(CH_3CN)_2$ $(PF_6)_2$ Data set 1
$t_{\max}=3630$ (81 h exposure) $\bar{P}=0·024$

Standard	Observations	A	B	k_t max
1	18	37185	0·41	0·96
2	21	14299	0·21	0·95
3	21	16506	−0·04	1·01
4	20	16695	−0·00	1·00
5	21	23676	−0·07	1·01
6	20	7046	0·04	0·98
7	21	33393	−0·19	1·02

$K_{\max}=0·990$ $S(K_{\max})=0·027$ $S(K_{\max})/PK_{\max}=1·14$

Crystal 2 Data set 2
$t_{\max}=3807$ (85 h exposure) $\bar{P}=0·001$

Standard	Observations	A	B	k_t max
1	18	16015	0·04	0·991
2	20	55237	−0·15	1·010
3	20	114090	−0·52	1·018
4	18	115113	−0·29	1·010
5	19	86721	−0·28	1·012
6	18	41511	−0·08	1·007
7	19	778773	−1·98	1·010
8	20	7642	−0·01	1·005
9	20	1709461	1·14	0·997
10	17	153822	−0·96	1·024
11	17	828454	1·85	0·992
12	19	17376	−0·09	1·020
13	19	17905	−0·12	1·026
14	19	115928	−0·44	1·015
15	19	25230	−0·01	1·002
16	19	34929	−0·17	1·019

$K_{\max}=1·010$ $S(K_{\max})=0·010$ $S(K_{\max})/PK_{\max}=9·90$

The results suggest the following technique for monitoring crystal and instrumental instability:

(1) A rather large number* of standard reflections should be measured several times throughout the period of data collection. These reflections should be a representative sample of the data being collected and thus should exhibit a range of intensities and be distributed throughout the region of reciprocal space spanning the experiment. These measurements then constitute a data base for analyzing the scaling parameter.

(2) A small subset of the total standard set should be measured frequently during the data collection in order to assess the overall status of the experiment. At least one fairly intense reflection should be included in the subset to be used in calculating the experimental instability constant.

Summary

The central theme of this paper is: how can the uncertainties inherent in the collection of X-ray data be assessed? The usual procedure with regard to guessing 'ignorance factors' seems to be yielding a 'good' value. We note that for crystal 1, the sum of $S^2(K)$ and $K^2\bar{P}^2$ is $7·95\times10^{-4}$ when evaluated at completion of half of the data set. This corresponds to an 'inflated' P of 0·028, a value one might take to be reasonable for a crystal which shows some decomposition. The 'ignorance factor' approach, however, completely ignores the time dependence of the uncertainty arising from the necessity of placing the data on a common scale.

The X-ray experiment itself frequently perturbs the crystal significantly and systematically. We emphasize that it is the inconsistent and/or divergent behavior of the standard reflections which contributes in a major way to the uncertainty in the scaling parameter and often accounts for the largest portion of the variance in excess of the Poisson contribution for reflections with large intensities. Furthermore, the time dependence of the scaling factor and its uncertainty becomes an important factor in experimental design. If questions are being asked which largely have their answers in a subset of the data (*e.g.*, questions about bonding electron density†), then it is wise to collect that

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* The IUCr's recommendation (S. C. Abrahams, 1973) of three strong, three medium, and three weak reflections distributed throughout reciprocal space would seem to be the *minimum* number of standard reflections needed.

† Radiation damage may initially manifest itself as an increase in crystal mosaicity. The resulting decrease in extinction would primarily influence strong, low-angle reflections. Thus it would be important in attempting to collect data containing information about bonding electron density, to monitor several strong, low-angle reflections. The pertinent data could then be collected after any initial period of rapid change in extinction. This procedure would lead to lower extinction corrections and a more self-consistent set of data.

subset first. This procedure insures maximum self-consistency within the subset of interest.

Other implications also arise. Suppose that as one monitors the several standard reflections, one finds significantly divergent behavior resulting in increasing $S^2(K)$. What might one choose to do short of mounting a fresh crystal? Perhaps the data can be significantly improved by measuring backgrounds for shorter periods and/or by using faster scan rates. The answers to such questions lie in the intelligent use of standard analysis as a feedback loop in experimental design. It is not hard to imagine in this age of mini-computer-controlled experiments a diffractometer programmed to ask and answer such questions.

The authors wish to thank V. Schomaker and L. H. Jensen for encouragement during the early part of this work. E. C. Lingafelter, G. J. B. Williams and J. P. Glusker read manuscripts, gave support, and offered valuable suggestions and criticism. G. J. B. W. suggested the title and also gave accounts of similar work performed by himself and J. Sygusch. We thank E. C. Lingafelter, H. Warren Smith, and N. J. Rose for the use of their standards. One of us (L.C.A.) wishes to acknowledge the U.S. Atomic Energy Commission under whose auspices some of this work was performed.

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Acta Cryst. (1975). A**31**, 249

The Debye–Waller Factors of the Rubidium and Cesium Halides

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(*Received* 9 *July* 1974; *accepted* 8 *November* 1974)

Computed mean-square displacements and Debye–Waller B_K factors, derived using the deformation dipole model, are reported for the rubidium and cesium halides at 4·2, 80, and 300°K. Experimental X-ray diffraction Debye–Waller factors, obtained at 300°K, are reported for CsCl, CsBr, and CsI. The calculated B_K values are compared with these and other experimental values wherever such data exist. The differences between calculated and measured values at 4·2°K are not large but in three out of four cases lie outside the small experimental uncertainties quoted. At 300°K, on the other hand, the differences tend to be larger, but in about half of the cases are less than the experimental uncertainty.

Introduction

The mean-square displacements of ions in the rubidium halides have been calculated by Govindarajan (1973) using a shell model where 11 to 14 parameters are fitted to the measured phonon dispersion curves. The Debye–Waller factors have not so far been measured for all of these eight crystals. However, Hafemeister, De Pasquali & De Waard (1964) have measured the recoilless fraction f_a for the I^- ion in several alkali halide crystals at 80°K using the Mössbauer effect, and Boyle & Perlow (1966) have made similar measurements at 4·2°K for the Cs^+ ion in the cesium halides. Barnea & Post (1966) have measured B_K values for Cs^+ and Cl^- ions in CsCl. Recently Beaver & Weymouth (Beaver, 1974) have measured B_K values on powder samples of CsCl, CsBr, and CsI at 300°K using X-ray diffraction measurements.

The purpose of this paper is to compare the measured values and computed values that are based on lattice-dynamical models which have fewer parameters, and fit the dispersion curves equally well. Moreover the parameters are determined mainly by fitting to macroscopic data (*e.g.*, static and high-frequency dielectric constants). Thus, although the calculated dispersion curves are mainly theoretical predictions, their agreement with experiment indicates that the models are producing dynamical matrices which are probably good for any phonon wave vector and not merely for those lying along a restricted class of high-symmetry