Conclusions

The results described above indicate two important features of silicates in the pyroxenoid group. As was previously supposed, crystallization of these structures is, in effect, a continual process where the structure type adopted gradually changes as the temperature is lowered, *via* a series of disordered intergrowth structures, to an equilibrium, or near-equilibrium arrangement. The material appears to adapt continually in the crystallization process, by means of metastable intermediate states, until the appropriate structural type is attained, with no evidence of the more normal nucleation and growth from the initial glassy product.

The most surprising feature indicated by these results, however, is in the degree of structural adaptability shown. In particular, no previous evidence for intersecting defects which appear to involve so little structural strain has been noted: these defect structures, which almost certainly involve breaking or branching of the metasilicate chains, suggest that the adaptability of these chains to thermodynamic and kinetic factors is far greater than was previously suspected. Subsequent results in the (Mg,Mn)SiO_3 structures (Pugh & Jefferson, 1981) have shown this even more clearly, especially if still shorter annealing times are used. It is interesting to speculate whether this behaviour will enable these silicates to form metastable states even in the very initial stages of crystallization from the glass.

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The Three-Colored Three-Dimensional Space Groups

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Abstract

This article contains a table of the groups of combined geometrical and color-permutational symmetry operations that leave a certain kind of three-colored, three-dimensionally periodic object apparently unchanged. The asymmetric units – 'motifs' – of the object are all either geometrically congruent to, or are mirror images of, one another. Each motif has a 'color' representing a scalar quality of some kind, and three different colors of motifs are assumed to occur in the object. Two types of three-colored space groups exist: type I in which all of the geometrical lattice translations leave all the motifs unchanged in color, and type II in which at least one of the geometrical lattice translations requires a permutation of the three colors in order to restore the original appearance. There are 88 three-colored space groups of type I, and 341 of

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type II. Type I can belong only to the trigonal, hexagonal and cubic systems; type II can belong to any system, except the cubic. A notation for the three-colored, three-dimensional space groups is proposed. It is based on similar principles to those used in the article on colored point groups by Harker [*Acta Cryst.* (1976), A**32**, 133–139].

Introduction

The definition of a three-colored, three-dimensional space group used here is based on the ideas of van der Waerden & Burckhardt (1961). Let an object K possess the geometrical space group G, and let a subgroup H' of index 3 of this Fedorov (or geometrical) space group G be present. Now choose an asymmetrical motif M in the object K, and find all the other motifs that are produced by the operations of this subgroup H'. These, together with M, are all given a certain color, say 1. The motifs which are derived from the first one, M, by the operations of one of the cosets of the subgroup H' are given a different color, say 2, and the motifs derived by using the remaining coset of H' are given a third color, say 3. In this way the three-dimensionally periodic object K possessing the three-dimensional space group G has been decomposed into three subsets, each containing the same number of motifs and each assigned a different color.

Each geometrical operation g_j of the space group G will replace each motif of K by another which may or may not have a different color. Thus each geometrical operaton g_j must be accompanied by a color permutation p_j (perhaps the identity permutation) in order to produce an object indistinguishable from K. The set of permutations $\{p_j\}$ obtained in this way constitutes a group P and the mapping $g_j \to p_j$ is a homomorphism of the group G onto P. The combined operation (g_j, p_j) is then a symmetry operation. The set of operations $\{g_j, p_j\}$ forms a group under the multiplication law $(g_j, p_j)(g_k, p_k) = (g_j\, g_k, p_j\, p_k)$. Since each motif in K has only one color, while, in general, several motifs can have the same color, it is G that is homomorphic onto P, *i.e.* $G \to P$. (In some cases, G and P are isomorphic, $G \leftrightarrow P$.) P is, therefore, isomorphic to a factor group G/H, where H is an invariant subgroup of G, *i.e.* a normal divisor of G. H is the subgroup of G that consists of all the g_j's associated with the identity permutation of the colors, (–) or **e**. (Some crystallographers call H the 'real' space group of K.) H is the intersection of H' with all its conjugate subgroups, or else $H' = H$ and is self-conjugate.

Two types of three-colored space groups exist: I. Those in which the group T of all lattice translations is included in H, i.e. all lattice translations are themselves symmetry operations, and are associated only with the identity permutation (–) of the colors present in K. II. The translation group T' of H is a proper subgroup of T, so that some translations in T must be associated with non-trivial permutations of the colors present. It has been shown by Harker (1978*a*) that the permutation subgroup associated with T must be Abelian, hence is $A_3 \equiv C_3$, the cyclic group of order three, in the case that only three colors are present.

Notation

In this work, the three-colored space groups will be symbolized thus: $G(\mathbf{t})H'|H$. Here, G is the geometrical, or Federov, space group; it is the symmetry group of the object K as observed by a 'color-blind' person; (**t**) is the matrix defining the basis vectors of the translation group (lattice) T' associated with the identity permutation of the colors, in terms of those of the translation group T of G (more discussion of T' and T will be given later); H' is the subgroup of G that contains the operations which interchange the motifs of one single color; H is the subgroup of H' that consists of the operations of G associated with the identity permutation (–) = **e** of all the colors. If $H = H'$ the three-colored space group is symbolized $G(\mathbf{t})H$.

