quence of these additional effects there may be large differences between observed and theoretical directions, and curved dislocation lines may occur. In such cases the determination of Burgers vectors from the directions of dislocation lines is questionable or impossible.

Conclusion

This study gives a further confirmation that the directions of grown-in straight dislocation lines are in many cases predominantly influenced by the tendency to minimize the elastic dislocation energy per unit growth length. Some consequences resulting from this theory and concerning the effect of elastic anisotropy and the determination of Burgers vectors, as well as the influence of the lattice structure are discussed. These subjects, however, require further investigations which this work may stimulate.

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On the Reliability of the $\sum_2$ Relation. I. Real Structures in $P2_1/c$

By H. Schenk

Laboratory for Crystallography, University of Amsterdam, Nieuwe Prinsengracht 126, *Amsterdam, The Netherlands*

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It is shown for real structures in $P2_1/c$ that the percentages of failures of the $\sum_2$ relation do not agree with the theoretical values based on the probability formula. Moreover there is some evidence that the probability of a multiple-sign relation is less reliable than that of a single-sign relation. In practice therefore, the probability formula cannot be used to estimate the reliability of a sign indication. An alternative method is proposed, in which only the ten to twenty triplets with highest *EEE* product are used directly. All other signs have to be determined by at least two independent sign indications. It is also shown that in difficult cases the strengthened quartet relation [Schenk (1973). *Acta Cryst.* A**29**, 77–82] is very helpful.

Introduction

During the last decade the number of successful structure determinations by means of direct phasing has increased enormously. The $\sum_2$ relation

$$\Phi_H = \frac{\sum_K |E_K E_{H-K}|(\Phi_K + \Phi_{H-K})}{\sum\limits_K |E_K E_{H-K}|} \qquad (1)$$

has proved to be the most successful phase relationship. In centrosymmetric space groups a probability formula (6) is associated with the $\sum_2$ relation.

In our laboratory a large number of centrosymmetric structures have been solved by means of the symbolic-addition method (Karle & Karle, 1966), in which a rule of thumb based on the probability formula (6) is used for the acceptance of sign indication. The rule says that a sign indication is accepted if the probability (6) fulfills the condition $P_+(H) > A$ or $P_+(H) < 1 - A$, in which for instance $A = 0{\cdot}97$, as suggested by Karle & Karle (1966). If the probabilities from (6) are reliable then for all structures the same value of A should lead to a correct sign determination. However, in our experience A must be given a wide variety of values

Table 1. *Crystal data and intensity statistics of nine structures in $P2_1/c$*

Number of the structure	Theoretical values for centrosymmetric structures	1	2	3	4	5	6	7	8	9
Molecular formula		$C_{34}O_6N_2H_{36}$	$C_{19}H_{26}O_2$	$C_{14}H_{22}N_2O_2$	$C_{12}H_{18}O_2$	$C_9H_{13}N_3O_6$	$C_9H_{13}N_3O_5$	$C_{19}H_{23}NO_3S.CH_3NO_2$	$C_{20}H_{28}O_2$	$C_{25}H_{16}$
Space group		$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a(Å)		9·288	9·487	8·383	9·043	13·304	6·423	13·847	8·078	10·173
b		20·976	8·260	23·999	9·812	6·350	6·937	6·154	34·104	10·241
c		14·866	22·472	7·320	15·290	13·263	24·416	26·141	7·387	16·722
β (°)		100·30	95·94	111·48	123·14	105·30	99·88	106·36	118·76	96·52
Z			4	4	4	4	4	4	4	4
Number of non-hydrogen atoms in the unit cell		168	84	72	56	72	68	112	88	100
Number of measured reflexions		3576	2377	2536	2444	2006	1999	2805	3298	3203
Number of non-zero reflexions		2021	1585	1968	1772	1837	1393	1567	2790	2600
$\sigma_3^2\sigma_2^{-3/2}$		0·077	0·106	0·115	0·131	0·118	0·122	0·106	0·104	0·098
$\langle\lvert E\rvert\rangle$	0·798	0·652	0·707	0·772	0·675	0·779	0·753	0·676	0·754	0·744
$\langle\lvert E^2-1\rvert\rangle$	0·968	1·282	1·112	1·015	1·096	1·040	1·027	1·170	1·025	1·026
$\langle\lvert E^2\rvert\rangle$	1·000	1·064	0·979	1·015	0·902	1·015	1·012	1·033	0·948	0·952
$\lvert E\rvert > 3·0$ (%)	0·27	2·18	0·93	0·47	0·74	0·35	0·60	0·61	0·61	0·47
$\lvert E\rvert > 2·5$	1·24	3·30	2·69	1·74	2·05	1·69	1·35	2·39	1·64	1·90
$\lvert E\rvert > 2·0$	4·55	6·60	5·85	4·93	5·16	5·53	5·00	6·38	4·28	5·00
$\lvert E\rvert > 1·8$	7·19	8·67	8·08	7·89	7·49	7·98	7·85	9·13	7·40	6·99
$\lvert E\rvert > 1·6$	10·96	11·47	11·19	11·59	10·72	12·21	11·66	12·98	11·28	10·05
$\lvert E\rvert > 1·4$	16·15	14·40	15·48	16·29	14·44	17·65	16·51	17·90	15·55	14·95
$\lvert E\rvert > 1·2$	23·01	18·62	20·28	23·50	20·05	23·93	23·76	24·96	21·65	22·01
$\lvert E\rvert > 1·0$	31·73	24·89	28·36	32·93	27·62	32·10	33·52	32·69	30·05	30·35

