HIRSHFELD: On the tail end of the curve shown, the difference between the total Hartree–Fock and core contributions is small; that is, one might conclude that the valence electrons are not contributing much – yet there seems to be a significant discrepancy in that region between calculated and experimental values for carbon black. Do you interpret this as due to a significant effect core electrons?

WEISS: Not at the present time. The difference could still be due to valence electrons. The reason is that since this is essentially a measurement of momentum density, it gives the probability of having an electron of a certain momentum and you can determine the kinetic energy. You can integrate what you think is the valence electron contribution, that is, everything above the four-electron contribution and get the total kinetic energy which is some sort of measure of the energy in the bond. We could not, however, rule out the possibility that there was still some valence electron contribution. We have found a few cases where we consider we could rub out this possibility and where the core electrons have indicated an alteration from the free atom state.

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Accuracies of Experimental Structure Factor Values

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A survey of the present status of the error problem concerning the experimental structure factor values (*F*-values) is given, with special reference to the fluctuation, or the reproducibility, of original data obtained by various methods under different experimental conditions. It is pointed out that in most methods the reproducibility of *F*-values approaches the range of 1% ~0·5% in favourable cases; the absolute accuracy is lower than this in all but a few examples.

Introduction

Experimental determination of accurate values of the crystal structure factors, or, in short, the *F*-values, becomes increasingly important not only for traditional crystal structure determinations but also for X-ray crystallography as a whole in relation to problems in solid state physics. This paper gives a survey of the present status of the error problem concerning experimental *F*-values. However, too detailed considerations of this sort of problem are not only difficult but will not be fruitful in view of the involved nature of the errors in general. Therefore, discussions in what follows are concerned only with restricted aspects of the subject.

Table 1. *Methods for determination of F-values*

A. X-ray methods:
  (1) Intensity measurements
    (*a*) Single crystals.
      (i) Kinematical formula, with correction for extinctions.
      (ii) Dynamical formula, for perfect crystals.
    (*b*) Powders. Kinematical formula.
  (2) Reflexion-profile method. Dynamical formula, for perfect crystals.
  (3) Pendellösung-fringe method. Dynamical formula, for perfect crystals.

B. Electron diffraction methods:
  (1) Intensity measurement
  (2) Dynamical-interaction method (Kikuchi-line method).

Table 1 lists the experimental methods available for obtaining accurate *F*-values and the principle of each method.

Before discussing individual problems, the so-called error in *F*-values must be distinguished as being of two kinds. The first is the fluctuation in the original data due to differences in specimens, series of measurements, methods, researchers, laboratories, *etc.* They may be of either statistical or systematic nature. The second one is the error which is introduced by the processing of the original data. For instance, in the powder method we have to take account of various quantities and effects, such as Debye–Waller factors, dispersion terms, the correction of thermal diffuse scattering, and of extinctions, the effect of porosity and surface roughness, *etc.* These two kinds of error cannot always be separated from each other; in particular, those due to Debye–Waller factors influence the data presented in Tables 5–7 and in Figs. 5 and 6. However, the absolute accuracy of the final data will receive little discussion and in the following sections we shall be concerned mainly with the first kind of error, namely with the fluctuation, or in other words, with the reproducibility of the original data. Where the experimental errors have a Gaussian distribution the 'fluctuation' or 'reproducibility' is measured by the standard deviation. However, in general, the error distribution is not strictly Gaussian.

Pendellösung-fringe method

The Pendellösung method (Kato & Lang, 1959) has high merit because of its firm theoretical basis in the dynamical theory, and its experimental method is essentially simple. Therefore, if this method is applied under ideal conditions, a high accuracy, better than 0·5%, may readily be expected. However, this is not always feasible and, in reality, there are considerable fluctuations in experimental data, mainly due to difficulties in controlling the wedge shape, and to lattice distortions within the crystals. Table 2 shows the fluctuations in the experiments of Kato and his group on silicon crystals (Hattori, Kuriyama & Kato, 1965). As seen here the *F*-values obtained scatter over the range of about 1–1·5%. If the measurements are repeated several times under conditions as independent as possible, say five times, then we may expect a typical accuracy of about 0·5 to 0·7% in this case.

