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Results of the I.U.Cr. precision lattice-parameter project. By WILLIAM PARRISH, *Philips Laboratories, Irvington-on-Hudson, New York, U.S.A.*

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This paper presents the results of an international project conducted by the I.U.Cr. Commission on Crystallographic Apparatus. The 16 laboratories that participated were located in the following nations: U.S.A. 4, U.S.S.R. 3, Germany 2, U.K. 2, and 1 each in Australia, Canada, France, the Netherlands and Spain. Each laboratory was given uniform powder samples of diamond, silicon and tungsten and used the same values for wavelengths, coefficients of thermal expansion and refraction corrections. Most of the laboratories used various conventional film methods which are briefly described. The table below shows the composite mean value $\bar{a}$ in Å at 25 °C., the standard deviation σ computed from the reported mean values and the number of mean values used (omitting one mean value which exceeded 3σ for each substance), the approximate number of films and observers and the per-cent agreement calculated from (highest − lowest)/mean. The agreement among the laboratories was about 1 part in 10^4; this includes random and systematic errors. This is much lower than the precision generally reported by the individual laboratories and often claimed in the literature.

	$\bar{a}$	σ	No. values used	No. films	No. obs.	% Agreement
Diamond	3·56703	± 0·00010	6	22	10	0·009
Silicon	5·43054	± 0·00017	25	77	33	0·012
Tungsten	3·16522	± 0·00009	14	43	20	0·010

1. Introduction

At meetings of the International Union of Crystallography Commission on Crystallographic Apparatus held at Madrid, Spain, April 1956, it was decided to sponsor a project on the precision measurement of lattice parameters and the author was selected to organize it. The primary objective was to determine the attainable accuracy by comparing results obtained in several laboratories using the same specimens and constants. Invitations to participate were sent to well-known specialists, and secretaries of the various national groups adhering to I.U.Cr. were invited to suggest additional participants. Reports were received from 16 laboratories in the following nations: Australia 1, Canada 1, France 1, Germany 2, the Netherlands 1, Spain 1, U.K. 2, U.S.A. 4, and U.S.S.R. 3. The results described in this paper show the importance of scientific collaboration on an international scale.

The work was carried on from 1957 to 1959, was described in two preliminary reports (Parrish, 1957, 1958) and was the subject of one of the Conferences of the Commission held in Stockholm, Sweden, June 1959 (see *Acta Cryst.* **12**, 1054, 1959). The purpose of this paper is to summarize the results of the first phase of the project, which was limited to measurements of three cubic powder samples: diamond, silicon and tungsten, in order to simplify the interpretation of the results. Most of the work was done using film methods and conventional procedures which are described in the literature; see for example, Straumanis & Ieviņš (1940), Klug & Alexander (1954), Edmunds, Lipson & Steeple (Peiser, Rooksby & Wilson, 1955), Azároff & Buerger (1958), and Parrish & Wilson (1959).

There have been many publications in which a precision of 1 part in 50,000, or 0·002%, has been reported. The highest precision appearing in the literature is that of Straumanis & Aka (1952), who report 0·00005% for a sample of high purity germanium. Weyerer (1956*a*, *b*, *c*), comparing four different experimental methods, reported a statistical error of ± 0·0002% and an uncertainty of 0·001% in his results. The agreement among the various laboratories in the present tests was 0·01%, calculated from (highest − lowest)/mean. This involves systematic and random errors and is much lower than the reported precision of the individual laboratories.

2. Specimens

Many factors were considered in the selection of the substances for the tests. The most important factor was to have a large enough quantity of the substance to allow distribution of uniform samples to all the investigators.* Cubic substances were chosen because they require the measurement of only a single parameter and also are convenient as internal calibration standards. Indexed diffractometer charts of the back-reflection region using unfiltered Cu K radiation are shown in Fig. 1.

The specimens were not ideal in all respects, nor is it possible to find the ideal specimen to fit all the conditions. For example, specimen transparency may be the source of large systematic errors, and hence low absorption is desirable for transmission methods and high absorption for reflection. Diamond with only a few lines and none at very high angles (for Cu K radiation) made it somewhat unfavorable for extrapolation methods, but its extremely narrow lines and high peak-to-background ratio were ideally suited for precision angle measurements. Silicon had a larger number of narrow lines, but the tungsten gave rather broad lines. Nevertheless, the substances used were probably better than many substances that would be met in practice.

Diamond powder is widely available throughout the world for various industrial purposes. It is supposed to be remarkably uniform because the powder is 'averaged' by crushing many thousands of diamond crystals. It is frequently adulterated by the addition of quartz, corundum and other hard colorless substances. An unadulterated sample of Congo diamond powder with crystallites between 6μ and 12μ was used. No chemical analysis was made.

Silicon powder and single crystals are widely available for transistor and other solid-state devices. Unfortunately the powder tends to be coated with a thin layer of amorphous silicon dioxide and its effect on the lattice parameter has not yet been fully established. Several batches

* Samples of the silicon and tungsten used in the tests are available free of charge by application to the author.

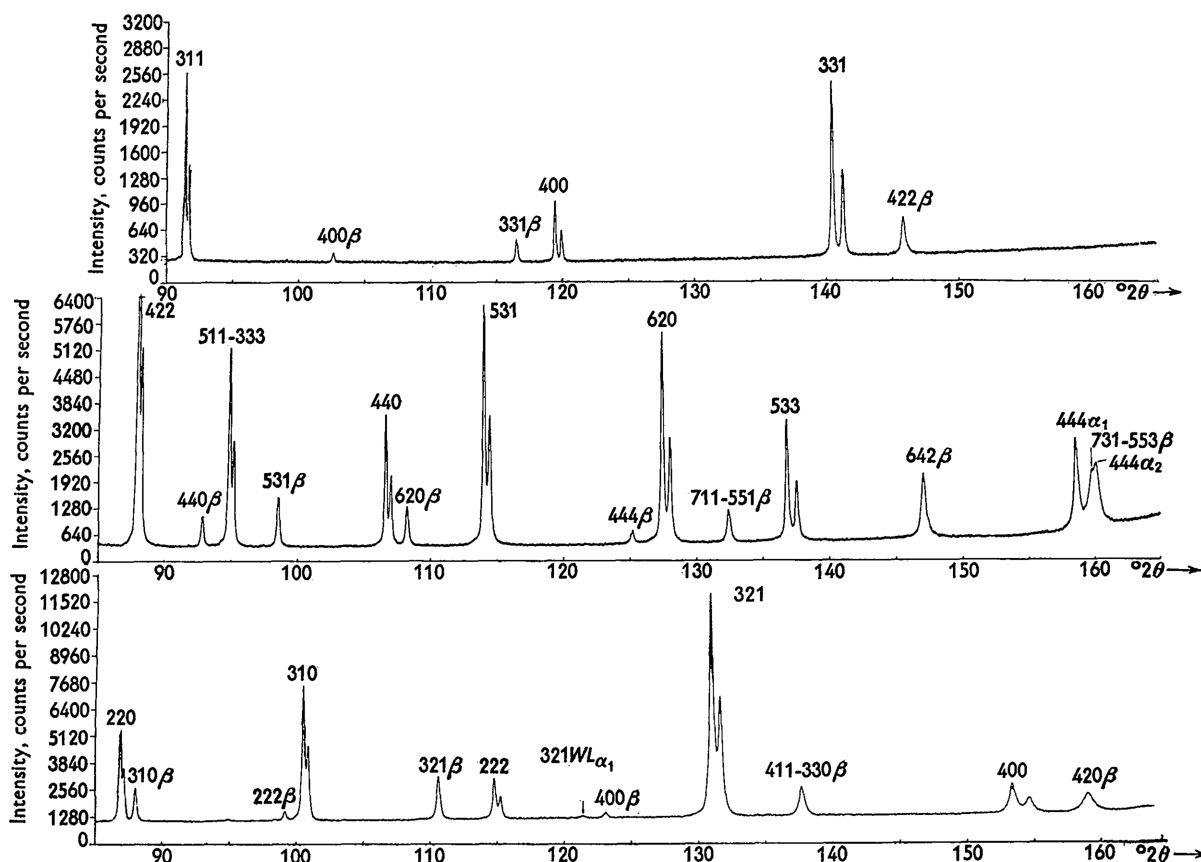

Fig. 1. Diffractometer ratemeter recordings of the back-reflection regions of diamond (top), silicon (middle), and tungsten (bottom). Cu K radiation, 40 kVp., 20 ma., full-wave rectified, line focus 1·6 × 10 mm. viewed at 3°, angular aperture 4°, two sets of Soller slits each with 4·5° aperture, receiving slit 0·10°, scanning speed $\frac{1}{4}$° 2θ min.$^{-1}$, scintillation counter with pulse-amplitude discrimination.

of powder were subjected to (optical) spectrographic, chemical and X-ray diffraction analysis. A thin layer of powder in an open fused quartz vessel was placed in a fused quartz firing chamber and heated to 1000 °C. in a stream of chlorine. The silicon passed out of the chamber as $SiCl_4$ leaving a non-volatile white residue of amorphous silica. The residue was tested by X-ray diffraction patterns sensitive to 0·1% of crystalline silicon. The amounts of crystalline silicon and amorphous silica were determined by weight differences. Analyses of different crystallite-size fractions prepared by air elutriation showed that the percentage of amorphous silica increased inversely with crystallite size. Analysis of the powder used in this project was: $< 5\mu$, 11·7% amorphous silica; 10–20μ, 1·5%; 30–50μ, 0·63%. Since a large fraction of the powder was $< 10\mu$ it was decided to use the powder as received without air elutriation; its analysis was 3·5% amorphous silica, 96·5% crystalline silicon. Unfortunately there were enough larger crystallites (between 40μ and 60μ) to cause spotty lines when the specimen was not rotated. The investigators were asked to use the powder as received, and the few cases where the powder was sieved are indicated below. Spectrographic analysis indicates that the sample contained trace amounts of Ca, Mg, Mn, Cu, Al, B, Ti and Fe. No attempt was made to determine the concentrations quantitatively, but it is unlikely that the total exceeds 0·1%.

