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Derivative Crystal Structures

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There exists a class of crystal structures which are derived from others by generalization. These are here designated *derivative structures*. A special case of derivative structure is the popular "superstructure." The symmetry of a derivative structure is a subgroup of the symmetry of the basic structure. Here the term "subgroup" is used in a wider sense than common in mathematical crystallography, and includes subgroups with multiple cells. The methods of finding the derivative symmetries are discussed. There are two important kinds of derivative structures, here designated *substitution structures* and *distortion structures*. Substitution structures result when a set of different atoms is substituted for a set of like atoms in the basic structure. For a given kind of substitution, it is possible to predict the cell dimensions of the crystal resulting from the substitution, as well as all the possible symmetries it could have. Examples are cited of the applications of derivative structure theory to several branches of crystallography.

INTRODUCTION

IN this paper some relations are discussed which obtain between a crystal structure and those crystal structures derived from it by generalization. The original crystal structure will be called the *basic structure* and the structures derived from it by generalization will be called *derivative structures*.

One special case of derivative structures has been given a certain amount of casual attention, namely those structures which are commonly known as *superstructures*. About the only relation which has been recognized between a superstructure and its basic structure is that one or more edges of the superstructure cell are multiples of the corresponding edge or edges of the cell of the basic structure. Apparently no attention has been paid to other geometrical relations between superstructure and basic structure, and

consequently the very existence of the more general class of derivative structures has escaped attention.

If the currently recognized relation between superstructure and basic structure is expressed in appropriate language, then the extreme specialization of the concept of superstructure becomes evident, and the extension of the notion becomes obvious. In terms of symmetry theory, a superstructure can be derived from a basic structure by suppression of certain sets of the operations of translation in the space group of the basic structure. Stated this way, it is evident that one particular kind of operation of a group of operations has been singled out for consideration. It is evident that structures can be derived from a basic structure by the suppression of sets of any kind of operations or combination of operations. Consequently, we define as a *derivative structure*

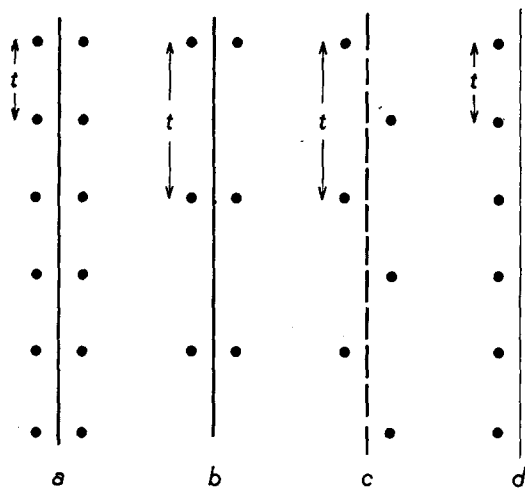


FIG. 1. The repetitions corresponding to a group based on a reflection and a translation, Fig. 1(a). In Figs. 1(b), (c), and (d) are shown the repetitions corresponding with the three types of infinite subgroups. The translation periods are labeled t .

any structure derived from a basic structure by the suppression of one or more sets of operations of the space group of the basic structure (due account being given to the requirements of group theory). Obviously, derivative structures include the class of superstructures.

The reason for the recognition of superstructures and the non-recognition of derivative structures lies in the comparative ease with which the operation of translation can be detected experimentally. Superstructures are commonly recognized in the field of metallography in connection with the formation of ordered phases. In such cases, if a set of translations is suppressed by the ordering process, it is easily detected by the change in dimensions of the cell edges. On the other hand, the suppression of certain other sets of symmetry operations leaves no diffraction record in a powder photograph. Suppose, for example, that the space group of the basic structure is $P2/m$, and suppose the set of all twofold rotations is suppressed. The derivative structure has the space group Pm , and its powder photograph is qualitatively no different from that of the original basic structure. The existence of the derivative structure may consequently escape detection unless its crystal structure has been worked out in detail.

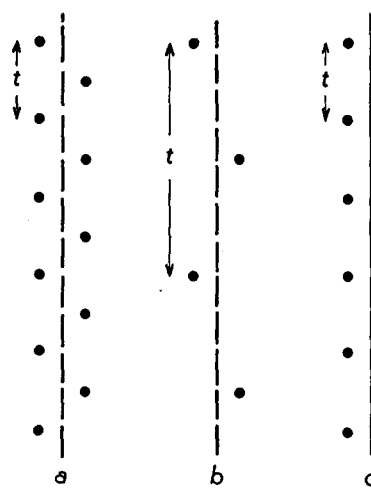


FIG. 2. The repetitions corresponding to a group of glide reflections, Fig. 2(a). In Figs. 2(b) and 2(c) are shown the repetitions corresponding with the two types of infinite subgroups. The translation periods are labeled t .

CHARACTERISTICS OF DERIVATIVE STRUCTURES

Symmetries of Derivative Structures

It is important to know how the symmetry of a derivative structure is related to that of its basic structure. The derivative symmetry is composed of some, but not all, the operations of the basic structure group, the missing operations being suppressed. The remaining operations must, of course, also form a group, and since this group is composed of operations contained in the original basic-structure group, it must be a subgroup of it. Thus, it is evident that the symmetry of a derivative structure is a subgroup of the space group of the basic structure. From this it immediately follows that the totality of possible derivative structure symmetries is composed of all the possible subgroups of the space group of the basic structure.

These conclusions are subject to possible misinterpretation. It does not follow from what has been said that the subgroups necessarily have the same cell dimensions as the cell of the basic group. The primitive cell of the subgroup is bound to be different from that of the basic group if any operations of lattice translation are among the suppressed set of operations. When the unit cell of the basic structure is non-primitive, and the suppressed group of operations includes

primitive translations, then the unit cell of the derivative structure may still be the same as the conventional unit cell of the basic structure, or it may have multiple edges. In the latter case, the derivative structure is the particular variety currently recognized as a superstructure.

Furthermore, it does not necessarily follow that the total number of possible derivative structures is equal to the total number of subgroup symmetries of the basic group. This is because for each derivative symmetry there may correspond more than one derivative structure. This matter will be discussed further.

Derivatives of Symmetry Planes Combined with One Translation

Some of the principles implied in the foregoing section can be simply illustrated by certain one-

dimensional space groups which amount to certain symmetry elements with one-dimensional translations. In Fig. 1(a) is shown a diagrammatic representation of such a group containing a reflection plane and a parallel translation. The fundamental operations are a reflection, S , and a translation, τ . The operations of the group are

$$\begin{array}{cccccccc} 1 & \tau & \tau^2 & \tau^3 & \tau^4 & \cdot & \cdot & \\ S & S\tau & S\tau^2 & S\tau^3 & S\tau^4 & \cdot & \cdot & \end{array} \quad (1)$$

and their inverses. This group has an infinite number of proper subgroups, but, provided that all translations are not suppressed, they all fall into three categories. Only the simplest representatives of the three categories are diagrammed in Figs. 1(b), (c), and (d). These simplest representatives have the following operations and their inverses:

$$\begin{array}{lcl} \text{I:} & 1 & \tau^2 & \tau^4 & \tau^6 & \cdot \\ \text{(Fig. 1(b)) } S & & S\tau & S\tau^4 & S\tau^6 & \cdot \end{array} \quad (2)$$

$$\begin{array}{lcl} \text{II:} & 1 & \tau^2 & \tau^4 & \tau^6 & \cdot \\ \text{(Fig. 1(c)) } S\tau & & S\tau^3 & S\tau^5 & \cdot & \\ (=g) & & (=g^3) & (=g^5) & & \end{array} \quad (3)$$

$$\begin{array}{lcl} \text{III:} & 1 & \tau & \tau^2 & \tau^3 & \tau^4 & \tau^5 & \tau^6 & \cdot & \cdot & \cdot \\ \text{(Fig. 1(d))} & & & & & & & & & & \end{array} \quad (4)$$

where g represents the operation of glide reflection with translation component τ .

