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The Extension Concept and Its Role in the Probabilistic Theory of the Structure Seminvariants*

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By embedding the structure seminvariant T and symmetry-related variants of T in suitable structure invariants Q the values of which, because of the space-group-dependent relations among the phases, are related to T, one reduces the probabilistic theory of the structure seminvariants to that of the structure invariants, which is well developed. The structure invariants Q are said to be extensions of the structure seminvariant T.

1. Introduction

It is assumed that the reader is familiar with the idea of 'neighborhood of a structure invariant or seminvariant', the 'neighborhood principle', and the roles these concepts play in the probabilistic theory of the structure invariants and seminvariants (see, for example, Hauptman, 1975, 1976; Green & Hauptman, 1976). Systems of neighborhoods of the structure invariants are now well known (see, for example, Hauptman, 1977*a*,*b*), and neighborhoods for selected structure seminvariants have also been identified (see, for example, Green & Hauptman, 1978).

The major goal of the present paper is to show how to determine in a systematic and unambiguous way neighborhoods of the structure seminvariants in general by exploiting the symmetries deriving from the space groups. The method is to embed a given structure seminvariant T and its symmetry-related variants in suitable structure invariants Q to which T is related *via* the space-group symmetries. Then the neighborhoods of T are determined by the known neighborhoods of Q. The structure invariant Q is said to be an extension of the structure seminvariant T. Recently secured methods may then be employed to derive suitable conditional probability distributions leading to estimates of the structure seminvariants in terms of the magnitudes in their neighborhoods.

The method will be illustrated by examples in space groups $P1$, $P\bar{1}$, $P2_1$ and $P2_12_12_1$ but is clearly of sufficient generality to be applicable to structure seminvariants in general.

Although the idea of embedding a structure seminvariant in an appropriate structure invariant is not new (Giacovazzo, 1975; Hauptman, 1976; Green & Hauptman, 1978) the present paper appears to be the first in which the interplay between the space-group symmetries and the neighborhood concept is systematically exploited. However, see Hauptman (1976) and Giacovazzo (1977*b*) for different techniques for obtaining neighborhoods of the structure seminvariants.

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2. The second neighborhoods of the three-phase structure invariant in $P1$ and $P\bar{1}$

The linear combination of three phases

$$T = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}}, \tag{2.1}$$

is a structure invariant if

$$\mathbf{h} + \mathbf{k} + \mathbf{l} = 0. \tag{2.2}$$

The first neighborhood of T consists of the three magnitudes

$$|E_{\mathbf{h}}|,\ |E_{\mathbf{k}}|,\ |E_{\mathbf{l}}|. \tag{2.3}$$

Embed T in a quintet (five-phase structure invariant) Q by means of

$$Q = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{q}} + \varphi_{-\mathbf{q}} \tag{2.4}$$

or, because of (2.1),

$$Q = T + \varphi_{\mathbf{q}} + \varphi_{-\mathbf{q}}, \tag{2.5}$$

where $\mathbf{q}$ is an arbitrary reciprocal vector, so that, in view of (2.2), Q is a structure invariant and

$$Q = T. \tag{2.6}$$

The second neighborhood of T is defined to be the second neighborhood of Q, which is well known (Schenk, 1975; Hauptman, 1977*b*). Although Q is a special quintet, its second neighborhood is obtained formally in the same way as if it were general. However, because of its special character, not all magnitudes in the second neighborhood are distinct. Thus the second neighborhood of T consists of the three magnitudes (2.3) and the additional seven magnitudes

$$|E_{\mathbf{q}}|; \tag{2.7}$$

$$|E_{\mathbf{h}+\mathbf{q}}|,\ |E_{\mathbf{k}+\mathbf{q}}|,\ |E_{\mathbf{l}+\mathbf{q}}|; \tag{2.8}$$

$$|E_{\mathbf{h}-\mathbf{q}}|,\ |E_{\mathbf{k}-\mathbf{q}}|,\ |E_{\mathbf{l}-\mathbf{q}}|. \tag{2.9}$$

Since $\mathbf{q}$ is an arbitrary reciprocal vector, there are many second neighborhoods. Strictly speaking, the structure factor magnitude $|E_{\mathbf{q}-\mathbf{q}}| = |E_0|$ should be added to the sets (2.7), (2.8) and (2.9). However, $|E_0|$ has a fixed value, independent of $\mathbf{h}$, $\mathbf{k}$, $\mathbf{l}$ and $\mathbf{q}$, and thus cannot be a proper random variable; it is therefore omitted from the second neighborhood.

