COOPER, M. J. & NATHANS, R. (1968). *Acta Cryst.* A **24**, 481.
FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual.* Milwaukee: General Electric Company.
HAMILTON, W. C. & ABRAHAMS, S. C. (1969). *Acta Cryst.* A**26**, 18.
HAMILTON, W. C., ROLLETT, J. S. & SPARKS, R. A. (1965). *Acta Cryst.* **18**, 129.
International Union of Crystallography (1959). *Acta Cryst.* **12**, 1054.
International Union of Crystallography (1964*a*). *Acta Cryst.* **17**, 1183.
International Union of Crystallography (1964*b*). *Acta Cryst.* **17**, 1616.
MACKENZIE, J. K. & MASLEN, V. W. (1968). *Acta Cryst.* A**24**, 628.
MATHIESON, A. McL. (1969). *Acta Cryst.* A**25**, 264.

Acta Cryst. (1970). A**26**, 18

International Union of Crystallography Commission on Crystallographic Apparatus Single-Crystal Intensity Measurement Project Report II. Least-Squares Refinements of Structural Parameters

BY WALTER C. HAMILTON

Brookhaven National Laboratory, Upton, New York 11973, *U.S.A.*

AND S. C. ABRAHAMS

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey 07974, *U.S.A.*

(*Received* 21 *July* 1969)

The structure factors measured by the participants in the single-crystal intensity project of the I.U.Cr. Commission on Crystallographic Apparatus on D(+)-tartaric acid have been used in least-squares refinement of the structural parameters. The structure factors submitted by each participant were subjected to two refinements – once with heavy atoms only and once with all atoms including hydrogen. The parameters resulting from these refinements differ by magnitudes which suggest that the estimated standard deviations of the positional parameters obtained in the least-squares refinements are not infrequently a factor of about two too small and about $\sqrt{2}$ too small on the average. The agreement for the thermal vibration parameters may be even worse – by an additional factor of about two. These results are consistent with the indications of serious systematic errors in some of the experiments revealed in part I of this report. A modal group of six experiments with good interexperimental agreement leads to least-squares refined position parameters that are also in fair agreement; the maximum value of the ratio of the externally estimated standard deviation to the internal estimate from the least-squares refinements is about 2·5. The finding that results of possible high precision but low accuracy are not uncommon in single crystal-structure investigations is confirmed.

Introduction

In part I of this report (Abrahams, Hamilton & Mathieson, 1969), later referred to as part I, the interexperimental agreement factors and classical analysis-of-variance techniques have revealed the presence of systematic errors in many diffractometer experiments. Such errors cause differences between relative structure factors, measured by different experimenters on different specimens of the same substance, to be much larger than the internal consistency of the individual experiments would suggest. The analysis-of-variance techniques used in part I are appropriate for revealing the nature of the systematic differences among experiments without recourse to a theoretical model. Nevertheless, it is of interest to examine the results of applying the usual least-squares refinement procedure to the structure factors to determine how the possible systematic errors are manifested in the refined positional and thermal parameters.*

Refinement procedure

Each set of structure factors was subjected to least-squares refinement, using the usual model for the oxygen and carbon atoms that

$$F(hkl) = K \sum_j f_j \exp\left[2\pi i(hx+ky+lz)\right] \exp\left[-\sum_{ik} h_i h_k \beta_{ik}\right]$$

* Since limited data sets consisting of no more than 332 independent reflections were used, none of the results below should be taken as definitive determinations of the average parameters in the D(+)-tartaric acid structure, especially since the reflections used extended only to $\sin\theta/\lambda = 0{\cdot}5$ Å^{-1}.

and replacing the anisotropic thermal vibration term by $\exp\{-B(\sin\theta/\lambda)^2\}$ for the hydrogen atoms, where $\{h_i: i=1,2,3\}$ is identical to $\{h,k,l\}$. The parameters refined were the overall scale factor K and, for each atom, x,y,z and $\{\beta_{ik}: i=1,3;\ k=1,3\}$ or B for hydrogen atoms. Free-atom atomic scattering factors were used for all atoms (*International Tables for X-ray Crystallography*, 1962); no corrections were made for anomalous scattering (which is small). The space group was assumed to be $P2_1$ (Stern & Beevers, 1950). The numbering of the atoms is presented in Table 1 and agrees with that used by Okaya, Stemple & Kay (OSK, 1966) in the most recent published refinement of this structure. The heavy atom parameters of OSK were used as initial values in the full matrix least-squares refinements (Busing, Martin & Levy, 1962). The quantity minimized was $\Sigma w(|F_{obs}|-|F_{calc}|)^2$, where the weight w was assumed equal to $(0{\cdot}1|F_{obs}|)^{-2}$.* For each set of data an attempt was made to carry out two refinements, one with the ten heavy atoms only, and one including hydrogen atoms. In the latter case, the initial hydrogen atom parameters were taken from some preliminary neutron diffraction results of Cox, Sabine & Taylor (1966). In all the refinements, the y parameter of atom 1 was held fixed at 0·0343 – the final value of OSK; this is possible because of the one degree of freedom in the choice of origin in this space group.

Table 1. *Atom numbering scheme*

	Number		Number
O(1)	1	C(3)	9
O(2)	2	C(4)	10
O(3)	3	H(1)	11
O(4)	4	H(2)	12
O(5)	5	H(3)	13
O(6)	6	H(4)	14
C(1)	7	H(5)	15
C(2)	8	H(6)	16

Results

In Table 2 are presented the results of the heavy atom refinements.† Since experimenters 6 and 10 supplied one zone of data only, it was not possible to refine these data sets. (There was in fact insufficient data from these two experiments for an anisotropic two-dimensional refinement.) The parameters (P) are numbered in the order $x,y,z,\beta_{11},\beta_{22},\beta_{33},\beta_{12},\beta_{13},\beta_{23}$. Table 2 contains the following data:

(i) In the last fifteen columns are the parameters P_i obtained from the individual refinements; the least-squares estimated standard deviations are not given but may be inferred from the standard deviation of the mean (see σ below).

(ii) The MAXIMUM and MINIMUM of the fifteen parameter values obtained.

(ii) The mean parameter value (labelled AVERAGE) defined by

$$\mu=\sum_i\left(\frac{P_i}{\sigma_i^2}\right)/\sum_i\left(\frac{1}{\sigma_i^2}\right)$$

where σ_i^2 is the estimated variance of the parameter from the least-squares refinement obtained in the usual way from the inverse matrix of the normal equations by multiplication by the goodness-of-fit parameter $\Sigma w(\Delta F)^2/(n-m)$.

(iv) The parameter value reported by OSK (1966) for the X-ray refinement.

(v) The estimated standard deviation of the weighted mean based on the agreement among the experiments:

$$\sigma_{EXT}=\left[\frac{\sum_i\frac{(P_i-\mu)^2}{\sigma_i^2}}{(n-1)\sum\frac{1}{\sigma_i^2}}\right]^{1/2}$$

(vi) The estimated standard deviation of the mean based on the individually estimated standard deviations:

$$\sigma_{INT}=\left[\sum_i\frac{1}{\sigma_i^2}\right]^{-1/2}.$$

(vii) The variance ratio

$$\text{RATIO}=(\sigma_{EXT}/\sigma_{INT})^2.$$

In the absence of systematic error RATIO is expected to have, on the average, a value close to unity. Except for the variance ratio, all numbers in Table 2 have been multiplied by 10^5.