The operations of the general groups of which the above three are the simplest proper representatives are:

$$\begin{array}{lcl} \text{I:} & 1 & \tau^{1+n} & \tau^{2(1+n)} & \tau^{3(1+n)} & \tau^{4(1+n)} & \cdot \\ S & & S\tau^{1+n} & S\tau^{2(1+n)} & S\tau^{3(1+n)} & S\tau^{4(1+n)} & \cdot \end{array} \quad (5)$$

$$\begin{array}{lcl} \text{II:} & 1 & \tau^{2(1+n)} & \tau^{4(1+n)} & \cdot \\ S\tau^{1+n} & & S\tau^{3(1+n)} & \cdot \end{array} \quad (6)$$

$$\begin{array}{lcl} \text{III:} & 1 & \tau^{1+n} & \tau^{2(1+n)} & \tau^{3(1+n)} & \tau^{4(1+n)} & \cdot \end{array} \quad (7)$$

where n is a non-negative integer.

Fewer categories occur for the derivatives of the group of operations representing glide symmetry, Fig. 2(a). The operations of this group are:

$$\begin{array}{cccccccccccc} 1 & S\tau & \tau^2 & S\tau^3 & \tau^4 & S\tau^5 & \tau^6 & S\tau^7 & \tau^8 & S\tau^9 & \cdot \\ (=g) & (=g^3) & (=g^5) & (=g^7) & (=g^9) & & & & & & \end{array} \quad (8)$$

The subgroup categories are represented by the following simplest examples:

$$\begin{array}{lcl} \text{I:} & 1 & S\tau^3 & \tau^6 & S\tau^9 & \cdot \\ \text{(Fig. 2(b)) } (=g^3) & & & & (=g^9) & \end{array} \quad (9)$$

$$\begin{array}{lcl} \text{II:} & 1 & \tau^2 & \tau^4 & \tau^6 & \tau^8 & \cdot \\ \text{(Fig. 2(c))} & & & & & & \end{array} \quad (10)$$

These examples are the simplest proper representatives of the two general categories of subgroups which have the following operations:

$$\text{I:} \quad 1 \quad S\tau^{1+2n} \quad \tau^{2(1+2n)} \quad S\tau^{3(1+2n)} \quad \cdot \quad (11) \\ (=g^{1+2n}) \quad (=g^{3(1+2n)})$$

$$\text{II:} \quad 1 \quad \tau^{2+2n} \quad \tau^{2(2+2n)} \quad \cdot \quad (12)$$

From this it is possible to draw the following conclusions with regard to the derivatives of these symmetry elements combined with a single parallel translation: The derivative of a reflection plane can be

- either: (1) a reflection plane parallel to which the translation is multiplied (Fig. 1(b)),
 or: (2) a glide plane with component parallel to the translation, the translation period being $2+2n$ ($=2, 4, 6, \dots$) times that of the basic translation (Fig. 1(c)),
 or: (3) a translation of 1, 2, 3, \dots times that of the basic translation, without reflection (Fig. 1(d)).

On the other hand, the derivative of a glide plane combined with a single parallel translation is

- either: (1) a glide plane with component parallel to the translation, the new translation being $2+4n$ basic glides, or $1+2n$ ($=1, 3, 5, \dots$) times that of the basic translation (Fig. 2(b)).
 or: (2) a translation of 1, 2, 3, \dots times that of the basic translation, without reflection (Fig. 2(c)).

Thus, a reflection plane can have as derivative a reflection plane, a glide plane, or a parallel translation, while a glide plane can have as derivative only a glide plane or a parallel translation. A glide plane cannot have a reflection plane as derivative.

These derivatives of simplified groups illustrate some of the fundamental features of the derivatives of space groups. Two general features to be observed are:

- (1) Each symmetry has a limited number of derivative types. Certain derivatives can be expected from a given basic symmetry while others cannot.
- (2) Certain derivative symmetries permit, among others, the same translation as the basic symmetry; other derivative symmetries permit only translations which are particular multiples of the basic translation. Those permitting the same translation are the standard subgroups listed in tables of space group characteristics.

Derivatives of Symmetry Planes

The information about the derivatives of symmetry planes is not yet in very useful form, for in crystals a reflection is always normal to a possible lattice net. Consequently, it is important to know the derivatives of reflections combined with the two translations of the net. As a preliminary to this, the derivatives of the net will first be discussed. (The derivatives of lattices will be discussed in another paper since lattice derivatives are not specifically required for the understanding of what follows.)

Derivatives of Nets

To simplify the discussion a primitive cell of the net is chosen and all translation operations are referred to the primitive translations, τ_1 and τ_2 . The general translation of the net, in vectorial form, is then $e\tau_1 + f\tau_2$, where e and f are any integers. The product form of this is $\tau_1^e \tau_2^f$. These operations form a group whose table is represented by the following origin portion of the quadrant with positive powers:

$$\begin{array}{cccccc} 1 & \tau_1 & \tau_1^2 & \tau_1^3 & \tau_1^4 & \cdot \\ \tau_2 & \tau_1\tau_2 & \tau_1^2\tau_2 & \tau_1^3\tau_2 & \tau_1^4\tau_2 & \cdot \\ \tau_2^2 & \tau_1\tau_2^2 & \tau_1^2\tau_2^2 & \tau_1^3\tau_2^2 & \tau_1^4\tau_2^2 & \cdot \\ \tau_2^3 & \tau_1\tau_2^3 & \tau_1^2\tau_2^3 & \tau_1^3\tau_2^3 & \tau_1^4\tau_2^3 & \cdot \\ \tau_2^4 & \tau_1\tau_2^4 & \tau_1^2\tau_2^4 & \tau_1^3\tau_2^4 & \tau_1^4\tau_2^4 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{array} \quad (13)$$

Two kinds of subgroups involving both τ_1 and τ_2 can be selected from (13). These are represented by the following two simple examples:

$$P: \begin{array}{cccc} 1 & \tau_1^2 & \tau_1^4 & \cdot \\ \tau_2^2 & \tau_1^2\tau_2^2 & \tau_1^4\tau_2^2 & \cdot \\ \tau_2^4 & \tau_1^2\tau_2^4 & \tau_1^4\tau_2^4 & \cdot \end{array} \quad (14)$$

$$C: \begin{array}{cccc} 1 & \tau_1^2 & \tau_1^4 & \cdot \\ \tau_2^2 & \tau_1\tau_2 & \tau_1^3\tau_2 & \cdot \\ \tau_2^4 & \tau_1\tau_2^3 & \tau_1^3\tau_2^3 & \cdot \\ \tau_2^2 & \tau_1^2\tau_2^2 & \tau_1^4\tau_2^2 & \cdot \\ \tau_2^4 & \tau_1^2\tau_2^4 & \tau_1^4\tau_2^4 & \cdot \end{array} \quad (15)$$

The first example represents the operations of a primitive net while the second represents the operations of a centered net. Thus, a primitive net can have as derivatives both primitive nets and centered nets. It can easily be shown that the primitive derivatives can have any translation multiplicities, while the centered derivatives can only have translation multiplicities which are even. (This assumes that the cell edges of basic and derivative cells are taken in the same direction. If they are not taken in the same direction, then the edges of the derivative cell in terms of the edges of the basic cell are given by

$$\mathbf{A} = e_1\mathbf{a} + f_1\mathbf{b}, \quad \mathbf{B} = e_2\mathbf{a} + f_2\mathbf{b}.$$

The condition that the derivative cell can be a centered cell is that $e_1 + e_2$ must be even and that $f_1 + f_2$ must be even.)

