

The Subdivision of the Hexagonal Net and the Systematic Generation of Crystal Structures*

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A classification of all crystal structures containing closely packed ions is based on the stacking of partially or totally occupied hexagonal nets. It is shown that the symmetry of the hexagonal net is preserved only if the fraction of the net occupied is an integral multiple of $1/(k^2 + kl + l^2)$, where k and l are integers. On this basis the plausibility of some existing structures and the non-existence of others is discussed.

Introduction

Crystal structures in which some ions are closely packed while the remaining ones occupy interstices may be described in terms of stacked hexagonal nets, each of which is partially or totally occupied by ions (Iida, 1957; Loeb, 1958; Morris & Loeb, 1960; Loeb, 1962).

The description of crystal structures given by Morris & Loeb involves the stacking of the nets and the distribution of ions over the points of each net. The stacking of nets in cubic and hexagonal structures is outlined by the algorithms reviewed in the following section. The distribution of ions over the points of a hexagonal net necessitates discrimination between these points. Previous articles included subdivision into three, four, nine, and twelve subarrays (Morris & Loeb, 1960; Iida, 1957) and into seven subarrays (Iida, 1957). In each of these instances every subarray is itself a hexagonal net; *i.e.* the symmetry of the

original net is preserved but the area of a unit mesh of a subnet is an integral multiple of the area of a unit mesh of the original net (Fig. 1). In the present paper we shall derive a general expression for the number of hexagonal subarrays into which a hexagonal net may be divided. This expression will eliminate certain subdivisions, thus providing rules for generating crystal structures when the chemical formula, the mode of packing of the closely packed ions, and the coordination of interstitial ions are known.

Coordinates and stacking of nets

For a description of crystal structures in which some ions are closely packed, a hexagonal coordinate system was defined having its origin on a closely packed ion (Morris & Loeb, 1960). The planes $h = \text{const.}$ are defined parallel to a plane of closest packing; within each closest-packed plane the directions $u = \text{const.}$, $v = \text{const.}$, and $w = \text{const.}$ coincide with closest-packed rows. Adjacent close-packed planes differ from each other by two units in h ; within any plane $h = \text{const.}$ adjacent close-packed rows differ from each other by three units in u , v , or w . The latter coordinates are related by the expression $u + v + w = 0$.

In terms of this hexagonal system, the location of the centers of the close-packed ions as well as the location of the centers of the tetrahedral and octahedral interstices between these ions are described by the following algorithms:

$$\left. \begin{aligned} v_{\text{mod } 3} &= [f(h)]_{\text{mod } 3}; & w_{\text{mod } 3} &= [f(h)]_{\text{mod } 3}; \\ \text{where} & & f(h) &= 2h, \\ & & \text{for structures in which the closely packed ions} & \\ & & \text{are cubically stacked;} & \\ \text{and} & & f(h) &= 4 - 2|h_{\text{mod } 4} - 2|, \\ & & \text{for structures in which the closely packed ions} & \\ & & \text{are hexagonally stacked.} & \end{aligned} \right\} (1)$$

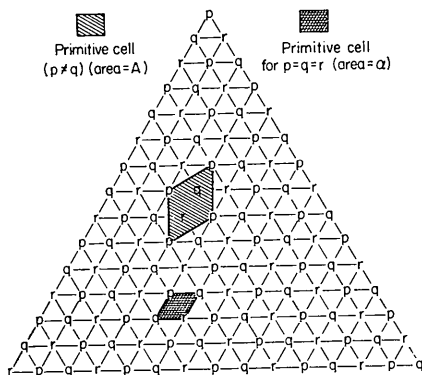


Fig. 1. A subdivided hexagonal net (subdivision into three subnets).

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All centers of closely packed ions have $h_{\text{mod } 2} = 0$; all centers of octahedral interstices have $h_{\text{mod } 2} = 1$; all centers of tetrahedral interstices have $h_{\text{mod } 2} = \pm \frac{1}{2}$. Tetrahedra whose centers are located in plane $h_{\text{mod } 2} = +\frac{1}{2}$ are called 'positive,' while those whose centers are in planes $h_{\text{mod } 2} = -\frac{1}{2}$ are called 'negative.'

