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Reproducibility of Intensity Measurements by X-ray Diffractometers. A New Assessment of Data from the Single-Crystal Intensity Project of the American Crystallographic Association

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The seven sets of X-ray intensity data for CaF_2 obtained in the ACA project are compared. The data are graded so as to reduce statistical errors in mean values, and deviations from these means are plotted against angle of reflexion and measured intensity. The plots reveal systematic errors depending on both of these variables; this dependence was partly obscured in the ACA analysis. A rank correlation method is used both to confirm the significance of this systematic dependence and also to search for any dominant dependence on unsuspected and unspecified variables; none is found.

The data for the important reflexions 111, 002, 022 are grossly discordant and low-angle reflexions must receive prime attention in any future development of experimental techniques. Further guidance is provided by the results of the present analysis. The deviations for the other reflexions are everywhere large for the device using a fixed crystal and fixed detector, but while they are large at the lower angles for that using an ω-scan without monochromator, they are reasonably small for the other ω-scan and $\omega/2\theta$-scan devices. It is suggested that particular systematic errors are associated with incorrect calibration of attenuator factors, with change of filters and with counting statistics.

Introduction

When a variety of techniques are used to measure a common set of physical quantities there will inevitably be differences between the measurements, and there arises a need to compare them carefully and critically. The aim of such a comparison should be to assess the relative magnitudes of the random and of the various systematic errors and, if possible, to assign these errors to physical causes. The random component provides a measure of the greatest degree of internal consistency currently attainable. Moreover, if the source of any error can be identified then a correction may be made immediately; otherwise there is useful guidance for the future development of the technique. We believe that, with the advent of automated instruments, such comparisons will become increasingly important.

The means of making effective comparisons are largely provided by established statistical procedures and the success of a particular approach can be measured by the extent to which it achieves the above aims. Maslen (1967) has reported a comparison of X-ray intensity data for sodium chloride, but these data originated from diverse sources and the conclusions were thereby limited. More suitable data have recently been published in the report of the American Crystallographic Association (ACA) Single-Crystal Intensity Project (Abrahams, Alexander, Furnas, Hamilton, Ladell, Okaya, Young & Zalkin, 1967). This report contains the only X-ray intensity data of coherent origin which are currently available and provides the opportunity of making a detailed test of the effectiveness of some procedures for comparing data. Thus, in this paper, we present an analysis of the ACA data whereby we extract more information than did the ACA report, about the nature of the errors and their possible association with specific individual techniques.

In the ACA project seven X-ray diffractometers were used to measure the relative intensities of a number of reflections from the same crystal of calcium fluoride. In their analysis of the data, the authors of the ACA report did not carry through the necessary preliminary grading of the data according to internal consistency. They therefore detected only the grossest of the systematic errors and came to weaker conclusions than the data permit. Furthermore, we do not agree with their main conclusion that 'the agreement between the experiments is good'. A glance at the data in Table 1 shows a disturbing spread in the measured intensities ($|F|^2$) of some low angle reflexions; there are differences of up to 50% between experiments whereas an accuracy of better than 2% is considered essential to electron density studies.

Our analysis proceeds in three main stages: In the first stage we grade the data, take account of the fact that the sets are only approximately on the same scale, and calculate the deviation of every measurement from an appropriately chosen mean value. We begin by showing that two sets of data differ significantly from the remaining five. Even within these five, agreement deteriorates for reflexions at both ends of the angular range. Thus, in order to determine mutually consistent scale factors for each of the five sets, we use a concordant subset which includes reflexions from only the middle angular range. Mean values of the intensity of every reflexion are then determined from the five sets of rescaled measures (after rejecting three outlying low angle measures). Finally, these mean values are used

to estimate scale factors for the two remaining sets and deviations are computed for every measurement. The reduction in the statistical error of the estimated mean values which is achieved by this process has enabled us to detect systematic errors which might otherwise have been obscured, and were so in the ACA analysis.

In the second stage, we look for a systematic dependence of the deviations on two specifically named variables. For this purpose the individual deviations are plotted as functions of the angle of reflexion and of the measured intensity. Inspection of these plots by eye provides visible evidence of trends, and of the relative magnitudes of the random and the systematic errors. Finally, in the third stage, we have employed a rank correlation method to examine the possibility that there are other major trends depending on unsuspected and unspecified variables; none is found. In all these ways we have been able to come closer to fulfilling the intentions of the ACA project.

The ACA project

The aims of the ACA project have already been discussed in broad terms. We shall now summarize and comment on some of the more relevant details.

A single crystal of calcium fluoride was ground to a sphere and presented to each of seven experimenters who were asked to measure the relative intensities of all

Table 1. $|F|^2$ *for various experiments on arbitrary scale*
(Uncorrected for extinction)

				Experiment						
h	*k*	*l*	*s*	1	2	3	4	5	6	7
1	1	1	3	314·1*	486·2	578·3	477·0	501·4	519·9	—
0	0	2	4	4·5	5·1	5·5	4·5	4·6	6·5	—
0	2	2	8	663·4*	1040·5	1086·3	1009·4	1035·3	859·9	890·3
1	1	3	11	462·3	465·0	497·7	443·4	465·5	538·9	475·0
2	2	2	12	41·3	43·4	45·3	39·0	38·8	47·0	40·0
0	0	4	16	850·7	852·6	913·0	824·6	842·8	962·4	—
1	3	3	19	423·9	396·8	458·2	389·6	414·9	386·6	413·2
2	2	4	24	719·0	697·8	729·9	701·4	719·7	777·0	713·1
3	3	3	27	362·1	356·5	381·1	351·6	360·0	382·8	364·8
1	1	5	27	376·0	357·0	363·6	363·5	362·3	429·1	370·5
0	4	4	32	679·3	633·9	698·2	649·0	666·0	585·3	653·3
1	3	5	35	330·8	321·1	327·1	324·2	328·5	358·2	—
0	0	6	36	77·7	75·5	79·2	74·6	74·0	89·4	72·4
2	4	4	36	78·6	76·7	79·5	74·9	73·9	74·3	74·9
3	3	5	43	302·1	294·7	278·4	290·7	291·1	321·5	288·2
2	2	6	44	81·2	78·8	76·3	76·1	77·1	89·5	77·6
4	4	4	48	522·8	497·7	483·4	507·4	523·4	510·3	495·1
1	5	5	51	279·5	277·4	269·6	268·1	280·2	245·1	264·9
1	1	7	51	284·3	278·5	260·0	267·2	270·9	296·9	265·3
3	5	5	59	254·7	245·6	240·1	242·7	242·7	232·9	239·8
1	3	7	59	244·5	247·3	235·0	242·5	244·3	255·3	—
0	0	8	64	450·4	425·1	409·9	424·2	423·3	462·8	414·4
3	3	7	67	228·9	225·9	216·0	217·2	218·2	238·3	217·4
4	4	6	68	73·0	69·6	68·8	68·1	68·8	71·6	68·6
0	6	6	72	398·9	372·6	370·8	384·7	379·4	325·8	378·8
2	2	8	72	396·8	376·2	360·9	377·3	380·3	395·7	378·2
5	5	5	75	202·4	194·4	189·9	192·4	193·2	182·2	194·3
2	6	6	76	67·8	67·1	63·6	64·6	62·8	57·4	—
1	1	9	83	187·9	176·8	172·0	179·9	178·2	183·2	181·2
4	6	6	88	315·1	305·4	293·2†	304·2	303·4	263·0	307·0
4	4	8	96	285·8	268·4	256·7	277·7	273·2	249·9	276·5
1	7	7	99	150·6	144·5	137·8	144·0	143·0	114·1	144·8
3	3	9	99	150·5	138·6	137·0	142·4	143·6	132·4	143·4
5	5	7	99	152·5	147·8	141·5	145·8	145·8	129·8	146·9
0	0	10	100	52·0	49·0	47·3	49·4	46·1	—	50·5
3	7	7	107	—	132·0	—	128·8	131·0	—	—
6	6	6	108	45·9	42·1	43·5	43·8	42·4	35·6	43·6
2	2	10	108	46·4	42·6	41·9	44·1	43·4	—	45·5
1	1	11	123	—	98·1	—	105·1	—	—	—
5	7	7	123	—	98·5	—	102·2	—	—	—
0	8	8	128	—	178·1	—	189·4	—	—	—
5	5	9	131	—	85·3	—	91·7	—	—	—
2	8	8	132	—	30·3	—	32·1	—	—	—
4	4	10	132	—	29·0	—	30·2	—	—	—
6	6	8	136	—	149·1	—	171·4	—	—	—

