

## Group-Theoretical Considerations Concerning Domain Formation in Ordered Alloys\*

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Domain formation in ordered alloys has been studied from the group-theoretical point of view. A method is derived to determine the number of orientation variants as well as the number of translation variants from the point groups and lattices of the ordered and disordered structures. The number of orientation variants is found to be equal to the order of the point group of the disordered phase divided by that of the ordered phase. It has been shown that under certain conditions the set of operations that produce all variants from a given original variant can be chosen so as to form a group. The operations relating the orientation variants are the elements of this group called the *variant generating group*. The results of the theory derived in this paper are general and can be applied to any disorder-order transformation. A few examples are worked out explicitly to illustrate the different theorems.

### Introduction

The study of the substructure of ordered alloys has been the subject of numerous papers, especially since electron-microscopic methods have become available to observe directly the different structural variants. However, most of these papers are concerned with 'case studies' of particular alloys. It would therefore be of interest to have some guiding principles for such studies that would allow the derivation of the number of variants; translation variants and orientation variants as well the set of operations that relate these variants one to the other. A similar problem exists in relation to the domain structure of ferroelectrics and magnetics and a number of papers have been devoted to the subject, (Aizu, 1966, 1967, 1969, 1970). We shall follow a somewhat similar line of reasoning to that used by Aizu (1970).

Somewhat related work, although with a quite different purpose, was done by Altmann (1963*a, b*), who decomposed the point groups into semi-direct products and by Melvin (1956) who introduced the weak direct product for this purpose.

In order to make the paper more readable we have repeated some of the elementary concepts of group theory. More background informations may be found *e.g.*, in books by Janssen & Boon (1967), Boerner (1969), and Buerger (1963).

### 1. Symmetry considerations – notations

Domain formation is clearly a consequence of the fact that on going through the disorder-order transformation different variants of the ordered phase have equal probability of being generated if their structures are related by a symmetry operation of the disordered

matrix, which is not a symmetry operation of the ordered phase.

We shall introduce the following notations: The point group of the disordered parent phase will be represented by  $G$ , of order  $p$  with elements  $g_j$ .

We shall assume that the ordered structure is a superstructure, *i.e.* the same atomic sites as those present in the disordered structure are also occupied in the ordered structure. However, whereas they were occupied at random by the different atomic species in the disordered phase, they will be occupied by well-defined atoms in the ordered phase. The small changes in the lattice that accompany ordering will be ignored since they are unimportant in determining the number of variants. We shall afterwards generalize our considerations to other situations.

The ordering is usually accompanied by a decrease in symmetry in such a way that the point group of the ordered structure  $H$  of order  $q$  is a subgroup of  $G$ , *i.e.*  $H \subset G$ . We shall further call  $G_i$  and  $H_i$  the point groups of the lattices of the disordered and ordered structures respectively. We then have  $G \subset G_i$  and  $H \subset H_i$ , *i.e.* the symmetry of the structure may be lower than that of the lattice, as well for the ordered as for the disordered structure. The lattice translations of the parent phase will be represented by the group  $T$ , whereas those of the ordered lattice will be represented by  $T^{(o)}$  according to our assumptions  $T^{(o)} \subset T$ .

The structure of the different variants will be denoted by  $V_j$  and their point group by  $H_j$ ; the  $H_j$  can only differ in the orientation of their elements. It is clear that as well the structures as the point groups are related by operations of  $G$  which are not elements of  $H$ . Let *e.g.*  $gV_i = V_j$  with  $g \in G$  but  $g \notin H_i$  then  $H_j = gH_i g^{-1}$ , *i.e.* the point groups of the different variants are conjugate in  $G$ .

If for all  $g \in G$ ,  $H_j = H_i$  the subgroup  $H$  is invariant in  $G$ . This is often not the case, moreover the configuration of the elements of  $H_i$  can mostly adopt different orientations with respect to the elements of  $G$ .

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Generally more than one operation transforms a given variant  $V_i$  into another given variant  $V_j$ . It is shown easily that if  $g$  is an operation such that  $gV_i = V_j$ , the complete set is given by  $gH_i$  or  $H_jg$ .

## 2. Decomposition of $G$ into cosets

Let  $gV_i = V_j$  then we have just shown that the complete set of operations that transforms  $V_i$  into  $V_j$  is given by  $gH_i$  (or  $H_jg$ ). Similarly the complete set of operations that transforms  $V_i$  into  $V_k$  is given by  $fH_i$  (or  $H_kf$ ) if  $fV_i = V_k$ .

The sets  $gH_i$  and  $fH_i$  have no element in common for if they had, this common element would have to transform  $V_i$  into two different variants which is clearly impossible.

We can now construct the sets of operations that transform an arbitrarily chosen original variant, say  $V_i$ , respectively into all other variants. Let  $g_jV_i = V_j$  then in particular  $g_1 = E$  (identity operation) and we obtain the following sets:

$$g_1H_i, g_2H_i, \dots, g_jH_i, \dots, g_nH_i.$$

We note that:

(i) all elements in each set are elements of  $G$  since they consist of products of elements of  $G$ .

(ii) two sets have not elements in common as was shown above, *i.e.* each set contains  $q$  different elements of  $G$ , which differ from those in any other set.

(iii) we can continue to construct sets until  $nq = p$  because then we have used all elements of  $G$ .

We conclude that we can write down  $G$  as the set-theoretic sum:

$$G = g_1H_i + g_2H_i + \dots + g_nH_i,$$

where the  $g_j$  are not elements of  $H_i$  (except  $g_1 = E$ ). This leads immediately to the well-known theorem of Lagrange which in our case has a particularly simple geometrical interpretation.

We have in fact developed  $G$  into cosets of  $H_i$  and each coset represents the complete set of operations leading from a given variant  $V_i$  to another given variant from the set  $V_1, \dots, V_n$ .

We can conclude that:

(i) The number of variants is given by  $n = p/q$ .

(ii) The set of operations that generates all variants can be obtained by taking one operation from each coset in the development of  $G$  into cosets of  $H$ .

## 3. The variant generating group

It is clear that there are a large number of different ways of choosing the variant generating set; there are, in fact,  $q^n$  ways of selecting  $n$  elements by selecting one out of each coset of  $q$  elements. Some of these variant generating sets will form a group which we shall call  $V$ , the variant generating group (V.G.G.). Other sets will not form a group; in some cases it will not be possible to select a set forming a group. Clearly it is of interest

to represent the variant generating operations as a group whenever possible, since the properties of groups can then be made use of; in particular the closure property.