Table 2. *Pendellösung method on* Si (*Kato et.al*)

Condition	Fluctuation (ε_s)
Different portions in a specimen	0·8–1·0%
Different specimens	1·0–2·0%
Different wavelengths	1·0–1·5%
Different series of measurements	1·0–1·2%

$$\varepsilon=\frac{\varepsilon_s}{\sqrt{m}}\sim 0{\cdot}5\%\text{–}0{\cdot}7\%\ (m=5)$$

Powder method. Statistical error in photon counting

A disadvantage of the Pendellösung method at present is that it can be applied to only a few kinds of crystals which are very perfect. On the other hand in the powder method, which has a wider applicability, there are numerous sources of error, such as those due to preferred orientation, state of packing, determination of the background level, error in the primary X-ray intensity, and, in particular, the statistical fluctuation in the photon counting, and also the stability of the measuring system including that of the X-ray source and of the detecting system. Of these, the statistical fluctuation in the photon counting is unavoidable in any intensity measurement. In practice, there is a limit to the countable number of the photons in a single measurement of the integrated intensity of Debye line. Besides, there is a statistical error in the background level which is to be subtracted from the total count.

In order to consider these circumstances we replace a diffraction peak by a rectangle as shown in Fig. 1. The total count J measured by scanning a counter over an angular range AB for a time interval t is given by:

$$J=(I_h+I_B)t\pm\Delta_1$$
$$\Delta_1=\sqrt{(I_h+I_B)t}\,. \tag{1}$$

The background intensity is usually determined independently by measuring the total count b, by setting the counter at a position, say A, for a time interval, say, t again. The value of b is given by

$$b=I_Bt\pm\Delta_2$$
$$\Delta_2=\sqrt{I_Bt}\,. \tag{2}$$

The accuracy ε_s of the integrated intensity $J_h=J-b$ for the h-reflexion per cent is therefore given by

$$\varepsilon_s(\%)=100\frac{\sqrt{\Delta_1^2+\Delta_2^2}}{I_ht}=\frac{100}{\sqrt{I_ht}}\left\{1+2\frac{I_B}{I_h}\right\}^{\frac{1}{2}} \tag{3}$$

or

$$\varepsilon_s(\%)=\varepsilon_h\{1+2r\}^{\frac{1}{2}},\text{ where }\varepsilon_h=\frac{100}{\sqrt{I_ht}}\,,\quad r=\frac{I_B}{I_h}\,. \tag{4}$$

For strong reflexions, the value of I_ht in a single measurement may be ten to twenty thousand or more, and the value of the ratio r may be $\frac{1}{5}$ or less, whereas for weak ones the value of I_ht may be only two to three thousand, or even less, and the value of r may be 1 to 2 or even more. Thus, the accuracy which is limited by the statistical error will be in the range of about 1% for strong reflexions to about 7% for weak ones.

In the above, the instrumental error ε_i, which includes that due to the stability of X-ray source, is not taken into account. In an absolute intensity measurement, there is also the statistical error concerning the primary X-ray intensity ε_p. Thus, the accuracy in the case of the absolute intensity measurement is given by

$$\varepsilon_A^I=(\varepsilon_s^2+\varepsilon_p^2+2\varepsilon_i^2)^{\frac{1}{2}}, \tag{5}$$

and that for the relative measurement by

$$\varepsilon_R^I=(\varepsilon_s^2+\varepsilon_i^2)^{\frac{1}{2}}\,. \tag{6}$$

The statistical error ε_p may be assumed to be about 1%. Although it is, in general, very difficult to assess the instrumental error ε_i, we assume it tentatively to be 2% by taking account of various complicated factors involved. Then, we obtain

$$\varepsilon_A^I\sim 3-8\%\,,\quad \varepsilon_R^I\sim 2-7\%\,.$$

The numerical values adopted in the above estimation are somewhat arbitrary. However, according to the experience in the author's laboratory, the fluctuation or the reproducibility is in fact found to be contained approximately within these ranges.