In Table 3 are presented similar results for the refinements which include the six hydrogen atoms. The fourth parameter for each hydrogen atom is the isotropic thermal parameter B. The data of experiments 1, 3, 12 and 14 did not lead to successful refinements; the positional and thermal parameters of the hydrogen atoms varied widely, and the refinements diverged. (It is possible that careful individual analysis in each of these cases would have led to non-divergent refinement. We note here only that a routine refinement starting from the initial neutron diffraction values was not possible for these four experiments, as it was for the others.) These experiments are thus omitted from Table 3.

* This weighting formula was found to be suitable by an analysis of the average value of $\Delta F/\sigma$ as a function of F. There were few reflections of low enough intensity to be overweighted by this formulation.

† It was not possible to refine the data for experiment 11*b* to a satisfactory solution. Non-positive-definite thermal parameters were obtained, and the convergence procedure became unstable, the agreement factor getting suddenly worse and then better. This was possibly due to the small number of independent structure factors that was available for this data set. Nevertheless, a set of parameters for this experiment is included in Table 2; this set corresponds to the lowest value for the agreement ratio obtained during the refinement procedure. The omission of this experiment from the analysis presented in Table 2 did not affect any of the conclusions.

As a further summary of the refinements, we present in Table 4 the values of the agreement ratios

$$R=\Sigma\,||F_{\rm obs}|-|F_{\rm calc}||/\Sigma\,|F_{\rm obs}|\,,$$

$$wR=[\Sigma\,\{w^{1/2}(|F_{\rm obs}|-|F_{\rm calc}|)\}^2/\Sigma\,(w^{1/2}|F_{\rm obs}|)^2]^{1/2}.$$

In addition, for the heavy atom refinements, typical values of the least-squares estimated standard deviations (σ) for the x-positional parameter are also quoted.

Discussion

It will be left for the reader to analyze the variation among the parameter sets in detail, but some conclusions will be given here. The results of the refinements confirm the conclusions of part I. There are systematic differences among the experiments. Again this is most obvious for experiment 13, where β_{33} is about a factor of four larger than the average value of β_{33} obtained over all experiments; a systematic error as a function of l is thus clearly indicated. Despite this great discrepancy, the R, wR and $\sigma(x)$ values (see Table 4) for this experiment are comparable with those for the other experiments.

The most important figures in Tables 2 and 3 are the variance ratios $\sigma^2_{\rm EXT}/\sigma^2_{\rm INT}$ (RATIO). In the absence of systematic error, these quantities should be distributed with a mean of approximately 1·0 and variance approximately $\{2(n-1)\}^{1/2}$ where n is the number of experiments compared. Inspection of Table 2 reveals a maximum value of 4·3 for a position coordinate and 35·7 for a thermal vibration parameter. The corre-

Table 2. *Results of heavy atom refinements of the project data*

The atom numbering scheme is given in Table 1, and explanation of the contents of the Table is given in the text. For fifteen degrees of freedom, values of RATIO exceeding 1·66 are significant at the 95% level.

