Acta Cryst. (1964). **17**, 1421

The Role of Molecular Structure in the Direct Determination of Phase

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(*Received* 11 *June* 1963 *and in revised form* 16 *December* 1963)

A major revision of the direct methods of phase determination is undertaken in order to extend the domain of validity of the methods to those structures having atoms with rationally dependent coordinates. The new formulation, strongly dependent on a critical analysis of the nature of the interactions which may occur among Patterson peaks, has the additional advantage that it is capable of using partial or complete *a priori* information concerning molecular structure.

1. Introduction

The method of solving crystal structures based on the direct determination of the phases of the structure factors had its serious beginnings only about a dozen years ago. Yet its development has been so vigorous that it has already achieved several notable successes (*e.g.* Christ & Clark, 1956; Karle, Hauptman, Karle & Wing, 1958; Hauptman, Karle & Karle, 1960). The most remarkable aspect of these applications of the direct method, however, does not appear to have been sufficiently stressed. This is simply that, in contrast to most other methods of crystal structure determination, no *a priori* knowledge of molecular structure is employed by the direct methods. The fact that the direct approach is not dependent on a previous knowledge of molecular structure is of course an advantage of the method when such previous knowledge is not available. However, in the case that such knowledge does exist, it is to be considered a weakness of the direct method that it is unable to utilize this information. In view of the fact that complete, or even partial, knowledge of the molecular structure would reduce substantially the number of unknown parameters required to fix the crystal structure, it is surely to be expected that the ability to make use of such *a priori* structural information would enhance the power of the method.

The direct method has been limited too by the fact that, for their exact validity, most of the phase determining formulas require that a special type of rational dependence among atomic coordinates be not present. Owing to the symmetries which seem to occur all too frequently in real crystals, this limitation has proved to be much more serious than originally expected, particularly in the non-centrosymmetric space groups. Although it has been found possible to surmount this difficulty for some of the special relationships by means of the so-called renormalization of structure factors (Hauptman & Karle, 1959*c*), it has become increasingly clear that what is called for is nothing less than a major revision of the whole formalism of the direct methods. It is the purpose of this paper to carry out such a revision.

Instead of avoiding the annoying question of rational dependence of atomic coordinates, it is assumed from the outset that the kind of rational dependence which causes trouble may in fact be present. By a critical re-examination of the earlier methods, coupled with a careful study of the nature of the interactions which may exist among Patterson peaks, it is shown how the formalism is to be modified in order to accommodate the existing rational dependence, if any. This more general point of view has the additional advantage that it makes transparent the manner in which previous knowledge of molecular structure is to be used. Even if only partial information concerning the molecular structure is available, the new formalism is capable of utilizing it. Naturally, however, the more complete the *a priori* knowledge of the molecular structure the more accurate the final phase determination will be.

A device often employed in this paper is to compute expected values of different random variables and to equate two expected values if the corresponding probability distributions are approximately the same. This technique naturally introduces certain errors into the calculations the magnitudes of which it would be desirable to estimate. However, a detailed study of the errors involved in the final formulas must be postponed in order to keep the present treatment within reasonable bounds. Since the present formulation includes as special cases those in which no rational dependence exists and no previous knowledge of molecular structure is available, it is possible to specialize some of our formulas suitably so that comparison with existing theory may be made. There are four points at which such contacts with earlier, known results are here made. In every case the agreement with the exact formulas is acceptable, the errors being of the order of $1/\sqrt{N}$ or less, where N is the number of atoms in the unit cell.

In this paper the final formulas express the magnitudes of certain linear combinations of the phases, the so-called structure invariants, in terms of the observed magnitudes of the structure factors. There remains the problem of evaluating the individual phases from the structure invariants. How this is to be done for the centrosymmetric space groups has already been spelled out in detail in an earlier series of papers (Karle & Hauptman, 1959*a*, *b*, 1960, 1961; Hauptman & Karle, 1959*a*, *b*, 1960). These procedures have been worked out also for certain of the non-centrosymmetric space groups (Karle & Hauptman, 1956, 1957). However, complete details for all the non-centrosymmetric space groups will be published at a later date.

In § 2 we give a formula for the average value of $\exp\{2\pi i(\mathbf{h}.\mathbf{r}+\mathbf{h}'.\mathbf{r}')\}$. This result is of fundamental importance for this paper. However, owing to the length of the analysis, the proof is omitted.*

2. The average value of exp $\{2\pi i(\boldsymbol{h}.\boldsymbol{r}+\boldsymbol{h}'.\boldsymbol{r}')\}$

Debye (1915) obtained the average value of $\exp(2\pi i\mathbf{h}.\mathbf{r})$ where $\mathbf{h}$ is a fixed vector, the magnitude of the vector $\mathbf{r}$ is fixed, and all orientations of $\mathbf{r}$ are equally probable. He found that

$$\langle\exp(2\pi i\mathbf{h}.\mathbf{r})\rangle=\frac{\sin 2\pi qr}{2\pi qr}\,, \qquad (2\cdot1)$$

where $q=|\mathbf{h}|$ is the magnitude of $\mathbf{h}$ and $r=|\mathbf{r}|$ is the magnitude of $\mathbf{r}$. This result proved to be of basic importance for the interpretation of the scattering of electrons by gas molecules. We note that in Debye's application of (2·1) the vector $\mathbf{r}$ is identified with an interatomic vector $\mathbf{r}_{jj'}$ which is assumed to be randomly oriented.

For our purposes it turns out to be necessary to average, not over all orientations of an interatomic vector $\mathbf{r}_{jj'}$, but instead over all orientations of an interatomic triangle $\mathbf{r}_{\mu\nu}$, $\mathbf{r}_{\nu\varrho}$, $\mathbf{r}_{\varrho\mu}$ where $\mathbf{r}_{\mu\nu}$ is the vector joining atom μ to atom ν, *etc.* However, except for its position and orientation in space, such a triangle is determined by the magnitudes of any two of its sides and the angle between them. In this way we are led to consider a generalization of (2·1). Assume that the vectors $\mathbf{h}$ and $\mathbf{h}'$ are given. The magnitudes r and r' of the vectors $\mathbf{r}$ and $\mathbf{r}'$ respectively, as well as the angle φ_r between $\mathbf{r}$ and $\mathbf{r}'$, are also specified. We imagine that all orientations of the triangle determined by r, r', and φ_r are equally probable and we seek, under these conditions, the average value of $\exp\{2\pi i(\mathbf{h}.\mathbf{r}+\mathbf{h}'.\mathbf{r}')\}$. The final result is a function, which we shall denote by $B(z,t)$, of two parameters z and t each of which is in turn expressible in terms of the six known quantities $q, q', \varphi_q, r, r', \varphi_r$, where q and q' are the magnitudes of $\mathbf{h}$ and $\mathbf{h}'$ respectively, φ_q is the angle between $\mathbf{h}$ and $\mathbf{h}'$, and r, r', and φ_r have already been defined. With this notation we have

THEOREM 2·1.

$$\langle\exp\{2\pi i(\mathbf{h}.\mathbf{r}+\mathbf{h}'.\mathbf{r}')\}\rangle=B(z,t)$$

$$=\sqrt{\frac{\pi}{2z}}\sum_{n=0}^{\infty}\frac{t^{2n}}{(n!)^2}J_{\frac{1}{2}(4n+1)}(z)\,, \qquad (2\cdot2)$$

where

$$z=2\pi\sqrt{(q^2r^2+2qrq'r'\cos\varphi_q\cos\varphi_r+q'^2r'^2)}\,, \qquad (2\cdot3)$$

$$t=\frac{\pi qrq'r'\sin\varphi_q\sin\varphi_r}{\sqrt{(q^2r^2+2qrq'r'\cos\varphi_q\cos\varphi_r+q'^2r'^2)}}\,, \qquad (2\cdot4)$$

and $J_{\frac{1}{2}(n+1)}(z)$ is the Bessel function of the first kind.

We note first that the same result is obtained if $\mathbf{r}$ and $\mathbf{r}'$ are replaced by $-\mathbf{r}$ and $-\mathbf{r}'$ respectively. Hence also

$$\langle\cos 2\pi(\mathbf{h}.\mathbf{r}+\mathbf{h}'.\mathbf{r}')\rangle=B(z,t)\,. \qquad (2\cdot5)$$

Next we observe that in the special case that $\varphi_q=0$ or π or that $\varphi_r=0$ or π, then $t=0$, and, in view of

$$J_{\frac{1}{2}}(z)=\sqrt{(2/(\pi z))}\sin z\,, \qquad (2\cdot6)$$

equation (2·2) reduces to $(\sin z)/z$, *i.e.* to Debye's result (2·1), as it should.

We remark finally that, since the pairs $(\mathbf{h},\mathbf{h}')$ and $(\mathbf{r},\mathbf{r}')$ occur symmetrically in Theorem 2·1, we may interchange their roles. Hence Theorem 2·1 is valid also in the case that the vectors $\mathbf{r}$ and $\mathbf{r}'$ are fixed and the average is taken over all orientations in reciprocal space of the triangle with sides q, q' and with included angle φ_q. We shall make important use of this observation in the sequel.

From (2·3) and (2·4) it follows easily that

$$z(z\pm 4t)\geq 0 \qquad (2\cdot7)$$

whence

$$|t|\leq\tfrac{1}{4}z\,. \qquad (2\cdot8)$$

Since $B(z,t)$ is an even function of t, $B(z,t)$ need be computed therefore only in the range

$$0\leq t\leq\tfrac{1}{4}z\,. \qquad (2\cdot9)$$

In order to apply the methods described in this paper, it is necessary to have a table of values of the function $B(z,t)$. Table 1 gives the values of this function for z in the range $0\leq z\leq 40$ and for t satisfying (2·9) approximately. If it should prove necessary, a more extensive table will be published at a future date. Inspection of Table 1 shows that, in the range defined by (2·9), the magnitude of no entry exceeds unity, in agreement with the interpretation of the function $B(z,t)$ as an average of the cosine. It is of some interest, however, that outside the range defined by (2·9), computation shows that $B(z,t)$ increases with extreme rapidity. For future

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* This analysis will appear in a forthcoming issue of *Z. Kristallogr.* (1965).