Chemical formula

The numbers of octahedral interstices, of positive tetrahedral interstices, and of negative tetrahedral interstices all equal the number of closely packed ions. Therefore the chemical formula of a crystal in which the closely packed ions are denoted by X, the tetrahedrally coordinated ions by A, and the octahedrally coordinated ions by B is:

$$F(n, x, y) = A_{2xn} B_{yn} X_n, \quad (2)$$

where x = fraction of tetrahedral interstices occupied, y = fraction of octahedral interstices occupied, and $n, 2xn$, and yn are integers.

Geometrical postulates

The distribution of ions over available interstices should be such as to minimize electrostatic repulsions and maximize entropy. It will be postulated here that an array of equally charged ions located in the interstices of an oppositely charged close-packed array has minimum free energy when as many interionic distances are equal to each other as is permitted by geometric constraints. In the distribution of ions over the nodes of a hexagonal net this means that the hexagonal symmetry of the net must be preserved; increasing the distance between one pair of ions leads to a decrease in other interionic distances, and the nature of Coulomb repulsion is such that the latter more than offsets the stabilization due to the former effect. We therefore postulate that clustering of equally charged ions would be energetically unfavorable. From the entropy point of view clustering would also be unfavorable, for entropy is maximized by uniform distribution.

Primitive meshes

An equilateral parallelogram (rhomb) whose corners are adjacent nodes in the hexagonal net can be considered as a primitive mesh of the net. The area of this mesh will be called α (Fig. 1).

When all nodes of the hexagonal net are identically occupied, then the area of any primitive mesh of the resulting array equals α as well. On the other hand, if the nodes are occupied by a variety of different ions, or if some of the nodes remain unoccupied, then an array results whose primitive mesh has an area, A , equal to an integral multiple of α . Since we have postulated hexagonal symmetry for this array, its

primitive mesh can be an equilateral parallelogram as shown in Fig. 1.

Subdivision of the hexagonal net

The nodes of the hexagonal net can be subdivided into a number of subarrays, each of which has hexagonal symmetry. In Fig. 2 a representative node P_0 is joined to its six nearest nodes by the six vectors $\pm \mathbf{a}_1, \pm \mathbf{a}_2, \pm (\mathbf{a}_1 + \mathbf{a}_2)$. The same node P_0 is also joined to the six nearest nodes belonging to the same subarray as does P_0 by the six vectors $\pm \mathbf{A}_1, \pm \mathbf{A}_2, \pm (\mathbf{A}_1 + \mathbf{A}_2)$.

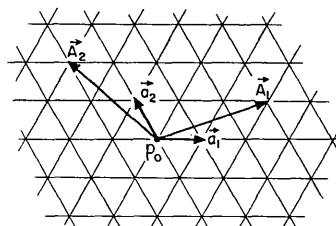


Fig. 2. Subdivision of hexagonal net (drawn for $k = +3; l = -1$).

If all subarrays are equivalent except for a translation, then the number of subarrays constituting the hexagonal net equals the ratio of the area of a primitive mesh of each subarray to the area of a primitive mesh of the hexagonal net. To find this ratio, expand \mathbf{A}_1 in terms of \mathbf{a}_1 and \mathbf{a}_2 :

$$\mathbf{A}_1 = k\mathbf{a}_1 - l\mathbf{a}_2 \quad (3)$$

where k and l are integers.

Therefore

$$A_1^2 = k^2 a_1^2 + l^2 a_2^2 - 2kl \mathbf{a}_1 \cdot \mathbf{a}_2.$$

Since

$$a_1 = a_2, \text{ and } \mathbf{a}_1 \cdot \mathbf{a}_2 = -\frac{1}{2} a_1^2,$$

$$A_1^2 = a_1^2 (k^2 + l^2 + kl)$$

and

$$A/\alpha = A_1^2/a_1^2 = k^2 + kl + l^2. \quad (4)$$

Therefore the number of subarrays = $k^2 + kl + l^2$.

