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Two-Dimensional Icosahedral B_{12} Networks in Boron-Rich Crystals

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Abstract. Two-dimensional icosahedral B_{12} networks in boron-rich crystals have been examined on the basis of crystal structure data. The linkages between the icosahedral B_{12} units within the networks are effected approximately along the five-fold axis of B_{12} icosahedron. Features of the icosahedral B_{12} networks as well as the external appearances of individual icosahedral B_{12} units are discussed in connection with the crystal structure-type in which the B_{12} networks are present. The crystal phases used for the calculations of icosahedral B_{12} structures are as follows: α-rhombohedral boron, β-rhombohedral boron, α-tetragonal boron, α-AlB_{12}, γ-AlB_{12}, $AlMgB_{14}$, $AlB_{24}C_4$, YB_{66} and $YB_{41}Si_{1.2}$.

1. Introduction

Boron-rich solids differ from ordinary solids in that it is impossible to interpret their bondings in terms of the conventional rule of valence. As a result, these materials manifest a number of unique properties (such as high-hardness, high-melting points, high-electrical or -thermal conductivity, optical or semi-conducting properties, etc.), which in many cases are of possible technological importance giving rise to a growing interest in their physics and chemistry.

In relation with forms of atomic arrangements, the boron-rich solids are unique in that the boron atoms tend to gather themselves, making up various types of chains and polyhedral units. With increase of the boron content in boride compounds, boron atoms form a pair, a (single, branched, double and triple) zigzag chain, a hexagonal network, B_6 octahedron, B_{12} cubooctahedron and B_{12} icosahedron (Fig. 1).

A great many boron-rich crystals principally made up of icosahedral B_{12} units have so far been synthesized and their structures determined. In the icosahedral B_{12} crystals, the linkage between B_{12} icosahedra is almost always performed approximately along their five-fold axes. It is impossible, however, to utilize five-fold rotation symmetry in a two- or three-dimensional periodic network. For that reason the largest boron cluster made up of only the B_{12} icosahedron is the $B_{12}(B_{12})_{12}$ unit (Fig. 2), which was discovered in the structure of YB_{66} (RICHARD and KASPER, 1969) and is often referred to as a giant icosahedron. Consequently, three dimensional arrangements of B_{12} icosahedra actually form open although rigid three dimensional frameworks. Except α-rhomboheral boron

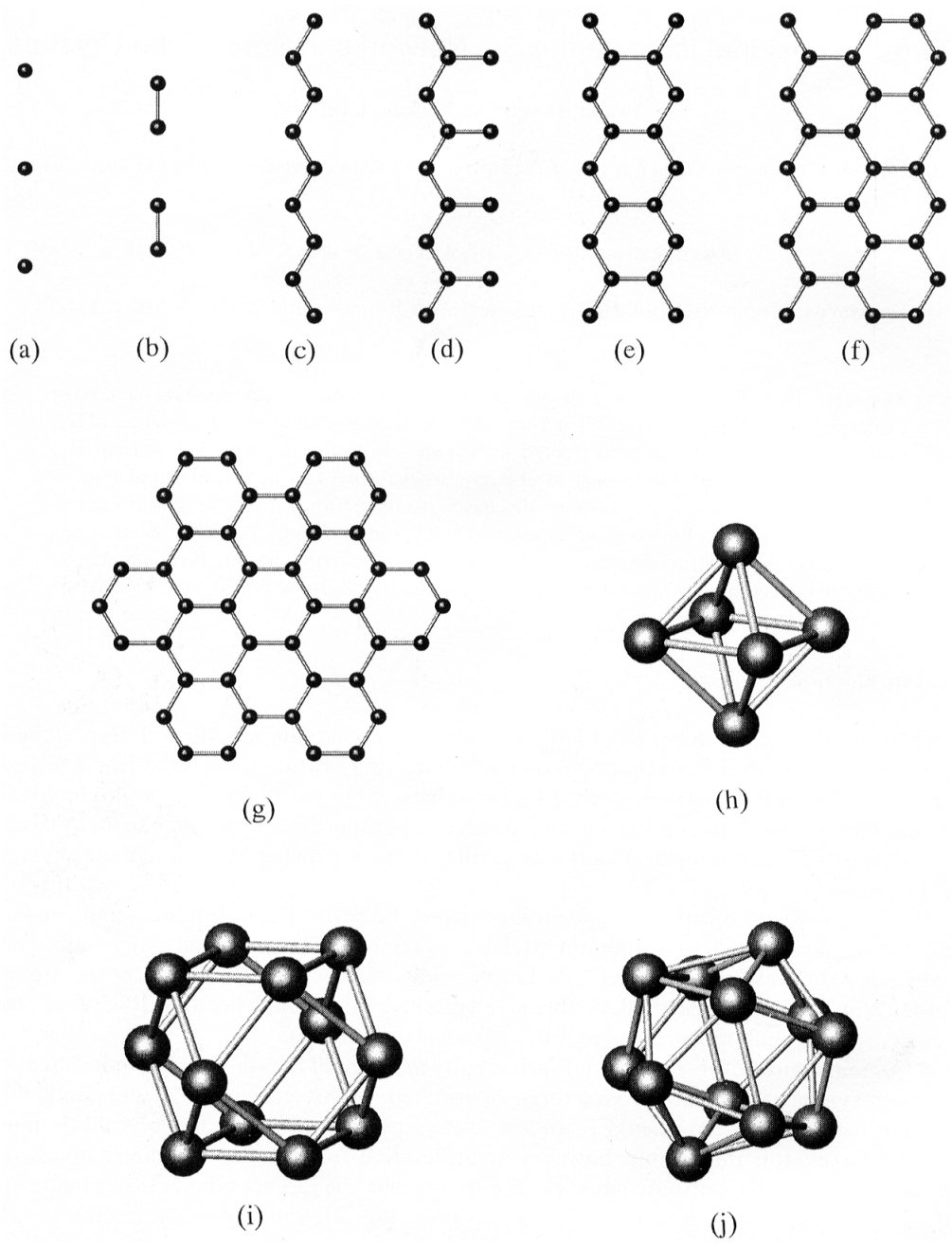


Fig. 1. Variation in bonding nature of boron atoms with increase of the boron content of boride compounds. (a) isolated atoms, (b) pairs, (c) zigzag chain, (d) branched chain, (e) double chain, (f) triple chain, (g) two-dimensional network, (h) octahedron, (I) cubooctahedron, (j) icosahedron.