* Possibly in error due to faulty calibration of attenuation factors. See Table 1 of Abrahams *et al.*
† Corrected entry. See Table 6 of Abrahams *et al.*

the reflexions *hkl* within a radius of $\sin\theta/\lambda = 1{\cdot}00$ Å^{-1}, using Mo $K\alpha$ radiation; they were also asked to measure the complete sets {135} and {137}. We repeat in Table 1 the results of these measurements given by the ACA report. In this table and in what follows $s = h^2+k^2+l^2$ and we refer to the data obtained by experimenter 1 simply as **1** and so on. The seven experiments were representative of the most widely used diffractometer methods for measuring integrated intensities and the resulting structure factors. Some of the salient features of these experiments are summarized in Table 2. We also mention that the data **3** and **4** were obtained with equi-inclination instruments and the remainder with 4-circle instruments, but we must refer the reader to the original report for such further information as is available.

Since the same crystal was used, each experimenter made a measure, for each reflexion, of essentially the same physical quantity. Thus, apart from changes in the Lorentz and polarization factors, the project limited itself to testing the reproducibility of intensity measurements as affected by technique and experimenter. The spherical shape of the crystal ensured that equivalent reflexions would have closely similar intensities for any one experimenter and the ACA report states that there were, in fact, no significant differences. However, we have no access to these data since the entries in Table 1 are averages over both equivalent reflexions and any reflexions measured more than once; the numbers of reflexions involved are not stated.

It seems likely, though the report does not explicitly say so, that the crystal was mounted with $[1\bar{1}0]$ along the axis of the goniometer head and that all reflexions except {135} and {137} were measured in the zero layer. Since the geometries of both equi-inclination and 4-circle devices are equivalent for the zero layer, the project did not provide much information concerning systematic differences between these two classes of instrument; a dependence on layer, for example, could be detected only from the measurements of {135} or {137}.

The values reported in Table 1 have been obtained from the raw intensity data after a number of manipulations. They have been averaged, as already mentioned, and have been brought to approximately the same scale. They have not been corrected for either extinction or thermal diffuse scattering. However, they have been modified by Lorentz and polarization factors, and corrected for absorption. It will be assumed later in this paper, when deriving values of measured intensities from the tabulated values of $|F|^2$, that all measurements were made in the zero layer for which the combined Lorentz and polarization factors are:

$$\mathrm{Lp} = (1+\cos^2 2\theta)/(2\sin 2\theta)\,. \qquad (1)$$

Strictly speaking, a slightly different factor should be used for **4**, since the monochromator would have partially polarized the X-ray beam. This difference, here ignored, is unlikely to upset the results of the ensuing analysis.

The ACA report used a fixed-effects analysis of variance technique to analyse the data of Table 1 by grouping them into six levels of angle of reflexion, and four of measured intensity. They found strong evidence for effects depending on angle of reflexion but little or no evidence for effects depending on intensity. These conclusions were the same whether or not they included the reflexions 111, 002 and 022, which were observed to be unexpectedly discordant. They also found that **6** differs significantly from the remainder and that angle dependent effects remain even when **6** is removed from the analysis.

We shall see later that **6** is indeed an outlier. Furthermore, it is apparent both from Fig. 1 of the ACA report and Fig. 1 of the present paper that most of the angle dependent effects which remain when **6** is removed are due to the low angle data in **3**. Indeed, it is not until **3** is also removed that some smaller effects, depending on both intensity and angle, can be revealed in the intercomparison of the remaining data.

Examination of the data

A concordant subset

The first step in our analysis of the data of Table 1 is to find a concordant subset. A reasonable subset turns out to comprise measurements for reflexions in the range $27 \le s \le 108$ from the group **1,2,4,5,7**. This subset was selected by (*a*) rejecting those sets which disagree strongly with the others, (*b*) rejecting those reflexions which appear to be poorly determined and (*c*) retaining a majority of the data.

In the first place, since the seven sets of data must be regarded as being only approximately on the same scale, it is desirable to use a scale-independent test to examine them. A suitable test is the comparison, be-

Table 2. *Partial summary of techniques and of our assessment of the data*

Type of scan	Data set	Miscellaneous	Consistency	Errors
none	**6**	—	very poor	angle
ω-scan	**4**	monochromator	good	—
	3	balanced filters	poor at low θ	angle
	5		fair	intensity and/or
$\omega/2\theta$-scan	**1**	attenuator troubles at low θ	fair	angle
	2	low count rate, poor power supply	fair	statistical
	7	no filter/β filter	fair	angle

tween the sets of data, of the spread in $|F|^2$ for reflexions with the same s; such reflexions are expected on theoretical grounds to have closely similar X-ray intensities and this has been verified experimentally for CaF_2 by Weiss, Witte & Wölfel (1957). It is seen from Table 1 that the separations of these $|F|^2$ are generally several times greater for **6** than for any of the others, thereby suggesting that **6** is anomalous.

Confirmation of the anomalous nature of **6** is provided by the R_{ij}-factors shown in Table 3. These do, however, depend upon scale, since

$$R_{ij}=\frac{\sum_h \left||F_{hi}|/g_i^{\frac{1}{2}}-|F_{hj}|/g_j^{\frac{1}{2}}\right|}{\frac{1}{2}\sum_h (|F_{hi}|/g_i^{\frac{1}{2}}+|F_{hj}|/g_j^{\frac{1}{2}})}, \qquad (2)$$

where i, j are experiment indices and the summation index h extends over all reflexions except 111, 002 and 022 (see later). The inverse scale-factors g_i were calculated by applying the method of Hamilton, Rollett & Sparks (1965) to all the data except the above-mentioned reflexions, with the assumption that $\sigma(|F|^2)\propto |F|^2$. (The matter of suitable weighting is discussed below.) Table 3 shows not only that **6** is anomalous in that the factors R_{6j} are excessively large, but also that **3** is significantly different from the remaining sets, though less so than **6**.

The ACA report includes a comparable calculation of R factors, based on $|F|^2$ rather than $|F|$, but the anomalous natures of **6** and **3** are not as easily seen there due to the large R factors involving **1**. We believe that these large values of R are due to the inclusion in **1** of the data for 111 and 022, data which are reported to be associated with possible calibration errors in attenuation factors. Since the values given by **1** for these reflexions are about 50% lower than the majority of other values it seems fair to treat these values as anomalous and omit them both from the calculation of R and from the concordant subset.