Optical spectrographic examination of the tungsten powder showed small amounts of Ca, Mg, Si, B and Cr. The weight loss on firing in dry hydrogen at 1000 °C. to constant weight was 0·08%. A wet chemical analysis showed 99·27% W, 0·19% Fe_2O_3, and 0·06% SiO_2. By direct chlorination of the tungsten powder 0·08% residue was obtained. Thus the powder was between 99·27% and 99·92% W.

3. Procedure

To avoid differences which would occur from the use of different constants in the calculations, a report (Parrish, 1957) was sent to all participants listing the values to be used by all investigators. *All lattice parameters listed in this paper are in Ångström units at* 25 °C. *and corrected for refraction.*

Wavelengths

The wavelengths used were those published by Lonsdale (1950), who multiplied the values in the Cauchois & Hulubei Tables (1947) by 1·00202 to convert kX to Å. (This conversion factor now appears to be low and probably 1·002037 (Bearden & Thomsen, 1959; DuMond, 1959) should be used, but this does not influence the

interpretation of the results reported here). Where the doublet was unresolved, the weighted mean $(2K\alpha_1+K\alpha_2)/3$ was used. Most of the work was done with Cu K radiation.

Table 1. *Compilation of individual results for diamond, Å, 25 °C.*

Code No.	Observations	Lattice parameter[a)]
1a	Film 1, Obs. *A*	3·56673±0·00008[b)]
1b	Film 1, Obs. *B*	680 006[b)]
1c	Film 2, Obs. *A*	607 021[b)]
1d	Film 2, Obs. *B*	672 011[b)]
1e	Avg. 1a to 1d	**3·56658±0·00013[c)]**
3a	Film 1, avg. 2 obs.	3·56684
3b	Film 2, avg. 2 obs.	682
3c	Film 3, avg. 2 obs.	686
3d	Film 4, avg. 2 obs.	695
3e	Film 5, avg. 2 obs.	690
3f	Film 6, avg. 2 obs.	687
3g	Film 7, avg. 2 obs.	690
3h	Avg. 3a to 3g	**3·56688±0·00003[d)]**
6a	Film 1, Obs. *A*	3·56706
6b	Film 2, Obs. *A*	683
6c	Film 3, Obs. *A*	730
6d	Film 4, Obs. *A*	665
6e	Film 5, Obs. *A*	715
6f	Avg. 6a to 6e	*3·56700±0·00021[e)]*
6g	Film 1, Obs. *B*	3·56717
6h	Film 2, Obs. *B*	691
6i	Film 3, Obs. *B*	700
6j	Film 4, Obs. *B*	718
6k	Film 5, Obs. *B*	3·56704
6l	Avg. 6g to 6k	*3·56706±0·00009[e)]*
6m	Avg. 6f and 6l	**3·56703±0·00006[f), g)]**
11	Avg. 3 obs.	**3·56719±0·00006[f)]**
13a	Diffract. method (a)	**3·56709±0·00013[h)]**
13b	Diffract. method (b)	**3·56705±0·00009[h)]**
16	Avg. 7 films	**3·56696±0·00007[i)]**

a) See description of each Code for discussion of error limits.
b) Variance.
c) Variance of variances.
d) Probable error.
e) 95 % confidence level.
f) Standard deviation.
g) 95 % confidence level limits ±0·00014.
h) Method of computing errors not given.
i) Standard deviation of instrumental and measurement errors, see text.
j) Maximum error.
k) Error limits estimated.
l) Deviations of results of different readings from mean value of a single film.
m) First number refers to diameter of glass fibre and second number to overall specimen diameter.

Table 2. *Compilation of individual results for silicon, Å, 25 °C.*

Code No.	Observations	Lattice parameter[a)]
1a	Film 1, Obs. *A*	5·43052±0·00006[b)]
1b	Film 1, Obs. *B*	116 018[b)]
1c	Film 2, Obs. *A*	054 004[b)]
1d	Film 2, Obs. *B*	062 004[b)]
1e	Avg. 1a to 1d	**5·43071±0·00010[c)]**

Table 2 (*cont.*)

Code No.	Observations	Lattice parameter[a)]
2a	Unicam, Film 1, Camera 1	5·43045
2b	Unicam, Film 2, Camera 2	046
2c	Unicam, Film 3, Camera 2	051
2d	Avg. 2a to 2c	**5·43047±0·00005[f)]**
2e	Philips, Film 1	5·43051
2f	Philips, Film 2	059
2g	Avg. 2e and 2f	**5·43055±0·00007[f)]**
3a	Film 1, Obs. *A*	5·43056
3b	Film 1, Obs. *B*	057
3c	Film 2, Obs. *A*	032
3d	Film 2, Obs. *B*	036
3e	Film 3, Obs. *A*	053
3f	Film 3, Obs. *B*	043
3g	Film 4, Obs. *A*	023
3h	Film 4, Obs. *B*	017
3i	Film 5, Obs. *A*	036
3j	Film 5, Obs. *B*	039
3k	Film 6, Obs. *A*	051
3l	Film 6, Obs. *B*	050
3m	Avg. films 1 to 6, Obs. *A*	*5·43041*
3n	Avg. films 1 to 6, Obs. *B*	*5·43040*
3o	Avg. 3a to 3l	**5·43041±0·00009[d)]**
4a	Film 1	5·43064
4b	Film 2	079
4c	Film 3	073
4d	Avg. 4a to 4c	**5·43072±0·00008[i)]**
5a	Spec. 1, Obs. *A*	5·4308x
5b	Spec. 2, Obs. *B*	07x
5c	Spec. 1, Obs. *A*	08x
5d	Spec. 2, Obs. *B*	07x
5e	Avg. 5a to 5d	**5·43076±0·00007[k)]**
6a	Film 1, Obs. *A*	5·42991
6b	Film 2, Obs. *A*	5·43026
6c	Film 3, Obs. *A*	054
6d	Film 4, Obs. *A*	038
6e	Avg. 6a to 6d	*5·43027±0·00019[e)]*
6f	Film 2, Obs. *A*	5·43030
6g	Film 2, Obs. *B*	5·42997
6h	Film 2, Obs. *C*	5·42961
6i	Film 2, Obs. *D*	5·43065
6j	Avg. 6f to 6i	*5·43013±0·00032[e)]*
6k	Film 2, Obs. *A*	5·43017
6l	Avg. 6b, 6f and 6k	*5·43034±0·00005[f)]*
6m	Avg. 6e and 6j	**5·43020±0·00011[f)]**
7a	Film 1	5·43092
7b	Film 2	080
7c	Film 3	086
7d	Avg. 7a to 7c	**5·43086±0·00004[h)]**
8	(?)	**5·42949±0·00005[h)]**
9a	Avg. 7 films, 2 D.-S. cameras	**5·43040±0·00005[h)]**
9b	Avg. 3 films, Foc. mono.	**5·4305x±0·0002x[h)]**
10a	Avg. 6 films, coarse coll.	*5·4304x±0·0006x[h)]*
10b	Avg. 6 films, fine coll.	*5·4304x±0·0006x[h)]*
10c	Avg. 10a and 10b	**5·4304x±0·0006x[h)]**
11	Avg. 3 obs.	**5·43052±0·00006[f)]**
12a	Cr K	**5·43056±0·00015[a)]**
12b	Cu K	**5·43061±0·00015[a)]**

Table 2 (*cont.*)

Code No.	Observations	Lattice parameter[a)]
13a	Diffract. method (a)	**5·43019±0·00015**[h)]
13b	Diffract. method (b)	**5·43034±0·00015**[h)]
13c	D.-S. camera	**5·4303x±0·0002x**[h)]
14a	D.-S., Cu, Ni, Co unfilt.	5·43070
14b	D.-S., Cu, Ni, Co unfilt.	071
14c	D.-S., Cu, Ni, Co unfilt.	057
14d	Avg. 14a to 14c	**5·43066±0·00004**[a)]
14e	D.-S., Cu unfilt.	5·43057
14f	D.-S., Cu unfilt.	052
14g	Avg. 14e and 14f	**5·43055±0·00004(?)**[a)]
14h	Flat plate, Cu filt., Co unfilt.	5·43068
14i	Flat plate, Cu filt., Ni & Co unfilt.	070
14j	Flat plate, Cu filt., Ni & Co unfilt.	067
14k	Flat plate, Cu filt., Ni & Co unfilt.	069
14l	Flat plate, Cu filt., Ni & Co unfilt.	069
14m	Avg. 14h to 14l	**5·43069±0·00001**[a)]
14n	Symm. b.r.f., Cu filt., Ni & Co unfilt.	5·43061
14o	Symm. b.r.f., Cu filt., Ni & Co unfilt.	055
14p	Symm. b.r.f., Cu filt., Ni & Co unfilt.	065
14q	Symm. b.r.f., Cu filt., Ni & Co unfilt.	067
14r	Symm. b.r.f., Cu filt., Ni & Co unfilt.	065
14s	Avg. 14n to 14r	**5·43063±0·00002**[a)]
15a	Peaks	5·43065
15b	Peaks	068
15c	Peaks	068
15d	Avg. 15a to 15c	**5·43067±0·00003**[h)]
16a	Avg. 3 films, Cr $K\beta$	**5·43063±0·00016**[i)]
16b	Avg. 5 films, Co $K\alpha_{1,2}$	**5·43051±0·00011**[i)]
16c	Avg. 5 films, Cu $K\alpha_1$	**5·43058±0·00008**[i)]

For explanation of superscripts see the footnote of Table 1.