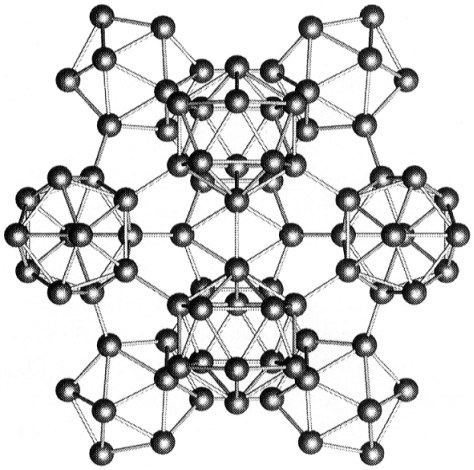


Fig. 2. $B_{12}(B_{12})_{12}$ giant icosahedron as seen along the two-fold axis.

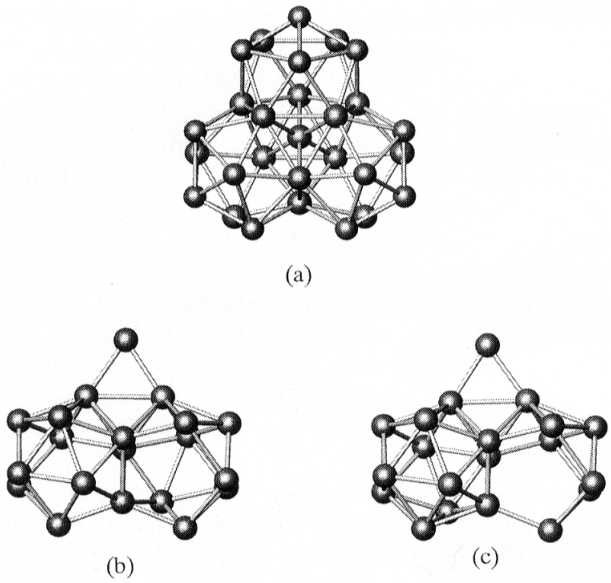


Fig. 3.

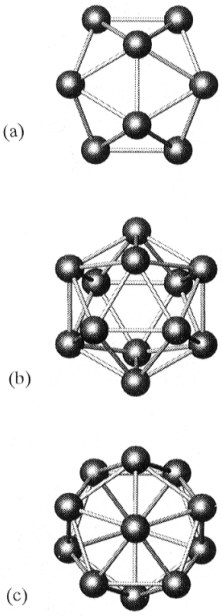


Fig. 4.

Fig. 3. (a) B_{28} unit as seen along the three-fold rotation-inversion axis, (b) B_{20}-(C_2) unit, (c) B_{20}-(C_s) unit. The B_{20}-(C_2) unit has a vacant apical site at each side of the unit, and the B_{20}-(C_s) unit two vacant apical sites at one side.

Fig. 4. The B_{12} icosahedron as seen along the (a) two-fold axis, (b) three-fold rotation-inversion axis, (c) fivefold axis.

(DECKER and KASPER, 1959), icosahedral B_{12} crystals need additional structural entities such as B_{28} (HOARD *et al*., 1970), B_{22} (VLASSE *et al*., 1979) and B_{20} units (HIGASHI *et al*., 1977; HUGHES *et al*., 1977; HIGASHI, 1983) and isolated boron atoms to fill openings within the three dimensional B_{12} frameworks. The boron units B_{28}, B_{22} and B_{20} are condensed icosahedra made up of 3, 2, and 2 icosahedra, respectively (Fig. 3).

In this paper we describe two-dimensional icosahedral B_{12} networks which extend parallel to or laying on typical crystallographic planes of boron-rich crystals. The icosahedral B_{12} structures of following materials have been examined. (1) α-rhombohedral boron and B_6O (α-rhombohedral boron-type), (2) β-rhombohedral boron (β-rhombohedral boron-type), (3) α-tetragonal boron (α-tetragonal boron-type), (4) α-AlB_{12} (β-tetragonal boron-type) and γ-AlB_{12} (γ-AlB_{12}-type or related compound of α-AlB_{12}), (5) $AlMgB_{14}$ ($AlMgB_{14}$-type), (6) $AlB_{24}C_4$ ($AlB_{24}C_4$-type), (7) YB_{66} (YB_{66}-type) and $YB_{41}Si_{1.2}$ (related compound of YB_{66}). For reference or comparison with the figures in the text, the B_{12} icosahedron is projected in Fig. 4 along its two-fold, three-fold (rotation-inversion), and five-fold axes.

