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# Translation-Permutation Operator Algebra for the Description of Crystal Structures. I. Ideal Closest Packing

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The foundation of an abstract algebra for the description of crystal structures is developed in terms of ideally closest-packed structures. All the spatial information of closest-packed structures can be derived in terms of (*a*) the geometry of the atoms (*A* positions) and the plane, triangular interstices (*B* and *C* positions) of a closest-packed *p*6*mm* monolayer, and (*b*) the permutations induced among these *A*, *B*, and *C* positions by translations from one monolayer midplane to another. The mathematical device used to correlate this information is a translation-permutation vector operator. Since this operator is closely related to the basic concept of a layer-by-layer crystal growth process, the algebra is readily extensible to crystal structures that are defective owing to many kinds of non-periodic elements of structure. Some examples are presented of the application of the algebra to closest-packed structures that are either ideal or exhibit one of two kinds of defect: classical stacking faults or point defects.

## 1. Introduction

An algebra for the description of crystal structures is herein presented which has its axiomatic foundation based upon a concept that is central to the general ideas concerning crystal growth: namely that crystals grow by the successive laying down of new layers of atoms upon the underlying substrate. The present paper, which is the first of a planned series of papers, lays the foundation of the algebra and is restricted to the case of ideal closest packing. In later papers it is planned to extend the algebra to cover both increasingly greater deviations from ideal closest packing and non-periodic elements of structure such as dislocations.

One aim of the algebra is to meet an increasingly greater need, in the field of crystal physics calculations, for the description of highly defective solids in a natural mathematical fashion. Another aim is to serve a heuristic purpose by exposing the logical foundations of complicated crystal structures so that interrelationships between structures can be discovered and useful modifications of known structures suggested.

Although the outward form of the present algebra is quite distinct from the modular crystal algebra of Loeb (1958, 1962) and Morris & Loeb (1960), the two algebras can be shown to be mathematically isomorphic. However, the present algebra has certain advantages in the ease of treatment of non-ideal and defective crystals, particularly those with non-periodic elements of structure.

## 2. The closest-packed monolayer and the fundamental generating operation of closest packing

Infinite, three-dimensional arrays of closest-packed spheres can be described in terms of the *closest-packed monolayer* and a *generating operation* by means of which the monolayers are combined. A closest-packed monolayer is a planar array of rigid spheres of equal size that are packed together as densely as possible with each sphere tangentially contacting six other spheres and with the centers of the rigid spheres defining the two-dimensional space group *p*6*mm*. The fundamental generating operation of closest packing is the physical operation of placing one closest-packed monolayer in contact with another monolayer in as close a fashion as possible, *i.e.* so that the atoms of each monolayer lie in the triangular hollows of the adjacent monolayer and tangentially contact three of its atoms (*cf.* Patterson & Kasper, 1959).

## 3. The coordinate systems

It is convenient to use simultaneously both a hexagonal coordinate system ($a_1, a_2, c$) and a cartesian coordinate system ($x, y, z$) with a common origin at the center of a closest-packed atom, coincident $a_2$ and $y$ axes, and coincident $c$ and $z$ axes (Fig. 1). The unit of distance along the $a_1, a_2, x, y$, and $z$ axes is taken as $2r_{\text{cp}}$, where $r_{\text{cp}}$ is the radius of the closest-packed spheres. However, it is useful to use a different unit of distance along the $c$ axis, namely $t_c=\sqrt{\frac{8}{3}}\cdot r_{\text{cp}}=1\cdot6330r_{\text{cp}}$ which is the minimum separation distance between the midplanes of ideally closest-packed monolayers; thus $z$ and $c$ coordinate readings are related by the equation $z=\sqrt{\frac{2}{3}}\cdot c$.

## 4. Definition of the *A*, *B*, and *C* positions

Three types of position within the closest-packed monolayer, the *A*, *B*, and *C* positions (Fig. 1), are used as the basis for the notational system of the algebra developed in the present paper. The center

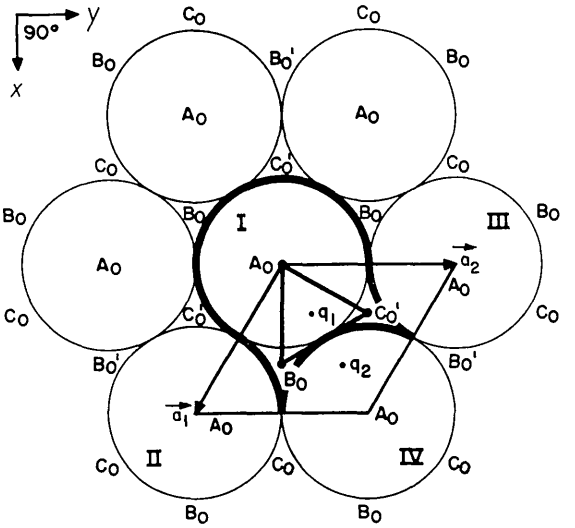

Fig. 1. Illustration of: (*a*) the distribution of the $A, B, C$ positions of the closest packed *reference* monolayer with $c=z=0$ (denoted by the 0-subscripts); (*b*) the correlation of the $x$, $y$ and $a_1$, $a_2$ axes; and (*c*) the intersection of the TPO unit cell with the midplane of the reference monolayer (heavy curved line).

of each closest-packed sphere is defined as an $A$ position. If the curved triangular interstices are considered as two-dimensional arrowheads, the centers of those plane triangular interstices which point in the positive $x$ direction are defined as $B$ positions, and the centers of those plane triangular interstices which point in the negative $x$ direction are defined as $C$ positions.