The matrix (t)

The translation groups T and T' can be represented by lattices. Lattices can have 14 difference kinds of geometrical symmetry. These are called the Bravais lattices. Primitive unit cells can be chosen for each Bravais type; these are defined by the vector triples **a**, **b**, and **c** shown in Fig. 1. The one-colored lattices T' are referred to axes **a**′, **b**′, **c**′ which are defined in terms of the axes **a**, **b**, **c** of the geometrical lattice T by the equations

$$\mathbf{a}' = t_{11}\,\mathbf{a} + t_{12}\,\mathbf{b} + t_{13}\,\mathbf{c}$$

$$\mathbf{b}' = t_{21}\,\mathbf{a} + t_{22}\,\mathbf{b} + t_{23}\,\mathbf{c}$$

$$\mathbf{c}' = t_{31}\,\mathbf{a} + t_{32}\,\mathbf{b} + t_{33}\,\mathbf{c}.$$

The matrix (t_{jk}) must have a determinant $\Delta = |t_{jk}|$ of magnitude 1 for three-colored space groups of type I, and of magnitude 3 for those of type II. For type I it is sufficient to take (t_{jk}) to be (100/010/001) which will be denoted (**E**) in this paper. For type II, it is convenient to use the symbols for (t_{jk}) listed in Table 1 in the column headed (**t**), and symbols derived from these by changes of setting, as described in the *Notes* for Table 1.

The three-colored space groups

The three-colored space groups of type I are listed in Table 2, and of type II in Table 3. In both tables, space groups for which $H = H'$ exist. In these cases the operations of G are associated only with the three cyclic permutations of the three colors: (–), (123), (132), since the index of H in G is 3. This group is known as the alternating group or cyclic group of order three, $A_3 \equiv C_3$. These cases can be recognized by the fact that their symbols contain only one International space-group symbol after the matrix symbol. The other

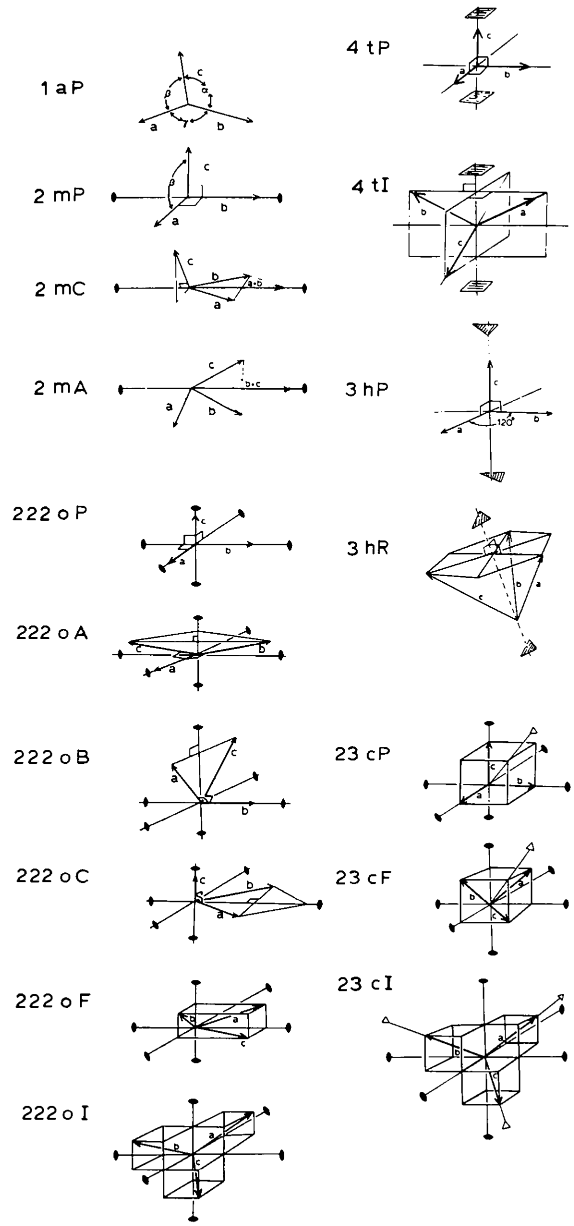

Fig. 1. Axes that define primitive unit cells for the Bravais lattices. The symbol above and to the left of the drawing of each set of axes **a**, **b**, **c** indicates in International notation the minimum rotational symmetry of the lattice $\mathbf{L} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c}$. Then follow the symbols of the Bravais lattice and its centering. (a for anorthic = triclinic; m for monoclinic; o for orthorhombic; t for tetragonal; h for hexagonal; c for cubic; P for primitive; A, B, C for centerings in, respectively, the a, b, c faces; F for all faces centered; I for body centered; R for rhombohedral centering.) The matrices connecting the axes of Fig. 1 with the traditional axes are as follows: P (100/010/001); A(100/011/0$\bar{1}$1) or (100/01$\bar{1}$/011); B (10$\bar{1}$/010/101); C (1$\bar{1}$0/110/001); F ($\bar{1}$11/1$\bar{1}$1/11$\bar{1}$); I (011/101/110); R (1$\bar{1}$0/01$\bar{1}$/111).

Table 1. *The three-colored lattices*

Symbol	(t_{jk})	(**t**)	Prominent one-colored nets
aP/P	(100/010/003)	(3**c**)	∥ c face
mP/P	(100/030/001)	(3**b**)	⊥ b axis
	(100/010/003)	(3**c**)	∥ c face
mC/C	(1$\bar{2}$0/2$\bar{1}$0/001)	(3**a**)	Rectangular nets ∥ 2-fold axis
	(210/120/001)	(3**b**)	⊥ 2-fold axis
	(100/010/003)	(3**c**)	Centered nets ∥ 2-fold axis
oP/P	(100/010/003)	(3**c**)	⊥ c
oC/C	(210/120/001)	(3**b**)	Rectangular nets ⊥ 2-fold axis
	(100/010/003)	(3**c**)	Centered nets ⊥ 2-fold axis
oF/F	(21$\bar{1}$/12$\bar{1}$/001)	(3**c**)	Centered nets ⊥ 2-fold axis
oI/I	(210/120/$\bar{1}\bar{1}$1)	(3**c**)	Rectangular nets ⊥ 2-fold axis
tP/P	(100/010/003)	(3**c**)	⊥ 4-fold axis
tI/I	(210/120/$\bar{1}\bar{1}$1)	(3**c**)	⊥ 4-fold axis
hP/P	(210/$\bar{1}$10/001)	(3**a**)	∥ 3-fold axis
	(100/010/003)	(3**c**)	⊥ 3-fold axis
hP/R	(101/011/$\bar{1}\bar{1}$1)	(3**r**)	∥ rhombohedral cell faces
hR/P	(1$\bar{1}$0/01$\bar{1}$/111)	(3**h**)	⊥ 3-fold axis