Table 3. *Compilation of individual results for tungsten*, Å, 25 °C.

Code No.	Observations	Lattice parameter[a)]
1a	Film 1, Obs. *A*	3·16530±0·00020[b)]
1b	Film 1, Obs. *B*	533 030[b)]
1c	Film 2, Obs. *A*	517 018[b)]
1d	Film 2, Obs. *B*	520 018[b)]
1e	Avg. 1a to 1d	**3·16525±0·00022**[c)]
2a	Unicam, undil. spec., 90/120[m)], 1st read.	3·16524
2b	Unicam, undil. spec., 90/120[m)], 2nd read.	508
2c	Unicam, undil. spec., 90/120[m)], 3rd read.	527
2d	Avg. 2a to 2c	*3·16519±0·00008*[l)]
2e	Unicam, dil. spec., 70/130, 1st read.	3·16522
2f	Unicam, dil. spec., 70/130, 2nd read.	515
2g	Unicam, dil. spec., 70/130, 3rd read.	525
2h	Avg. 2e to 2g	*3·16521±0·00004*[l)]
2i	Unicam, dil. spec., 40/260, 1st read.	3·16515
2j	Unicam, dil. spec., 40/260, 2nd read.	511
2k	Unicam, dil. spec., 40/260, 3rd read.	503
2l	Avg. 2i to 2k	*3·16509±0·00005*[l)]
2m	Unicam, dil. spec., 40/260, 1st read.	3·16496
2n	Unicam, dil. spec., 40/260, 2nd read.	504
2o	Unicam, dil. spec., 40/260, 3rd read.	504
2p	Unicam, dil. spec., 40/260, 4th read.	505
2q	Avg. 2m to 2p	*3·16502±0·00004*[l)]
2r	Avg. 2d, 2h, 2l, 2g	**3·16513±0·00005**[f)]
2s	Philips, undil. spec., 110/170, 1st read.	3·16534
2t	Philips, undil. spec., 110/170, 2nd read.	3·16537
2u	Philips, undil. spec., 110/170, 3rd read.	536
2v	Avg. 2s to 2u	*3·16536±0·00002*[l)]
2w	Philips, dil. spec., 160/360, 1st read.	3·16525
2x	Philips, dil. spec., 160/360, 2nd read.	520
2y	Philips, dil. spec., 160/360, 3rd read.	528
2z	Avg. 2w to 2y	*3·16524±0·00003*[l)]
2z′	Avg. 2v and 2z	**3·16530±0·00003**[f)]
3a	Film 1, $(400)\alpha_1$	3·16509
3b	Film 1, $(420)\beta$	525
3c	Film 2, $(400)\alpha_1$	510
3d	Film 2, $(420)\beta$	518
3e	Film 3, $(400)\alpha_1$	512
3f	Film 3, $(420)\beta$	500
3g	Film 4, $(400)\alpha_1$	509
3h	Film 4, $(420)\beta$	520
3i	Film 5, $(400)\alpha_1$	526
3j	Film 5, $(420)\beta$	516
3k	Film 6, $(400)\alpha_1$	510
3l	Film 6, $(420)\beta$	514
3m	Avg. 6 films, $(400)\alpha_1$	*3·16513*[d)]
3n	Avg. 6 films, $(420)\beta$	*3·16515*
3o	Avg. 6 films, $(400)\alpha_1$ and $(420)\beta$	**3·16514±0·00005**[d)]
6a	Film 1, Obs. *A*	3·16500
6b	Film 2, Obs. *A*	483
6c	Film 3, Obs. *A*, 1st read.	466
6d	Film 3, Obs. *A*, 2nd read.	487
6e	Film 4, Obs. *A*	510
6f	Avg. 6a to 6e	*3·16489±0·00013*[e)]
6g	Film 1, Obs. *B*	3·16495
6h	Film 2, Obs. *B*	479
6i	Film 3, Obs. *B*, 1st read.	518
6j	Film 3, Obs. *B*, 2nd read.	557
6k	Film 4, Obs. *B*	505
6l	Avg. 6g to 6k	*3·16511±0·000021*[e)]
6m	Avg. 6f to 6l	**3·16500±0·00008**[f)]
8	(?)	**3·16491±0·00005**[h)]
9a	Avg. 7 films, 2 spec. 0·1 mm., RKU 95 & 114	*3·16531*

Table 3 (*cont.*)

Code No.	Observations	Lattice parameter[a]
9b	Avg. 3 films, 1 spec. 0·1 mm., RKU 95	*3·16530*
9c	Avg. 4 films, 3 spec. 0·1 mm., RKU 95 & 114	*3·16527*
9d	Avg. 2 films, 1 spec. 0·4 mm., RKU 95 & 114	*3·16532*
9e	Avg. 9a to 9d	**3·16530 ± 0·00004**[h]
11	Avg. 3 obs.	**3·16523 ± 0·00004**[f]
12a	Cu $K\alpha_{1,2}$	**3·16531 ± 0·00010**[a]
12b	W $L\alpha_1$	**3·16532 ± 0·00010**[a]
13a	Diffract. method (a)	**3·16528 ± 0·00013**[h]
13b	Diffract. method (b)	**3·16517 ± 0·00007**[h]
13c	D.-S. camera	**3·16533 ± 0·00030**[h]
16a	Avg. 4 films, Co $K\alpha_{1,2}$	**3·16519 ± 0·00006**[i]
16b	Avg. 4 films, Cu $K\alpha_{1,2}$, $K\beta$	**3·16521 ± 0·00007**[i]

For explanation of superscripts see also footnote of Table 1.

The X-ray spectral lines normally used for this application have different breadths and asymmetries (Bearden & Shaw, 1935), which may influence the determination of the reflection angles, and hence the value derived for the lattice parameter. In fact, the $K\alpha_1$, $K\alpha_2$ and $K\beta$ lines from the same target usually show considerable difference. Separate average values are therefore given in Tables 1–2 and Figs. 2–4 for each X-ray tube target used, even though this procedure allowed two or three values from some laboratories. However, the format of some reports did not permit this separation and in no case was it possible to separate data derived from the individual spectral lines of the same target. This problem will have to be considered in future precision work.

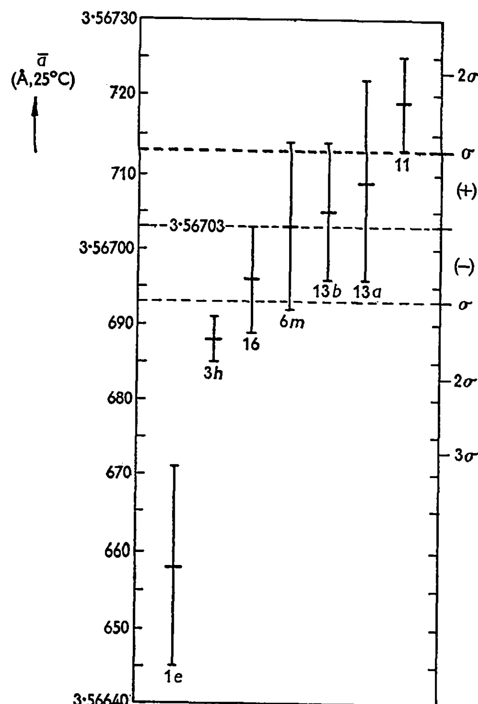

Fig. 2. Distribution of individual mean values (heavy short horizontal lines) of lattice parameter of diamond and ± error limits (vertical lines) reported by various laboratories (Code numbers on bottom). The dotted lines show the composite mean of the mean values and the standard deviation, Code No. 1*e* omitted.

*Thermal expansion**

In most cases the equipments were provided with thermostatic control of the specimen, but in some cases the ambient temperature was controlled and recorded to apply the temperature correction. All measurements were made near room temperature. The coefficient of thermal expansion α was low for all substances: diamond $1·1 \times 10^{-6}$ (Skinner, 1957); silicon $4·2 \times 10^{-6}$ (Straumanis & Aka, 1952); and tungsten $4·3 \times 10^{-6}$ (Michel, 1938). All values listed in the tables have been corrected to 25 °C. by means of the formula

$$a_{T_2} = a_{T_1}[1 + \alpha(T_2 - T_1)] .$$

Refraction

All measurements were corrected for refraction by adding to the lattice parameter obtained from extrapolation or least squares, etc., an amount $(1-n)a$, which can be calculated for cubic crystals from the expression

$$(1-n)a = 4·47 \times 10^{-6}(\lambda/a)^2 \Sigma A ,$$

where n is the refractive index, a the lattice parameter, λ the wavelength in Ånström units, and ΣA the sum of the atomic numbers of the atoms in the unit cell (Lipson & Wilson, 1941). The corrections for Cu $K\alpha$ are: diamond 0·00004, silicon 0·00004, and tungsten 0·00016 Å.

4. Instrumentation and methods

The instruments and methods employed were described in the reports submitted by the various investigators and are abstracted below. When well-known methods were

* *Note Added in Proof.*—The exact value of the coefficient of thermal expansion α of diamond powder at room temperature is not known. Prof. B. Post (private communication, 14 Aug. 1960) using a counter diffractometer obtained an average value $0·33 \times 10^{-6}$ on a clear single crystal plate cut parallel to (111) in the temperature range 100 to 300 °K and found that α was increasing rapidly in the vicinity of room temperature. Skinner (1957) reports an average value of his measurements on single crystals and powders, and those of others, to be $1·06 \times 10^{-6}$ at 25 °C; he obtained $0·844 \times 10^{-6}$ for commercial diamond powder. Straumanis and Aka (1951*b*) give an average value of $1·32 \times 10^{-6}$ for white clear diamond bort in the temperature range 10–50 °C., and Straumanis (1953) gives $1·38 \times 10^{-6}$ for white diamond powder. Dame K. Lonsdale (private communication, 13 June 1960) points out 1) she obtained values of $a = 3·56000 \pm 0·00005$ to $3·55942 \pm 0·00010$ kX. on various diamond single crystals using the divergent beam method, 2) diamonds from different localities may give different values of a and α depending on their impurity content, 3) synthetic diamond powder contains up to about 4% of impurities, mostly Si and Ni.