2. Icosahedral B_{12} Networks in the α-Rhomnohedral Boron Structure

The crystal structure of α-rhombohedral boron (Space group: R $\bar{3}$m; a = 0.5057 nm, α = 58.07°) is shown in Fig. 5, in which each circle centered at the corner of the rhombohedral unit cell stands for the B_{12} icosahedron. Linkages between the icosahedra are effected along the five-fold axis in the direction of the crystallographic main axes. There appear three icosahedral B_{12} networks every periodic translation along the [111] axis. They are all crystallographically equivalent, extending parallel to the (111) plane. In Fig. 6, the icosahedral B_{12} network as seen along the [111] axis is presented, where every boron atom is depicted with a small circle. The linkages between B_{12} icosahedra within each network are performed by the three-centered bond which is indicated (in Fig. 6) with the thin lines connecting adjacent apical B atoms. On the other hand, linkages between icosahedral B_{12} networks, each of which appears every 1/3 periodic translation along the [111] axis, are made by two-centered bond along the five-fold axes of icosahedra in the direction of the crystallographic main axes (Fig. 5). Two kinds of linkages (two-centered and three-centered bonds) are seen on the icosahedral B_{12} network on the {100} planes of the rhombohedral structure (Fig. 7). The two-centered-bond is effected along the five-fold axis of the B_{12} icosahedron in the <100> directions, and the three centered bond is formed in the <110> directions; the latter is presented (in Fig. 7) with a thinner line lying perpendicularly to the [111] direction.

In the structure of $B_{12}O_2$ (α-rhombohedral boron structure-type, a = 0.5150 nm, α = 62.95°), two oxygen atoms are located on the [111] axis in such a way that each of which is enclosed with three B_{12} icosahedra (Fig. 8) (BORMGREN *et al*., 1990; HIGASHI *et al*., 1990). Owing to the incorporation of oxygen atoms, the rhombohedral unit cell volume is increased slightly with a variation of the angle α from 58.07° to 62.95°. Figure 9 shows the icosahedral B_{12} network as seen along the [111] axis, which is almost the same as that in α-rhombohedral boron except the presence of oxygen atoms; each oxygen atom is located at the center of a triangle formed with three B_{12} icosahedra. The icosahedral B_{12} network on the {100} plane in this compound is almost the same as that in α-rhombohedral boron (Fig. 7).

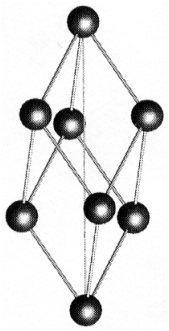
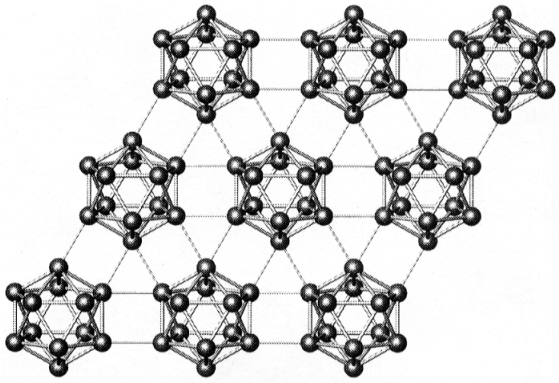


Fig. 5.



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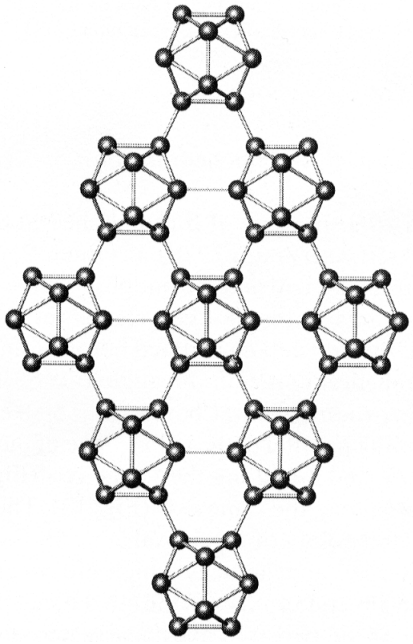
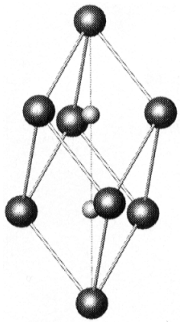


Fig. 7.

Fig. 5. Structure of α-rhombohedral boron (space group: R $\overline{3}$m; a = 0.5057 nm, α = 58.07°). Each circle at the lattice point stands for the B_{12} icosahedron.

Fig. 6. Icosahedral B_{12} network in the α-rhombohedral boron structure as seen along the [111] axis.

Fig. 7. Icosahedral B_{12} network in the α-rhombohedral boron structure extending on the {100} planes.



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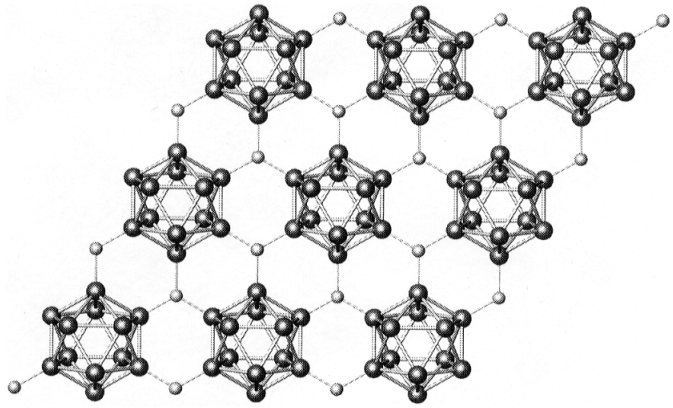


Fig. 9.

Fig. 8. Structure of B_6O (α-rhombohedral boron structure-type, a = 0.5150 nm, α = 62.9°). Each circle at the lattice point stands for the B_{12} icosahedron and smaller ones on the [111] axis oxygen atoms.
Fig. 9. Icosahedral B_{12} network in the structure of B_6O as seen along the [111] axis. the smaller circles stand for the oxygen atom.