Derivatives of Mirrors

To investigate the derivatives of a mirror, the translations of the net, (13), must be combined with the reflection S^q , where q has the values 0 or 1. The general operation is then $\tau^e S^q$. These operations form a group represented by the following origin portion of the quadrant with positive powers (in this table, the terms containing S can be thought of as constituting an upper level in the third dimension):

$$\begin{array}{cccccc} 1 & \tau_1 & \tau_1^2 & \tau_1^3 & \tau_1^4 & \cdot \\ S & S\tau_1 & S\tau_1^2 & S\tau_1^3 & S\tau_1^4 & \cdot \\ \tau_2 & \tau_1\tau_2 & \tau_1^2\tau_2 & \tau_1^3\tau_2 & \tau_1^4\tau_2 & \cdot \\ S\tau_2 & S\tau_1\tau_2 & S\tau_1^2\tau_2 & S\tau_1^3\tau_2 & S\tau_1^4\tau_2 & \cdot \\ \tau_2^2 & \tau_1\tau_2^2 & \tau_1^2\tau_2^2 & \tau_1^3\tau_2^2 & \tau_1^4\tau_2^2 & \cdot \\ S\tau_2^2 & S\tau_1\tau_2^2 & S\tau_1^2\tau_2^2 & S\tau_1^3\tau_2^2 & S\tau_1^4\tau_2^2 & \cdot \\ \tau_2^3 & \tau_1\tau_2^3 & \tau_1^2\tau_2^3 & \tau_1^3\tau_2^3 & \tau_1^4\tau_2^3 & \cdot \\ S\tau_2^3 & S\tau_1\tau_2^3 & S\tau_1^2\tau_2^3 & S\tau_1^3\tau_2^3 & S\tau_1^4\tau_2^3 & \cdot \\ \tau_2^4 & \tau_1\tau_2^4 & \tau_1^2\tau_2^4 & \tau_1^3\tau_2^4 & \tau_1^4\tau_2^4 & \cdot \\ S\tau_2^4 & S\tau_1\tau_2^4 & S\tau_1^2\tau_2^4 & S\tau_1^3\tau_2^4 & S\tau_1^4\tau_2^4 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{array} \quad (16)$$

The subgroups of (16) are restricted by the requirements that (a), they must all be based upon translation subgroups P , (14), or C , (15), and that (b), all radial lines of operations containing the identical operation at the origin must

conform to subgroups of types I, II, or III, (2), (3), (4) and (5), (6), (7). Thus the borders and main diagonal of the subgroups of (16) must be of types I, II, or III. To find the subgroups of (16), therefore, one assumes translation subgroup

TABLE I. Derivatives of symmetry planes (referred to a single translation)

Basic symmetry element	Derivative symmetry element	Translation multiplicity of derivative (n is a non-negative integer)
m	m g (glide) 1	$(1+n)2 = 1+n$ $2+2n$ $1+n$
g	g 1	$(\frac{1}{2}+n)2 = 1+2n$ $1+n$

TABLE II. Derivatives of symmetry planes, and their translation multiplicities (referred to the axes of the primitive net parallel to the symmetry plane).

Basic symmetry	Derivative symmetry	Translation multiplicity of derivative (n_1 and n_2 are non-negative integers) $\parallel \tau_a$ $\parallel \tau_b$	
Pm	Pm	$1+n_1$	$1+n_2$
	Pa	$2+2n_1$	$1+n_2$
	Pb	$1+n_1$	$2+2n_2$
	Pn	$2+2n_1$	$2+2n_2$
	$P1$	$1+n_1$	$1+n_2$
	Cm	$2+2n_1$	$2+2n_2$
	$Ca = Cb$	$2+2n_1$	$2+2n_2$
	Cd	$4+4n_1$	$4+4n_2$
Pa	$C1$	$2+2n_1$	$2+2n_2$
	Pa	$1+2n_1$	$1+n_2$
	Pn	$1+2n_1$	$2+2n_2$
	$P1$	$1+n_1$	$1+n_2$
	Cd	$2+4n_1$	$4+4n_2$
Pb	$C1$	$2+2n_1$	$2+2n_2$
	Pb	$1+n_1$	$1+2n_2$
	Pn	$2+2n_1$	$1+2n_2$
	$P1$	$1+n_1$	$1+n_2$
	Cd	$4+4n_1$	$2+4n_2$
Pn	$C1$	$2+2n_1$	$2+2n_2$
	Pn	$1+2n_1$	$1+2n_2$
	$P1$	$1+n_1$	$1+n_2$
	Cd	$2+4n_1$	$2+4n_2$

either P or C and then assumes that the left border, upper border, and diagonal each have one of the forms of I, II, or III. Not all such combinations form groups. The ones which do are the following:

Combination			Designation
τ_1	τ_2	$\tau_1\tau_2$	
P	I	I	Pm
P	II	III	Pa
P	III	II	Pb
P	III	III	Pn
P	III	III	$P1$
C	I	I	Cm
C	II	II	$Ca = Cb$
C	III	III	Cd
C	III	III	$C1$

TABLE III. Derivatives of axial symmetry elements and their translation multiplicity

Basic symmetry element	Derivative symmetry elements	Translation multiplicity of derivative (n is a non-negative integer)
$\bar{1}$	$\bar{1}$ 1	$1+n$ $1+n$
2	2 2 ₁ 1	$1+n$ $(1+n)2 = 2+2n$ $1+n$
2 ₁	2 ₁ 1	$(\frac{1}{2}+n)2 = 1+2n$ $1+n$
3	3 3 ₁ , 3 ₂ 1	$1+n$ $(1+n)3 = 3+3n$ $1+n$
3 ₁ (3 ₂)	3 ₁ (3 ₂) 3 ₂ (3 ₁) 1(1)	$(\frac{1}{3}+n)3 = 1+3n$ $(\frac{2}{3}+n)3 = 2+3n$ $1+n$
$\bar{4}$	$\bar{4}$ 2 2 ₁ 1	$1+n$ $1+n$ $(1+n)2 = 2+2n$ $1+n$
4	4 4 ₁ , 4 ₂ 4 ₂ 2 2 ₁ 1	$1+n$ $(1+n)4 = 4+4n$ $(1+n)2 = 2+2n$ $1+n$ $(1+n)2 = 2+2n$ $1+n$
4 ₁ (4 ₂)	4 ₁ (4 ₂) 4 ₂ (4 ₁) 2 ₁ (2 ₁) 1(1)	$(\frac{1}{2}+n)4 = 1+4n$ $(\frac{3}{2}+n)4 = 3+4n$ $(\frac{1}{2}+n)2 = 1+2n$ $1+n$
4 ₂	4 ₂ 4 ₁ , 4 ₂ 2 2 ₁ 1	$1+n$ $(\frac{1}{2}+n)4 = 2+4n$ $1+n$ $(1+n)2 = 2+2n$ $1+n$
6	6 6 ₁ , 6 ₅ 6 ₂ , 6 ₄ 6 ₃ 3 3 ₁ , 3 ₂ 2 2 ₁ 1	$1+n$ $(1+n)6 = 6+6n$ $(1+n)3 = 3+3n$ $(1+n)2 = 2+2n$ $1+n$ $(1+n)3 = 3+3n$ $1+n$ $(1+n)2 = 2+2n$ $1+n$
6 ₁ (6 ₅)	6 ₁ (6 ₅) 6 ₅ (6 ₁) 3 ₁ (3 ₂) 3 ₂ (3 ₁) 2 ₁ (2 ₁) 1(1)	$(\frac{1}{3}+n)6 = 1+6n$ $(\frac{2}{3}+n)6 = 5+6n$ $(\frac{1}{3}+n)3 = 1+3n$ $(\frac{2}{3}+n)3 = 2+3n$ $(\frac{1}{3}+n)2 = 1+2n$ $1+n$
6 ₂ (6 ₄)	6 ₂ (6 ₄) 6 ₄ (6 ₂) 2(2) 2 ₁ (2 ₁) 1(1)	$(\frac{1}{3}+n)3 = 1+3n$ $(\frac{2}{3}+n)3 = 2+3n$ $1+n$ $(1+n)2 = 2+2n$ $1+n$
6 ₃	6 ₃ 3 3 ₁ , 3 ₂ 2 ₁ 1	$(\frac{1}{3}+n)2 = 1+2n$ $1+n$ $(1+n)3 = 3+3n$ $(\frac{1}{3}+n)2 = 1+2n$ $1+n$

