JEFFERSON, D. A. & THOMAS, J. M. (1975). *Mater. Res. Bull.* **10**, 761–768.
LEVINSON, A. A. (1953). *Amer. Min.* **38**, 88–107.
LOPES-VIEIRA, A. & ZUSSMAN, J. (1969). *Miner. Mag.* **37**, 49–60.
LYNCH, D. F., MOODIE, A. F. & O'KEEFE, M. A. (1975). *Acta Cryst.* A**31**, 300–307.
MCCAULEY, J. W. & NEWNHAM, R. E. (1971). *Amer. Min.* **56**, 1626–1637.
NAKAJIMA, Y., MORIMOTO, N. & WATANABE, E. (1975). *Proc. Japan Acad.* **51**, 173–178.
PHAKEY, P. P., CURTISS, C. D. & OERTEL, G. (1972). *Clays Clay Min.* **20**, 193–197.
RADOSLOVICH, E. W. (1959). *Nature, Lond.* **183**, 253.
RADOSLOVICH, E. W. (1960). *Acta Cryst.* **13**, 919–932.
SHIROZU, H. & BAILEY, S. W. (1965). *Amer. Min.* **50**, 868–885.
SMITH, J. V. & YODER, H. S. (1956). *Miner. Mag.* **31**, 209–235.
SMITH, M. L. & FRONDEL, C. (1968). *Miner. Mag.* **36**, 893–913.
STEADMAN, R. & NUTTALL, P. M. (1963). *Acta Cryst.* **16**, 1–8.
STEADMAN, R. & NUTTALL, P. M. (1964). *Acta Cryst.* **17**, 404–407.
SUITO, E., ARAKAWA, M. & YOSHIDA, T. (1969). *Proc. Int. Clay Conf. Tokyo*, **1**, 757.
TAKEDA, H. & BURNHAM, C. W. (1969). *Miner. J. Japan*, **6**, 102–109.
VAN LANDUYT, J., AMELINCKX, S., KOHN, J. A. & ECKART, D. W. (1974). *J. Solid State Chem.* **9**, 103–119.

Acta Cryst. (1977). A**33**, 553–555

A Sequence of Nested Neighborhoods of the Structure Invariant $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}$

BY HERBERT HAUPTMAN

Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203, *USA*

(*Received* 14 *June* 1976; *accepted* 21 *January* 1977)

A sequence of nested neighborhoods of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}$ is derived. Each neighborhood is a subset of the succeeding ones and consists of the small number of structure factor magnitudes $|E|$ upon which, in favorable cases, the value of φ mostly depends. Thus the stage is set for deriving reliable estimates for φ in terms of known magnitudes $|E|$ *via* appropriate conditional probability distributions.

1. Introduction

In recent work on the theory of the structure invariants and seminvariants (Hauptman, 1975*a,b*) a novel probabilistic background was formulated and mathematical methods introduced in order to obtain a new class of probability distributions. These lead to estimates of the structure invariants and seminvariants φ which are particularly good in the favorable case that the variance of the distribution happens to be small. The major result was that the value of φ is mostly determined by one or more appropriately chosen small sets of structure factor magnitudes $|E|$, the neighborhoods of φ, and is relatively insensitive to the values of the great bulk of the remaining magnitudes. In particular, a principle of nested neighborhoods was formulated which posits the existence of one or more sequences of nested neighborhoods of φ, each neighborhood a subset of the succeeding one, with the property that φ may be estimated in terms of the magnitudes $|E|$ constituting any neighborhood (or a suitable subset) of φ and that the more magnitudes in the neighborhood the better the estimate 'in the probabilistic sense', *i.e.* with more magnitudes there is a greater potential for obtaining a distribution with a small variance.

More recently (Hauptman, 1976), the identity of the first two neighborhoods of each of the structure seminvariants φ, $\varphi_1+\varphi_2$, $\varphi_1+\varphi_2+\varphi_3$, $\varphi_1+\varphi_2+\varphi_3+\varphi_4$ in the space group $P\bar{1}$ was determined and, for some of these neighborhoods, the associated conditional probability distribution of the structure seminvariant derived (Green & Hauptman, 1976, 1977; Hauptman & Green, 1977). This preliminary work confirms the importance of the neighborhood concept, and its central role in future developments now seems assured. In view of the earlier work it appears likely too that the problem of deriving the conditional probability distribution of a structure invariant or seminvariant, given an arbitrary set of magnitudes $|E|$, will present no insuperable obstacle, although the analysis may be long and tedious. There remains therefore first the problem of identifying a suitable sequence of nested neighborhoods for a given structure invariant or seminvariant. The present paper is devoted to the solution of this problem for the four-phase structure invariant (quartet)

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}} \tag{1.1}$$

where

$$\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}=0\,. \tag{1.2}$$

In the accompanying papers (Hauptman, 1977*a,b*) the related probability distributions in $P1$ and $P\bar{1}$ are derived and, in subsequent papers, the importance of these distributions in the applications will be demonstrated.

