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DISCUSSION

CHAIRMAN (HERBSTEIN): Professor Kurki-Suonio should be congratulated on the way in which he presented this paper.

POST: When you rotate the Borrmann crystal, the anomalously transmitted beam will rotate in a circle of radius $t \sin \theta$.

KURKI-SUONIO: This comes to about 0·2 mm, which is insignificant.

WEISS: Inkinen used an expression which I suggested to correct for porosity. I would not use this expression myself! The expression attempts to eliminate effects by comparing the fluorescence with that of a smooth sample.

FURNAS: The energy discriminating properties of a Li-drifted Si radiation detector are such that if it is used with a multi-channel pulse-height analyser, one can record simultaneously all diffraction effects due to the subharmonics of the monochromatic wavelength which are reflected by the monochromator crystal.

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G2·1

Current Status of the I.U.Cr.Powder Intensity Project

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The eventual objective of powder intensity measurements, in the present context, is to obtain absolute integrated Bragg intensities from specimens which are ideal with respect to all parameters such as extinction, preferred orientation, *etc.* At present, the Project has been limited to a comparison of X-ray techniques on a number of samples of carbonyl process nickel which are known to be non-ideal, but which were determined by actual measurement to yield identical integrated intensities using Cu $K\alpha$ radiation. Eleven samples have been measured in ten laboratories and six of these have been standardized by measurement of the incident beam. The results show that integrated intensities may not be relied on to better than 5%, even on a relative basis. It appears that, at the present time, the techniques for making an accurate measurement of the incident beam may be more reliable than those for measuring relative intensities.

Background

The study of electron density in crystals through the measurement of X-ray structure factors may be broadly classified into the study (*a*) of the positions of atoms within the unit cell and (*b*) of the details of the electron distribution once the position of the atoms is known. This latter case may be subdivided into effects arising from the thermal motion of the atoms and into those arising from the actual electronic distribution within the atom. It is well established that this distribution differs by only a few per cent from a distribution obtained by superposing free atoms having electron distributions calculated by modern approximation schemes. Thus, it is clear that a study of the influence of crystalline environment on such atoms will require an accuracy of better than, say, 1%. Furthermore, it is the outermost electrons which are most influenced by this environment and it is likely to be the lowest order Bragg reflections which are of greatest interest. The primary motive for making measurements of such reflexions on powders is the possibility of varying preparation conditions over a wide range so as to be better able to assess the effects of extinction than is possible with single crystals.

If attention is restricted to simple materials for which the Bragg peaks are intense and widely separated, modern diffractometers are able to reproduce integrated intensities to a precision approaching 0·1%. It has become clear, however, that the actual accuracy with which structure factors could be measured is far less. Because of this situation, it appeared that it would be fruitful to conduct an international project under the auspices of the Commission on Crystallographic Apparatus of the IUC to assess the actual accuracy possible. From the outset, it was visualized that the

Project should be a purely experimental one, *i.e.* there should be as little recourse as possible to theoretical models. In particular, the scaling factor should be determined experimentally and not through comparison with any model. Furthermore, for the reasons outlined above, the emphasis should be on low order reflections.

In order to formulate a Project, the views of a large number of diffractionists were solicited and discussed at an informal session at the Moscow IUC-Congress in 1966. As a result of these discussions, attention was concentrated on nickel metal. In principle, it would only be necessary to require each participant to supply his measured value for the structure factors of nickel, but it seemed advisable to restrict the first part of the Project to the purely X-ray aspects of the problem. Accordingly, we prepared a number of pressed specimens of carbonyl process nickel powder and studied their properties using Cu $K\alpha$ radiation. We chose Cu $K\alpha$ because of higher intensity and lack of fluorescence as compared to a harder radiation. The disadvantages of large extinction and dispersion correction seemed of lesser consequence in the context of the Project. The specimens were found to display preferred orientation, porosity effects, and probably extinction, but we were able to prepare specimens which yielded values of integrated intensity of each of the first three reflections that were well within $\frac{1}{2}$% of the average. Such a sample was sent to each participant, who was asked to measure the integrated intensities of the Bragg reflections using Cu $K\alpha$ radiation so that he might compare his X-ray technique with that of other participants. Beyond this request, we were deliberately vague about how the measurements were to be carried out and reported, in the hope that each worker would detail to us those considerations which were important from his own experience.

