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Some New Relationships Among the Structure Invariants

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For structures consisting of identical point atoms, formulas expressing the magnitudes of the structure factors in terms of the phases are obtained. Thus the crystal structure is uniquely determined by the values of the phases alone. It is already known that also the magnitudes suffice to determine the crystal structure. However, evidence is presented which suggests that, in a sense to be described, the structure is more strongly dependent on the values of the phases than on the values of the magnitudes of the structure factors.

1. Introduction

An important by-product of attempts to discover relationships among the structure factors has been the gradual realization of the central role played by the structure invariants. Initially (Hauptman & Karle, 1953, 1956) the structure invariants were defined to be those linear combinations of the phases whose values are determined by the structure alone and are independent of the choice of permissible origin. Since the permissible origins are space group dependent, the structure invariants also depend on the space group. In the two references cited all the structure invariants were determined for those space groups for which the unit cell is chosen, by convention, to be primitive. In two subsequent publications (Hauptman & Karle, 1959; Karle & Hauptman, 1961) the invariants for the remaining space groups were determined.

The most important structure invariants are the linear combinations

$$\varphi_1+\varphi_2+\varphi_3\,, \tag{1·1}$$

where

$$\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0\,, \tag{1·2}$$

and in which the abbreviations

$$\varphi_j=\varphi_{\mathbf{h}_j},\quad j=1,\,2,\,3\,, \tag{1·3}$$

have been used. In (1·3) $\varphi_{\mathbf{h}_j}$ is the phase of the normalized structure factor $E_{\mathbf{h}_j}=E_j$ defined by

$$\begin{aligned}E_j&=|E_j|\exp(i\varphi_j)\\&=(1/\sigma_2^{1/2})\sum_{\nu=1}^{N}Z_\nu\exp(2\pi i\mathbf{h}_j.\mathbf{r}_\nu)\,,\end{aligned} \tag{1·4}$$

where N is the number of atoms in the unit cell, $\mathbf{r}_\nu$ is the position vector of the νth atom, the atomic number of which is Z_ν, and

$$\sigma_2=\sum_{\nu=1}^{N}Z_\nu^2\,. \tag{1·5}$$

The importance of the structure invariants (1·1) is threefold. First, the linear combinations (1·1) are structure invariants for all the space groups. Secondly, all those structure invariants (involving three or fewer phases) which are appropriate to any particular space group are obtainable from (1·1) and those relationships among the phases which arise from the symmetries of the space group. Finally, the values of the magnitudes of the invariants (1·1), together with the appropriate (space group dependent) procedure for fixing the origin and enantiomorph (Hauptman & Karle, 1956), suffice to determine the values of all the phases.

In addition to the (relatively new) set (1·1), there are two other fundamental sets of structure invariants which have been known for some time but which have not been called structure invariants. They are the magnitudes of the structure factors,

$$|E_{\mathbf{h}}|\,, \tag{1·6}$$

and the interatomic vectors,

$$\mathbf{r}_{\mu\nu}=\mathbf{r}_\mu-\mathbf{r}_\nu\,. \tag{1·7}$$

It is natural to call the elements of the sets (1·6) and (1·7) structure invariants because, as with the elements of the set (1·1), they are uniquely determined by the structure and are independent of the choice of origin. It is occasionally convenient to replace the set (1·7) by the equivalent Patterson function $P(\mathbf{r})$:

$$P(\mathbf{r})=\langle(|E_{\mathbf{h}}|^2-1)\cos 2\pi\mathbf{h}.\mathbf{r}\rangle_{\mathbf{h}} \tag{1·8}$$

$$\left.\begin{aligned}&=Z_\mu Z_\nu/\sigma_2 \quad \text{if}\quad \mathbf{r}=\mathbf{r}_{\mu\nu}\\&=0 \quad\qquad \text{if}\quad \mathbf{r}\neq\mathbf{r}_{\mu\nu}\,,\end{aligned}\right\} \tag{1·9}$$

so that $P(\mathbf{r})$ may also be regarded as a structure invariant.