We shall therefore investigate under what circumstances a V.G.G. can be found. We make use here of the following theorem: If a group  $G$  has two subgroups  $H$  and  $V$  which only have the unit element in common then each coset (left or right) of  $H$  in  $G$  contains at most one element of  $V$ . If moreover the product of the orders of the subgroups  $H$  and  $V$ , respectively  $q$  and  $n$ , is equal to the order of the group  $G$ , the statement can be made more stringent; each coset of  $H$  in  $G$  now contains *one and only one element of  $V$* .

We can summarize these statements now somewhat differently: let  $G$  be decomposed into cosets of  $H$ ; we then have a number of cosets equal to  $p/q$ . If we can find a subgroup  $V$  of  $G$  of order  $n = p/q$  which has no element in common with  $H$  other than the unit element, then we know that each of the cosets will contain one and only one of the elements of the group  $V$ . The group  $V$  then clearly qualifies as a V.G.G. So, if a V.G.G.  $V$  exists we can always develop  $G$  into cosets of  $H$  in such a way that the 'coefficients' in the development are the elements of  $V$ . If  $H$  is an invariant subgroup of  $G$  the factor group  $G/H$  constitutes a representation of the V.G.G.  $V$  (if it exists).

From the development of  $G$ :

$$G = v_1H + v_2H + \dots + v_nH$$

where the  $v_j$  are the elements of a group  $V$ , it follows immediately that  $G$  can be written as a product of two groups  $G = V.H = H.V$ . This can also be shown directly as follows:

(i) Each product  $v_ih_i$  is an element of  $G$

(ii) All products are different

(iii) The set of products  $v_ih_i$  contains  $nq = p$  different elements of  $G$  and is therefore  $G$  itself.

(iv) The same reasoning applies to the product  $h_iv_i$  and therefore the multiplication is commutative.

The multiplication of individual elements is not commutative however, and therefore multiplying out  $H.V$  and  $V.H$  will lead to the same set of elements but they will be generated in a different order.

The product  $V.H$  is the so-called weak direct product (Melvin, 1956) of the groups  $V$  and  $H$ , where the term weak indicates that the products of the elements of the groups  $V$  and  $H$  need not be commutative.

If one of the two groups  $H$  or  $V$ , say  $H$ , is invariant,  $G$  may be written as the semi-direct product  $G = H \Delta V$ , where the convention is made that the invariant subgroup is written first since the multiplication of individual elements is still not commutative. Such products have been studied by Altmann (1963a, b).

If both  $H$  and  $V$  are invariant, then  $G$  is called the direct product of  $H$  and  $V$ ;  $G = H \times V$ . In this case also the multiplication of the individual elements is commutative. Neither of these products has any particular significance for our purpose however.

#### 4. Uniqueness theorem

For a given group  $H$  usually more than one group can be found that qualifies as a V.G.G. Let  $V$  and  $V'$  be two such groups which are both subgroups of  $G$ , have no element in common with  $H$  and are of the order  $n = p/q$ , then it is easy to show that  $V$  and  $V'$  generate the same set of variants, although by making use of different operations of  $G$ . As a result of this theorem it is sufficient to find one V.G.G. for a given  $G$  and  $H$  group, since all the others are equivalent, *i.e.* lead to the same set of variants. Since  $V$  and  $V'$  produce the same set of variants we can always write the decomposition of  $G$  in such a way that the cosets having coefficients with the same index generate the same variants, *e.g.* in

$$G = v_1H + v_2H + \dots + v_nH = v'_1H + v'_2H + \dots + v'_nH$$

$v_iH$  and  $v'_iH$  generate the same variant. Moreover we know that in both expansions each element of  $G$ , written as a product  $v_ih$  or  $v'_ih$  has to occur once and only once.

#### 5. Reciprocity theorem

The relationship between the groups  $H$  and  $V$  in  $G$ , *i.e.*  $G = H \cdot V = V \cdot H$ , is symmetrical. It is therefore clear that the  $H$  group plays the role of the V.G.G. if the  $V$  group is the point group of the ordered phase, *i.e.*  $G$  can be decomposed according to two essentially different schemes:

$$G = v_1H_i + v_2H_i + \dots + v_nH_i = h_1V_i + h_2V_i + \dots + h_qV_i.$$

The reciprocity principle can be used to shorten the labour in establishing the table of V.G.G.'s for the 32 point groups and all their subgroups (see Appendix).

#### 6. Relations between $V$ and $H$

We shall make use of the fact that two groups  $M$  and  $M'$  related by a relation of the type

$$M' = p^{-1}Mp,$$

where  $p$  is an arbitrary operation not necessarily belonging to  $M$ , are isomorphic.

Very often the group  $H$  can adopt several configurations within the same group  $G$ . This will for instance be the case if there exists an operation  $p$  that transforms  $G$  into itself without  $p$  being an element of  $G$ . Such operations are, *e.g.*, a rotation over an odd number of times  $45^\circ$  about the fourfold axis in the point group  $4/m2/m2/m$  or a rotation over an odd number of times  $30^\circ$  about the sixfold axis in the group  $6/m2/m2/m$ .

Such an operation interchanges the two classes of twofold axis as well as the two classes of vertical mirrors occurring in these point groups. If we ignore for the moment the distinction between these two different classes of symmetry elements of the same type we can

say that  $p$  transforms  $G$  into itself, *i.e.*  $G = p^{-1}Gp$ . Such an operation  $p$  will in general transform the subgroup  $H$  into a different subgroup  $H'$  such that  $H' = p^{-1}Hp$ . The V.G.G.'s  $V$  and  $V'$  corresponding respectively to  $H$  and  $H'$  are then related in the same manner, *i.e.*  $V' = p^{-1}Vp$ . To prove this it is sufficient to demonstrate that if the two subgroups  $V$  and  $H$  have no element in common except  $E$ , the product of their orders being equal to the order of  $G$ , this is also the case for  $V'$  and  $H'$ . This follows immediately from the fact that  $V$  and  $V'$  as well as  $H$  and  $H'$  are isomorphic.

It is true that also

$$V \cdot H = G = p^{-1}Gp = p^{-1}(V \cdot H)p = p^{-1}Vpp^{-1}Hp = V' \cdot H'$$

which shows that  $V'$  is indeed the V.G.G. corresponding to  $H'$  in  $G$ . However since  $p$  is not an operation of  $G$  the two positions of  $H, H$  and  $H'$ , are not crystallographically equivalent and either one or the other will occur in a given physical situation but never both simultaneously. In our derivation of all possible subgroups (Appendix) we have *a priori* to consider the two cases as different. However, we have now shown that if  $V$  undergoes the same transformation as  $H$  we obtain the  $V$  group belonging to the transformed  $H$  group. This remark allows us to limit ourselves to *one* configuration of  $H$  in  $G$ .