## 5. Abstract algebra of the TPO; reduction to a simplified notation; unit TPO; symmetry operations of the TPO

Infinite, three-dimensional arrays of closest-packed spheres are built up by successive applications of the fundamental generating operation described in § 2. Each time the generating operation is applied a translation is effected from one monolayer midplane to the next and a definite permutative relationship exists between the $A$, $B$, $C$ positions of the newest monolayer added to the stack and the $A$, $B$, $C$ positions of all the previous monolayers in the stack. By keeping track of the permutative relationships between the $A$, $B$, $C$ positions of the separate monolayers the present algebra leads to a simple description of all the spatial properties of ideal closest packing.

The correlations of the $A$, $B$, $C$, positions of different monolayers are stated in terms of translation-permutation vector operators denoted by the symbol:

$$\mathrm{TPO} = \{P \mid \mathbf{T}_c\},^* \tag{1}$$

where $\mathbf{T}_c$ is a mathematical translation operator acting in the $c$ direction, $P$ is a permutation operator representing the permutation induced by the overall translation operation, and TPO is an abbreviation for the full name 'translation-permutation operator'. These operators are of three types:

$$\{I \mid (n-m)t_c\}(A, B, C)_m=(A, B, C)_n\,, \tag{2}$$

$$\{R \mid (n-m)t_c\}(A, B, C)_m=(B, C, A)_n\,, \tag{3}$$

$$\{L \mid (n-m)t_c\}(A, B, C)_m=(C, A, B)_n \tag{4}$$

where $t_c$ is the magnitude of the unit translation vector parallel to the $c$ axis, $n$ and $m$ are integral values of the $c$ coordinate, and $I, R, L$ are the three possible choices of $P$. Multiplication of TP-operators is carried out by vector addition of the $\mathbf{T}_c$ operators and by permutation multiplication of the $P$ operators:

$$\{P \mid (n-m)t_c\}\{P' \mid (p-n)t_c\}=\{PP' \mid (p-m)t_c\}\,. \tag{5}$$

Equation (5) holds regardless of the algebraic magnitude of the $c$ coordinates $m$, $n$, $p$, but, without any loss of generality, it will be assumed that the TPO all act in the positive $z$ direction and that $m \le n \le p$, with the exceptions of inverse and horizontally reflected TP-operators where $m \ge n \ge p$. Hence, unless otherwise specified, *left-to-right* in the TPO formulae corresponds to the *positive c direction* in the crystal structures.

It is convenient to indicate the magnitude of the translation by the use of subscripts and thus redefine (2), (3), (4) as (6), (7), (8) respectively; thus:

$$I_{mn} = (A_mA_n, B_mB_n, C_mC_n) = ((A)(B)(C))_{mn}\,, \tag{6}$$

$$R_{mn} = (A_mB_n, B_mC_n, C_mA_n) = (ABC)_{mn}\,, \tag{7}$$

$$L_{mn} = (A_mC_n, C_mB_n, B_mA_n) = (ACB)_{mn}\,, \tag{8}$$

where the letter couples, $X_mX_n$, are entities, directed parallel to the $c$ axis, called *permutation subvectors* which connect the positions $X_m$ ($X=A$, $B$, or $C$) of the monolayer midplane with $c$ coordinate $c=m$ with the positions $X_n$ of the monolayer midplane at $c=n$. The permutation subvectors differ from true vectors in that subvector addition,

$$X_mX_n+X_nX_p=X_mX_p\,, \tag{9}$$

is not commutative in general since the starting position $X_n$ of the subvector $X_nX_p$ must be identical with the terminating position $X_n$ of the subvector $X_mX_n$. The combinations of three subvectors in the middle terms of equations (6), (7), (8) further differ from true vectors in that their subvectors do not emanate from a common origin as do ordinary vector components but instead are all parallel to the $z$ axis; hence these subvector-combinations are called *permutation pseudovectors*.

Unit TPO are defined by setting $n=m+1$ in equations (6), (7), (8). However, of the nine subvectors

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* This notation has been adapted from a rotation–translation operator notation first suggested by Seitz (1934, 1935, 1936) and recently used by Koster (1957).

in those equations, the three in equation (6) are forbidden for the case $n=m+1$ by the definition of closest packing in § 2; *i.e.* the identity operator $I_{mn}$ is defined for $n=m$ and for $n \geq m+2$ but not for $n=m+1$. In the case of the unit TPO it is convenient to eliminate the subscripts except where they are necessary as in the case of inverse and horizontally reflected unit TPO. This permits a final simplification of the formulae for the two possible types of unit TPO to:

$$R = (AB, BC, CA) = (ABC)\,, \qquad (10)$$

$$L = (AC, CB, BA) = (ACB)\,. \qquad (11)$$

The algebra of the TP-operators is a mathematical group with many (but not all) of the properties of a one-dimensional vector group of infinite order under vector addition. The group multiplication table is shown in Table 1.