Table 1. *The function $B(z, t)$ defined by equation* (2·2), *where z and t are given by* (2·3) *and* (2·4)

The entries are the values of $10^4 \times B(z, t)$

z \ t		6.0	5.6	5.2	4.8	4.4	4.0	3.6	3.2	2.8	2.4	2.0	1.6	1.2	0.8	0.4	0.0	t / z
0.0	10000	37068	+1478	-91	+28	-107	-16	+123	+120	+17	-65	-70	-27	+13	+20	+5	-4	22.0
0.2	+9933	+9935	+4125	-172	+73	-58	-33	+114	+145	+37	-90	-134	-85	+10	+101	+158	+177	21.6
0.4	+9735	+9740	+9168	-111	+83	+13	-42	+82	+145	+52	-100	-178	-133	+6	+168	+291	+335	21.2
0.6	+9411	+9420	17859	+324	+42	+89	-37	+33	+118	+59	-92	-194	-160	+0	+211	+382	+447	20.8
0.8	+8967	+8983	31788	+1499	-36	+149	-17	-24	+67	+55	-69	-178	-162	-6	+221	+415	+490	20.4
1.0	+8415	+8440	+8514	+3952	-95	+170	+16	-77	-1	+41	-32	-131	-138	-12	+196	+382	+456	20.0
1.2	+7767	+7802	+7906	+8408	-13	+133	+55	-113	-73	+17	+12	-59	-90	-16	+137	+287	+348	19.6
1.4	+7039	+7084	+7221	15802	+421	+39	+87	-124	-135	-13	+54	+25	-24	-18	+54	+141	+179	19.2
1.6	+6247	+6304	+6474	27271	+1521	-86	+96	-106	-176	-45	+88	+110	+48	-17	-42	-34	-26	18.8
1.8	+5410	+5478	+5683	+6026	+3724	-171	+69	-61	-183	-71	+107	+179	+117	-13	-135	-211	-236	18.4
2.0	+4546	+4626	+4865	+5265	+7593	-91	+1	-0	-154	-88	+106	+221	+169	-6	-210	-362	-417	18.0
2.2	+3675	+3765	+4036	+4492	13815	+346	-98	+59	-89	-89	+86	+227	+196	+3	-254	-461	-539	17.6
2.4	+2814	+2914	+3215	+3720	23182	+1407	-194	+98	+0	-71	+49	+193	+192	+12	-258	-490	-580	17.2
2.6	+1983	+2091	+2417	+2966	+3747	+3437	-215	+100	+98	-36	+1	+125	+155	+20	-221	-441	-528	16.8
2.8	+1196	+1311	+1658	+2243	+3078	+5853	-52	+58	+181	+13	-48	+30	+90	+25	-145	-318	-389	16.4
3.0	+470	+590	+952	+1564	+2439	12130	+455	-19	+229	+68	-88	-74	+6	+26	-42	-137	-180	16.0
3.2	-182	-60	+311	+939	+1842	19784	+1516	-93	+223	+118	-112	-172	-84	+23	+74	+76	+69	15.6
3.4	-752	-629	-256	+379	+1295	+2520	+3386	-98	+156	+150	-112	-244	-166	+15	+184	+287	+320	15.2
3.6	-1229	-1108	-740	-111	+803	+2033	+6357	+69	+34	+152	-89	-277	-225	+3	+269	+463	+533	14.8
3.8	-1610	-1493	-1136	-523	+372	+1588	10746	+547	-113	+117	-45	-261	-250	-10	+314	+573	+671	14.4
4.0	-1892	-1781	-1442	-857	+5	+1188	16866	+1508	-233	+42	+10	-196	-233	-24	+310	+597	+708	14.0
4.2	-2075	-1972	-1657	-1110	-295	+835	+2346	+3148	-250	-64	+63	-90	-175	-35	+254	+524	+632	13.6
4.4	-2163	-2070	-1784	-1283	-529	+532	+1972	+5672	-62	-183	+100	+40	-81	-41	+152	+361	+449	13.2
4.6	-2160	-2079	-1827	-1381	-699	+277	+1627	+9282	+449	-279	+109	+172	+35	-40	+18	+128	+181	12.8
4.8	-2075	-2007	-1793	-1409	-808	+71	+1314	14151	+1412	-304	+82	+281	+155	-31	-128	-140	-134	12.4
5.0	-1918	-1863	-1690	-1372	-861	-90	+1032	+2621	+2957	-197	+23	+342	+258	-15	-262	-404	-447	12.0
5.2	-1699	-1659	-1528	-1279	-862	-206	+783	+2230	+5202	+115	-54	+337	+325	+8	-361	-619	-709	11.6
5.4	-1431	-1405	-1317	-1139	-816	-284	+565	+1858	+8241	+712	-120	+261	+340	+33	-405	-748	-874	11.2
5.6	-1127	-1115	-1070	-961	-738	-325	+379	+1510	12131	+1671	-130	+119	+293	+56	-385	-763	-908	10.8
5.8	-801	-803	-798	-757	-628	-336	+224	+1188	+2736	+3063	-30	-66	+186	+73	-296	-653	-796	10.4
6.0	-466	-480	-513	-535	-496	-321	+96	+894	+2254	+4943	+246	-253	+27	+78	-150	-426	-544	10.0
6.2	-134	-159	-226	-307	-351	-285	-5	+629	+1800	+7343	+765	-393	-159	+67	+35	-109	-182	9.6
6.4	+182	+147	+50	-81	-199	-233	-81	+394	+1378	10265	+1587	-425	-343	+39	+231	+255	+242	9.2
6.6	+472	+429	+308	+134	-49	-171	-136	+191	+994	+2514	+2760	-288	-486	-6	+404	+609	+665	8.8
6.8	+727	+678	+537	+330	+95	-103	-171	+20	+650	+1960	+4311	+75	-549	-62	+522	+895	+1017	8.4
7.0	+939	+885	+732	+500	+225	-33	-190	-120	+349	+1454	+6235	+703	-492	-121	+559	+1061	+1237	8.0
7.2	+1102	+1047	+887	+640	+338	+34	-194	-229	+93	+1003	+8498	+1620	-286	-171	+498	+1064	+1274	7.6
z / t	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8								

t \ z	22.4	22.8	23.2	23.6	24.0	24.4	24.8	25.2	25.6	26.0	26.4	26.8
0.0	-177	-317	-403	-423	-377	-274	-132	+27	+176	+293	+361	+371
0.4	-143	-263	-339	-359	-323	-237	-118	+16	+143	+244	+304	+315
0.8	-61	-130	-176	-193	-179	-137	-76	-4	+66	+123	+159	+170
1.2	+13	+11	+7	+3	-2	-6	-9	-10	-10	-8	-5	-1
1.6	+34	+87	+124	+140	+134	+107	+64	+12	-40	-84	-113	-123
2.0	+3	+73	+128	+161	+167	+146	+103	+44	-20	-79	-123	-146
2.4	-30	+10	+46	+74	+89	+88	+73	+47	+13	-22	-53	-74
2.8	-4	-22	-35	-41	-40	-32	-20	-5	+9	+21	+29	+31
3.2	+75	+19	-37	-83	-114	-123	-112	-82	-39	+8	+52	+85
3.6	+107	+72	+24	-28	-72	-103	-114	-104	-76	-35	+11	+53
4.0	+3	+19	+27	+27	+19	+5	-9	-22	-29	-29	-22	-11
4.4	-126	-115	-81	-34	+16	+57	+83	+91	+80	+55	+22	-12
4.8	-32	-82	-108	-103	-71	-21	+33	+77	+104	+107	+88	+50
5.2	+6	+65	+75	+51	+14	-18	-34	-31	-15	+8	+28	+38
5.6	+293	-89	-98	+8	+100	+132	+107	+47	-19	-69	-92	-87
6.0	20309	10165	+4466	+1579	+334	-54	-75	+4	+59	+59	+17	-37
6.4			75358	43168	23041	11186	+4720	+1554	+249	-124	-116	-16
6.8							89416	50012	26003	12256	+4999	+1587

t \ z	27.2	27.6	28.0	28.4	28.8	29.2	29.6	30.0	30.4	30.8	31.2	31.6
0.0	+323	+226	+97	-44	-174	-274	-328	-329	-280	-188	-69	+58
0.4	+276	+196	+87	-32	-143	-229	-276	-280	-239	-162	-62	+45
0.8	+153	+113	+57	-7	-68	-117	-146	-151	-133	-94	-42	+16
1.2	+2	+5	+7	+8	+7	+6	+3	+0	-3	-5	-6	-6
1.6	-114	-87	-48	-2	+43	+80	+103	+110	+98	+72	+35	-6
2.0	-145	-121	-79	-25	+31	+81	+116	+132	+127	+101	+61	+11
2.4	-82	-77	-59	-32	-1	+30	+55	+71	+75	+66	+47	+21
2.8	+28	+21	+11	-0	-11	-19	-23	-24	-20	-14	-6	+3
3.2	+103	+103	+86	+56	+17	-23	-57	-82	-92	-86	-67	-38
3.6	+86	+102	+101	+82	+50	+10	-31	-65	-88	-95	-86	-63
4.0	+4	+18	+28	+33	+31	+23	+11	-4	-19	-29	-35	-34
4.4	-41	-60	-67	-61	-44	-21	+4	+26	+43	+51	+49	+39
4.8	+4	-41	-77	-96	-96	-78	-46	-7	+33	+65	+84	+87
5.2	+37	+24	+3	-20	-39	-50	-49	-37	-16	+8	+31	+48
5.6	-61	-24	+13	+41	+55	+54	+42	+22	+0	-18	-30	-33
6.0	-79	-92	-74	-34	+14	+58	+85	+90	+73	+41	+1	-37
6.4	+54	+67	+40	+2	-25	-32	-19	+5	+28	+42	+41	+26
6.8	+259	-78	-43	+57	+106	+89	+34	-25	-65	-75	-59	-29
7.2	29434	13540	+5385	+1668	+270	-75	-51	+26	+51	+22	-29	-67
7.6				66926	33197	14848	+5692	+1655	+205	-116	-63	+30
8.0								77083	37358	16287	+6071	+1721

t \ z	32.0	32.4	32.8	33.2	33.6	34.0	34.4	34.8	35.2	35.6	36.0
0.0	+172	+257	+300	+294	+243	+156	+46	-69	-170	-243	-275
0.4	+142	+215	+253	+250	+208	+135	+42	-55	-141	-204	-233
0.8	+70	+111	+134	+136	+116	+78	+29	-23	-71	-106	-124
1.2	-6	-4	-2	+0	+3	+4	+5	+5	+4	+3	+1
1.6	-46	-77	-95	-98	-86	-60	-25	+12	+47	+74	+88
2.0	-39	-81	-110	-120	-111	-85	-46	-0	+44	+81	+104
2.4	-8	-35	-56	-67	-68	-57	-38	-13	+14	+38	+55
2.8	+11	+17	+19	+19	+15	+10	+3	-4	-10	-15	-16
3.2	-3	+31	+59	+77	+81	+73	+53	+24	-7	-36	-59
3.6	-30	+7	+4	+70	+85	+85	+72	+47	+15	-19	-49
4.0	-27	-15	+0	+15	+27	+34	+35	+30	+20	+6	-8
4.4	+23	+4	-14	-29	-38	-40	-35	-25	-11	+4	+18
4.8	+74	+49	+16	-19	-49	-70	-78	-72	-54	-27	+4
5.2	+56	+52	+38	+17	-8	-31	-49	-57	-54	-42	-22
5.6	-28	-18	-6	+6	+15	+19	+18	+13	+6	-1	-8
6.0	-65	-77	-73	-55	-26	+6	+35	+56	+64	+60	+45
6.4	+1	-25	-46	-56	-53	-36	-11	+17	+41	+57	+61
6.8	+3	+28	+39	+36	+24	+7	-8	-17	-20	-15	-5
7.2	-76	-54	-13	+30	+63	+76	+67	+42	+8	-25	-49
7.6	+65	+44	+5	-24	-28	-12	+14	+34	+42	+32	+10
8.0	+233	-66	-5	+74	+82	+37	-21	-58	-63	-44	-14
8.4	42074	17917	+6505	+1784	+220	-84	-30	+35	+32	-11	-51
8.8					47232	19604	+6887	+1791	+179	-97	-20
9.2									52971	21484	+7363

t \ z	36.4	36.8	37.2	37.6	38.0	38.4	38.8	39.2	39.6	40.0
0.0	-265	-213	-129	-26	+78	+168	+230	+254	+239	+186
0.4	-225	-182	-112	-25	+63	+140	+193	+215	+203	+159
0.8	-122	-101	-65	-19	+29	+71	+101	+115	+111	+89
1.2	-1	-3	-2	-4	-4	-3	-2	-1	+1	+2
1.6	+88	+75	+50	+17	-17	-48	-71	-82	-80	-66
2.0	+110	+98	+71	+34	-8	-48	-79	-98	-100	-87
2.4	+63	+61	+49	+30	+6	-18	-39	-53	-59	-55
2.8	-15	-12	-7	-1	+5	+10	+13	+14	+12	+9
3.2	-71	-72	-61	-41	-14	+14	+39	+57	+66	+64
3.6	-70	-80	-76	-59	-34	-3	+28	+53	+69	+74
4.0	-21	-31	-35	-33	-26	-14	+0	+14	+26	+32
4.4	+28	+32	+31	+25	+15	+3	-9	-19	-25	-27
4.8	+33	+56	+68	+69	+57	+37	+10	-17	-40	-57
5.2	+2	+25	+44	+54	+55	+46	+29	+7	-16	-36
5.6	-12	-12	-15	-5	+1	+6	+10	+11	+10	+6
6.0	+22	-3	-27	-44	-53	-51	-40	-23	-2	+18
6.4	+52	+32	+6	-20	-43	-57	-60	-51	-32	-8
6.8	+5	+13	+16	+14	+8	-2	-11	-18	-21	-19
7.2	-60	-56	-40	-17	+8	+29	+41	+44	+38	+24
7.6	-17	-41	-54	-52	-37	-13	+15	+39	+54	+57
8.0	+14	+29	+30	+19	+4	-10	-17	-16	-7	+4
8.4	-63	-43	-4	+35	+59	+63	+47	+20	-11	-35
8.8	+54	+56	+17	-17	-27	-12	+13	+33	+37	+23
9.2	+1876	+210	-56	+18	+71	+48	-7	-49	-58	-39
9.6		59377	23543	+7855	+1925	+182	-83	-11	+35	+12
10.0						66394	25714	+8334	+1957	+164

application we observe that $B(z, t)$ approaches zero with increasing z, *i.e.*, in view of (2·3), with increasing r or r' or q or q'.