ATOM	P	MAXIMUM	MINIMUM	AVERAGE	DSK	SIGMA(EXT)	SIGMA(INT)	RATIO	1	2	3	4	5	7	8	9	11A	11B	12	13	14	15	16
1	1	33941	33174	33747	33820	28	16	3.2086	33941	33798	33174	33831	33726	33796	33805	33808	33797	33440	33500	33707	33807	33546	33775
1	2	3430	3430	3430	3430	0	0	0.0000	3430	3430	3430	3430	3430	3430	3430	3430	3430	3430	3430	3430	3430	3430	3430
1	3	51635	50701	51057	51020	42	24	3.1206	51162	51179	51639	51180	50963	51047	51138	51006	50948	51313	51469	50950	51071	50701	51039
1	4	2492	476	826	965	61	26	5.4660	597	522	1320	476	856	736	717	845	774	1480	2492	1000	709	992	740
1	5	2469	1039	1855	2355	94	54	3.0018	2158	1039	1736	1624	2064	1734	1269	2143	2357	1363	1384	2469	2176	1948	1826
1	6	5850	-961	1199	1149	262	55	22.3950	1446	670	1618	1047	1183	951	1342	549	1002	1452	-961	5850	1146	1421	1093
1	7	374	-271	26	-2	29	34	.6996	-136	4	243	8	21	16	5	120	23	50	174	8	304	-271	53
1	8	466	-410	238	284	21	27	.6016	64	186	-90	180	272	252	189	221	466	-410	319	141	313	258	261
1	9	771	42	341	289	43	50	.7404	60	307	116	42	426	309	179	240	276	403	249	771	647	259	405
2	1	43610	42896	42988	42960	21	15	1.9898	43065	42967	43186	42905	42941	42945	43012	43004	43127	43610	43362	42960	42896	43008	43044
2	2	-3101	-3804	-3382	-3249	41	39	1.1182	-3695	-3539	-3322	-3616	-3405	-3460	-3593	-3106	-3406	-3145	-3804	-3379	-3472	-3101	-3325
2	3	-1921	-2610	-2140	-2189	25	24	1.0640	-2169	-2123	-2467	-2239	-2118	-2170	-2113	-2229	-1983	-2610	-2281	-1921	-2043	-2105	-2118
2	4	1562	404	769	725	51	24	4.4475	1103	429	1016	404	850	769	594	672	442	1306	1562	984	841	815	689
2	5	3934	1511	2345	2213	91	66	1.9250	1927	1511	2864	2381	2590	2135	2151	1963	3034	2731	2491	2549	2230	2478	2172
2	6	6736	-779	1139	1412	246	53	21.5131	682	854	1282	1074	909	955	1249	1863	1063	6736	-779	6078	937	1615	997
2	7	583	25	305	186	33	36	.8435	395	306	583	247	369	348	266	72	353	295	349	298	449	25	347
2	8	386	69	284	407	18	30	.3564	380	172	159	229	325	318	386	328	370	69	258	143	254	345	233
2	9	27	-1730	-220	-298	50	50	.9747	-397	-165	-883	-343	-161	-142	-275	-165	-224	-1730	-195	-138	27	-424	-146
3	1	61420	60840	60955	60840	18	16	1.1340	60914	60843	60993	60840	60956	60979	60908	60883	61075	61420	60853	60973	61060	60978	60966
3	2	1499	225	550	500	50	42	1.4305	227	350	410	350	540	406	225	682	770	1499	375	643	591	883	594
3	3	30369	29289	30104	30050	28	26	1.0982	30152	30046	30369	29905	30107	30092	30143	29944	30155	29289	30127	30181	30112	30205	30140
3	4	1230	86	490	578	46	25	3.2413	929	277	686	401	476	329	428	569	86	735	1230	734	305	640	495
3	5	2681	960	1778	2274	98	64	2.3546	960	1010	2073	1737	1944	1648	1299	1831	2681	2165	1279	2153	2202	2100	1570
3	6	6339	385	1833	1634	259	49	27.0481	917	1064	2979	1298	1818	1721	1473	2018	2165	2779	385	6339	1796	2223	1589
3	7	437	-193	40	116	30	31	.9479	236	124	-193	437	4	74	147	-2	401	-192	176	2	244	-2	17
3	8	346	-74	175	303	25	32	.5994	544	98	2	306	191	121	16	258	207	92	192	184	120	275	140
3	9	861	34	271	440	41	47	.7607	194	327	861	410	333	292	233	34	114	589	273	173	241	536	149
4	1	30852	30624	30729	30630	14	16	.8063	30696	30852	30763	30825	30758	30733	30805	30706	30630	30783	30624	30724	30698	30651	30676
4	2	42424	41357	41748	41730	64	37	2.9914	41357	41423	41885	41411	41706	41589	41435	41986	41781	42129	41620	41805	41500	42424	41780
4	3	23852	22476	23553	23350	33	25	1.7105	23211	23528	23599	23547	23567	23546	23624	23828	23579	22476	23064	23563	23498	23598	23547
4	4	1567	220	572	648	38	24	2.3972	342	352	645	363	635	544	591	518	220	1567	1043	717	607	539	545
4	5	1516	646	1027	1708	64	50	1.6643	1432	646	1054	1488	1178	859	943	862	1516	1267	786	1343	1502	875	792
4	6	5966	-157	1410	1018	290	48	35.7153	1045	612	1671	699	1167	1179	971	2530	2276	4131	-357	5966	1059	2926	1214
4	7	397	-563	-9	-199	30	33	.7901	-563	55	-176	-58	-5	28	38	-26	142	-138	387	-103	32	61	8
4	8	619	-591	320	171	36	27	1.8221	306	227	289	284	336	254	433	509	461	-591	278	313	137	619	245
4	9	369	-871	119	58	25	42	.3578	-49	181	129	124	128	134	248	63	23	-871	221	133	369	28	87
5	1	-7550	-8018	-7750	-7649	26	18	2.1311	-8001	-7704	-7922	-7674	-7674	-7792	-7753	-7550	-7853	-8004	-8018	-7787	-7802	-7812	-7821
5	2	8341	7719	7926	7920	43	45	.9305	8260	7802	7953	7754	7813	7805	7767	8162	7972	8341	7885	8103	7719	8168	8060
5	3	18284	17592	17854	17900	43	31	.9751	17916	17715	17954	17592	17776	17783	17623	18284	17862	18180	18039	18053	18024	17911	17830
5	4	1712	484	780	640	55	25	4.6508	725	484	1289	751	829	676	750	578	489	929	1712	931	648	1090	705
5	5	3427	1987	2520	2688	94	77	1.4700	3427	2027	2090	3295	2661	2461	2603	2567	2044	2934	2633	2985	2981	1987	2378
5	6	7841	-4	2134	2342	275	54	25.4250	1904	1355	2775	1380	2056	1941	1715	2663	2477	7841	-4	6709	1879	2289	2020
5	7	38	-1005	-296	-380	31	43	.5469	38	-303	-547	-447	-247	-317	-342	-406	-212	-1005	-51	-210	-104	-325	-286
5	8	612	-374	406	511	40	30	1.7606	500	321	-374	605	-89	476	337	334	460	151	-61	310	378	612	402
5	9	-316	-1254	-861	-861	37	59	.3957	-1254	-943	-878	-1185	-857	-930	-928	-825	-551	-316	-652	-892	-648	-1042	-766
6	1	-2015	-2504	-2086	-2169	20	17	1.4722	-2223	-2040	-2198	-2199	-2055	-2016	-2105	-2222	-2044	-2504	-2132	-2138	-2015	-2095	-2033
6	2	41215	40093	40448	40720	72	46	2.4070	40327	40198	40238	40093	40268	40303	40214	40851	40431	41215	40388	40528	40331	41158	40583
6	3	35637	34659	34962	34990	43	31	1.9135	34744	34925	34859	34914	35033	35036	34732	34741	34839	35637	34749	34764	35169	35293	35017
6	4	1859	208	843	920	61	32	3.5775	616	474	839	927	848	815	736	798	208	829	1859	1171	803	1189	790
6	5	3537	1471	2288	2641	105	75	1.9592	1471	1763	3028	2425	2588	2112	2059	2186	3537	2008	1867	2544	2519	2016	2008
6	6	6807	691	2424	2492	272	61	19.7586	2925	1764	2725	1636	2330	2111	2069	2573	2061	3365	691	6807	2189	3010	2206
6	7	174	-257	-59	-1	22	45	.2502	-96	-118	-69	-257	-139	-84	-69	47	174	6	7	-206	-10	-8	-8
6	8	687	179	542	655	24	34	.5030	567	428	362	405	623	536	462	504	687	686	179	636	439	640	529
6	9	-37	-1403	-750	-885	64	67	.9238	-1009	-501	-37	-553	-736	-710	-457	-919	-833	-949	-832	-632	-1403	-1090	-737
7	1	29565	28303	29257	29410	33	24	1.7654	28951	29207	29565	29092	29319	29249	29151	29353	29259	28303	28956	29289	29212	29083	29338
7	2	1915	1156	1579	1590	45	53	.7251	1220	1492	1156	1680	1486	1588	1633	1915	1729	1709	1330	1674	1199	1607	1684
7	3	30882	27476	28224	28320	60	39	2.2958	27684	28177	27476	28105	28290	28227	28131	28664	28352	30882	27859	28217	28309	28424	28137
7	4	1491	46	586	510	70	35	3.9408	1451	109	1355	46	575	502	356	557	458	685	1491	764	406	950	732
7	5	2380	963	1597	1611	95	85	1.2355	1490	963	2380	1503	1813	1316	1258	1474	2090	2036	1089	2041	1798	1674	1301
7	6	5714	-131	1212	1266	240	72	11.1256	40	995	1478	930	1184	1179	1046	2152	988	4437	487	5714	978	-131	1041
7	7	767	-82	252	111	32	50	.4193	437	160	27	394	294	211	401	340	-82	19	767	153	111	195	266
7	8	870	-861	403	194	62	41	2.2273	419	413	-861	322	496	439	483	870	658	-396	-585	102	558	55	298
7	9	860	-185	52	168	53	67	.6328	289	92	335	171	-71	-131	262	402	145	860	272	45	246	290	-185
8	1	47066	45867	46354	46400	30	24	1.5779	46498	46448	45867	46529	46318	46349	46551	46338	46615	47066	46423	46295	46336	46265	46297
8	2	-129	-1244	-705	-679	66	46	2.0517	-1041	-1000	-1244	-1016	-680	-753	-1033	-642	-658	-278	-789	-497	-916	-129	-586
8	3	19385	18027	18909	19110	47	38	1.5407	19115	19024	19385	19202	18851	18847	19264	18942	18530	18027	19106	18880	18632	18721	18822
8	4	2984	39	464	665	80	43	3.4539	54	39	1115	72	542	407	497	245	104	2984	670	829	412	973	462
8	5	2115	-27	845	1161	97	74	1.6877	-27	270	1202	1170	954	558	382	708	2115	479	920	1145	1492	1121	726
8	6	6160	-242	1336	1502	255	78	10.6694	876	707	3968	802	1451	1463	765	1461	1179	1926	-242	6160	1001	1066	1112
8	7	423	-457	-109	-11	34	44	.5900	423	-161	-296	-457	-122	-21	-288	-99	-195	399	-8	-142	-96	-205	-33
8	8	482	-1069	174	278	54	44	1.5416	482	160	-1069	166	337	311	183	-91	482	-961	-276	345	-279	227	110
8	9	687	-581	157	161	45	65	.4940	231	196	393	21	20	208	-33	322	262	-581	687	371	116	-187	191
9	1	20502	19792	20103	20030	32	23	2.0227	19905	20191	20070	20259	20122	20133	20088	19893	20502	20256	19792	20065	20110	20011	20205
9	2	22911	22332	22578	22730	39	53	.5408	22523	22483	22454	22332	22431	22550	22497	22880	22557	22897	22911	22702	22682	22709	22640
9	3	18144	15001	17929	18110	81	39	4.2781	17787	18025	18044	17963	17981	17970	17880	17455	17951	15001	17627	18144	17898	17597	18144
9	4	617	-374	111	442	51	32	2.4282	-93	-86	-188	-58	236	274	155	7	-99	617	-374	348	262	-134	139
9	5	2213	961	1315	1532	74	67	1.2303	2213	961	1519	1923	1232	1220	979	1053	1682	1893	1596	1574	2170	1567	1046
9	6	5807	-284	1109	954	320	69	21.2697	969	220	83	190	1050	866	700	2129	2340	2463	-284	5807	664	3694	884
9	7	986	-770	-366	-3	59	48	1.5340	-770	-632	-252	-768	-274	-517	-586	-198	-418	986	-458	-215	-766	-44	-465
9	8	1468	0	160	142	60	41	2.1633	3	14	1468	135	52	210	142	54	662	1143	217	9	52	349	200
9	9	440	-669	-124	33	62	69	.8128	-528	-250	-24	-533	68	-110	-447	32	-226	-362	-152	-52	440	-669	-118
10	1	2517	1676	2216	2190	29	25	1.3212	2279	2209	2517	2149	2192	2173	2105	2140	2242	1676	2274	2274	2215	2467	2232
10	2	25736	24998	25409	25280	47	56	.7053	25296	25189	25638	25193	25368	25330	25058	25333	25547	24998	25257	25351	25614	25736	25599
10	3	24699	24566	24985	24900	65	38	2.9083	24795	24744	24781	24659	24971	24908	24566	25184	25416	24699	25190	25359	25263	25427	24964
10	4	922	-368	561	496	71	43	2.7076	384	343	922	279	830	482	588	521	183	-368	-115	896	495	579	516
10	5	2573	595	1250	1802	78	86	.8180	1253	727	1271	1373	1181	1233	995	1431	1600	2573	1321	1469	825	1890	1120
10	6	5197	473	1165	1203	264	81	10.6790	868	473	1531	775	930	932	1060	1065	660	3952	1283	5197	965	1721	904
10	7	626	-253	-3	82	51	55	.8756	169	146	626	9	-24	25	34	-81	430	-8	-176	11	-253	-189	-188
10	8	1167	-327	-73	26	48	48	1.0084	-223	-60	185	-301	-103	-77	-227	-154	633	1167	18	-80	-327	-10	-88
10	9	706	-721	-73	-20	75	72	1.0819	-202	-268	-690	-527	-34	-172	-259	203	-284	-721	14	203	-352	706	-32