In earlier work (Hauptman & Karle, 1953, p. 48; Simerska, 1956; Schenk, 1973; Schenk & de Jong, 1973; Hauptman, 1975*b*) the first neighborhood of the structure invariant (1.1) was found to consist of the four magnitudes

$$|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{l}}|, |E_{\mathbf{m}}|, \tag{1.3}$$

and the second to consist of the four magnitudes (1.3) and the three additional magnitudes

$$|E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{k}+\mathbf{l}}|, |E_{\mathbf{l}+\mathbf{h}}| . \tag{1.4}$$

The third neighborhoods are found next.

2. The third neighborhoods of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}$

If **p** and **q** are arbitrary reciprocal vectors which satisfy

$$\mathbf{h}+\mathbf{k}+\mathbf{p}+\mathbf{q}=0 \tag{2.1}$$

then

$$\varphi_{pq}=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{p}}+\varphi_{\mathbf{q}} \tag{2.2}$$

is a structure invariant and, in view of (1.2),

$$\mathbf{l}+\mathbf{m}-\mathbf{p}-\mathbf{q}=0, \tag{2.3}$$

so that

$$\psi_{pq}=\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}-\varphi_{\mathbf{p}}-\varphi_{\mathbf{q}} \tag{2.4}$$

is also a structure invariant. In view of earlier work (Hauptman, 1975*b*) φ is estimated by means of the seven magnitudes in its second neighborhood,

$$|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{l}}|, |E_{\mathbf{m}}|, |E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{k}+\mathbf{l}}|, |E_{\mathbf{l}+\mathbf{h}}|, \tag{2.5}$$

φ_{pq} by means of the seven magnitudes in its second neighborhood,

$$|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{p}}|, |E_{\mathbf{q}}|, |E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{k}+\mathbf{p}}|, |E_{\mathbf{p}+\mathbf{h}}|, \tag{2.6}$$

and ψ_{pq} by means of the seven magnitudes in its second neighborhood,

$$|E_{\mathbf{l}}|, |E_{\mathbf{m}}|, |E_{\mathbf{p}}|, |E_{\mathbf{q}}|, |E_{\mathbf{l}+\mathbf{m}}|, |E_{\mathbf{m}-\mathbf{p}}|, |E_{-\mathbf{p}+\mathbf{l}}| . \tag{2.7}$$

However, from (1.1), (2.2) and (2.4) it is clear that

$$\varphi-\varphi_{pq}-\psi_{pq}\equiv 0 . \tag{2.8}$$

It is therefore to be expected that, in the favorable case that the seven magnitude estimates yield values for φ, φ_{pq} and ψ_{pq} in accord with (2.8), φ will be well estimated in terms of the 21 magnitudes (2.5), (2.6) and (2.7), of which only the following 13 are distinct:

$$|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{l}}|, |E_{\mathbf{m}}|, |E_{\mathbf{p}}|, |E_{\mathbf{q}}| , \tag{2.9}$$

$$|E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{k}+\mathbf{l}}|, |E_{\mathbf{l}+\mathbf{h}}|, |E_{\mathbf{h}+\mathbf{p}}|, |E_{\mathbf{k}+\mathbf{p}}|, |E_{\mathbf{l}-\mathbf{p}}|, |E_{\mathbf{m}-\mathbf{p}}| . \tag{2.10}$$

Hence the third (13-magnitude) neighborhood of φ is obtained by adjoining to the second (seven magnitude) neighborhood (1.3) and (1.4) the additional six magnitudes

$$|E_{\mathbf{p}}|, |E_{\mathbf{q}}|, |E_{\mathbf{h}+\mathbf{p}}|, |E_{\mathbf{k}+\mathbf{p}}|, |E_{\mathbf{l}-\mathbf{p}}|, |E_{\mathbf{m}-\mathbf{p}}| , \tag{2.11}$$

where **p** is an arbitrary reciprocal vector; thus there are many third neighborhoods.