3. The structure invariants $|E|^2-1$

In this section we introduce the basic definitions and notation and prove some preliminary results which will be needed later.

The central theme in this section is the formula (Hauptman & Karle, 1955)

$$|E_{\mathbf{h}}|^2-1=N\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}\,, \quad (3\cdot1)$$

valid for the case of N identical atoms per unit cell and under the restriction that no two interatomic vectors coincide, *i.e.* that the Patterson function contain no overlapping peaks.* The latter requirement rules out, for example, the space group $P\bar{1}$, for which the correct formula is (Cochran, 1954)

$$|E_{\mathbf{h}}|^2-1 \approx (N/2)\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}\,, \qquad (3\cdot2)$$

subject now to the restriction that, except for symmetry-related vectors, no two interatomic vectors coincide. The symbol $\approx$ in (3·2) replaces the exact equality of (3·1) since, for simplicity, a term of the order of $1/\sqrt{N}$ has been suppressed in (3·2). A major aim of this section is to exhibit (3·1) and (3·2) as special cases of a single, more general formula, valid, at least approximately, in the case of unequal atoms and, of greater significance, in the case that arbitrary numbers of interatomic vectors coincide. In particular, our main formula (equation (3·20)), in contrast to (3·1) and (3·2), is space-group independent, contains (3·1) and (3·2) as special cases, and clearly shows the origin of the discrepancy between (3·1) and (3·2).

As usual, in the following definitions, $\mathbf{r}_j$ is the position vector of the jth atom, the atomic number of which is Z_j, and N is the number of atoms in the unit cell.

Def. 3·1. $\sigma_n = \sum\limits_{j=1}^{N} Z_j^n$.

Def. 3·2. $E_{\mathbf{k}} = (1/\sigma_2^{1/2})\sum\limits_{j=1}^{N} Z_j \exp(2\pi i\mathbf{k}.\mathbf{r}_j)$.

Def. 3·3. $\mathbf{r}_{jk}=\mathbf{r}_j-\mathbf{r}_k$.

Def. 3·4. If $j\neq k$ we define Z_{jk} by means of

$$Z_{jk}=Z_jZ_k\,.$$

We list next, as immediate consequences of Def. 3·1–3·4, the following formulas:

$$|E_{\mathbf{k}}|^2-1 = (1/\sigma_2)\sum_{\substack{j\neq j'\\1}}^{N} Z_{jj'}\exp(2\pi i\mathbf{k}.\mathbf{r}_{jj'})\,; \qquad (3\cdot3)$$

$$\langle|E_{\mathbf{k}}|^2-1\rangle_{\mathbf{k}}=0\,; \qquad (3\cdot4)$$

$$E_0 = \sigma_1/\sigma_2^{1/2}\,; \qquad (3\cdot5)$$

$$\sum_{\substack{j,j'\\1}}^{N} Z_{jj'} = \sigma_1^2\,; \qquad (3\cdot6)$$

$$\sum_{\substack{j\neq j'\\1}}^{N} Z_{jj'} = \sigma_1^2-\sigma_2\,; \qquad (3\cdot7)$$

$$\sum_{\substack{j,j'\\1}}^{N} Z_{jj'}^2 = \sigma_2^2\,; \qquad (3\cdot8)$$

$$\sum_{\substack{j\neq j'\\1}}^{N} Z_{jj'}^2 = \sigma_2^2-\sigma_4\,. \qquad (3\cdot9)$$

Def. 3·5. If $j\neq k$ we define w_{jk}, the 'weight' of the vector $\mathbf{r}_{jk}$, by means of

$$w_{jk} = \sum_{j'\neq k'} Z_{j'k'}\,, \qquad (3\cdot10)$$

where the summation is extended over all pairs (j', k') such that

$$\mathbf{r}_{jk}+\mathbf{r}_{j'k'} = 0\,. \qquad (3\cdot11)$$

If $j=k$ we define w_{jk} to be zero.

Def. 3·6. The symbol ε_{jk} is defined by means of

$$\varepsilon_{jk}=w_{jk}/Z_{jk} \qquad (3\cdot12)$$

if $j\neq k$. If $j=k$, ε_{jk} is defined to be zero.

Since the equation

$$\mathbf{r}_{jk}+\mathbf{r}_{kj}=0 \qquad (3\cdot13)$$

implies that (3·11) always has at least the one solution $j'=k$, $k'=j$, and since $Z_{jk}=Z_{kj}$, it follows that

$$\varepsilon_{jk} \geq 1 \quad \text{if} \quad j\neq k\,. \qquad (3\cdot14)$$

Again, in view of $\mathbf{r}_{jk} = -\mathbf{r}_{kj}$, (3·11) implies $\mathbf{r}_{kj}+\mathbf{r}_{k'j'}=0$, and conversely. Hence, in view of $Z_{jk}=Z_{kj}$, (3·1), and (3·12),

$$w_{jk}=w_{kj}, \quad \varepsilon_{jk}=\varepsilon_{kj}\,. \qquad (3\cdot15)$$

Theorem 3·1. For arbitrary structures

$$\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}} = (1/\sigma_2^2)\sum_{\substack{j\neq k\\1}}^{N} Z_{jk}^2\varepsilon_{jk}\exp(2\pi i\mathbf{h}.\mathbf{r}_{jk})\,. \qquad (3\cdot16)$$

Proof: Appendix I.

Corollary. For a structure consisting of N identical atoms ε_{jk} may be interpreted as the number of vectors $\mathbf{r}_{j'k'}$ satisfying (3·11), and we have

$$\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}} = (1/N^2)\sum_{\substack{j\neq k\\1}}^{N} \varepsilon_{jk}\exp(2\pi i\mathbf{h}.\mathbf{r}_{jk})\,. \qquad (3\cdot17)$$

It is an important property of the ε_{jk} that their (weighted) average is the average of $(|E_{\mathbf{k}}|^2-1)^2$. In fact, setting $\mathbf{h}=0$ in theorem 3·1, we obtain

Theorem 3·2. For arbitrary structures

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* It should be emphasized that, under the conditions stated, (3·1) has exact validity provided that the average on the right is taken over all vectors $\mathbf{k}$ in reciprocal space. In the attempt to confirm (3·1) with experimental data one is faced with the complication introduced by the necessity of averaging over only a finite sample from the infinite population of vectors $\mathbf{k}$. One approach to the problem of estimating the errors arising from such finite sampling has already been described by Vaughan (1959). The further consideration of this problem is outside the scope of this paper. Similar remarks apply to § 5.

$$\langle(|E_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}} = (1/\sigma_2^2)\sum_{\substack{j\neq k\\1}}^{N} Z_{jk}^2\varepsilon_{jk} = \frac{\sum\limits_{\substack{j,k\\1}}^{N} Z_{jk}^2\,\varepsilon_{jk}}{\sum\limits_{\substack{j,k\\1}}^{N} Z_{jk}^2} \qquad (3{\cdot}18)$$

Corollary. For a structure consisting of N identical atoms we have

$$\langle(|E_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}} = (1/N^2)\sum_{\substack{j,k\\1}}^{N} \varepsilon_{jk}\,. \qquad (3{\cdot}19)$$

The main result of this section is contained in

Theorem 3·3. For arbitrary structures

$$|E_{\mathbf{h}}|^2-1 \approx \left(\frac{\sigma_1^2}{\sigma_2}-1\right)\frac{\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h+k}}|^2-1)\rangle_{\mathbf{k}}}{\langle(|E_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}}}\,. \qquad (3{\cdot}20)$$

Proof: Appendix II.

Corollary. For a structure consisting of N identical atoms we have

$$|E_{\mathbf{h}}|^2-1 \approx \frac{N-1}{\langle(|E_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}}}\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h+k}}|^2-1)\rangle_{\mathbf{k}}\,. \qquad (3{\cdot}21)$$

We conclude this section by showing how our formulas are specialized to yield the known results (3·1) and (3·2).

We assume first that no two interatomic vectors coincide. Then $\varepsilon_{jk}=1$ for $j\neq k$ and, in view of (3·9), equations (3·18) and (3·19) reduce to

$$\langle(|E_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}}=1-\sigma_4/\sigma_2^2 \qquad (3{\cdot}22)$$

and

$$\langle(|E_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}}=1-1/N \qquad (3{\cdot}23)$$

respectively. Hence equations (3·20) and (3·21) now become

$$|E_{\mathbf{h}}|^2-1 \approx \frac{(\sigma_1^2/\sigma_2)-1}{1-(\sigma_4/\sigma_2^2)}\cdot\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h+k}}|^2-1)\rangle_{\mathbf{k}} \qquad (3{\cdot}24)$$

and

$$|E_{\mathbf{h}}|^2-1 \approx N\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h+k}}|^2-1)\rangle_{\mathbf{k}} \qquad (3{\cdot}25)$$

respectively, the second of which is the exact formula (3·1).

Finally, we assume that the space group is $P\bar{1}$ and that, except for symmetry-related vectors, no two interatomic vectors coincide. Then, if $j\neq k$, $\varepsilon_{jk}=2$ except for the case that $\mathbf{r}_j = -\mathbf{r}_k$ when $\varepsilon_{jk} = 1$.

Theorem 3·2 now becomes

$$\langle(|E_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}} = (2/\sigma_2^2)\sum_{\substack{j\neq k\\1}}^{N} Z_{jk}^2-(1/\sigma_2^2)\sum_{j=1}^{N} Z_j^4$$
$$= (2/\sigma_2^2)(\sigma_2^2-\sigma_4)-\sigma_4/\sigma_2^2=2-3\sigma_4/\sigma_2^2\,. \qquad (3{\cdot}26)$$

Theorem 3·3 now reduces to

$$|E_{\mathbf{h}}|^2-1 \approx \frac{(\sigma_1^2/\sigma_2)-1}{2-(3\sigma_4/\sigma_2^2)}\cdot\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h+k}}|^2-1)\rangle_{\mathbf{k}}\,, \qquad (3{\cdot}27)$$

or, for the case of N identical atoms, to

$$|E_{\mathbf{h}}|^2-1 \approx \frac{N-1}{2-3/N}\cdot\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h+k}}|^2-1)\rangle_{\mathbf{k}}, \qquad (3{\cdot}28)$$

i.e., except for terms of the order of $1/N$, to equation (3·2).