Notes

In the first column are the symbols for the colored lattices as defined by Harker (1978*b*). The first letter gives the system: a anorthic=triclinic; m monoclinic; o orthorhombic; t tetragonal; h hexagonal. The second letter gives the centering of the geometrical or 'color blind' lattice, and the third letter (after the slash) gives the centering of the 'one-colored' lattice: P primitive; C c-face centered; F all faces centered; I body centered; R rhombohedral centering of the hexagonal lattice.

The second column gives the matrix relating the axes of the 'one-colored' lattice T' to those of the 'color-blind' lattice T; the unit cells of both lattices are primitive in these axes – they are shown in Fig. 1. The centerings in column one are present in the traditional unit cells, not in the primitive unit cells of the lattices in Fig. 1.

Column three gives abbreviated symbols for the matrices of column two. In Tables 2 and 3 this notation for (**t**) is used.

Column four gives the directions of prominent one-colored nets in these lattices.

Shubnikov & Koptsik (1974) have overlooked the three-colored lattice *mC/C* with the matrix (3**c**).

The 17 three-colored lattices in Table 1 all have different colored symmetry. In Tables 2 and 3 a few of these occur in different settings to conform better with conventional International space-group notation. The changes in notation required by these changes are listed below.

Notations for (t_{jk}) and (**t**) for settings in Table 1			Notations for (t_{jk}) and (**t**) for settings with same symmetry occurring in Tables 2 and 3		
mP/P	(100/010/003)	(3**c**)	*mP/P*	(300/010/001)	(3**a**)
oP/P	(100/010/003)	(3**c**)	*oP/P*	(100/030/001)	(3**b**)
oP/P	(100/010/003)	(3**c**)	*oP/P*	(300/010/001)	(3**a**)
oC/C	(210/120/001)	(3**b**)	*oC/C*	(1$\bar{2}$0/2$\bar{1}$0/001)	(3**a**)
oC/C	(210/120/001)	(3**b**)	*oA/A*	(100/021/012)	(3**c**)
oC/C	(210/120/001)	(3**b**)	*oA/A*	(100/01$\bar{2}$/02$\bar{1}$)	(3**b**)
oC/C	(100/010/003)	(3**c**)	*oA/A*	(300/010/001)	(3**a**)
oF/F	(21$\bar{1}$/12$\bar{1}$/001)	(3**c**)	*oF/F*	(100/$\bar{1}$21/$\bar{1}$12)	(3**a**)
oI/I	(210/120/$\bar{1}\bar{1}$1)	(3**c**)	*oI/I*	(201/$\bar{1}$1$\bar{1}$/102)	(3**b**)
oI/I	(210/120/$\bar{1}\bar{1}$1)	(3**c**)	*oI/I*	(1$\bar{1}\bar{1}$/021/012)	(3**a**)

three-colored space groups – those for which H is a subgroup of H' of index 2 – make use of all six permutations of the three colors: (–), (123), (132), (12), (13), (23), since the index of H in G is 6, and that is the order of $S_3 \equiv D_3$, the symmetric group on three letters.

A few examples may be helpful at this point. Consider the entry $R\bar{3}(\mathbf{E})P\bar{1}$ in Table 2. The geometrical space group G is $R\bar{3}$, the set of six motifs is repeated by the translations of a rhombohedral lattice, and each of the three pairs of motifs in a set related by its center of inversion has only one of the three colors present. The operation of each such center in the infinite object K interchanges motifs of the same color so that $H = H'$ and only $H = P\bar{1}$ occurs in the symbol. The operations of the three-fold inversion axes are

Table 2. *Type* I. *No lattice translations require color permutations*

The unit cells of the colored and geometrical ('color-blind') lattices are the same. Only hexagonal, trigonal and cubic three-colored space groups can exist under this restriction. There are 88 three-colored space groups of type I.

1. Trigonal Three-Colored Space Groups of Type I

$P3(E)P1$
$P3_1(E)P1$
$P3_2(E)P1$
$R3(E)P1$

$P\bar{3}(E)P\bar{1}$
$R\bar{3}(E)P\bar{1}$

$P312(E)C2 \mid P1$
$P321(E)C2 \mid P1$
$P3_112(E)C2 \mid P1$
$P3_121(E)C2 \mid P1$
$P3_212(E)C2 \mid P1$
$P3_221(E)C2 \mid P1$
$R32(E)C2 \mid P1$

$P3m1(E)Cm \mid P1$
$P31m(E)Cm \mid P1$
$P3c1(E)Cc \mid P1$
$P31c(E)Cc \mid P1$
$R3m(E)Cm \mid P1$
$R3c(E)Cc \mid P1$

$P\bar{3}1m(E)C2/m \mid P\bar{1}$
$P\bar{3}1c(E)C2/c \mid P\bar{1}$
$P\bar{3}m1(E)C2/m \mid P\bar{1}$
$P\bar{3}c1(E)C2/c \mid P\bar{1}$
$R\bar{3}m(E)C2/m \mid P\bar{1}$
$R\bar{3}c(E)C2/c \mid P\bar{1}$