One naturally anticipates that the conditional variance of the structure invariant φ, given the 13 magnitudes in its third neighborhood, will be small if the three seven-magnitude subsets of the third neighborhood which are the respective second neighborhoods of the structure invariants φ, φ_{pq}, ψ_{pq} yield reliable estimates for the latter in accord with the identity (2.8). Thus (Hauptman, 1977*a*,*b*) only those third neighborhoods are useful for which $|E_{\mathbf{p}}|$ and $|E_{\mathbf{q}}|$ are both large, where **p** and **q** satisfy (2.1).

3. The fourth neighborhoods of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}$

Proceed as in § 2 and denote by **r** and **s** two reciprocal vectors which satisfy

$$\mathbf{h}+\mathbf{k}+\mathbf{r}+\mathbf{s}=0 \tag{3.1}$$

so that

$$\varphi_{rs}=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{r}}+\varphi_{\mathbf{s}} \tag{3.2}$$

is a structure invariant. Now it follows from (1.2), (2.1) and (3.1) that

$$\mathbf{l}+\mathbf{m}-\mathbf{r}-\mathbf{s}=0 \tag{3.3}$$

and

$$\mathbf{p}+\mathbf{q}-\mathbf{r}-\mathbf{s}=0 \tag{3.4}$$

so that

$$\psi_{rs}=\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}-\varphi_{\mathbf{r}}-\varphi_{\mathbf{s}} \tag{3.5}$$

and

$$\chi_{rs}=\varphi_{\mathbf{p}}+\varphi_{\mathbf{q}}-\varphi_{\mathbf{r}}-\varphi_{\mathbf{s}} \tag{3.6}$$

are also structure invariants. The invariant φ_{rs} is approximated by means of the seven magnitudes

$$|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{r}}|, |E_{\mathbf{s}}|, |E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{k}+\mathbf{r}}|, |E_{\mathbf{r}+\mathbf{h}}|, \tag{3.7}$$

in its second neighborhood, ψ_{rs} by means of the seven magnitudes

$$|E_{\mathbf{l}}|, |E_{\mathbf{m}}|, |E_{\mathbf{r}}|, |E_{\mathbf{s}}|, |E_{\mathbf{l}+\mathbf{m}}|, |E_{\mathbf{m}-\mathbf{r}}|, |E_{-\mathbf{r}+\mathbf{l}}|, \tag{3.8}$$

in its second neighborhood, and χ_{rs} by means of the seven magnitudes

$$|E_{\mathbf{p}}|, |E_{\mathbf{q}}|, |E_{\mathbf{r}}|, |E_{\mathbf{s}}|, |E_{\mathbf{p}+\mathbf{q}}|, |E_{\mathbf{q}-\mathbf{r}}|, |E_{-\mathbf{r}+\mathbf{p}}|, \tag{3.9}$$

in its second neighborhood. Now, in addition to the identity (2.8), there are the two additional identities

$$\varphi-\varphi_{rs}-\psi_{rs}\equiv 0 \tag{3.10}$$

and

$$\varphi_{pq}-\varphi_{rs}+\chi_{rs}\equiv 0 \tag{3.11}$$

which must be satisfied. Hence, in view of (3.7)–(3.9), the fourth (21-magnitude) neighborhood of φ is obtained from the 13-magnitude third neighborhood (1.3), (1.4) and (2.11) by adjoining the additional eight magnitudes

$$|E_{\mathbf{r}}|, |E_{\mathbf{s}}|, |E_{\mathbf{h}+\mathbf{r}}|, |E_{\mathbf{k}+\mathbf{r}}|, |E_{\mathbf{l}-\mathbf{r}}|, |E_{\mathbf{m}-\mathbf{r}}|, |E_{\mathbf{p}-\mathbf{r}}|, |E_{\mathbf{q}-\mathbf{r}}|. \quad (3.12)$$

Again, since $\mathbf{r}$ is arbitrary, there are many fourth neighborhoods, but only those are useful for which $|E_{\mathbf{r}}|$and $|E_{\mathbf{s}}|$ are both large, where $\mathbf{r}$ and $\mathbf{s}$ satisfy (3.1).