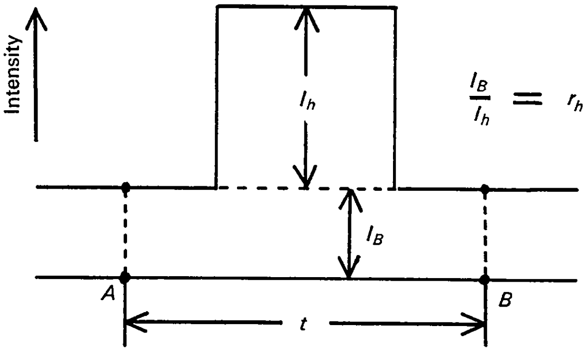

Fig. 1. Diagrammatic representation of relationship between measured intensity and other variables.

If the measurements are repeated m times, the fluctuation with respect to the F-value finally obtained may be given by

$$\varepsilon_A^F = \tfrac{1}{2}\frac{\varepsilon_A^I}{\sqrt{m}}\,. \tag{7}$$

If $m=5$, we have

$\varepsilon_A^F \sim 0{\cdot}7\,\%$ (strong reflexions) $-$ 2 % (weak reflexions)
$\varepsilon_R^F \sim 0{\cdot}5\,\%$ (strong reflexions) $-$ 2 % (weak reflexions) .

The fluctuation will naturally increase a little or sometimes appreciably by the difference in specimens, measuring instruments, laboratories, *etc.* What we can expect from the above considerations, however, is that the reproducibility of F-values in the powder method can reach the range between 0·5 to 1 %, under the most favourable conditions.

As shown above, the accuracy of F-values by the intensity method is limited by the statistical errors, especially for weak reflexions. Of course, this error may be reduced by the use of a strong X-ray source, in particular for powders whose reflexion lines are generally weak. For the same reason, the measurement on single crystals is much more favourable because the X-ray reflexions are much stronger, and, moreover, the background level is generally very low. In reality, however, the maximum counting rate of photons is practically limited by the linearity range of the counting system. Without an extension of this linearity range, the reproducibility of about 0·5 % in F for strong reflexions will not be improved appreciably.

Intensity measurements on single crystals

For the reasons already mentioned, it can be expected that the reproducibility of the F values in the measurement on single crystals may reach the range 0·5 to to 1 % for weak as well as strong reflexions.

For perfect single crystals, we can use the formula of the dynamical theory which is most reliable. In the study on silicon perfect crystals made by DeMarco & Weiss (1965), a general agreement with theoretical values and other experimental data was obtained, although the deviations of their data from those of Kato and his group, (Hattori, Kuriyama & Kato, 1965) obtained by the Pendellösung method, were of a similar order of magnitude to the deviations of other data obtained by the powder method, as shown in Table 3. There are also measurements on perfect copper crystals by Jennings, Chipman & DeMarco (1964), and by others (Nicklow, Sherril & Young, 1965; Baldwin, Young & Merlini, 1967). So far, however, accurate intensity measurements on perfect crystals are still only a few. Since this method is one of the most fundamental means for the determination of accurate F-values, it is very important to make more effort along this direction in future.

When this method is used for single crystals which are less perfect, there is the problem of extinction. Recently, Zachariasen (1967, 1968) has developed an improved theory of secondary extinction. In fact, a data analysis for quartz crystals made by Yamamoto, Homma & Kato (1968) showed that a reduction of F values by the extinction effect amounting to 10 % or more can be corrected to an accuracy of the order of about 2 %. It is admirable and even surprising that the new theory of secondary extinction can reach this extent of accuracy. One cannot, however, hope for a further increase in accuracy by this method for reflexions subject to strong extinction, because of the more or less phenomenological nature of the theory of extinction.

The barrier of 0·5 % accuracy

One of the efforts towards the accurate X-ray intensity measurement has been related to a study of the so-called solid state effect, in particular that in metals. Theoretical calculations showed that this effect on F values is very small. Table 4 shows the results of the calculation on Cu and Fe (Wakoh & Yamashita, 1966;

Table 3. *f-values* for* Si (20 °C)