3. Icosahedral B_{12} Networks in β-Rhombohedral Boron

Figure 10 shows the crystal structure of β-rhombohedral boron (Space group: R $\bar{3}$m; a = 1.0145 nm, α = 65.17°) (HOARD *et al.*, 1970), in which B_{12} icosahedra are centered at the corner of the rhombohedral unit cell and the midpoint of the unit cell edges. The largest circles situated on the [111] axis of the unit cell stands for the B_{28} unit (Fig. 3) and the smallest one at the center of the unit cell an isolated boron atom. With the incorporation of the B_{28} unit into the rhombohedral unit cell, the angle α (=65.17°) becomes significantly larger compared to that of α-rhombohedral boron (α = 58.07°). There are two kinds of icosahedral networks extending parallel to the (111) plane of the crystal. One appears at the periodic translation of 0, 2/6, and 4/6 along the [111] axis (Fig. 11), and the other at the translation of 1/6, 3/6 and 5/6 along the same axis (Fig. 12). The former is made up of both B_{12} and B_{28} units and the latter solely of B_{12} icosahedra. In Fig. 11, the B_{12} and B_{28} units are displaying their well-formed appearances which are precisely projected along their respective threefold rotation-inversion axis. On the other hand, in Fig. 12 the B_{12} icosahedra are arranged with their one of the two-fold axes nearly perpendicularly to the projection plane, thus forming a 3636 kagomé net (PEASON, 1972) as will be seen in some other structure types described in this paper. Another important icosahedral B_{12} network is that which extends on the {100} plane (Fig. 13). In this network, every B_{12} icosahedron is situated so as to have its one of the mirror planes just on the (100) plane, forming linear linkages with adjacent icosahedra almost precisely along the five-fold axes. Considering the periodic nature of the crystal structure, the icosahedral B_{12} network on the (100) plane should be a 3636 kagomé net.

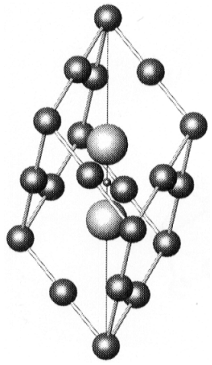


Fig. 10.

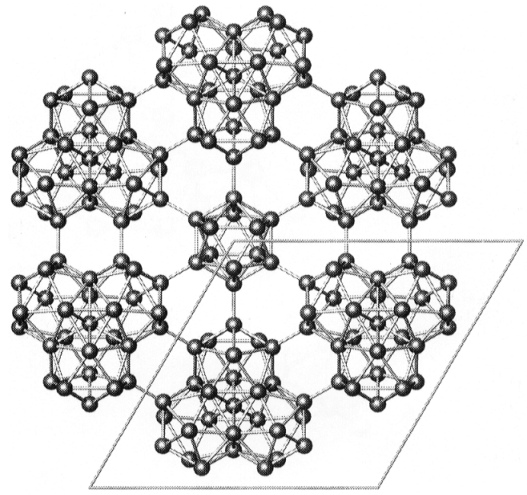


Fig. 11.

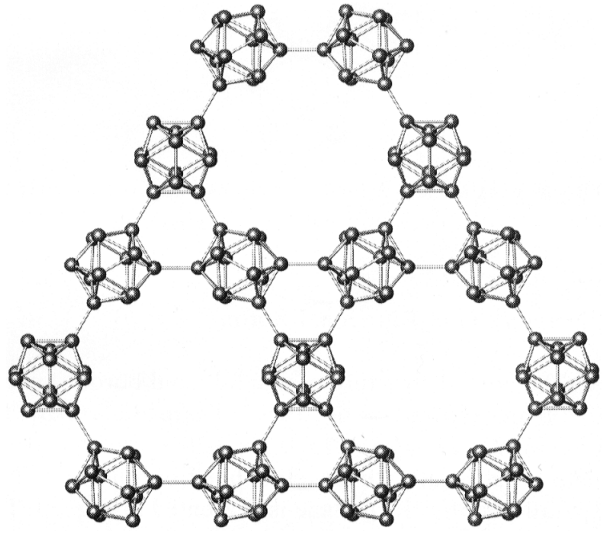


Fig. 12.

Fig. 10. Structure of α-rhombohedral boron (space group: R $\bar{3}$m; a = 1.0145 nm, α = 65.17°). Each circle at the lattice point and the midpoints of the unit cell edges stands for the B_{12} icosahedron. The largest circles on the [111] axis stand for the B_{28} unit and the smallest one at the unit cell center an isolated boron atom.

Fig. 11. Icosahedral B_{12} network in the β-rhombohedral boron structure as seen along the [111] axis. This network is consisting of the B_{12} icosahedron and the B_{28} unit (condensed icosahedra), and appears every periodic translation of 0, 1/3 and 2/3 along the [111] axis. The rhombus drawn in the figure indicates the hexagonal unit plane $(001)_{hex}$.

Fig. 12. Icosahedral B_{12} network in the β-rhombohedral boron structure as seen along the [111] axis. It appears every periodic translation of 1/6, 3/6 and 5/6 along the [111] axis.