Results

Up to the present time, we have received results on eleven samples studied in ten laboratories in seven countries. We are greatly indebted to all these workers, some of whom have performed extensive researches in connection with the Project; we have listed all the participants at the end of the paper. On the other hand, this response is sufficiently limited that we feel it is possible to view the results directly in tabular form; it is not considered necessary or advisable at this stage to employ complicated schemes for their assessment. In order to prepare such tables it was, of course, necessary to put all the results on a comparable scale, and we should like to discuss some necessary considerations.

Polarization factor

Since we had in mind that the results should be placed on an absolute scale, almost all the participants made use of a monochromator. This introduces a polarization factor of $(1+k\cos^2 2\theta)/(1+k)$, where k is the polarization ratio of the monochromator. Some participants evaluated k for their apparatus using one of four techniques: (1) use of a moderately thick perfect crystal in transmission (Borrmann polarizer), (2) comparison of scattering at 90° in two perpendicular directions, (3) comparison of relative integrated intensities with the monochromator to those in an unpolarized, non-monochromatic beam, and (4) calculating k from the integrated intensity of the monochromator. The other participants assumed that their monochromator reflected as an ideal mosaic. One set of relative measurements was carried out with filtered, presumably unpolarized radiation. In this case, difficulties in evaluating k are replaced by difficulties in assessing the background properly.

Geometrical considerations

Two of the participants made use of wide slits so that it was necessary only to measure the height of the slit and the integrated intensities could be measured without scanning. The remainder presumably used relatively narrow slits. Some of the participants mentioned explicitly that they made use of X-rays to determine the slit dimensions and that they shaped the slits in such a way as to eliminate deleterious effects from divergences. No participant reported the necessity of making any corrections for aberrations, but several explicitly mentioned that they studied the possibility.

Direct beam

All workers who measured the direct beam did so by reducing its intensity with calibrated foils. Some participants reduced it further by scanning the direct beam with their receiving slit, thereby obviating the necessity of measuring the slit width or angular velocity.

Wavelength

A number of quantities entering into the interpretation of the integrated intensities depend on wavelength. We have corrected the results reported by the participants to the weighted average of $K\alpha_1$ and $K\alpha_2$ or have assumed that this was the average wavelength used in those cases where none was reported. One should note that, in the case on hand, the influence of the dispersion correction in this connection is far from negligible.

Thermal diffuse scattering (TDS)

Because the TDS peaks at the same positions as the Bragg reflections, it is necessary to consider it explicitly when evaluating the Bragg integrated intensity. For the purposes of the present Project, the contribution of TDS could be included as part of the integrated intensity if the peaks were so widely separated that the TDS dropped to a negligible value between them. This, however, is not the case, and it is necessary to take ex-

plicit account of the TDS in the region between closely neighboring peaks. Two respondents detailed their techniques for doing this, mentioning explicitly that it was impossible to obtain background correctly between closely neighboring peaks. Several other respondents indicated that they had taken account of the TDS. In view of these considerations, we concluded that it would be most appropriate to compare results as corrected for TDS. In those cases where the participant did not make his own corrections, we subtracted a fraction $0{\cdot}016 \cos\theta\ (\sin\theta/\lambda)^2\Delta$, with Δ the width of the scan measured in degrees of 2θ. This approximation (Chipman & Paskin, 1959) does not differ greatly from the more complicated calculation of Suortti (1967). The entire amount of the correction is slightly greater than 1% in the worst case and we feel that the question of TDS does not introduce an error of more than about 0·3% in the *comparison* of various respondents' intensity data.