Table 3. *Results of refinement of all atom parameters for the project data*

Only those experiments which led to successful hydrogen atom refinements are included. For nine degrees of freedom, a value of RATIO greater than 1·88 is significant at the 95% significance level.

ATOM	P	MAXIMUM	MINIMUM	AVERAGE	OSK	SIGMA(EXT)	SIGMA(INT)	RATIO	2	4	5	7	8	9	11A	13	15	16
1	1	33825	33618	33738	33820	15	15	1.0550	33715	33825	33735	33788	33780	33618	33711	33795	33721	33735
1	2	3430	3430	3430	3430	0	0	0.0000	3430	3430	3430	3430	3430	3430	3430	3430	3430	3430
1	3	51197	50909	51034	51020	21	20	1.1335	51157	51197	51046	51075	51127	50941	51045	51035	50909	50992
1	4	895	384	688	965	38	23	2.5907	433	384	677	625	711	789	518	827	889	655
1	5	2545	1035	1918	2355	101	45	4.8994	1035	1913	2069	1760	1347	1728	2421	2545	2003	1946
1	6	5729	709	1108	1149	299	47	39.1066	709	893	1025	902	1270	1082	1302	5729	950	845
1	7	83	-300	-34	-2	20	31	.4177	-163	-151	-54	-33	-5	1	-300	83	-24	-21
1	8	496	133	282	284	21	24	.7861	215	357	287	246	329	364	456	133	397	259
1	9	681	-93	226	289	48	42	1.3106	114	-65	273	159	-93	188	168	681	77	311
2	1	43062	42570	42809	42960	31	16	3.6106	42628	42570	42728	42780	42714	42836	43002	42873	42910	42905
2	2	-3096	-3757	-3343	-3249	40	33	1.4237	-3578	-3757	-3392	-3395	-3449	-3096	-3362	-3407	-3173	-3318
2	3	-1890	-2378	-2145	-2189	38	26	2.1522	-1958	-2074	-2101	-2131	-2083	-2378	-1948	-1974	-1890	-2248
2	4	808	157	582	725	48	22	2.5828	212	157	565	559	467	808	365	803	712	544
2	5	3187	1857	2362	2713	112	58	3.6940	1857	2738	2687	2126	2466	1910	3187	2544	2776	2071
2	6	6343	977	1436	1412	275	53	27.0927	1127	1646	1326	1205	1720	1533	977	6343	1495	1254
2	7	321	15	238	186	33	31	1.1062	153	141	309	231	126	189	68	295	15	321
2	8	909	261	477	407	58	29	4.0367	596	731	596	542	831	261	433	344	909	321
2	9	196	-580	-151	-298	68	44	2.3841	39	196	-14	-40	96	-580	-462	-65	-538	-186
3	1	60928	60740	60859	60840	13	13	.9967	60791	60787	60870	60890	60874	60740	60928	60912	60865	60856
3	2	1129	105	665	500	74	35	4.4061	358	105	551	542	217	857	896	718	1129	725
3	3	30171	29937	30091	30050	20	21	.9534	30117	29995	30136	30118	30165	29937	30038	30171	30117	30042
3	4	651	75	289	578	42	21	3.9747	92	173	282	182	190	377	75	651	325	282
3	5	3106	1182	2065	2374	95	55	2.9847	1182	1862	2163	1973	1450	2232	3106	2233	2301	2026
3	6	6076	889	1514	1634	302	39	57.6759	889	1154	1318	1329	1176	2061	1897	6076	2196	1264
3	7	325	17	152	116	20	26	.6017	214	325	186	219	133	17	115	133	120	101
3	8	190	-116	110	303	24	24	.8788	91	190	151	122	12	167	186	185	116	93
3	9	742	120	394	440	47	39	1.4475	431	517	501	403	334	269	120	204	742	260
4	1	30867	30607	30716	30630	20	15	1.7910	30867	30827	30715	30725	30733	30798	30737	30662	30607	30669
4	2	42479	41390	41814	41730	84	35	5.7912	41531	41390	41646	41724	41673	42008	42041	41643	42479	41893
4	3	23643	23004	23431	23350	46	25	3.2664	23569	23663	23402	23439	23646	23603	23571	23004	23076	23384
4	4	926	198	543	648	48	23	4.3650	235	198	590	519	617	580	230	926	643	503
4	5	1803	847	1416	1708	73	51	2.0259	847	1417	1518	1275	1082	1500	1803	1702	1755	1286
4	6	5087	322	820	1018	239	50	22.4216	322	592	501	717	925	1681	1794	5087	1367	758
4	7	-12	-185	-104	-199	18	30	.3924	-12	-108	-94	-91	-29	-93	-19	-185	-15	-175
4	8	554	8	166	171	40	24	2.6706	87	206	201	198	329	378	554	128	119	8
4	9	394	-96	161	58	39	38	1.1028	353	384	169	236	363	-96	-92	-84	149	123
5	1	-7658	-7895	-7719	-7649	16	19	.7235	-7717	-7759	-7658	-7749	-7827	-7684	-7895	-7732	-7730	-7749
5	2	8228	7602	7956	7920	53	38	1.9683	7704	7602	7796	7896	7829	8043	8068	8143	8228	8066
5	3	18155	17614	17958	17900	36	27	1.7747	17855	17614	17985	17922	17683	18076	17818	18155	17948	18005
5	4	655	155	432	640	48	23	2.7184	155	441	411	344	373	361	208	655	631	455
5	5	3288	1896	2427	2688	97	62	2.4916	1896	3288	2549	2384	2309	2605	2791	3014	2003	2292
5	6	6746	1550	2364	2362	313	50	38.6457	1550	1565	2194	2194	1928	2845	2627	6746	2342	2144
5	7	-26	-436	-290	-382	27	36	5.5685	-237	-227	-245	-312	-24	-258	-368	-240	-436	-308
5	8	774	332	565	511	31	27	1.2713	497	774	561	611	332	743	576	416	510	572
5	9	-765	-1438	-949	-861	41	47	.7874	-1096	-1438	-942	-1001	-1042	-765	-827	-866	-1076	-833
6	1	-2003	-2217	-2071	-2169	16	13	1.3247	-2079	-2217	-2058	-2067	-2149	-2003	-2061	-2184	-2101	-2038
6	2	41084	40003	40629	40720	77	46	3.7265	40269	40003	40427	40527	40517	40879	40681	40643	41084	40772
6	3	35351	34799	35095	34960	37	26	2.0800	34977	35029	35127	35120	34933	35016	34852	34799	35351	35133
6	4	1125	165	785	920	60	26	5.4237	359	782	715	752	647	728	165	1125	1035	847
6	5	3198	1571	2012	2641	94	59	2.5281	1571	2171	2303	1936	1912	1840	3198	2220	1992	1718
6	6	7008	1707	2486	2492	327	51	39.8069	1781	1870	2295	2077	2154	2700	2289	7008	3159	2192
6	7	346	57	131	-1	23	36	.4243	156	176	57	84	384	228	285	132	155	139
6	8	802	232	537	655	40	28	2.0956	396	232	567	522	442	301	577	673	802	577
6	9	-826	-1095	-946	-885	34	53	.4246	-857	-842	-1095	-1008	-834	-974	-859	-881	-826	-858
7	1	29473	29208	29397	29410	20	20	.9636	29279	29208	29415	29352	29343	29473	29388	29367	29371	29470
7	2	1831	1534	1658	1590	25	44	.3457	1534	1609	1571	1610	1831	1746	1739	1723	1691	1724
7	3	28490	28176	28314	28320	29	32	.6184	28265	28176	28385	28286	28345	28400	28275	28381	28490	28208
7	4	606	6	386	510	40	31	1.6957	6	222	374	304	299	389	252	606	410	503