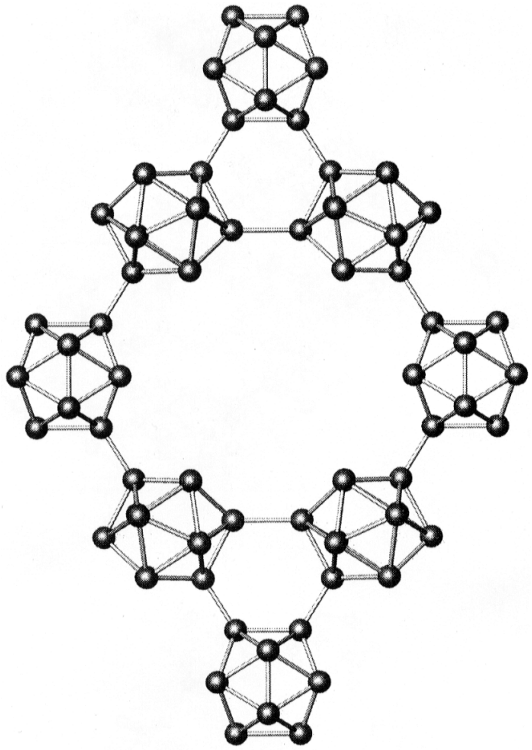


Fig. 13. Icosahedral B_{12} network in the β-rhombohedral boron structure extending on the {100} planes.

4. Icosahedral B_{12} Network in α-Tetragonal Boron

Figure 14 shows the crystal structure of α-tetragonal boron (Space group: $P4_2/nnm$; a = 0.875 nm, c = 0.506 nm) (HOARD *et al.*, 1958). There are four B_{12} icosahedra per unit cell, centering the positions: 0.25, 0.25, 0.75; 0,75, 0.25, 0.25; 0.25, 0.75, 0.25; 0.75, 0.75, 0.75. They coordinate tetrahedrally about an isolated boron atom. The icosahedral B_{12} network extending parallel to the (100) plane is presented in Fig. 15. There are two kinds of icosahedral B_{12} chains; one is those running along the <100> directions and the other those running along the <101> directions. The linkages between B_{12} icosahedra in the former are effected almost along the five-fold axis, on the other hand, those in the latter deviate approximately 20° from the five-fold axis (Fig. 16). It has been reported that the accurate chemical composition of this crystal phase is $B_{50}C_2$ or $B_{50}N_2$, and the isolated boron atoms should be replaced with either carbon or nitrogen atoms (WILL and KOSSOBUTZKI, 1976). The icosahedral networks in $B_{50}C_2$ or $B_{50}N_2$ are, however, exactly the same as those in α-tetragonal boron which had previously been reported (HOARD *et al.*, 1958).

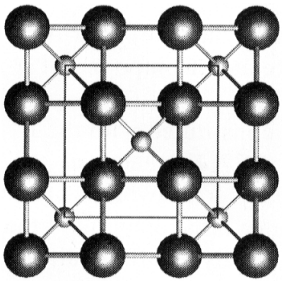
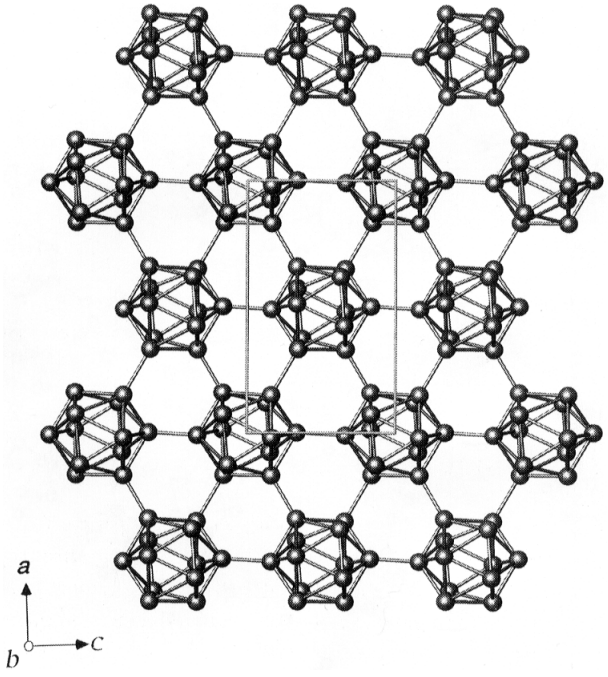


Fig. 14.



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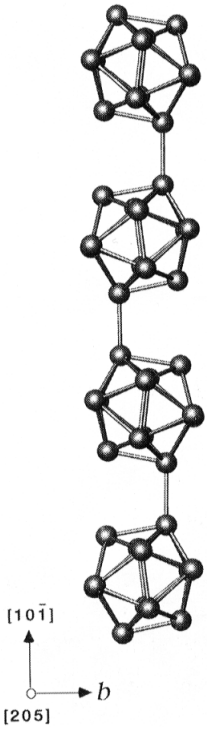


Fig. 16.

Fig. 14. Structure of α-tetragonal boron as seen along the *c* axis (space group: $P4_2/nnm$; $a = 0.875$ nm, $c = 0.506$ nm). The larger cycles stands for the B_{12} icosahedron and the smaller one for an isolated boron atom. Each of the isolated boron atoms is tetrahedrally coordinated with four B_{12} icosahedra.

Fig. 15. Icosahedral B_{12} network in the α-tetragonal boron structure extending parallel to the {100} planes.

Fig. 16. Icosahedral B_{12} chain in the α-tetragonal boron structure running along the <101> direction. It shows a significant deviation of B_{12}-B_{12} linkage from the five-fold axis of the B_{12} icosahedron.