Even for **1**, **2**, **4**, **5** and **7** there remains an appreciable scatter in $|F|^2$ for low-order reflexions. Furthermore, **2** always lies below **4** in the region $s>108$. For these reasons, only data within the range $27\leq s\leq 108$ have been included in the calculation of consistent scale factors for these sets.

Weighting of the data

Having located a concordant subset of data, there remains the question of how to weight them. It is here that one feels the need for data rather more basic than those provided by the ACA report. The vital data are the individual counts, times, details of attenuation and the number of reflexions involved in forming the averaged entries of Table 1. This type of information would have been particularly helpful, too, for our later discussion of some aspects of **2**.

If the same number of observations contributes to each reflexion, if variations of correction factors (such as Lorentz, polarization and absorption factors) are neglected, and if counting statistics dominate the total error variance, then the assumption $\sigma(|F|^2)\propto|F|$ is appropriate for an experiment conducted with fixed counting time and fixed attenuators; the assumption $\sigma(|F|^2)\propto|F|^2$ is appropriate if the attenuator and counting time are adjusted to give a constant total count. Any actual experimental arrangement seems likely to fall between these two extremes.

Lacking information about proper weights, we have carried out all computations for these two weighting schemes; as found by the ACA report, no very significant differences occur. All numerical details in the remainder of this paper are based on the assumption that $\sigma(|F|^2)\propto|F|$. This weighting is not that favoured by the ACA report but it seems to us to give a more realistic weighting to the weakest reflexions than does the alternative (see later). Note that the weights used are the same for all sets.

Means and scale factors for concordant subset

For each reflexion h we introduce a mean structure factor F_h and for each set of observations an inverse scale factor g_i. Then $|F_{hi}|^2-g_i|F_h|^2$ is the deviation of an observation from its estimated value and the method of Hamilton *et al.* determines the $|F_h|^2$ and g_i by minimising the weighted sum of squares

$$S=\sum_h w_h S_h=\sum_h w_h \sum_i (|F_{hi}|^2-g_i|F_h|^2)^2, \qquad (3)$$

where the weighting factor $w_h\propto 1/\sigma^2(|F_h|^2)$ is independent of the index i. For given g_i, the least-squares estimate of $|F_h|^2$ is found, by minimizing S_h, to be the weighted mean value:

$$|F_h|^2=\sum_i g_i|F_{hi}|^2/\sum_i g_i^2, \qquad (4)$$

and the resulting partial residual sum of squares is

$$S_{h\min}=\sum_i (|F_{hi}|^2)^2-(\sum_i g_i|F_{hi}|^2)^2/\sum_i g_i^2. \qquad (5)$$

Table 3. *Interexperiment R-factors based on* $|F|$

(Reflexions 111, 002 and 022 omitted)

	6	3	4	1	2	5	7	Technique
6		0·047	0·050	0·052	0·045	0·049	0·049	Fixed crystal, fixed counter, 4-circle
3	0·047		0·025	0·026	0·024	0·022	0·020	ω-scan, equi-inclination
4	0·050	0·025		0·006	0·014	0·010	0·009	ω-scan, equi-inclination + monochromator
1	0·052	0·026	0·006		0·011	0·011	0·009	$\omega/2\theta$-scan, 4-circle
2	0·045	0·024	0·014	0·011		0·011	0·012	$\omega/2\theta$-scan, 4-circle
5	0·049	0·022	0·010	0·011	0·011		0·009	$\omega/2\theta$-scan, 4-circle
7	0·049	0·020	0·009	0·009	0·012	0·009		$\omega/2\theta$-scan, 4-circle

The estimated standard deviation of $|F_{hi}|^2$, from $g_i|F_h|^2$, is

$$\sigma_h=[S_{h\min}/(n_h-1)]^{1/2}\,, \qquad (6)$$

where n_h is the number of sets which contain data for reflexion h.

The relative values of g_i are determined numerically by steepest descent from an initial set of values ($g_i=1$), holding a suitable g_j equal to 1. Given a set of values of g_i, equation (5) determines $S_{h\min}$ for each h and thus a value $S=\sum_h w_h S_{h\min}$ is obtained which is already minimized with respect to variation of $|F_h|^2$. Selection of a new neighbouring set of g_i gives a new value of S and by suitable iteration S is minimized.

In this way the values of the scale factors g_i for **1**, **2**, **4**, **5** and **7** are determined. At the same time we obtain values of $|F_h|^2$ and σ_h for the range $27\leq s\leq 108$. These values are listed among the entries in Table 4.

Extension to the remaining data

From the same group **1**, **2**, **4**, **5** and **7**, mean values $|F_h|^2$ and standard deviations σ_h for reflexions outside the range $27\leq s\leq 108$ were estimated from relations (4) and (6) using the g values just determined. In this calculation, reflexions 111 and 022 of **1** and 022 of **7** were omitted; the first two data were discussed previously and the third also seems unduly low.

Finally, using the $|F_h|^2$ already determined, scale factors for **3** and **6** were chosen to minimize for $i=3,6$ the sum of squares

Table 4. *Estimated inverse scale factors, mean values and deviations for the data of Table* 1

