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A Formula for the Invariant cos $(\varphi_h+\varphi_k+\varphi_l-\varphi_{h+k+l})$ in the Procedures for Phase Solution

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Several random structures are investigated to test formulae given in the preceding paper [Giacovazzo (1976). *Acta Cryst.* A**32**, 91–99]. As the values of the cosine invariant cos $(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$ are generally overestimated, an empirical scaling factor is introduced. The reliability of the phase indications in quartets is then similar to that in triplets, justifying the simultaneous use of triplets and quartets in tangent procedures for phase determination.

Introduction

In the preceding paper (Giacovazzo, 1976*b*) a probabilistic theory of the cosine invariant cos $(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$ was given in $P1$ in terms of the magnitudes of $|E_{\mathbf{h}}|,|E_{\mathbf{k}}|,|E_{\mathbf{l}}|,|E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|,|E_{\mathbf{h}+\mathbf{k}}|,|E_{\mathbf{h}+\mathbf{l}}|,|E_{\mathbf{k}+\mathbf{l}}|$. By means of the joint probability distribution functions a number of conditional expected values were derived: the most significant is given by

$$\langle\cos \Phi_{\mathbf{h},\mathbf{k},\mathbf{l}}\rangle=\langle\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})\rangle=\frac{I_1(G)}{I_0(G)}\,, \tag{1}$$

where

$$G=2N^{-1}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}+R^2_{\mathbf{k}+\mathbf{l}}-2) \tag{2}$$

when all three cross vectors are in the set of measured reflexions, and

$$G=2N^{-1}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}-1) \tag{3}$$

when only two cross vectors, $\mathbf{h}+\mathbf{k}$ and $\mathbf{h}+\mathbf{l}$ are present. The variance of the cosine is

$$\mathrm{Var}\,[\cos \Phi_{\mathbf{h},\mathbf{k},\mathbf{l}}]=1-\frac{I_1(G)}{GI_0(G)}-\frac{I_1^2(G)}{I_0^2(G)}\,. \tag{4}$$

(1) and (4) were obtained by taking terms up to order $1/N\sqrt{N}$ into account.

It is the aim of this paper to verify the reliability of (1). It was suggested from theoretical considerations that (1) should lead to an overestimate of the values of the cosine invariants when large values of G are involved. As the calculation of the terms of order $1/N^2$ in the probability distribution function would discourage the use of quartets in procedures for crystal structure solution, a further task of this paper is to find a simple scaling factor which assigns to the quartet relationships a reliability similar to that of the triplets. This condition is essential for simultaneous use of triplets and quartets in procedures for phase solution.

The role of the special quartets

Special quartets of type $2\mathbf{h},\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k}$ have been investigated in $P1$ by Giacovazzo (1976*c*) for deriving the conditional expectation values of cos $(\varphi_{2\mathbf{h}}-2\varphi_{\mathbf{h}})$. Probabilistic calculations led to

$$\langle\cos(\varphi_{2\mathbf{h}}-\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}-\mathbf{k}})\rangle=\frac{I_1(G)}{I_0(G)} \tag{5}$$

where

$$G=2N^{-1}R_{2\mathbf{h}}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{h}-\mathbf{k}}(R^2_{2\mathbf{h}-\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{k}}-1)\,. \tag{6}$$

The second of the cross vectors, $\mathbf{h}+\mathbf{k},\mathbf{h},2\mathbf{h}-\mathbf{k}$, coincides with a vector which is part of the quartet and is not relevant for defining the sign of cos $(\varphi_{2\mathbf{h}}-\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}-\mathbf{k}})$. Even if the number of special quartets is a small percentage of the observable quartets, the overall phase reliability will be improved if special formulae are used for special quartets. As (5) and (6) are formally very like (1) and (3), we will hereafter use for special quartets the same formulae as for quartets in which only two cross vectors are measured.