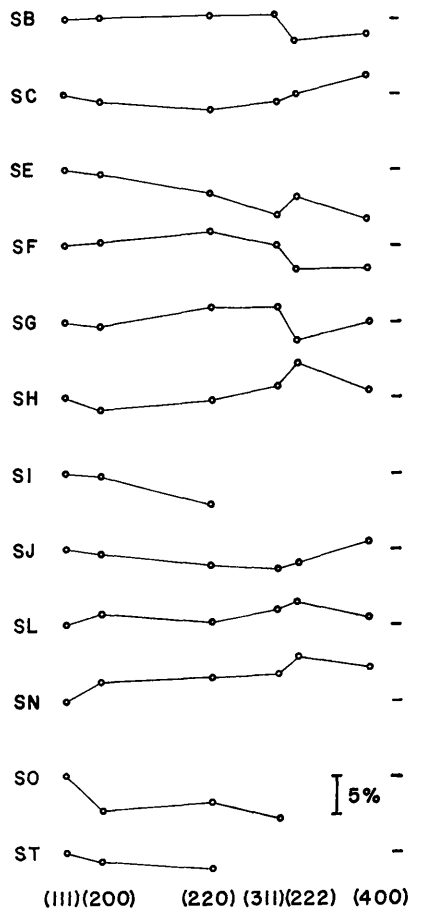

Fig. 1. For each sample, the ratio of each relative value of F to the average for each reflection. The values are taken from Table 3 and are normalized to the 111 reflection so that the point on the left is plotted at unity for each sample. The vertical scale is the same for all samples and is given in the lower right hand corner. The abscissa is proportional to $\sin\theta$. One may note that there is an overall angular dependence for most samples. Superposed on this are fluctuations whose source is not determined, but one way surmise that different techniques for separating the intensity belonging to the closely neighbouring peaks 311 and 222 may give rise to the sharp breaks in this region.

Presentation of results

Making use of the above considerations, we were able to evaluate relative values of F^2/μ. Most of the respondents gave, in addition, enough information to evaluate this quantity on an absolute basis. Although the choice of μ is important to an evaluation of f, we did not consider it important to the present Project, and we did not attempt to go further than the evaluation of F^2/μ. For the sake of clarity, we note that $F^2=[(f_0+\Delta f')^2+(\Delta f'')^2]\,e^{-2M}$, where f_0 is the quantity that is usually tabulated.

The current results of the Project are thus given in Table 1, which presents absolute values of F^2/μ. However, since some participants have supplied only relative values and because of the interest in the possibility of obtaining scaling factors from a treatment of accurate relative data, we also gives tables of relative data. In Table 2, we give data standardized so that the sum of the first four reflections is 10^4. This standardization tends to obscure systematic angular dependence and therefore gives perhaps the most optimistic possible view; discrepancies are revealed only in the highest reflections. In order better to display the angular dependences, it would be most satisfactory to extrapolate each set of results to zero angle and to scale each set from this value. It is not clear, however, how such an extrapolation should be carried out, so we have instead scaled each set of data to the 111 reflection with the results shown in Table 3. The 111 is the strongest as well as the lowest angle reflection (almost all workers report an error less than $\frac{1}{2}$%) and is thus the most suitable for the purpose. Thus, we feel that the range of values shown for the various reflections in Table 3 is a realistic assessment of the situa-

Table 1. *Absolute values of* $F^2/\mu \times 10^4$

	(111)	(200)	(220)	(311)	(222)	(400)	(331)
SB	6657	6192	3375	2235	1884	1321	
SC	6402	5889	3163	2116	1862	1323	
SE	6377	5889	3111	2004	1792	1207	
SF	6618	6172	3402	2209	1872	1300	
SJ	6401	5906	3154	2082	1832	1307	
SL	6271	5905	3173	2132	1880	1281	
SN	6544	6233	3395	2267	2014	1381	1016
SO	7274	6453	3541	2290			

tion. This same information is depicted graphically in Fig. 1.