Dame Lonsdale also notes that there are no X-ray measurements of the thermal expansion of tungsten. The value given by Michel (1938) is $\alpha = 4·3 \times 10^{-6}$ at 100 °C. without giving references, experimental data or other justification. Nix and Mac Nair (*Phys. Rev.* **61**, 74, 1942) obtained a value of $4·7 \times 10^{-6}$ for the range 0 to 27·5 °C. by macroscopic measurements.

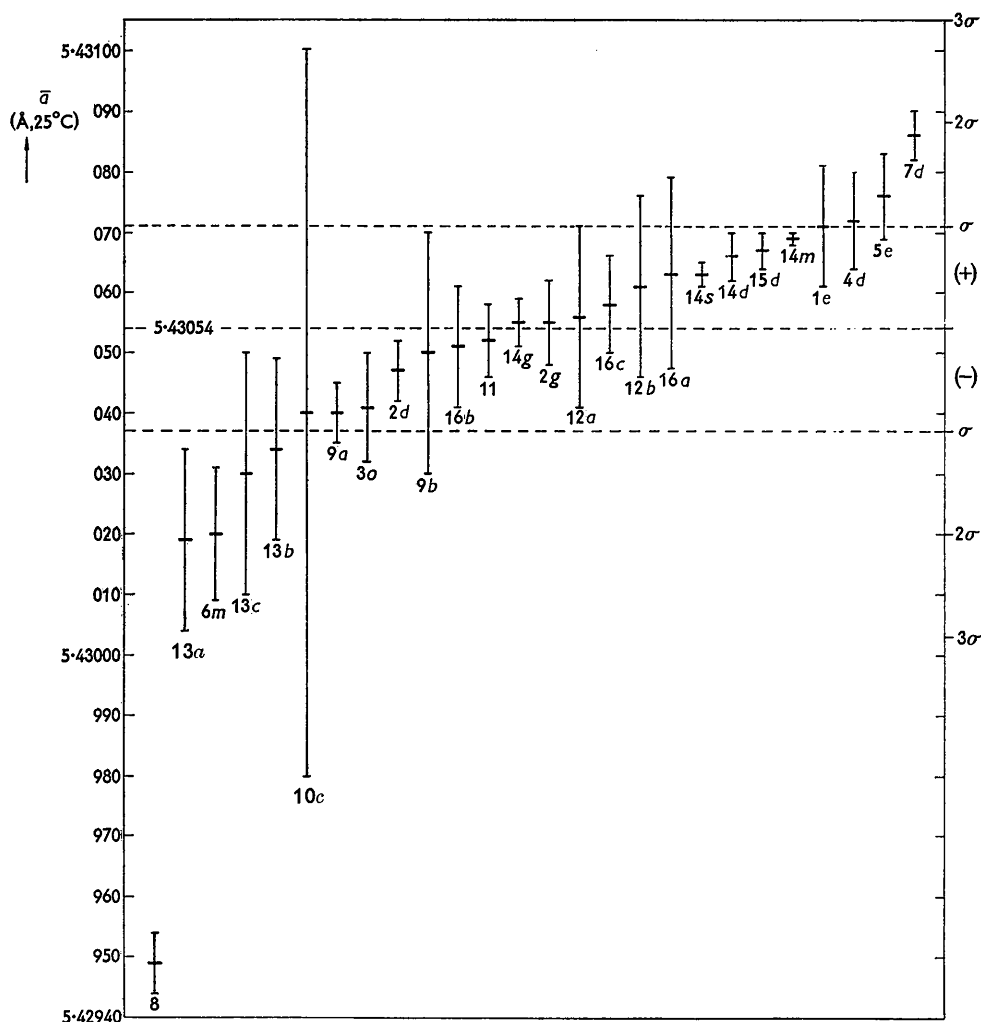

Fig. 3. Distribution of individual mean values (heavy short horizontal lines) of lattice parameter of silicon and ± error limits (vertical lines) reported by various laboratories (Code numbers on bottom). The dotted lines show the composite mean of the mean values and the standard deviation, Code No. 8 omitted.

used the descriptions have been limited to the information pertinent to the proper understanding of the conditions employed. Rather longer descriptions are given for the less well-known methods. The size of the camera is always indicated by the diameter in centimeters or the specimen-to-film distance in the flat-cassette cameras.

Cylindrical Debye–Scherrer cameras were used for most of the work: 19 cm. (6 sets of data), 11·46 cm. (14), 9 cm. (2), and 6·4 cm. (5); symmetrical back-reflection focussing camera (4), flat cassette in back-reflection (5), focussing-monochromator camera (1), and counter diffractometer (5). This section is thus a compilation of the methods currently employed with film instrumentation for precision lattice-parameter determination.

Unless otherwise stated extrapolations refer to the linear extrapolation of the data to $2\theta = 180°$ using the function

$$\xi = \tfrac{1}{2}[(\cos^2\theta)/(\sin\theta) + (\cos^2\theta)/(\theta)]$$

derived by Taylor & Sinclair (1945) and Nelson & Riley (1945). Those cases where the higher-angle reflections were weighted (Hess, 1951) are indicated. Not all the investigators used extrapolation methods and at the Stockholm Conferences a number of speakers debated the value of such procedures.

A code number is used for each laboratory only to facilitate identification of the data in the tables and figures with their source, and the number has no other meaning. The code number usually is followed by a letter to separate the individual sets of data from the same laboratory.

Code No. 1

W. G. Perdok, Kristallografisch Instituut, Rijksuniversiteit, Groningen, the Netherlands.

Unicam S70 camera, 19 cm. modified and calibrated by De Boer (1957) for precision measurements. Specimen thermostatically controlled at 25° ± 0·05 °C. Radiation: Cu $K\alpha_{1,2}$.

Visual comparator readings of films to 0·001 mm. Two films of the same specimen of each substance

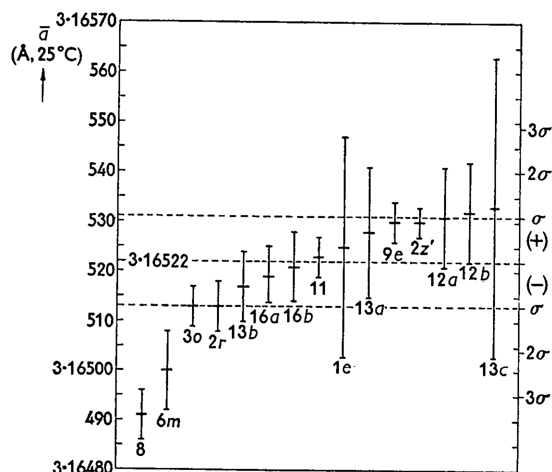

Fig. 4. Distribution of individual mean values (heavy short horizontal lines) of lattice parameter of tungsten and ± error limits (vertical lines) reported by various laboratories (Code numbers on bottom). The dotted lines show the composite mean of the mean values and the standard deviation, Code No. 8 omitted.

measured by two observers. Lines measured: diamond (331), (400); silicon (444), (531), (620); tungsten (400), (321).

Least-squares method (Cohen, 1935) applied without weighting using

$$A_0\alpha_i + Dd_i = \sin^2 \theta_{(\text{calc.})} .$$

The error limits in the lattice parameter (Jette & Foote, 1935) were calculated from the variance of

$$\Delta \sin^2 \theta = \sin^2 \theta_{(\text{calc.})} - \sin^2 \theta_{(\text{meas.})} .$$

The error limits of the average values were calculated from the variance of the variances of the different films.

Code No. 2

M. H. Francombe (silicon) and A. A. Balchin (tungsten), Research Laboratory, The General Electric Co., Ltd., Wembley, U.K.

Two cameras: Unicam 19 cm. and Philips (Parrish & Cisney, 1948) 11·46 cm. Unicam calibrated by direct measurement of knife edges to 3 parts in 10^5 (Lipson & Wilson, 1941). Unicam aperture about 1·6°; 'high-resolution' collimator used in Philips camera. Specimens centered with low-power microscope. Room temperature control; estimate of specimen temperature to about 1 °C. for silicon and ±0·1 °C. for tungsten. Cu $K\alpha_{1,2}$, Cu $K\beta$. Films measured with travelling microscope and vernier reading to 0·01 mm. Corrections were applied for film shrinkage, which was assumed to be uniform. Films of silicon read by 2 or 3 different observers, each observer repeating readings twice. Films of tungsten read 3 or 4 times by same observer; readings checked by differences and those with inconsistencies were repeated.

Silicon mixed with equal volume of gum tragacanth, mounted on 0·07 to 0·12 mm. diameter Lindemann-glass fibres; overall specimen diameter 0·20 to 0·28 mm., the smaller sizes used in Philips camera. Tungsten prepared undiluted and also diluted with three volumes of gum tragacanth and several fibre diameters used.

Silicon: extrapolations without weighting of all values of $\xi < 0·33$. Error limits based on maximum difference between extrapolated values obtained by each camera (Unicam, 0·00006 Å; Philips, 0·00008 Å), errors in the extrapolation procedure and those due to temperature control (±0·00002 Å). Tungsten: extrapolations with each value weighted (Hess, 1951) proportional to $csc^2(180° - 2\theta)$ for $\xi < 0·5$. Error limits correspond approximately to the deviations of results of different readings from the mean value of a single film. The limits of the average value of all the averages was computed as the standard deviation.