Calculations

In a given structure the quartets for which only two cross vectors are in the set of measurements may constitute a high percentage of the observable quartets (Giacovazzo, 1976*a*). So separate tests will be made for quartets in which only two cross vectors have measured intentities and for quartets in which all three cross vectors are present. Given $\Phi_{\mathbf{h},\mathbf{k}}=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}$ (Hauptman, 1972)

$$\langle\cos \Phi_{\mathbf{h},\mathbf{k}}\rangle=\frac{I_1(G)}{I_0(G)}\,,$$
$$\mathrm{Var}\,[\cos \Phi_{\mathbf{h},\mathbf{k}}]=1-\frac{I_1(G)}{GI_0(G)}-\frac{I_1^2(G)}{I_0^2(G)}\,, \tag{7}$$

where $G=2R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{h}+\mathbf{k}}/\sqrt{N}$. Triplet and quartet reliabilities may therefore be compared, giving in fixed ranges of G the number of cosine invariants, the percentage of the cosines whose sign is in accordance with the theory, the average error

$$\langle\Delta\cos\rangle=\langle\cos\Phi_{\text{true}}-\cos\Phi_{\text{calc}}\rangle\,,$$

and the average magnitude of the error $\langle|\Delta\cos|\rangle$. In order to check the formulae for a satisfactory range of structural complexity, four random structures have

Table 1. *Number of cosines (nr), percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and negative quartets for a 20-atom model structure*

Negative quartets are given when only two cross vectors are within the set of measurements.

	Triplets				Negative quartets (3)				Negative quartets (9)			
$\lvert G\rvert$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$
0·4					1888	72·7	−0·099	0·573	1264	73·7	−0·096	0·569
0·8					80	75·0	−0·015	0·585	40	90·0	−0·225	0·515
1·2	93	94·6	0·137	0·339	7	100	−0·316	0·316	5	100	−0·280	0·280
1·6	249	99·6	0·163	0·251								

Table 2. *Number of cosines (nr), percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and negative quartets for a 20-atom model structure*

Negative quartets are given when all three cross vectors are within the set of measurements.

	Triplets				Negative quartets (2)				Negative quartets (8)			
$\lvert G\rvert$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$
0·4					1152	78·8	−0·149	0·504	923	82·7	−0·252	0·516
0·8					415	86·5	−0·226	0·443	195	85·7	−0·239	0·444
1·2	93	94·6	0·137	0·339	40	90·0	−0·044	0·351	20	80·0	−0·004	0·531
1·6	249	99·6	0·163	0·251	3	100	−0·276	0·276				
2·0	190	99·5	0·120	0·201								

Table 3. *Number of cosines (nr), percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and positive quartets for a 20-atom model structure*

Positive quartets are given when only two cross vectors are in the set of measurements.

	Triplets				Positive quartets (3)				Positive quartets (9)			
G	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$
0·4					8893	72·1	0·049	0·542	16657	83·3	0·225	0·489
0·8					8259	81·7	0·040	0·432	11464	91·9	0·223	0·394
1·2	93	94·6	0·137	0·339	7656	86·9	0·017	0·373	7669	95·3	0·160	0·318
1·6	249	99·6	0·163	0·251	6049	91·4	0·003	0·304	4408	97·3	0·110	0·254
2·0	190	99·5	0·120	0·201	4702	93·7	−0·037	0·264	2384	99·0	0·059	0·220
2·4	155	100	0·087	0·146	5873	95·2	−0·065	0·231	1873	99·8	0·025	0·185
3·0	52	100	0·080	0·113	3449	96·8	−0·073	0·210	735	99·5	0·020	0·148
3·5	16	100	0·047	0·086	2237	98·2	−0·070	0·189	306	100	0·006	0·122
4·0	4	100	0·084	0·084	2770	99·0	−0·084	0·182	275	100	−0·041	0·138
5·0	2	100	0·049	0·049	2155	99·8	−0·098	0·150	137	100	−0·026	0·105
7·0					494	100	−0·107	0·131	11	100	−0·082	0·107
9·0					221	100	−0·107	0·121	3	100	−0·104	0·104
15·0					8	100	−0·142	0·142				

Table 4. *Number of cosines (nr), percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and positive quartets for a 20-atom model structure*

Positive quartets are given when all three cross vectors are in the set of measurements.