	Kato *et al.*(1) (Pendel.)	Wölfel *et al.*(2) (Powder)	Hosoya *et al.*(3) (Powder)	DeMarco *et al.*(4) (Perfect single)
111	10·91	10·75	11·04	10·71
220	8·51	8·48	8·50	8·47
311	7·71	7·80	7·73	7·77
400	6·95	7·02	6·85	7·27
331	6·82	6·94	6·93	6·93
422	6·13	6·34	6·23	6·27
333	5·79	5·93	5·79	5·90
511	5·75			5·95
440	5·34	5·39	5·33	5·39
531	5·13	5·11	5·01	
	$\langle\lvert\Delta\rvert\rangle$	1·8 %	1·0 %	1·9 %

* Corrected for dispersion.
(1) Ag $K\alpha$ and Mo $K\alpha$, $\Delta f' \sim 0{\cdot}07$.
(2) Mo $K\alpha$, $\Delta f'$ (?). (Göttlicher & Wölfel, 1959).
(3) Unpublished data. Cu $K\alpha$, $\Delta f' = 0{\cdot}23$ (Cromer). (Hosoya & Yamagishi, 1964).
(4) Mo $K\alpha$, $\Delta f' = 0{\cdot}07$ (Weiss). (DeMarco & Weiss, 1965; Weiss, 1966).

1968). As seen in the Table, the magnitude of the reduction which may be expected compared with the free-atom value is of the order of 1 or 2%, or less. Thus, in order to investigate the solid state effect experimentally, it is necessary to ensure an accuracy in *F*-values of at least 0·5%.

Whether an accuracy of 0·5% in experimental *F*-values has already been attained is still not very certain in any method at present, even in better examples. Table 5 shows *F*-values for magnesium oxide by the powder method which were obtained quite independently in two laboratories in Japan (Togawa, 1965; Uno, unpublished). Togawa's values are the original data obtained by the method of absolute measurement with Cu *Kα* while Uno's somewhat earlier values were averaged using Cu*Kα*, Cr*Kα* and Fe*Kα*, making an allowance for scaling factors and dispersion terms. It is, however, noteworthy that many of the measurements agree to within 0·5%, except for less important discrepancies for weak reflexions. As discussed by Hosoya (1969) from a slightly different viewpoint, the agreement of these data with those of Burley (1965) and of Raccah & Arnott (1967) is also essentially good. Therefore, it seems that a reproducibility better than 1%, or even very nearly 0·5%, can be insisted on for most of the strong reflexions in the case of magnesium oxide.

As another example showing a reproducibility of the order of 0·5% or less, the elaborate measurement for rare gases performed by Chipman & Jennings (1963) should be mentioned.

Table 6 shows some recent results for Fe by the powder method using carbonyl iron (Paakkari &

Table 4. *Theoretical f-values for copper and iron atoms*

Cu *f*	111	200	220	311	222	400	331	420
Free Atom*	22·14	20·75	16·76	14·74	14·19	12·39	11·39	11·11
Metal**	21·72	20·46	16·63	14·64	14·10	12·34	11·35	11·07
Δ (%)	−1·7	−1·4	−0·8	−0·7	−0·7	−0·4	−0·4	−0·4

Fe *f*	110	200	211	220	310	222	321	400
Free Atom*	18·51	15·27	13·13	11·61	10·49			
Metal**	18·34	15·12	12·99	11·48	10·36	9·59	8·96	8·43
Δ (%)	−1·0	−0·9	−1·2	−1·3	−1·0			

* Freeman & Watson (1961).
** Wakoh & Yamashita (1968).

Table 5. F_{hkl}* *for* MgO (20°C) Cu *Kα*

	111	200	220	311	222	400	331	420	422
Togawa (1965)	11·60	54·16	42·24	12·76	34·88	29·92	10·24	26·28	23·16
Uno† (1963–1967)	11·55	54·70	42·25	12·99	34·73	29·07	9·92	26·07	23·10
Δ (%)	+0·5	−1·0	∼0	−2·0	+0·5	+3	+3	+0·8	+0·3
Theory‡	10·91	54·51	42·31	12·95	34·95	29·83	10·35	26·15	23·41

* Including dispersion.
† Unpublished data. $\Delta f'_{\text{theo}}(\text{Mg})=0{\cdot}15$ (Cromer).
‡ Using Yamashita-Tokonami's *f*-values for oxygen atom (Tokonami, 1965). $B_{\text{Mg}}=0{\cdot}24$ Å^2, $B_{\text{O}}=0{\cdot}19$ Å^2.

