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# Periodic Arrays of Identical Ions Packed with 10, 11, and 12 Nearest Neighbors

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The relationships between 10, 11, and 12 coordination identical-sphere packing arrangements are discussed. Primitive tetragonal packing, which is adopted with minor distortions by rutile, has 11 coordination and may be regarded as an intimate intergrowth of close packing (12 coordination) and body-centered tetragonal (10 coordination) packing. Several other known and postulated structures are shown to represent different arrangements of the 50–50 intergrowth of *c*-axis square channel and *c*-axis strings of edge-shared octahedra typical of body-centered tetragonal packing and close packings, respectively. Partial cation occupancy of the square channels in such anion arrays would provide conduction pathways for small cations such as $Li^+$. It is also shown that body-centered tetragonal packing is an intermediate of cubic and hexagonal close packing.

Close-packed anion or cation configurations play a prominent role in the discussion of crystal structures (*1*). Numerous inorganic compounds can best be visualized in terms of hexagonal-close-packed (HCP) or cubic-close-packed (CCP) anion arrays (Fig. 1). In addition to these two packing schemes, in which each close-packed ion is coordinated by 12 crystallographically identical ions, it has recently been shown (*2, 3*) that there is a third packing scheme, primitive tetragonal packing (PTP) (Fig. 1), in which each ion is coordinated by 11 crystallographically identical ions; it is adopted, with minor distortions, by a number of important structures such as rutile. Primitive tetragonal packing is different from the body-centered tetragonal packing (BCTP) (Fig. 1), described by Wells (*1*), in which each ion is surrounded by 10 equidistant identical ions. (This occurs at an ideal $c/a$ ratio of $\sqrt{(2/3)} = 0.8165$). Although the BCTP scheme is adopted by few structures, it is shown here that it nevertheless plays an important role in the discussion of "close"-packed arrays. In particular, it is shown that BCTP is intermediate between HCP and CCP and that the square interstitial channels in primitive tetragonal packing are identical to those in BCTP. This letter thus outlines the structural relationships between the packing of identical spheres into periodic arrays with 10, 11, and 12 coordination.

Primitive tetragonal packing may be regarded in terms of a distorted HCP configuration; such a description has commonly been given for the rutile structure. However, the creation of a $4_2$ screw axis (the "undistorted" HCP equivalent structure is orthorhombic) and the change in coordination from 12 to 11 justifies the proposal that

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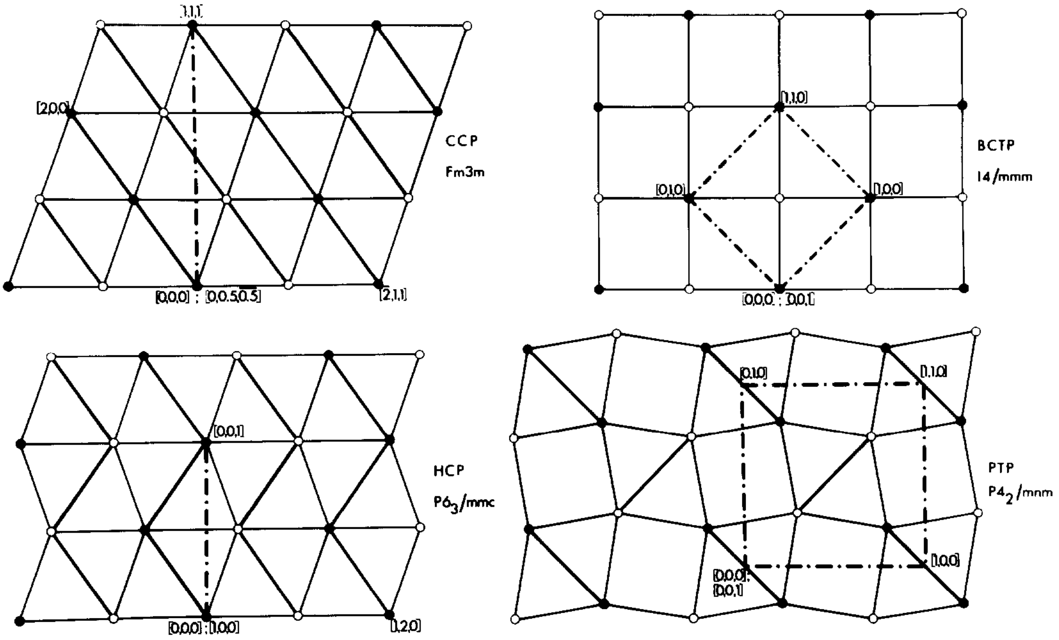