Since the expressions (1·1), (1·6), (1·7), and (1·8) all depend on the crystal structure alone, it is to be anticipated that relationships among them exist. Initially the set (1·6) is known from experiment, so that the problem of determining the crystal structure is equivalent to that of determining the phases of the structure factors. It was natural therefore that the first relationships among structure invariants

to be discovered should express the linear combinations (1·1) in terms of the elements of the sets (1·6) and (1·8) (Hauptman & Karle, 1957, 1962; Karle & Hauptman, 1957; Vaughan, 1958). Equation (1·8) already expresses $P(\mathbf{r})$, *i.e.* the elements of the set (1·7), in terms of the magnitudes (1·6), while (1·4) implies

$$|E_{\mathbf{h}}|^2 = (1/\sigma_2)\sum_{\substack{\mu,\nu \\ 1}}^{N} Z_\mu Z_\nu \exp(2\pi i \mathbf{h}.\mathbf{r}_{\mu\nu}) , \quad (1\cdot10)$$

which expresses the magnitudes (1·6) in terms of the interatomic vectors (1·7). Thus, in order to clarify completely the interrelationships among the various structure invariants, there remains only the problem of expressing the structure factor magnitudes, (1·6), in terms of the invariants (1·1), *i.e.* in terms of the phases of the structure factors. The present paper is devoted to the solution of this problem.

2. Analysis

The starting point of our investigation is the joint probability distribution of the pair of normalized structure factors $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$ in which the vector $\mathbf{h}$ is fixed while the vector $\mathbf{k}$ is assumed to range uniformly throughout reciprocal space.

2·1. *The non-centrosymmetric space groups*

We denote by $P(R_0, R_1; \Phi_0, \Phi_1)$ the joint probability distribution of the pair $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$ so that

$$P(R_0, R_1; \Phi_0, \Phi_1)dR_0 dR_1 d\Phi_0 d\Phi_1$$

is the probability of the compound event:

$\lvert E_{\mathbf{k}}\rvert$	lies between	R_0	and R_0+dR_0 ,
$\lvert E_{\mathbf{h}+\mathbf{k}}\rvert$	lies between	R_1	and R_1+dR_1 ,
$\varphi_{\mathbf{k}}$	lies between	Φ_0	and $\Phi_0+d\Phi_0$,
$\varphi_{\mathbf{h}+\mathbf{k}}$	lies between	Φ_1	and $\Phi_1+d\Phi_1$.

The probability distribution $P(R_0, R_1; \Phi_0, \Phi_1)$ is readily found by methods described elsewhere (Karle & Hauptman, 1958) or by integrating, with respect to R_2 and Φ_2, in equation (3·1·10) of the same reference. We observe that, for the accuracy required in this paper, we find in all the non-centrosymmetric space groups the same probability distribution as for space group $P1$. We obtain, for $R_0 \geq 0$, $R_1 \geq 0$,

$$P(R_0, R_1; \Phi_0, \Phi_1) = (R_0 R_1/\pi^2)\exp(-R_0^2-R_1^2)\{1 + (2/N^{1/2})R_0 R_1|E_{\mathbf{h}}|\cos(\varphi_{\mathbf{h}}+\Phi_0-\Phi_1)+\ldots\}. \quad (2\cdot1\cdot1)$$

The expected value of $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}})$ is next found by a straightforward integration:

$$\begin{aligned}\langle\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}})\rangle_{\mathbf{k}} &= \int_{\Phi_1=0}^{2\pi}\int_{\Phi_0=0}^{2\pi}\int_{R_1=0}^{\infty}\int_{R_0=0}^{\infty}\cos(\varphi_{\mathbf{h}}+\Phi_0-\Phi_1) \times P(R_0, R_1; \Phi_0, \Phi_1)dR_0 dR_1 d\Phi_0 d\Phi_1 \quad (2\cdot1\cdot2)\\ &= \int_0^{\infty}\int_0^{\infty}(4/N^{1/2})|E_{\mathbf{h}}|R_0^2 R_1^2 \exp(-R_0^2-R_1^2)dR_0 dR_1 + \ldots \\ &= \pi/(4N^{1/2})|E_{\mathbf{h}}| + \ldots . \quad (2\cdot1\cdot3)\end{aligned}$$

Hence we obtain our first main result,

$$|E_{\mathbf{h}}| = (4/\pi)N^{1/2}\langle\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{-\mathbf{h}-\mathbf{k}})\rangle_{\mathbf{k}}+\ldots , \quad (2\cdot1\cdot4)$$

which expresses the invariants (1·6) in terms of the invariants (1·1), *i.e.* the magnitudes of the structure factors in terms of the phases.