Since the borders define the translations of the group, the translations multiplicities of the subgroups can be found from the individual translation multiplicities of the borders, which are listed in Table I. Centered derivatives occur only for even multiplicities, as mentioned in the last section. The two translation multiplicities of all derivatives of mirrors are found listed in Table II.

Derivatives of Glide Planes

The derivatives of glide planes combined with nets can be investigated in the same way as the derivatives of mirrors. The derivations will not be given in detail. The kinds of derivatives of each kind of glide can be predicted from the following considerations: In the case of the axial glide, a , the translation vector associated with the elementary glide operation is $\frac{1}{2}\tau_1$. The other glide operations of the group consist of this glide plus, vectorially, the translations of the net, giving $(\frac{1}{2}+e)\tau_1+f\tau_2$, where e and f are integers. All these glides are candidates for the elementary glide of the derivative symmetry. Thus the translation component of the derivative glide has the form $(\frac{1}{2}+e)\tau_1+f\tau_2$. Note that this derivative glide can have components along both a and b axes, showing that diagonal glides are among the derivatives. Similarly, when f is zero, the

derivative has a translation component along a only, showing that parallel axial glides are among the derivatives. On the other hand, no derivative can have zero component along a . Hence the derivatives of the axial glide, a , include the glides n , d , and a , but not b .

In the case of the diagonal glide, the translation component of the elementary glide is $\frac{1}{2}\tau_1+\frac{1}{2}\tau_2$. When this is combined with the translations of the net there results $(\frac{1}{2}+e)\tau_1+(\frac{1}{2}+f)\tau_2$. This is the translation of the general glide operation of the group and is a candidate for the elementary glide of the derivative symmetry. Note that neither coefficient can ever be zero. Therefore, the derivatives of the diagonal glide include n and d but not a or b .

The derivatives of all types of reflection planes and their translation multiplicities are listed in Table II.

Derivatives of Rotation Axes with a Parallel Translation

The derivatives of the rotation axes may be found in the manner illustrated by the following example: In the screw 3_1 , the group is composed of operations $(R\tau)^f$, where f is any integer. The rotational components, R^f , have the following identities:

$$\begin{array}{llll} \cdot & \cdot & R^{-3}=R^0=R^3=R^6 & \cdot & \cdot \\ \cdot & \cdot & R^{-2}=R^1=R^4=R^7 & \cdot & \cdot \\ \cdot & \cdot & R^{-1}=R^2=R^5=R^8 & \cdot & \cdot \end{array}$$

The operations of the group may therefore be written

$$1 \quad R\tau \quad R^2\tau^2 \quad \tau^3 \quad R\tau^4 \quad R^2\tau^5 \quad \tau^6 \quad \cdot \quad \cdot \quad (17)$$

By selecting some operation, $(R\tau)^f$, as a primitive operation, a new set of operations $((R\tau)^f)^g$ may be arranged in a group table, for example:

$$1 \quad R^2\tau^2 \quad R\tau^4 \quad \tau^6 \quad \cdot \quad \cdot \quad (18)$$

By virtue of the above identities, and by substituting τ_1 for τ^2 , this may be rewritten

$$1 \quad R^{-1}\tau_1 \quad R^{-2}\tau_1^2 \quad \tau_1^3 \quad \cdot \quad \cdot \quad (19)$$

The subgroup is now recognized as defining the group of operations of a screw 3_2 . Other subgroups of the same symmetry can be formed from (17) by taking as the primitive operation of the subgroup any term separated from $R^2\tau^2$ by n basic translations. The first term of this new group thus represents $(\frac{2}{3}+n)$ basic translations. Since this is the primitive operation of 3_2 , it is only $\frac{1}{3}$ of the derivative translation. The derivative translation is thus $3(\frac{2}{3}+n)=2+3n$ basic translations. The numeral, 2, indicates that the smallest translation period a derivative can have is 2 basic primitive translations.

The derivatives of the several rotation axes and their translation multiplicities are given in Table III. Table IV is another arrangement of this material of use in quickly determining the possible derivatives of a rotation axis for a given translation multiplicity.

TABLE IV. Derivatives of axial symmetry elements for particular parallel translations (excluding trivial derivative, 1).

Basic symmetry element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$
2	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁
2 ₁	2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁	
3	3	3	3 3 _{1,2}	3	3	3 3 _{1,2}	3	3	3 3 _{1,2}	3	3	3 3 _{1,2}	3	3	3 3 _{1,2}	3	3 3 _{1,2}	3	3 3 _{1,2}	3
3 ₁ (For basic 3 ₂ , inter- change 3 ₁ and 3 ₂ in derivatives)	3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂
$\bar{4}$	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁	$\bar{4}$ 2	$\bar{4}$ 2 2 ₁
4	4	4	4	4 4 _{1,3}	4	4	4	4	4	4	4	4 4 _{1,3}	4	4	4	4	4 4 _{1,3}	4	4	4 4 _{1,3}
		4 ₂ 2 2 ₁	2	4 ₂ 2 2 ₁	2	4 ₂ 2 2 ₁	2	4 ₂ 2 2 ₁	2	4 ₂ 2 2 ₁	2	4 ₂ 2 2 ₁	2	4 ₂ 2 2 ₁	2	4 ₂ 2 2 ₁	2	4 ₂ 2 2 ₁	2	4 ₂ 2 2 ₁
4 ₁ (For basic 4 ₃ , inter- change 4 ₁ and 4 ₃ in derivatives)	4 ₁		4 ₃ 2 ₁		4 ₁		4 ₃ 2 ₁		4 ₁		4 ₃ 2 ₁		4 ₁		4 ₃ 2 ₁		4 ₁		4 ₃ 2 ₁	
4 ₂	4 ₂	4 ₂ 4 _{1,3}	4 ₂	4 ₂	4 ₂	4 ₂ 4 _{1,3}	4 ₂	4 ₂	4 ₂	4 ₂ 4 _{1,3}	4 ₂	4 ₂	4 ₂	4 ₂ 4 _{1,3}	4 ₂	4 ₂	4 ₂	4 ₂ 4 _{1,3}	4 ₂	4 ₂
	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁
6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
			6 _{2,4}			6 _{2,4}			6 _{2,4}			6 _{2,4}			6 _{2,4}			6 _{2,4}		
	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁
6 ₁ (For basic 6 ₆ , inter- change 6 ₁ and 6 ₆ , also 3 ₁ and 3 ₂ in derivative)	6 ₁			6 ₆			6 ₁			6 ₆			6 ₁			6 ₆			6 ₁	
	3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂		3 ₁	3 ₂
	2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁	
6 ₂ (For basic 6 ₄ , inter- change 6 ₂ and 6 ₄ in derivative)	6 ₂	6 ₄		6 ₂	6 ₄		6 ₂	6 ₄		6 ₂	6 ₄		6 ₂	6 ₄		6 ₂	6 ₄		6 ₂	6 ₄
	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁	2	2 2 ₁
6 ₃	6 ₃ 3	3	6 ₃ 3 3 _{1,2}	3	6 ₃ 3	3 3 _{1,2}	3	6 ₃ 3	3 3 _{1,2}	3	6 ₃ 3	3 3 _{1,2}	3	6 ₃ 3	3	6 ₃ 3 3 _{1,2}	3	6 ₃ 3 3 _{1,2}	3	6 ₃ 3
	2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁		2 ₁	