Code No. 3

M. E. Straumanis and W. J. James, School of Mines and Metallurgy, University of Missouri, Rolla, Missouri, U.S.A.

Straumanis (1949) precision 6·4 cm. camera. Specimen temperature thermostatically controlled to 30±0·02 °C. (Straumanis, 1953).

Precision film-measuring device (Straumanis, 1953). Each film measured twice, once by each investigator. φ-angle given to 0·0001°, although differences exceeding 0·05° are listed for some readings. Six films of the same specimen mount obtained for each of the three substances. Diamond: Co $K\beta$ (331); values listed in Table 1 were calculated from the mean φ-angle obtained by both investigators on each film. Silicon: Cu $K\alpha_1$ (444); values listed in Table 2 were calculated from φ-angles measured by each investigator. Tungsten: Cu $K\alpha_1$ (400) and Cu $K\beta$ (420); values listed in Table 3 were calculated from the mean φ-angle of each reflection measured by both investigators on each film.

Specimens mounted on Lindemann-glass fibres 0·09 mm. diameter using a thin layer of a mixture of oil and stopcock grease. Overall specimen diameters 0·12 mm. for silicon and diamond, 0·10 to 0·11 mm. for tungsten.

Lattice parameters calculated from mean observed φ-angles of a single reflection on each film of diamond and silicon, and two reflections of tungsten. The error limits of the final average value are given in terms of the probable error. No extrapolations used and no corrections applied for systematic errors as investigators state such errors are negligible in their method. For further details of this widely used method, see Straumanis & Ieviņš (1940), Straumanis (1949, 1953).

Code No. 4

J. Adam, Metallurgy Division, Atomic Energy Research Establishment, Harwell, Didcot, Berks, U.K..

Precision 19 cm. camera calibrated to 0·002° (Adam, 1954). Specimen temperature controlled to ±0·2 °C. Cu K unfiltered.

To avoid errors due to non-uniform film shrinkage a scale from an accurate glass negative was printed on each film before processing and was subsequently used as a reference. A series of measurements showed that the greatest deviations from uniform film shrinkage occurred at the ends of the film, and therefore are probably associated with the drying process. Film measuring device constructed in their laboratory uses an illuminated glass fibre projected onto the film as a reference line. Measurements were made with respect to the printed scale on each film. Stated accuracy

attainable $\pm 0{\cdot}005$ mm. and reproducibility on sharp X-ray lines $\pm 0{\cdot}01$ mm.

Specimen powder placed in thin-walled silica capillary 0·3 mm. diameter and 10 mm. long.

Extrapolation to $\theta = 90°$. Error limits given as the maximum deviation.

Code No. 5

L. E. Alexander and G. G. Summer, Department of Research in Chemical Physics, Mellon Institute of Industrial Research, Pittsburgh 13, Pennsylvania, U.S.A.

Norelco 11·46 cm. standard camera (Parrish & Cisney, 1948). Temperature controlled to $22{\cdot}8 \pm 0{\cdot}5$ °C. by regulating air-conditioning of laboratory. Exposures 12 hr. Cu $K\alpha_{1,2}$.

Device for measuring films improved over one previously described (Klug & Alexander, 1954, p. 322). Precision $\pm 0{\cdot}01$ mm. attainable but quality of films reduced precision to about $\pm 0{\cdot}02$ mm. Two films of two specimen mounts, each measured by both authors.

Specimen powder packed in thin-walled glass capillaries 0·3 mm. inside diameter. Powder was ground to eliminate larger particles.

Extrapolated best straight line based on points with $\xi < 0{\cdot}8$, giving most weight to points from resolved lines. The error limits are estimated.

Code No. 6

Karl E. Beu, Physical Measurements Department, Goodyear Atomic Corp., Portsmouth, Ohio, U.S.A.

Norelco 11·46 cm. standard camera and collimator. Line focus of X-ray tube used to obtain sharper rings than could be obtained with square focus (but no special correction appears to have been made to allow for the increased axial divergence). Room temperature recorded adjacent to camera during exposure, and average specimen temperature taken as one-half of the sum of the extremes. Cu $K\alpha_{1,2}$, Cu $K\beta$.

Norelco film-measuring device reading directly to 0·05 mm. and estimates made to one-half this value; linearity of scale not checked. Four of five films prepared from one specimen mount of each substance. Four investigators measured the films of silicon and two measured the films of diamond and tungsten.

Undiluted powders packed in thin-walled glass capillaries 0·2 mm. inside diameter. Two straight extrapolation lines, one of maximum and the other of minimum slope were drawn through all points with $\xi < 0{\cdot}33$, without weighting. The lattice parameter for each determination was taken as the value lying midway between the intercepts of these lines at $\xi = 0$. Standard deviations and 95% confidence limits were calculated from 10 such determinations each for diamond and tungsten and 9 for silicon, and the type of error limits is indicated in the tables; the error limits in the figures represent standard deviations.

Code No. 7

B. M. Rovinskij and E. P. Kostjukova, Institute of Machine Sciences, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

Precision back-reflection flat-cassette camera with specimen-to-film distance about 6 cm. Collimator consists of two parallel slits 0·008 cm. wide and 4 cm. apart. Room temperature controlled and average specimen temperature estimated to $\pm 0{\cdot}5$ °C. in one exposure and $\pm 0{\cdot}2$ °C. in other two exposures. Specimen and film rotated. Emulsion on one side of double-coated film removed. Exposures 10 to 16 hr. Cu $K\alpha_1$.

Films measured with comparator (I3A–2) to 0·001 mm. Diameter of each ring measured 30 times on each of 3 photographs. Two reflections (533) and (444) were used.

Powder mixed with amyl acetate binder and prepared as a flat surface 0·6 cm. diameter, 0·05 cm. thick.

Writers state the ratio of the diameters of two arbitrarily chosen Debye–Scherrer rings in the back-reflection region is independent of sample-to-film distance, film shrinkage and similar factors, so that

$$d_1(h_1k_1l_1)/d_2(h_2k_2l_2) = \tan(\pi - 2\theta_1)/\tan(\pi - 2\theta_2) = f(a) = K\,.$$

A graphical plot was used to determine $K = d(533)/d(444)$, using the mean values of the 30 readings. They assume instrumental and geometrical errors to cause $< 0{\cdot}00001$ Å error in the lattice parameter and thus no corrections are required. A description of the method has recently been published in English (Rovinskij & Kostiukova, 1958, see also Rovinskij, 1940).

Code No. 8

A. F. Ieviņš, Chemistry Department, Latvian State University, Riga, Latvian S.S.R., U.S.S.R.

Debye–Scherrer 6·3 cm. camera (Straumanis & Ieviņš, 1940) with cylindrical 0·08 cm. diameter diaphragm. Measurements on silicon made at 21·8 °C., and those on tungsten at 27·25 °C. Cu $K\alpha_1$ for silicon and Ni $K\alpha_1$ for tungsten.

Film-measuring device stated to have precision of 0·01 mm.

Silicon powder mounted on Lindemann glass fibre 0·07 mm. diameter and overall specimen diameter was 0·1 mm.

No extrapolations used. Lattice parameter determined from single line: (444) for silicon, (331) for tungsten.

[Author's note: No details are available as to the number of films, calculation of error limits, wavelengths used, etc.]

Code No. 9

M. M. Umanskij, Z. K. Zolina and V. V. Zubenko, Department of Solid State Physics, Moscow State University, Moscow, U.S.S.R.

Three types of powder cameras were used:

RKU–95. Debye–Scherrer cylindrical camera 9·56 cm. with Straumanis film mounting. Collimator consists of two 0·8 mm. diameter diaphragms 5·5 cm. apart; two 0·5 mm. diameter diaphragms 4 cm. apart used for angles $> 174°$ 2θ. Line breadth 0·1 to 0·2 mm. and $K\alpha$-doublet separation becomes apparent at about 80° (2θ). Temperature of air in camera controlled to 0·1 to 0·2 °C. with potentiometer and thermocouples in contact with camera body; temperature read with glass thermometer to 0·1 °C. Specimens prepared by packing powder into celluloid(?) capillary 0·10 to 0·15 mm. internal diameter, mounted on goniometer head, and rotated by motor outside thermostat. Tungsten measurements made on large camera of similar design—RKU-114, 11·46 cm. diameter.

RKF–86–*T*/2. Symmetrical back-reflection focussing

camera (Zubenko & Umanskij, 1956). Entrance slit 0·2 by 0·2 mm. on focussing circle and line widths up to 0·3 mm. Angular range 120–176°(2θ). Entire camera together with specimen and film are placed in a thermostat which controls temperature to $\pm 0{\cdot}1$ °C. Effective camera diameter determined from two pairs of light marks recorded on film at the temperature of the investigation. Film pressed against camera body but ends not rigidly fastened to allow for thermal expansion of film. Double-coated film used and the back emulsion removed.

KMSP/1. Focussing quartz crystal (10·1) monochromator with camera body diameter 17·19 cm. ($2\pi R = 54$ cm., $1°\theta = 12$ mm. on film), in symmetrical focussing arrangement (Kvitka, Kolontsova & Umanskij, 1952). Effective camera diameter determined from pairs of light marks. No thermostatic control and only those films used in which the temperature variation was < 1 °C. during the exposure as determined from measurements of the camera body.

Films measured with a comparator having a precision of 0·001 mm. and a magnification of $2\times$ or $6\times$. Each line was measured 3 to 10 times by each of the three investigators. The maximum differences did not exceed 0·03 mm. and the average observed θ-angles were used for the calculations. The average deviation of lines measured were: RKU 10 to 20 sec., RKF 30 sec., KMSP 20 sec. The effective film length was measured twice, before and after measuring the lines, to a precision of 0·02 mm. Calculations done with electric desk calculator and seven-place trigonometric tables.