We shall have occasion to compare (2·1·4) with the known result (Karle & Hauptman, 1957; Vaughan, 1958)

$$\begin{aligned}\cos(\varphi_1+\varphi_2+\varphi_3) = {} & \frac{N^{3/2}}{2|E_1 E_2 E_3|} \times\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{h}_2+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}} \\ & + \frac{1}{N^{1/2}|E_1 E_2 E_3|}(|E_1|^2+|E_2|^2+|E_3|^2-2) \quad (2\cdot1\cdot5)\end{aligned}$$

in which it is assumed that (1·2) holds and the abbreviations of § 1 are employed. It is to be emphasized that the exact validity of (2·1·5) is subject to the non-existence of a special kind of rational dependence among the atomic coordinates which has been previously described (Karle & Hauptman, 1957).

2·2. *The centrosymmetric space groups*

Now we denote by $P(X_0, X_1)$ the joint probability distribution of the pair $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$ so that $P(X_0, X_1)dX_0 dX_1$ is the probability that $E_{\mathbf{k}}$ lie between X_0 and X_0+dX_0 and that $E_{\mathbf{h}+\mathbf{k}}$ lie between X_1 and X_1+dX_1. Referring to equation (3·3·1) of a previous paper (Hauptman & Karle, 1958) we readily find

$$P(X_0, X_1) = 1/2\pi \exp[-\tfrac{1}{2}(X_0^2+X_1^2)] \times\left\{1+\frac{X_0 X_1 E_{\mathbf{h}}}{N^{1/2}}+\ldots\right\} \quad (2\cdot2\cdot1)$$

and observe that, for the accuracy required in this paper, the same formula holds for all the centrosymmetric space groups.

Employing the fact that each phase is now either 0 or π, so that

$$\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}) = +1$$

or -1 according as $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}$ is positive or negative, we find the expected value of $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}})$ as before:

$$\begin{aligned}\langle\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}})\rangle_{\mathbf{k}} &= \left\langle\frac{|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|}{E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}}\right\rangle_{\mathbf{k}} \quad (2\cdot2\cdot2)\\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{|X_0 X_1 E_{\mathbf{h}}|}{X_0 X_1 E_{\mathbf{h}}}P(X_0, X_1)dX_0 dX_1 \quad (2\cdot2\cdot3)\end{aligned}$$

$$= \frac{|E_{\mathbf{h}}|}{2\pi N^{1/2}} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |X_0 X_1| \times \exp\left[-\tfrac{1}{2}(X_0^2+X_1^2)\right] dX_0 dX_1 + \ldots = \frac{2|E_{\mathbf{h}}|}{\pi N^{1/2}} + \ldots . \quad (2\cdot2\cdot4)$$

Thus we obtain our second main result, the analogue of (2·1·4) in the centrosymmetric space groups,

$$|E_{\mathbf{h}}| = \frac{\pi}{2} N^{1/2} \langle \cos(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{-\mathbf{h}-\mathbf{k}}) \rangle_{\mathbf{k}} + \ldots . \quad (2\cdot2\cdot5)$$

Since now every phase has the value 0 or π, each contributor to the average in (2·2·5) has the value ± 1.

Again, for future reference, we write the analogue of (2·1·5) in the centrosymmetric space groups (Hauptman & Karle, 1957; Vaughan, 1958):

$$\cos(\varphi_1+\varphi_2+\varphi_3) = \frac{N^{3/2}}{8|E_1E_2E_3|} \langle (|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{k}}|^2-1)(|E_{\mathbf{h}_1+\mathbf{h}_2+\mathbf{k}}|^2-1) \rangle_{\mathbf{k}} + \frac{1}{N^{1/2}|E_1E_2E_3|} (|E_1|^2+|E_2|^2+|E_3|^2-2) + \ldots , \quad (2\cdot2\cdot6)$$

where again $\mathbf{h}_1$, $\mathbf{h}_2$ and $\mathbf{h}_3$ satisfy (1·2) and the abbreviations of § 1 are used.

Needless to say, additional correction terms in the series expressions (2·1·4) and (2·2·5), of the order of $1/N^{1/2}$ (or perhaps $1/N$), may readily be found if desired by simply carrying more terms in the probability distributions (2·1·1) and (2·2·1) respectively.