Table 6. Fe *f*

		110	200	211	220	310
1	Hosoya & Fukamachi* (1968*a*)	18·44	15·12	13·17	11·58	10·34
2	Paakkari & Suortti (1967)	18·19	15·19	13·01	11·60	10·47
	(2)–(1) (%)	−1·2	+0·2	−1·2	+0·1	+1·3
3	Paakkari & Suortti* (1968) corrected	18·50	15·27	13·17	11·61	10·49
	(3)–(1) (%)	0·3	1·0	0·0	0·3	1·5
4	Theory Freeman–Watson	18·51	15·27	13·13	11·61	10·49
	Theory Wakoh & Yamashita* (1968)	18·34	15·12	12·99	11·48	10·36

* Unpublished data.

Suortti, 1967, 1968; Hosoya & Fukamachi, 1968). They are related directly to the problem of the solid state effect. The comparison of these data suggests that the reproducibility of data obtained at different places is almost within 1 %, and also strongly suggests that the reduction exceeding 2 % from the free-atom values does not exist. [See also the measurements on nickel shown in Fig. 5(*b*).]

Under these circumstances, it will be of great value if an independent method is available to give check points for conventional methods. In this respect, the dynamical-interaction method of electron diffraction [*B*(2) in Table 1] developed by Watanabe & Uyeda (Watanabe, Uyeda & Kogiso, 1968, Watanabe, Uyeda & Fukuhara, 1968) is very important. The reproducibility of the data in this method is fairly good because of the essentially simple experimental procedure using a zero method. As they have discussed, the error in *f*-values obtained was estimated to be about 0·5 %. At present, the number of these investigations is still small. In Table 7 results by this method on Fe and Al are compared with theoretical values and also with data by other methods. It is remarkable that the experimental values of *f* for 110 of iron and 111 of aluminum (Watanabe, Uyeda & Fukuhara, 1968) show reductions of about 1 % from the free-atom values, and agree fairly well with Wakoh & Yamashita's (1968) calculations based on the band theory of solid metals. At the same time, this comparison will give some idea as to the reliability of other data.

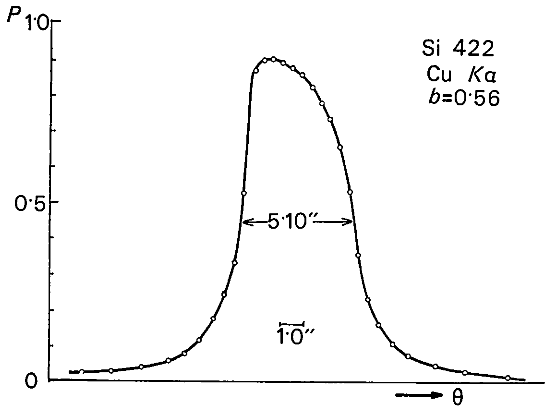

Fig. 2. Reflexion intensity curve for 422 of Si, using two asymmetry cut crystals as a monochromator. The *b*-factor (the asymmetry factor (Kohra & Kikuta, 1968) concerns that for the sample (the third) crystal. Ordinate: ratio of the X-ray flux of reflected beam to that of incident beam.

Reflexion-profile method

In what follows the reflexion-profile method [*A*(2) in Table 1] is reviewed. This method consists of comparing the reflexion curve of X-rays from a perfect crystal with the relevant theoretical one. The reflexion curve obtained by the usual double crystal spectrometer gives a convolution function of the intrinsic reflexion curve; the intrinsic curve is that reflexion curve which would be obtained with ideally parallel and monochromatic X-rays. Comparison of experimental and theoretical curves may be made more accurately with an intrinsic curve than with the relevant convoluted one.