Table 1. TPO *group multiplication table*

| | $I_{np}$ | $R_{np}$ | $L_{np}$ |
|---|---|---|---|
| $I_{mn}$ | $I_{mp}$ | $R_{mp}$ | $L_{mp}$ |
| $R_{mn}$ | $R_{mp}$ | $L_{mp}$ | $I_{mp}$ |
| $L_{mn}$ | $L_{mp}$ | $I_{mp}$ | $R_{mp}$ |

A complication arises with respect to the uniqueness of the group elements for $n \geq m+6$ due to the onset of isomerism (see § 6). To insure the well-behaved nature of the TPO group it is necessary that a group element $Y_{m,m+k}$ ($Y=I$, $R$, or $L$; $k=$ a positive integer) be considered as a *sum* of $k$ unit TPO and not as a single TPO of magnitude $kt_c$. However, for some usages, *e.g.* stating the correlations between widely separated planes without regard to the intervening structure, it is convenient to set rigor on the side and consider the TPO vector to have the magnitude $kt_c$.

A second restriction must be placed on the TPO formulae for the purpose of defining crystallographic unit cells. In order to limit the TPO group to a single structure in a given discussion it is necessary to specify both the sequence of unit TPO and the number, $N$, of unit TPO in the crystallographic repeat unit of the given structure. The result is a periodic group of infinite order with a period $N$.

It is important to note the difference in the physical effect of taking the inverse of a TPO and the effect of two other symmetry operations, namely rotation of the TPO by 60° about the $c$ axis, $\mathscr{C}$ (60°), and horizontal reflection of the TPO in the $xy$ plane, $\sigma_h$. The physical effect of these three symmetry operations is compared and summarized in Table 2 for both a general and a unit TPO, where an $R$ TPO has been arbitrarily chosen as the operand.

Table 2. *Symmetry operations of the* TPO

| | |
|---|---|
| $(R_{mn})^{-1} = L_{nm}$ | $(R_{01})^{-1} = L_{10}$ |
| $\mathscr{C}(60°)R_{mn} = L_{mn}$ | $\mathscr{C}(60°)R_{01} = L_{01}$ |
| $\sigma_h R_{mn} = R_{-m,-n}$ | $\sigma_h R_{01} = R_{0,-1}$ |

## 6. Atom lattices

Closest-packed atom lattices are simply represented by TPO formulae which consist of sequences of unit TPO. Since these unit TPO can have one of only two possible values, $R$ or $L$, the resulting formulae are directly related to the classification scheme developed by Zhdanov (1945) and later extended by Patterson & Kasper (1959).*

A sequence of $k$ unit TPO ($k$ an integer) represents a crystallographic unit cell if the group product of the given sequence of $R$ and $L$ unit TPO is an identity element of either the form $I_{m,m+k}$ or $I_{m,m+3k}$ (*i.e.* either $N=k$ or $N=3k$). The former form holds if $(n_R - n_L) \equiv 0$ (modulo 3) and the latter form holds if $(n_R - n_L) \not\equiv 0$ (modulo 3), where $n_R$ and $n_L$ are the numbers of $R$ and $L$ unit TPO respectively in the overall TPO formula and $n_R + n_L = k$.

As representative examples the cases $1 \leq k \leq 6$ are listed in Table 3 where for simplicity $m$ has been set equal to zero. $I_{01}$ is of course forbidden by the definition of closest packing in § 2. $I_{02}, I_{03}, I_{04}$ and $I_{05}$ represent unique structures, but the case $k=6$ exhibits a structural isomerism, $I_{06}(1)$ and $I_{06}(2)$, a phenomenon which will be quite prevalent for $k \geq 6$.

Use was purposely made of the letters $A, B, C$ in the present notation since it contains and, in fact, defines the classic three-letter *layer notation* using the same letters. However, to insure clarity in the

Table 3. *Closest-packed unit cells,* $I_{m,m+k}$ $(1 \leq k \leq 6)$

| | | |
|---|---|---|
| $I_{01}$ | is forbidden by the definition of closest packing | |
| $I_{02}$ | $= RL$ | $= (ABC)(ACB) =$ h.c.p.<br>$= (A_0B_1A_2,\ B_0C_1B_2,\ C_0A_1C_2)$ |
| $I_{03}$ | $= RRR$ | $= (ABC)(ABC)(ABC) =$ c.c.p.<br>$= (A_0B_1C_2A_3,\ B_0C_1A_2B_3,\ C_0A_1B_2C_3)$ |
| $I_{04}$ | $= RRLL$ | $= (ABC)(ABC)(ACB)(ACB)$<br>$=$ double-hexagonal c.p.<br>$= (A_0B_1C_2B_3A_4,\ B_0C_1A_2C_3B_4,\ C_0A_1B_2A_3C_4)$ |
| $I_{05}$ | $= RRRRL$ | $= (ABC)(ABC)(ABC)(ABC)(ACB)$<br>$= (A_0B_1C_2A_3B_4A_5,\ B_0C_1A_2B_3C_4B_5,$<br>$C_0A_1B_2C_3A_4C_5)$ |
| $I_{06}(1)$ | $= RRRLLL$ | $= (ABC)(ABC)(ABC)(ACB)(ACB)(ACB)$<br>$= (A_0B_1C_2A_3C_4B_5A_6,\ B_0C_1A_2B_3A_4C_5B_6,$<br>$C_0A_1B_2C_3B_4A_5C_6)$ |
| $I_{06}(2)$ | $= RRLLRL$ | $= (ABC)(ABC)(ACB)(ACB)(ABC)(ACB)$<br>$= (A_0B_1C_2B_3A_4B_5A_6,\ B_0C_1A_2C_3B_4C_5B_6,$<br>$C_0A_1B_2A_3C_4A_5C_6)$ |