2·3. *Additional relationships*

Because of their simple interpretation, we are primarily concerned in this paper with equations (2·1·4) and (2·2·5) However many other relationships may be derived in the same way First we shall need the preliminary integral formula

$$\int_0^{\infty} x^n \exp(-ax^2)\,dx = \frac{\Gamma(\frac{1}{2}(n+1))}{2a^{\frac{1}{2}(n+1)}} , \quad (2\cdot3\cdot1)$$

where Γ is the Gamma-function and $n>-1$, $a>0$. Then from (2·1·1) we find, for example, if $p>-3$, $q>-3$,

$$\langle |E_{\mathbf{k}}|^p |E_{\mathbf{h}+\mathbf{k}}|^q \cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}) \rangle_{\mathbf{k}} = \int_{\Phi_1=0}^{2\pi}\int_{\Phi_0=0}^{2\pi}\int_{R_1=0}^{\infty}\int_{R_0=0}^{\infty} R_0^p R_1^q \cos(\varphi_{\mathbf{h}}+\Phi_0-\Phi_1) \times P(R_0, R_1; \Phi_0, \Phi_1)\,dR_0\,dR_1\,d\Phi_0\,d\Phi_1 \quad (2\cdot3\cdot2)$$

$$= \frac{|E_{\mathbf{h}}|}{N^{1/2}} \Gamma\left(\frac{p+3}{2}\right) \Gamma\left(\frac{q+3}{2}\right) + \ldots . \quad (2\cdot3\cdot3)$$

Thus, for the non-centrosymmetric space groups,

$$|E_{\mathbf{h}}| = \frac{N^{1/2}}{\Gamma\left(\frac{p+3}{2}\right)\Gamma\left(\frac{q+3}{2}\right)} \times \langle |E_{\mathbf{k}}|^p |E_{\mathbf{h}+\mathbf{k}}|^q \cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{-\mathbf{h}-\mathbf{k}}) \rangle_{\mathbf{k}} + \ldots , \quad (2\cdot3\cdot4)$$

the special case $p=q=0$ of which is (2·1·4).

Again, from (2·2·1), if $p>-2$, $q>-2$,

$$\langle |E_{\mathbf{k}}|^p |E_{\mathbf{h}+\mathbf{k}}|^q \cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}) \rangle_{\mathbf{k}} = \left\langle \frac{|E_{\mathbf{k}}|^p |E_{\mathbf{h}+\mathbf{k}}|^q |E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}+\mathbf{k}}|}{E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}+\mathbf{k}}} \right\rangle_{\mathbf{k}} \quad (2\cdot3\cdot5)$$

$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{|X_0|^{p+1}|X_1|^{q+1}|E_{\mathbf{h}}|}{X_0 X_1 E_{\mathbf{h}}} P(X_0, X_1)\,dX_0\,dX_1 \quad (2\cdot3\cdot6)$$

$$= \frac{2^{\frac{1}{2}(p+q+2)}}{\pi N^{1/2}} |E_{\mathbf{h}}| \Gamma\left(\frac{p+2}{2}\right)\Gamma\left(\frac{q+2}{2}\right) + \ldots . \quad (2\cdot3\cdot7)$$

Hence, for the centrosymmetric space groups,

$$|E_{\mathbf{h}}| = \frac{\pi N^{1/2}}{2^{\frac{1}{2}(p+q+2)}\Gamma\left(\frac{p+2}{2}\right)\Gamma\left(\frac{q+2}{2}\right)} \times \langle |E_{\mathbf{k}}|^p |E_{\mathbf{h}+\mathbf{k}}|^q \cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{-\mathbf{h}-\mathbf{k}}) \rangle_{\mathbf{k}} + \ldots , \quad (2\cdot3\cdot8)$$

the special case $p=q=0$ of which is (2·2·5).

The case $p=q=1$ of (2·3·4) and (2·3·8) yields one and the same equation valid for all the space groups, non-centrosymmetric and centrosymmetric,

$$|E_{\mathbf{h}}| \approx N^{1/2} \langle |E_{\mathbf{k}} E_{\mathbf{h}+\mathbf{k}}| \cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{-\mathbf{h}-\mathbf{k}}) \rangle_{\mathbf{k}} . \quad (2\cdot3\cdot9)$$

It is easily verified that

$$\langle |E_{\mathbf{k}} E_{\mathbf{h}+\mathbf{k}}| \sin(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{-\mathbf{h}-\mathbf{k}}) \rangle_{\mathbf{k}} = 0 . \quad (2\cdot3\cdot10)$$

Hence

$$E_{\mathbf{h}} = |E_{\mathbf{h}}| \exp(i\varphi_{\mathbf{h}}) \approx N^{1/2} \times \langle |E_{-\mathbf{k}} E_{\mathbf{h}+\mathbf{k}}| \exp(-i\varphi_{\mathbf{k}} + i\varphi_{\mathbf{h}+\mathbf{k}}) \rangle_{\mathbf{k}} = N^{1/2} \langle E_{-\mathbf{k}} E_{\mathbf{h}+\mathbf{k}} \rangle_{\mathbf{k}} = N^{1/2} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}} , \quad (2\cdot3\cdot11)$$

so that (2·3·9) and (2·3·10) are equivalent to (2·3·11), the Hughes–Sayre formula (Hughes, 1953; Sayre, 1952). The derivation of (2·3·9) and (2·3·11) given here is instructive in that it makes clear why these relationships are valid, at least to a first approximation, for all the space groups.