	Triplets				Positive quartets (2)				Positive quartets (8)			
G	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$	nr.	%	$\langle \Delta \cos\rangle$	$\langle \lvert\Delta \cos\rvert\rangle$
0·4					2588	72·8	0·055	0·489	5046	83·3	0·215	0·471
0·8					2553	81·7	0·044	0·440	4719	91·9	0·190	0·370
1·2	93	94·6	0·137	0·339	2500	88·3	0·006	0·348	3375	95·4	0·141	0·313
1·6	249	99·6	0·163	0·251	2465	91·1	−0·034	0·303	2484	98·7	0·111	0·248
2·0	190	99·5	0·120	0·201	2050	93·8	−0·064	0·271	1363	99·1	0·055	0·196
2·4	155	100	0·087	0·146	2541	95·3	−0·079	0·238	1143	99·7	0·030	0·172
3·0	52	100	0·080	0·113	1716	97·7	−0·086	0·221	554	100	0·030	0·134
3·5	16	100	0·047	0·086	1390	99·1	−0·075	0·181	360	100	0·021	0·136
4·0	4	100	0·084	0·084	1563	99·0	−0·085	0·165	288	100	−0·004	0·126
5·0	2	100	0·049	0·049	1373	100	−0·087	0·139	136	100	0·006	0·060
7·0					545	100	−0·082	0·117	21	100	0·008	0·060
9·0					228	100	−0·065	0·079	13	100	−0·063	0·063
15·0					13	100	−0·003	0·022				

Table 5. *Number of cosines, percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and negative quartets for a 40-atom model structure*

Negative quartets are given when all three cross vectors are in the set of measurements.

	Triplets				Negative quartets (2)				Negative quartets (8)			
$\|G\|$	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$
0·4					166	72·9	−0·067	0·561	114	80·7	−0·164	0·545
0·8	27	85·2	0·114	0·469	17	88·2	−0·134	0·439	13	80·0	−0·066	0·532
1·2	125	91·2	0·118	0·363	3	100	−0·346	0·346	2	100	−0·321	0·321
1·6	131	95·4	0·102	0·275								

Table 6. *Number of cosines (nr), percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and positive quartets for a 40-atom model structure*

Positive quartets are given when only two cross vectors are in the set of measurements.

	Triplets				Positive quartets (3)				Positive quartets (9)			
G	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$
0·4					1288	69·5	0·036	0·574	1621	81·0	0·204	0·529
0·8	27	85·2	0·114	0·469	880	79·1	−0·003	0·484	683	90·3	0·212	0·423
1·2	125	91·2	0·118	0·363	634	85·3	0·009	0·404	319	95·9	0·193	0·328
1·6	131	95·4	0·102	0·275	389	89·7	−0·007	0·321	127	96·1	0·113	0·301
2·0	62	100	0·130	0·204	258	91·1	−0·071	0·313	44	100	0·095	0·213
2·4	34	100	0·084	0·156	254	96·5	−0·020	0·220	27	100	0·127	0·153
3·0	6	100	−0·019	0·165	129	96·9	−0·078	0·229	2	100	−0·048	0·236
3·5	2	100	0·099	0·099	59	96·6	−0·040	0·183	2	100	−0·026	0·175
4·0					53	100	−0·040	0·144				
5·0					20	100	−0·018	0·107				
7·0					2	100	−0·119	0·178				
9·0												

Table 7. *Number of cosines (nr), percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and positive quartets for a 40-atom model structure*

Positive quartets are given when all three cross vectors are in the set of measurements.