The reasoning used above holds *a fortiori* if  $p$  is an element of  $G$ ,  $g$  because then  $g^{-1}Gg = G$ , even when making the distinction between different classes of similar elements. If  $p$  is an element of  $H$ , *e.g.*  $p \equiv h$  (and therefore not of  $V$ ), one has  $H' = H$  and hence with one  $H$  group different V.G.G.'s may correspond; they are given by  $V' = h^{-1}Vh$  and are different representations of the same V.G.G. However,  $p$  may also be an element of  $V$  and thus no element of  $H$ , *e.g.*  $p \equiv v$ ; then we have  $V' = V$  but  $H' = v^{-1}Hv$ , *i.e.* with one  $V$  group now different  $H$  groups correspond. These different  $H$  groups are in fact the point groups of the different variants. If  $V_j = vV_i$  then  $H_j = v^{-1}H_i v$  as shown before.

It is clear that the relations  $V' = h^{-1}Vh$  and  $H' = v^{-1}Hv$  can be derived one from the other by means of the reciprocity theorem.

If  $V$  is an invariant subgroup of  $G$ , we have  $g^{-1}Vg = V$  and in particular  $h^{-1}Vh = V$ , *i.e.* only one  $V$  group is generated in this way. However, other  $V$  groups can be generated by multiplying the elements of  $V$  by an element of  $H$ ; in general one will have to use different elements of  $H$  for different elements of  $V$  in order to generate a new group, if it exists. The conclusions of this paragraph can be summarized as follows:

(i) If  $H$  can occur in  $G$  in several configurations not related by operations of  $G$ , then the corresponding  $V$  groups are related by the same operations, *i.e.* from  $H' = p^{-1}Hp$  follows  $V' = p^{-1}Vp$  even if  $p \notin G$  but  $p^{-1}Gp = G$ .

(ii) Different representations of the V.G.G. belonging to a given  $H$  group can be derived from one of them,  $V$ , by the relation  $V' = h^{-1}Vh$ .

(iii) Different  $H$  groups leading to the same  $V$  group can be derived from one of them by means of the relation

$$H' = v^{-1}Hv.$$

(iv) The pointgroups of the different variants can be derived from one of them,  $H_i$ , by the relation

$$H_j = v^{-1}H_i v.$$

### 7. Variant generating sets

It is not always possible to find a point group that represents all the operations of the set  $V$ , even though  $H$  is an invariant subgroup. The simplest way to prove this statement is to present an example.

Let  $G$  be the pointgroup 4 and  $H$  the point group 2. The elements of  $G$  are  $(E, C_4^1, C_4^2, C_4^3)$  and the elements of  $H$   $(E, C_2^1)$ .  $H$  is an invariant subgroup of  $G$ . One can decompose  $G$  as follows

$$G = (E, C_4^2) + C_4^1(E, C_4^2)$$

or

$$G = (E, C_2^1) + C_4^3(E, C_2^1).$$

The set  $V$  is  $(E, C_4^1)$  or  $(E, C_4^3)$  and it is clear that none of these forms a group. The reciprocity principle is clearly not applicable in such cases since the  $V$  group does not exist. In cases where a V.G.G. exists, it is also possible to find variant generating sets. One can construct such sets by multiplying the group  $V$  with elements of  $H$ , i.e.  $V' = hV = Vh$ . The  $V'$  are now not groups. They nevertheless generate the same set of variants as the groups: multiplying by an element  $H$ , which is a symmetry operation for the variant, does not change the resulting structure. In many cases one can also generate other groups from a given group (see § 3).

### 8. Crystallographically different interfaces

We shall say that the interface  $I_{ij}$  between  $V_i$  and  $V_j$  is crystallographically equivalent with the interface  $I_{kl}$  between  $V_k$  and  $V_l$  if  $V_k$  is derived from  $V_i$  by means of the same, or equivalent, operation as  $V_l$  is derived from  $V_j$ . We shall associate an operation of the V.G.G. with each interface.

Let  $V_\alpha = v_\alpha V_0$  when  $V_0$  is an arbitrary chosen original variant then  $V_l = v_l V_0 = v_l v_k^{-1} V_k = v_q V_k$ . The interface between  $V_l$  and  $V_k$  is then characterized by the operator  $v_q$ , which is in fact the operator that transforms the structure  $V_k$  into  $V_l$ ; the point groups are then related by  $H_l = v_q^{-1} H_k v_q$ . Similarly one can associate the operation  $v_p$  with the interfaces between  $V_j$  and  $V_i$   $V_j = v_p V_i$ ; the relation between the point groups is then  $H_j = v_p^{-1} H_i v_p$ .

According to our definition two interfaces are crystallographically equivalent if  $v_q$  and  $v_p$  are transformed one into the other by a symmetry operation of the group  $G$ , i.e. if

$$v_p = g^{-1} v_q g.$$

This follows immediately by expressing the relation between  $V_l$  and  $V_i$  in two different ways:

$$V_l = v_q g V_i \text{ and } V_l = g v_p V_i$$

which leads to

$$g v_p = v_q g \text{ or } v_p = g^{-1} v_q g.$$

This relation means that  $v_p$  and  $v_q$  are conjugate or are transformed one into the other by means of an operation of  $G$ . Conversely different interfaces correspond to operations of  $V$  which are not conjugate.

### Translation variants

We shall now discuss the consequences of translation symmetry and look for the number of different ways the superstructure can be built in a parallel orientation within a given orientation variant of the structure. We shall call these translation variants.

More quantitatively if the symmetry operation  $g$  that transforms one variant into another, and for which we have  $g \in G$  is such that  $g \notin H$ , one can still have either  $g \in H_i$  or  $g \notin H_i$ . In the first hypothesis the lattices are parallel, this is the case we are considering now.

The number of different translation variants for a given orientation variant is given by the number of translation vectors  $\tau$  such that  $\tau \in T$  but  $\tau \notin T^{(o)}$ . (If  $\tau \notin T$  we have a stacking fault). It is clear that all essentially different  $\tau$  vectors are those leading from the origin of a primitive unit cell of the superstructure to lattice points of  $T$  located within or in the side faces of this superlattice unit cell. These vectors are not necessarily the shortest; however one can always add a lattice vector of  $T$  to  $\tau$  in order to obtain the shortest equivalent  $\tau$  vector.