Derivatives of Groups of Operations in a Plane

An interesting aspect of derivative structures may be illustrated by the simplified cases of operations confined to a plane. Fig. 3(a) shows a basic structure for a simple group consisting of rotations and perpendicular one-dimensional translations. The group is based on operation $A(\pi)$, i.e., a

rotation about the axis A through the angle π , and translation t . The group contains the following operations and their inverses:

$$\begin{array}{cccccccc} 1 & t & t^2 & t^3 & t^4 & t^5 & t^6 & \cdot & \cdot \\ A(\pi) & A(\pi)t & A(\pi)t^2 & A(\pi)t^3 & A(\pi)t^4 & A(\pi)t^5 & A(\pi)t^6 & \cdot & \cdot \end{array} \quad (20)$$

Each of the operations which are the result of combining t^n with $A(\pi)$ is equivalent to a rotation of π about an axis half a translation away from A . The axes fall into two classes, A and A' , which are shown with different orientations in Fig. 3(a). The A 's are translation-equivalent and the A'' 's are translation-equivalent, but the A 's and A'' 's are non-equivalent.

The following two kinds of subgroups can be formed from the operations of (20) by suppressing half the operations:

$$\text{I:} \quad \begin{array}{ccccccc} 1 & & t^2 & & t^4 & & t^6 & \cdot & \cdot \\ A(\pi) & & A(\pi)t^2 & & A(\pi)t^4 & & A(\pi)t^6 & \cdot & \cdot \end{array} \quad (21)$$

$$\text{II:} \quad \begin{array}{ccccccc} 1 & t & t^2 & t^3 & t^4 & t^5 & t^6 & \cdot & \cdot \end{array} \quad (22)$$

Consider, now, the first kind of subgroup, (21), in relation to the structure itself. The operation at the bottom of the first column of the basic group, (20), can be either $A(\pi)$, or $A'(\pi)$, depending on choice of origin. The subgroup (21) has the same form in both cases, but in one case all axes are of type A , in the other they are all A' . This amounts to saying that, in the derivative structure, Figs. 3(b) and 3(c), either axes of A' or A are entirely suppressed. The resulting two derivative structures have the same symmetry but have structures which are quite different, as shown in Figs. 3(b) and 3(c).

In (20) the even columns were retained to form subgroup (21). If columns divisible by 3 are retained, the subgroup becomes

$$\begin{array}{cccc} 1 & t^3 & t^6 & t^9 \cdot \\ A(\pi) & A(\pi)t^3 & A(\pi)t^6 & A(\pi)t^9 \cdot \\ (=A) & (=A') & (=A_2) & (=A_2') \end{array} \quad (23)$$

This subgroup contains both A and A' varieties of original axes, and its origin can be chosen in any one of three places, namely A , A' , or A_2 . The three resulting structures, Fig. 3(d), are identical with change of origin.

In a corresponding way, subgroups may be chosen in several ways from the other combinations of permissible operations with translations in a plane. In general, if the subgroup is composed of operations originally equivalent, several derivative structures are possible and these are found by placing the origin of the group at the several similar but non-equivalent points of the basic group. On the other hand, if the subgroup contains a sampling of all the elements of the original basic group, only one kind of derivative structure results.

In a diagrammatic way, Fig. 4 illustrates some of the derivatives of basic structures for other groups in a plane.

Derivatives of Space Groups

The total number of possible derivatives of a space group consist of all its subgroups in the wide sense. The number of these is infinite. They belong to the following categories:

(1) Subgroups having the same translation group, i.e., having the same lattice mode and cell dimensions as the basic structure. These are the subgroups ordinarily found listed in subgroup tables.¹

(2) Subgroups having different translation groups, i.e., referable to different cells than the basic structure either with regard to lattice mode or to cell dimensions. The primitive cell of such a subgroup is always a multiple of that of

¹ Paul Niggli, *Geometrische Kristallographie des Diskontinuums* (Gebrüder Borntraeger, Leipzig, 1919) pp. 125-131. The *International Tables for the Determination of Crystal Structures* also list the subgroups of each space group in the description of that group.

the basic group. Unfortunately, lists of such subgroups are not available.

The subgroups consistent with a specific derivative cell can be found by forming the possible groups of the derivatives of the symmetry elements of the basic structure. (Naturally, these derivative space groups will be isomorphous with the possible subgroups of the point groups of the basic structure.) To illustrate how these subgroups may be found, an example is given of the process:

Derivatives for a Particular Cell

To illustrate the finding of the derivatives of a structure for a specific relation between derivative cell and basic cell, the case of finding the derivatives of marcasite consistent with the

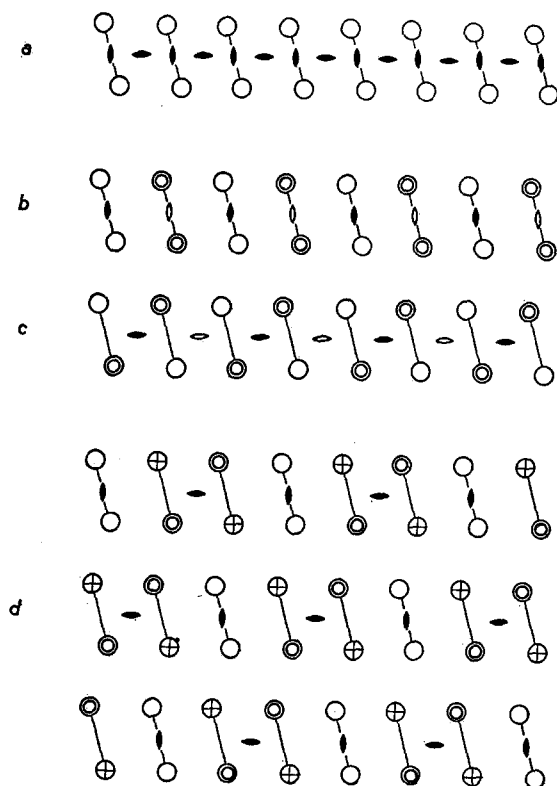


FIG. 3. The kinds of derivative structures based on the same subgroup. Fig. 3(a) is the basic structure. Figs. 3(b) and 3(c) show two different structures based on the same subgroup. Fig. 3(d) illustrates that such different structures do not arise when the subgroup contains a sampling of the several kinds of symmetry elements in the basic structure.

arsenopyrite cell is offered. This problem has been solved by other methods.²

The basic cell (marcasite, FeS_2) has symmetry $Pmnn$. It is desired to find the derivative symmetries consistent with a C -centered cell of multiplicity 2. The derivative cell in terms of the basic cell is represented by the matrix

$$\begin{vmatrix} 1 & 1 & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{vmatrix}. \quad (24)$$

The upper part of Fig. 5 diagrammatically represents the symmetry $Pmnn$ and the shape and dimensions of the derivative cell. Fig. 5 illustrates the following discussion:

Consider first the symmetry axes:

Parallel to a : The basic structure has twofold rotation axes. The derivatives of 2 for $2t$ are 2, 2_1 , and 1. Owing to the fact that a face parallel to a , namely C , is centered, rotations and screws must occur mixed, so that the only possible derivative symmetries are $(2+2_1)$ and 1.