						1	**2**	**3**	**4**	**5**	**6**	**7**
					Inverse scale factor g_i	1·0000	0·9590	0·9493	0·9593	0·9661	0·9595	0·9586
h	k	l	s	$\|F_h\|^2$	σ_h	Deviations $\|F_{hi}\|^2-g_i\|F_h\|^2$						
1	1	1	3	507·79	10·50	−193·69	−0·75	96·25	−10·15	10·82	32·67	—
0	0	2	4	4·81	0·34	−0·31	0·49	0·93	−0·12	−0·05	1·88	—
0	2	2	8	1069·62	15·84	−406·22	14·78	70·91	−16·73	1·95	−166·41	−135·00
1	1	3	11	477·10	14·25	−14·80	7·48	44·79	−14·30	4·57	81·12	17·67
2	2	2	12	41·81	1·93	−0·51	3·31	5·61	−1·11	−1·59	6·89	−0·07
0	0	4	16	867·58	16·24	−16·88	20·63	89·41	−7·70	4·64	129·96	—
1	3	3	19	420·94	10·25	2·96	−6·86	58·61	−14·22	8·24	−17·29	9·71
2	2	4	24	733·12	10·82	−14·12	−5·24	33·95	−1·91	11·44	73·57	10·36
3	3	3	27	370·57	6·78	−8·47	1·14	29·32	−3·90	2·00	27·24	9·59
1	1	5	27	377·70	5·23	−1·70	−5·20	5·05	1·15	−2·60	66·69	8·45
0	4	4	32	677·61	10·00	1·69	−15·91	54·94	−1·06	11·36	−64·87	3·77
1	3	5	35	335·81	3·95	−5·01	−0·93	8·32	2·04	4·08	35·99	—
0	0	6	36	77·27	1·18	0·43	1·40	5·85	0·47	−0·65	15·26	−1·67
2	4	4	36	78·26	1·21	0·34	1·65	5·21	−0·18	−1·71	−0·79	−0·12
3	3	5	43	302·86	2·53	−0·76	4·27	−9·11	0·15	−1·50	30·90	−2·11
2	2	6	44	80·70	1·09	0·50	1·41	−0·31	−1·32	−0·86	12·07	0·25
4	4	4	48	525·79	9·72	−2·99	−6·52	−15·73	2·99	15·43	5·80	−8·90
1	5	5	51	282·89	6·06	−3·39	6·12	1·06	−3·29	6·91	−26·33	−6·26
1	1	7	51	282·12	5·22	2·18	7·96	−7·81	−3·45	−1·65	26·21	−5·13
3	5	5	59	253·06	2·35	1·64	2·93	−0·13	−0·07	−1·78	−9·91	−2·77
1	3	7	59	251·85	5·45	−7·35	5·78	−4·08	0·89	0·99	13·65	—
0	0	8	64	441·42	6·53	8·98	1·80	−9·14	0·73	−3·15	39·26	−8·73
3	3	7	67	228·70	3·84	0·20	6·59	−1·11	−2·20	−2·75	18·86	−1·82
4	4	6	68	71·89	0·86	1·11	0·66	0·56	−0·86	−0·65	2·63	−0·31
0	6	6	72	395·32	4·77	3·58	−6·50	−4·48	5·45	−2·52	−53·52	−0·14
2	2	8	72	394·16	1·67	2·64	−1·79	−13·28	−0·84	−0·50	17·50	0·37
5	5	5	75	201·68	1·26	0·72	1·00	−1·55	−1·08	−1·64	−11·31	0·98
2	6	6	76	67·53	1·96	0·28	2·35	−0·50	−0·18	−2·44	−7·39	—
1	1	9	83	186·67	2·05	1·23	−2·21	−5·21	0·82	−2·14	4·09	2·27
4	6	6	88	316·95	2·43	−1·85	1·45	−7·69	0·13	−2·81	−41·12	3·18
4	4	8	96	285·28	3·82	0·52	−5·17	−14·12	4·02	−2·41	−23·83	3·04
1	7	7	99	150·10	1·17	0·51	0·56	−4·69	0·01	−2·01	−29·92	0·92
3	3	9	99	148·38	2·21	2·12	−3·69	−3·86	0·05	0·25	−9·97	1·17
5	5	7	99	152·55	1·18	−0·05	1·51	−3·31	−0·55	−1·58	−16·57	0·67
0	0	10	100	51·01	1·86	0·99	0·09	−1·12	0·47	−3·18	—	1·61
3	7	7	107	135·83	1·64	—	1·74	—	−1·51	−0·23	—	—
6	6	6	108	44·98	0·96	0·92	−1·03	0·80	0·65	−1·05	−7·56	0·49
2	2	10	108	45·84	1·16	0·56	−1·36	−1·62	0·12	−0·89	—	1·56
1	1	11	123	105·93	4·92	—	−3·48	—	3·48	—	—	—
5	7	7	123	104·62	2·59	—	−1·83	—	1·83	—	—	—
0	8	8	128	191·58	7·94	—	−5·62	—	5·61	—	—	—
5	5	9	131	92·27	4·50	—	−3·18	—	3·18	—	—	—
2	8	8	132	32·53	1·26	—	−0·89	—	0·89	—	—	—
4	4	10	132	30·86	0·84	—	−0·59	—	0·59	—	—	—
6	6	8	136	167·08	15·73	—	−11·12	—	11·12	—	—	—

$$\sum_h w_h(|F_{hi}|^2-g_i|F_h|^2)^2\ ,\ 27\leq s\leq 108\ ,$$

for variation of g_i alone.

The complete sets of values of g_i, $|F_h|^2$, σ_h and the deviations $|F_{hi}|^2-g_i|F_h|^2$ are collected in Table 4.

Reconsideration of weights and concordant subset

If the weights $w_h(\propto 1/|F_h|^2)$ have been properly chosen, the estimated values of $w_h\sigma_h^2$ should be statistically compatible with a constant value and distributed as χ^2 with four degrees of freedom.

The estimated values of $w_h\sigma_h^2$ for $27\leq s\leq 108$ vary over a range of 25 to 1. While this large ratio is not by itself statistically significant (Owen, 1962, p. 101), the overall distribution of values has a just significant excess of both large and small values over the numbers expected for a χ^2 distribution. The alternative weighting scheme, $w_h\propto 1/|F_h|^4$, suffers similarly and, moreover, it appears to give undue weight to the weak reflexions.

As previously noted, the subsequent conclusions of this paper are not affected by which weighting scheme is used and, in the absence of further information relevant to the weighting, we have not thought it worth while to consider any more elaborate scheme.

The concordance of **1**, **2**, **4**, **5** and **7** for $27\leq s\leq 108$ can be judged by comparing the variances of the weighted residuals,

$$\sigma_i^2=\sum_h w_h(|F_{hi}|^2-g_i|F_h|^2)^2/(n_i-1) \qquad (7)$$

for each experiment; n_i being the number of reflexions contributing to the summation, and (n_i-1) the number of degrees of freedom. The relevant numbers are given in the first line of Table 5. Naive use of standard statistical tests* shows that the variance of 1·43 for **4** is significantly lower than the next greatest value 3·49 for **1** and that the ratio of the greatest value 7·01 for **2** to 3·49 for **1** is not significant. Thus, we could conclude that while **1**, **2**, **5** and **7** have about the same experimental errors, **4** has a significantly lower error. Although this may be true, the next line of Table 5 shows that with the inclusion of additional low angle reflexions **4** is not markedly superior to the others, and we have chosen not to give **4** any additional weight.

The entries in Table 5 show clearly that the subset chosen as concordant comprises over half the data and, moreover, has the property that any increase in size, either from adding reflexions or from increasing the number of sets, would lead to a sharp increase in the overall group variance. We feel therefore that the scale factors are well determined and that we have found an adequate basis for comparing all the data.

* In applying the various statistical tests referred to above (*e.g.* the variance-ratio or *F*-test) we have made the usual assumptions that the errors in individual measurements are independent normal variates with zero mean and constant variance. Thus, the deviations $|F_{hi}|^2-g_i|F_h|^2$ for the *i*th set are independent normal variates with constant variance but, because the mean $|F_h|^2$ involves values from both the *i*th and the *j*th sets, the deviations for the *j*th set are correlated with those for the *i*th set and the correlation coefficient is $-\frac{1}{4}$. It follows that, although the sum of squares of the deviations for the *i*th set has a χ^2 distribution, it is not independent of the sum of squares for the *j*th set of deviations, but has a correlation coefficient of $\frac{1}{16}$. We feel that this correlation is sufficiently small not to influence unduly the significance limits obtained from the usual *F*-distribution tables. In any case, with the possible exception of the tests for homogeneity of the concordant subset, there is always an ample safety margin and the subsequent conclusions are unlikely to be changed.

Table 5. *Variances of the weighted residuals for each experiment and various groups of reflexions*

The numbers of contributing reflexions are shown in brackets. For **4**, **1**, **5**, **7** and **2** the italicized entries differ significantly from the remainder. (See Owen, pp. 82, 87, 101.)