2. Hexagonal Three-Colored Space Groups of Type I

$P\bar{6}(E)Pm$

$P6(E)P2$
$P6_1(E)P2_1$
$P6_5(E)P2_1$
$P6_2(E)P2$
$P6_4(E)P2$
$P6_3(E)P2_1$

$P6/m(E)P2/m$
$P6_3/m(E)P2_1/m$

$P\bar{6}m2(E)Cm2m \mid Pm$
$P\bar{6}c2(E)Cc2m \mid Pm$
$P\bar{6}2m(E)Cm2m \mid Pm$
$P\bar{6}2c(E)Cc2m \mid Pm$

$P6mm(E)Cmm2 \mid P2$
$P6cc(E)Ccc2 \mid P2$
$P6_3cm(E)Cmc2 \mid P2_1$
$P6_3mc(E)Ccm2_1 \mid P2_1$

$P622(E)C222 \mid P2$
$P6_122(E)C222_1 \mid P2_1$
$P6_522(E)C222_1 \mid P2_1$
$P6_222(E)C222 \mid P2$
$P6_422(E)C222 \mid P2$
$P6_322(E)C222_1 \mid P2_1$

$P6/mmm(E)Cmmm \mid P2/m$
$P6/mcc(E)Cccm \mid P2/m$
$P6_3/mcm(E)Ccmm \mid P2_1/m$
$P6_3/mmc(E)Cmcm \mid P2_1/m$

Table 2 (*cont.*)

3. Cubic Three-Colored Space Groups of Type I

$P23(E)P222$
$F23(E)F222$
$I23(E)I222$
$P2_13(E)P2_12_12_1$
$I2_13(E)I2_12_12_1$

$Pm3(E)Pmmm$
$Pn3(E)Pnnn$
$Fm3(E)Fmmm$
$Fd3(E)Fddd$
$Im3(E)Immm$
$Pa3(E)Pbca$
$Ia3(E)Ibca$

$P\bar{4}3m(E)P\bar{4}2m \mid P222$
$F\bar{4}3m(E)F\bar{4}2m \mid F222$
$I\bar{4}3m(E)I\bar{4}2m \mid I222$
$P\bar{4}3n(E)P\bar{4}2c \mid P222$
$F\bar{4}3c(E)F\bar{4}2c \mid F222$
$I\bar{4}3d(E)I\bar{4}2d \mid I2_12_12_1$

$P432(E)P422 \mid P222$
$P4_232(E)P4_222 \mid P222$
$F432(E)F422 \mid F222$
$F4_132(E)F4_122 \mid F222$
$I432(E)I422 \mid I222$
$P4_332(E)P4_322 \mid P2_12_12_1$
$P4_132(E)P4_122 \mid P2_12_12_1$
$I4_132(E)I4_122 \mid I2_12_12_1$

$Pm3m(E)P4/mmm \mid Pmmm$
$Pn3n(E)P4/nnc \mid Pnnn$
$Pm3n(E)P4/mmc \mid Pmmm$
$Pn3m(E)P4/nnm \mid Pnnn$
$Fm3m(E)F4/mmm \mid Fmmm$
$Fm3c(E)F4/mcm \mid Fmmm$
$Fd3m(E)F4/ddm \mid Fddd$
$Fd3c(E)F4/ddc \mid Fddd$
$Im3m(E)I4/mmm \mid Immm$
$Ia3d(E)I4/acd \mid Ibca$

Table 3. *Type* II. *These contain three-colored lattice translations*

The unit cell of the subgroup lattice with translations that do not require color permutations has three times the volume of the geometrical ('color-blind') unit cell. There are no three-colored cubic space groups of this type. There are 341 three-colored space groups of type II.

1. Triclinic Three-Colored Space Groups of Type II

$P1(3c)P1$

$P\bar{1}(3c)P\bar{1} \mid P1$

2. Monoclinic Three-Colored Space Groups of Type II

$Pm(3c)Pm$
$Pm(3b)Pm \mid P1$
$Pc(3c)Pc$
$Pc(3b)Pc \mid P1$
$Pc(3a)Pc$
$Cm(3c)Cm$
$Cm(3b)Cm \mid P1$
$Cm(3a)Cm$
$Cc(3c)Cc$
$Cc(3b)Cc \mid P1$
$Cc(3a)Cc$

$P2(3c)P2 \mid P1$
$P2(3b)P2$
$P2_1(3c)P2_1 \mid P1$
$P2_1(3b)P2_1$
$C2(3c)C2 \mid P1$
$C2(3b)C2$
$C2(3a)C2 \mid P1$

$P2/m(3c)P2/m \mid Pm$
$P2/m(3b)P2/m \mid P2$
$P2_1/m(3c)P2_1/m \mid Pm$
$P2_1/m(3b)P2_1/m \mid P2_1$
$C2/m(3c)C2/m \mid Cm$
$C2/m(3b)C2/m \mid C2$
$C2/m(3a)C2/m \mid Cm$
$P2/c(3c)P2/c \mid Pc$
$P2/c(3b)P2/c \mid P2$
$P2/c(3a)P2/c \mid Pc$
$P2_1/c(3c)P2_1/c \mid Pc$
$P2_1/c(3b)P2_1/c \mid P2_1$
$P2_1/c(3a)P2_1/c \mid Pc$
$C2/c(3c)C2/c \mid Cc$
$C2/c(3b)C2/c \mid C2$
$C2/c(3a)C2/c \mid Cc$

Table 3 (*cont.*)

3. Orthorhombic Three-Colored Space Groups of Type II

P222(3c)P222 |P112
P222$_1$(3c)P222$_1$ |P112$_1$
P222$_1$(3a)P222$_1$ |P211
P2$_1$2$_1$2(3c)P2$_1$2$_1$2 |P112
P2$_1$2$_1$2(3a)P2$_1$2$_1$2|P2$_1$11
P2$_1$2$_1$2$_1$(3c)P2$_1$2$_1$2$_1$ |P112$_1$
C222$_1$(3c)C222$_1$ |C112$_1$
C222$_1$(3a)C222$_1$ |C211
C222(3c)C222 |C112
C222(3a)C222 |C211
F222(3c)F222 |F112
I222(3c)I222 |I112
I2$_1$2$_1$2$_1$(3c)I2$_1$2$_1$2$_1$|I112