Not only does the argument given in the preceding paragraph define the second neighborhood of T, but (2.6) and the known relation between Q and the magnitudes of its second neighborhood serve to predict, in a qualitative way, what the relation between T and the ten magnitudes (2.3) and (2.7)–(2.9) must be. Thus, if all ten magnitudes (2.3), (2.7)–(2.9) are large then, with near certainty,

$$T \simeq 0. \tag{2.10}$$

If, on the other hand, (2.7) is very large and the three elements of one of the sets (2.8), (2.9) are all very large and of the other all very small, then

$$T \not\simeq 0. \tag{2.11}$$

Finally, it turns out, as shown elsewhere (Green, Hauptman & Kruger, 1978), that if (2.7) is small and the six magnitudes (2.8), (2.9) are all large, then (2.11) again holds. The relation (2.11) is particularly likely to be valid, and the deviation of T from 0 particularly likely to be large, if the required conditions hold for several reciprocal vectors $\mathbf{q}$ and if the three magnitudes (2.3) are only moderately large (*i.e.* not extremely large). The qualitative relation of these results to the MDKS formula (Hauptman, 1972) and some recent results of Giacovazzo (1976; 1977*a*) should be noted.

It should be stressed that the argument of the preceding paragraph is heuristic only, especially in view of the omission of $|E_0|$, the duplication of certain magnitudes in the second neighborhood of the special quintet, Q, *etc.* The purpose of embedding the structure seminvariant T in the structure invariant Q, the value of which is simply related to that of T, is simply to identify the magnitudes $|E|$ on which the value of T primarily depends, *i.e.* the neighborhoods of T. There remains the task of deriving the conditional probability distribution of T, given the magnitudes $|E|$ in any of its neighborhoods, employing for this purpose techniques described elsewhere (see, for example, Hauptman, 1975). In the favorable case that the variance of a distribution happens to be small, one obtains a reliable estimate for T in terms of the chosen magnitudes $|E|$.

3. The first two neighborhoods of the three-phase structure seminvariant in $P2_1$

3.1. *The extensions*

The linear combination of three phases,

$$T_0 = \varphi_{h_1k_1l_1} + \varphi_{h_2k_2l_2} + \varphi_{h_3k_3l_3}, \tag{3.1}$$

is a structure seminvariant in $P2_1$ if and only if

$$k_1 + k_2 + k_3 = 0 \tag{3.2}$$

and

$$h_1 + h_2 + h_3 \equiv l_1 + l_2 + l_3 \equiv 0 \pmod 2), \tag{3.3}$$

i.e. $h_1 + h_2 + h_3$ and $l_1 + l_2 + l_3$ are even integers. It follows that the eight integers $\pm h_1 \pm h_2 \pm h_3$ and the eight integers $\pm l_1 \pm l_2 \pm l_3$ are also even, so that the linear combinations of three phases,

$$T_1 = \varphi_{\bar{h}_1k_1\bar{l}_1} + \varphi_{h_2k_2l_2} + \varphi_{h_3k_3l_3}, \tag{3.4}$$

$$T_2 = \varphi_{h_1k_1l_1} + \varphi_{\bar{h}_2k_2\bar{l}_2} + \varphi_{h_3k_3l_3}, \tag{3.5}$$

and

$$T_3 = \varphi_{h_1k_1l_1} + \varphi_{h_2k_2l_2} + \varphi_{\bar{h}_3k_3\bar{l}_3}, \tag{3.6}$$

are also structure seminvariants. Furthermore, because of the space-group-dependent relations among the phases, T_0 is related to T_1, T_2 and T_3 by means of

$$T_0 = T_i + \pi(\tfrac{1}{2} - \tfrac{1}{2}\cos \pi k_i), \quad i = 1, 2, 3. \tag{3.7}$$