Comparison of equations (3·18), (3·22) and (3·26) clearly shows that the presence of coincident interatomic vectors or, what is the same thing, overlap in the Patterson function results in an increase in the average value of $(|E_{\mathbf{k}}|^2-1)^2$. As has already been observed, the occurrence of such coincidences spoils the exact validity of (3·1), but the more general formula (3·20) is not adversely affected. It should be pointed out that, although the occurrence of coincident interatomic vectors affects the average value of $(|E_{\mathbf{k}}|^2-1)^2$, the average value of $|E_{\mathbf{k}}|^2$ is always unity. Hence the usual method (*e.g.* Karle, Hauptman & Christ, 1958) for placing the $|E_{\mathbf{k}}|^2$ on an absolute scale remains valid.

4. The three kinds of interaction

Def. 4·1. The notation $\mu\neq\nu\neq\varrho$ shall mean that $\mu\neq\nu$, $\nu\neq\varrho$, and $\varrho\neq\mu$.

Def. 4·2. A triple of interatomic vectors $(\mathbf{r}_{jk}, \mathbf{r}_{j'k'}, \mathbf{r}_{j''k''})$, with $j\neq k, j'\neq k', j''\neq k''$, is said to constitute an interaction if they satisfy the equation

$$\mathbf{r}_{jk}+\mathbf{r}_{j'k'}+\mathbf{r}_{j''k''}=0\,. \qquad (4{\cdot}1)$$

Permuting the vectors in an interaction, or reversing the order of each of the three pairs of subscripts yields, in general, twelve interactions (six if two pairs of subscripts coincide) which, however, will be considered to be the same interaction.

Def. 4·3. Two interactions are said to be equivalent if the three vectors constituting the first interaction are equal, in some order, to the three vectors (or their negatives) of the second interaction. In particular, any interaction is equivalent to itself.

Def. 4·4. An interaction is said to be a valid interaction if, by suitable arrangement of its elements, it may be written in the form $(\mathbf{r}_{\mu\nu}, \mathbf{r}_{\nu\varrho}, \mathbf{r}_{\varrho\mu})$. Thus the valid interactions are identified with the interatomic triangles, including the degenerate ones which arise when three atoms happen to lie on the same straight line.

Def. 4·5. An interaction is said to be an induced interaction if it is equivalent to a valid interaction.

In particular every valid interaction is also an induced interaction.

Evidently a structure contains induced interactions (other than valid ones) if and only if certain interatomic vectors coincide.

Def. 4·6. A chance interaction is one which is not an induced interaction (or a valid one).

Def. 4·7. The symbol $Z_{\mu\nu\varrho}$ is defined by

$$Z_{\mu\nu\varrho}=Z_\mu Z_\nu Z_\varrho \tag{4·2}$$

where $\mu\neq\nu\neq\varrho$.

Def. 4·8. If $\mu\neq\nu\neq\varrho$, the symbol $\eta_{\mu\nu\varrho}$ is defined to be the number of valid interactions equivalent to the valid interaction $(\mathbf{r}_{\mu\nu}, \mathbf{r}_{\nu\varrho}, \mathbf{r}_{\varrho\mu})$.

Since every valid interaction is equivalent to itself it follows that

$$\eta_{\mu\nu\varrho} \geq 1 \quad \text{if} \quad \mu\neq\nu\neq\varrho\,. \tag{4·3}$$

Evidently, also, the value of $\eta_{\mu\nu\varrho}$ is unchanged under all permutations of the indices.

Def. 4·9. If $\mu\neq\nu\neq\varrho$, the symbol $\varepsilon_{\mu\nu\varrho}$ is defined by means of

$$\varepsilon_{\mu\nu\varrho}=2\varepsilon_{\mu\nu}\varepsilon_{\nu\varrho}\varepsilon_{\varrho\mu}/\eta_{\mu\nu\varrho}\,. \tag{4·4}$$

If any two or all three of μ, ν, ϱ are equal, then $\varepsilon_{\mu\nu\varrho}$ is defined to be zero.

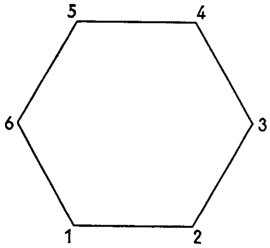

Fig. 1. Structure consisting of six identical atoms at the vertices of a regular hexagon.

The structure consisting of the vertices of a regular hexagon labeled as in Fig. 1 readily yields examples of the three kinds of interactions (Table 2). The three interactions listed in the second column are equivalent, in the same order, to the valid interactions shown in the first column.

Table 2. *Classification of several interactions obtained from the structure of Fig.* 1

Valid interactions	Induced interactions	Chance interactions
$(\mathbf{r}_{12}, \mathbf{r}_{23}, \mathbf{r}_{31})$	$(\mathbf{r}_{12}, \mathbf{r}_{65}, \mathbf{r}_{46})$	$(\mathbf{r}_{12}, \mathbf{r}_{34}, \mathbf{r}_{56})$
$(\mathbf{r}_{12}, \mathbf{r}_{41}, \mathbf{r}_{24})$	$(\mathbf{r}_{12}, \mathbf{r}_{15}, \mathbf{r}_{41})$	$(\mathbf{r}_{12}, \mathbf{r}_{54}, \mathbf{r}_{36})$
$(\mathbf{r}_{13}, \mathbf{r}_{51}, \mathbf{r}_{35})$	$(\mathbf{r}_{62}, \mathbf{r}_{46}, \mathbf{r}_{15})$	$(\mathbf{r}_{12}, \mathbf{r}_{12}, \mathbf{r}_{36})$

If the atoms in the structure of Fig. 1 are identical, then evidently $\varepsilon_{12}=\varepsilon_{13}=2$ whereas $\varepsilon_{14}=1$. Again, $\eta_{123}=2$ since the valid interactions represented by $(\mathbf{r}_{12}, \mathbf{r}_{23}, \mathbf{r}_{31})$ and $(\mathbf{r}_{45}, \mathbf{r}_{56}, \mathbf{r}_{64})$ are the only ones equivalent to the former. Similarly $\eta_{124}=\eta_{135}=2$. It follows that $\varepsilon_{123}=\varepsilon_{135}=8$ while $\varepsilon_{124}=4$.

5. The structure invariants $\varphi_1+\varphi_2+\varphi_3$

The central theme in this section is the formula (Karle & Hauptman, 1957; Vaughan, 1958)

$$\begin{aligned}&|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3)\\&\quad=(N^{3/2}/2)\,.\,\langle(|E_\mathbf{k}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_\mathbf{k}\\&\quad+(1/N^{1/2})(|E_1|^2+|E_2|^2+|E_3|^2-2)\,,\end{aligned} \tag{5·1}$$

in which we have written E_i for $E_{\mathbf{h}_i}$, φ_i for the phase $\varphi_{\mathbf{h}_i}$ of the normalized structure factor $E_{\mathbf{h}_i}$, $i=1, 2, 3$, and where we have assumed (and shall assume throughout) that

$$\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0\,, \tag{5·2}$$

so that $\varphi_1+\varphi_2+\varphi_3$ is a structure invariant. Equation (5·1) has exact validity if the structure consists of N identical atoms per unit cell and if the only interactions are valid ones. The latter requirement rules out, for example, the space group $P\bar{1}$, for which the correct formula is (Hauptman & Karle, 1957; Vaughan, 1958)

$$\begin{aligned}&|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3)\\&\quad\approx(N^{3/2}/8)\,.\,\langle(|E_\mathbf{k}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_\mathbf{k}\\&\quad+(1/N^{1/2})(|E_1|^2+|E_2|^2+|E_3|^2-2)\,,\end{aligned} \tag{5·3}$$

provided that, in each asymmetric unit, the only interactions which occur are valid ones. The symbol $\approx$ in (5·3) replaces the exact equality of (5·1) since, for simplicity, a term of the order of $1/\sqrt{N}$ has been suppressed in (5·3). A major aim of this section is to exhibit (5·1) and (5·3) as special cases of a single, more general formula, valid, at least approximately, not only in the case that the structure contains unequal atoms but, of much greater importance, in the case that arbitrary numbers of induced interactions are present, *i.e.* that arbitrary numbers of interatomic vectors coincide. In fact, our main formula (equation (5·12)), in contrast to (5·1) and (5·3), is space group independent, contains (5·1) and (5·3) as special cases, and clearly shows the origin of the discrepancy between (5·1) and (5·3). In § 6 and § 7 we generalize the results of this section to the case that chance interactions may also occur and, at the same time, show how previous knowledge of molecular structure is to be used.

We begin with the following result which we assume to be known (Hauptman & Karle, 1962, equation (2·3·7)):

Theorem 5·1. If $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$, then

$$|E_1E_2E_3|\cos(\varphi_1+\varphi_2+\varphi_3)$$
$$\approx 1/\sigma_2^{3/2})\sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z_{\mu\nu\varrho}\cos 2\pi(\mathbf{h}_1\,.\,\mathbf{r}_{\mu\nu}-\mathbf{h}_3\,.\,\mathbf{r}_{\nu\varrho})$$
$$+(\sigma_3/\sigma_2^{3/2})(|E_1|^2+|E_2|^2+|E_3|^2-2)\,. \tag{5·4}$$

Def. 5·1. A structure is said to be determinate if it has no chance interactions.

Theorem 5·2. For determinate structures

$$\langle(|E_\mathbf{k}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_\mathbf{k}$$
$$=(1/\sigma_2^3)\sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho}\cos 2\pi(\mathbf{h}_1\,.\,\mathbf{r}_{\mu\nu}-\mathbf{h}_3\,.\,\mathbf{r}_{\nu\varrho})\,. \tag{5·5}$$

Proof: Appendix III.

Just as a suitable weighted average of the ε_{jk} was found to be equal to the average of $(|E_\mathbf{k}|^2-1)^2$ (Theorem 3·2), so now we find that, for determinate structures, a weighted average of the $\varepsilon_{\mu\nu\varrho}$ is equal to the average of $(|E_\mathbf{k}|^2-1)^3$. More precisely, we have

Theorem 5·3. For determinate structures

$$\langle(|E_\mathbf{k}|^2-1)^3\rangle_\mathbf{k}=(1/\sigma_2^3)\sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho}=\frac{\sum\limits_{\substack{\mu,\nu,\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho}}{\sum\limits_{\substack{\mu,\nu,\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}}\,. \tag{5·6}$$

Proof: Set $\mathbf{h}_1=\mathbf{h}_3=0$ in Theorem 5·2 and employ the fact that $\varepsilon_{\mu\nu\varrho}=0$ if any two or all three indices coincide, as well as the identity

$$\sigma_2^3=\sum_{\substack{\mu,\nu,\varrho\\1}}^{N} Z^2_\mu Z^2_\nu Z^2_\varrho=\sum_{\substack{\mu,\nu,\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}\,. \tag{5·7}$$

Using Def. 3·1, a straightforward computation yields

Theorem 5·4.

$$\sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z_{\mu\nu\varrho}=\sigma_1^3-3\sigma_1\sigma_2+2\sigma_3\,, \tag{5·8}$$

$$\sum_{\substack{\mu\neq\nu\\1}}^{N} Z^2_\mu Z_\nu=\sigma_1\sigma_2-\sigma_3\,. \tag{5·9}$$

Corollary.

$$\sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}=\sigma_2^3-3\sigma_2\sigma_4+2\sigma_6\,, \tag{5·10}$$

$$\sum_{\substack{\mu\neq\nu\\1}}^{N} Z^4_\mu Z^2_\nu=\sigma_2\sigma_4-\sigma_6\,. \tag{5·11}$$

The main result of this section is given by

Theorem 5·5. For determinate structures

$$|E_1E_2E_3|\cos(\varphi_1+\varphi_2+\varphi_3)\approx\frac{\sigma_1^3-3\sigma_1\sigma_2+2\sigma_3}{\sigma_2^{3/2}\langle(|E_\mathbf{k}|^2-1)^3\rangle_\mathbf{k}}$$
$$\times\langle(|E_\mathbf{k}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_\mathbf{k}$$
$$+(\sigma_3/\sigma_2^{3/2})(|E_1|^2+|E_2|^2+|E_3|^2-2)\,. \tag{5·12}$$

Proof: Appendix IV.