5. Icosahedral B_{12} Networks in the Structure of α-AlB_{12} (β-Tetragonal Boron-Type) and γ-AlB_{12} (γ-AlB_{12}-Type or Related Compound of α-AlB_{12})

The structure of α-AlB_{12} is constituted with the B_{12} icosahedron and one of the two sorts of B_{20} units (HIGASHI *et al.*, 1977; KASPER *et al.*, 1977; HIGASHI, 1983). Full structure of three-dimensional icosahedral B_{12} framework is presented in Fig. 17. The B_{20} (B_{20}-(C_2) in Fig. 3) unit is accommodated in a large opening of the icosahedral B_{12} framework. The Al atoms are situated within relatively small openings outside the B_{12} or B_{20} units. The structure belongs to the tetragonal system (space group $P4_12_12$ or $P4_32_12$) with the lattice constants a = 1.017 nm and c = 1.428 nm, and is isostructural with β-tetragonal boron

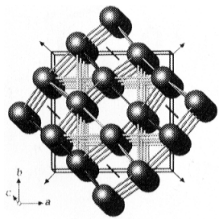


Fig. 17.

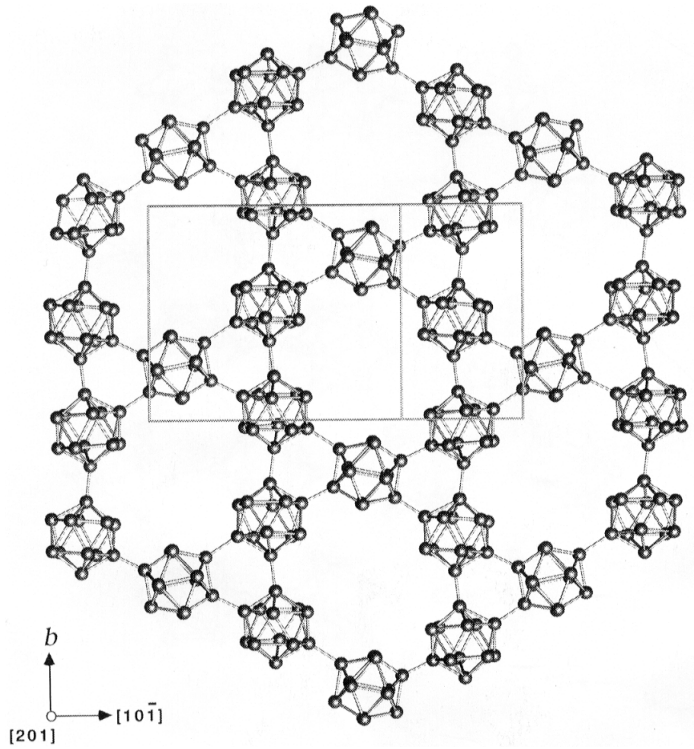


Fig. 18.

Fig. 17. Structure of α-AlB_{12} (tetragonal, space group: $P4_12_12$ or $P4_32_12$; a = 1.017 nm and c = 1.428 nm). Each circle stands for the B_{12} icosahedron. This type of structure has four-fold and two-fold screw axes (see the text).

Fig. 18. Icosahedral B_{12} network in the α-AlB_{12} structure extending parallel to the {101} planes. As to the three sections of the unit plane, an explanation is made in the text.

(VLASSE *et al*., 1979). It has 4_1 or 4_3 screw axes in the *c* axes direction at the positions of (0.1/2, *z*) and (0, 1/2, *z*), and 2_1 screw axes in the <110> directions at $z = 0$ or 1/2. In the α-AlB_{12} structure, two dimensional icosahedral B_{12} networks are observed only parallel with the {101} planes (Fig. 18). All the B_{12} icosahedra in this structure are crystallographically equivalent. Almost the same icosahedral B_{12} network as in the α-AlB_{12} structure is present in the γ-AlB_{12} structure (Orthorhombic, space group: $P2_12_12_1$; a = 1.657 nm, b = 1.751 nm, c = 1.014 nm) in parallel to the (100) plane. The icosahedral B_{12} network in this structure is shown in Fig. 19 in a larger scale than that of Fig. 18. Unlike the α-AlB_{12} structure, three B_{12} icosahedra forming a triangle are crystallographically independent from each other, and two sorts of B_{20} units {B_{20}-(C_2) and B_{20}-(C_s)} (Fig. 3) are accommodated within openings of the icosahedral B_{12} framework (HUGHES *et al*., 1977; HIGASHI, 1983). In Fig. 20, the relationship of the unit cells and the structures of α-AlB_{12} and γ-AlB_{12} in the syntactically intergrown crystal of both phases is given (HIGASHI, 2000). The division of the (101) unit plane in Fig. 18 into three equal parts indicates that equivalent positions of adjacent networks are shifted in the [101] direction by one-third the periodic distance.

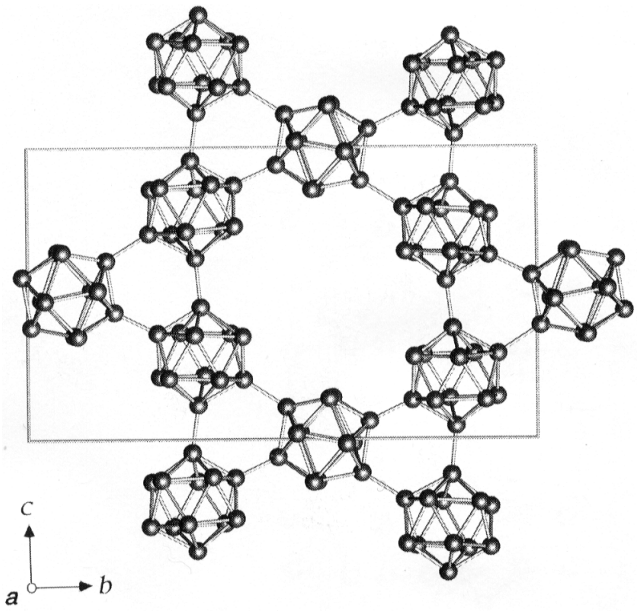


Fig. 19.