Very recently, it has become possible to obtain a reflexion curve which reproduces the intrinsic one very closely, owing to a technical advance of producing extremely parallel X-ray beams by the use of X-ray reflexions on two or three asymmetrically cut crystals (Kohra & Kikuta, 1968). They observed the 422 reflexion with Cu *Kα*, for which the reflected X-rays are almost perfectly polarized because the relevant Bragg angle is 44°. The angular divergence of the X-ray beam used was about 0·01″. Figs. 2 and 3 (Kikuta & Kohra, 1968) show the profiles of experimental and theoretical curves for the 422-reflexion from silicon crystals. The profiles of these experimental curves show features

Table 7. *f*(110) *for* Fe

f(110) for Fe

Theory		Experiment			
		E.D.	Powder Mo *Kα*, $\Delta f'=0·35$		
free atom	metal	W–U (1968)	Pa–Su (1967)	Ho–Fu* (1968*a*)	B–Ch–DeM (1961)
18·51	18·34	18·34 ± 0·11	18·19 ± 0·20 (18·50)	18·44 ± 0·15	17·63 ± 0·20

* Unpublished data.

f(111) for Al

Theory		Experiment			
		E.D.	Powder Mo *Kα*, $\Delta f'=0·35$		Single
free atom	metal	W–U (1968)	Bensch *et al.* (1955)	B–Ch–DeM (1961)	DeM (1967)
8·95	–	8·87 ± 0·05	8·55	8·63 ± 0·14	8·69

W–U: Watanabe & Uyeda, Pa–Su: Paakkari & Suortti, Ho–Fu: Hosoya & Fukamachi (Yamagishi), B–Ch–DeM: Batterman, Chipman & DeMarco, DeM: DeMarco, Bensch *et al.*: Bensch, Witte & Wölfel (1955).

which are typical of the intrinsic curve. The determination of the *F* value is feasible by finding out the best fit between experimental and theoretical curves. The *f*-value obtained is shown in Table 8. Because of its rather laborious experimental technique at the present stage, the accuracy of this method for a single measurement seems to correspond to a fluctuation of about 3–4% at the moment.

Table 8. *f-value* Si 422 (20°C)

Profile-method	Pendel-method
Kikuta–Kohra	Hattori *et al.*
(1968) (Cu Kα)	(1965) (Mo Kα)
5·95 (1%)	6·12 (1%)

(Corrected for dispersion [Cromer]).

Although the reflexion-profile method is still not well established as a general procedure for the determination of accurate *F*-values, it is probable that this method will also be able to supply valuable check points for other methods in the near future. Of course, the use of convoluted reflexion curves is also promising for the same purpose.

Concluding remark

So far, the accuracy of each method has been discussed mainly with respect to the fluctuation in the original data. It is interesting to compare the various methods as shown schematically in Fig. 4. Here each measurement is assumed to have been repeated five times. The breadth of a strip shows the applicability of each method. However, it is to be emphasized that the ranges indicated here are the accuracies which are the goals that may be expected to be reached in measurements of reasonable quality in each method at the present stage, but do not mean that those accuracies have already been established in every case. Furthermore, errors of the second kind are not taken into account.

The second kind of error will be the most appreciable for the powder method and also for intensity measurements on less perfect crystals. These errors require separate detailed discussions. In this connexion, it is worth pointing out that some recent measurements by the powder method show a common trend: instead of a reduction, observed *F*-values show a small increment compared with the theoretical values for the metallic state. Figs. 5(*a*) and 5(*b*) show the cases of copper and nickel. The same trend is also observed to some extent in the case of iron shown in Table 6. Such a common trend suggests that there might still exist some kind of systematic error of the order of 0·5% – 1% in the powder method, in particular in the determination of the scale factor.

It is also to be noted in Fig. 5(*a*) for copper that the data of Jennings, Chipman & DeMarco (1964) obtained by intensity measurement on perfect single crystals show a fairly good agreement with Wakoh & Yamashita's values.

Since we can hope to have data of an absolute accuracy of about 0·5%, it is very important to be supplied with theoretical values of the dispersion terms which are more reliable than those available at present. For instance, the tabulated values of $\Delta f'$ of iron for Mo *Kα* range from 0·4 (Dauben & Templeton, 1955) 0·37 (Cromer, 1965) to 0·27 (Weiss, 1966), and this range brings about an uncertainty of 0·7% and 0·9% in the reflexions 110 and 111, respectively.