The number of  $\tau$  vectors is hence equal to the number of lattice nodes of  $T$ , within a primitive unit cell of  $T^{(o)}$ . This number can be obtained by dividing the volume of the primitive unit cell of the superlattice by the volume of the primitive unit cell of the disordered structure, ignoring small changes in dimensions due to ordering. (If the unit cells are not primitive one should divide by their multiplicity, e.g. by four for an f.c.c. cell and two for a b.c.c. cell.) Let the quotient be  $t$ ; the total number of variants is then  $(m_1/m_2)t$  where  $m_1$  and  $m_2$  are the multiplicities of disordered and ordered structures respectively.

A somewhat more elegant way of formulating the same result is based on the transformation matrix  $M$  from the primitive base of the disordered structure  $(\bar{a}_1, \bar{a}_2, \bar{a}_3)$  to the primitive base of the ordered structure  $(\bar{a}_{1,o}, \bar{a}_{2,o}, \bar{a}_{3,o})$ .

One has:

$$\begin{pmatrix} \bar{a}_{1,o} \\ \bar{a}_{2,o} \\ \bar{a}_{3,o} \end{pmatrix} = \begin{pmatrix} M \end{pmatrix} \begin{pmatrix} \bar{a}_1 \\ \bar{a}_2 \\ \bar{a}_3 \end{pmatrix}.$$

The volumes  $V$  and  $V_o$  respectively of the primitive unit cell of the disordered and the ordered structures are

given by

$$V_o = (\bar{a}_{1,o} \times \bar{a}_{2,o}) \cdot \bar{a}_{3,o} \text{ and } V = (\bar{a}_1 \times \bar{a}_2) \cdot \bar{a}_3$$

which leads to

$$V_o = |M|V$$

where  $|M|$  is the determinant value of the matrix  $M$ . According to the foregoing discussion we can also write:

$$t = |M|.$$

If the unit cells are not primitive the same correction factors as discussed above should be applied.

### Applications

The results obtained above were derived with a specific model in mind, the ordering of a substitutional alloy on a superlattice. However, the derivation is in fact not specifically based on this model and it is therefore of more general validity. It can be applied directly to the case of a structure resulting from the ordering of structural vacancies, as for instance in pyrrhotite (Van Landuyt & Amelinckx, 1972) or  $\beta$ -indium sulphide (Van

Landuyt & Amelinckx, 1969). The  $G$  group is then the point group of the structure without structural vacancies, whereas the  $H$  group is the point group of the structure with ordered vacancies. Similarly the results can also be applied to structures resulting from the ordering of interstitials. In fact, there is no essential difference from the previous case, since it is possible to describe this alternatively as the ordering of vacancies in a partially filled sublattice.

The results can also be applied to ordered alloys in cases where the disordered form is unknown or non-existent, but where the symmetry of the lattice is higher than that of the structure, *i.e.* where the point group of the structure is a subgroup of the point group of the lattice. This is for instance the case in the  $\delta$ -phase alloy NiMo (see below).

The results are furthermore also applicable to domain structures resulting from small displacements of atoms or small deformations, so-called 'displacive transformations' like those occurring in ferroelectrics and antiferromagnetics; in this case  $G$  is the point group of the prototype phase and  $H$  the point group of the ferroelectric or antiferromagnetic phase.

### Examples

We shall now work out a number of examples following the principles set out in the theory.

1. Let the group  $G$  be  $4/m\bar{2}/m\bar{2}/m$

A stereogram of the symmetry elements of this group is shown in Fig. 1. It contains 16 elements in ten classes

$$[E]; [C_2, C_2']; [C_2', C_2'']; [m', m''']; [m, m']; [C_4^1, C_4^3]; [C_4^{-1}, C_4^{-3}]; [I]; [C_4^{-2} \equiv \sigma]; [C_2^4].$$

Let the subgroup  $H$  be  $222$ ; it contains four elements in four classes:

$$[E]; [C_2]; [C_2']; [C_2''].$$

Since we have complete classes of  $G$  in  $H$ ,  $H$  is invariant.  $H$  can adopt two different orientations in  $G$  differing by a rotation over an angle of  $45^\circ$  about the fourfold axis; these two orientations are not crystallographically equivalent; they are shown in Fig. 2. We shall only consider the first since the V.G.G.'s for the second orientation can be derived from those of the first by a rotation over  $45^\circ$  about the fourfold axis (see § 6). The V.G.G. has to be a subgroup of order 4 of  $G$ . Several candidates can be found:  $222$ ;  $\bar{4}$ ;  $4$ ;  $2mm$ ;  $2/m$ . Only the last group qualifies as a  $V$  group because it is the only one that can be oriented so as to have no element in common with  $222$ . It can in fact occur in two orientations for one given orientation of  $H$ : they are both shown in Fig. 3. The two solutions are  $V(E, I, C_2'', m''')$  and  $V'(E, I, C_2', m')$ . The groups  $V$  and  $V'$  are related by the twofold rotations  $C_2$  and  $C_2'$  of  $H$ . The

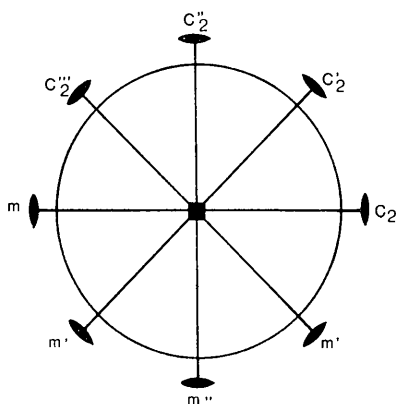


Fig. 1. Stereographic projection of the pointgroup  $G \left( \frac{4}{m} \frac{2}{m} \frac{2}{m} \right)$  of the NiMo lattice.

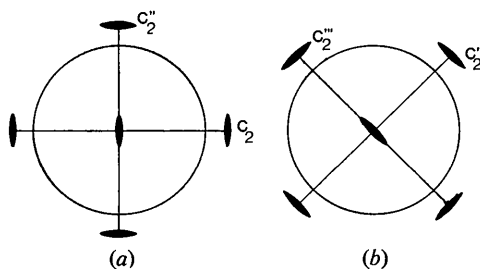


Fig. 2. Stereogram illustrating the two orientations of  $H(222)$  within  $G \left( \frac{4}{m} \frac{2}{m} \frac{2}{m} \right)$ . They differ by a rotation over  $45^\circ$ .

rotation  $C_4^2$  does not change the  $V$  group. It is clear that the operations of  $V$  belong to four different classes of  $G$ ; they therefore lead to three different interfaces.

(i) Inversion boundaries; separating domains related by the inversion operation  $I$ .

(ii) Permutation boundaries; separating domains related by the twofold rotation  $C_2'$ , which leads to permutation of the axes  $a$  and  $b$  of the orthorhombic ordered phase.