Range of s	**4**	**1**	**5**	**7**	**2**	**3**	**6**
27–108	*1·43* (30)	3·49 (29)	5·48 (30)	5·54 (26)	7·01 (30)	41·11 (29)	282·41 (27)
11–108	4·23 (35)	6·26 (34)	6·08 (35)	8·32 (30)	9·02 (35)	108·01 (34)	374·13 (32)
3–108	5·21 (38)	*677·86* (37)	6·22 (38)	*70·04* (31)	9·02 (38)	164·21 (37)	432·47 (35)
3–136	7·22 (45)	—	—	—	10·42 (45)	—	—

Table 6. *Measured intensities in increasing order of magnitude*

h k l	I_{meas}	h k l	I_{meas}	h k l	I_{meas}	h k l	I_{meas}
4 4 10	6·11	2 2 6	26·22	3 3 7	55·74	1 3 5	127·40
0 0 2	6·36	0 0 6	28·77	4 4 8	56·67	4 4 4	160·95
2 8 8	6·44	2 4 4	29·14	4 6 6	65·53	3 3 3	166·45
6 6 6	8·66	3 3 9	29·15	1 3 7	66·89	1 1 5	169·65
2 2 10	8·83	1 7 7	29·49	3 5 5	67·21	1 3 3	235·22
0 0 10	9·99	5 5 7	29·97	1 1 7	82·83	0 4 4	272·74
2 6 6	15·18	2 2 2	30·53	1 5 5	83·05	2 2 4	354·86
4 4 6	17·35	6 6 8	33·58	2 2 8	91·67	1 1 3	365·88
5 5 9	18·19	0 8 8	37·43	0 6 6	91·94	0 0 4	536·94
5 7 7	20·23	1 1 9	39·83	3 3 5	99·95	1 1 1	779·34
1 1 11	20·48	5 5 5	45·72	0 0 8	110·92	0 2 2	977·43
3 7 7	26·20						

Table 5 also highlights the anomalous character of the measurements of 111 and 022 for **1** and of 022 for **7**. These data alone account for almost the whole of the catastrophic increase in variance seen in the third line of Table 5. We therefore feel justified in omitting these data in forming the means in Table 4. Furthermore, the high values of the variances for **3** and the even higher values for **6** confirm the earlier conclusions, based on the R factors in Table 3, that both **3** and **6** are of qualitatively different accuracies from the remaining sets.

Discussion of deviations

General remarks

We now turn to the following question. Are the deviations in Table 4 due entirely to random errors or do they suggest a systematic dependence on some as yet unknown variables? We shall find that there are systematic errors which depend mainly on either angle of reflexion or measured intensity.

In so far as we can guess at possible variables it is appropriate to plot the deviations against these variables, and to look at least for any major dependence by visual inspection. Moreover, we believe that it is desirable in the first place to plot the deviations individually, rather than as values averaged over some small subset, so as not to lose the possibility of detecting some unsuspected dependence; the eye is well known for its tendency to average scattered points over small subsets.

Below we consider explicitly a possible dependence on angle of reflexion, measured intensity* and type of reflexion.† Furthermore, we have applied a rank correlation method, outlined in the next section, to detect any dominant but unsuspected dependence (on, for example, the l index) and also as a check on the dependence deduced from the angle and intensity plots.

The analysis in the ACA report considers only the possibility of a dependence on angle of reflexion and measured intensity. The data are grouped (averaged over subsets) and, using a model, a separation of the deviations is made into angle and intensity dependent components. However, because of the strong correlation between angle and intensity of a reflexion, such a separation is not well-defined. (See discussion of **1** below.) For this reason, we have not attempted such a separation.

The large range of the deviations, resulting from the 160:1 range of measured intensities, has made it necessary to plot fractional deviations in order to separate all the points adequately from one another. This method of plotting has two advantages. Firstly, the fractional deviations, like the actual deviations and the means $|F_h|$ are substantially independent of the weighting system used and, secondly, fractional values are not affected by the introduction of arbitrary multiplicative factors such as corrections for absorption or the Lorentz and polarization factors. On the other hand, there is the minor disadvantage that the statistical significance of a fractional deviation depends upon the weight of the corresponding observation; it is constant only for the weighting $w \propto 1/|F|^4$, while for the weighting $w \propto 1/|F|^2$ used here a given value is more significant for a strong reflexion than for a weak one. This disadvantage is to some extent alleviated by the coding of the points in Figs. 1 and 2 according to the type of reflexion involved.

The fractional deviations, $(|F_{hi}|^2 - g_i|F_h|^2)/|F_h|^2$, are expressed as percentages and plotted for sets 1–7 in Fig. 1 as functions of $s = h^2+k^2+l^2$ and in Fig. 2 as functions of measured intensity. The values of $100\sigma_h/|F_h|^2$ are also plotted. The identification of the reflexion corresponding to a particular point in Fig. 2 is readily made with the aid of the ordered list of measured intensities in Table 6.

Main features and interpretation of deviations

Inspection of Figs. 1 and 2 leads us to make the following observations about the data. These findings also appear in condensed form in Table 2. They should be regarded as tentative rather than conclusive, as we are dealing with deviations from mean values rather than from true values. Note that the scales are such that the deviations for **3** are twice as great and those for **6**, four times as great as they may immediately appear to be.

Set 1: There appear to be systematic trends with both angle and intensity. Although the deviation of 002 is anomalous with respect to the trend with intensity, its magnitude is less than one standard deviation.

The following argument shows that both trends can be accounted for by an intensity dependence alone. Consider the two groups of reflexions 111, 002, 022 and 113, 004, 224, which account almost entirely for the apparent trend with angle. We know that the deviation of 002 may not be significant and, as mentioned previously, 111 and 022 are possibly subject to errors in the calibration of attenuation factors. The deviations for reflexions in the first group may therefore be assigned to an intensity effect and removed from both plots. Removal of the second group of reflexions leaves almost no trend with angle while the trend with intensity remains substantially unaffected. Thus, it seems to us possible that the trend is mainly dependent on intensity.

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* Apart from a constant factor which we neglect, the measured intensity is equal to Lp $|F|^2/A^*$, where Lp is given by equation (1) and A^* is an absorption correction factor. Numerical values for A^* were obtained by interpolation in Table 5.3.6B of Vol II of *International Tables for X-ray Crystallography* (1962), using the value $\mu R = 0{\cdot}725$. Values of measured intensity for all reflexions are given in Table 6. These values fit only approximately into the four levels indicated in Table 2 of the ACA report.

† The reflexions from CaF_2 may be divided into three types according to the value of $h+k+l$: (*i*) strong, with $h+k+l = 4n$ (Ca+2F), (*ii*) medium, with $h+k+l = 4n \pm 1$ (Ca) and (*iii*) weak, with $h+k+l = 4n+2$ (Ca−2F).

Set 2: The data for $s > 108$ (enclosed in squares in Fig. 2) arise from **2** and **4** alone and are discussed separately below. Disregarding these data, it is evident both from Figs. 1 and 2 and from Table 5 that the scatter of deviations is larger for **2** than for the other members, **1**, **4**, **5** and **7**, of the concordant group. The scatter is largest for the weak reflexions and there are no significant trends with either angle or intensity.

A scatter which is largest for the weak reflexions suggests that an appreciable part of the overall scatter may be due to counting statistics arising from a fixed time of count for each reflexion. We note that, of all the sets, **2** had the lowest maximum count rate and also the poorest stability of power supply. In the absence of more detailed information, these sources of random variation seem to be the most obvious possible causes for the larger variability of this set.

We shall now discuss the data for $s > 108$ arising from **2** and **4**. Fig. 1 shows that the deviations are all negative for **2**, and so all positive for **4**. They are so systematic and of such magnitude as to make it quite clear that **2** and **4** differ significantly for these reflexions and that at least one of these sets is in error. Comparison of the deviations for $s > 108$ with others in the same set shows that the former are more in conformity with expectations for **2** than for **4**; the scatter for **2** is greater than that for **4**. It is tempting to ascribe to **2** an angle dependent error at the larger angles.