Corollary. For determinate structures consisting of N identical atoms

$$|E_1E_2E_3|\cos(\varphi_1+\varphi_2+\varphi_3)\approx\frac{(N-1)(N-2)}{N^{1/2}\langle(|E_\mathbf{k}|^2-1)^3\rangle_\mathbf{k}}$$
$$\times\langle(|E_\mathbf{k}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_\mathbf{k}$$
$$+(1/N^{1/2})(|E_1|^2+|E_2|^2+|E_3|^2-2)\,. \tag{5·13}$$

We conclude this section by showing how our main formula (5·12) is suitably specialized to yield the known results (5·1) and (5·3).

We assume first that no two interatomic vectors coincide and that the structure is determinate. Then $\varepsilon_{\mu\nu}=\varepsilon_{\nu\varrho}=\varepsilon_{\varrho\mu}=\eta_{\mu\nu\varrho}=1$ while $\varepsilon_{\mu\nu\varrho}=2$ if $\mu\neq\nu\neq\varrho$. Next, in view of (5·10), (5·6) becomes

$$\langle(|E_\mathbf{k}|^2-1)^3\rangle_\mathbf{k}=2(\sigma_2^3-3\sigma_2\sigma_4+2\sigma_6)/\sigma_2^3\,, \tag{5·14}$$

or, for the case of N identical atoms per unit cell,

$$\langle(|E_\mathbf{k}|^2-1)^3\rangle_\mathbf{k}=\frac{2(N-1)(N-2)}{N^2}\,. \tag{5·15}$$

Equation (5·12) now reduces to

$$|E_1E_2E_3|\cos(\varphi_1+\varphi_2+\varphi_3)\approx\frac{\sigma_2^{3/2}(\sigma_1^3-3\sigma_1\sigma_2+2\sigma_3)}{2(\sigma_2^3-3\sigma_2\sigma_4+2\sigma_6)}$$
$$\times\langle(|E_\mathbf{k}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_\mathbf{k}$$
$$+(\sigma_3/\sigma_2^{3/2})(|E_1|^2+|E_2|^2+|E_3|^2-2) \tag{5·16}$$

or, for the case of N identical atoms per unit cell, to equation (5·1).

Finally, we assume that the space group is $P\bar{1}$, that, except for symmetry related vectors, no two interatomic vectors coincide, and that the structure is determinate. Now $\varepsilon_{\mu\nu}=\varepsilon_{\nu\varrho}=\varepsilon_{\varrho\mu}=2$ if $\mu\neq\nu\neq\varrho$ except that if $\mathbf{r}_\mu=-\mathbf{r}_\nu$ then $\varepsilon_{\mu\nu}=1$, if $\mathbf{r}_\nu=-\mathbf{r}_\varrho$ then $\varepsilon_{\nu\varrho}=1$, and if $\mathbf{r}_\varrho=-\mathbf{r}_\mu$ then $\varepsilon_{\varrho\mu}=1$. Again, if $\mu\neq\nu\neq\varrho$, then $\eta_{\mu\nu\varrho}=2$ so that $\varepsilon_{\mu\nu\varrho}=8$ unless $\mathbf{r}_\mu=-\mathbf{r}_\nu$ or $\mathbf{r}_\nu=-\mathbf{r}_\varrho$ or $\mathbf{r}_\varrho=-\mathbf{r}_\mu$ in which cases $\varepsilon_{\mu\nu\varrho}=4$.

Now (5·6) becomes, in view of (5·10) and (5·11),

$$\langle(|E_\mathbf{k}|^2-1)^3\rangle_\mathbf{k}=(8/\sigma_2^3)\sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}-(12/\sigma_2^3)\sum_{\substack{\mu\neq\nu\\1}}^{N} Z^4_\mu Z^2_\nu$$
$$+(12/\sigma_2^3)\sum_{\mu=1}^{N} Z^6_\mu$$
$$=(8/\sigma_2^3)(\sigma_2^3-3\sigma_2\sigma_4+2\sigma_6)$$
$$-(12/\sigma_2^3)(\sigma_2\sigma_4-\sigma_6)+(12/\sigma_2^3)\sigma_6$$
$$=8-(36\sigma_4/\sigma_2^2)+(40\sigma_6/\sigma_2^3) \tag{5·17}$$

or, for the case of N identical atoms per unit cell,

$$\langle(|E_{\mathbf{k}}|^2-1)^3\rangle_{\mathbf{k}}=4(N-2)(2N-5)/N^2. \qquad (5{\cdot}18)$$

Equation (5·12) now reduces to

$$|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3) \approx \frac{\sigma_2^{3/2}(\sigma_1^3-3\sigma_1\sigma_2+2\sigma_3)}{4(2\sigma_2^3-9\sigma_2\sigma_4+10\sigma_6)}$$

$$\times\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}$$

$$+\ (\sigma_3/\sigma_2^{3/2})(|E_1|^2+|E_2|^2+|E_3|^2-2) \qquad (5{\cdot}19)$$

or, for the case of N identical atoms per unit cell, to

$$|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3)$$

$$\approx \frac{N^{3/2}(N-1)}{4(2N-5)}\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}$$

$$+\ (1/N^{1/2})(|E_1|^2+|E_2|^2+|E_3|^2-2)\ , \qquad (5{\cdot}20)$$

i.e., except for terms of the order of $1/N$, to equation (5·3).

Our discussion clearly shows how the presence of the induced interactions results in an increase in the average value of $(|E_{\mathbf{k}}|^2-1)^3$.

6. A generalization

In this section we extend the results of § 5 to arbitrary structures and, at the same time, show how the known features of the molecular structure may be used. Since now we permit the occurrence of chance interactions, equation (III·2) no longer implies (5·5). Instead, by averaging over all vectors $\mathbf{k}$, (III·2) leads to

$$\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}$$

$$=1/\sigma_2^3 \sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho}\cos 2\pi(\mathbf{h}_1.\mathbf{r}_{\mu\nu}-\mathbf{h}_3.\mathbf{r}_{\nu\varrho})$$

$$+C(\mathbf{h}_1,\ -\mathbf{h}_3)\ , \qquad (6{\cdot}1)$$

where

$$C(\mathbf{h},\ \mathbf{h}') = (1/\sigma_2^3)\sum_{\chi} Z_{jk}Z_{j'k'}Z_{j''k''}$$

$$\times\exp[2\pi i(\mathbf{h}.\mathbf{r}_{jk}+\mathbf{h}'.\mathbf{r}_{j'k'})], \qquad (6{\cdot}2)$$

and $\sum_{\chi}$ means that the sum is extended over all indices, j, k, j', k', j'', k'' corresponding to the chance interactions. (We observe that, in general, there will be twelve contributors to the total sum corresponding to each change interaction since the elements of the triple (j, k), (j', k'), (j'', k''), associated with the chance interaction $(\mathbf{r}_{jk}, \mathbf{r}_{j'k'}, \mathbf{r}_{j''k''})$ may be permuted, *e.g.* (j', k'), (j, k), (j'', k''), and the order of the elements of the three pairs in each such triple may be simultaneously reversed, *e.g.* (k, j), (k', j'), (k'', j''). If however $j=j'$ and $k=k'$, for example, then only six contributors to the total sum correspond to the interaction.)

Next we employ Theorem 2·1 to replace $\exp[2\pi i(\mathbf{h}.\mathbf{r}_{jk}+\mathbf{h}'.\mathbf{r}_{j'k'})]$ by its average value $B(z, t)$ in order to obtain the following estimate of $C(\mathbf{h}, \mathbf{h}')$:

$$C(\mathbf{h},\ \mathbf{h}') \approx (1/\sigma_2^3)\sum_{\chi} Z_{jk}Z_{j'k'}Z_{j''k''}B(z, t)\ . \qquad (6{\cdot}3)$$

We observe that $B(z, t)$ is given by equation (2·2) while z and t are obtained from (2·3) and (2·4) respectively. The latter equations require a knowledge of q, q', and φ_q, which are known once the vectors $\mathbf{h}$ and $\mathbf{h}'$ have been specified, as well as a knowledge of $r=r_{jk}$, $r'=r_{j'k'}$, and φ_r. However, r_{jk} and $r_{j'k'}$ are the magnitudes of the vectors $\mathbf{r}_{jk}$ and $\mathbf{r}_{j'k'}$ respectively while φ_r is the angle between these vectors. Thus one possible method of utilizing the known features of the molecular structure immediately suggests itself: Use all the known chance interactions (*i.e.* those triples $(\mathbf{r}_{jk}, \mathbf{r}_{j'k'}, \mathbf{r}_{j''k''})$ which are neither valid nor induced interactions but which satisfy $\mathbf{r}_{jk}+\mathbf{r}_{j'k'}+\mathbf{r}_{j''k''}=0$ and are such that the magnitudes of $\mathbf{r}_{jk}$, $\mathbf{r}_{j'k'}$, $\mathbf{r}_{j''k''}$ are known) to compute as many terms of (6·3) as possible. Naturally the more complete the previous knowledge of molecular structure the more terms in (6·3) may be computed and the better will the resulting estimate of (6·3) approximate the desired value of $C(\mathbf{h}, \mathbf{h}')$ as given by (6·2). We shall assume then that $C(\mathbf{h}, \mathbf{h}')$ is known as a function of the vectors $\mathbf{h}$ and $\mathbf{h}'$.

We shall need a preliminary theorem obtained by setting $\mathbf{h}_1=\mathbf{h}_3=0$ in equations (6·1) and (6·3):

THEOREM 6·1. For arbitrary structures,

$$\langle(|E_{\mathbf{k}}|^2-1)^3\rangle_{\mathbf{k}} = (1/\sigma_2^3)\sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho}+C(0,0) \qquad (6{\cdot}4)$$

where

$$C(0,0) = (1/\sigma_2^3)\sum_{\chi} Z_{jk}Z_{j'k'}Z_{j''k''} \qquad (6{\cdot}5)$$

and $\sum_{\chi}$ means that the sum is to be taken over all the chance interactions, each such interaction being counted twelve (or possibly six) times as already explained.

Comparison of equations (6·4) and (5·6) shows clearly how the presence of the chance interactions increases the average value of $(|E_{\mathbf{k}}|^2-1)^3$.