	Triplets				Positive quartets (2)				Positive quartets (8)			
G	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$
0·4					534	63·9	−0·094	0·574	744	77·0	0·116	0·518
0·8	27	85·2	0·114	0·469	395	75·9	−0·053	0·485	429	89·5	0·191	0·406
1·2	125	91·2	0·118	0·363	298	80·2	−0·115	0·447	243	90·9	0·118	0·359
1·6	131	95·4	0·102	0·275	241	88·0	−0·052	0·340	108	95·4	0·052	0·284
2·0	62	100	0·130	0·204	160	93·8	−0·026	0·263	61	98·4	0·078	0·228
2·4	34	100	0·084	0·156	198	91·4	−0·102	0·274	28	100	0·051	0·168
3·0	6	100	−0·019	0·165	88	93·2	−0·091	0·239	4	100	0·018	0·128
3·5	2	100	0·099	0·099	51	96·1	−0·184	0·268	3	100	−0·146	0·257
4·0					70	98·6	−0·063	0·164				
5·0					23	100	−0·085	0·148				
7·0					4	100	−0·254	0·258				
9·0												
15·0												

Table 8. *Number of cosines (nr), percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and positive quartets for a 60-atom model structure*

Positive quartets are given when only two cross-vectors are in the set of measurements.

	Triplets				Positive quartets (3)				Positive quartets (9)			
G	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$	nr.	%	$\langle\Delta \cos\rangle$	$\langle\|\Delta \cos\|\rangle$
0·4	49	61·2	−0·085	0·529	4276	65·2	−0·040	0·584	2169	70·2	0·053	0·559
0·8	394	77·4	−0·012	0·514	1504	68·7	−0·138	0·538	243	85·2	0·127	0·467
1·2	229	92·1	0·067	0·335	530	74·9	−0·165	0·511	19	94·7	0·138	0·304
1·6	54	87·0	0·000	0·342	165	80·6	−0·171	0·453	4	100	0·286	0·286
2·0	14	100	−0·002	0·261	70	94·3	−0·018	0·263				
2·4	2	100	0·201	0·201	18	94·4	−0·110	0·227				
3·0	2	100	0·172	0·172	3	100	0·102	0·102				
3·5					2	100	0·102	0·102				
4·0												

been tested, with 20, 40, 60, 90 atoms in the unit cell: the results are shown in Tables 1–11. Corresponding to any G_i value in the first column of the tables, the triplets and the quartets are given for which $G_i < G \le G_j$, where G_j is the value which immediately follows G_i. To save computing time a limit L for $R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h+k}}$ in the triplets and for $R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{l}}, R_{\mathbf{h+k+l}}$ in the quartets has been introduced: $L=1\cdot40$ for the random structures with $N=20,40,60$; $L=1\cdot45$ for $N=90$.

As the negative cosine invariants have a specific use in procedures for resolving the ambiguities of direct solutions in symmorphic space groups, distinct tests are made on these invariants in the random structures with $N=20,40$. Tables 1–11 suggest that, when G is given by (2) or (3), (1) overestimates the values of the quartet cosine invariants: on the other hand (7) underestimates the values of the triplet cosines. This situation would be unsuitable when triplet and quartet relationships are simultaneously used in a tangent procedure for phase solution since it would strongly overestimate the quartet contribution.

More favourable results are obtained when the values of G as provided by (2) and (3) are empirically rescaled. Suitable new values of G seem to be

$$G=\frac{2N^{-1}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h+k+l}}(R^2_{\mathbf{h+k}}+R^2_{\mathbf{h+l}}+R^2_{\mathbf{k+l}}-2)}{1+\tanh\,[(R^2_{\mathbf{h+k}}+R^2_{\mathbf{h+l}}+R^2_{\mathbf{k+l}})/3]} \quad (8)$$

Table 9. *Number of cosines (nr), percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and positive quartets for a* 60-*atom model structure*

Positive quartets are given when all three cross vectors are in the set of measurements.