One embeds the structure seminvariants T_j in suitable quintets (five-phase structure invariants) Q_j by means of

$$Q_j = T_j + \varphi_{H_jK_jL_j} + \varphi_{\bar{H}_jK_j\bar{L}_j}, \quad j = 0, 1, 2, 3, \tag{3.8}$$

where the H_j and L_j are defined by

$$H_0 = \tfrac{1}{2}(h_1 + h_2 + h_3), \quad L_0 = \tfrac{1}{2}(l_1 + l_2 + l_3), \tag{3.9}$$

$$H_1 = \tfrac{1}{2}(-h_1 + h_2 + h_3), \quad L_1 = \tfrac{1}{2}(-l_1 + l_2 + l_3), \tag{3.10}$$

$$H_2 = \tfrac{1}{2}(h_1 - h_2 + h_3), \quad L_2 = \tfrac{1}{2}(l_1 - l_2 + l_3), \tag{3.11}$$

$$H_3 = \tfrac{1}{2}(h_1 + h_2 - h_3), \quad L_3 = \tfrac{1}{2}(l_1 + l_2 - l_3), \tag{3.12}$$

and the four integers K_j, $j = 0, 1, 2, 3$, are arbitrary. In view of (3.3) the H_j and L_j are integers. Further, (3.2)–(3.6) imply that the Q_j are structure invariants. It follows from (3.8) and the relations

$$\varphi_{\bar{H}_jK_j\bar{L}_j} + \varphi_{\bar{H}_j\bar{K}_j\bar{L}_j} = \pi(\tfrac{1}{2} - \tfrac{1}{2}\cos \pi K_j) \tag{3.13}$$

that

$$T_j = Q_j + \pi(\tfrac{1}{2} - \tfrac{1}{2}\cos \pi K_j), \quad j = 0, 1, 2, 3. \tag{3.14}$$

In view of (3.7) and (3.14), the structure seminvariant T_0 is related to the four quintets Q_j by means of

$$T_0 = Q_j + \pi[\tfrac{1}{2} - \tfrac{1}{2}\cos \pi(k_j + K_j)], \quad j = 0, 1, 2, 3 \tag{3.15}$$

provided that k_0 is defined by

$$k_0 = 0. \tag{3.16}$$

Because of the relation (3.15) the probabilistic theory of the three-phase structure seminvariant T_0 is made to depend on that of the four quintets Q_j, which is well developed. Thus the first neighborhood of T_0 is defined to be the set-theory union of the first neighborhoods of the Q_j, the second neighborhood of T_0 the set-theory union of the second neighborhoods of the Q_j, *etc.* Since the integers K_0, K_1, K_2 and K_3 are arbitrary, T_0 has many first neighborhoods, many second neighborhoods, *etc.*

3.2. *The first neighborhood(s)*

Following the procedure described in the preceding paragraphs and employing the known first neighborhood of the quintet (Hauptman, 1977*b*), one finds that the first neighborhood of T_0 consists of the seven magnitudes

$$|E_{h_ik_il_i}|, \quad i = 1, 2, 3, \tag{3.17}$$

and

$$|E_{H_jK_jL_j}|, \quad j = 0, 1, 2, 3, \tag{3.18}$$

where the integers H_j and L_j are defined by (3.9)–(3.12) and the K_j are arbitrary integers. Thus there are many first neighborhoods. If the seven magnitudes (3.17) and (3.18) are all large then, in view of (3.15) and quintet theory, according as

$$k_j + K_j \text{ is even or odd}, j = 0, 1, 2, 3, \tag{3.19}$$

$$T_0 \simeq 0 \text{ or } \pi, \tag{3.20}$$

respectively, but the relation (3.20) is relatively weak. A more reliable relation is obtained *via* the second neighborhood(s).

3.3. *The second neighborhood(s)*

Again, following the recipe described in § 3.1 and employing the known second neighborhoods of the quintets (Schenk, 1975; Hauptman, 1977*b*) one finds that the second neighborhood of T_0 consists of 41 magnitudes, the seven magnitudes (3.17), (3.18) in the first neighborhood, and the additional 34 magnitudes

$$|E_{h_1+h_2,k_3,l_1+l_2}|, \; |E_{h_1-h_2,k_3,l_1-l_2}|; \tag{3.21}$$

$$|E_{h_2+h_3,k_1,l_2+l_3}|, \; |E_{h_2-h_3,k_1,l_2-l_3}|; \tag{3.22}$$

$$|E_{h_3+h_1,k_2,l_3+l_1}|, \; |E_{h_3-h_1,k_2,l_3-l_1}|; \tag{3.23}$$

$$|E_{H_1,k_1\pm K_0,L_1}|, \; |E_{H_2,k_2\pm K_0,L_2}|, \; |E_{H_3,k_3\pm K_0,L_3}|; \tag{3.24}$$

$$|E_{H_0,k_1\pm K_1,L_0}|, \; |E_{H_3,k_2\pm K_1,L_3}|, \; |E_{H_2,k_3\pm K_1,L_2}|; \tag{3.25}$$