(iii) Permutation inversion boundaries, or twin boundaries between domains related by the mirror  $m' = C_2'I$ .

In the  $\delta$  phase NiMo these four variants and the associated interfaces have been identified (Van Tendeloo & Amelinckx, 1973). Since we have an invariant subgroup one can define the factor group. We decompose  $G$  in the following manner:

$$G = (E, C_2, C_2'', C_4^2) + (I, m, m', C_4^{-2} \equiv \sigma) + (C_2', C_4', C_4^3, C_2''') + (m', C_4^{-1}, C_4^{-3}, m''') = (EH + IH + C_2'H + m'H) = V \cdot H.$$

We introduce the notation for cosets:

$$C_1 = (E, C_2, C_2'', C_4^2) \quad C_2 = (I, m, m', C_4^{-2}) \\ C_3 = (C_2', C_4', C_4^3, C_2''') \quad C_4 = (m, C_4^{-1}, C_4^{-3}, m''').$$

Then we can establish the multiplication tables for the factor group (Table 1) and for the  $V$  group (Table 2).

Table 1. Multiplication table for the factor group

	$C_1$	$C_2$	$C_3$	$C_4$
$C_1$	$E \equiv C_1$	$C_2$	$C_3$	$C_4$
$C_2$	$C_2$	$E$	$C_4$	$C_3$
$C_3$	$C_3$	$C_4$	$E$	$C_2$
$C_4$	$C_4$	$C_3$	$C_2$	$E$

Table 2. Multiplication table for the  $V$  group

	$E$	$I$	$C_2'$	$m'$
$E$	$E$	$I$	$C_2'$	$m'$
$I$	$I$	$E$	$m'$	$C_2'$
$C_2'$	$C_2'$	$m'$	$E$	$I$
$m'$	$m'$	$C_2'$	$I$	$E$

It is clear that the two multiplication tables are the same if one makes the following mapping:

$$C_1 \equiv E, \quad C_2 \equiv I, \quad C_3 \equiv C_2', \quad C_4 \equiv m'.$$

This shows in an example that the  $V$  group and the factor group are isomorphic.

2. Let the group  $G$  be  $6/m2/m2/m$ ; its 24 elements are represented in the stereogram of Fig. 4

The 24 elements belong to 12 different classes. The decomposition into classes is as follows:

$$[E] [I] [C_6^1, C_6^5] [C_6^2, C_6^4] [C_6^3] [C_{2,1}, C_{2,2}, C_{2,3}] \\ [C_{2,1}', C_{2,2}', C_{2,3}'] [m_1, m_2, m_3] [m_1', m_2', m_3'] [C_6^{-2}, C_6^{-4}] \\ [C_6^{-1}, C_6^{-5}] [C_6^{-3} \equiv \sigma].$$

Let the  $H$  group be  $2/m$ ; it can be built in six different ways in  $G$ ; they are three by three crystallographically equivalent. Two different situations may therefore

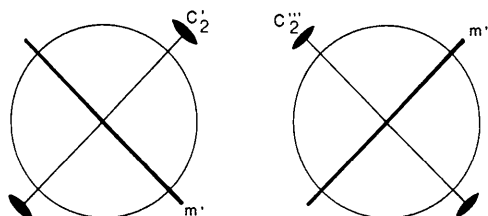


Fig. 3. The two different orientations within  $G \left( \frac{4}{m} \frac{2}{m} \frac{2}{m} \right)$  which the resulting variant generating group  $2/m$  may adopt. They differ by a rotation of  $90^\circ$  about the fourfold axis.

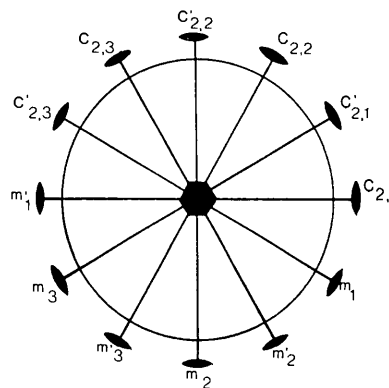


Fig. 4. Stereographic projection of the pointgroup  $G \left( \frac{6}{m} \frac{2}{m} \frac{2}{m} \right)$ , representing the point group of a disordered hexagonal NbTe<sub>2</sub> structure.

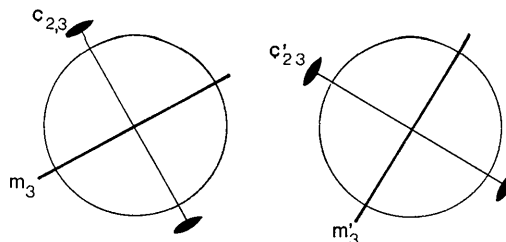


Fig. 5. Stereogram of the two possible orientations of  $H(2/m)$  in  $G \left( \frac{6}{m} \frac{2}{m} \frac{2}{m} \right)$  differing by a rotation of  $30^\circ$  around the sixfold axis.

arise; for instance either (Fig. 5),

$$H[E, I, m_3, C_{2,3}] \text{ or } H'[E, I, m'_3, C'_{2,3}].$$

We shall only treat the first case; the second differs in orientation by  $30^\circ$ .

The group does not contain complete classes of  $G$ ; it is therefore not invariant and a factor group does not exist. In order to find the V.G.G. we have to look for a subgroup of  $G$  of order six which has no element in common with  $H$ . Different point groups qualify:  $6, \bar{6} \equiv 3/m, 32, 3m$ ; their stereographic projections are

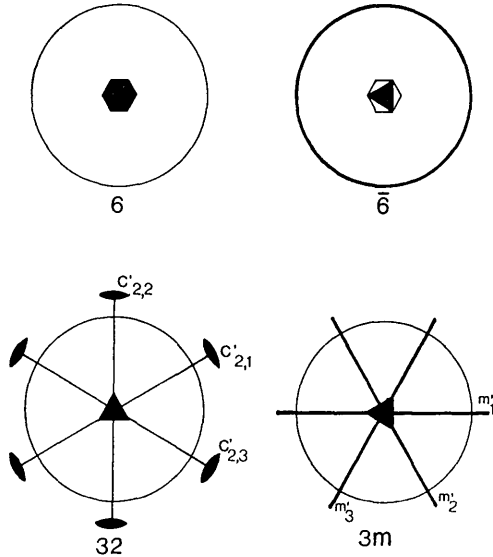


Fig. 6. Stereogram of the four variant generating groups,  $6, \bar{6}, 32$  and  $3m$ , for  $G \left( \begin{smallmatrix} 6 & 2 & 2 \\ m & m & m \end{smallmatrix} \right)$  and  $H(2/m)$ .