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* It should be noted that the $+$, $-$ symbols of Patterson & Kasper have a one-to-one relationship respectively to the present $L, R$ symbols for closest-packed double layers, but that Zhdanov's $c, h$ symbols refer to a triple layer, *i.e.* his $c=RR=LL$ and his $h=RL=LR$. Thus if one applies the physical meaning of Zhdanov's $c, h$ symbols in terms of $R$ and $L$ unit TPO to his sequential formulae, the correlation of his formal formulae with physical structures is destroyed; *e.g.* 3113 in the $c, h$ notation implies space group $F\bar{6}m2$ but actually corresponds to the real structure 4211 of space group $R3m$. However, Zhdanov's tables are correct since they only make use of the twofold aspect of his definitions and not their physical meaning (Gehman, 1963*a*).

mathematical formulae, the $c$ coordinate of *monolayer positions* will be indicated by subscripts, *e.g.* $A_n$, $B_n$, $C_n$, for a layer at $c=n$, but the $c$ coordinate of the *layer* will be indicated in parentheses, *e.g.* $B(n)$ for a $B$ layer at $c=n$. The reference monolayer is arbitrarily defined as an $A$ layer, $A(0)$, in both notations. Then, an $A(m)$ layer is one which has its atom centers or $A_m$ positions directly above the $A_0$ positions (in the sense of a projection parallel to the $c$ axis); thus $A(m) \equiv I_{0m}$. A $B(n)$ layer has its $A_n$ positions over $B_0$ positions; thus, using equation (8), $B(n) \equiv L_{0n}$. Similarly, a $C(p)$ layer is defined as $C(p) \equiv R_{0p}$. In these definitions $m \neq 1$, *i.e.* $AA$ subvectors are forbidden, and, in a given structure, $m \neq n \neq p$.

## 7. Interstice lattices

Interstice lattices are defined by the closest-packed atom lattices. For many crystal physics considerations, *e.g.* the ordering of the cations in spinel (Verwey & Heilmann, 1947; Verwey, Haayman & Romeijn, 1947), it is convenient for a first approximation to separate the physics of the interstice lattices completely from the physics of the closest-packed atom lattice, and to allow the interactions between the two lattices to enter only at a higher stage of approximation.

In two dimensions there is one lattice of the $B$ positions and one of the $C$ positions. Spatially, these two interstice lattices are exactly equivalent to the defining atom lattice but are respectively displaced from it by translations of $\pm\sqrt{\frac{4}{3}}\cdot r_{\text{cp}}$ parallel to the $x$ axis (Gehman, 1961).

In three dimensions, lattices of the familiar octahedral and tetrahedral interstices (abbreviated as oct. and tet. respectively) arise. The octahedral interstices are represented in the TPO algebra by unit interstice-interstice permutation subvectors of the form $BC$ and $CB$, and the tetrahedral interstices by unit atom-interstice subvectors of the form $AB$, $AC$, $BA$, and $CA$. The tetrahedral interstices can be further subdivided into two subclasses according as the atom ($A$ position) lies below or above the plane triangular interstice ($B$ or $C$ position); thus $AB$ and $AC$ represent negative tetrahedral interstices, $(-)$-tet., and $BA$ and $CA$ represent positive tetrahedral interstices, $(+)$-tet.[*]

The $c$ coordinate of the plane of the centers of the three types of three-dimensional interstices, between the two midplanes at $c=n$ and $c=n+1$, is $(n+\frac{1}{4})$ for $(+)$-tet., $(n+\frac{1}{2})$ for oct., and $(n+\frac{3}{4})$ for $(-)$-tet.

The identification of the three-dimensional interstices with the unit permutation subvectors permits a simple verification of the following stoichiometric ratio rules:

$$n_{\text{cp}}:n_{\text{tet}}:n_{\text{oct}}=1:2:1\ , \tag{12}$$

$$n_{\text{cp}}=n_{(+)\text{-tet}}=n_{(-)\text{-tet}}=n_{\text{oct}}\ , \tag{13}$$

where $n_{\text{cp}}$, $n_{\text{oct}}$, $n_{(+)\text{-tet}}$, and $n_{(-)\text{-tet}}$ stand for the numbers of closest-packed atoms, octahedral interstices, positive tetrahedral interstices, and negative tetrahedral interstices respectively, and where $n_{\text{tet}}=n_{(+)\text{-tet}}+n_{(-)\text{-tet}}$. The rules follow by inspection of either of the unit TPO definitions, equations (10) and (11), in which it should be noted that the $A$ positions represent crystallographic half-atoms.