It was our hope that each worker would prepare his results with as little influence as possible from the results of others. To this end, we did not circulate our compilation except to those who had already submitted their results to us. However, to give other participants the same opportunities as we ourselves had and to minimize the chances of typographical errors, we submitted the tabulated results to each respondent. The tabulations presented here show the corrected values sent to us by each respondent.

Remarks and conclusions

It is clear that there are a number of entries in each Table which must differ from the true value by about 5%. It is our opinion that differences among the samples or from our TDS corrections give rise to less than 1% of this. Furthermore, we have omitted the statistical errors quoted by the various respondents in as much as they are in general less than 1% for the first four reflections and only slightly more for the higher reflections. It is thus our conclusion that, at the present time, errors in relative integrated intensities of the order of 5% must be anticipated. It is unfortunate that not more of the results have been put on an absolute scale. It does appear, however, that (with the exception of one set) the absolute measurements do not show markedly more range than the relative measurements. It is thus our opinion that at least as much attention needs to be directed toward the measurement of accurate relative intensities as toward the measurement of the incident power. In addition, one must bear in mind that these results take no account of errors in scattering factors arising from non-ideal samples.

I should like to thank my collaborators D. R. Chipman and B. W. Batterman for their help in initiating and carrying out the Project. F. H. Herbstein is the member of the Apparatus Commission in charge of the Project; both he and the Commission Chairman, A. McL. Mathieson, have given much attention and encouragement to the Project. Thanks are also due to the other Commission members and to those diffractionists who have given us suggestions for carrying out the Project.

The Project was made possible at all only through the generous response of the participants. It may yet be that there will be additional respondents, but we should like to give thanks here to those who have provided data for inclusion at this time: J. Urban, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin; R. Uno, Nihon University, Tokyo; S. Hosoya, University of Tokyo; U. Korhonen, E. Rantavuori, and M. Linkoaho, Institute of Technology, Otaniemi (Helsinki); O. Inkinen, T. Paakkari, and P. Suortti,

Table 2. *Relative values of F^2, normalized to sum of first four reflections*

	(111)	(200)	(220)	(311)	(222)	(400)	(331)
SB	3606	3354	1828	1211	1021	716	
SC	3644	3352	1800	1204	1060	753	
SE	3669	3388	1790	1153	1031	695	
SF	3597	3354	1849	1200	1017	706	
SG	3600	3322	1853	1225	1021	727	
SH	3629	3314	1827	1231	1104	741	558
SI	3674	3402	1778				
SJ	3649	3367	1798	1187	1044	754	
SL	3587	3378	1815	1220	1075	733	
SN	3549	3380	1841	1229	1092	749	551
SO	3719	3299	1811	1171			
ST	3652	3356	1803				
Range	4·7%	3·1%	4·1%	5·5%	7·8%	8·0%	

Table 3. *Relative values of F^2, normalized to first reflection*

	(111)	(200)	(220)	(311)	(222)	(400)	(331)
SB	1000	930	507	336	283	198	
SC	1000	920	494	330	291	207	
SE	1000	923	488	314	281	189	
SF	1000	933	514	334	283	196	
SG	1000	923	515	340	284	202	
SH	1000	913	503	339	304	204	154
SI	1000	926	484				
SJ	1000	923	493	325	286	204	
SL	1000	942	506	340	300	204	
SN	1000	952	519	346	308	211	155
SO	1000	887	487	315			
ST	1000	919	494				
Range		7%	7%	10%	9%	11%	

University of Helsinki; P. J. Black and G. G. S. Millar, University of Birmingham (England); G. C. Verschoor, Rijksuniversiteit, Leiden; N. N. Sirota, E. M. Gololobov, N. M. Olekhnovich, and A. U. Sheleg, Institute of Solids and Semiconductors, Minsk; P. Trucano and B. W. Batterman, Cornell University, Ithaca (New York); L. D. Jennings, Army Research Center, Watertown (Massachusetts); and G. Albrecht and B. Dietrich, Physikalisches Institut der Friedrich-Schiller-Universität, Jena (DDR).