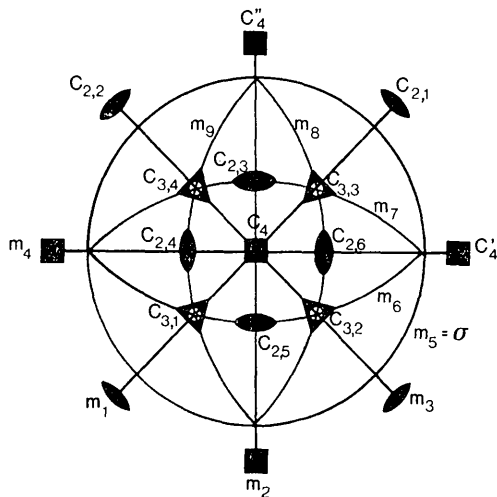


Fig. 7. Stereographic projection of the pointgroup  $\frac{4}{m} \bar{3} \frac{2}{m}$ , representing the point group of an f.c.c. structure.

shown in Fig. 6 in the correct orientations with respect to  $G$  and  $H$ . The simplest choice is  $6$ .

We can then decompose  $G$  as follows:

$$G = EH + C_6^1 H + C_6^2 H + C_6^3 H + C_6^4 H + C_6^5 H = V_1 \cdot H$$

and the  $V$  group is:

$$V_1(E, C_6^1, C_6^2, C_6^3, C_6^4, C_6^5).$$

Alternative decompositions are:

$$G = EH + m'_1 H + m'_2 H + m'_3 H + C_6^2 H + C_6^4 H$$

with

$$V_2(E, m'_1, m'_2, m'_3, C_6^2, C_6^4) \text{ of the type } 3m;$$

$$G = EH + C'_{2,1} H + C'_{2,2} H + C'_{2,3} H + C_6^2 H + C_6^4 H$$

with

$$V_3(E, C'_{2,1}, C'_{2,2}, C'_{2,3}, C_6^2, C_6^4) \text{ of the type } 32;$$

$$G = EH + C_6^{-1} H + C_6^{-2} H + C_6^{-3} H + C_6^{-4} H + C_6^{-5} H$$

of the type  $\bar{6}$

with

$$V_4(E, C_6^{-1}, C_6^{-2}, C_6^{-3}, C_6^{-4}, C_6^{-5}).$$

We thus obtain four different  $V$  groups which however are all equivalent and produce the same variants.

The first group  $V_1$  has a simple meaning; the six variants can be obtained by rotation about the hexagonal axis over angles which are multiples of  $60^\circ$ . The number of different interfaces is only three however, since in the group  $6/m 2/m 2/m$  the rotations about the sixfold axis belong to three classes (apart from the unit element):

$$[C_6^2, C_6^4], [C_6^1, C_6^5] \text{ and } [C_6^3].$$

For the  $\text{NbTe}_2$  crystal which has a disordered high-temperature hexagonal phase ( $6/m 2/m 2/m$ ) and is ordered monoclinic ( $2/m$ ), these three different resulting boundaries have been called ortho-, meta- and paraboundaries (Van Landuyt, Remaut & Amelinckx, 1970).

To know the number of translation variants for this  $\text{NbTe}_2$  structure we have to consider the transformation matrix between the disordered hexagonal and the ordered monoclinic structures:

$$M = \begin{pmatrix} 3 & \bar{1} & \bar{1} \\ 3 & 1 & \bar{1} \\ 0 & 0 & 1 \end{pmatrix}$$

which has a determinant value of 6. Since the monoclinic unit cell is twofold however, one obtains three translation variants giving rise to two different anti-phase boundaries. These again have been considered and used as evidence by Van Landuyt, Remaut & Amelinckx (1970).

3. Let the group  $G$  be  $\frac{4}{m} \bar{3} \frac{2}{m}$

This is the largest point group and contains 48 elements divided into ten classes; they are shown in Fig. 7:

- [E]
- [I]
- [C<sub>2,1</sub>, C<sub>2,2</sub>, C<sub>2,3</sub>, C<sub>2,4</sub>, C<sub>2,5</sub>, C<sub>2,6</sub>]
- [m<sub>1</sub>, m<sub>3</sub>, m<sub>6</sub>, m<sub>7</sub>, m<sub>8</sub>, m<sub>9</sub>] [m<sub>2</sub>, m<sub>4</sub>, m<sub>5</sub>]
- [C<sub>4</sub><sup>1</sup>, C<sub>4</sub><sup>3</sup>, C<sub>4</sub><sup>1</sup>, C<sub>4</sub><sup>3</sup>, C<sub>4</sub><sup>1</sup>, C<sub>4</sub><sup>3</sup>]
- [C<sub>4</sub><sup>2</sup>, C<sub>4</sub><sup>2</sup>, C<sub>4</sub><sup>2</sup>]
- [C<sub>3,1</sub><sup>1</sup>, C<sub>3,2</sub><sup>1</sup>, C<sub>3,3</sub><sup>1</sup>, C<sub>3,4</sub><sup>1</sup>, C<sub>3,1</sub><sup>2</sup>, C<sub>3,2</sub><sup>2</sup>, C<sub>3,3</sub><sup>2</sup>, C<sub>3,4</sub><sup>2</sup>]
- [C<sub>3,1</sub><sup>-1</sup>, C<sub>3,2</sub><sup>-1</sup>, C<sub>3,3</sub><sup>-1</sup>, C<sub>3,4</sub><sup>-1</sup>, C<sub>3,1</sub><sup>-2</sup>, C<sub>3,2</sub><sup>-2</sup>, C<sub>3,3</sub><sup>-2</sup>, C<sub>3,4</sub><sup>-2</sup>]
- [C<sub>4</sub><sup>-1</sup>, C<sub>4</sub><sup>-1</sup>, C<sub>4</sub><sup>-1</sup>, C<sub>4</sub><sup>-3</sup>, C<sub>4</sub><sup>-3</sup>, C<sub>4</sub><sup>-3</sup>].

If the subgroup *H* is 4/*m* (as in Ni<sub>4</sub>Mo) it contains eight elements divided into eight classes (Fig. 8):

$$[E], [I], [C_4^1], [C_4^3], [C_4^2], [C_4^{-1}], [C_4^{-3}], [\sigma = m_5].$$

This subgroup is clearly not invariant in the *G* group, since it does not contain complete classes of *G*; therefore there is no factor group. The *H* group can adopt three different orientations in *G*, but they are all crystallographically equivalent and related by a symmetry operation of *G*.