3. Concluding remarks

The obvious conclusion to be drawn from (2·1·4) and (2·2·5) is that the magnitudes of the structure factors are determined by the values of the phases. Thus we obtain the unexpected result that the phases of the structure factors suffice to determine the crystal structure.

Comparison of equations (2·1·4) and (2·1·5) is even

more revealing. We observe first that the factor multiplying the average on the right in (2·1·4) is of the order of $N^{1/2}$ while in (2·1·5) this factor is of the order of $N^{3/2}$. Assuming that these averages are estimated by means of only a finite sample from the infinite population of phases or magnitudes respectively, and hence subject to sampling errors, it follows that the accuracy of magnitude determination from known phases using (2·1·4) is greater than the accuracy of phase determination from known magnitudes using (2·1·5). Since the electron density appears to be just about as sensitive to errors in the magnitudes as in the phases of the structure factors, it would seem that a given set of phases contains more structural information than the corresponding set of magnitudes. In this sense then the crystal structure appears to be more intimately related to the phases than to the magnitudes of the structure factors (naturally for large N). This is somewhat unfortunate for X-ray crystallography since it is the magnitudes of the structure factors, not the phases, which are obtained from experiment.

There is another way of interpreting the pair of equations (2·1·4) and (2·1·5) which is particularly illuminating. We may regard (2·1·5) as an infinite system of simultaneous equations in which the structure invariants (1·1) are assumed to be known and the magnitudes are the unknowns. Then, if the phases are the ones appropriate to some underlying crystal structure, (2·1·4) gives the solution of this system of equations. Alternatively, and more relevant for X-ray crystallography, we may regard (2·1·4) as an infinite system of equations in which the magnitudes (1·6) are assumed to be known and the invariants (1·1) are the unknowns. Then, again under the assumption that the magnitudes do in fact correspond to some crystal structure, the solution of this system of equations is given by (2·1·5). It should be emphasized again that the fact that the relations (2·1·4) are 'strong', in the sense that the relatively small power $N^{1/2}$ appears, does not imply that the inverse relations (2·1·5), the solution of the system (2·1·4), are equally strong. On the contrary, the occurrence of the higher power, $N^{3/2}$, in (2·1·5) suggests that the solution of the system (2·1·4), however it may be expressed, is not likely to be as powerful a relationship as the system (2·1·4). Of course this is just another way of saying that magnitudes are more accurately determined from phases than *vice versa*. It should however be emphasized that the results obtained so far, however suggestive, do not preclude the possibility that relationships as powerful as (2·1·4) may exist which express the phases in terms of the magnitudes of the structure factors. An important contribution to our knowledge would be the definitive resolution of this question, one way or the other.*

Instead of the system (2·1·4) we consider next the Hughes–Sayre relation (2·3·11), which may also be written

$$|E_{\mathbf{h}}| \exp(i\varphi_{\mathbf{h}}) = N^{1/2}\langle |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \exp(i\varphi_{\mathbf{k}}+i\varphi_{\mathbf{h}-\mathbf{k}})\rangle_{\mathbf{k}} . \tag{3·1}$$

We may regard (3·1) as an infinite system of equations in which the magnitudes (1·6) are known and the phases are the unknowns. The solution of this system of equations is again given by (2·1·5). As before, the fact that the relationships (3·1), like (2·1·4), are powerful ones does not imply that by solving the system (3·1) we necessarily obtain just as powerful expressions for the phases in terms of the magnitudes. The available evidence, while not conclusive, suggests that the opposite is the case.

Similar remarks evidently apply to the centrosymmetric space groups for which the appropriate systems of equations are (2·2·5), (2·2·6) and (3·1).

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* The fact that special cases of (space group dependent) 'strong' relationships exist which express the phases in terms of the magnitudes (*e.g.*, if $hl \neq 0$,

$$\cos \varphi_{2h,0,2l} = N^{1/2}/(|E_{2h,0,2l}|)\langle |E_{hkl}|^2 - 1\rangle_k$$

in the space group $P222$) is not relevant. In all such cases the averages are extended over some (one or two-dimensional) subset of the vectors in reciprocal space, while in (2·1·4) and (2·1·5) the averages are taken over all vectors in reciprocal space.