$$|E_{H_3,k_1\pm K_2,L_3}|, \; |E_{H_0,k_2\pm K_2,L_0}|, \; |E_{H_1,k_3\pm K_2,L_1}|; \tag{3.26}$$

$$|E_{H_2,k_1\pm K_3,L_2}|, \; |E_{H_1,k_2\pm K_3,L_1}|, \; |E_{H_0,k_3\pm K_3,L_0}|; \tag{3.27}$$

$$|E_{2H_j,0,2L_j}|, \quad j = 0, 1, 2, 3. \tag{3.28}$$

Again the integers H_j and L_j are defined by (3.9)–(3.12) and the K_j are arbitrary integers, so that there are many second neighborhoods.

4. The first two neighborhoods of special three-phase structure seminvariants in $P2_12_12_1$

The linear combination of three phases

$$T_0 \; \varphi_{h_1k_1l_1} + \varphi_{h_2k_2l_2} + \varphi_{h_3k_3l_3} \tag{4.1}$$

is a structure seminvariant in $P2_12_12_1$ if, and only if,

$$h_1 + h_2 + h_3 \equiv k_1 + k_2 + k_3$$
$$\equiv l_1 + l_2 + l_3 \equiv 0 \pmod 2, \tag{4.2}$$

i.e. if, and only if, $h_1 + h_2 + h_3$, $k_1 + k_2 + k_3$ and $l_1 + l_2 + l_3$ are even integers. One obtains a special class of structure seminvariants by assuming that

$$k_1 + k_2 + k_3 = 0, \text{ an even integer.} \tag{4.3}$$

In this special case the argument used in § 3 for $P2_1$ may be carried over without essential change to $P2_12_12_1$, and one obtains as before the 7-magnitude first neighborhoods and the 41-magnitude second neighborhoods.

By permuting the indices h, k, l one obtains two additional special classes of three-phase structure seminvariants. These are derived by assuming, in addition to (4.2), first, that

$$l_1 + l_2 + l_3 = 0, \text{ an even integer,} \tag{4.4}$$

and, second, that

$$h_1 + h_2 + h_3 = 0, \text{ an even integer.} \tag{4.5}$$

Thus there are in all three special classes of three-phase structure seminvariant, those in which (4.3) holds, those in which (4.4) holds, and those in which (4.5) holds. In each case, the first neighborhoods contain 7 magnitudes and the second neighborhoods contain 41 magnitudes. Because the derivation of these neighborhoods is so similar to that given in §3 for $P2_1$, no further details for $P2_12_12_1$ are given here.

5. Concluding remarks

By embedding a given structure seminvariant T and its symmetry-related variants in appropriate structure invariants Q, one obtains the extensions of T and in this way reduces the probabilistic theory of the structure seminvariants to that of the structure invariants. Details have been described for the three-phase structure invariants in $P1$ and $P\bar{1}$, the three-phase structure seminvariants in $P2_1$, and three kinds of special three-phase structure seminvariants in $P2_12_12_1$. The method is clearly capable of extension to the structure seminvariants in general. There remains the task of deriving the associated conditional probability distributions leading to estimates of the structure seminvariants. Because the full second neighborhoods often contain so many magnitudes $|E|$, not all of which may be in the observable sphere of reflections, it will in general be necessary to derive distributions which assume as known only certain subsets of these neighborhoods. Finally, it should be pointed out that the discriminant of the structure seminvariant, a polynomial in the presumed known magnitudes $|E|$, which is easily derived, easily computed and strongly correlated with the true value of the structure seminvariant [compare, for example, the discriminant for quintets (Fortier & Hauptman, 1977)], may often serve as a substitute for the true distribution, especially in those cases when sufficiently accurate and computable forms for the latter are particularly difficult or even impossible, as yet, to derive.

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Determinantal Equations for the Scale Factor, Temperature Factors and Quantitative Chemical Contents of the Unit Cell

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A class of determinantal equations for the scale factor, the temperature factors and quantitative chemical contents of the unit cell is derived assuming non-penetrating atoms but without making use of statistical arguments. A new method for the determination of the scale and Debye–Waller factors is developed on the basis of these equations and applied to the structure factors of $Al(OH)_3$, giving results with errors of about 2%.

The various methods of structure analysis require the knowledge of the moduli of a sufficient number of Fourier coefficients of the scattering density function of the crystal to be analysed and a more or less complete knowledge of the form factors of the atoms present in its elementary cell.

Except for the scale factor and the temperature

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