To find the V.G.G. we have to look for a group of order 6, which is a subgroup of *G* and which has no elements in common with the 4/*m* group. In the Ni<sub>4</sub>Mo structure these six elements of the *V* group represent the six possible ways of building up the ordered tetragonal Ni<sub>4</sub>Mo from the disordered f.c.c. structure. Three of them correspond to the three possible orientations of the tetragonal *c* axis along one of the cube axes of the f.c.c. parent; whereas for each of these there are two further orientations of the *a* axis of the tetragonal lattice with respect to the cube directions of the parent. Different *V* groups are 3*m* and 32 with the threefold axis oriented along one of the threefold axes of the parent point group (Fig. 9). They can therefore be oriented in four crystallographically equivalent ways, related by symmetry operations of *H*, so that we have only to consider one orientation. To find the number of different interfaces we have to look for the number of 'classes' of *V* in *G*.

$$3m = \{[E], [C_{3,1}^1, C_{3,1}^2], [m_1, m_6, m_9]\}$$

$$32 = \{[E], [C_{3,1}^1, C_{3,1}^2], [C_{2,2}, C_{2,3}, C_{2,6}]\}.$$

So, apart from the unity element, every *V* group contains two different classes representing the two interfaces which have been called (Ruedl, Delavignette & Amelinckx, 1968; Fu-Wen Ling & Starke, 1971)

- antiparallel twins
- perpendicular twins.

We can decompose *G* therefore as follows:

$$G = H + C_{3,1}^1 H + C_{3,1}^2 H + m_1 H + m_6 H + m_9 H$$

or

$$G = H + C_{3,1}^1 H + C_{3,1}^2 H + C_{2,2} H + C_{2,3} H + C_{2,6} H.$$

We have worked this out explicitly for the first decomposition (Table 3).

Table 3. The decomposition of *G*

<i>H</i>	<i>E</i>	C <sub>4</sub> <sup>1</sup>	C <sub>4</sub> <sup>2</sup>	C <sub>4</sub> <sup>3</sup>	C <sub>4</sub> <sup>-1</sup>	C <sub>4</sub> <sup>-3</sup>	σ	<i>I</i>
<i>V</i>	<i>E</i>	C <sub>4</sub> <sup>1</sup>	C <sub>4</sub> <sup>2</sup>	C <sub>4</sub> <sup>3</sup>	C <sub>4</sub> <sup>-1</sup>	C <sub>4</sub> <sup>-3</sup>	σ	<i>I</i>
C <sub>3,1</sub> <sup>1</sup>	C <sub>3,1</sub> <sup>1</sup>	C <sub>3,5</sub> <sup>1</sup>	C <sub>3,2</sub> <sup>2</sup>	C <sub>4</sub> <sup>3</sup>	m <sub>7</sub>	C <sub>4</sub> <sup>-</sup>	C <sub>3,2</sub> <sup>-2</sup>	C <sub>3,1</sub> <sup>-1</sup>
C <sub>3,1</sub> <sup>2</sup>	C <sub>3,1</sub> <sup>2</sup>	C <sub>4</sub> <sup>1</sup>	C <sub>3,4</sub> <sup>1</sup>	C <sub>4</sub> <sup>2</sup>	C <sub>4</sub> <sup>1</sup>	m <sub>8</sub>	C <sub>3,4</sub> <sup>-1</sup>	C <sub>3,1</sub> <sup>-2</sup>
m <sub>1</sub>	m <sub>1</sub>	m <sub>2</sub>	m <sub>3</sub>	m <sub>4</sub>	C <sub>4</sub> <sup>2</sup>	C <sub>2</sub> <sup>2</sup>	C <sub>2,1</sub>	C <sub>2,2</sub>
m <sub>6</sub>	m <sub>6</sub>	C <sub>3,4</sub> <sup>-2</sup>	C <sub>4</sub> <sup>-1</sup>	C <sub>3,3</sub> <sup>-1</sup>	C <sub>4</sub> <sup>3</sup>	C <sub>3,3</sub> <sup>1</sup>	C <sub>4</sub> <sup>1</sup>	C <sub>2,3</sub>
m <sub>9</sub>	m <sub>9</sub>	C <sub>3,3</sub> <sup>-2</sup>	C <sub>4</sub> <sup>-3</sup>	C <sub>3,2</sub> <sup>-1</sup>	C <sub>3,3</sub> <sup>2</sup>	C <sub>3,2</sub>	C <sub>4</sub> <sup>3</sup>	C <sub>2,6</sub>

The number of translation variants for each orientation can be derived from the transformation matrix *M* between the ordered tetragonal cell and the disordered f.c.c. unit cell:

$$M = \begin{pmatrix} \frac{3}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{3}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The determinant value is  $\frac{5}{2}$ . As the unit cell of the ordered phase is twofold and that of the disordered fourfold, *i.e.*

$$2V_0 = \frac{5}{2}V$$

or

$$t = \frac{V_0}{V} = 5,$$

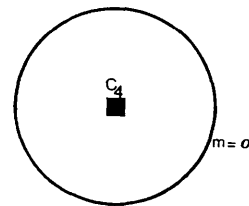


Fig. 8. Stereogram of the subgroup *H*(4/*m*) in the exact orientation compared to the *G* group  $\frac{4}{m} \frac{3}{3} \frac{2}{m}$ .

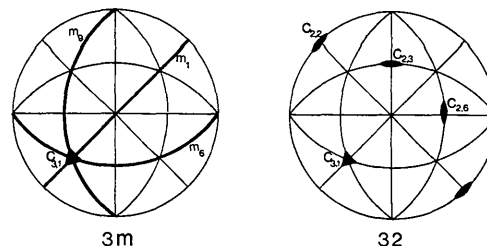


Fig. 9. Stereographic projection of the resulting variant generating groups 3*m* and 32 in the exact orientation with respect to  $\frac{4}{m} \frac{3}{3} \frac{2}{m}$  and *H*(4/*m*).



one finds five translation variants and four kinds of anti-phase boundaries. They have also been discussed by Ruedl, Delavignette & Amelinckx (1968), Chakravarti, Starke & LeFevre (1970) and Okamoto & Thomas (1971).

4. Let the group  $G$  as in the previous example be  $\frac{4}{m} \bar{3} \frac{2}{m}$ , of order 48, divided into 10 classes

Let the subgroup be  $H=3m$ ; it contains six elements in three classes

$$[E], [C_3^1, C_3^2], [m_1, m_6, m_9].$$

Clearly this subgroup is not invariant in  $G$ . It can adopt four orientations in  $G$ , but they are all related by symmetry operations of  $G$ .