7	5	1854	362	1042	1411	117	71	2.6872	411	717	1087	746	362	1313	1654	1591	1514	869
7	6	5733	341	996	1266	298	62	22.8905	348	476	872	875	849	1315	966	5733	341	934
7	7	169	-487	-21	111	33	43	.5707	-161	-81	10	-28	-29	-66	-487	2	169	-112
7	8	422	-34	111	194	37	35	1.1113	55	81	170	102	172	147	422	54	359	-34
7	9	400	-178	176	168	39	56	.4956	319	159	257	87	400	204	-178	264	302	43
8	1	46638	46303	46366	46400	22	22	1.0075	46381	46533	46333	46333	46638	46357	46473	46303	46362	46383
8	2	-236	-855	-542	-679	43	38	1.2889	-694	-755	-615	-594	-607	-470	-635	-486	-236	-520
8	3	19415	18690	19203	19110	36	31	1.3523	19095	19411	19278	19140	19415	19108	18690	19181	19062	19180
8	4	1435	165	692	665	76	39	3.6965	320	408	695	605	870	447	165	802	1435	769
8	5	1796	8	651	1161	121	64	3.6115	200	1158	978	424	489	8	1796	1167	685	431
8	6	5926	153	981	1502	300	62	23.2918	153	175	841	954	308	1873	1346	5926	752	958
8	7	196	-574	-23	-11	40	36	1.2176	-122	-574	-41	51	-375	-23	-146	14	196	-19
8	8	794	-88	426	278	50	37	1.8630	396	463	440	420	424	488	667	-88	794	413
8	9	261	-79	84	161	32	53	.3696	100	-71	-18	205	-79	48	60	261	75	139
9	1	20278	19784	19997	20030	34	21	2.4511	20071	20100	19984	20034	19870	19784	20278	20017	19840	20091
9	2	22966	22530	22717	22730	44	43	1.0755	22614	22530	22574	22728	22727	22966	22850	22909	22902	22680
9	3	18328	17507	17971	18110	59	34	2.9454	18037	17844	17998	17979	17715	17670	17844	18328	17507	18118
9	4	536	9	361	442	48	31	2.2586	115	9	439	472	124	485	55	536	400	242
9	5	1845	466	1110	1532	88	59	2.2082	466	1137	1137	954	679	878	1845	1641	1371	1049
9	6	4912	108	650	954	292	67	18.8739	108	120	420	471	412	831	1309	4912	741	443
9	7	14	-549	-209	-3	42	42	1.0108	-476	-549	-163	-395	-260	14	-85	-294	-101	-152
9	8	622	-339	60	142	54	37	2.1066	-8	51	-50	172	0	272	622	-339	229	78
9	9	156	-409	-113	33	36	60	.3673	-191	-409	-72	-221	-180	-41	156	-295	-145	-10
10	1	2381	2086	2265	2190	19	19	.9624	2303	2190	2252	2245	2086	2381	2276	2249	2353	2268
10	2	25536	25200	25431	25280	28	44	.3984	25333	25270	25414	25475	25413	25200	25380	25465	25536	25481
10	3	25559	24867	25115	24960	35	30	1.3509	24994	24900	25165	25070	24867	25231	25559	25312	25124	25096
10	4	651	-91	354	496	59	36	2.6708	-23	-91	450	169	249	333	168	651	567	361
10	5	1762	601	1222	1802	84	69	1.4885	737	1282	1157	1264	601	1640	1762	1504	1547	1022
10	6	4938	543	1052	1203	304	63	23.2128	543	842	757	912	855	1175	998	4938	1033	781
10	7	275	-245	-11	82	36	44	.6833	93	-245	70	36	-177	-229	275	40	42	-118
10	8	616	-351	-73	26	52	38	1.7950	-60	-186	-129	-50	-140	-351	616	0	296	-67
10	9	247	-107	91	-20	31	57	.3087	-107	-83	155	-6	-10	80	-102	257	207	79
11	1	26024	22440	23427	24100	293	232	1.6027	24174	26024	23424	22462	24811	23556	23030	22440	23069	23189
11	2	-9701	-14592	-11198	-11599	360	382	.8878	-10516	-11198	-11246	-10561	-9901	-11750	-11849	-11133	-14592	-10651
11	3	25166	22606	23386	23600	163	305	.2849	22606	23064	23179	23195	23117	23219	25166	23480	22928	24098
11	4	625789	-4297*4	-179954	-129099	73698	38C90	3.7437	-385557	-429734	-198965	-250740	-418352	25129	-214257	625789	164848	-163431
12	1	18443	16832	17385	18200	166	166	.9910	17633	17701	16987	17590	18157	17803	17912	17035	18443	16832
12	2	24885	19771	20979	20200	454	319	2.0308	23461	24885	20220	21065	21462	19771	22387	20791	20808	20916
12	3	4822	-3737	1655	2800	496	300	2.7235	2691	1772	2729	2299	902	1088	-3737	4822	-1998	1241
12	4	-37547	-506795	-243313	-119999	37784	28293	1.7834	-239181	-506795	-135985	-180553	-280647	-339677	-69415	-37547	-90771	-274656
13	1	26878	20477	23714	25300	374	294	1.6234	21199	20477	24015	23835	26878	22855	22864	22382	22988	25030
13	2	6133	-3076	9	3700	460	445	1.0685	1641	1786	362	2313	6133	-1056	-3076	376	-504	-729
13	3	58181	51553	55155	55500	596	375	2.1985	52671	51553	52981	54005	56919	56785	54686	54096	58181	55977
13	4	590157	-244697	45538	640000	79069	49682	2.5329	175557	590357	204966	229631	447739	-244697	44171	564525	142068	-43896
14	1	51788	45200	49263	51500	426	273	2.4257	48370	48056	49122	48967	48309	45200	48083	50998	49816	51788
14	2	-845	-5624	-2842	-4599	287	428	.4495	-2381	-2220	-3214	-2192	-2435	-5624	-2470	-4437	-845	-3961
14	3	-5549	-17737	-7733	-8599	599	319	3.5209	-6485	-5549	-7198	-8517	-6448	-17737	-12955	-11908	-11676	-8390
14	4	682016	-757215	-344943	440000	89088	47087	3.5795	-648353	-757215	-353775	-256839	-530621	682016	-31750	117597	-336092	41586
15	1	35063	28666	32925	34200	196	235	.6957	32908	32106	33071	32873	35063	31203	28666	32105	33177	33216
15	2	48749	38270	43670	43800	503	381	1.7413	43379	38270	44705	43820	38754	42996	48749	45009	41322	42925
15	3	42945	32883	35621	36700	646	374	2.9874	38230	41285	35246	36527	42545	38447	33518	32883	36501	35504
15	4	591467	-353778	-135720	180000	90421	48432	1.0838	-84944	122403	-202524	45919	442673	161091	591467	-194797	-353778	-53842
16	1	-16476	-19035	-17125	-18199	253	266	.9061	-17872	-19035	-17139	-16564	-18851	-16814	-18973	-17866	-18423	-16474
16	2	12382	8015	8948	4900	319	365	.7665	10881	10458	9393	8454	12382	8015	8504	8281	9400	8514
16	3	21682	18067	21591	20300	534	296	3.2547	19787	18816	20459	20860	18067	21682	20108	23682	21967	21965
16	4	314259	-217055	-59382	530000	45722	43800	1.0897	-142417	-60801	3498	-147089	-47262	-217055	-79410	260063	314259	-114972