Silicon: Two RKU cameras used to obtain 5 films with Cu K and 2 films with Co K at various temperatures around 25 °C. Extrapolations used for lines with $\xi < 0{\cdot}32$. RKF films not used because the lines were too spotty for accurate measurements. The KMSP camera was used for 3 films using Cu K and the extrapolation function $\varphi \tan \varphi (< 0{\cdot}5)$. Tungsten: Three series of films obtained using RKU–95–114 and RKF–86 cameras, 0·1 and 0·4 mm. diameter samples for former two and flat sample for latter, Cu K, 25 °C. Each film was measured 3 or 6 times, the average θ for each line calculated from each series of films and extrapolations used to determine the lattice parameters.

Code No. 10

J. L. Amorós, Cátedra de Cristalografiá, Museo de Ciencias Naturales, Madrid, Spain.

Standard Philips camera, 11·46 cm. Six films using the 'coarse' and 3 films with the 'fine' collimator were measured. Best line drawn through experimental values of a plotted against 2θ and extrapolated to $2\theta = 180°$.

Code No. 11

C. F. Kempter, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.

Norelco symmetrical back-reflection focussing camera, 12 cm. Temperature about 25 °C. Cu $K\alpha_{1,2}$.

Norelco film-measuring device with fluorescent tube substituted for Lumiline lamp. Film allowed to come to constant temperature with unit on for one hour before measuring. Film shrinkage determined from fiducial edges of camera which are in contact with film. Double-coated film used and back emulsion removed (Parrish, 1955). Three investigators measured each film. Diamond (400), (331); silicon (620), (533), (444); tungsten (321), (400).

Powder screened through 325-mesh screen and thin layer sprinkled on cardboard coated with rubber cement.

The lattice parameters and their standard deviations were determined on an I.B.M. 704 computer (Vogel & Kempter, 1959) assuming all systematic errors in a were directly proportional to $\varphi \tan \varphi$.

Code No. 12

C. M. Mitchell, Physical Metallurgy Division, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada.

Modified Norelco 11·46 cm. camera (Mitchell, 1952). Collimator is a 3° tapered slit with smallest opening 0·11 by 3·0 mm. set at film cylinder. Source-to-specimen distance R_1 was equal to the camera radius R_0. The square focus of the X-ray tube is used. A small auxiliary camera attached to the exit port is used to photograph the emergent beam in order to check axial alignment and to measure irradiated specimen length. Camera specimen shaft concentricity checked to $\pm 0{\cdot}005$ mm. Specimen mounted in universal specimen chuck containing thermocouple, and aligned with cathetometer. With specimens of high absorption, sharp ('focussed') lines are obtained over the low-2θ range. The optimum value of specimen diameter for minimum exposure time is four times the slit width for slit widths with aperture $< 0{\cdot}2°$. Accuracy of line-center measurement in the low-2θ range is independent of specimen diameter and proportional to slit width. Specimen temperature regulated to $\pm 0{\cdot}10$ °C. in the range 30° to 31° for periods of 24 to 36 hr. Silicon: Cu and Cr $K\alpha_{1,2}, K\beta$; tungsten Cu $K\alpha_{1,2}$, W $L\alpha_1(\lambda = 1{\cdot}47635$ Å).

Films measured with Cambridge Universal Measuring Machine accurate to 0·002 mm. Each film measured twice with forward- and back-reflection regions reversed. The diffraction-line centers and film axis were checked for systematic errors produced by film misalignment in the camera. All lines on each film used.

Powder packed in Lindemann-glass capillary of 0·01 mm. wall thickness and diameter tapered less than 0·005 mm. per cm. of length. Specimen density determined by weighing and dimensions of capillary, and linear absorption coefficient calculated.

Systematic errors are assumed to be caused primarily by specimen absorption effects. Assuming symmetrical intensity distributions in the source and the characteristic X-ray lines, the Warren (1945) (first equation below) correction can be applied directly. The $q_0(=1/a^2)$ value for a was corrected for each (hkl) line, plotted against the Warren relation and resulted in a straight line with small negative slope. The residual slope is believed to have been due to inaccurate measurement of the specimen diameter arising from the particle sizes. The experimental data show that direct extraction of the absorption displacement term gives precision values over the whole pattern, approaching the limit set by the accuracy of the film measurements. The systematic absorption error relations (Mitchell, 1960) used were

$$\frac{\delta q}{q} = \left[r_s \left(\frac{1}{R_0} + \frac{1}{R_1} \right) F(\theta) \right] - \left[\frac{1}{2\mu_m \varrho} \left(\frac{1}{R_0} + \frac{1}{R_1} \right) A(\theta) \right]$$

$$F(\theta) = \cot \theta \cdot \frac{\cos \theta}{4} \left[\frac{\sin 2\theta - 2\theta \cos 2\theta}{\sin \theta - \cos^2 \theta \log_e \tan (\frac{1}{4}\pi + \frac{1}{2}\theta)} \right]$$

$$A(\theta) = \left[\frac{\cot\theta \, . \frac{2}{3} \sin^2\theta \cos\theta}{\sin\theta - \cos^2\theta \log_e \tan(\frac{1}{4}\pi + \frac{1}{2}\theta)}\right] - \cot^2\theta \cot^2\theta$$

where r_s is the specimen length, μ_m the mass absorption coefficient and ϱ the specimen density.

The root-mean-square deviation of d was $\delta d/d = 1/15{,}000$ for $2\theta > 100°$ and $1/5000$ for $2\theta > 40°$, except for silicon with Cu K at the limit $\mu r \approx 1$ where $1/2000$ for $2\theta > 40°$.

Code No. 13

M. Tournarie, Commissariat de l'Energie Atomique, Centre d'Études Nucléaires de Saclay, Gif-Sur-Yvette, S. et O., France.

Norelco diffractometer (Parrish, Hamacher & Lowitzsch, 1954) with Philips generator. Cu K, angle of view 3°, angular apertures 0·5°, 1°, 4°, receiving slit 0·15°. Angular calibration with knife edge (Tournarie, 1954*a*). MECl Speedomax recorder modified for automatic marking of angles in 0·1° or 0·02°(2θ) increments by rapid lateral movement of recorder pen. Geiger counter, scanning speed $\frac{1}{8}°(2\theta)$ min.$^{-1}$. Ratemeter (intégrateur C.E.A.) modified so that 2% probable-error fluctuation is obtained when the full-scale reading is 1000 counts sec.$^{-1}$ with a 5·6 sec. time constant, and 300 counts sec.$^{-1}$ with a 19 sec. time constant. Each reflection corrected for time-constant displacement (Tournarie, 1954*b*).

Thin specimens $< 50\mu$ were prepared by mixing the powder with amorphous Seccotine and spreading on a glass plate. The position of the effective reflecting surface could be estimated to better than 25μ. The correction for displacement of the specimen surface from the goniometer axis of rotation was made by extrapolation of $\lambda^2/2a^2$ of each reflection against $\cos^2\theta/\sin\theta$. If the slope of the extrapolated line indicated the displacement was $> 20\mu$, the specimen was translated the required amount and direction. (This method is susceptible to considerable error if the angular calibration is incorrect.) This method is listed as 13*a*, and in an alternative method 13*b*, the specimen position was adjusted with a micrometer prior to making the recording.

When the $K\alpha_{1,2}$ doublet was fairly well resolved, the center of a horizontal chord drawn at 60·3% of the peak height of the $K\alpha_1$ line was taken as the reflection angle. The author states this point corresponds sufficiently well with the centroid of the reflection. (The wavelengths used, however, are the same as those used by the other investigators.)

A Philips 11·46 cm. powder camera modified for regulating the specimen temperature to ±2 °C. was also used. The square X-ray focus was viewed at 6°.

Code No. 14

H. Weyerer, Physikalisch-Technische Bundesanstalt, Braunschweig, Germany.

Used three camera methods and separate results were reported for each.

1) Debye–Scherrer, 5·7 cm., Straumanis film mount, collimator design of Parrish & Cisney (1948) with 0·3 by 1·2 mm. slit and 0·5 mm. diameter diaphragm. Specimen mounted on 0·09 mm. Lindemann-glass fibre with overall diameter 0·2 mm. $\cos^2\theta$ extrapolation. For further details see Weyerer (1956*a*).

2) Flat rotating specimen and flat film back-reflection method. Single slit 0·3 by 1·2 mm., film-to-specimen distance 5·01 cm., film shrinkage determined from light marks to 0·01 mm. $\tan\varphi . \sin 4\varphi$ extrapolation. For further details see Weyerer (1956*c*).

3) Symmetrical back-reflection focussing camera, 5·7 cm. with 0·2 mm. wide slit. Specimen oscillated during exposure. Specimen surface moved back 0·21 mm. to compensate for film emulsion thickness. $\cos^2\theta$ extrapolation. For further details see Weyerer (1956*b*), where, however, $\varphi \tan\varphi$ extrapolation was used.

Cameras placed in vacuum thermostat regulated to ±0·02 °C. (Weyerer, 1955); exposures made nearly at 25 °C. so that no temperature corrections were required.

Five films were obtained with each method and measured on a precision device (Hoffrogge & Weyerer, 1954). Three different observers measured each line five times and the measurements were repeated after several weeks. The differences among the observers were less than the systematic errors. The average values were used for the calculations.

In most cases all films were exposed successively to unfiltered Ni K and Co K radiations and Cu K with Ni filter. A *single* extrapolation line was drawn through all reflections from all the wavelengths for each film. An average refraction correction of +0·00005 was then applied to the extrapolated value. The averages were calculated as the arithmetic mean. In computing the error limits the extrapolated value from each film was given a weight equal to the number of X-ray tubes used to obtain that film, i.e., 1 for Cu tube filtered or unfiltered, 3 for Cu, Ni and Co, etc. In the tables and figures it was not possible to separate the values obtained with the different radiations, except in the one case where only Cu K was used, and hence the mean values are separated only on the basis of methods used.