Parallel to b : The basic structure has twofold screws. The derivatives of 2_1 for $2t$ are 2_1 and 1. Since a face parallel to b , namely C , is centered, rotations and screws must occur mixed. Since 2 is not a derivative of 2_1 , the mixture $(2+2_1)$ cannot be a derivative, hence the only derivative symmetry is 1.

Parallel to c : The basic structure has twofold screws. The derivatives of 2_1 for $1t$ are 2_1 and 1.

The axial derivatives are thus

$\parallel a$	$\parallel b$	$\parallel c$	
$(2+2_1)$	1	2_1	(25)
and 1	1	and 1.	

These can only be combined into the following groups: $C211$, $C112_1$, $C1$.

Consider next the symmetry planes:

Parallel to (100) : The basic structure has a mirror. The derivatives of m are m , g (glide) and 1. The only possible glide for translations $(2t_b; t_c)$ is b . Hence the only derivatives of m for $(2t_b; t_c)$ are m , b , and 1. However, since the cell is C -centered, glides and mirrors must occur mixed, so the only derivatives are $(m+b)$ and 1.

² M. J. Buerger, "A systematic method of investigating superstructures, applied to the arsenopyrite crystal structural type," *Zeits. f. Krist. (A)* **94**, 425-438 (1936).

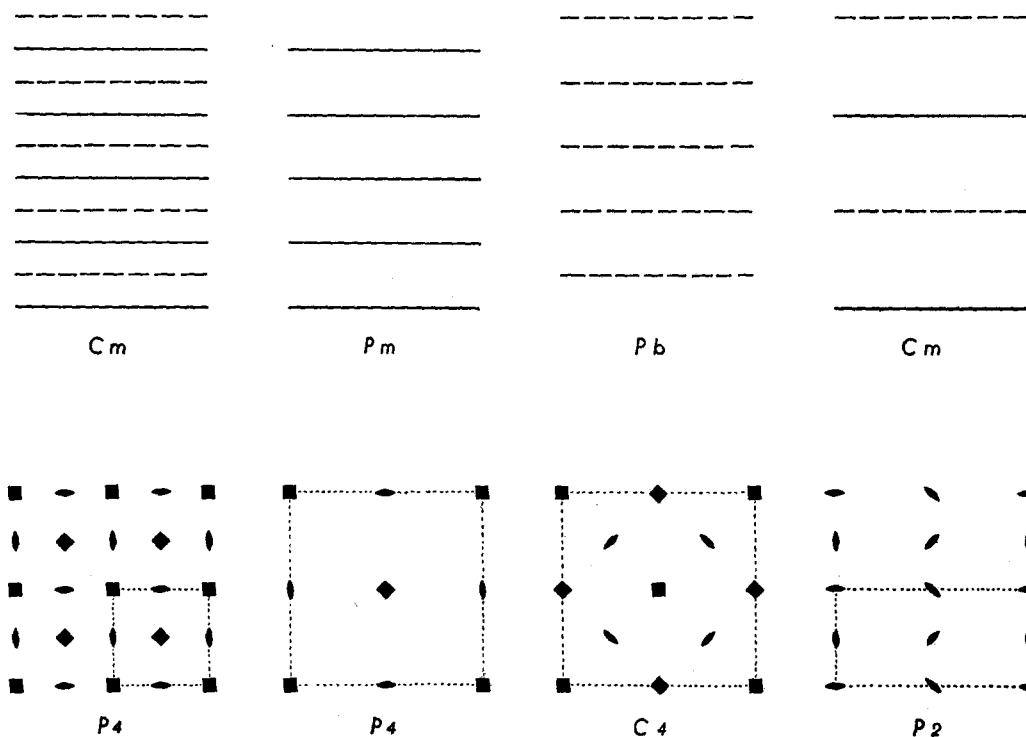


FIG. 4. Examples of derivative symmetries for the two basic symmetries, Cm and $P4$. In each case the basic symmetry is shown at the left. To the right of it are three examples of derivative symmetry.

Parallel to (010): The basic structure has a glide n . The only derivatives of a glide for translations ($2t_a; t_c$) is 1.

Parallel to (001): The basic structure has a glide n . The derivatives of a glide n for translations ($t_{a+b}; t_{a-b}$) are n and 1.

The derivatives of the symmetry planes are thus

$$\begin{array}{ccc} \parallel(100) & \parallel(010) & \parallel(001) \\ (m+b) & & n \\ \text{and 1} & 1 & \text{and 1.} \end{array} \quad (26)$$

By combining the derivatives of plane symmetry, (26), with the derivatives of axial symmetry, (25), there result the following possible derivative symmetries:

$C2/m 1 1$, and subgroups $C2 1 1$, $Cm 1 1$ } and $C1$.
 $C 1 1 2_1/n$ and subgroups $C1 1 2$, $C 1 1 n$ }

The symmetry $C1$ is inconsistent with the theory of substitution structures, discussed beyond. The remaining symmetries each determine two derivative structures differing in a manner similar to Figs. 3(b) and 3(c).

KINDS OF DERIVATIVE STRUCTURES

There are two distinct kinds of derivative structures. These are here designated *substitution structures* and *distortion structures*. The distinction between these can be illustrated by one-dimensional examples. Suppose the basic structure is a linear array of equally spaced atoms, A , thus:

$$A \quad A \quad A \quad A \quad A \quad A. \quad (27)$$

$\leftarrow t \rightarrow$

If another kind of atom, B , is substituted for every alternate atom A , there results:

$$A \quad B \quad A \quad B \quad A \quad B. \quad (28)$$

$\leftarrow t \rightarrow$

The substitution doubles the translation period, t . This is an instance of the suppression of a set of operations, thus leaving only a subgroup of operations, and therefore a derivative symmetry and a derivative structure, (28). The specific case of the operation of translation has been used for illustration, but obviously substitution can occur within any periodic operation, thus giving

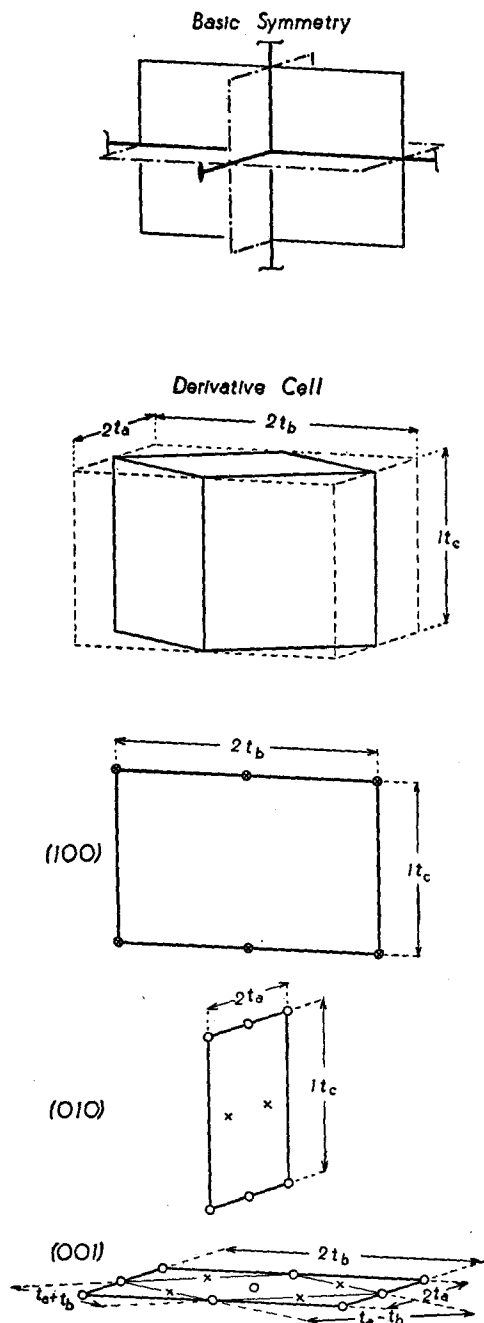


FIG. 5. Diagrams to illustrate the finding of the derivative symmetries of marcasite, FeS_2 , for a particular derivative cell. Open circles and x 's are reflection-equivalent points.

rise to derivative structures by substitution. Substitution structure may be regarded as formally including the case of structures with regularly arranged holes, by the device of substituting

holes for certain atoms A . Similarly the notion may be extended to include substitution of two or more atoms for a single atom, A .