sponding values in Table 3 are 5·8 and 57·7. The average value for the positional parameters is about 2 and for the thermal parameters about 5. (The mean value should be 1·0, $\sigma=0{\cdot}4$.) Thus, if the agreement among experiments is taken as a criterion of accuracy, the internal estimates of the standard deviations from the least-squares refinements are too low by a factor of $(\text{RATIO})^{1/2}$. If any one of the experimenters had reported his least-squares derived standard deviations, a false picture of the accuracy of these parameters could have been presented. The internal standard deviations for positional parameters could be as much as a factor of 2 too small: those for thermal parameters would not infrequently be an additional factor of 2 or 3 too small. It is of course possible that one or more experiments may be more accurate than the others and that the standard deviations reported in such experiments are a reliable indication of accuracy; it is clear however that the average accuracy is not as great as the precision of the individual refinements. Furthermore, the *average* parameter values differ from the OSK values by as much as 6·4 σ_{EXT} for O(3)x and by 10·7 σ_{EXT} for O(4)β_{22}.*

* The mean values in Tables 2 and 3 are probably less accurate than the results of OSK, since the latter are based on data extending to higher scattering angles. On the other hand, there is no reason to assume that the results of OSK are not subject to some systematic error which would render the quoted standard deviations too low by a factor of 2 or 3. Without any evidence to the contrary, the definitive parameters for this structure should be taken as those of OSK rather than any of those quoted here. The estimated σ's of OSK are much smaller than the σ_{EXT} in this study.

The maximum variation between a position coordinate determined in an individual experiment and the average value for that coordinate in Table 2 is 0·043 Å.† The maximum variation from the value found by OSK is somewhat larger, 0·052 Å. In terms of the individual standard deviations from the least-squares refinements, such atomic position differences would be considered significant. However, use of a factor of 2 or 3 to obtain a more meaningful standard deviation, as suggested by the comparison between the external and internal estimates, would render most of the differences not statistically significant.

It is instructive to examine the least-squares refined structural parameters based on one group of experiments which were considered to have the best internal consistency as judged by a number of indicators (see part I for details). This *modal* group consisted of experiments 1, 2, 3, 5, 7 and 16. We have already noted that experiment 3 gave divergent results on attempting to refine the parameters for all atoms including hydrogen. In the following, we therefore compare only the *heavy* atom parameters. The results are listed in Table 5 in the same form as Table 2.

Excluding the β_{ij} values for $i\neq j$, which are particularly susceptible to anisotropic error, there are 539 different parameter values in Table 5. The range in each parameter value for the *modal* group may also be taken as a measure of consistency. The *average* range for the position parameters is 11·4 σ_{INT}; for the thermal parameters it is 16·5 σ_{INT}. Individual ranges, of

† Except for experiment 11*b*, which did not converge.

Table 4. *Agreement ratios R and wR for the least-squares refinement of the data*

$\sigma(x)$ is a typical value of the estimated standard deviation of a positional parameter in the heavy atom refinement.