4. The remaining neighborhoods

One continues as in §§ 2 and 3 in order to derive the fifth and higher neighborhoods of φ. Thus the fifth (31-magnitude) neighborhoods are obtained from a fourth (21-magnitude) neighborhood by adjoining the ten additional magnitudes

$$|E_{\mathbf{t}}|, |E_{\mathbf{u}}|, |E_{\mathbf{h}+\mathbf{t}}|, |E_{\mathbf{k}+\mathbf{t}}|, |E_{\mathbf{l}-\mathbf{t}}|, |E_{\mathbf{m}-\mathbf{t}}|, |E_{\mathbf{p}-\mathbf{t}}|, |E_{\mathbf{q}-\mathbf{t}}|, |E_{\mathbf{r}-\mathbf{t}}|, |E_{\mathbf{s}-\mathbf{t}}| \quad (4.1)$$

where $\mathbf{t}$ and $\mathbf{u}$ are reciprocal vectors which satisfy

$$\mathbf{h}+\mathbf{k}+\mathbf{t}+\mathbf{u}=0\,, \quad (4.2)$$

but are otherwise arbitrary, so that again there are many fifth neighborhoods; but only those are useful for which $|E_{\mathbf{t}}|$ and $|E_{\mathbf{u}}|$ are both large.

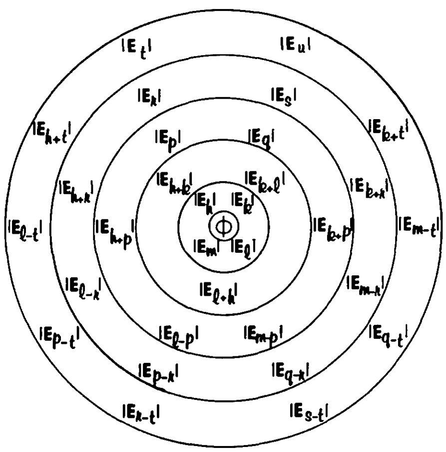

Fig. 1. A sequence of nested neighborhoods of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}$. The reciprocal vectors **h**, **k**, **l**, **m**, **p**, **q**, **r**, **s**, **t**, **u** satisfy $\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}=\mathbf{h}+\mathbf{k}+\mathbf{p}+\mathbf{q}=\mathbf{h}+\mathbf{k}+\mathbf{r}+\mathbf{s}=\mathbf{h}+\mathbf{k}+\mathbf{t}+\mathbf{u}=0$, but are otherwise arbitrary.

One continues in this way to obtain the sixth (43-magnitude) neighborhoods, *etc.* The first five of this sequence of nested neighborhoods are conveniently exhibited in Fig. 1 in which the four magnitudes of the first shell define the first neighborhood, the seven magnitudes of the first two shells the second neighborhood, *etc.*

5. Concluding remarks

A sequence of nested neighborhoods of the quartet invariant φ has been obtained. It remains to derive the associated conditional probability distributions and corresponding estimates for φ in the expectation that as more and more magnitudes $|E|$ are used the estimates will become more and more reliable. In the accompanying papers (Hauptman, 1977*a,b*) this task is begun for the space groups $P1$ and $P\bar{1}$. The initial applications, to be described in future publications, confirm the expectation that the estimates for φ become better as more magnitudes $|E|$ are used. There remains the task of deriving the distributions for the remaining space groups.

This research was supported in part by Grant No. MPS73-04992 from the National Science Foundation.

References

GREEN, E. & HAUPTMAN, H. (1976). *Acta Cryst.* A**32**, 940–944.
GREEN, E. & HAUPTMAN, H. (1977). *Acta Cryst.* A**33**. To be submitted.
HAUPTMAN, H. (1975*a*). *Acta Cryst.* A**31**, 671–679.
HAUPTMAN, H. (1975*b*). *Acta Cryst.* A**31**, 680–687.
HAUPTMAN, H. (1976). *Acta Cryst.* A**32**, 934–940.
HAUPTMAN, H. (1977*a*). *Acta Cryst.* A**33**, 556–564.
HAUPTMAN, H. (1977*b*). *Acta Cryst.* A**33**, 565–568.
HAUPTMAN, H. & GREEN, E. (1977). *Acta Cryst.* A**33**. To be submitted.
HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem.* I. *The Centrosymmetric Crystal.* Pittsburgh: Polycrystal Book Service.
SCHENK, H. (1973). *Acta Cryst.* A**29**, 77–82.
SCHENK, H. & DE JONG, J. G. H. (1973). *Acta Cryst.* A**29**, 31–34.
SIMERSKA, M. (1956). *Czech. J. Phys.* **6**, 1–7.