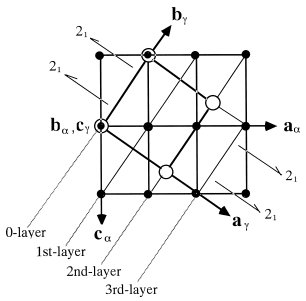


Fig. 20.

Fig. 19. Icosahedral B_{12} network in the γ-AlB_{12} structure extending parallel to the (100) plane.
Fig. 20. Relationship of the unit cells and the structures of α-AlB_{12} and γ-AlB_{12}.

6. Icosahedral B_{12} Networks in the $AlMgB_{14}$ Structure

The $AlMgB_{14}$ compound belongs to the orthorhombic system (space group: Imam) with the lattice constants a = 0.5848 nm, b = 0. 8112 nm, c = 1.0312 nm (MATKOVICH and ECONOMY, 1970; HIGASHI and ITO, 1983). Its structure (Fig. 21) is made up of four B_{12} icosahedra and eight isolated boron atoms per unit cell. The icosahedra are centered at the positions 0,0,0; 1/2,1/2,0; 0,0,1/2 and 1/2,1/2,1/2. Each icosahedron directly links to six icosahedra (first neighbors) approximately along the five-fold axes and to six icosahedra (second neighbors) via isolated boron atoms. The Al and Mg atoms are accommodated within openings outside the icosahedral B_{12} framework. The B_{12} icosahedra are oriented so as to have one of their mirror planes just on the structural mirror planes situated at the levels of x = 0 and 1/2. Two kinds of icosahedral B_{12} networks extending parallel to the (001) plane and (110) planes are shown in Figs. 22 and 23, respectively. In Fig. 22, every icosahedron is oriented so that one of its five-fold axes is approximately perpendicular to the (001) plane. A deviation of B_{12}-B_{12} bond from the five-fold axes can been seen from the icosahedral B_{12} chains running along the [110] direction (Fig. 23). Such a large deviation is unusual except for that in the α-tetragonal boron structure (Fig. 16). In Fig. 24, a feature of the deviation (about 17°) of B_{12}-B_{12} bond from the five-fold axis is demonstrated with the icosahedral B_{12} chain running in the [110] direction.

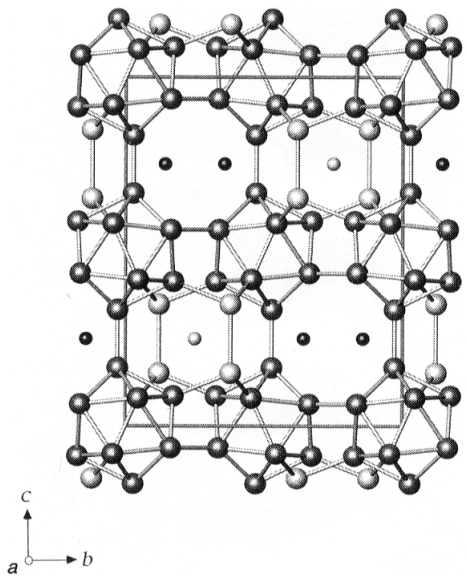


Fig. 21. Structure of $AlMgB_{14}$ as seen along the a axis (orthorhombic, space group: Imam; a = 0.5848 nm, b = 0. 8112 nm, c = 1.0312 nm). Small circles stand for Mg (dark) and Al (gray) atoms. The less dark circles linking to the icosahedral apical atoms are isolated boron atoms.

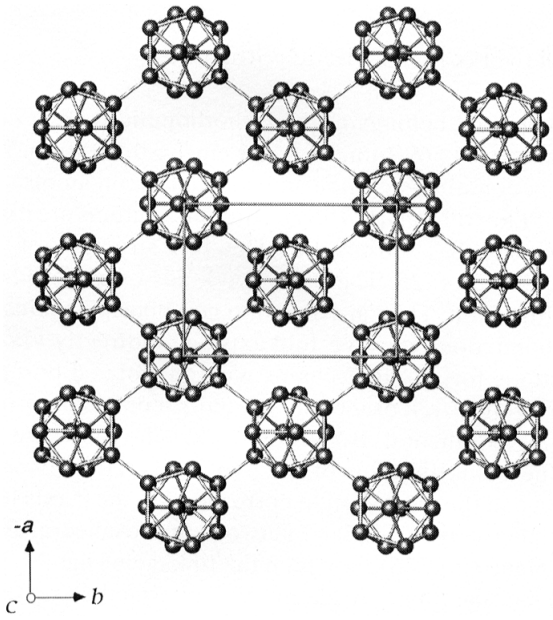


Fig. 22.

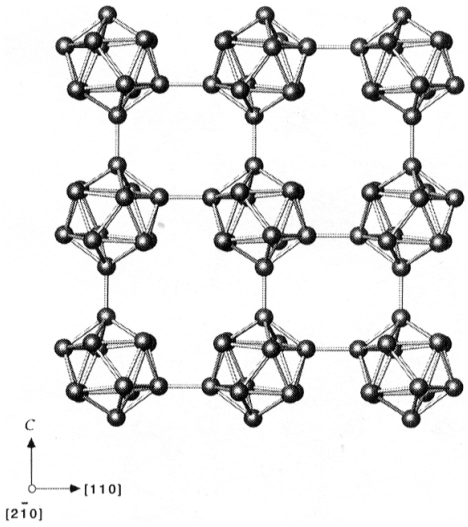


Fig. 23.