FIG. 1. 10 (BCTP), 11 (PTP), and 12 (HCP/CCP) periodic sphere packing arrangements. Lattice vectors are labeled according to the specified space groups. Open and filled circles represent ions at zero and half heights, respectively, of the lattice repeat perpendicular to the plane of the projection.

primitive tetragonal packing should be regarded as a separate and independent packing arrangement. Additionally, viewing PTP as a distorted HCP variant results in a misleading description of the interstitial space in PTP; an error of some consequence may result since PTP-related anion arrangements are adopted by many solid electrolytes (*3*), in which ionic conduction occurs principally within the interstitial channels. In the rutile structure, for example, cations occupy the edge-shared chains of distorted octahedra running parallel to the *c* axis of the PTP array, and the interstitial space consists of square channels running parallel to the *c* axis of the tetragonal cell as can be seen from Fig. 1.

From Fig. 1, it can also be seen by inspection that the *c*-axis square channels of a PTP array are identical to the *c*-axis channels of BCTP. The two structures differ in the coordination of these channels. In a PTP array, the square edge-shared *c*-axis channels are surrounded by four strings of edge-shared, distorted octahedra whereas BCTP has only *c*-axis square channels sharing faces and edges. Thus a PTP array may be regarded as an intergrowth of BCTP *c*-axis channels and *c*-axis strings of edge-shared octahedra typical of HCP or CCP arrays (Fig. 2). This observation does not negate the statement that primitive tetragonal packing, with its unique symmetry characteristics, is a distinct arrangement of identical, periodically packed spheres; rather, it reveals a particular structural relationship between packing with 10 (BCTP), 11 (PTP), and 12 (HCP/CCP) nearest-neighbor spheres.

To establish that primitive tetragonal packing may be regarded as an intergrowth of BCTP *c*-axis channels and strings of edge-shared octahedra, we note that the close-packed ions of an ideal PTP array sit on the $4f$ positions at $(x,x,0)$, where $x = 1/(2 + \sqrt{2}) = 0.2929$ of the space group $P4_2/mnm$ $(D_{4h}^{14})$ which has an ideal tetragonal $c/a$ ratio $(2 - \sqrt{2}) = 0.5858$. From geometrical considerations the diagonal distance $d$ across the square interstitial channels is related to the unit-cell length $a$ by the formula

$$d = a\sqrt{[1 - 4x + 8x^2]}.$$

Thus, in terms of the PTP $c$-axis length,

$$d = \sqrt{(3/2)}c.$$

This is, as required, equal to the ideal $a/c$ ratio for the BCTP scheme.

TABLE I

COMPARISON OF THE INTERSTITIAL SITES IN THE INTERMEDIATE BCTP LAYERED STRUCTURE WITH THOSE IN THE $CdI_2$ AND $CdCl_2$ STRUCTURES

| | $B2/m$ $(C_{2h}^3)$[a] | $CdI_2$ (HCP) $P\bar{3}m1$ $(D_{3d}^3)$ | $CdCl_2$ (CCP) $R\bar{3}m$ $(D_{3d}^5)$ |
|---|---|---|---|
| Close-packed ion | $4i$ | $2d$ | $2c$ |
| Octahedral site | $2a$ | $1a$ | $1a$ |
| Tetrahedral site | $4i$ | $2d$ | $2c$ |
| Distorted octahedral sites | $2c$ | $1b$ | — |
| | $2d$ | — | $1b$ |
| Distorted tetrahedral sites | $4i$ | $2d$ | — |
| | $4i$ | — | $2c$ |
| Distorted tetrahedral sites | $4h$[b] | — | — |

[a] The $B2/m$ cell is twice the size of the HCP and CCP cells. Hence there are twice the number of positions in the $B2/m$ cell.