Experiment number	Heavy atom refinement			Hydrogen atom refinement		Number of reflections* in refinement
	R	wR	$\sigma(x)$	R	wR	
1	0·063	0·094	0·0016	†	†	239
2	0·091	0·110	0·0006	0·076	0·091	368
3	0·049	0·060	0·0011	†	†	277
4	0·104	0·127	0·0008	0·089	0·107	331
5	0·034	0·064	0·0003	0·029	0·043	607
6	‡	‡	‡	‡	‡	96
7	0·063	0·077	0·0004	0·047	0·052	429
8	0·079	0·114	0·0007	0·065	0·093	355
9	0·064	0·090	0·0005	0·048	0·066	366
10	‡	‡	‡	‡	‡	129
11*a*	0·075	0·133	0·0010	0·063	0·123	342
11*b*‖	0·097	0·163	0·0022	§	§	164
12	0·112	0·178	0·0016	†	†	403
13	0·057	0·071	0·0006	0·047	0·060	417
14	0·081	0·104	0·0008	†	†	273
15	0·047	0·063	0·0008	0·029	0·039	324
16	0·049	0·070	0·0004	0·034	0·043	429

* The numbers greater than 332 occurred because of the appearance of equivalent reflections which were not averaged before the refinement.
† Diverged on attempted hydrogen atom refinement.
‡ Insufficient data for refinement.
§ Hydrogen atom refinement not attempted.
‖ Did not converge. These were lowest R factors obtained.

course, are larger with maximum values of 38 σ_{INT} for O(1)x and 34 for C(2)β_{33}. The expected value is 6 σ_{INT} for a normal distribution with this number of degrees of freedom. The frequency with which a given experiment is associated with an extremum of a range for the 539 parameters in question is also revealing, as shown

Table 5. *Results of heavy atom refinements for the modal experimental group*

For five degrees of freedom, a value of RATIO greater than 2·21 is significant at the 95% level.

ATOM	P	MAXIMUM	MINIMUM	AVERAGE	OSK	SIGMA(EXT)	SIGMA(INT)	RATIO	1	2	3	5	7	16
1	1	33941	33174	33747	33820	49	20	6.0105	33941	33798	33174	33726	33796	33775
1	2	3430	3430	3430	3430	0	0	0.0000	3430	3430	3430	3430	3430	3430
1	3	51635	50963	51070	51020	69	30	5.2234	51162	51179	51635	50963	51047	51039
1	4	1320	522	786	965	69	33	4.3489	597	522	1320	856	736	740
1	5	2158	1039	1812	2355	129	67	3.7063	2158	1039	1736	2064	1734	1826
1	6	1618	670	1086	1149	97	66	2.1755	1468	670	1618	1183	951	1093
1	7	243	-136	35	-2	26	44	.3590	-136	4	243	21	16	53
1	8	272	-90	243	284	26	34	.5754	64	186	-90	272	252	261
1	9	426	60	348	289	45	65	.4755	60	307	116	426	309	405
2	1	43186	42941	42978	42960	25	19	1.5940	43065	42947	43186	42941	42945	43044
2	2	-3322	-3695	-3409	-3249	39	50	.6100	-3695	-3539	-3322	-3405	-3460	-3325
2	3	-2118	-2467	-2149	-2189	34	29	1.3690	-2169	-2123	-2467	-2118	-2170	-2118
2	4	1103	429	762	725	62	30	4.0544	1103	429	1016	850	769	689
2	5	2864	1511	2301	2713	158	83	3.6170	1927	1511	2864	2590	2135	2172
2	6	1282	682	953	1412	51	61	.6776	682	854	1282	909	955	997
2	7	583	306	367	186	26	47	.3167	395	306	583	369	348	347
2	8	380	159	282	407	26	37	.4736	380	172	159	325	318	231
2	9	-142	-883	-216	-298	85	64	1.7739	-397	-165	-883	-161	-142	-146
3	1	60993	60843	60955	60840	16	21	.6115	60914	60843	60993	60956	60979	60966
3	2	594	227	483	500	45	54	.6812	227	350	410	540	406	594
3	3	30369	30046	30120	30050	27	33	.6774	30152	30046	30369	30107	30092	30140
3	4	929	277	453	578	53	32	2.7107	929	277	686	476	329	495
3	5	2073	960	1668	2374	146	82	3.1603	960	1010	2073	1944	1648	1570
3	6	2979	917	1645	1634	159	60	7.0195	917	1064	2979	1818	1721	1589
3	7	236	-193	15	116	36	40	.8225	236	126	-193	4	74	-37
3	8	546	2	160	303	37	41	.8010	546	98	2	191	121	140
3	9	861	149	290	440	64	60	1.1363	194	327	861	333	292	149
4	1	30852	30676	30739	30630	21	20	1.0983	30696	30852	30763	30758	30733	30676
4	2	41885	41357	41683	41730	58	47	1.5442	41357	41423	41885	41706	41589	41780
4	3	23599	23211	23542	23350	29	31	.9064	23211	23528	23599	23567	23546	23547
4	4	645	342	558	648	35	32	1.2581	342	352	645	615	544	545
4	5	1432	646	974	1708	90	63	2.0700	1432	646	1054	1178	859	792
4	6	1671	612	1150	1018	98	57	2.9162	1045	612	1671	1167	1179	1214
4	7	55	-563	-21	-199	49	43	1.2982	-563	55	-176	-5	28	6
4	8	336	227	280	171	19	35	.3012	306	227	289	336	254	245
4	9	181	-49	114	58	20	53	.1515	-49	181	129	128	134	87
5	1	-7674	-8001	-7758	-7649	37	23	2.6114	-8001	-7704	-7922	-7674	-7792	-7821
5	2	8260	7753	7874	7920	57	56	1.0436	8260	7802	7753	7813	7805	8060
5	3	17954	17716	17802	17900	26	39	.4447	17916	17716	17954	17776	17783	17830
5	4	1289	484	754	640	71	33	4.6510	725	484	1289	829	676	705
5	5	3427	2027	2455	2688	122	100	1.4923	3427	2027	2090	2661	2461	2378
5	6	2775	1355	1973	2362	132	66	3.9988	1504	1355	2775	2056	1949	2020
5	7	38	-547	-293	-380	43	56	.6030	38	-303	-547	-247	-317	-286
5	8	500	-374	419	511	68	39	3.0895	500	321	-374	489	476	402
5	9	-766	-1254	-078	-861	46	78	.3444	-1254	-943	-878	-857	-930	-766
6	1	-2016	-2223	-2054	-2169	22	21	1.0946	-2223	-2040	-2198	-2055	-2016	-2033
6	2	40583	40198	40346	40720	61	59	1.0946	40327	40198	40238	40268	40303	40583
6	3	35036	34659	34982	34960	47	39	1.4402	34744	34925	34659	35033	35036	35017
6	4	848	474	783	920	48	41	1.3867	616	474	839	848	815	790
6	5	3028	1471	2261	2641	173	96	3.2577	1471	1763	3028	2588	2112	2008
6	6	2925	1764	2233	2492	105	76	1.9081	2925	1764	2725	2330	2111	2206
6	7	-8	-139	-86	-1	22	57	.1514	-94	-118	-69	-139	-88	-8
6	8	623	362	550	655	30	44	.4704	567	428	362	623	536	529
6	9	-37	-1009	-681	-885	83	86	.9409	-1009	-501	-37	-736	-710	-737
7	1	29565	28951	29296	29410	36	32	1.3057	28951	29207	29565	29319	29249	29338
7	2	1684	1156	1525	1590	65	69	.8721	1320	1492	1156	1486	1588	1684
7	3	28290	27476	28173	28320	77	49	2.4615	27684	28177	27476	28290	28227	28137
7	4	1451	109	580	510	104	45	5.2177	1451	109	1355	575	502	732
7	5	2380	963	1551	1411	168	109	2.3513	1490	963	2380	1813	1316	1301
7	6	1478	40	1074	1266	117	86	1.8690	40	995	1478	1184	1179	1041
7	7	437	27	247	111	31	65	.2271	437	160	27	294	211	266
7	8	496	-861	408	194	62	52	1.4184	419	413	-861	496	439	298
7	9	335	-185	-64	168	62	85	.5396	289	92	335	-71	-131	-185
8	1	46498	45867	46327	46400	40	31	1.6406	46498	46448	45867	46318	46349	46297
8	2	-566	-1244	-760	-679	88	59	2.1696	-1041	-1000	-1244	-680	-753	-566
8	3	19385	18822	18888	19110	48	47	1.0266	19115	19024	19385	18851	18847	18822
8	4	1115	39	431	665	80	54	2.1523	54	39	1115	542	407	462
8	5	1202	-27	739	1161	133	94	1.9730	-27	270	1202	954	558	726
8	6	3968	707	1274	1502	185	95	3.8185	876	707	3968	1451	1463	1112
8	7	423	-296	-70	-11	51	57	.8205	423	-161	-296	-122	-21	-33
8	8	337	-1669	227	278	79	57	1.9369	-42	180	-1669	337	311	110
8	9	393	20	151	161	43	84	.2713	231	196	393	20	208	191
9	1	20205	19905	20143	20030	23	29	.6360	19905	20191	20070	20122	20133	20205
9	2	22640	22431	22516	22730	37	67	.3038	22523	22483	22454	22431	22550	22640
9	3	18144	17787	18021	18110	36	48	.5726	17787	18025	18034	17981	17970	18144
9	4	276	-188	149	442	67	42	2.4553	-93	-86	-188	236	276	139
9	5	2213	961	1222	1532	93	86	1.1898	2213	961	1519	1232	1220	1046
9	6	1050	83	800	954	140	82	2.8513	969	220	83	1050	866	884
9	7	-252	-770	-414	-3	62	62	1.0122	-770	-632	-252	-274	-517	-465
9	8	1468	0	153	142	100	52	3.6037	0	14	1468	52	210	200
9	9	68	-528	-78	33	59	88	.4572	-528	-250	-24	68	-110	-118
10	1	2517	2173	2219	2190	34	32	1.1260	2279	2209	2517	2192	2173	2232
10	2	25638	25189	25424	25280	64	73	.7728	25296	25189	25638	25368	25330	25599
10	3	24971	24744	24914	24960	35	46	.5707	24795	24744	24781	24971	24908	24964
10	4	922	343	623	496	85	57	2.1689	364	343	922	830	482	516
10	5	1271	727	1154	1802	59	110	.2961	1253	727	1271	1181	1233	1120
10	6	1531	473	881	1203	86	98	.7676	869	473	1531	930	932	904
10	7	626	-188	13	82	90	71	1.6133	169	146	626	-24	25	-188
10	8	185	-223	-87	26	20	62	.1069	-223	-60	185	-103	-77	-88
10	9	-32	-690	-130	-20	72	92	.6233	-202	-268	-690	-34	-172	-32