An obvious extension of the present notation permits a classification of the interstice layers as $A, B, C$ layers, as can be seen by subdividing a unit TPO into *fractional* TPO as follows:

$$L_{01} = L_{0,\frac{1}{4}}L_{\frac{1}{4},\frac{1}{2}}L_{\frac{1}{2},\frac{3}{4}}L_{\frac{3}{4},1}\ , \tag{14}$$

or

$$R_{01} = R_{0,\frac{1}{4}}R_{\frac{1}{4},\frac{1}{2}}R_{\frac{1}{2},\frac{3}{4}}R_{\frac{3}{4},1}\ . \tag{15}$$

It also follows from (14) and (15) that the $(+)$-tet. and $(-)$-tet. space lattices are individually identical with the closest-packed atom lattice but are displaced from it along the $c$ axis by $\mp\frac{3}{4}t_c$ respectively. However, the octahedral interstice lattice is the same as the closest-packed atom lattice only for the single case of c.c.p. All other closest-packed lattices have at least one $RL$ or $LR$ pair of adjacent unit TPO in their TPO formulae which implies an adjacent pair of octahedral interstices parallel to the $c$ axis (see $I_{02}$ in Table 3), and this configuration cannot be matched by closest-packed atoms.

## 8. Information content of the TPO; geometrical display form

An important feature of the TPO crystal algebra is that, as the algebraic TPO formula for a given structure is being generated by writing down a sequence of $R$ and $L$ unit TPO, all of the crystallographic information of the structure is simultaneously generated and stored in the final TPO formula. As examples, consider the cases of h.c.p., c.c.p., and double hexagonal closest packing. From Table 3 it follows that the number of crystallographic layers in the repeat units are 2, 3, and 4 respectively for these structures since their permutation subvectors contain 3, 4 and 5 letter symbols respectively. Table 3 also contains the well known information that the atoms are contained in single equivalent sets in h.c.p. and c.c.p., but are contained in two distinct sets in the double hexagonal case. This can be readily seen by considering the stoichiometric ratios, $n_{\text{cp}}:n_{\text{tet}}:n_{\text{oct}}$, of the individual subvectors which differ in the three structures. All the atoms ($A$ positions) lie on three equivalent subvectors in c.c.p., and in h.c.p. the atoms lie on only two subvectors (those starting at $A_0$ and $C_0$) that are equivalent to each other but which differ from the third subvector which contains octahedral interstices exclusively. But in the double hexagonal case the atoms lie in two separate sets: one set in the subvector starting at $C_0$ which contains only atoms and tetrahedral interstices, and the other set in the

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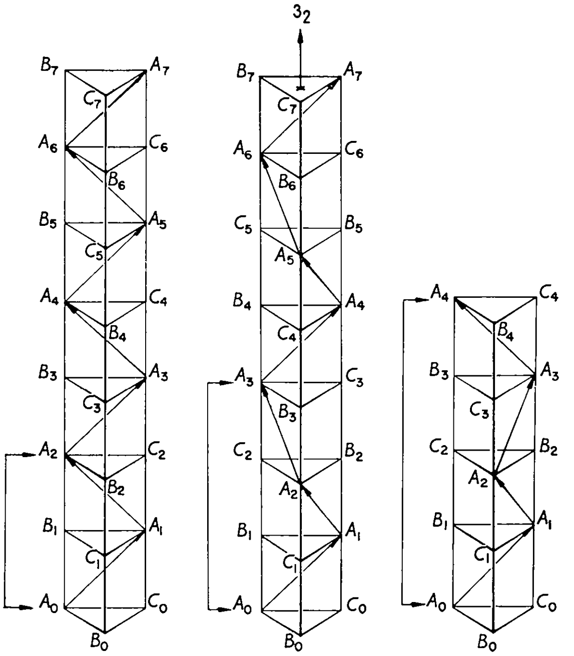
[*] *N.B.* The $B$ and $C$ position are distinguished by direction along the $x$ axis whereas the $(-)$-tet. and $(+)$-tet. interstices are distinguished by direction along the $z$ axis.

two remaining subvectors which also contain octahedral interstices.

The information content of the TPO formulation can be made even more graphic by converting the linear display forms of Table 3 to *geometrical display forms* such as those illustrated in Fig. 2. The trigonal columns are constructed by arranging the three permutation subvectors, of the overall permutation pseudovector of the given structure, in a parallel fashion, their $c=0$ positions being located at the apices of the triangle of $A_0$, $B_0$, $C_0'$ positions illustrated in heavy outline in Fig. 1.



h.c.p. = *RL*... c.c.p. = *RRR*... Double hexagonal = *RRLL*...

Fig. 2. Geometrical display forms of the TPO for h.c.p., c.c.p., and double hexagonal closest packing. Double headed arrows indicate the crystallographic repeat unit, and the *AA skew vectors* connect adjacent *A* positions (travelling upward).

In Fig. 2 a single crystallographic repeat unit of double hexagonal closest packing is illustrated but 7/2 and 7/3 of repeat units are illustrated in the case of h.c.p. and c.c.p. respectively in order to show the coincidence of certain double layers in the three structures. For example, all three structures have identical pairs of monolayers and interleaved planes of octahedral and tetrahedral interstices for $c$ coordinates of $c=0, 1$; h.c.p. and c.c.p. next have identical double layers at $c=6, 7$; h.c.p. and double hexagonal next have identical double layers at $c=3, 4$; and c.c.p. and double hexagonal would next have identical double layers at $c=12, 13$.