[b] These "extra" distorted tetrahedral sites have no equivalent interstitial sites in either $CdI_2$ or $CdCl_2$ structures.

Having established that primitive tetragonal packing may be regarded as an intimate intergrowth of closest packing and BCTP schemes, it is a straightforward matter to extend this notion to more complex structures such as ramsdellite and hollandite (*1*) (Fig. 2). Indeed it is possible to imagine new "intergrowth" structures such as "antihollandite" (Fig. 2) and a structure intermediate between $CdI_2$ (HCP) and $CdCl_2$ (CCP) (Fig. 3) that have packing densities equivalent to that of primitive tetragonal packing. The intermediate structure of Fig. 3 possesses BCTP interstitial layers between close-packed layers: it adopts the monoclinic space group $B2/m$ $(C_{2h}^3)$. In Table I the Wyckoff positions of all the interstitial sites of the intermediate structure are listed alongside the equivalent sites in $CdI_2$ and $CdCl_2$. For instance the $2c$ site in the $B2/m$ structure is at the same position as the $1b$ site in $CdI_2$: there is no equivalent interstitial site in the $CdCl_2$ structure. Similarly the $2d$ site ($B2/m$) is equivalent to the $1b$ octahedral site in $CdCl_2$ and has no equivalent in $CdI_2$. Table I thus shows that the interstitial sites of both CCP and HCP are present in the intermediate $B2/m$ structure, thus confirming that this structure is intermediate between $CdI_2$ and $CdCl_2$ and that in general BCTP is intermediate between CCP and HCP.

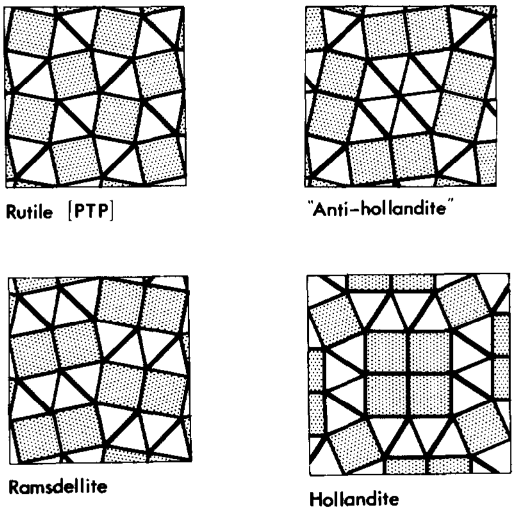

FIG. 2. Diagrammatic representation of various CCP/BCTP intergrowth structures. Shaded regions represent BCTP interstitial channels.

No known compound adopts this intermediate layered structure; the attractive Van der Waals interactions between the close-packed layers tend to minimize the interstitial space and hence to give either CCP or HCP structures. This is in contrast to the rutile structure in which the intersti-