Forbidden subdivisions

Table 1 lists the function $(k^2 + kl + l^2)$ for a number of values of k and l . (Note that equation (4) is sym-

Table 1. Possible numbers of subdivisions of the hexagonal net

		$k \rightarrow$					
		-2	-1	0	1	2	3
$l \downarrow$	-2	12	7	4	3	4	7
	-1	7	3	1	1	3	7
	0	4	1	0	1	4	9
	1	3	1	1	3	7	13
	2	4	3	4	7	12	19
	3	7	7	9	13	19	27

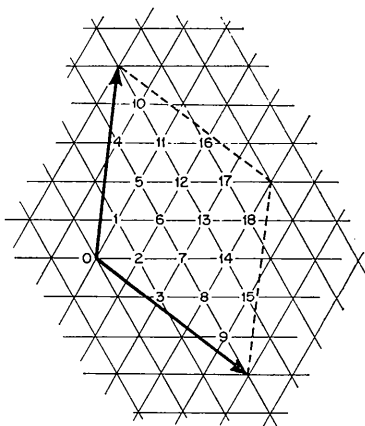


Fig. 3. Subdivision of hexagonal net into nineteen subnets ($A/\alpha = 19$).

metrical in k and l , so that the table is symmetrical about its principal diagonal.) This information, combined with Fig. 2, provides a means of constructing a primitive cell for any array; for instance, an array containing 19 distinct subarrays could be constructed by choosing $k=2$, $l=3$.

Familiar entries in Table 1 are the subdivisions into 3, used for corundum; 4, used for spinel and cuprite; 12, used for quartz; and 7, mentioned by Iida, though not for any particular existing structure.

Notable among the missing are subdivisions into 2 and into 8; it is not possible to subdivide a hexagonal net into two or eight hexagonal subnets. The former impossibility was surmised by Morris & Loeb in their discussion of the olivine structure.

These forbidden subdivisions are relevant to such structures as sphalerite or wurtzite, in which one half of all tetrahedral interstices are occupied; as cadmium iodide and chloride, in which one half of all octahedral interstices are occupied; and as spinel, in which one eighth of all tetrahedral and one half of all octahedral interstices are occupied.

Applications to crystal structures

It has been pointed out (Morris & Loeb, 1960; Loeb & Pearsall, 1963) that for all the structures under consideration models can be built from two basic types of building blocks. One type of block is a regular tetrahedron, the other a regular octahedron; each may but does not necessarily contain a sphere at its center. When blocks of these basic types are assembled in appropriate permutations and combinations, models result in which the corners of the blocks represent centers of (cubically or hexagonally) closely-packed ions, and a sphere at the center of a block, if present, represents an interstitially located ion. When each octahedron shares two faces with other octahedra, the close-packing is hexagonal; when all

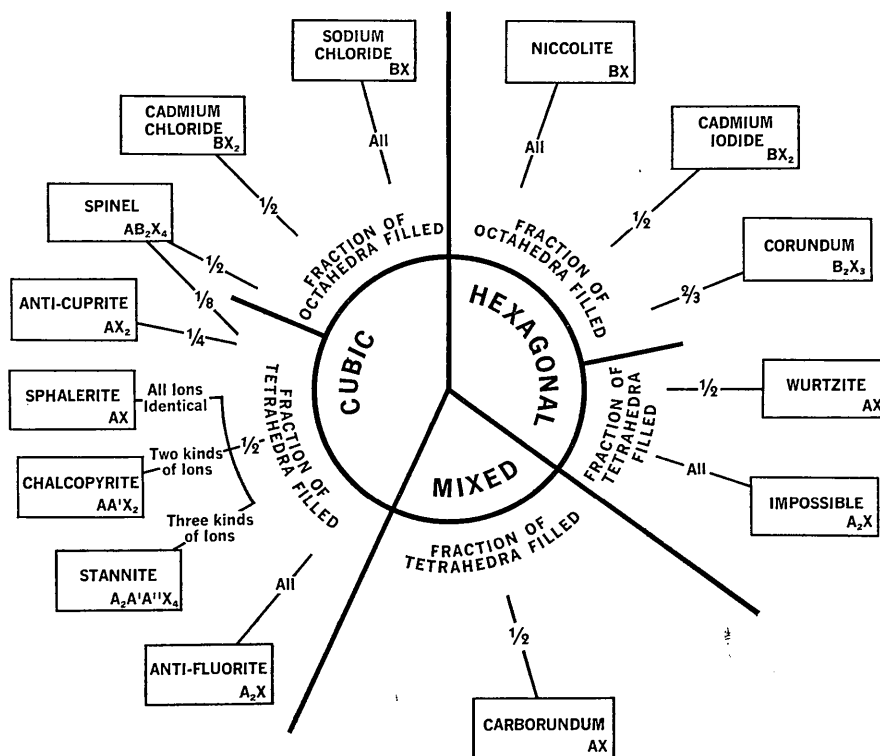


Fig. 4. The classification system.

eight faces of each octahedron are shared with tetrahedra, the structure is cubically close-packed.