Next, returning to equation (6·1) we find

$$\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}-C(\mathbf{h}_1,\ -\mathbf{h}_3)$$

$$=(1/\sigma_2^3)\sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho}$$

$$\times\left\{\frac{\sum\limits_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho}\cos 2\pi(\mathbf{h}_1.\mathbf{r}_{\mu\nu}-\mathbf{h}_3.\mathbf{r}_{\nu\varrho})}{\sum\limits_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho}}\right\} \qquad (6{\cdot}6)$$

and observe that the expression in braces is the average value of $\cos 2\pi(\mathbf{h}_1 . \mathbf{r}_{\mu\nu} - \mathbf{h}_3 . \mathbf{r}_{\nu\varrho})$. However equation (IV·2), a consequence of Theorem 5·1 and therefore valid for arbitrary structures (determinate or not), yields another expression for the average value, with different weights, of $\cos 2\pi(\mathbf{h}_1 . \mathbf{r}_{\mu\nu} - \mathbf{h}_3 . \mathbf{r}_{\nu\varrho})$. Substituting from (IV·2) into (6·6), and employing also (6·4) and (5·8), we find

$$\begin{aligned}
&\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}} - C(\mathbf{h}_1, -\mathbf{h}_3) \\
&\approx (1/\sigma_2^3) \sum_{\substack{\mu\neq\nu\neq\varrho \\ 1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho} \left\{ \frac{\sigma_2^{3/2}}{\sum\limits_{\substack{\mu\neq\nu\neq\varrho \\ 1}}^{N} Z_{\mu\nu\varrho}} |E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3) - \frac{\sigma_3(|E_1|^2+|E_2|^2+|E_3|^2-2)}{\sum\limits_{\substack{\mu\neq\nu\neq\varrho \\ 1}}^{N} Z_{\mu\nu\varrho}} \right\} \\
&\approx \{\langle(|E_{\mathbf{k}}|^2-1)^3\rangle_{\mathbf{k}} - C(0, 0)\} \left\{ \frac{\sigma_2^{3/2}|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3) - \sigma_3(|E_1|^2+|E_2|^2+|E_3|^2-2)}{\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3} \right\} . \qquad (6·7)
\end{aligned}$$

Finally, solving (6·7) for $|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3)$ we are led to the first main result of this paper:

THEOREM 6·2. For arbitrary structures

$$\begin{aligned}
|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3) &\approx \frac{\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3}{\sigma_2^{3/2}} \times \\
&\frac{\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}} - C(\mathbf{h}_1, -\mathbf{h}_3)}{\langle(|E_{\mathbf{k}}|^2-1)^3\rangle_{\mathbf{k}} - C(0, 0)} \\
&+ (\sigma_3/\sigma_2^{3/2})(|E_1|^2+|E_2|^2+|E_3|^2-2) . \qquad (6·8)
\end{aligned}$$

In view of Theorem 6·1 we also have the

COROLLARY. For arbitrary structures

$$\begin{aligned}
|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3) &\approx \frac{\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3}{\sigma_2^{3/2}} \times \\
&\frac{\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}} - C(\mathbf{h}_1, -\mathbf{h}_3)}{(1/\sigma_2^{3/2}) \sum\limits_{\substack{\mu\neq\nu\neq\varrho \\ 1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho}} \\
&+ (\sigma_3/\sigma_2^{3/2})(|E_1|^2+|E_2|^2+|E_3|^2-2) . \qquad (6·9)
\end{aligned}$$

It is to be noted that the expressions $C(0, 0)$ and

$$(1/\sigma_{2/}^{3/2}) \sum_{\substack{\mu\neq\nu\neq\varrho \\ 1}}^{N} Z^2_{\mu\nu\varrho}\varepsilon_{\mu\nu\varrho} , \qquad (6·10)$$

which occur in (6·8) and (6·9), may, since they are sums of positive terms, be accurately computed only if the complete molecular structure is known. If only partial information concerning molecular structure is available, then it is possible only to estimate the sums (6·5) and (6·10) by computing those of their contributors which are known from the molecular structure. Thus equations (6·8) and (6·9), while an improvement over the analogous formula (5·12) when chance interactions are present, are still subject to error when, in practical application, the amount of previous structural information is small. Again, it is difficult to see how to employ equations (6·8) and (6·9) to cope with the problem arising from the occurrence of approximate chance interactions which one would expect, in view of the limited number of data usually available from experiment, should somehow be taken into account. In the next section we show how to overcome these difficulties.

7. An alternative

We introduce the notation

$$r(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3) = (\sigma_3/\sigma_2^{3/2})(|E_1|^2+|E_2|^2+|E_3|^2-2) , \qquad (7·1)$$

so that $r(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$ is a known function (of the order $1/\sqrt{N}$) of the three vectors $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$. Then, assuming as always that $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$, Theorem 5·1 may be written

$$\begin{aligned}
&|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3) \\
&\quad\approx (1/\sigma_2^{3/2}) \sum_{\substack{\mu\neq\nu\neq\varrho \\ 1}}^{N} Z_{\mu\nu\varrho} \cos 2\pi(\mathbf{h}_1 . \mathbf{r}_{\mu\nu} - \mathbf{h}_3 . \mathbf{r}_{\nu\varrho}) \\
&\quad + r(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3) . \qquad (7·2)
\end{aligned}$$

We imagine that $\mathbf{h}_1$, $\mathbf{h}_2$, and $\mathbf{h}_3$ are fixed and write $q_i = |\mathbf{h}_i|$, $i=1, 2, 3$. Next, replace the vectors $\mathbf{h}_i$ in (7·2) by vectors $\mathbf{k}_i$, $i=1, 2, 3$, where the $\mathbf{k}_i$ are arbitrary vectors subject only to the condition $|\mathbf{k}_i| = q_i$, $i=1, 2, 3$ (whence $\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0$). We then average both sides of (7·2) over all such vectors $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$ and observe that this is equivalent to averaging over all orientations in reciprocal space of the triangle whose sides are the vectors $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$. We employ Theorem 2·1 to replace $\langle\cos 2\pi(\mathbf{k}_1 . \mathbf{r}_{\mu\nu} - \mathbf{k}_3 . \mathbf{r}_{\nu\varrho})\rangle_{\mathbf{k}}$ by $B(z, t)$ which, in view of (2·3) and (2·4), depends only on the magnitudes q_1, q_2, q_3 of the vectors $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$, assumed fixed over the present averaging process, as well as on the magnitudes of the interatomic vectors $\mathbf{r}_{\mu\nu}$, $\mathbf{r}_{\nu\varrho}$ and the angle between them. Knowledge of the latter is equivalent to that of the sides $r_{\mu\nu}, r_{\nu\varrho}, r_{\varrho\mu}$ of the interatomic triangle $\mathbf{r}_{\mu\nu}$, $\mathbf{r}_{\nu\varrho}$, $\mathbf{r}_{\varrho\mu}$. In order to emphasize this dependence we shall replace $B(z, t)$ by $B(q_1, q_2, q_3;\, r_{\mu\nu}, r_{\nu\varrho}, r_{\varrho\mu})$. Thus we obtain

$$\begin{aligned}
&\langle|E_{\mathbf{k}_1}E_{\mathbf{k}_2}E_{\mathbf{k}_3}| \cos(\varphi_{\mathbf{k}_1}+\varphi_{\mathbf{k}_2}+\varphi_{\mathbf{k}_3})\rangle_{|\mathbf{k}_i|=q_i} \\
&\quad\approx (1/\sigma_2^{3/2}) \sum_{\substack{\mu\neq\nu\neq\varrho \\ 1}}^{N} Z_{\mu\nu\varrho} B(q_1, q_2, q_3;\, r_{\mu\nu}, r_{\nu\varrho}, r_{\varrho\mu}) \\
&\quad + R(q_1, q_2, q_3) , \qquad (7·3)
\end{aligned}$$

in which we have written

$$R(q_1, q_2, q_3) = \langle r(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)\rangle_{|\mathbf{k}_i|=q_i} \qquad (7{\cdot}4)$$

so that, in view of (7·1), $R(q_1, q_2, q_3)$ is a known function of q_1, q_2, q_3.

Since $B(q_1, q_2, q_3;\ r_{\mu\nu}, r_{\nu\varrho}, r_{\varrho\mu})$ depends in a known way on $q_1, q_2, q_3, r_{\mu\nu}, r_{\nu\varrho}, r_{\varrho\mu}$, the right hand side of (7·3) may be computed, for fixed q_1, q_2, q_3, provided that (the sides of) all interatomic triangles (including the occasional degenerate triangles which arise when three atoms lie on the same straight line) are known. Now knowledge of some or all of the molecular structure implies that at least some of the smaller interatomic triangles are known. Many or most of the larger interatomic triangles may not be known. However, as has already been pointed out, the value of the B function is relatively small for the larger interatomic triangles. Since the B function takes on negative as well as positive values, it follows that, in general, we may obtain a valid estimate of the triple sum on the right hand side of (7·3) by including only those contributors for which the corresponding interatomic triangles are known. Naturally the more complete our *a priori* knowledge of the molecular structure, the closer will this approximation be to the correct value. Henceforth we shall assume therefore that the value of the left hand side of (7·3) is known as a function of q_1, q_2, q_3 and shall denote it by $D(q_1, q_2, q_3)$:

$$D(q_1, q_2, q_3) = \langle |E_{\mathbf{k}_1}E_{\mathbf{k}_2}E_{\mathbf{k}_3}| \cos(\varphi_{\mathbf{k}_1}+\varphi_{\mathbf{k}_2}+\varphi_{\mathbf{k}_3})\rangle_{|\mathbf{k}_i|=q_i}, \qquad (7{\cdot}5)$$

where, naturally, $\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0$.

We return now to equation (6·8) which we write in the form

$$|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3) \approx K\{a(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)-S(q_1, q_2, q_3)\}+r(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3), \qquad (7{\cdot}6)$$

where

$$K = \frac{\sigma_1^3-3\sigma_1\sigma_2+2\sigma_3}{\sigma_2^{3/2}(\langle(|E_{\mathbf{k}}|^2-1)^3\rangle_{\mathbf{k}}-C(0, 0))} \qquad (7{\cdot}7)$$

is an absolute constant,

$$S(q_1, q_2, q_3)=C(\mathbf{h}_1, -\mathbf{h}_3), \qquad (7{\cdot}8)$$

in view of (6·3), is a function only of q_1, q_2, q_3, $r(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$ is given by (7·1), and $a(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$ is defined by means of

$$a(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3) = \langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}, \qquad (7{\cdot}9)$$

so that $a(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$ is a known function of the vectors $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$. There remains only the problem of determining K and $S(q_1, q_2, q_3)$.

We rewrite (7·6) in the form

$$\frac{|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3)-r(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)}{K} \approx a(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)-S(q_1, q_2, q_3), \qquad (7{\cdot}10)$$

and average over all orientations in reciprocal space of the triangle with sides $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$. Writing

$$\langle a(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)\rangle_{|\mathbf{k}_i|=q_i} = A(q_1, q_2, q_3), \qquad (7{\cdot}11)$$

where $q_i=|\mathbf{h}_i|=|\mathbf{k}_i|$, $i=1, 2, 3$, so that, in view of (7·9), $A(q_1, q_2, q_3)$ may be assumed to be known as a function of q_1, q_2, q_3, we find, using (7·5) and (7·4),

$$S(q_1, q_2, q_3) \approx A(q_1, q_2, q_3) - \frac{D(q_1, q_2, q_3)-R(q_1, q_2, q_3)}{K}. \qquad (7{\cdot}12)$$

Hence (7·10) may be written

$$|E_1E_2E_3| \cos(\varphi_1+\varphi_2+\varphi_3) \approx K\{a(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)-A(q_1, q_2, q_3)\} + D(q_1, q_2, q_3)+r(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)-R(q_1, q_2, q_3). \qquad (7{\cdot}13)$$

In order to obtain the constant K from (7·13) it would be sufficient to substitute any values for $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ satisfying (5·2) except for the fact that, in general, the corresponding value of $\varphi_1+\varphi_2+\varphi_3$ is not known. However, for all space groups other than $P1$, it is always possible to choose $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ in such a way that, as a consequence of the space group symmetries, $\varphi_1+\varphi_2+\varphi_3$ is 0 or π. With such a choice for $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$, the value of $\cos(\varphi_1+\varphi_2+\varphi_3)$ appearing in (7·13) is ± 1. The ambiguity may be resolved by observing firstly that, in view of (7·1), (7·4) and (7·5), the last three terms of (7·13) are relatively small, and secondly, from (7·7) and (6·4), that K must be positive. Hence $\cos(\varphi_1+\varphi_2+\varphi_3)=+1$ or -1 according as the coefficient of K in (7·13) is positive or negative. Naturally, in practice, $\mathbf{h}_1, \mathbf{h}_2$, and $\mathbf{h}_3$ are further restricted by the requirement that $|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|$ be relatively large. In order to improve the accuracy with which K is determined, it is desirable also to employ several triples $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ subject to the conditions already described. Once K has been determined, then $S(q_1, q_2, q_3)$ is found from (7·12).