Set 3: The deviations show a strong dependence on angle but there is little evidence of any simple dependence on intensity. The dependence on angle divides fairly sharply into two regions at $s \simeq 36$. For $s > 36$ there is a small negative slope and, bearing in mind the different scales, the scatter of the deviations is no more than that for **2**. By contrast, for the low angle reflexions with $s < 36$, the scatter is large and the deviations, which are all positive, increase rapidly as s decreases.

The data **3** were obtained with balanced filters and an ω-scan, a method which has often been criticized (Burbank, 1964; Arndt & Willis, 1966, p. 267). In this method a fixed detector aperture would imply the acceptance of an increasing band of wavelengths as the angle of reflexion decreases. Thus, one might expect the intensities of low angle reflexions to be overestimated, as is, in fact observed. Could the sharp break at $s \simeq 36$ indicate a change of experimental technique, or could it indicate the point where the band width determined by the aperture size is first matched with that of the balanced filters?

Set 4: The data lie remarkably close to the set of mean values; only five deviations exceed σ_h and none exceeds $1{\cdot}5\sigma_h$. The deviations are consistently negative for $s < 27$ and there is no evidence up to $s = 108$ of any further trend with either angle or intensity. The deviations for $s > 108$ have already been discussed and seem more likely to be associated with **2** than with **4**.

The consistently negative deviations for $s < 27$ differ significantly from zero when judged in terms of the scatter of the deviations for **4** alone but are not significant when judged in terms of the scatter of the deviations for the concordant group as a whole. The deviations for **2**, **5** and **7** are predominantly positive in this range and the negative deviations for **4** could simply be a consequence of the zero sum constraint on deviations of an individual reflexion when summed over the concordant group **1**, **2**, **4**, **5** and **7**. On the other hand, they could be due to angle setting difficulties which are known to beset a linear diffractometer at low angles (Arndt & Willis, 1966, p. 93).

We note that both **3** and **4** were obtained with an ω-scan but that a monochromator was used for **4** in contrast to the balanced filter technique for **3**. The clear superiority of **4** over **3** would seem amply to justify the use of a monochromator with an ω-scan.

Set 5: The deviations show a trend with intensity and possibly a weaker trend with angle. In Fig. 1 the weak reflexions lie uniformly below the remainder across the whole angular range, but the same downward trend with increase of angle seems to be present in both groups taken separately. Since the scatter in the deviations is greater in the angular plot than in the intensity plot it would seem that a dependence on intensity dominates.

A trend with intensity suggests that the principal source of error may lie in the determination of attenuation factors. Inasmuch as the deviations are mainly negative for measured intensities below 128 and mainly positive thereafter, there is some slight evidence for a change of attenuator at this intensity and an associated error in the attenuation factor.

Set 6: The deviations are very large and show a marked dependence on angle but no obvious dependence on intensity.

The large deviations provide striking practical confirmation of the known hazards associated with a fixed-crystal, fixed-counter technique (Arndt & Willis, 1966, p. 265).

Set 7: The data for this set are incomplete. In particular, the important low angle reflexions 111, 002 and 004 are missing, while the first low angle reflexion measured, 022, is anomalously low. With the exception of this reflexion, the deviations fall very close to a V-like curve when plotted against s, and there appears to be also a parabolic dependence on intensity. Careful consideration of this mutual dependence shows it to be what would be expected from the correlation between angle and intensity. Since the angle dependence has the lower scatter we believe this to be the principal variable.

The ACA report tells us that a change was made from no filter to a β filter. Such a change is normally made at some specific angle. If this angle corresponded to $s \simeq 50$ we might begin to understand the intriguing V-like dependence of the deviations in terms of changes in technique associated with the change of filters. Unfortunately, such details of technique are unavailable to us.

Values of σ_h: These values give an overall estimate of the errors of the group **1, 2, 4, 5** and **7**. They lie generally below 2% of $|F_h|^2$ and have an average value of about 1%. The most notable exceptions occur for weak reflexions and for the region $s > 108$, which we henceforth disregard for lack of sufficient data. The σ_h values of the low angle, high intensity reflexions also tend to be high, in spite of the removal of anomalous data.

The values of σ_h for the weak reflexions tend to be high for all angles of reflexion so that the rise seems to be an intensity effect. It is probably due to counting statistics and provides some support for our preference for the weights $w \propto 1/|F|^2$. For the low angle, high intensity reflexions, the preceding discussion of the individual sets shows that the principal cause of error varies from one technique to another.

An application of rank correlation

We have applied a rank correlation method (Kendall, 1955) and have convinced ourselves, firstly, that the dependence on angle and on intensity already found