The structure types that can be so represented are shown in Fig. 4. In rock salt and nickel arsenide all tetrahedral sites are empty and all octahedral ones occupied. In (anti) fluorite all tetrahedral sites are occupied. These structures are therefore easily defined in terms of the building blocks. The corundum structure, with its hexagonally close-packed oxide ions and with two-thirds of the octahedral sites occupied by aluminum ions, is easily described in terms of a subdivision into three hexagonal nets (Loeb, 1962); *i.e.* by setting $k=l=1$ in equation (4).

Of special interest here is a comparison of the structure of ZnS with that of $\text{Zn}(\text{CN})_2$. The chemical formulas of these compounds correspond to the following constants: in equation (2): For ZnS $n=1$, $x=\frac{1}{2}$, $y=0$, while for $\text{Zn}(\text{CN})_2$ $n=2$, $x=\frac{1}{4}$, $y=0$. Accordingly, in $\text{Zn}(\text{CN})_2$ the cyanide ions are closely-packed and the zinc ions occupy one quarter of all tetrahedral sites; this structure is described by subdivision of all hexagonal nets having $h_{\text{mod } 2} = \pm \frac{1}{2}$ into four subnets (Loeb, 1962), *i.e.* by setting $k=2$, $l=0$ in equation (4). The occupancy of the subnets is such that all the occupied sites have the same values of $v_{\text{mod } 2}$ and $w_{\text{mod } 2}$ (Morris & Loeb, 1960). On the other hand, in the two forms of ZnS, sphalerite and wurtzite, one half of all tetrahedral interstices is occupied; since equation (4) does not permit subdivision of a hexagonal net into two equivalent hexagonal nets, the distribution of Zn ions over available sites is such that the nets are alternately completely occupied or completely empty: If the nets having $h_{\text{mod } 2} = +\frac{1}{2}$ are occupied, all nets having $h_{\text{mod } 2} = -\frac{1}{2}$ are empty, and *vice versa*. This distribution accounts for the electrical polarity of sphalerite and wurtzite; since in zinc cyanide the cations are distributed equally over nets having $h_{\text{mod } 2} = +\frac{1}{2}$ and those having $h_{\text{mod } 2} = -\frac{1}{2}$, crystals of zinc cyanide are non-polar.

A similar distribution is observed in CdCl_2 and CdI_2 crystals, where the anions are respectively cubically and hexagonally close-packed, and the cations occupy octahedral interstices. For these compounds $n=2$, $x=0$, and $y=\frac{1}{2}$; the distribution of cadmium ions

over octahedral sites cannot, according to equation (4), be accomplished by subdivision of hexagonal nets. Therefore, alternate nets of octahedral sites are empty and occupied in both cadmium chloride and cadmium iodide.

Equation (4) has further applicability in the description of the spinel structure, AB_2O_4 ($n=4$, $x=\frac{1}{3}$, $y=\frac{1}{2}$). Since subdivision of hexagonal nets into two or eight nets is forbidden by equation (4), the distribution of ions over interstices must alternate. As shown by Morris & Loeb, half of the octahedral nets are three-quarters occupied, while the remainder are one-quarter occupied; of the tetrahedral nets half are one-quarter occupied, the other half empty.

Summary and conclusions

Previous descriptions of crystal structures in terms of partially or totally occupied stacked hexagonal nets are supplemented by the observation that the distribution of ions over the points of a hexagonal net tends to preserve the hexagonal symmetry of the net; the number of subnets is thus limited to $(k^2 + kl + l^2)$, where k and l are integers. This limitation explains the lack of uniformity of the ion distribution along the threefold symmetry axis, in particular the resulting polarity of sphalerite and the curious alternating distribution of ions in spinel.

The class of crystal structures in which part of the ions is closely-packed can, on this basis, be logically classified.

It is a pleasure to acknowledge stimulating discussions with Prof. Philippe LeCorbeiller that led to a simplification of the derivation of Table I and equation (4).

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