The chief result of this paper is contained in equation (7·6), where K is obtained from (7·13) in the manner described, $a(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$, $A(q_1, q_2, q_3)$, $r(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$, $R(q_1, q_2, q_3)$ are given by (7·9), (7·11), (7·1), (7·4) respectively, $D(q_1, q_2, q_3)$, defined by (7·5), is found from the right-hand side of (7·3) (employing naturally all the known interatomic triangles, as well as Table 1), and $S(q_1, q_2, q_3)$ is then obtained from (7·12).

8. Concluding remarks

In this paper the problem of determining the phases of the structure factors directly from their magnitudes has been formulated with great generality. The resulting formalism is sufficient to cope, not only with the annoying obstacle arising from the presence of rational dependence among the atomic coordinates, but also with the problem of utilizing whatever previous information concerning molecular structure may be available. The treatment is admittedly an approximate one, so that two directions for further research are suggested: (1) to estimate accurately the magnitudes of the errors involved (presumably of the order of $1/\sqrt{N}$) and (2) to improve the accuracy of the formulas here derived.

Our formulation leads to two procedures, the second of which appears superior, for the actual determination of the phases. In order to facilitate the implementation of these methods, a short table of the important function $B(z, t)$ has been included.

APPENDIX I

Proof of Theorem 3·1:

$$\begin{aligned}(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}+\mathbf{k}}|^2-1) &= (1/\sigma_2^2) \sum_{\substack{j\neq k\\ j'\neq k'\\ 1}}^{N} Z_{jk}Z_{j'k'} \\ &\quad\times \exp(2\pi i\mathbf{k}.\mathbf{r}_{j'k'}) \exp[2\pi i(\mathbf{h}+\mathbf{k}).\mathbf{r}_{jk}] \\ &= (1/\sigma_2^2) \sum_{\substack{j\neq k\\ j'\neq k\\ 1}}^{N} Z_{jk}Z_{j'k'} \\ &\quad\times \exp(2\pi i\mathbf{h}.\mathbf{r}_{jk}) \exp[2\pi i\mathbf{k}.(\mathbf{r}_{jk}+\mathbf{r}_{j'k'})]\,. \qquad (\mathrm{I{\cdot}1})\end{aligned}$$

Averaging (I·1) over all vectors $\mathbf{k}$ we find that all terms on the right vanish except those for which $\mathbf{r}_{jk}+\mathbf{r}_{j'k'}=0$. For each fixed pair (j, k) summation of $Z_{j'k'}$ over all $j'\neq k'$ such that $\mathbf{r}_{jk}+\mathbf{r}_{j'k'}=0$ yields $w_{jk}=Z_{jk}\varepsilon_{jk}$, and (3·16) follows immediately.

APPENDIX II

Proof of Theorem 3·3: From Theorem 3·1,

$$\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}} = \frac{\sum\limits_{\substack{j\neq k\\1}}^{N} Z_{jk}^2\varepsilon_{jk}}{\sigma_2^2}\left\{\frac{\sum\limits_{\substack{j\neq k\\1}}^{N} Z_{jk}^2\varepsilon_{jk}\exp(2\pi i\mathbf{h}.\mathbf{r}_{jk})}{\sum\limits_{\substack{j\neq k\\1}}^{N} Z_{jk}^2\varepsilon_{jk}}\right\}. \qquad (\mathrm{II{\cdot}1})$$

The expression in braces is a weighted average of $\exp(2\pi i\mathbf{h}.\mathbf{r}_{jk})$. However, (3·3), with $\mathbf{k}$ replaced by $\mathbf{h}$, yields the following formula for the average (with different weights) of $\exp(2\pi i\mathbf{h}.\mathbf{r}_{jk})$:

$$\frac{\sum\limits_{\substack{j\neq k\\1}}^{N} Z_{jk}\exp(2\pi i\mathbf{h}.\mathbf{r}_{jk})}{\sum\limits_{\substack{j\neq k\\1}}^{N} Z_{jk}} = \frac{\sigma_2(|E_{\mathbf{h}}|^2-1)}{\sigma_1^2-\sigma_2}\,, \qquad (\mathrm{II{\cdot}2})$$

in which we have also used (3·7) to replace

$$\sum_{\substack{j\neq k\\1}}^{N} Z_{jk} \quad \text{by} \quad \sigma_1^2-\sigma_2\,.$$

Identifying these two averages of $\exp(2\pi i\mathbf{h}.\mathbf{r}_{jk})$, we substitute from (II·2) into the last factor (in braces) of (II·1) and, employing also Theorem 3·2, obtain the approximate formula (3·20).

APPENDIX III

Proof of Theorem 5·2:

$$\begin{aligned}(|E_{\mathbf{k}}|^2-1)&(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1) \\ &= (1/\sigma_2^3) \sum_{\substack{j\neq k\\ j'\neq k'\\ j''\neq k''\\ 1}}^{N} Z_{jk}Z_{j'k'}Z_{j''k''}\exp(2\pi i\mathbf{k}.\mathbf{r}_{jk}) \\ &\quad\times \exp[2\pi i(\mathbf{h}_1+\mathbf{k}).\mathbf{r}_{j'k'}] \exp[2\pi i(-\mathbf{h}_3+\mathbf{k}).\mathbf{r}_{j''k''}] \qquad (\mathrm{III{\cdot}1}) \\ &= (1/\sigma_2^3) \sum_{\substack{j\neq k\\ j'\neq k'\\ j''\neq k''\\ 1}}^{N} Z_{jk}Z_{j'k'}Z_{j''k''}\exp[2\pi i(\mathbf{h}_1.\mathbf{r}_{jk}-\mathbf{h}_3.\mathbf{r}_{j'k'})] \\ &\quad\times \exp[2\pi i\mathbf{k}.(\mathbf{r}_{jk}+\mathbf{r}_{j'k'}+\mathbf{r}_{j''k''})]\,. \qquad (\mathrm{III{\cdot}2})\end{aligned}$$

Next we average (III·2) over all vectors $\mathbf{k}$ and observe that all contributors to the average of the right-hand side vanish except those for which $\mathbf{r}_{jk}+\mathbf{r}_{j'k'}+\mathbf{r}_{j''k''}=0$. Since the structure is determinate, it has no chance interactions so that the only non-zero contributors are those corresponding to the valid interactions or the induced interactions. There remains only the problem of summing those contributions to the average which correspond to such interactions, with the aim of reducing the sextuple sum (III·2) to a triple sum over the valid interactions or, more precisely, to the triple sum shown in (5·5).

We first find those contributors to the average corresponding to the valid interactions. Two cases arise. For each fixed pair $(j, k)=(\mu, \nu)$ the interaction $(\mathbf{r}_{jk}, \mathbf{r}_{j'k'}, \mathbf{r}_{j''k''})$ assumes either the form $(\mathbf{r}_{\mu\nu}, \mathbf{r}_{\nu\varrho}, \mathbf{r}_{\varrho\mu})$ or the form $(\mathbf{r}_{\mu\nu}, \mathbf{r}_{\varrho\mu}, \mathbf{r}_{\nu\varrho})$. Hence the contributors to the average corresponding to the valid interactions may be written

$$\begin{aligned}(1/\sigma_2^3)&\sum_{\substack{\mu\neq\nu\\1}}^{N} Z_{\mu\nu}\sum_{\substack{\varrho=1\\ \varrho\neq\mu\\ \varrho\neq\nu}}^{N} Z_{\nu\varrho}Z_{\varrho\mu}\{\exp[2\pi i(\mathbf{h}_1.\mathbf{r}_{\mu\nu}-\mathbf{h}_3.\mathbf{r}_{\nu\varrho})] \\ &\quad+\exp[-2\pi i(\mathbf{h}_1.\mathbf{r}_{\nu\mu}-\mathbf{h}_3.\mathbf{r}_{\mu\varrho})]\} \\ &= (2/\sigma_2^3)\sum_{\substack{\mu\neq\nu\neq\varrho\\1}}^{N} Z_{\mu\nu\varrho}^2\cos 2\pi(\mathbf{h}_1.\mathbf{r}_{\mu\nu}-\mathbf{h}_3.\mathbf{r}_{\nu\varrho})\,. \qquad (\mathrm{III{\cdot}3})\end{aligned}$$

Next, corresponding to each fixed valid interaction $(\mathbf{r}_{\mu\nu}, \mathbf{r}_{\nu\varrho}, \mathbf{r}_{\varrho\mu})$ are those contributors to the average associated with all the induced interactions $(\mathbf{r}_{jk}, \mathbf{r}_{j'k'}, \mathbf{r}_{j''k''})$, including the interaction $(\mathbf{r}_{\mu\nu}, \mathbf{r}_{\nu\varrho}, \mathbf{r}_{\varrho\mu})$ itself, which are equivalent to $(\mathbf{r}_{\mu\nu}, \mathbf{r}_{\nu\varrho}, \mathbf{r}_{\varrho\mu})$:

$$(1/\sigma_2^3) \sum_{\substack{j \neq k \\ j' \neq k' \\ j'' \neq k''}} Z_{jk} Z_{j'k'} Z_{j''k''} \exp\left[2\pi i(\mathbf{h}_1 . \mathbf{r}_{jk} - \mathbf{h}_3 . \mathbf{r}_{j'k'})\right] \tag{III·4}$$

where the summation is extended over all j, k, j', k', j'', k'' such that the three vectors $\mathbf{r}_{jk}, \mathbf{r}_{j'k'}, \mathbf{r}_{j''k''}$ are equal, in some order, to the three vectors $\mathbf{r}_{\mu\nu}, \mathbf{r}_{\nu\varrho}, \mathbf{r}_{\varrho\mu}$, or to their negatives.