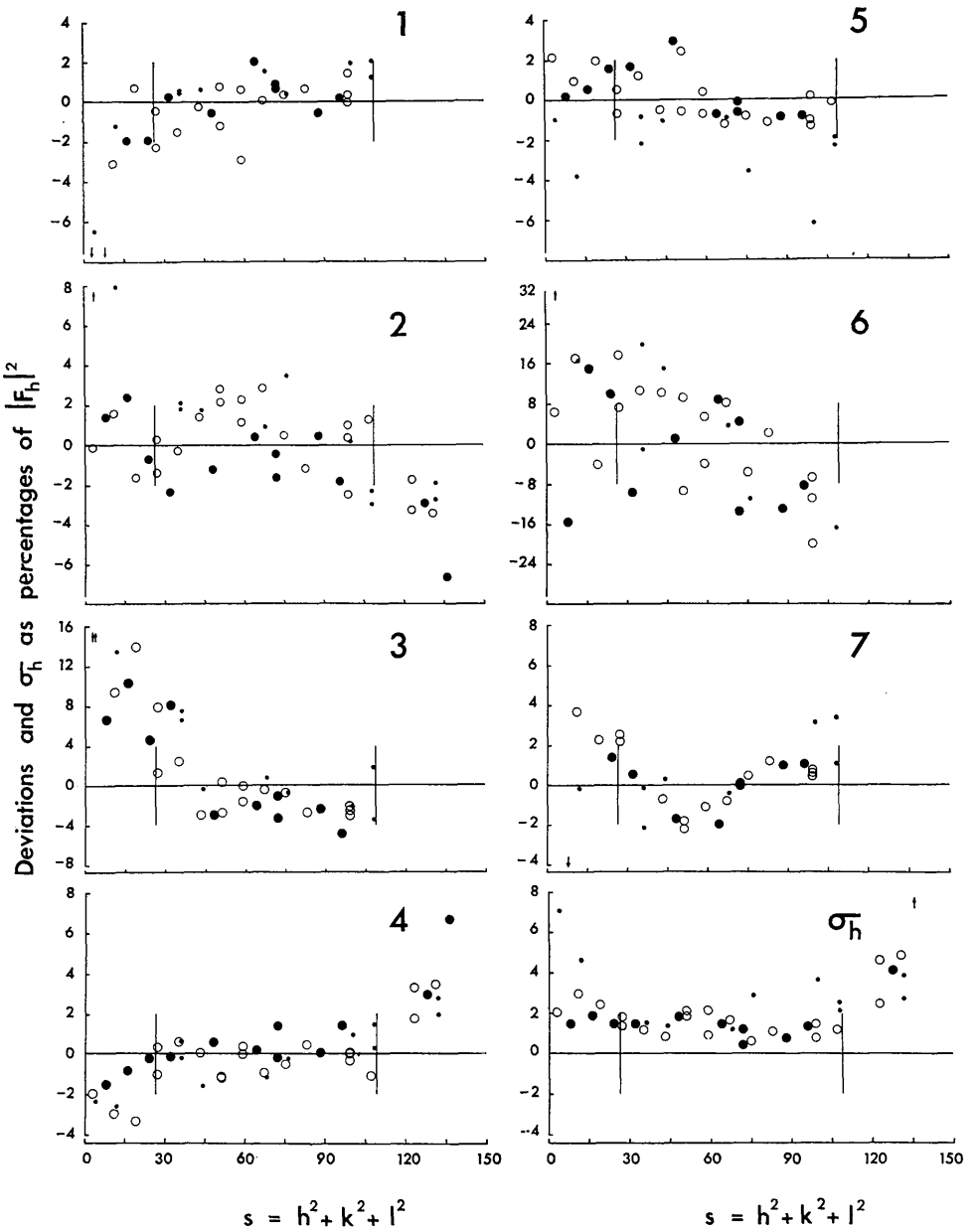

Fig. 1. Percentage deviations of individual sets of data *versus* s, with $100\sigma_h/|F_h^2|$ shown for comparison. The range $27 \leq s \leq 108$ is indicated by vertical lines. Note the exceptional scales for **3** and **6**. Symbols: ●, $h+k+l=4n$; ○, $h+k+l=4n\pm1$; •, $h+k+l=4n\pm2$; ⇅, ordinate exceeds 4 scale units.

is statistically significant and, secondly, that there is no dependence of an unsuspected nature which dominates these. The following brief outline of the way in which we have adapted a rank correlation method to the needs of the present analysis may be of interest to some; others may wish to pass directly to the conclusions.

We start with a subset of reflexions for each of which we know both the values of the deviations obtained in a given experiment, and the values of another variable, for example, the angle of reflexion. The reflexions are then ranked twice: in order of decreasing algebraic value of the deviations and in order of the other variable (angle). These two rankings are compared.

If the deviations are independent of angle (the other variable) the two rankings are expected to be completely different. On the other hand, if there is a strictly monotonic increasing/decreasing relationship between them, the two rankings will be exactly the same/opposite. Furthermore, it is at least intuitively clear that, as the existence of a relationship becomes less certain, the agreement between the rankings will become less

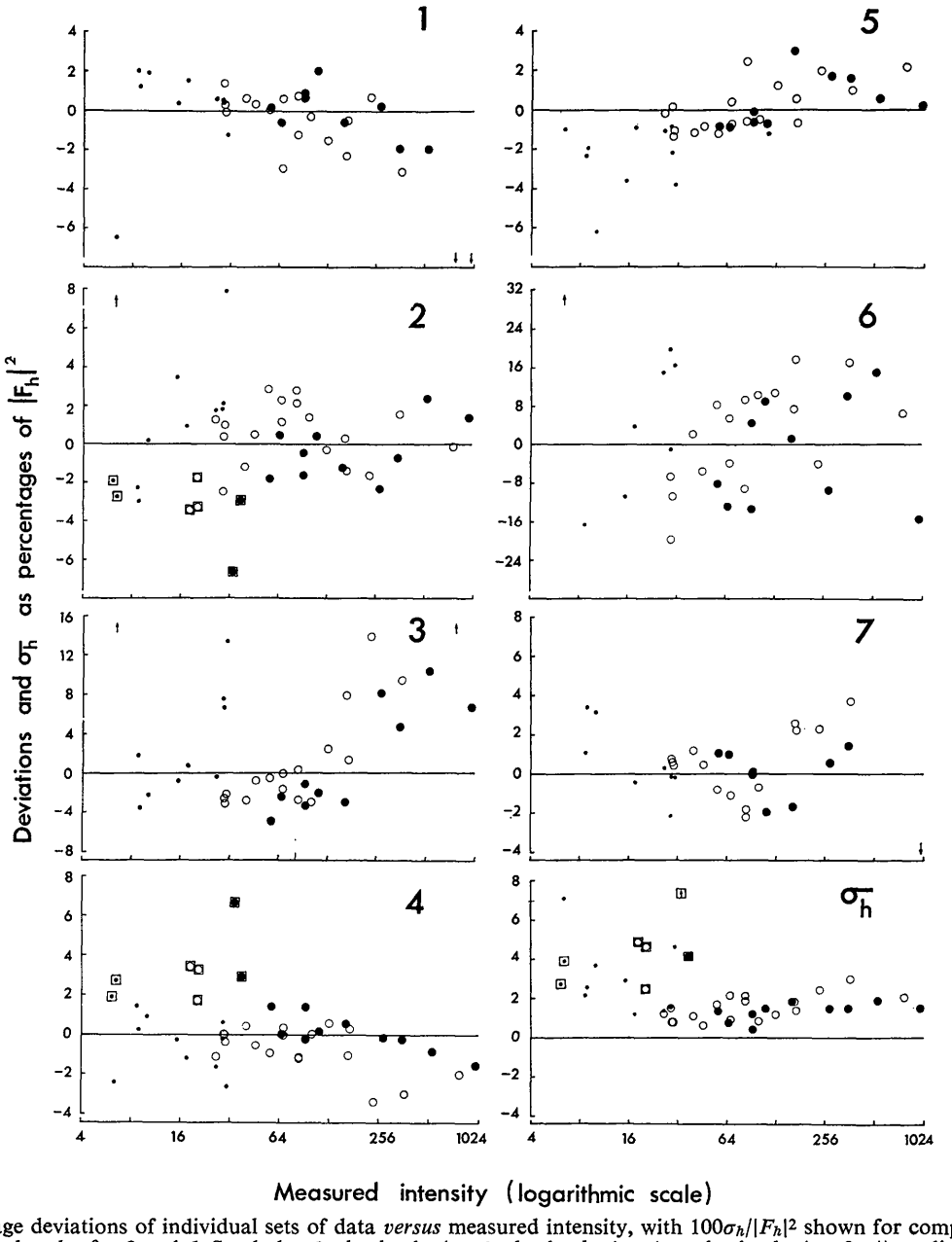

Fig. 2. Percentage deviations of individual sets of data *versus* measured intensity, with $100\sigma_h/|F_h|^2$ shown for comparison. Note the exceptional scales for 3 and 6. Symbols: ●, $h+k+l=4n$; ○, $h+k+l=4n\pm1$; •, $h+k+l=4n\pm2$; ↑↓, ordinate exceeds 4 scale units; □, $s>108$.

pronounced. It is also clear that when the relationship is strictly monotonic the identity of the rankings remains, irrespective of the detailed nature of the relationship. More generally, a given pair of rankings will remain substantially unchanged for even quite large changes in the magnitude of the functional dependence. This insensitivity to the precise nature of the functional relationship is one of the main advantages of rank correlation methods.

Two rankings are compared by counting the least number Q of interchanges required to transform either ranking into the other. Then, Kendall's rank correlation coefficient is given by

$$\tau = 1 - 2Q/[\tfrac{1}{2}n(n-1)] ,$$

where n is the number of reflexions in the subset being ranked. If the two rankings are identical, $Q=0$ and $\tau=+1$; if they are exactly opposite, Q takes its greatest value $\frac{1}{2}n(n-1)$ and $\tau=-1$; in all other cases τ lies between -1 and $+1$. When the two rankings are independent and due solely to chance, τ has, for $n>10$, a normal distribution with zero mean and variance $2(2n+5)/9n(n-1)$. This fact is the basis on which we have tested for significance a possible dependence on either angle or intensity.