Table 4. *Information concerning experimental techni quesused*

We did not ask the various respondents to fill out a questionnaire; we felt that the very framing of such a questionnaire would bias the respondents toward our own views. The objective was to compare results for each worker using his customary techniques. In response to requests at the Intensity Meeting, we have prepared this table from information available to us; any omissions should be interpreted simply to indicate that the information was not available to us in time for inclusion here.

						Percentage error[5]			
Sample	Polarization ratio, k[1]	Monochromator[2]	Wavelength[3]	TDS[4]	Slit[3]	111	222	400	Incident beam
SB[6]	Borrmann crystal	Ge	—	J(E)	–	–	–	–	–
SF									
SC	Borrmann crystal	SiO_2 (after)	1·5418	S	Narrow	0·2[5]	0·8	1·3	1·0
SE	Miyake method	LiF	—	C & P	Narrow	0·3	2·4	0·9	[5]
SG	Borrmann crystal	LiF	—	C & P	Narrow	0·2	0·7	1·4	–
SH	Unity	Filtered radiation	—	J(E)	Narrow	1·0	1·0	2	–
SI	k_M	SiO_2	1·542	J(E)	–	0·3[5]	–	–	–
SJ	Miyake method	SiO_2 (after)	—	J	Narrow	[5]	0·8	1·3	2·8
SL	90 degree scattering	LiF	1·5412	C & P[4]	Wide	0·1[5]	0·5	0·4	0·3
SN	Miyake method	SiO_2	—	J(E)	Narrow	–	–	–	–
SO	Integrated intensity	Si	—	C & P	Narrow	2	–	–	–
ST	Average of k_P and k_M	SiO_2	—	J(E)	Wide	0·5	–	–	–

[1] The polarization ratio k was measured or estimated in the following ways: (*a*) A perfect (Borrmann) crystal of Si, so thick that it transmits only a single polarization of that radiation which fulfills the Bragg condition, is placed in the customary position of the sample. The integrated intensity for each of the two polarizations is measured and their ratio is k. If the monochromator is between the X-ray source and the sample position, the integrated intensity is that obtained by rocking the Borrmann crystal; if the monochromator is between the sample position and the detector, it is that obtained by rocking the monochromator. (*b*) The Miyake method compares the integrated intensities of a powder sample using a monochromatic beam whose k value is to be determined with those obtained in an unpolarized, non-monochromatic beam. (*c*) The integrated intensity of a crystal which Bragg scatters at a 2θ value of 90° is proportional to the power in the σ polarized component in the incident beam. The ratio of integrated intensities from rocking such a crystal in two perpendicular planes is k. (*d*) The integrated intensity of the monochromating crystal itself gives information about its perfection from which one may infer a k value. (*e*) From general knowledge of diffraction, one may estimate the value of k by calculating the mosaic value $k_m = \cos^2 2\theta_M$ and the perfect crystal value $k_p = \cos 2\theta_M$, where θ_M is the Bragg angle of the monochromator. It should be noted that there is much less range between the limiting values k_m and unity in the case of SiO_2 than in the case of LiF.

[2] In each case, the lowest angle reflection of the material indicated was used for monochromatization. The position of the monochromator is between the X-ray source and the sample except where it is indicated as being after the sample.

[3] See text for a discussion of these points.