(from 0·98 up to 0·99999) in order to arrive at the correct solution, so that the usefulness of (6) in real structure determinations is doubtful.

The purpose of this paper is to present full details of the $\sum_2$ relationships for a number of structures in space group $P2_1/c$ in order to show the discrepancies between the theoretical and experimental probabilities of the triplet sign relations. Furthermore the way in which the apparent practical difficulties in the sign determinations may be remedied is indicated.

Theory of the probability relations

The theory of the probability relations is based on the assumption that the positions of atoms are random variables. This implies that the theoretical results are averages obtained for all conceivable combinations of atomic positions. It is known that overlap of Patterson peaks decreases the reliability of these results (Cochran, 1958). Thus when probability relations are applied to individual structures it may be expected that structures without Patterson overlap, that is to say structures without physical reality, will give the best fit with the theoretical results. Physically significant structures, however, in which considerable Patterson overlap occurs, will be expected to show discrepancies.

It is not the purpose of this paragraph to go into the details of the theory [see *e.g.* Karle & Karle (1966) and Klug (1958) and the references cited there], but two expressions have to be mentioned here:

(*a*). The probability of the truth of a sign relation

$$s(H)s(K)s(H-K)=+1 \qquad (3)$$

is given by

$$P_+(E_HE_KE_{H-K})=\tfrac{1}{2}+\tfrac{1}{2}\tanh \sigma_3\sigma_2^{-3/2}|E_HE_KE_{H-K}| \qquad (4)$$

in which $\sigma_n=\sum_{j=1}^{N} Z_j^n$ (N is the number of atoms in the unit cell and Z is the number of electrons of an atom).

(*b*). The probability that

$$s(H)=s(\sum_K E_KE_{H-K}) \qquad (5)$$

is given by

$$P_+(H)=\tfrac{1}{2}+\tfrac{1}{2}\tanh \sigma_3\sigma_2^{-3/2}\,|E_H|\sum_K E_KE_{H-K}\,. \qquad (6)$$

Both expressions have been derived by Cochran & Woolfson (1955) using the assumption of randomness. Actually (4) and (6) are approximations and with a more exact treatment Klug (1958) proved that the probability given by (4) is an underestimate, especially for larger values of $|E_HE_KE_{H-K}|$.

From (4) it follows that the percentage of failures of the $\sum_2$ relation for a given value of $E_3=\sigma_3\sigma_2^{-3/2}|E_HE_KE_{H-K}|$ is given by

$$F(E_3)=[1-P_+(|E_HE_KE_{H-K}|)]\times 100\,\%\,. \qquad (7)$$

The results of Klug (1958) suggests that true percentages of failures should be less than $F(E_3)$.