It is interesting to consider the connectivity of the atoms ($A$ positions) along the TPO vector. This can most easily be done in terms of entities that are called *AA skew vectors* since they are necessarily skewed with respect to the $c$ axis. In Fig. 2 a difference in the atom types in h.c.p. and c.c.p. can be established by noting that each atom connects two $AA$ skew vectors that always lie in the *same* face of the trigonal column in h.c.p., but which always lie in *adjacent* faces in c.c.p. This difference also demonstrates the existence of two sets of equivalent atoms in double hexagonal closest packing since half of the atoms are of the h.c.p. type and the other half of the c.c.p. type.

The $AA$ skew vectors illustrate an interesting anti-parity property since they spiral around the $RRR$ = c.c.p. column in Fig. 2 like a left-handed screw ($LLL$ leads to a right-handed spiral). Algebraically, this anti-parity is illustrated by the $I_{03}$ = c.c.p. case in Table 3 where a sequence of $R=(ABC)$ unit TPO leads to an $ACBA$ sequence of layers which is left-handed from a permutation viewpoint. It should be emphasized that this anti-parity property is a fundamental characteristic of closest packing and not a peculiarity of the TPO algebra that might be removed by a different formulation.

The $AA$ skew vectors can be extended linearly to infinity only in the single case of c.c.p. where they define the $\langle 110 \rangle$ directions. This can be seen from Fig. 1 where it should be noted that the three extended skew vectors, $\dots A_0A_1A_2\dots$, that pass through the origin have their $c=1$ and $c=2$ positions directly above the $C_0'$ and $B_0'$ positions respectively. This is the TPO statement of the existence of a center-of-symmetry in c.c.p.

Fig. 2. also shows that both h.c.p. and double hexagonal closest packing possess mirror planes of symmetry: for all integral values of the $c$ coordinate, $n$, in the h.c.p. case, but only for even values of $n$ in the $RRLL$ double hexagonal case. Finally, in h.c.p., the subvector starting at $B_0$ in Fig. 2 clearly shows that the planar $p6mm$ lattice of the octahedral interstices can form a *simple* hexagonal lattice when extended to three-dimensions.

## 9. Standard ionic crystal structures

The standard ionic crystal structures are defined as those structures which have either a cubic or hexagonal closest-packed structure of large atoms (usually anions) and which have the individual planes of octahedral and tetrahedral interstices either completely filled by small atoms (usually cations) or completely empty (Gehman, 1963*b*). This gives rise to the ten structures listed in Table 4, where the three digital entries in parentheses after each unit TPO represent the complete occupancy or non-occupancy, 1 or 0 respectively, of the (+)-tet., oct., and (−)-tet. interstice-layers respectively. In the $CdX_2$ and ZnS TPO formulae, changing the *or* to *and* mixes the two possibilities together and leads to the concept of interstice lattice stacking faults which is the subject of part II of this series.

In writing a FORTRAN computer program for the calculation of a given solid state property of the standard crystal structures, the meaning of the $R$ and $L$ unit TPO would be defined in terms of the coordinate translations (as listed by Patterson & Kasper, 1959, Table 7.1.5A) and any other parameters of interest would also be defined. Then the high-speed computer would be instructed to generate the standard crystal structure of interest by entering-in the appropriate instruction from Table 4.

Table 4. TPO *representation of the standard crystal structures for a high-speed electronic computer program*

c.c.p.:

$Li_3Bi$ = $L(111)L(111)L(111)$
NaCl = $L(010)L(010)L(010)$
$CdCl_2$ = $L(010)L(000)L(010)L(000)L(010)L(000)$ *or* $L(000)L(010)L(000)L(010)L(000)L(010)$
$Li_2O$ = $L(101)L(101)L(101)$
ZnS = $L(100)L(100)L(100)$ *or* $L(001)L(001)L(001)$

h.c.p.:

hex-$Li_3Bi$ = $L(111)R(111)$
NiAs = $L(010)R(010)$
$CdI_2$ = $L(010)R(000)$ *or* $L(000)R(010)$
hex-$Li_2O$ = $L(101)R(101)$
ZnS = $L(100)R(100)$ *or* $L(001)R(001)$

## 10. TPO containing a multiplicity of permutation pseudovectors; TPO unit cells

In Table 4, a single permutation pseudovector per TPO is sufficient since the layers of interstices are either completely empty or completely full in the standard ionic crystal structures. However, in the case of many important crystal structures the interstice layers are only *partially* occupied, *e.g.* $\alpha$-$Al_2O_3$ has its layers of octahedral interstices only two-thirds occupied by Al ions. Partial occupancy by a given type of atom can even occur in the closest-packed atom monolayers, *e.g.* the perovskite structure of $KMgF_3$ has its closest-packed monolayers made up of K and F ions in a 1:3 proportion (Wells, 1962). The TPO formulae for such structures necessarily contain more than one permutation pseudovector. For example, in spinel, four pseudovectors, I, II, III, IV, are required in the TPO formula, as shown in formula (16):

$$\begin{aligned}
&\text{I. } R(001)R(000)R(100)R(010)R(010)R(010)\\
&\text{II. } R(100)R(010)R(010)R(010)R(001)R(000)\\
&\text{III. } R(010)R(010)R(001)R(000)R(100)R(010)\\
&\text{IV. } R(000)R(010)R(000)R(010)R(000)R(010)\,. \qquad (16)
\end{aligned}$$

The $A$ positions of the reference monolayer are clustered in the arrangement indicated by the roman numerals I through IV in Fig. 1 which requires that the hexagonal unit cell in Fig. 1 must have its edges doubled in the $a_1$ and $a_2$ directions. In general, the *multiplicity*, or the number of permutation pseudovectors required in the TPO formula, *is equal to the highest common denominator of the occupation-fractions of the layers of interstices*.