[4] An S indicates that the corrections were made following Suortti (1967). In this case, the background was fitted over a range of suitable angles. C & P indicates that the respondent made his own TDS corrections following the procedures of Chipman & Paskin (1959). In the case of SL, the intensity between closely neighboring peaks was assigned to each peak with use of symmetry considerations before application of the C & P corrections to each peak. J indicated that the corrections were made by me, using the considerations discussed in the text. Anticipating the need for this calculation, we had specifically asked each worker for 'the details of the background subtraction (because of the peaking of thermal diffuse scattering)'. Nevertheless, we did not have information on the length of scan in some cases and it was necessary for us to make an estimate. These cases give rise to the 0·3% uncertainty mentioned in the text and we have indicated them by (E) in the table.

[5] The objective of the Project, as stated several times, was to obtain results significant to 1% or better. We assume that this goal was borne in mind by each worker. Some respondents did, however, indicate error limits. Except in the following cases the significance of these was not specified. SC: The stated errors include an estimate of all relevant factors except the composition of the sample. SE: The stated errors apply to the absolute measurements. SI and SL: The stated errors are standard deviations arising from counting statistics alone. It is stated that systematic errors may amount to ½–1%. SJ: The errors stated for relative accuracy include the error in 111. For all samples, the errors given for 200, 220 and 311 are in general appreciably smaller than the lesser of those given for 222 and 400.

[6] Samples SB and SF were assigned to one laboratory which has several powder diffractometers available.

APPENDIX

In response to numerous requests at the Cambridge Intensity Meeting, we have appended Table 4, which gives some information about experimental details. Although we feel that Tables 1–3 give a fair representation of the reliability of published data, Table 4 may aid in an assessment of techniques.

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DISCUSSION

ABRAHAMS: Do you plan to analyse statistically the results of your powder intensity Project, and particularly, how do you propose to treat the outlying experiments, since you have already indicated that it is possible that such an outlier might be closer to the true values than the mean of the experiments?

JENNINGS: Our situation is rather different from a project dealing with single crystals. Whereas single-crystal studies are bound to continue unabated and the accuracy aspects are of direct significance, powder measurements are only done occasionally and the error limits hoped for require to be lower. Hence, because of the limited number of reflections involved, I feel that my role is to present the spread of results, so as to stimulate individual laboratories to look more closely into factors which influence accuracy in their technique. I rather doubt if further project studies of this type are worthwhile or warranted at the present.

ALEXANDER: Is there an intention to carry out a statistical analysis of the results as has occurred for the angle crystal projects?

JENNINGS: No. The paucity of data in each set does not encourage this approach.

MILLEDGE: Can one correlate trends in the results with the experimental techniques which were used?

JENNINGS: There was some variety in the techniques but my strong opinion is that the differences do not arise from any basic factors but merely from the way in which the work was done.

KATZ: Did the individual workers give any indication of the internal consistency of their own results?

EDITOR'S COMMENT: This question is answered in Dr Jennings's Appendix to his paper. [Footnotes, Table 4.]

BATTERMAN: What is the future of the project?

JENNINGS: My own opinion does not differ very greatly from that of the participants whom I have consulted. It is that we have published all that can be deduced from the results; future work should take the form of research projects in individual laboratories. Elaboration as part of a project does not seem advisable at present.

KAPLOW: I cannot see why the spread in the results should be as bad as it is when, for example, Chipman claims to be able to make *absolute* measurements well within 10%. What are people doing wrong and can they learn from one another?

JENNINGS: I really do not know what is wrong. Perhaps we might have learnt something if we had had three times as many participants. I am sure that we have all been educated: for instance, at the beginning no-one except the Japanese measured polarization ratios.

POST: I still think that a limited statistical study should be made. Statistical analysis is normally applied and is, indeed, only applicable, to the measurements which group together. It seems to me that if outliers are excluded the results are not as bad as all that.

GOMES DE MESQUITA: Perhaps the participants themselves can shed some light on possible sources of their own errors.

WARREN: Has there been any interchange of samples?

JENNINGS: No, but I measured three reflexions from each powder sample: if, for any given sample, I got a difference of more than 0·4% from the mean, I discarded that sample.