Code No. 15

R. A. Coyle and R. I. Garrod, Aeronautical Research Laboratories, Melbourne, Australia.

Philips diffractometer, angular aperture 4°, receiving slit 0·2°. Zero angle calibrated with knife edge (Tournarie, 1954*a*) and drift was less than 0·001°(2θ). Cu $K\alpha_1$. Mullard MX 118 Geiger counter. Manual goniometer settings and fixed-time measurements of lines, each set of lines measured three times. Specimen rotated in its own plane and temperature maintained to ±0·25 °C. during measurements. Silicon mixed with collodion diluted with amyl acetate, packed into 9/16 inch diameter Perspex mount, 0·020 inch thick, and levelled after drying. Peak angles used. $\cos^2\theta$ extrapolation of (444), (533), (620) and (531) lines. Some attempts were made to reduce the axial ('vertical') divergence and to use the centroid instead of the peak; these results are not included because they were preliminary.

Code No. 16

M. Wilkens, Institut für Metallphysik am Max Planck Institut für Metallforschung, Stuttgart, Germany.

Back-reflection flat-cassette camera. Horizontal and vertical divergence of primary beam limited to 0·4° (semi-angle) to avoid corrections. Specimen and film planes adjusted parallel to each other to better than 0·05° by means of two flat mirrors which take their place during alignment. Specimen-to-film distance (about 6 cm.) measured to 10μ with a vernier bar fixed to the cassette and a glass slide in place of the specimen, whose

position could be adjusted until a plastic film could be moved between the vernier bar and glass slide without excessive friction. Specimen mounted in holder which permits $\pm 2°$ precession about an axis in the specimen plane, and rotated continuously during exposure. Double-coated film used and only front side developed. Film and specimen mounted in brass cover whose hollow walls are warmed with water and temperature kept constant to at least within 0·05 °C. at about 25 °C.

A system of reference marks was exposed on the film before development and was measured with a comparator to 3μ. The films were measured with a special glass rod having 1 mm. divisions and a dial micrometer reading to 10μ. The rod was positioned with the upper part of the markings lined up with the diffraction ring. To eliminate the effect of film graininess, each film was measured at 5 different diameters at or near the equator and each measurement consisted of 5 to 10 detailed measurements. With strong sharp lines and 5 different exposures of each specimen the ring radius could be determined with a standard deviation of approximately 50μ.

Specimens prepared by sprinkling powder on a flat glass slide covered with a glue to make a translucent layer 20 to 30μ thick.

The errors were estimated as follows: film-to-specimen distance $\pm 0{\cdot}4 \times 10^{-5}$, film shrinkage $\pm 0{\cdot}4 \times 10^{-5}$, ring radius $\pm 0{\cdot}7 \times 10^{-5}$, for a total of $\pm 1{\cdot}5 \times 10^{-5}$.

Diamond: Co $K\beta$ (331) 7 films; silicon: Cr $K\beta$ (333/511) 3 films, Co $K\alpha_{1,2}$ (531) 5 films, Cu $K\alpha_1$ (444) 5 films; tungsten: Co $K\alpha_{1,2}$ (222) 4 films, Cu $K\alpha_{1,2}$ (400) 4 films, Cu $K\beta$ (420) 4 films.

5. Results

The reported individual results are listed in Tables 1, 2 and 3 for diamond, silicon and tungsten, respectively. The **bold-face** values are the arithmetic means of one or more series of values for each code number used for Figs. 2–4 and to compile the composite averages given below. When a laboratory used two or more different techniques or X-ray tube targets, two or more separate average values were listed for that code number, as for example **13a** and **13b** in Table 1. However, if two or more cameras of the same type, films, samples, observers, etc., were used, these averages are shown in *italics*, but such averages were not used separately in compiling the composite averages; see for example *6f* and *6l* in Table 1. In some cases the original reported data could not be separated into these two categories and are reported as a single average value, as for example **14d** in Table 2. The use of two or more average values from the same laboratory instead of only one value had practically no effect on the composite averages; diamond and tungsten were unchanged and the silicon value was changed by only 1 in the fifth decimal.

The lattice parameters were generally reported to five decimal places and when the fifth decimal was not reported an x was inserted to avoid confusion. The $\pm$ error is that reported by the investigator and is explained in the footnote to the tables. The standard deviation σ used below for the composite averages was calculated from the formula

$$\sigma = [1/(n-1) \sum_{j=1}^{n} (x_j - \overline{x})^2]^{\frac{1}{2}} ,$$

where x is the arithmetic mean and n is the number of independent measurements (Kendall, 1946).

Diamond

Six laboratories reported, five of which used cameras to obtain about 22 films read by 10 observers. Using seven average values the composite arithmetic mean and standard deviation were $3{\cdot}56697 \pm 0{\cdot}00018$. The difference between the largest and smallest average value was 0·00061 (0·017%). One value (**1e**) deviated from the average value by greater than 3σ, and if this is omitted the values become:

$$\mathbf{3{\cdot}56703 \pm 0{\cdot}00010} \quad (0{\cdot}009\%) .$$

Some previous precision measurements on diamond powder have been reported by Riley (1944), $3{\cdot}56687 \pm 0{\cdot}0001x$; Straumanis & Aka (1951), $3{\cdot}56679 \pm 0{\cdot}00016$; and Skinner (1957), $3{\cdot}56688 \pm 0{\cdot}00009$; the average of these three measurements is 3·56685, or 0·005% lower than the composite average value given above.

Silicon

Sixteen laboratories reported and only two of these used the diffractometer. About 77 films were read by 33 observers. Using 26 average values the composite arithmetic mean, standard deviation and % agreement were $5{\cdot}43050 \pm 0{\cdot}00026$ (0·025%). If value (**8**) is omitted because of its large deviation from the mean, the values become:

$$\mathbf{5{\cdot}43054 \pm 0{\cdot}00017} \quad (0{\cdot}012\%) .$$

Some previous precision measurements on silicon powder have been reported by Jette & Foote (1935), $5{\cdot}43077 \pm 0{\cdot}00034$; Straumanis & Ieviņš (1940), $5{\cdot}43074 \pm 0{\cdot}00005$; Lipson & Rogers (1944), $5{\cdot}43072 \pm 0{\cdot}00005$; Straumanis & Aka (1952), $5{\cdot}43097 \pm 0{\cdot}00003$; and Smakula & Kalnajs (1955), $5{\cdot}43068 \pm 0{\cdot}00001$; the average of these five values is 5·43078, or 0·004% larger than the composite average value given above.

Tungsten

Ten laboratories reported, and only one used the diffractometer. About 43 films were read by 20 observers. Using 15 average values the composite arithmetic mean, standard deviation and % agreement were $3{\cdot}16520 \pm 0{\cdot}00012$ (0·013%). If value (**8**) is omitted because it deviates from the mean by more than 3σ, the values become:

$$\mathbf{3{\cdot}16522 \pm 0{\cdot}00009} \quad (0{\cdot}010\%) .$$

Some previous precision measurements on tungsten powder have been reported by Jette & Foote (1935), $3{\cdot}16475 \pm 0{\cdot}00012$; Straumanis & Ieviņš (1936), $3{\cdot}1651x \pm 0{\cdot}0002x$; Lu & Chang (1941), $3{\cdot}1650x$; Swanson & Tatge (1953), $3{\cdot}1648x$; the average of these four values is 3·16491, or 0·01% smaller than the composite average value given above.

6. Conclusions

The percent agreement or spread of the reported mean values for each of the three substances was about 0·01%, a surprisingly poor agreement considering the experience of most of the participants. The reported small $\pm$ values of most of the individual mean values indicated that most

of the laboratories had much more confidence in their results than was justified by the spread among the laboratories. Of course most of the results were reported without the knowledge of the reports of the others.

All the participants made great efforts to minimize the accidental or random errors and their small $\pm$ values are mainly a measure of the reproducibility of their determinations. They also tried to reduce the systematic errors by use of extrapolation procedures, special experimental methods and other means, and it is likely that in this case they were less successful. The large spread among the reported mean values indicates that the systematic errors were not in all cases properly taken into account. The standard deviations calculated for the composite averages are thus a measure of the systematic and random errors and probably are principally systematic errors.

There is always a question as to the significance in applying statistical analysis to a relatively small number of observations, particularly if the form and nature of the error distributions are unknown. Nevertheless, the standard deviation serves as some measure of the confidence one should place in the determination. In the present results 3 of the 7 mean values of diamond deviated by more than σ from the composite average; 8 of 26 mean values of silicon and 4 of 15 mean values of tungsten exceeded σ. In each substance one value exceeded 3σ. One should expect about one-third of the determinations to exceed σ in a normal error distribution and the distribution of mean values is not inconsistent with such a distribution. It would thus appear that the individual treatments of the systematic errors resulted in a normal error distribution. This may mean that the computed composite averages are close to the 'correct' lattice parameters, although the confidence in these values should not be greater than that indicated by the standard deviation. There is even a possibility that the 'correct' value lies outside the standard deviation.

A study of the data separated on the basis of methods and instrumentation failed to reveal an obvious reason for the large spread, nor could any definite conclusion be drawn as to the advisability (or inadvisability) of using extrapolation procedures, least-squares analysis, *etc.* A wide range of film instruments and methods were used and no one method could be shown to yield results superior to the others. It was concluded at the Stockholm Conference that it would be desirable to study further the possible sources of the systematic errors before continuing with this project.