	Triplets				Positive quartets (2)				Positive quartets (8)			
G	nr.	%	$\langle \Delta \cos \rangle$	$\langle \lvert\Delta \cos\rvert \rangle$	nr.	%	$\langle \Delta \cos \rangle$	$\langle \lvert\Delta \cos\rvert \rangle$	nr.	%	$\langle \Delta \cos \rangle$	$\langle \lvert\Delta \cos\rvert \rangle$
0·4	49	61·2	−0·085	0·529	1866	66·5	−0·038	0·569	1175	74·1	0·104	0·555
0·8	394	77·4	−0·012	0·514	798	71·9	−0·093	0·527	149	86·6	0·143	0·456
1·2	229	92·1	0·067	0·335	295	78·6	−0·112	0·467	15	86·7	0·113	0·381
1·6	54	87·0	0·000	0·342	97	88·7	−0·071	0·360	1	100	−0·365	0·365
2·0	14	100	−0·002	0·261	45	84·4	−0·147	0·376	1	100	0·241	0·241
2·4	2	100	0·201	0·201	15	86·7	−0·120	0·315				
3·0	1	100	0·172	0·172	1	100	−0·567	0·567				
3·5												
4·0					1	100	0·091	0·091				
5·0												

Table 10. *Number of cosines (nr), percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and positive quartets for a* 90-*atom model structure*

Positive quartets are given when only two cross vectors are in the set of measurements.

	Triplets				Positive quartets (3)				Positive quartets (9)			
G	nr.	%	$\langle \Delta \cos \rangle$	$\langle \lvert\Delta \cos\rvert \rangle$	nr.	%	$\langle \Delta \cos \rangle$	$\langle \lvert\Delta \cos\rvert \rangle$	nr.	%	$\langle \Delta \cos \rangle$	$\langle \lvert\Delta \cos\rvert \rangle$
0·4	54	83·3	0·135	0·531	3962	64·0	−0·054	0·596	1354	71·8	0·092	0·570
0·8	368	78·5	0·019	0·497	1037	70·8	−0·097	0·539	90	75·6	0·032	0·509
1·2	199	85·4	0·037	0·409	266	75·9	−0·121	0·500	7	85·7	−0·038	0·297
1·6	35	91·4	−0·031	0·308	67	68·7	−0·261	0·551	2	100	0·166	0·166
2·0	9	100	0·236	0·236	23	95·7	−0·070	0·264				
2·4	1	100	−0·159	0·159	7	85·7	−0·275	0·347				
3·0					2	100	−0·038	0·144				
3·5												

Table 11. *Number of cosines, percentages of correct cosine signs, average errors and average magnitudes of the errors in triplets and positive quartets for a* 90-*atom model structure*

Positive quartets are given when all the three cross vectors are in the set of measurements.

	Triplets				Positive quartets (2)				Positive quartets (8)			
G	nr.	%	$\langle \Delta \cos \rangle$	$\langle \lvert\Delta \cos\rvert \rangle$	nr.	%	$\langle \Delta \cos \rangle$	$\langle \lvert\Delta \cos\rvert \rangle$	nr.	%	$\langle \Delta \cos \rangle$	$\langle \lvert\Delta \cos\rvert \rangle$
0·4	54	83·3	0·135	0·531	1383	62·5	−0·079	0·593	601	75·5	0·125	0·537
0·8	368	78·5	0·019	0·497	440	78·0	−0·021	0·475	54	83·3	0·077	0·487
1·2	199	85·4	0·037	0·409	125	75·2	−0·134	0·488	6	83·3	0·051	0·365
1·6	35	91·4	−0·031	0·308	43	81·4	−0·209	0·430				
2·0	9	100	0·236	0·236	11	81·8	−0·117	0·377				
2·4	1	100	−0·159	0·159	4	100	−0·095	0·317				
3·0					1	100	0·107	0·107				
3·5												