As already pointed out, the dynamical-interaction method of electron diffraction is fairly reliable as to the reproducibility of the data. However, in this method also, there is still a problem to be pursued

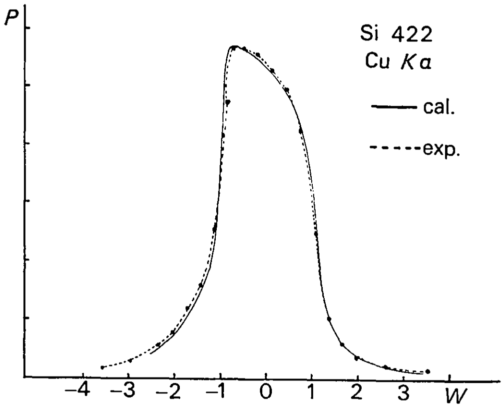

Fig. 3. *W*: normalized angular parameter used in the dynamical theory. Abscissa on arbitrary scale.

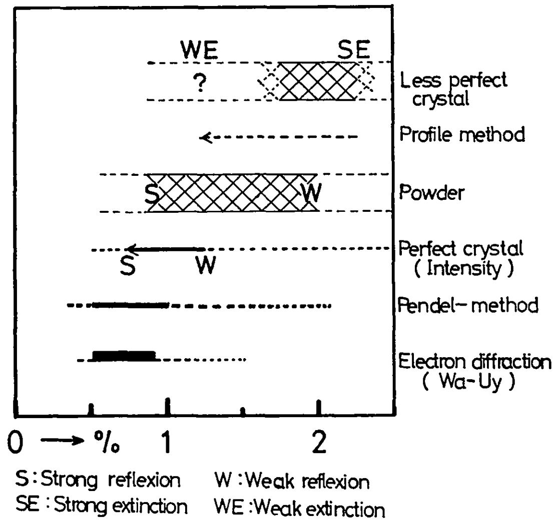

Fig. 4. Comparison of the various methods of measuring *f* values. Abscissa: accuracy. Wa–Uy: Watanabe, Uyeda & Fukuhara (1968).

further concerning an additional term to the Fourier potential. As formulated by Yoshioka (1957), the observed value of the Fourier potential $V_{h(\mathrm{obs})}$ contains an additional term to the crystal Fourier potential V_h, due to the inelastic scattering of electrons. The real part of the additional term ΔV_h, however, is a very cumbersome quantity to estimate. Therefore, a theoretical advance is also hoped for in this respect.

The conclusion of the survey made in this paper is that the reproducibility of experimental data of *F*-values is now approaching about 0·5% in various methods under favourable experimental conditions. On the other hand, the same accuracy does not seem to have been ensured in most cases with respect to the absolute experimental *F*-values. No doubt, however, the above assessment will quickly become obsolete in view of the very rapid progress of present-day experimental methods.

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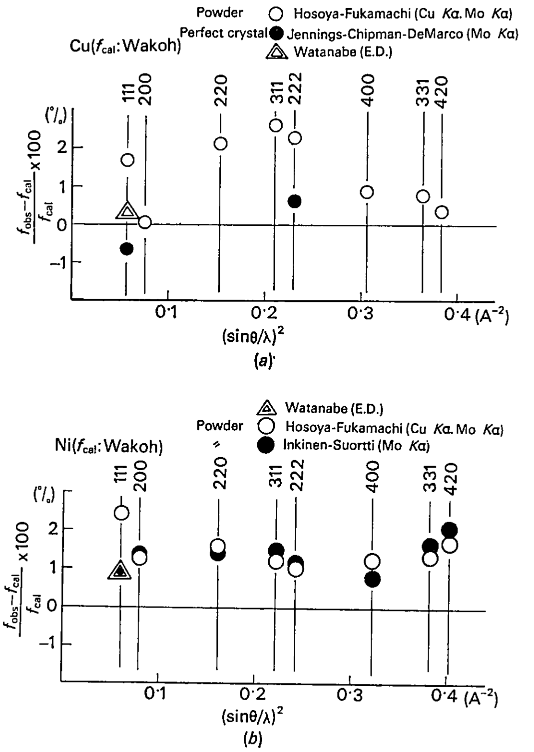

Fig. 5. *F*-values for (*a*) Cu and (*b*) Ni. f_{cal}: theoretical values of Wakoh & Yamashita (1968). f_{obs}: (*a*) Hosoya–Fukamachi (1966). Jennings–Chipman–DeMarco (1964). (*b*) Inkinen–Suortti (1964). Hosoya–Fukamachi (1968*b*).