Consider first those terms of (III·4) such that $\mathbf{r}_{jk} = \mathbf{r}_{\mu\nu}$, $\mathbf{r}_{j'k'} = \mathbf{r}_{\nu\varrho}$, $\mathbf{r}_{j''k''} = \mathbf{r}_{\varrho\mu}$. Then

$$\exp\left[2\pi i(\mathbf{h}_1 . \mathbf{r}_{jk} - \mathbf{h}_3 . \mathbf{r}_{j'k'})\right]$$

is constant with respect to the summation of (III·4) and is equal to $\exp\left[2\pi i(\mathbf{h}_1 . \mathbf{r}_{\mu\nu} - \mathbf{h}_3 . \mathbf{r}_{\nu\varrho})\right]$. These terms of (III·4) then reduce to

$$(1/\sigma_2^3) Z_{\mu\nu} \varepsilon_{\mu\nu} Z_{\nu\varrho} \varepsilon_{\nu\varrho} Z_{\varrho\mu} \varepsilon_{\varrho\mu} \exp\left[2\pi i(\mathbf{h}_1 . \mathbf{r}_{\mu\nu} - \mathbf{h}_3 . \mathbf{r}_{\nu\varrho})\right] . \tag{III·5}$$

Consider next those terms of (III·4) such that $\mathbf{r}_{jk} = \mathbf{r}_{\mu\nu}$, $\mathbf{r}_{j'k'} = \mathbf{r}_{\varrho\mu}$, $\mathbf{r}_{j''k''} = \mathbf{r}_{\nu\varrho}$. Again

$$\exp\left[2\pi i(\mathbf{h}_1 . \mathbf{r}_{jk} - \mathbf{h}_3 . \mathbf{r}_{j'k'})\right]$$

is constant with respect to the summation of (III·4) and is now equal to $\exp\left[-2\pi i(\mathbf{h}_1 . \mathbf{r}_{\nu\mu} - \mathbf{h}_3 . \mathbf{r}_{\mu\varrho})\right]$. Hence these terms of (III·4) reduce to

$$(1/\sigma_2^3) Z_{\mu\nu} \varepsilon_{\mu\nu} Z_{\nu\varrho} \varepsilon_{\nu\varrho} Z_{\varrho\mu} \varepsilon_{\varrho\mu} \exp\left[-2\pi i(\mathbf{h}_1 . \mathbf{r}_{\nu\mu} - \mathbf{h}_3 . \mathbf{r}_{\mu\varrho})\right] . \tag{III·6}$$

The remaining ten cases obtained by setting $\mathbf{r}_{jk} = \mathbf{r}_{\nu\varrho}$, $\mathbf{r}_{j'k'} = \mathbf{r}_{\mu\nu}$, $\mathbf{r}_{j''k''} = \mathbf{r}_{\varrho\mu}$; $\mathbf{r}_{jk} = \mathbf{r}_{\nu\varrho}$, $\mathbf{r}_{j'k'} = \mathbf{r}_{\varrho\mu}$, $\mathbf{r}_{j''k''} = \mathbf{r}_{\mu\nu}$; *etc.*, all reduce to terms like (III·5) or (III·6). We arrange these terms so as to combine exponentials to form cosines and obtain

$$(2/\sigma_2^3) Z_{\mu\nu\varrho}^2 \varepsilon_{\mu\nu} \varepsilon_{\nu\varrho} \varepsilon_{\varrho\mu} \mathop{\mathcal{S}}_{\mu,\nu,\varrho} \cos\left[2\pi(\mathbf{h}_1 . \mathbf{r}_{\mu\nu} - \mathbf{h}_3 . \mathbf{r}_{\nu\varrho})\right], \tag{III·7}$$

where the symbol $\mathop{\mathcal{S}}_{\mu,\nu,\varrho}$ means the sum over the six permutations of μ, ν, ϱ.

For each fixed triple μ, ν, ϱ, (III·7) would give the exact contribution to (III·4) corresponding to the induced interactions equivalent to $(\mathbf{r}_{\mu\nu}, \mathbf{r}_{\nu\varrho}, \mathbf{r}_{\varrho\mu})$ except for the fact that each such interaction is counted in (III·7) as often as there are valid interactions equivalent to $(\mathbf{r}_{\mu\nu}, \mathbf{r}_{\nu\varrho}, \mathbf{r}_{\varrho\mu})$, *i.e.* $\eta_{\mu\nu\varrho}$ times. Since we shall want to sum over all the valid interactions, more precisely over all $\mu \neq \nu \neq \varrho$, we must divide (III·7) by $\eta_{\mu\nu\varrho}$ so that we finally obtain (5·5).

APPENDIX IV

Proof of Theorem 5·5: We employ Theorem 5·2 to get

$$\langle(|E_{\mathbf{k}}|^2 - 1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2 - 1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2 - 1)\rangle_{\mathbf{k}} = \frac{\sum\limits_{\mu \neq \nu \neq \varrho}^{N}{}_{1}\, Z_{\mu\nu\varrho}^2 \varepsilon_{\mu\nu\varrho}}{\sigma_2^3}$$

$$\times \left\{ \frac{\sum\limits_{\mu \neq \nu \neq \varrho}^{N}{}_{1}\, Z_{\mu\nu\varrho}^2 \varepsilon_{\mu\nu\varrho} \cos\left[2\pi(\mathbf{h}_1 . \mathbf{r}_{\mu\nu} - \mathbf{h}_3 . \mathbf{r}_{\nu\varrho})\right]}{\sum\limits_{\mu \neq \nu \neq \varrho}^{N}{}_{1}\, Z_{\mu\nu\varrho}^2 \varepsilon_{\mu\nu\varrho}} \right\} . \tag{IV·1}$$

The weighted average of $\cos\left[2\pi(\mathbf{h}_1 . \mathbf{r}_{\mu\nu} - \mathbf{h}_3 . \mathbf{r}_{\nu\varrho})\right]$ in braces is approximately equal to the average (with different weights) given by Theorem 5·1:

$$\frac{\sum\limits_{\mu \neq \nu \neq \varrho}^{N}{}_{1}\, Z_{\mu\nu\varrho} \cos\left[2\pi(\mathbf{h}_1 . \mathbf{r}_{\mu\nu} - \mathbf{h}_3 . \mathbf{r}_{\nu\varrho})\right]}{\sum\limits_{\mu \neq \nu \neq \varrho}^{N}{}_{1}\, Z_{\mu\nu\varrho}}$$

$$\approx \frac{\sigma_2^3}{\sum\limits_{\mu \neq \nu \neq \varrho}^{N}{}_{1}\, Z_{\mu\nu\varrho}} |E_1 E_2 E_3| \cos(\varphi_1 + \varphi_2 + \varphi_3)$$

$$- \frac{\sigma_3}{\sum\limits_{\mu \neq \nu \neq \varrho}^{N}{}_{1}\, Z_{\mu\nu\varrho}} (|E_1|^2 + |E_2|^2 + |E_3|^2 - 2) . \tag{IV·2}$$

Substituting back into equation (IV·1) and employing also Theorems 5·3 and 5·4, we find

$$\langle(|E_{\mathbf{k}}|^2 - 1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2 - 1)(|E_{-\mathbf{h}_3+\mathbf{k}}|^2 - 1)\rangle_{\mathbf{k}}$$

$$\approx \langle(|E_{\mathbf{k}}|^2 - 1)^3\rangle_{\mathbf{k}} \left\{ \frac{\sigma_2^{3/2} |E_1 E_2 E_3| \cos(\varphi_1 + \varphi_2 + \varphi_3) - \sigma_3(|E_1|^2 + |E_2|^2 + |E_3|^2 - 2)}{\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3} \right\} . \tag{IV·3}$$

Solving (IV·3) for $|E_1 E_2 E_3| \cos(\varphi_1 + \varphi_2 + \varphi_3)$ yields (5·12).

The programming and computation of the function $B(z, t)$, which was performed on the NAREC, the Naval Research Laboratory automatic computer, were carried out by Mr Herbert Bixhorn. Some constructive criticism concerned with the computation of this function was offered by Dr. Benjamin Lepson and Mr Richard McGill of the Applied Mathematics Staff, Naval Research Laboratory. Their help and cooperation are gratefully acknowledged.

References

CHRIST, C. L. & CLARK, JOAN R. (1956). *Acta Cryst.* **9**, 830.

COCHRAN, W. (1954). *Acta Cryst.* **7**, 581.

DEBYE, P. (1915). *Ann. Phys., Lpz.* **46**, 809.

HAUPTMAN, H., KARLE, I. L. & KARLE, J. (1960). *Acta Cryst.* **13**, 451.

HAUPTMAN, H. & KARLE, J. (1955). *Acta Cryst.* **8**, 355.

HAUPTMAN, H. & KARLE, J. (1957). *Acta Cryst.* **10**, 267.

HAUPTMAN, H. & KARLE, J. (1959*a*). *Acta Cryst.* **12**, 553.

HAUPTMAN, H. & KARLE, J. (1959*b*). *Acta Cryst.* **12**, 802.

HAUPTMAN, H. & KARLE, J. (1959*c*). *Acta Cryst.* **12**, 846.

HAUPTMAN, H. & KARLE, J. (1960). *Acta Cryst.* **13**, 745.

HAUPTMAN, H. & KARLE, J. (1962). *Acta Cryst.* **15**, 547.

KARLE, I. L., HAUPTMAN, H., KARLE, J. & WING, A. B. (1958). *Acta Cryst.* **11**, 257.

KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.

KARLE, J. & HAUPTMAN, H. (1957). *Acta Cryst.* **10**, 515.

KARLE, J. & HAUPTMAN, H. (1959*a*). *Acta Cryst.* **12**, 404.

KARLE, J. & HAUPTMAN, H. (1959*b*). *Acta Cryst.* **12**, 590.

KARLE, J. & HAUPTMAN, H. (1960). *Acta Cryst.* **13**, 469.

KARLE, J. & HAUPTMAN, H. (1961). *Acta Cryst.* **14**, 105.

KARLE, J., HAUPTMAN, H. & CHRIST. C. L. (1958). *Acta Cryst.* **11**, 757.

VAUGHAN, P. A. (1958). *Acta Cryst.* **11**, 111.

VAUGHAN, P. A. (1959). *Acta Cryst.* **12**, 981.

Acta Cryst. (1964). **17**, 1433

The Structure and Mechanism of Formation of Pyrolytic Carbon from Cyanogen

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(*Received* 5 *November* 1963)

The structures of carbon deposits formed by pyrolysis of cyanogen on a carbon filament have been investigated by electron diffraction and the influence of cyanogen pressure and filament temperature has been determined. All the deposits show the existence of graphite layer planes and both the crystal size and the degree of preferred orientation parallel to the axis of the substrate increase with temperature of deposition. Possible mechanisms are discussed for the formation of carbon from cyanogen, methods of growth of deposits both along and normal to the graphite *c* axis being proposed.

Carbons produced by the decomposition of organic vapours on heated substrates, particularly carbon filaments, have been extensively studied (Grisdale, Pfister & van Roosbroeck, 1951; Tesner & Echeistova, 1952; Brown, Hall & Watt, 1953; Brown & Watt, 1958; Cullis, Manton, Thomas & Wilman, 1959; Blackman, Saunders & Ubbelohde, 1961). One factor which is of primary importance in determining the structure of the deposited carbon is the physical condition obtaining at the point of deposition, the carbons produced on a solid surface differing fundamentally from those formed in the gas phase. In the first case, the carbon is laid down in small crystallites which have a high degree of orientation and is easily graphitized at 2500 °C or above. Gas phase carbon is, however, a carbon black in which the individual particles are spherical, and does not graphitize well even at 3000 °C.

The physical properties of pyrolytic carbons depend too to a considerable extent on the temperature of deposition. A striking change has been found to occur as this temperature passes through a critical region around 1900 °C (Blackman, Saunders & Ubbelohde, 1961). Carbons prepared from methane below this temperature have low bulk densities, show only a comparatively small degree of preferred orientation and contain appreciable amounts of residual hydrogen. Deposition at higher temperatures results in carbons with bulk densities and other properties which tend towards those of perfect graphite. It seems probable that, at about 1900 °C, the rates of thermal annealing processes become of the same order as the rates of deposition of carbon, thus causing defect structures to be removed as rapidly as fresh deposits are laid down.

The influence of the starting material from which carbons are formed is, however, much less clear. Comparison of the carbonaceous deposits produced by pyrolysis of some hydrocarbons and chlorohydrocarbons shows that the more highly chlorinated compounds give rise to carbons in which the crystallites are smaller and the preferred orientation is less marked than in those derived from compounds containing little or no chlorine (Cullis, Manton, Thomas