Pmm2(3c)Pmm2
Pmm2(3a)Pmm2|P1m1
Pmc2$_1$(3c)Pmc2$_1$
Pmc2$_1$(3b)Pmc2$_1$|Pm11
Pmc2$_1$(3a)Pmc2$_1$|P1c1
Pcc2(3c)Pcc2
Pcc2(3b)Pcc2|Pc11
Pma2(3c)Pma2
Pma2(3b)Pma2|Pm11
Pma2(3a)Pma2|P1a1
Pca2$_1$(3c)Pca2$_1$
Pca2$_1$(3b)Pca2$_1$|Pc11
Pca2$_1$(3a)Pca2$_1$|P1a1
Pnc2(3c)Pnc2
Pnc2(3b)Pnc2|Pn11
Pnc2(3a)Pnc2|P1c1
Pmn2$_1$(3c)Pmn2$_1$
Pmn2$_1$(3b)Pmn2$_1$|Pm11
Pmn2$_1$(3a)Pmn2$_1$|P1n1
Pba2(3c)Pba2
Pba2(3b)Pba2|Pb11
Pba2(3a)Pba2|P1a1
Pna2$_1$(3c)Pna2$_1$
Pna2$_1$(3b)Pna2$_1$|Pn11
Pna2$_1$(3a)Pna2$_1$|P1a1
Pnn2$_1$(3c)Pnn2$_1$
Pnn2$_1$(3b)Pnn2$_1$|Pn11

Cmm2(3c)Cmm2
Cmm2(3b)Cmm2|Cm11
Cmc2$_1$(3c)Cmc2$_1$
Cmc2$_1$(3b)Cmc2$_1$|Cm11
Cmc2$_1$(3a)Cmc2$_1$|C1c1
Ccc2(3c)Ccc2
Ccc2(3b)Ccc2|Cc11
Amm2(3c)Amm2
Amm2(3b)Amma|Am11
Amm2(3a)Amm2|A1m1
Ama2(3c)Ama2
Ama2(3b)Ama2|Am11
Ama2(3a)Ama2|A1a1
Abm2(3c)Abm2
Abm2(3b)Abm2|Ab11
Abm2(3a)Abm2|A1m1
Aba2(3c)Aba2
Aba2(3b)Aba2|Ab11
Aba2(3a)Aba2|A1a1
Fmm2(3c)Fmm2
Fmm2(3a)Fmm2|F1m1
Fdd2(3c)Fdd2
Fdd2(3a)Fdda|F1d1
Imm2(3c)Imm2
Imm2(3a)Imm2|I1m1
Iba2(3c)Iba2
Iba2(3a)Iba2|I1a1
Ima2(3c)Ima2
Ima2(3b)Ima2|Im11
Ima2(3a)Ima2|I1a1

Pmmm(3c)Pmmm|Pmm2
Pnnn(3c)Pnnn|Pnn2
Pccm(3c)Pccm|Pcc2
Pccm(3a)Pccm|P2cm
Pban(3c)Pban|Pba2
Pban(3a)Pban|P2an
Pmma(3c)Pmma|Pmm2
Pmma(3b)Pmma|Pm2a
Pmma(3a)Pmma|P2ma
Pnna(3c)Pnna|Pnn2
Pnna(3b)Pnna|Pn2$_1$a
Pnna(3a)Pnna|P2na
Pmna(3c)Pmna|Pmm2$_1$
Pmna(3b)Pmna|Pm2a
Pmna(3a)Pmna|P2na
Pcca(3c)Pcca|Pcc2
Pcca(3b)Pcca|Pc2a
Pcca(3a)Pcca|P2$_1$ca
Pbam(3c)Pbam|Pba2
Pbam(3a)Pbam|P2$_1$am
Pccn(3c)Pccn|Pcc2
Pccn(3a)Pccn|Pc2$_1$n
Pbcm(3c)Pbcm|Pbc2$_1$
Pbcm(3b)Pbcm|Pb2$_1$m
Pbcm(3a)Pbcm|P2cm
Pnnm(3c)Pnnm|Pnn2
Pnnm(3a)Pnnm|Pn2$_1$m
Pmmn(3c)Pmmn|Pmm2
Pmmn(3a)Pmmn|P2$_1$mn
Pbcn(3c)Pbcn|Pbc2$_1$
Pbcn(3b)Pbcn|Pb2n
Pbcn(3a)Pbcn|P2$_1$cn
Pbca(3c)Pbca|Pbc2$_1$
Pnma(3c)Pnma|Pnm2$_1$
Pnma(3b)Pnma|Pn2$_1$a
Pnma(3a)Pnma|P2$_1$na

Cmcm(3c)Cmcm|Cmc2$_1$
Cmcm(3b)Cmcm|Cm2m
Cmcm(3a)Cmcm|Cmc2
Cmca(3c)Cmca|Cmc2$_1$
Cmca(3b)Cmca|Cm2a
Cmca(3a)Cmca|Cmc2
Cmmm(3c)Cmmm|Cmm2
Cmmm(3a)Cmmm|C2mm
Cccm(3c)Cccm|Ccc2
Cccm(3a)Cccm|C2cm
Cmma(3c)Cmma|Cmm2
Cmma(3a)Cmma|C2ma
Ccca(3c)Ccca|Ccc2
Ccca(3a)Ccca|C2ca
Fmmm(3c)Fmmm|Fmm2
Fddd(3c)Fddd|Fdd2
Immm(3c)Immm|Imm2
Ibam(3c)Ibam|Iba2
Ibam(3a)Ibam|I2am
Ibca(3c)Ibca|Iba2
Imma(3c)Imma|Imm2
Imma(3a)Imma|I2ma

Note added in proof: In Table 3, section 3, the entries *Pba*2(3**b**)*Pba*2|*Pb*11 and *Pba*2(3**a**)*Pba*2|*P*1*a*1 denote the same colored space group; one of them should be crossed out. Also, the colored space groups *Cmma*(3**b**)*Cmma*|*Cm*2*a* and *Ccca*(3**b**)*Ccca*|*Cc*2*a* should be inserted into the last column of the same section.

associated only with powers of the color permutation (123).