DISCUSSION

DESLATTES: The profile analysis curve which you have shown is one of the most beautiful I have ever seen. It is a most remarkable achievement. I should be grateful for further experimental details.

MIYAKE: They are to be found in the paper by Kohra & Kikuta (1968). Their further studies will be published shortly.

JENNINGS: The agreement between *measured* and *calculated* F-values which you have shown is, in several cases, rather better than the level of agreement between different sets of *measured* F-values evident in the Powder Project results which I showed yesterday (Paper G2·1). I would like to know whether in the cases you presented the B-factors were the same in all experiments or whether they were adjusted to give the best agreement of F_o and F_c.

MIYAKE: Different B-values were used in different experiments but this does not necessarily imply that artificial adjustments were made to give the best agreement of F_o and F_c for all reflexions.

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The Role of Intensity Measurement Projects

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The accuracy of the determination of X-ray intensities, and hence structure factor F-values, is of crucial importance to studies of the solid state, particularly at the present time when computational facilities allow exhaustive analysis of experimental data against theoretical models. Experimental errors are far less easy to estimate than appears from consideration of published individual experiments at a first, or even more careful, consideration; methods of both estimating and correcting for them need very careful elucidation. By far the best way to do this – and probably the only way that will yield reliable information as to where we are in this ill-defined field – is to organize group projects specifically to allow estimation of the magnitude of overall error, the identification of individual sources of error where possible and hence, the detection of specific experimental features, which should be either carefully assessed in each experiment to allow the magnitudes of errors to be kept as low as possible, or actually physically corrected. It is helpful in this regard to allow error-sources to be thought of as stabilized or variable according to the type of project planned. It is obvious that careful planning of a series of projects with different characteristics will be an even more powerful tool for the investigation of error-sources in depth. In this paper, two projects are considered in some detail – one originated by the I.U.Cr., the other by the A.C.A. – both having considerable similarities but also instructive differences. A method of comparing and also of editing the projects is considered using the correlation R factor $|R_{ij}|$ where $|R_{ij}| = \Sigma\,|F_i - F_j| / \frac{1}{2}\,\Sigma\,|F_i + F_j|$. This is seen to allow simple but important deductions.

Our basic concern is with the individual experiment from which structure factor F-values are derived – how to estimate its accuracy, to detect the error-sources responsible for its failure to attain greater accuracy and, having learned about these, to devise means to achieve the necessary improvement.

Most factors capable of producing errors in the measurement of intensities and hence F-values, have probably been recognized. However, the assessment of the magnitude of their individual contributions to errors in measurement is not, in each case, necessarily well-defined. In addition, there is the possiblity of other factors whose effects may have been underestimated and hence have not been fully explored. The elucidation of the influence of a wide range of factors, in a piecemeal fashion, by individual experiments, although obviously of great value, is extremely tedious. Furthermore such an approach to the task of determining the overall error magnitude does pose certain problems as, I trust, will become evident.

In particular, each scientist tends to be optimistic regarding the accuracy of his own measurements in that he feels that he has adequate knowledge and control of the variables involved in his experiments. Moreover since few experiments are repeated, the normal single experiment is unique and its accuracy is largely indeterminate although an estimate of precision from the internal details of the experiment can be made; but this may be optimistic if the full range of error-sources in the experiment is not appreciated. It is perhaps unfortunate that for such isolated situations, F-values calculated from atomic models have been used as a guide to the assessment of accuracy of experimental measurements. If the models are inadequate, the attempted estimate made in this manner can be misleading.

Opinions on levels of accuracy have been expressed on earlier occasions but such estimates remain personal assessments without backing numerical evidence.

A counterbalance to individual bias and a somewhat less subjective assessment of accuracy can be attained by comparison of F-values given in the literature. Unfortunately, opportunities to apply this procedure are few since it is only rarely that experimenters measure and publish new values concerning compounds already reported, except to prove some point in the de-