If a set of deviations depends strongly on an unknown variable, the rankings of the reflexions ordered by their deviations will be approximately the same as their rankings when ordered by the unknown variable. Again, if the deviations for each of two experiments depend strongly on some common but unknown variable, then there will be a strong correlation between the two rankings of the reflexions when ordered by the two sets of deviations; each of these rankings approximates to the ranking ordered by the common unknown variable. In both these situations we can try to guess the variable in question by inspection of the rankings, though this is not always successful. The importance of the second situation is that we have here the basis for testing for a dependence on a common variable without the need to specify its nature.

We have examined all possible pairs of experiments in this way. The only pairs showing signs of a significant dependence on a common variable are **3–6**, **3–1**, **1–4** and **2–4**. The last pair, **2–4**, is discussed in the next paragraph. On the basis of the angle- or intensity-dependent trends discussed above we might expect to find significant rank correlations for the pairs **3–6**, **3–1** and **1–4**, and also for the pairs **6–1** and **1–5**. A non-significant result for the last two pairs is not surprising in view of the large scatter in **6** and the ambiguity in the assignment of the deviations of **1** and **5** to either an angle or an intensity effect.

The tests of significance for pairs within the group **1**, **2**, **4**, **5** and **7** are not straightforward because the deviations are deviations from mean values and so are negatively correlated. One of us (Mackenzie) has constructed tables of the relevant significance levels. We believe that the unexpected significant result for the pair **2–4** arises from the disparity between the scatters of **2** and **4**; such a disparity leads to a more negative correlation between the deviations than was assumed in making the significance test.

Conclusions

We have used a variety of statistical methods to detect systematic errors in the ACA data and have attempted to associate these with particular experimental techniques. We hope that this will be a useful guide to those directly concerned with intensity measurements of the highest accuracy. These associations are of necessity very tentative and incomplete, owing mainly to lack of vital information. We cannot stress too strongly how important it is to know exact details of such apparently pedestrian matters as attenuation, counting statistics and at what point any changes were made in equipment parameters.

We can summarize our main conclusions, in decreasing order of confidence, as follows:

1. The data **6** and that part of **3** with $s<36$ differ substantially from the remaining data. With the exception of the low angle reflexions 111, 002 and 022 there is agreement between the sets comprising the remaining data to within $\pm 5\%$ in the measured intensity. (See Figs. 1 and 2.) The lack of agreement in the measurements of the above low angle reflexions amounts to a factor of almost 2 and is most unsatisfactory.

2. The majority of experiments suffer from systematic errors which depend on angle of reflexion and/or measured intensity. We can find no evidence for any other systematic dependence.

3. These systematic errors arise from either the techniques, the experimenters or both. In the absence of information to the contrary we have, in our discussion of the deviations, assigned the errors to the various techniques. Briefly, we find as follows:

(i) The fixed-crystal, fixed-detector technique (**6**) is currently unsuitable for measurements of high accuracy.
(ii) With ω-scan there is a clear need for using a monochromator (**4**) and not balanced filters (**3**). Balanced filters in conjunction with an $\omega/2\theta$-scan seems to be satisfactory (**5**).
(iii) All of the $\omega/2\theta$-scan techniques (**1**,**2**,**5**,**7**) are in close agreement but are afflicted to some extent by inadequate attenuator calibration or correction for filter characteristics.

4. Non-systematic errors due to counting statistics and/or power supply instabilities were suggested in only one case (**2**). However, once the grosser systematic errors have been removed or corrected, it may well be that these fluctuation errors will determine the accuracy.

Finally, we reiterate that the quantities referred to both here and in the ACA report as $|F|^2$ are uncorrected for extinction. Unlike the Lorentz and polarization factors and the correction for absorption, the correction for extinction is not calculable since it is a function of the unknown degree of perfection of the particular crystal being measured. Comparison of the mean values of $|F|^2$ in Table 4 with the data of Togawa (1964) and of Weiss *et al.* shows that the extinction correction for the strongest reflexions is a factor of about 5. For those contemplating an accuracy of $\pm 5\%$ in $|F|^2$ this is indeed a sobering thought.

We are greatly indebted to our colleagues Dr A. McL. Mathieson and Dr B. Dawson for advice on all aspects of this paper, particularly those relating to experimental techniques. We are also indebted both to them and to Dr D. A. Wright for helpful criticism of the manuscript. We wish to thank Miss A. G. Doig, Dr G. A. Watterson and Mr R. Birtwistle for advice on statistical matters.

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Mean Square Vibration Displacements and Atomic Scattering Factors of Aluminum Nitride Ions

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Absolute values of the squares of the structure amplitudes of AlN were measured with monochromatic Cu $K\alpha$ radiation in the temperature interval 85–670°K in order to determine the mean square vibration displacements and atomic scattering factors of Al and N ions. From the F^2 data, the parameter U_o/c controlling the separation of Al and N ions along the c axis was determined as $0{\cdot}386 \pm 0{\cdot}001$ compared with 0·375 for the case of the ideal structure ($c/a = 1{\cdot}633$) and 0·380 for the case of equality of all the nearest interatomic distances (at $c/a = 1{\cdot}600$). Temperature studies have shown that in AlN anisotropy of mean square vibration displacements ($\overline{U^2}$) occurs. Thus, $\overline{U^2_{xy}} = (0{\cdot}30 \pm 0{\cdot}02)\ 10^{-2}$Å^2, $\overline{U^2_z} = (0{\cdot}65 \pm 0{\cdot}03)10^{-2}$ Å^2 for Al ion and $\overline{U^2_{xy}} = (0{\cdot}52 \pm 0{\cdot}02)10^{-2}$ Å^2, $\overline{U^2_z} = (1{\cdot}00 \pm 0{\cdot}03)10^{-2}$ Å^2 for N ion at room temperature. The coefficient of linear expansion (α) is also anisotropic. In the temperature range 298–670°K $\alpha_z = (3{\cdot}0 \pm 0{\cdot}2)10^{-6}$ deg^{-1} and $\alpha_{xy} = (3{\cdot}8 \pm 0{\cdot}2)10^{-6}$ deg^{-1}. The values of F^2_{exp} at absolute zero are given and compared with F^2_{theor}.

The intensity of X-ray diffraction spectra of AlN has been measured in the temperature interval 85–670°K with the purpose of determining the mean square vibration displacements and atomic scattering factors of Al and N ions. Monocrystal aluminum nitride was prepared in the form of 'whiskers' by the method of gas transport reaction with ammonia. Transparent single crystals ground in the jasper mortar were used for X-ray investigation. The transparency of the selected single crystals (whiskers) of AlN was indicative of the nearness of their composition to the stoichiometric one.

The investigations were carried out on flat polycrystal samples with particle sizes 2–3μ in a vacuum chamber. The total intensity of the X-ray primary beam was compared with the integrated intensities of reflexions. Intensities of X-ray diffraction spectra of aluminum nitride were measured with the use of monochromatic Cu $K\alpha$ radiation and a scintillation counter with discriminator. Monochromatization of the radiation was realized by means of a bent single crystal of germanium. The measurements were made by determining the pulse amount at counting rate for point-by-point displacement of the counter.