The reliability of the single-sign relation

Expression (7) has been checked for nine structures of space group $P2_1/c$, all except one consisting of nearly equal atoms. The normalized structure factors E_H were calculated from the measured intensities applying the Wilson temperature and scale parameters. Cell constants, intensity statistics and other relevant information are given in Table 1. Judging from the $\langle|E|^2\rangle$ values, the Wilson parameters are reasonable approximations with the exception of structure 4. The signs of the structure factors were taken from the final least-

Table 2. *Total number* (NR) *of triplet sign relations above a variable* $E_3=\sigma_2^{-3/2}\,\sigma_3|E_HE_KE_{H-K}|$ *value with the percentage* (%) *of correct sign relations for nine structures in space group* $P2_1/c$

E_3	Structure 1		Structure 2		Structure 3		Structure 4		Structure 5		Structure 6		Structure 7		Structure 8		Structure 9	
	NR	%	NR	%	NR	%	NR	%	NR	%	NR	%	NR	%	NR	%	NR	%
15	1	100																
10	8	100																
8	30	100																
6	83	100	1	100									1	100				
5	149	99·3	4	100			3	100			1	100	1	100				
4·0	266	99·6	22	100	2	100	12	100			3	100	7	100	1	100		
3·6	348	99·7	32	100	3	100	19	100	1	100	7	100	13	100	5	100		
3·2	457	99·3	61	100	7	100	34	100	1	100	11	100	25	110	14	100	3	100
2·8	612	99·3	117	100	17	100	66	100	5	100	27	100	48	100	40	100	11	100
2·6	733	98·9	141	100	26	100	91	100	9	100	33	100	77	100	61	100	17	100
2·4	922	98·5	179	99·4	41	100	124	100	17	100	42	100	110	100	87	100	26	100
2·2	1120	98·0	255	99·2	67	98·5	174	100	32	100	67	100	166	98·8	135	100	35	100
2·0	1355	97·4	336	98·8	114	99·1	266	100	52	100	109	100	270	98·1	217	99·1	63	100
1·8	1725	96·5	473	97·1	206	99·5	394	100	103	98·1	177	100	456	96·5	345	98·3	135	99·3
1·6	2235	95·2	706	95·3	349	99·1	597	100	196	96·4	274	99·6	751	96·5	549	97·6	229	99·1
1·4	2935	94·0	1094	94·9	616	97·4	961	99·2	378	96·8	456	97·8	1300	94·3	870	96·8	468	97·9
1·2			1764	93·7	1130	96·3	1597	98·3	763	95·0	813	95·2	2303	93·5	1511	95·8	908	95·6
1·0			2910	92·4	2173	93·9	2782	96·8	1578	92·7	1607	92·8	4206	90·5	2905	93·4	1837	94·0
0·9			3842	91·1	3089	92·1	3798	95·7	2334	91·1	2319	91·1	5796	88·8	4123	92·1	2706	92·8
0·8			5104	89·7	4595	90·1	5299	94·2	3422	88·9	3437	89·2	8202	87·4	5952	89·7	4004	90·9
0·7			6941	87·7	6817	88·0	7509	91·7	5116	87·0	5039	86·5	11660	85·5	8749	87·4	6173	89·2

squares cycles. For 8 structures all triplet relations down to $E_3=0{\cdot}7$ have been calculated and for structure 1 the lower limit is 1·4. In Table 2 the total number of relations above a variable E_3 value, B, is given together with the percentage of correct relations. In Fig. 1 the percentage of failures of the $\sum_2$ relation is given for groups of at least 40 triplets relations with E_3 values within $B+0{\cdot}1\geq E_3>B$. The theoretical curve (7) is represented by the solid line F.

From Fig. 1 and Table 2 it can be seen that the results of the $\sum_2$ relation are fairly divergent. Structure 1 shows a percentage of failures which is about three times as high as the theoretical percentage, whereas the failure curve of structure 4 is better than the theoretical line. Therefore in practice the failure percentages of the $\sum_2$ relation differ to such an extent that the probability formulae (4) and (6) cannot be used as a measure of the correctness of a computed sign.