There also appears to be some confusion as to the significance of the *reproducibility* of measurements and the *accuracy* of the data. In this connection it appears appropriate to recall the Emperor of China story attributed to the astronomer Kapteyn, for which I am indebted to Prof. G. Uhlenbeck. The exact height of the Emperor could be obtained by asking each of the 500,000,000 Chinese to guess at his height. It was not necessary for any of his subjects to have seen him, or even his picture, because the application of statistical methods to so many 'individual observations' would give an answer for the Emperor's height to a precision of a few microns, or perhaps a few atom diameters! It is clear that millions of measurements of say a table with a meter stick will not give an average measurement accurate to an Ångström unit.

We are indebted to the many investigators who collaborated in this project. Members of the previous (1954–57) Commission on Crystallographic Apparatus offered useful suggestions for the organization of the project and members of the present Commission, Dr D. W. Smits and project collaborators kindly reviewed the first draft of the manuscript. Prof. R. W. G. Wyckoff and Dr A. C. Simonpietri (Office of Foreign Relations of U.S. National Research Council) arranged with the U.S. Department of State to ship the specimens abroad. The generous support of Philips Laboratories which provided funds for the purchase of the specimens, analyses and clerical aid, is deeply appreciated. Mr R. C. Hughes and Dr R. C. Sweet of this Laboratory made the chemical analyses.

References

ADAM, J. (1954). *J. Sci. Instrum.* **31**, 131.

AZÁROFF, L. V. & BUERGER, M. J. (1958). *The Powder Method in X-ray Crystallography*, chaps. 14 and 15. New York: Wiley.

BEARDEN, J. A. & SHAW, C. H. (1935). *Phys. Rev.* **48**, 18.

BEARDEN, J. A. & THOMSEN, J. S. (1959). *Amer. J. Phys.* **27**, 569.

CAUCHOIS, Y. & HULUBEI, H. (1947). *Longeurs d'Onde des Emissions X et des Discontinuites d'Absorption X.* Paris: Hermann & Cie.

COHEN, M. U. (1935). *Rev. Sci. Instrum.* **6**, 68.

COHEN, M. U. (1936). *Rev. Sci. Instrum.* **7**, 155.

DE BOER, TJ. H. (1957). Dissertation, Rijksuniversiteit te Groningen, Netherlands.

DUMOND, J. W. M. (1959). *Proc. Nat. Acad. Sci. Wash.* **45**, 1052.

HESS, J. B. (1951). *Acta Cryst.* **4**, 109.

HOFFROGGE, C. & WEYERER, H. (1954). *Z. angew. Phys.* **6**, 419.

JETTE, E. R. & FOOTE, F. (1935). *J. Chem. Phys.* **3**, 605.

KENDALL, M. G. (1946). *The Advanced Theory of Statistics*, vol. 2, chap. 17. London: Griffin.

KLUG, H. P. & ALEXANDER, L. E. (1954). *X-ray Diffraction Procedures*, chap. 8. New York: Wiley.

KVITKA, S. S., KOLONTSOVA, E. V. & UMANSKIJ, M. M. (1952). *Proc. Acad. Sci. U.S.S.R., Phys. Ser.* **16**, 372.

LIPSON, H. & ROGERS, L. E. R. (1944). *Phil. Mag.* **35**, 544.

LIPSON, H. & WILSON, A. J. C. (1941). *J. Sci. Instrum.* **18**, 144.

LONSDALE, K. (1950). *Acta Cryst.* **3**, 400.

LU, S. S. & CHANG, Y. L. (1941). *Proc. Phys. Soc.* **53**, 517.

MICHEL, J. (1938). *Bull. Classe Sci., Acad. Roy. Belg.* **24**, 333.

MITCHELL, C. M. (1952). Dissertation, Univ. of Toronto, Canada.

MITCHELL, C. M. (1960). In preparation.

NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160.

PARRISH, W. (1955). *Norelco Reporter*, **2**, 67.

PARRISH, W. (1957). *Precision Measurement of Lattice Parameters*, I.U.Cr. Rept. No. 1, March 7.

PARRISH, W. (1958). *Precision Measurement of Lattice Parameters*, I.U.Cr. Rept. No. 2, Sept. 12.

PARRISH, W. & CISNEY, E. A. (1948). *Philips Tech. Rev.* **10**, 157.

PARRISH, W., HAMACHER, E. A. & LOWITZSCH, K. (1954). *Philips Tech. Rev.* **16**, 123.

PARRISH, W. & WILSON, A. J. C. (1959). *International Tables for X-ray Crystallography*, vol. 2, 216. Birmingham: The Kynoch Press.

PEISER, H. S., ROOKSBY, H. P. & WILSON, A. J. C. (1955). *X-ray Diffraction by Polycrystalline Materials*, chap. 15. London: The Institute of Physics.

RILEY, D. P. (1944). *Nature, Lond.* **153**, 587.

ROVINSKIJ, B. M. (1940). *J. Techn. Phys. U.S.S.R.* **10**, 525.

ROVINSKIJ, B. M. & KOSTIUKOVA, E. P. (1958). *Kristallographya*, **3**, 382; transl. in *Soviet Physics-Crystallography*, **3**, 383 (1958).

SKINNER, B. J. (1957). *Amer. Min.* **42**, 39.

SMAKULA, A. & KALNAJS, J. (1955). *Phys. Rev.* **99**, 1737.

STRAUMANIS, M. E. (1949). *J. Appl. Phys.* **20**, 726.

STRAUMANIS, M. E. (1953). *Analyt. Chem.* **25**, 700.

STRAUMANIS, M. E. & AKA, E. Z. (1951). *J. Amer. Chem. Soc.* **73**, 5643.

STRAUMANIS, M. E. & AKA, E. Z. (1951*b*). *Rev. Sci. Instrum.* **22**, 843.

STRAUMANIS, M. E. & AKA, E. Z. (1952). *J. Appl. Phys.* **23**, 330.

STRAUMANIS, M. & IEVIŅŠ, A. (1936). *Z. Phys.* **98**, 461.

STRAUMANIS, M. & IEVIŅŠ, A. (1940). *Die Präzisionsbestimmung von Gitterkonstanten nach der asymmetrischen Methode*. Berlin: Springer. (Reprinted by Edwards Brothers, Inc., Ann Arbor, 1948.)

SWANSON, H. E. & TATGE, E. (1953). *Standard X-ray Diffraction Powder Patterns*, vol. 1, Nat. Bur. Standards Circular 539, Washington, D.C.

TAYLOR, A. & SINCLAIR, H. (1945). *Proc. Phys. Soc.* **57**, 108, 126.

TOURNARIE, M. (1954*a*). *J. Phys. Radium*, Supp. No. 1, **15**, 11A.

TOURNARIE, M. (1954*b*). *J. Phys. Radium*, Supp. No. 1, **15**, 16A.

VOGEL, R. E. & KEMPTER, C. P. (1959). Los Alamos Sci. Lab. Rept. LA-2317.

WARREN, B. E. (1945). *J. Appl. Phys.* **16**, 614.

WEYERER, H. (1955). *Z. angew. Phys.* **7**, 536.

WEYERER, H. (1956*a*). *Z. angew. Phys.* **8**, 202.

WEYERER, H. (1956*b*). *Z. angew. Phys.* **8**, 297.

WEYERER, H. (1956*c*). *Z. angew. Phys.* **8**, 553.

ZUBENKO, V. V. & UMANSKIJ, M. M. (1956). *Kristallographya*, **1**, 436.

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The space group of azulene.

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1. Introduction

There has been considerable controversy about the space group of azulene. The absent X-ray spectra indicate the centrosymmetric space group $P2_1/a$ and with only two non-centrosymmetric molecules in the unit cell this implies a disordered structure. A comparison of the entropies of azulene and naphthalene (Günthard, 1949) provides support for the possibility of disorder in the azulene crystal.

Two independent investigations of the crystal structure of azulene (Robertson & Shearer, 1956; Takeuchi & Pepinsky, 1956), however, led to an ordered arrangement of molecules in the non-centrosymmetric space group Pa with apparently satisfactory agreement between calculated and observed structure amplitudes in the principal zones. This choice of space group was supported by a study (Bernal, 1956) of the morphology of azulene crystals. Moreover Robertson & Shearer applied the $N(z)$ statistical test (Howells, Phillips & Rogers, 1950) to the $(h0l)$ intensity data and obtained results indicating an acentric distribution of intensities and hence supporting the assignment of Pa as the correct space group.

Subsequent refinement of the crystal structure, however, using full three-dimensional intensity data, showed that the ordered arrangement of molecules gives substantially poorer agreement between calculated and observed structure amplitudes than does a disordered centrosymmetric arrangement based on $P2_1/a$ as space group, the percentage discrepancies being 22·4 for the ordered structure and 13·5 for the disordered structure (Robertson, Shearer, Sim & Watson, 1958).

At a time when the alternative structures gave about equally good agreement between calculated and observed structure amplitudes, the actual overall percentage discrepancies being 21·4 and 22·4 for the centrosymmetrical and non-centrosymmetrical structures, respectively, the application of intensity statistics to the determination of the space group of azulene was reinvestigated with a view to providing evidence in favour of one or other of the molecular arrangements. It was found, in fact, that the intensity distribution obtained from the three-dimensional crystal data definitely favours the disordered structure.

2. Procedure

The X-ray spectra were divided into five groups with $\sin\theta = 0{\cdot}35-0{\cdot}45, \ldots, 0{\cdot}75-0{\cdot}85$, a total of 423 reflections being involved. In each group $\langle|F_o|^2\rangle$ was obtained and used to derive values of $z=|F_o|^2/\langle|F_o|^2\rangle$. Values of $_{\text{obs.}}N(z)$ for $z=0{\cdot}1, 0{\cdot}2, \ldots, 2{\cdot}0$ were calculated and the five values for each z were then averaged to yield the final values listed in Table 1, allowance being made for the different number of spectra in each group. As five independent results were used to derive each final $_{\text{obs.}}N(z)$ value it was possible to calculate a standard deviation for each such value. These standard deviations