Now consider the entry *R*32(**E**)*C*2|*P*1 in the same table. In this case a set of six motifs related by the point group 32 is repeated by the translations of a rhombohedral lattice. In each set, there are three pairs of motifs related by a given twofold axis, but the members of only one of these pairs have the same color, while the members of the other two pairs of motifs have different colors. Each of the three twofold axes of the set interchanges motifs with a different pair of colors, so that the operations of the three twofold axes must be associated with the three different color interchanges: (12), (13), and (23). The only geometrical operation that leaves the color arrangement in the set unchanged is the identity, so that $H = P1$, and $H' = C2$ (the three conjugate monoclinic subgroups of $R32$ having centered lattices). The operations of the threefold axes are associated with the powers of the color permutation (123), so that all six members of $S_3 \equiv D_3$ occur in this colored space group.

In Table 3, still other phenomena occur. For

Table 3 (*cont.*)

4. Tetragonal Three-Colored Space Groups of Type II

$P\bar{4}(3c)P\bar{4}|P2$
$I\bar{4}(3c)I\bar{4}|P2$

$P4(3c)P4$
$P4_1(3c)P4_3$
$P4_2(3c)P4_2$
$P4_3(3c)P4_1$
$I4(3c)I4$
$I4_1(3c)I4_1$

$P4/m(3c)P4/m|P4$
$P4_2/m(3c)P4_2/m|P4_2$
$P4/n(3c)P4/n|P4$
$P4_2/n(3c)P4_2/n|P4_2$
$I4/m(3c)I4/m|I4$
$I4_1/a(3c)I4_1/a|I4_1$

$C\bar{4}m2(3c)C\bar{4}m2|Cmm2$
$C\bar{4}c2(3c)C\bar{4}c2|Ccc2$
$C\bar{4}m2_1(3c)C\bar{4}m2_1|Cmm2$
$C\bar{4}c2_1(3c)C\bar{4}c2_1|Ccc2$
$P\bar{4}m2(3c)P\bar{4}m2|Pmm2$
$P\bar{4}c2(3c)P\bar{4}c2|Pcc2$
$P\bar{4}b2(3c)P\bar{4}b2|Pba2$
$P\bar{4}n2(3c)P\bar{4}n2|Pnn2$
$I\bar{4}m2(3c)I\bar{4}m2|Imm2$
$I\bar{4}c2(3c)I\bar{4}c2|Icc2$
$F\bar{4}m2(3c)F\bar{4}m2|Fmm2$
$F\bar{4}d2(3c)F\bar{4}d2|Fdd2$

$P4mm(3c)P4mm$
$P4bm(3c)P4bm$
$P4cm(3c)P4cm$
$P4nm(3c)P4nm$
$P4cc(3c)P4cc$
$P4nc(3c)P4nc$
$P4mc(3c)P4mc$
$P4bc(3c)P4bc$
$I4mm(3c)I4mm$
$I4cm(3c)I4cm$
$I4md(3c)I4md$
$I4cd(3c)I4cd$

$P422(3c)P422|P4$
$P42_12(3c)P42_12|P4$
$P4_122(3c)P4_322|P4_3$
$P4_12_12(3c)P4_32_12|P4_3$
$P4_222(3c)P4_222|P4_2$
$P4_22_12(3c)P4_22_12|P4_2$
$P4_322(3c)P4_122|P4_1$
$P4_32_12(3c)P4_122|P4_1$
$I422(3c)I422|I4$
$I4_122(3c)I4_122|I4_1$

$P4/mmm(3c)P4/mmm|P4mm$
$P4/mcc(3c)P4/mcc|P4cc$
$P4/nbm(3c)P4/nbm|P4bm$
$P4/nnc(3c)P4/nnc|P4nc$
$P4/mbm(3c)P4/mbm|P4bm$
$P4/mnc(3c)P4/mnc|P4nc$
$P4/nmm(3c)P4/nmm|P4mm$
$P4/ncc(3c)P4/ncc|P4cc$
$P4/mmc(3c)P4/mmc|P4mc$
$P4/mcm(3c)P4/mcm|P4cm$
$P4/nbc(3c)P4/nbc|P4bc$
$P4/nnm(3c)P4/nnm|P4nm$
$P4/mbc(3c)P4/mnc|P4bc$
$P4/mnm(3c)P4/mnm|P4nm$
$P4/nmc(3c)P4/nmc|P4mc$
$P4/ncm(3c)P4/ncm|P4cm$
$I4/mmm(3c)I4/mmm|I4mm$
$I4/mcm(3c)I4/mcm|I4cm$
$I4/amd(3c)I4/amd|I4md$
$I4/acd(3c)I4/acd|I4cd$

instance, compare the entries $Pma2(3\mathbf{c})Pma2$, $Pma2(3\mathbf{b})Pma2|Pm11$ and $Pma2(3\mathbf{a})Pma2|P1a1$. All three of these have three-colored translation groups. In the first, the colored translations are parallel to the twofold axes, the mirrors, and the glide planes; $H' = H$ and the associated permutation group is $A_3 \equiv C_3$. In the second and third cases the three-colored translations are parallel, respectively, only to the mirror planes, or only to the glide planes, so that only these can leave all the three colors unchanged. The corresponding subgroups H are $Pm11$ and $P1a1$. Both of these have index $2 \times 3 = 6$ in $G = Pma2$, their unit cells having three times the volume of the unit cell of G. Thus, the associated color-permutation group is $S_3 \equiv D_6$ in these two cases. Many examples of this kind occur in Table 3.