when all three cross vectors are in the set of measured reflexions, and

$$G=\frac{2N^{-1}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}-1)}{1+\tanh\left[(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}})/2\right]} \quad (9)$$

when only two cross-vectors, $\mathbf{h}+\mathbf{k}$ and $\mathbf{h}+\mathbf{l}$, are present. In particular, the trends of the average error and of the average magnitude of the errors seem to be similar in triplets and quartets when (8) and (9) are used. The simultaneous use of triplet and quartet relationship in tangent procedures is thus justified.

A further remark may be useful. The empirical scaling factor

$$SC=1+\tanh\left(\sum R_j^2/j\right), \quad j=2,3,$$

proposed in this paper is of course not unique. It occurred to the author both by analogy with the scaling factor successfully used for centrosymmetrical quartets (Giacovazzo, 1976*a*) and by its functional simplicity. SC nevertheless involves the magnitudes of the cross vectors alone, whereas the theoretical conditional variance given by the distribution function

$$P(\Phi_{\mathbf{h},\mathbf{k},\mathbf{l}}|R_{\mathbf{h}},R_{\mathbf{k}},R_{\mathbf{l}},R_{\mathbf{h}+\mathbf{k}+\mathbf{l}},R_{\mathbf{h}+\mathbf{k}},R_{\mathbf{h}+\mathbf{l}},R_{\mathbf{k}+\mathbf{l}})$$

suggests a scaling factor which takes all the magnitudes into account. It is hoped that further work in this direction will improve present results.

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X-ray Intensity Measurements on Large Crystals by Energy-Dispersive Diffractometry. I. Energy Dependences of Diffraction Intensities near the Absorption Edge

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The intensity variations of X-rays diffracted from a nearly perfect GaAs plate have been measured in symmetrical Laue and Bragg cases in the energy region near the As *K* absorption edge with small energy intervals, by the use of an energy-dispersive diffractometer and continuous X-rays from a sealed-off tube. The corresponding intensity variations have been calculated with the dynamical theory. These measurements and calculations have shown a good agreement. Moreover, the curve measured for the Bragg case on the same crystal, but after polishing, has shown good agreement with the corresponding curve calculated by the kinematical theory. However, there is a minor discrepancy in the energy region very near the absorption edge. This is probably due to the fact that the values of anomalous-scattering factors used for calculation are not precise enough to explain fine structures at the edge.

Introduction

Energy-dispersive diffractometry, with a solid-state detector (SSD) and continuous radiation from a normal X-ray tube, has various merits of its own, complementary to those of traditional angle-dispersive diffractometry. One of the merits is, as has been well known since early work (Giessen & Gordon, 1968), the possibility of carrying out rapid measurements comparatively easily even under extreme conditions. According to recent papers, the interplanar distances (Fukamachi, Hosoya & Terasaki, 1973), and the intensity values both for single crystals (Buras, Olsen, Gerward, Selsmark & Andersen, 1975) and for powder samples (Uno & Ishigaki, 1975) have been measured with considerable accuracy under normal conditions and even in extreme conditions (Inoue, 1975). Another merit is the possibility of carrying out the measurements with radiations of desired energy values. This has already been utilized for a rapid determination of polarity sense (Hosoya & Fukamachi, 1973), and for experimental determination of anomalous scattering factors at the energy values near the absorption edge (Fukamachi & Hosoya, 1975). Including the latter, various possibilities of determining the anomalous scattering factors and phases of reflexions have preliminarily been reviewed (Hosoya, 1975). In these papers, however, full formulation of the expressions for diffraction intensities and other quantities was not required. In the present work, such a formulation has been described in order to explain the measured energy dependences of intensities near the absorption edge in typical Laue and Bragg cases for mosaic and perfect crystal plates; for a mosaic

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