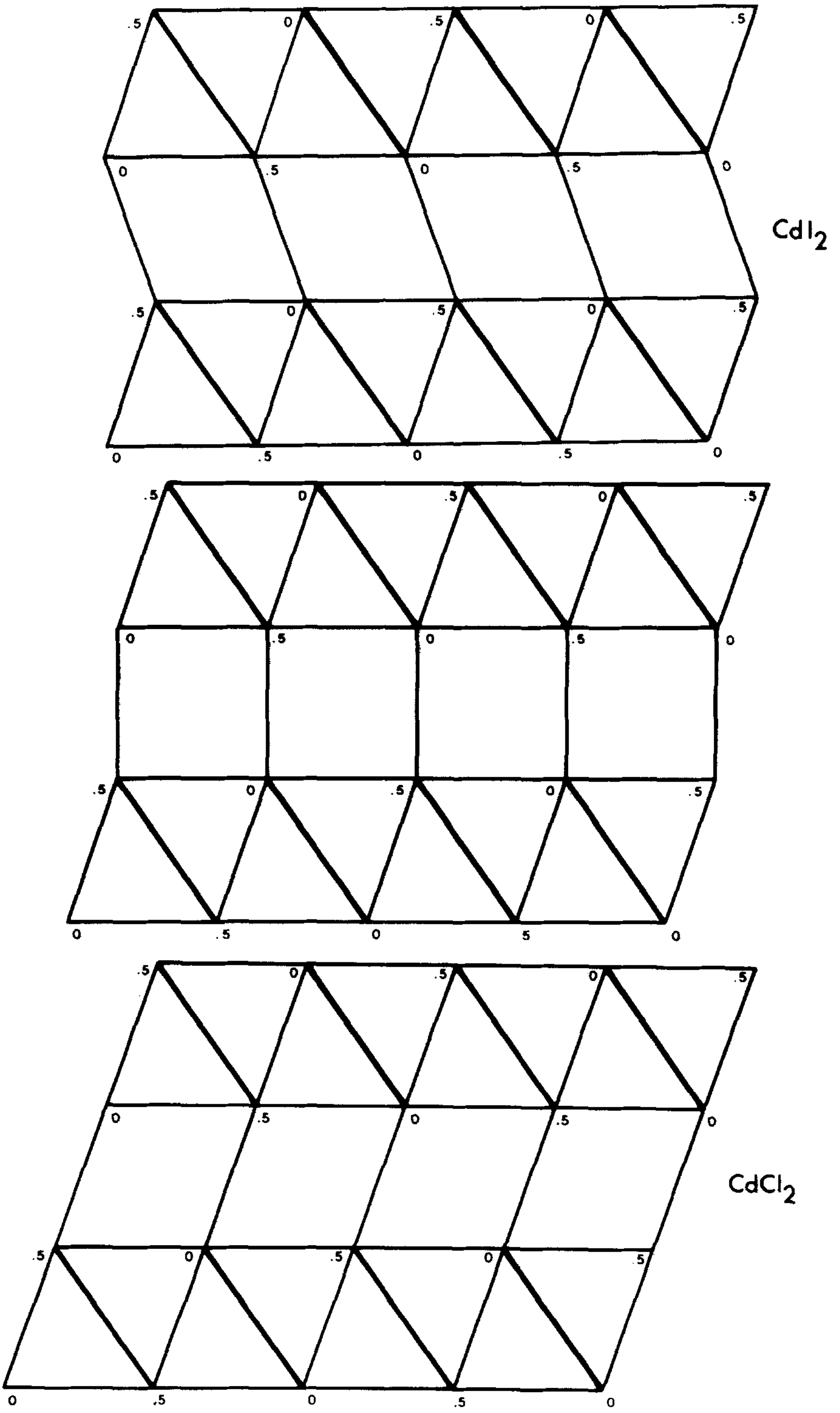

FIG. 3. CdI$_2$, CdCl$_2$, and intermediate layered structures. Heights of ions are expressed as fractional coordinates of the lattice repeat perpendicular to the plane of the projection.

tial space is maximized as a result of anion displacements from hexagonal close packing that screen the dominant cation–cation repulsions along the *c* axis. This observation suggests that, in general, if repulsion terms are dominant in such structures, then BCTP-type interstitial spaces may be expected; and conversely, if attractive terms dominate, then closest-packing (i.e., HCP/CCP) interstitial spaces will occur. The *c*-axis channels of BCTP interstitial space provide continuous conduction pathways in one dimension for small cations such as $Li^+$.

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