When G contains three- or sixfold axes in the $\mathbf{c}$ direction, then H' and H can contain either these axes or screw axes with translations of $\mathbf{c}$ or $2\mathbf{c}$. For instance, note the three entries: $P3(3\mathbf{c})P3$, $P3(3\mathbf{c})P3_1$ and $P3(3\mathbf{c})P3_2$, and also these: $P6(3\mathbf{c})P6$, $P6(3\mathbf{c})P6_2$ and $P6(3\mathbf{c})P6_4$.

There are several other similar situations in Table 3.

Previous work on three-dimensional three-colored space groups

A book in the Russian language, entitled *Tsvetnaya Simmetriya, yeyo Obobshcheniya i Prolozheniya* (*Colored Symmetry, its Generalization and Application*) by Zamorzaev, Galyarskii & Palistrant (1978)* contains tables on pages 184–213 listing colored three-dimensional space groups involving 3, 4, and 6 colors. This list contains only those colored space groups that involve cyclic permutations of the colors present, among them 111 three-colored space groups. My Tables 2 and 3 contain the same 111 three-colored space groups, as well as 318 others [including three of the ZGP type derived from the three-colored lattice mC/C with the matrix $(3\mathbf{c})$ overlooked by Russian workers]. There is, however, no serious discrepancy between my tables and those of ZGP, since theirs do not include colored space groups involving non-cyclic color permutations, while mine do.

I have not found any other listing of three-colored, three-dimensional space groups.

Applications

Crystals of substances containing molecules or ions in triplet states, *i.e.* with an electronic spin of magnitude 1, should sometimes have structures in which the spins of these groups have projections of +1, 0 and −1 onto local magnetic fields. If these three cases are present with equal frequency in an orderly array, then the magnetic space group of such a crystal should be one of those in Tables 2 or 3, provided that we symbolize the three projections of the spin with the three 'colors'.

* This book will be denoted ZGP in the rest of the text.

Table 3 (*cont.*)

5. Trigonal Three-Colored Space Groups of Type II

$P3(3\underset{\sim}{c})P3$
$P3(3\underset{\sim}{c})P3_1$
$P3(3\underset{\sim}{c})P3_2$
$P3(3\underset{\sim}{a})P3$
$P3(3\underset{\sim}{r})R3$
$P3_1(3\underset{\sim}{a})P3_1$
$P3_2(3\underset{\sim}{a})P3_2$
$R3(3\underset{\sim}{h})P3$
$R3(3\underset{\sim}{h})P3_1$
$R3(3\underset{\sim}{h})P3_2$

$P\bar{3}(3\underset{\sim}{c})P\bar{3}|P3$
$P\bar{3}(3\underset{\sim}{a})P\bar{3}|P3$
$P\bar{3}(3\underset{\sim}{r})R\bar{3}|R3$
$R\bar{3}(3\underset{\sim}{h})P\bar{3}|P3$

$P3m1(3\underset{\sim}{c})P3m1$
$P3m1(3\underset{\sim}{a})P31m|P3$
$P31m(3\underset{\sim}{c})P31m$
$P31m(3\underset{\sim}{a})P3m1$
$P31m(3\underset{\sim}{r})R3m$
$P3c1(3\underset{\sim}{c})P3c1$
$P3c1(3\underset{\sim}{a})P31c|P3$
$P31c(3\underset{\sim}{c})P31c$
$P31c(3\underset{\sim}{a})P3c1$
$P31c(3\underset{\sim}{r})R3c$
$R3m(3\underset{\sim}{h})P3m1$
$R3c(3\underset{\sim}{h})P3c1$

$P312(3\underset{\sim}{c})P312|P3$
$P312(3\underset{\sim}{a})P321|P3$
$P312(3\underset{\sim}{r})R32|R3$
$P321(3\underset{\sim}{c})P321|P3$
$P321(3\underset{\sim}{a})P312$
$P312(3\underset{\sim}{c})P3_112|P3_1$
$P312(3\underset{\sim}{c})P3_212|P3_2$
$P321(3\underset{\sim}{c})P3_121|P3_1$
$P321(3\underset{\sim}{c})P3_221|P3_2$
$P3_112(3\underset{\sim}{a})P3_121|P3_1$
$P3_212(3\underset{\sim}{a})P3_221|P3_2$
$P3_121(3\underset{\sim}{a})P3_112$
$P3_221(3\underset{\sim}{a})P3_212$
$R32(3\underset{\sim}{h})P321|P3$
$R32(3\underset{\sim}{h})P3_121|P3_1$
$R32(3\underset{\sim}{h})P3_221|P3_2$

$P\bar{3}1m(3\underset{\sim}{c})P\bar{3}1m|P31m$
$P\bar{3}1m(3\underset{\sim}{a})P\bar{3}m1|P3m1$
$P\bar{3}1m(3\underset{\sim}{r})R\bar{3}m|R3m$
$P\bar{3}m1(3\underset{\sim}{c})P\bar{3}m1|P3m1$
$P\bar{3}m1(3\underset{\sim}{a})P\bar{3}1m|P31m$
$P\bar{3}1c(3\underset{\sim}{c})P\bar{3}1c|P31c$
$P\bar{3}1c(3\underset{\sim}{a})P\bar{3}c1|P3c1$
$P\bar{3}1c(3\underset{\sim}{r})R\bar{3}c|R3c$
$P\bar{3}c1(3\underset{\sim}{c})P\bar{3}c1|P3c1$
$P\bar{3}c1(3\underset{\sim}{a})P\bar{3}1c|P31c$
$R\bar{3}m(3\underset{\sim}{h})P\bar{3}m1|P3m1$
$R\bar{3}c(3\underset{\sim}{h})P\bar{3}c1|P3c1$