The period of (27) can be multiplied by other means. Suppose alternate atoms A are slightly displaced by identical amount and direction, thus:

$$\begin{array}{ccccccc} A & A & & A & A & & A & A & . \end{array} \quad (29)$$

$\longleftrightarrow t$

Then the period of the array is again doubled. This amounts to a distortion of the basic structure, hence the designation *distortion structure*. Evidently such a structure can arise by the suppression of certain coincidence operations present in the basic structure; consequently a distortion structure is a derivative structure.

Substitution and distortion are obviously two different mechanisms for realizing the decreased symmetry of derivative structures. Consideration of these structures is important in many aspects of crystal relations.

SUBSTITUTION STRUCTURES

Kinds of Substitution Structures

If, for every series of like atoms, M , M , \dots in a crystal structure, there is substituted a sequence of unlike atoms, P , Q , \dots , then there results a new structure whose characteristics depend on the original symmetry relations between the M 's and also on how the substitution is effected. Depending upon these, the new structure may be one of several kinds:

I. If the original atoms, M , were related by any symmetry operation in the basic structure, then, depending on how the substitution is effected, two possible kinds of structures may result:

(a) If some regular plan is followed in substituting P , Q , \dots , for M , M , \dots , (Fig. 6(a)) as described in the last section, then some kind of alternation of P , Q , \dots , results. This necessarily suppresses the symmetry elements which carried one M atom into another. Such a structure may be called a *regular substitution structure* merely to distinguish it from the one which follows. Unless otherwise qualified, the term substitution structure will be taken to imply a regular substitution structure.

(b) If the unlike atoms, P , Q , \dots , are substi-

tuted for M, M, \dots without any plan or regularity, but at random, then the resulting substitution structure is in disorder with respect to the atoms P, Q, \dots . Such a structure is a *random substitution structure*. It has no true symmetry, for it lacks any periodicity in the repetition of P, Q, \dots . Insofar, however, as P, Q, \dots may together be regarded as statistically equivalent to the original M, M, \dots , the structure has periodicity. In this sense, it statistically has the exact symmetry of the basic structure.

(c) There is a possibility of a combination of the features of (a) and (b). For example, for the sequence of like atoms M, M, \dots there could be substituted the sequence $A, B, B, A, B, B, A, \dots$, where the B atoms may be either B' or B'' at random. While this kind of sequence has no true periodicity, it may be regarded as having, statistically, a symmetry controlled by the distribution of the similar A atoms.

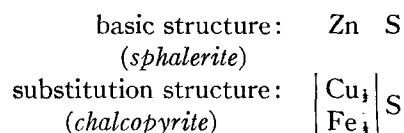
II. If the atoms M', M'', \dots are not equivalent by symmetry in the original structure (Fig. 6(b)), then the substitution of P, Q, \dots , for M', M'', \dots does not involve the suppression of any symmetry element of the crystal. An example of this is afforded by Fe_3O_4 . This crystal contains two structurally distinct kinds of Fe, so that its formula might well be written FeFe_2O_4 . In this case the replacement of the atoms FeFe_2 by MgAl_2 does not give rise to any loss of symmetry. MgAl_2 is not a "substitution" for FeFe_2 ; rather FeFe_2 is a degenerate case of MgAl_2 . This kind of "substitution" does not give rise to substitution structures in the sense here employed. Rather it gives rise to the non-degenerate case of a structure whose "basic" structure was degenerate.

Regular substitution structures constitute an important category of crystal structures. Recognition of the fact that an otherwise complicated structure is a substitution structure may become the key to its structural analysis. In order to handle such cases intelligently, the theory of regular substitution structures is briefly discussed below. Before entering into the theory, however, some examples will be given:

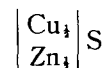
Examples of Substitution Structures

Mineralogy provides many structures which may be recognized as substitution structures. A

number are known which are based upon the sphalerite and wurtzite structures. The mineral chalcopyrite affords an example of a substitution structure based upon sphalerite. This may be brought out as follows:



In this case the Zn of the basic structure is replaced by half Cu and half Fe. The formula of chalcopyrite is customarily written CuFeS_2 , a form which tends to conceal the fact that it is a substitution structure based upon sphalerite, ZnS . The formula



brings out the relation to the basic structure, ZnS .

Substitution is by no means confined to half and half substitution. There are no restrictions on the proportions of the atoms entering into the substitution other than that they must be such as to fit into possible crystal structures. As an example of a more complicated substitu-

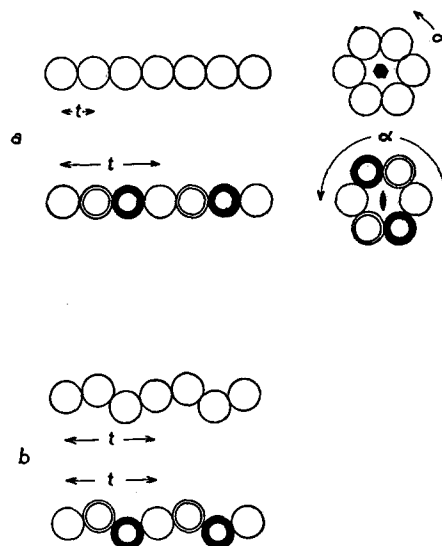
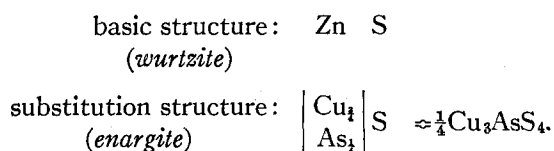
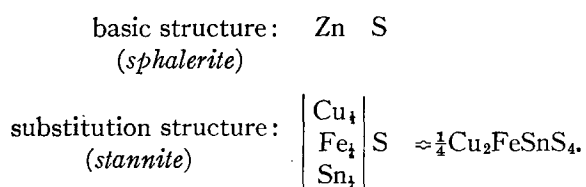


FIG. 6. In Fig. 6(a) is illustrated the increase in repetition period due to the regular substitution of unlike atoms for equivalent atoms. Figure 6(b) shows that this increase does not occur if the atoms in the basic structure are not equivalent. The translation repetition period is t , the angular repetition period is α .

tion there may be cited the structure formed by the substitution of Cu, Cu, Cu, As for Zn, Zn, Zn, Zn, in the basic wurtzite (ZnS) structure. This may be brought out with the following comparison:

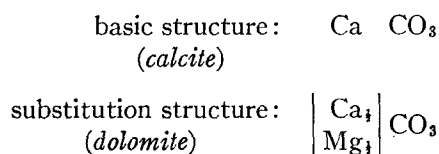


Furthermore, the substitution is not necessarily confined to substitution by two atoms. For example, stannite is a substitution structure based upon sphalerite in which the sequence Cu, Fe, Cu, Sn, is substituted for Zn, Zn, Zn, Zn, thus:

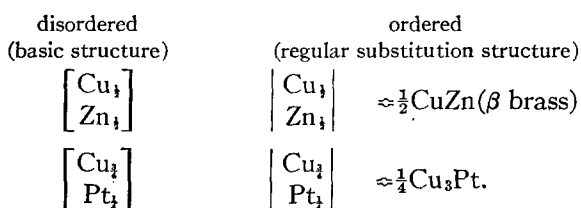


It appears likely that many apparently complex sulfosalt minerals will prove to have substitution structures based upon simple basic sulfide structures.