The repeat units of the trigonal columns in Fig. 2 are not crystallographic unit cells by themselves, but they do represent a construct that forms a true unit cell with respect to translation along the $a_1$, $a_2$, $c$ axes for TPO containing a single permutation pseudovector. This construct ($a$) has its surface made up of portions of the surfaces of closest packed atoms, octahedral interstices, and tetrahedral interstices, and ($b$) its intersection with the midplane of the reference monolayer at $c=0$ is shown by the heaviest line in Fig. 1 which outlines a single complete set of $A$, $B$, $C$ positions (equal to one full circle and two full, plane triangular interstices).

## 11. Surface TPO

Surface, TPO, $S$, are defined for the purpose of representing the abrupt termination of crystal periodicity that occurs at a crystal surface. These TPO which can be used to 'cap' ordinary TPO formulae represent infinite, two-dimensional planes of hemispherical *half-atoms* plus sites analogous to the ordinary (+)-tet., oct., and (−)-tet. interstices. An example of their use arises in connection with the crystal polarity of ZnS-like structures which have chemically and physically distinguishable closest-packed surfaces at each end of the crystal, *e.g.* (111) *versus* $(\bar{1}\bar{1}\bar{1})$ in c.c.p. and (0001) *versus* $(000\bar{1})$ in h.c.p. (Gatos & Lavine, 1960; Warekois, Lavine, Mariano & Gatos, 1962). Thus the TPO formulae for sphalerite in Table 4 can be rewritten as follows:

$$(000)SL(100)L(100)L(100)\ldots L(100)L(100)L(100)S(100)\,, \qquad (17)$$

$$(001)SL(001)L(001)L(001)\ldots L(001)L(001)L(001)S(000)\,. \qquad (18)$$

In (17), $(000)S$ is a surface TPO at the bottom of a crystal which has all its surface interstitial sites empty, and $S(100)$ is a surface TPO at the top of the crystal with the surface (+)-tet. sites occupied. Thus $(000)S$ represents the anionic or $(\bar{1}\bar{1}\bar{1})$ face of the crystal, whereas $S(100)$ represents the cationic or (111) face. In (18), the situation is just reversed with $(001)S$ representing the bottom, cationic face and $S(000)$ the top, anionic face.

## 12. Classical stacking faults; multiple TPO and point defects

Stacking faults of the classical type, *i.e.* in the closest-packed atom lattice, are described in the TPO algebra by simply scrambling the parity of the unit TPO. For example, in an $LLL\ldots$ sequence representing c.c.p. the inclusion of stacking faults would be indicated by entering a number of $R$-unit TPO either at random or in a statistically weighted fashion.

Heretofore only a single unit cell TPO, $I_{0m}$, was used to represent a crystal structure since, in the ideal case, a finite volume element of the crystal would be represented by simply multiplying the unit cell formula by an integer, $M$, or, in the case of a mole of the solid, by Avogadro's number, $\mathcal{N}$. With reference to Fig. 2, $M=qr$, *i.e.*, $q$ trigonal columns each of which contains $r$ crystallographic repeat units. However, to represent point defects more than one type of TPO or *multiple* TPO must be used. For example, to represent a defect NaCl structure in which some of the sodium cations have jumped into tetrahedral interstices, the following set of different types of unit TPO, $R$, might be used:

$$\begin{aligned}(3M-w-x-2y-2z)R(010)+wR(100)+xR(001)\\ +yR(110)+zR(011)+(y+z)R(000)\,, \quad (19)\end{aligned}$$

where $w, x, y, z$ are small compared to $M$, and where unit TPO are used since the crystallographic repeat unit, $RRR$, contains $R$-unit TPO exclusively. A given distribution of both the values of $w, x, y, z$ and the spatial locations of the individual defect unit TPO would constitute a '*snapshot*' of a given overall defect concentration at a given instant of time. The general scheme whereby successive snapshots might be generated in a computer study would involve the use of fractional occupational probability indices to indicate the *relative* probabilities of site occupation, *e.g.* $R(p, q, r)$ where $p+q+r=1$. Then, each individual 'snapshot' would be generated by the use of either a table of random numbers or by a statistically weighted scheme to mimic, say, a concentration gradient, with appropriate normalization in either case.