In our opinion the most important origin of the discrepancy between theory and practice is the fact that atomic positions are not random, but show regularities caused by bonding and packing, which are reflected in an appreciable overlap in the Patterson function. In a subsequent paper we shall demonstrate the effect of order in the atomic parameters by means of model structures.

Another cause of the lack of agreement between theory and practice will be the accidental and systematic errors in the $|E_H|$ values of real structures. The accidental errors in E_H are larger for larger values of θ and should be used to weight the triple products E_3 The systematic errors are caused by introducing the Wilson thermal and scale parameters instead of the true absolute scale parameter and individual anisotropic thermal parameters for all atoms. This can be partly remedied by measuring the absolute scale directly (Coppens, 1973) and calculating overall anisotropic corrections to the Wilson temperature parameter (Maslen, 1968). With respect to the latter, one has to be careful because anisotropy in the weighted reciprocal lattice need not be due to anisotropy of the thermal behaviour of the atoms but may be induced by the atomic arrangement instead.

Reliability of multiple-sign indications

Expression (6) gives the probability of a multiple-sign indication (5) and in view of the results of the preceding paragraph formula (6) will also be unreliable.

In order to solve structures it is necessary to use multiple-sign relations as well as single-sign relations. In our automated procedure a sign indication is accepted if the signs $s(H)$ of all component single indications are consistent and $\sum_K E_3>\text{LIM}$. In the sign determination of, for instance, structure 2 a value of $\text{LIM}=2{\cdot}6$ would be expected to lead to a correct solution, because according to Table 2 all single relations with $E_3>2{\cdot}6$ are correct. However in this way a set of incorrect signs is produced and in fact $\text{LIM}=4$ has to be used in order to arrive at the correct solution. From this and other analogous experiences a preliminary conclusion may be that if E_3, obtained from one single relation, is equal to $\sum E_3$, obtained from a multiple one, the reliability is larger for the single relation. This statement cannot at present be formulated quantitatively.

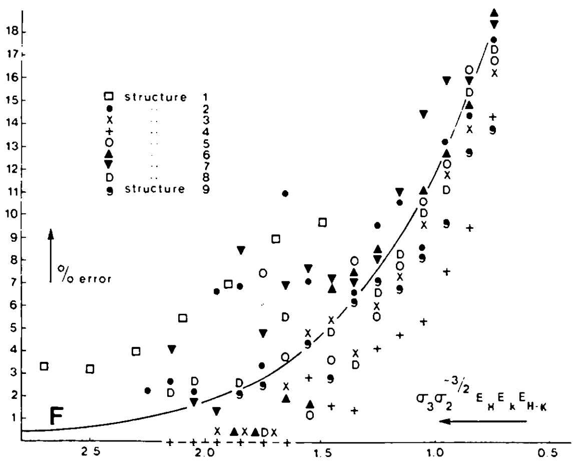

Fig. 1. Percentage of errors of the $\sum_2$ relation as a function of $E_3=\sigma_3\sigma_2^{-3/2}|E_HE_KE_{H-K}|$ for nine structures in $P2_1/c$. For reference the curve $F(E_3)$, based on the probability formula (4), has been indicated.

Structure determination

Although the practical results do not agree with the theory, structure determinations by means of the $\sum_2$ relation should be possible because in all $\sum_2$ sets the percentage of correct information is large (see Table 2). However in order to arrive at the correct solution a sign-acceptance criterion has to be used adapted to the E_3 values.

In our procedure we use $\sum E_3$ for estimating the reliability of a phase as long as we do not have a better measure. In order to overcome the difficulties described in the preceding paragraph the sign-acceptance criterion $\sum E_3>\text{LIM}$ is used with LIM chosen such that only the triplets corresponding to the 10 to 20 strongest E_3 values (Table 2) are accepted as correct. All other signs have to be determined by at least two relationships.

Eight out of nine structures could be solved by means of this procedure. In seven structures the solution of best $\sum_2$ consistency proved to be correct. In the sign determination of structure 1 the solution with the third best $\sum_2$ consistency was correct.