Many, but not all, double salts and other multiple salts have substitution structures. The double salt dolomite may be taken as an illustration. Its formula can be written as a double salt, $\text{CaCO}_3 \cdot \text{MgCO}_3$, or as $\text{CaMg}(\text{CO}_3)_2$. The relation to the calcite structure is brought out as follows:



Structures resulting from the ordering of disordered crystals (i.e., random substitution structures) are (regular) substitution structures. For example (notation taken from reference 6):



Cell Multiplicity of the Substitution Structure

A simple relation exists between the characteristics of the substitution and the size of the cell of the substitution structure. Let the volume of the cell of the substitution structure be m times the volume of the cell of the basic structure. Let the atom A , for which substitution is made, occupy an R -fold equipoint in the basic structure. Then in m cells there are mR atoms of A . In the substitution structure cell, the A atom occupies an r -fold equipoint. Thus r of the original mR atoms of A must remain if m cells are to be involved in the substitution. If F is the fraction of A remaining, then

$$F = r/mR. \quad (30)$$

It should be observed that since the group of operations carrying the A 's of r into each other is a subgroup of the operations carrying the A 's of R into each other, r cannot exceed R , nor can r be less than 1.

A useful form of (30) is

$$m = \frac{1}{F} \frac{r}{R} \left\{ \begin{array}{l} 1 \leq r \leq R \\ \text{or, } 1 > \frac{r}{R} > \frac{1}{R} \end{array} \right\}. \quad (31)$$

The maximum multiplicity, m , occurs when r/R is a maximum, namely 1. Therefore

$$m_{\max} = 1/F. \quad (32)$$

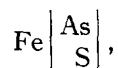
The minimum multiplicity, m , is 1. For this situation (30) becomes

$$F_{m=1} = r/R. \quad (33)$$

(In the above argument, it was assumed that the atoms A occupy one R -fold equipoint in the basic structure and that those remaining after substitution occupy one r -fold equipoint in the substitution structure. The argument remains valid if the atoms A occupy several R -fold equipoints in the basic structure and those remaining occupy several r -fold equipoints in the substitution structure, provided that in the above relations R is replaced by ΣR and r by Σr .)

These simple relations impose restrictions on substitution structures. To illustrate their use, suppose one wishes to know what maximum size cell could possibly come up for consideration in

a substitution structure of arsenopyrite,



derived from the basic structure FeS, marcasite. In this case half the S atoms are replaced by As atoms. Thus the fraction, F , of S atoms remaining is $\frac{1}{2}$. According to (32), $m_{\max} = 2$. Thus only cells having a multiplicity of 2 or less could exist having composition FeAsS and based upon the marcasite packing. Another characteristic of the substitution structure is the symmetry number, r , of the resulting space group. For this purpose, (30) may be solved for r . In this example, F was ascertained to be $\frac{1}{2}$. For marcasite, $R=4$ sulfur atoms per cell. For these values and $m=1$, (30) shows that $r=2$, and for $m=2$, $r=4$. Hence the derivative symmetries must have 2-fold equipoints if referred to a single cell or 4-fold equipoints if referred to a double cell. (This analysis eliminates the derivative symmetry $C1$ as determined above, since this space group has only 1-fold equipoints for a single (P) cell or 2-fold equipoints for a C -centered double cell.)

Thus for this substitution, only the following structure characteristics are possible

$$\text{I} \begin{cases} m=1 \\ r=2 \end{cases} \quad \text{II} \begin{cases} m=2 \\ r=4. \end{cases}$$

With the cell multiplicities, m , limited in this fashion, it is possible to write quickly the translation multiplicities of all possible substitution structures. For each of these, it is possible to pursue a derivative structure analysis of the type illustrated above under the heading "Derivatives for a Particular Cell." Therefore for a given substitution, all possible structures can be predicted. This procedure is an aid in the crystal analysis of structures which can be recognized as substitution structures.

DISTORTION STRUCTURES

The relation of distortion to basic structure is known to occur in two different ways:

(1) The atoms in two different kinds of crystals may be arranged in essentially the same way, yet differ in some slight detail. The result may be that one is the distortion equivalent of the

other. An example of this is afforded by the pair:

basic structure	distortion structure
PtS	CuO
(<i>Cooperite</i>)	(<i>Tenorite</i>)

Symmetry: $P4_2/m\ 2/m\ 2/c$ $C2/c$.

Both of these structures have square coordinated metals, tetrahedrally coordinated non-metals, and the structures are similarly linked. The CuO structure is, in effect, a slumped PtS structure. The derivative relation of the CuO structure to the PtS structure would be suspected by the comparable formulae, comparable cells and cell content, and derivative symmetry.

(2) Many rapid (*high-low*) inversions are polymorphic transformations from basic structure (high temperature, low pressure) to distortion structure (low temperature, high pressure). Good examples are afforded by the high-low inversions of quartz and cristobalite (in these examples, $m=1$):

	basic structure (high-T form)	distortion structure (low-T form)
quartz	$H6_2\ 2$	$H3_1\ 2$
cristobalite	$F4_1/d\ \bar{3}\ 2/m$	$P4_1\ 2_1$

The derivative natures of the low temperature structures are evident from the symmetries.

Distortion structures may be formally treated as substitution structures by the device of substituting distorted structure complexes for the undistorted complexes.

APPLICATIONS OF DERIVATIVE STRUCTURE THEORY

In this paper the elements of derivative structure theory and substitution structure theory have been presented. These relations are useful in several branches of crystallography. A few instances where they have been applied by the writer are mentioned below:

It is not generally possible to determine the space group symmetry of a crystal by qualitative x-ray means, although the crystal can be assigned to a diffraction group³ usually embracing several space groups. Between the space groups of this set one cannot decide by the methods of ordinary

³ M. J. Buerger, *X-Ray Crystallography* (John Wiley and Sons, New York, 1942), pp. 510-511.

qualitative x-ray crystallography. If, however, the crystal has a high-low inversion, the symmetries of the high form and low form are connected by derivative structure theory which restricts the symmetry possibilities for both forms. With the aid of this additional relation, it has been possible to determine the space groups of both⁴ high-Cu₂S and low-Cu₂S.

Derivative structure theory provides a basis for understanding certain varieties of twinning,⁵ particularly twinning which is the result of inversion. The number and orientation of the twins which descend by inversion from the high temperature form are readily provided⁵ by derivative structure theory. The results are appli-

cable to high-low inversions as well as to inversions due to ordering⁶ of a disordered structure.

For the special case of derivative structures which are substitution structures, the theory outlined under "Substitution Structures" permits one to predict, within a comparatively small group, the structures to be expected as the result of any given kind of substitution in any desired structure. In popular language, this enables one to predict the kinds of "superstructures" which could conceivably result from a selected substitution.

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⁴ M. J. Buerger and Newton W. Buerger, "Low-chalcocite and high-chalcocite," *Am. Mineral.* **29**, 55-65 (1944).

⁵ M. J. Buerger, "The genesis of twin crystals," *Am. Mineral.* **30**, 469-482 (1945).

⁶ M. J. Buerger, "The temperature-structure-composition behavior of certain crystals," *Proc. Nat. Acad. Sci.* **20**, 444-453 (1934).