6. Hexagonal Three-Colored Space Groups of Type II

$P\bar{6}(3\underset{\sim}{c})P\bar{6}|P3$
$P\bar{6}(3\underset{\sim}{a})P\bar{6}$

$P6(3\underset{\sim}{c})P6$
$P6(3\underset{\sim}{c})P6_2$
$P6(3\underset{\sim}{c})P6_4$
$P6(3\underset{\sim}{a})P6|P3$
$P6_1(3\underset{\sim}{a})P6_1|P3_1$
$P6_5(3\underset{\sim}{a})P6_5|P3_2$
$P6_2(3\underset{\sim}{a})P6_2|P3_2$
$P6_4(3\underset{\sim}{a})P6_4|P3_1$
$P6_3(3\underset{\sim}{c})P6_3$
$P6_3(3\underset{\sim}{c})P6_1$
$P6_3(3\underset{\sim}{c})P6_5$
$P6_3(3\underset{\sim}{a})P6_3|P3$

$P6/m(3\underset{\sim}{c})P6/m|P6$
$P6/m(3\underset{\sim}{a})P6/m|P\bar{6}$
$P6_3/m(3\underset{\sim}{c})P6_3/m|P6_3$
$P6_3/m(3\underset{\sim}{c})P6_3/m|P\bar{6}$

$P\bar{6}m2(3\underset{\sim}{c})P\bar{6}m2|P3m1$
$P\bar{6}m2(3\underset{\sim}{a})P\bar{6}2m|P\bar{6}$
$P\bar{6}2m(3\underset{\sim}{c})P\bar{6}2m|P31m$
$P\bar{6}2m(3\underset{\sim}{a})P\bar{6}m2$
$P\bar{6}c2(3\underset{\sim}{c})P\bar{6}c2|P3c$
$P\bar{6}c2(3\underset{\sim}{a})P\bar{6}2c|P\bar{6}$
$P\bar{6}2c(3\underset{\sim}{c})P\bar{6}2c|P3c$
$P\bar{6}2c(3\underset{\sim}{a})P\bar{6}c2$

$P6mm(3\underset{\sim}{c})P6mm$
$P6mm(3\underset{\sim}{a})P6mm|P31m$
$P6cc(3\underset{\sim}{c})P6cc$
$P6cc(3\underset{\sim}{a})P6cc|P31c$
$P6cm(3\underset{\sim}{c})P6cm$
$P6cm(3\underset{\sim}{a})P6mc|P3m1$
$P6mc(3\underset{\sim}{c})P6mc$
$P6mc(3\underset{\sim}{a})P6cm|P3c1$

$P622(3\underset{\sim}{c})P622|P6$
$P622(3\underset{\sim}{c})P6_222|P6_2$
$P622(3\underset{\sim}{c})P6_422|P6_4$
$P622(3\underset{\sim}{a})P622|P312$
$P6_122(3\underset{\sim}{a})P6_122|P3_112$
$P6_522(3\underset{\sim}{a})P6_522|P3_212$
$P6_222(3\underset{\sim}{a})P6_222|P3_212$
$P6_422(3\underset{\sim}{a})P6_422|P3_112$
$P6_322(3\underset{\sim}{c})P6_322|P6_3$
$P6_322(3\underset{\sim}{c})P6_122|P6_1$
$P6_322(3\underset{\sim}{c})P6_522|P6_5$
$P6_322(3\underset{\sim}{a})P6_322|P312$

$P6/mmm(3\underset{\sim}{c})P6/mmm|P6mm$
$P6/mmm(3\underset{\sim}{a})P6/mmm|P\bar{6}m2$
$P6/mcc(3\underset{\sim}{c})P6/mcc|P6cc$
$P6/mcc(3\underset{\sim}{a})P6/mcc|P\bar{6}c2$
$P6/mcm(3\underset{\sim}{c})P6/mcm|P6cm$
$P6/mcm(3\underset{\sim}{a})P6/mmc|P\bar{6}m2$
$P6/mmc(3\underset{\sim}{c})P6/mmc|P6mc$
$P6/mmc(3\underset{\sim}{a})P6/mcm|P6cm$

If three similar chemical groupings can exist in isomorphous crystals, *e.g.* Na^+, K^+, Rb^+ in NaCl, KCl, RbCl, then an equimolar solid solution may exist under certain conditions. If we consider the chemical natures of the three similar groups as 'colors', then ordered structures that may form from these solid solutions must have one of the 'three-colored' space groups described here. In the case of the equimolar solid solution of NaCl, KCl and RbCl mentioned above, the disordered structure would be that of NaCl, which is face-centered cubic with one alkali ion per lattice point. The completely ordered solid solution could not be cubic, but might be based on one of the tetragonal or trigonal three-colored space groups of type II, *viz* $I4mmm(3\mathbf{c})I4/mmm|I4mm$ with $c/a \simeq 3\sqrt{2}$, or $R\bar{3}m(3\mathbf{h})P\bar{3}m1|P3m1$ with $c/a \simeq 3\sqrt{6}$.

In organic crystals there are several triplets of groupings with similar geometrical packing characteristics, such as CH_3–, Cl– and Br–, for instance. Crystals containing 3-bromo-5-chlorotoluene might have a three-colored space group, if the corresponding disordered structure has threefold axes through the centres of those molecules. Many other possible examples can be imagined.

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