To indicate the presence of point defects involving the closest packed atoms as well as the interstitial atoms, the formulae in Table 4 would have to be modified to include additional occupational probability indices for the closest packed atoms. For convenience it would be best to have five such indices with the second, third, and fourth corresponding to the three indices in Table 4, and the first and fifth to the closest packed atoms (treated as hemispheres) at the top and bottom of the unit TPO. Then, as an example, an individual unit cell TPO for ideal h.c.p., $I_{02}$, would be written as $L(10001)R(10001)$, and an initial stage in the formation of a single Frenkel defect, in which a closest-packed atom has jumped into a neighboring octahedral site, might be indicated by a single defect TPO such as $L(10100)R(00001)$. It is important to note that the probability indices in neighboring unit TPO representing closest-packed atoms must be properly correlated, as in the last formula, to indicate properly the absences in the closest-packed atom structure and to avoid occurrences of closest-packed hemispheres.

## 13. Conclusions

An abstract algebra of translation permutation operators, TPO, has been developed to describe defective and deformed crystal structures. At the present stage the algebra is restricted to the hypothetical case of ideal closest packing which imposes three restrictions upon the TPO: (1) the magnitude of the unit TPO vector is $1{\cdot}6330r_{\text{cp}}$; (2) the TPO vector is perpendicular to the closest-packed planes; and (3) the monolayer positions, $A$ (or $B$ or $C$), form a *p6mm* net, the distance between nearest neighbor positions being $2r_{\text{cp}}$. More-complicated crystal structures can be described by modification of any one or all of these three restrictions. Even at the present idealized stage, however, the TPO Crystal Algebra is capable of effectively describing two types of crystal defects: (1) classical stacking faults; and (2) point defects.

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# The Crystal Structures of $Nb_3Se_4$ and $Nb_3Te_4$

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The compounds $Nb_3Se_4$ and $Nb_3Te_4$ are isostructural. The hexagonal unit cells have the dimensions:

$$Nb_3Se_4\colon\ a=10{\cdot}012,\ c=3{\cdot}4707\ \text{Å};$$
$$Nb_3Te_4\colon\ a=10{\cdot}671,\ c=3{\cdot}6468\ \text{Å}\ .$$

The space group is $P6_3/m$ ($C^2_{6h}$) and the unit cell contains 6 Nb and 8 Te(Se) in the positions:

$$6\,\text{Nb in }(h) \pm (x, y, \tfrac{1}{4};\ \bar{y}, x-y, \tfrac{1}{4};\ y-x, \bar{x}, \tfrac{1}{4})$$
$$\text{with } x_1=0{\cdot}4886,\ y_1=0{\cdot}1039.$$
$$2\,\text{Te in }(c) \pm (\tfrac{2}{3}, \tfrac{1}{3}, \tfrac{3}{4}).$$
$$6\,\text{Te in }(h)\text{ with } x_2=0{\cdot}3389,\ y_2=0{\cdot}2731.$$

The relationships to the $Ti_5Te_4$ type structure of the $Nb_5Se_4$ and $Nb_5Te_4$ phases and the $NbS_2$ (*H*)-like structure of the $Nb_{1+x}Se_2$ phase are discussed.

## Introduction

In recent communications by Selte & Kjekshus (1963, 1964) the crystallographic properties of the $Nb_5Te_4$, $Nb_5Se_4$ and $Nb_{1+x}Se_2$ phases have been described. The present paper is concerned with the crystal structures of two previously unknown niobium selenide and telluride* phases. The compositions were found to be $Nb_3Se_4$ and $Nb_3Te_4$ by X-ray and density measurements.

A variety of samples were prepared by heating accurately weighed quantities of the components (in different proportions) in evacuated and sealed silica tubes. The samples were heated at various temperatures between 500 and 1350 °C and quenching in ice water as well as slow cooling was used. Single crystals, grown from the vapour phase, were found in the telluride samples. Certain difficulties in the preparation of the samples resulted from reaction between the niobium and the silica (Selte & Kjekshus, 1963, 1964).

The atomic arrangement in these structures is of considerable interest, especially its resemblance to the neighbouring phases in the niobium–selenium and niobium–tellurium systems, *i.e.* the $Nb_5Se_4$, $Nb_{1+x}Se_2$, $Nb_5Te_4$ and $NbTe_2$ phases.

## Unit cell and space group

Guinier photographs (taken with strictly monochromatized Cu $K\alpha_1$ radiation, $\lambda_{\alpha_1}=1{\cdot}54050$ Å, with potassium chloride, $a=6{\cdot}2919$ Å (Hambling, 1953) added as internal standard) could be indexed on hexagonal axes with the following unit cell dimensions (*cf.* Table 1):

$$Nb_3Se_4;\ a=10{\cdot}012,\ c=3{\cdot}4707\ \text{Å},\ c/a=0{\cdot}3467.$$
$$Nb_3Te_4;\ a=10{\cdot}671,\ c=3{\cdot}6468\ \text{Å},\ c/a=0{\cdot}3418.$$

The lattice dimensions were approximately constant

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* The niobium tellurides have also been studied by Grigorjan, Simanov & Novoselova (1960) and by Novoselova, Grigorjan & Simanov (1960). They reported *inter alia* the existence of a phase with composition in the range $NbTe_{1{\cdot}00}$ to $NbTe_{1{\cdot}70}$. The available data indicate that their $NbTe_{1{\cdot}00-1{\cdot}70}$ phase is identical with the present $Nb_3Te_4$ phase.