The sign determination of structure 7 failed using 7 starting reflexions and $\text{LIM}=3{\cdot}6$ (only the 13 highest E_3 values were used directly). None of the 16 resulting $\sum_2$ solutions contained the correct signs. With $\text{LIM}=5{\cdot}0$ and a starting set of 26 reflexions the sign determination proceeded smoothly. This starting set was constructed by means of the mixed triplet and strengthened quartet relationships (Schenk, 1973) on the basis of the same 7 reflexions with an acceptance criterion LIM = 5·5.

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The Elastic Properties of Beryl

BY HYO SUB YOON* AND R. E. NEWNHAM

Materials Research Laboratory, The Pennsylvania State University, University Park, Pa. 16802, *U.S.A.*

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Using the pulse-superposition method, the second-order elastic stiffnesses of aquamarine were determined to be $C_{11}=3\cdot085$, $C_{33}=2\cdot834$, $C_{12}=1\cdot289$, $C_{13}=1\cdot185$, $C_{44}=0\cdot661$ Mbar. Results for goshenite beryl are very similar. Initial pressure derivatives were also determined.

The second-order adiabatic elastic stiffnesses of beryl and their initial pressure derivatives at 25 °C have been measured by the pulse-superposition method. Previous measurements (Voigt, 1887; Madelung & Fuchs, 1921; Bridgman, 1928; Sundara Rao, 1948) are not in agreement: bulk moduli measurements, for instance, differ by 20%. Chung & Buessem (1968) have questioned the validity of the elastic constants of beryl for a different reason. The compression anisotropy calculated from the elastic coefficients appears inconsistent with anisotropies observed in other hexagonal crystals.

Two Brazilian specimens were used in the investigation, a pale-blue aquamarine and a colorless goshenite beryl. The chemical compositions determined by wet chemical and spectroscopic analyses are presented in Table 1. As expected, the aquamarine is richer in iron, but the goshenite specimen contains more alkali ions. Densities were determined by the hydrostatic weighing method described by Smakula & Sils (1955). The goshenite specimen was slightly denser ($2\cdot7238 \pm 0\cdot0003$ g cm^{-3}) than the aquamarine ($2\cdot6976 \pm 0\cdot0003$ g cm^{-3}) because of the higher concentration of alkali ions and water molecules trapped in the structure. Both densities are significantly larger than the X-ray density of 2·640 g cm^{-3} calculated for a hexagonal unit cell measuring $a=9\cdot215$, $c=9\cdot192$ Å, and containing two ideal formula-units, 2 $Be_3Al_2Si_6O_{18}$ (Swanson, Cook, Isaacs & Evans, 1960).

Table 1. *Chemical analyses of two Brazilian beryls*

Analysts: J. DeVine, J. Bodkin and R. Raver.

	Ideal $Be_3Al_2Si_6O_{18}$	Pale blue aquamarine	Colorless goshenite
BeO	13·96 wt. %	13·60 %	12·66
Al_2O_3	18·97	18·20	18·24
SiO_2	67·07	65·92	65·18
Fe_2O_3		0·167	0·006
FeO		0·11	0·08
TiO_2		0·020	0·011
Li_2O		0·03	0·69
Na_2O		0·13	0·79
K_2O		0·013	0·05
Rb_2O		0·001	0·021
Cs_2O		0·075	0·16
H_2O^+		1·36	1·68
H_2O^-		0·02	0·02

Not detected: MnO, CaO, MgO, Cr_2O_3, Nb_2O_5, ZrO_2, SnO_2, Sc_2O_3.

Flawless rectangular prisms about 1 cm on edge were cut from the two large hexagonal crystals using the natural prism and pinacoid faces as a guide. After orientation by the back-reflection Laue method, the crystals were ground and polished with silicon carbide powders and diamond paste. Using specially-designed holders, orientations of better than 10 minutes of arc and flatnesses of 3×10^{-5} cm were achieved. Dimensions were measured with a Lufkin micrometer prior to the determination of the elastic constants from acoustic velocities.

In the pulse-superposition method (McSkimin & Andreatch, 1962; McSkimin, 1965) a high-frequency

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* Present address: Laboratory for Crystallographic Biophysics, Department of Physics, Rensselaer Polytechnic Institute, Troy, New York 12181, U. S. A.