The V.G.G. in this case is of order 8 and possible candidates are  $4/m$ ;  $422$ ;  $\bar{4}2m$ ;  $2/m2/m2/m$ ;  $4mm$ . The last one has to be eliminated because it has a mirror plane in common with  $H$ . For the  $2/m2/m2/m$  group the twofold axes have to be along the fourfold axis of the  $G$  group; otherwise it would also have common elements with  $H$ . These conditions occur for the  $\alpha$ -GeTe alloy which has been studied by Snykers, Delavignette & Amelinckx (1972), Goldak, Barrett, Innes & Youdelis (1966) and Stoemenos & Vincent (1972).

This and the previous example illustrate clearly what we have called in the general theory the reciprocity theorem. For the  $Ni_4Mo$  structure the subgroup  $H$  was  $4/m$  and one of the V.G.G. was  $3m$  while for GeTe where  $3m$  is the point group of the ordered structure, one of the V.G.G. was  $4/m$ .

5. A very simple example is the  $Ni_3Mo$  ordering

The  $G$  group is  $6/m2/m2/m$  which is of order 24 (Fig. 4). The elements belong to 12 different classes with the following decomposition.

$$\begin{aligned} & [E], [I], [C_6^1, C_6^5], [C_6^2, C_6^4], [C_6^3], [C_{2,1}, C_{2,2}, C_{2,3}] \\ & [C_{2,1}', C_{2,2}', C_{2,3}'], [m_1, m_2, m_3], [m_1', m_2', m_3'], [C_6^{-1}, C_6^{-5}] \\ & [C_6^{-2}, C_6^{-4}], [C_6^{-3} \equiv \sigma]. \end{aligned}$$

The point group of the ordered structure is  $2/m2/m2/m$  which is of order 8, the eight elements are divided into eight classes:

$$\{[E], [I], [C_6^3], [C_{2,1}], [C_{2,2}], [m_1], [m_2], [C_6^{-3} \equiv \sigma]\}$$

so that the  $H$  group is Abelian, but not invariant in  $G$ .

The only possible V.G.G. in this case is 3 which is evidently of order 3. The number of classes in  $G$  apart of the unit element is only one however. The decomposition of  $G$  can be made as follows:

$$\begin{aligned} G &= V. H = H + C_3^1 H + C_3^2 H \\ &= (E + I + C_6^3 + C_{2,1} + C_{2,2}' + m_1' + m_2 + \sigma) \\ &+ (C_6^2 + C_6^{-2} + C_6^5 + C_{2,3} + C_{2,1}' + m_2' \\ &+ m_3 + C_6^{-5}) + (C_6^4 + C_6^{-4} + C_6^1 + C_{2,2} \\ &+ C_{2,3}' + m_3' + m_1 + C_6^{-1}). \end{aligned}$$

These three possible orientation variants in  $Ni_3Mo$  have been observed and identified by Ruedl & Amelinckx (1969).

The number of translation variants follows from the transformation matrix  $M$  connecting the two primitive cells

$$M = \begin{pmatrix} 2 & -1 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and which has a determinant value 4. The number of different antiphase boundaries is therefore three. They have been studied in detail by Ruedl & Amelinckx (1971) and Van Tendeloo, Delavignette, Gevers & Amelinckx (1973).

Thanks are due to Professor Dr R. Gevers, Dr M. Bouten and D. Haentjens for useful discussions about the typical group-theoretical problems.

## APPENDIX

In an elaborated table we have systematically considered the 32 point groups, looked for all possible subgroups  $H$ , and if existing, noted the accompanying variant generating group  $V$ . If the same V.G.G.  $V$  can be obtained in different orientations, the number of ways to do so is noted. If ambiguity is possible or restrictions are to be made, this is also done. A last column indicates whether  $H$  is an invariant subgroup of  $G$  or not. For clarity, a stereographic projection of all these pointgroups, classified in decreasing order of the group is also shown. So, by means of this table it is possible if the point groups of the disordered and the ordered structure are known to predict for every kind of ordering not only the number of different orientation variants, but also the way to derive one variant from the other.

For brevity reasons this table is not published here, but it can be obtained free of charge from the authors.\*

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\* This table has also been deposited with the British Library Lending Division (Supplementary Publication No. SUP 30347). Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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## Generalized Structural Geometry

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Arbitrary combinations of bond lengths, bond angles and torsion angles can be used as generalized coordinates for describing molecular models. It is shown how these and the conventional Cartesian or fractional unit-cell coordinates can be interconverted. Algorithms are also given for the geometrical analysis of rigid structures of links joined by flexible connectors (where only bond lengths are specified). Properties of the connectivity matrix, as an alternative complete description of a structure, are developed. Several applications of the above procedures are described.

### Introduction

Given a set of parameters sufficient to define a general, unsymmetrical geometrical structure, such as a polyhedron (convex or otherwise), a molecule or a framework, it is often necessary to calculate certain consequential geometrical parameters. This calculation is often very difficult or tedious when done by exact algebraic means, since the solution of several simultaneous quadratic equations is usually necessary. For calculations of the energy and other parameters depending on pair interactions, for example, all interatomic distances must be found. Problems similar to those of molecular architecture occur also in real architecture, particularly with structures like the geodesic domes elaborated by Buckminster Fuller.

Modern computational facilities, especially those providing on-line access by time sharing, are now widely available. The procedures to be described show how geometrical models, very similar to the widely used ball-and-spoke models, but of indefinitely high accuracy, can be realized with a general computer. The programs have been written in BASIC and, since a program itself is very easily changed while using it from a teletypewriter keyboard, elaborate provisions for

all eventualities are not necessary. The programs (on paper tape) are available from the author.

### A general geometrical program

The primary or intrinsic parameters of an array of  $N$  points are the bond distances  $d_{ij}$  between pairs of points, the bond angles  $\theta_{ijk}$  defined by triplets of points and running from 0 to 180° and the torsion angles (or dihedral angles)  $\phi_{ijkl}$  which each require four points for identification and which run from -180 to 180°, a sense of rotation being defined in terms of a right-hand screw (Appendix). The secondary or derived parameters of the points are their coordinates  $x_i, y_i, z_i$  with respect either to orthogonal Cartesian axes or to crystallographic axes. The derived coordinates change with the axes and are not invariants of the structure. Following the Erlangen Programme of Klein (1872) wherever possible, quantities which are invariants of the structure and thus of physical significance are used. In each case  $3N-6$  parameters are needed to describe a structure of  $N$  points. Six further parameters clamp the grouping in a coordinate system.

Just as the solution of triangles is fundamental