below, the italicized value giving the frequency:

	Experiment					
	1	2	3	5	7	16
Maxima:	*11*	*1*	*31*	*6*	*3*	*7*
Minima:	*16*	*27*	*10*	*3*	*1*	*2*

The distribution of the maxima and minima differ significantly from the expected uniform distribution. That experiment 3 accounts for most of the maximum values and experiment 2 for the minimum values is further indication that the *modal* group still contains some systematic errors which are correlated with structural parameters.*

The low values found for the least-squares derived standard deviations are to be associated with the known systematic errors present in some, if not all, of the experiments. The formulas used to derive the internal standard deviations assume that only random errors are present in the observations. As this condition is increasingly violated, the apparent standard deviation, which is only a measure of the precision of fit between the model and the observations, becomes correspondingly unreliable as a measure of accuracy.

Conclusion

Systematic differences among structure factors from different experiments and different crystals are manifested in systematically different parameters when the data are subjected to least-squares refinement. Even if the parameters of an acceptable theoretical model refine without divergence, the derived parameters may be in error by several times the estimated standard deviations calculated from the goodness-of-fit achieved as a result of the least-squares refinement. Standard deviations on bond lengths and thermal parameters obtained in crystal structure refinements are realistic only if (1) there are no errors in the theoretical model and (2) if there are no systematic errors in the experiment. It is hoped that by projects such as this, the validity of (2) may be assessed so that we may direct our attention toward (1) – which includes all the questions of physical and chemical interest.

We would like to thank the following members and consultants of the 1963–1966 Commission on Crystallographic Apparatus of the I.U.Cr.: Professor M. M. Umanskij, Dr D. C. Phillips and Professor Y. Saito and, in particular, the chairman, A. McL. Mathieson, for exceedingly helpful comments. The project would of course not have been possible without the splendid cooperation of those who contributed data and who offered constructive criticism of earlier phases of the draft report.

* The large number of extrema for experiment 3 is partially influenced by the fact that, because of the smaller number of reflections, it has larger internally estimated standard deviations. On this basis, the number of extrema should be 3 to 4 times as great as for other members of the modal group.

References

ABRAHAMS, S. C., HAMILTON, W. C. & MATHIESON, A. McL (1969). *Acta Cryst.* A**25**, 1.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). USAEC Oak Ridge National Laboratory Report TM–305.

COX, G. W., SABINE, T. M. & TAYLOR, G. H. (1966). Private communication.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

OKAYA, Y., STEMPLE, N. R. & KAY, M. I. (1966). *Acta Cryst.* **21**, 237.

STERN, F. & BEEVERS, C. A. (1950). *Acta Cryst.* **3**, 341.

Acta Cryst. (1970). A**26**, 24

A Direct Method for the Determination of Polytype Structures. I. Theoretical Basis

BY K. DORNBERGER-SCHIFF

Deutsche Akademie der Wissenschaften zu Berlin, Institut für Strukturforschung, Berlin-Adlershof, Germany (DDR)

AND M. FARKAS-JAHNKE

Research Institute for Technical Physics of the Hungarian Academy of Sciences, Budapest, Hungary

(*Received* 6 *June* 1967 *and in revised form* 5 *June* 1969)

A direct method for the determination of polytype structures of SiC, ZnS and similar substances from X-ray data is described. It is based on the values of a Patterson-like function (the 'Pattersonian') which only depends on the stacking of the translationally equivalent layers of the structure. The way of obtaining the Pattersonian function from the experimental intensities is described and an algorithm given by which the sequence of layers may be deduced. This sequence is conveniently characterized by the sequence of the digits of a binary number. The influence of experimental errors in the intensities on the possibilities of determining the real sequence is discussed.

Introduction

It has been found recently that optical and electronic data of semiconducting substances, especially of ZnS and SiC, depend on the polytype present (Kholuyanov, 1964; Gobrecht, Nelkowski, Baars & Brandt, 1965; Hamilton, Patrick & Choyke, 1965; Patrick, 1965; Patrick, Choyke & Hamilton, 1965; Brafman & Stein-