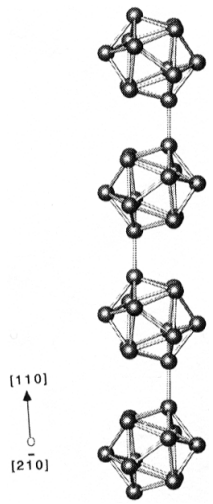


Fig. 24.

Fig. 22. Icosahedral B_{12} network in the $AlMgB_{14}$ structure extending parallel to the (001) plane.
Fig. 23. Icosahedral B_{12} network in the $AlMgB_{14}$ structure extending parallel to the {110} planes.
Fig. 24. Icosahedral B_{12} chain in the $AlMgB_{14}$ structure, showing a deviation of B_{12}-B_{12} linkage from the five-fold axis of the icosahedron.

7. Icosahedral B_{12} Networks in the $AlB_{24}C_4$ Structure

The $AlB_{24}C_4$ compound belongs to the orthorhombic system (space group, Cmam) with the lattice constants $a = 0.5690$ nm, $b = 0.881$ nm, $c = 0.9100$ nm. The structure consists of the B_{12} icosahedron, containing carbon and isolated boron atoms as essential structural entities (WILL, 1969; PERROTTA *et al.*, 1969). Aluminum atoms are distributed statistically among interstices outside B_{12} icosahedra. The full structure of the icosahedral B_{12} framework is presented in Fig. 25. There are two kinds of icosahedral B_{12} zigzag chains running in the [001] direction. They are linked to neighboring chains directly through the icosahedral B_{12}-B_{12} bond along the five-fold axis and indirectly via intermediary carbon atoms. The carbon atoms form C-B-C chains with an isolated boron atom. Each carbon atom in the chain linked to two icosahedral B_{12} units, contributing to the construction of the three-dimensional icosahedral B_{12} framework. The structure of $AlB_{24}C_4$ can be regarded as a pile in the *a* axis direction of wavy (or puckered) networks of icosahedral B_{12} units; the wave-length and the wave-height correspond to the *b* axis length and one-half of the *a* axis length, respectively. The plane network of icosahedral B_{12} units is extending parallel to the (001) plane (Fig. 26), in which the linkage of the B_{12} icosahedron with the second neighbor B_{12} icosahedra are made through intermediary carbon atoms.

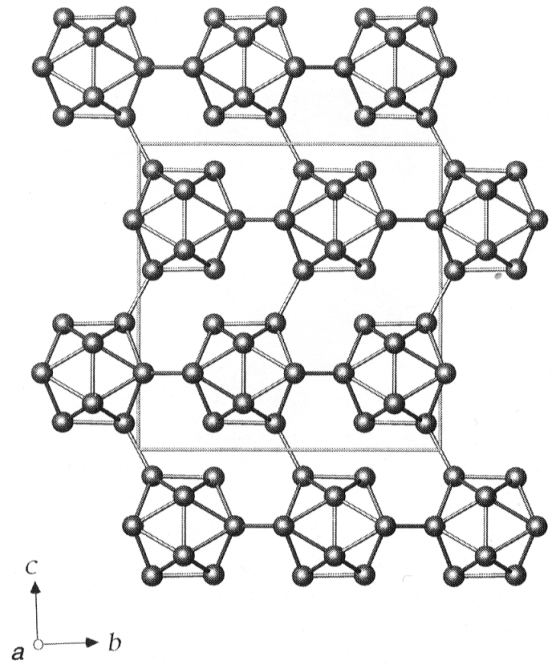


Fig. 25. Structure of $AlB_{24}C_4$ as seen along the *a* axis (orthorhombic, space group: Cmam; $a = 0.5690$ nm, $b = 0.881$ nm, $c = 0.9100$ nm). It corresponds to the projection of a puckered network of icosahedral B_{12} units (see the text).

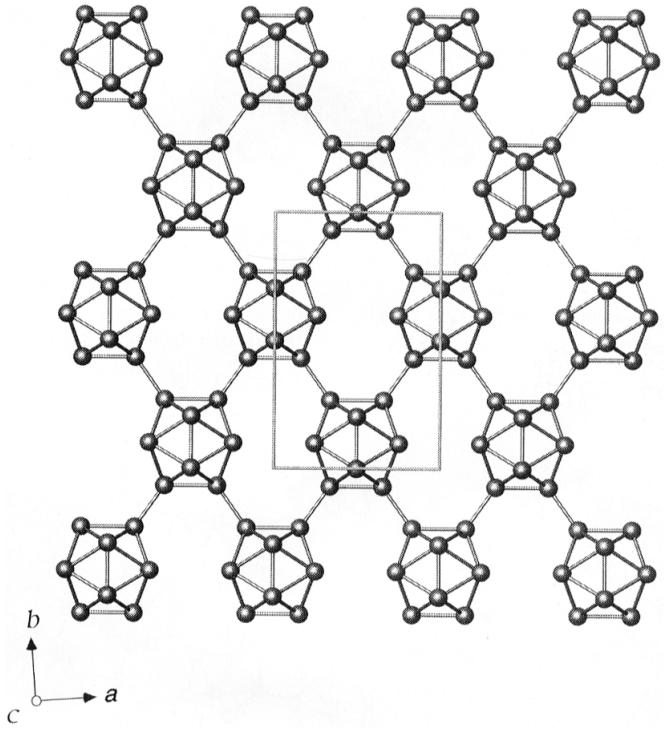


Fig. 26. Icosahedral B_{12} network in the $AlB_{24}C_4$ structure extending parallel to the (001) plane.

8. Icosahedral B_{12} Networks in the YB_{66} Structure

The YB_{66} compound (RICHARDS and KASPER, 1969) is the most boron-rich phase among the metal borides thus far reported. It crystallizes in a face centered-cubic structure (space group, Fm3c) with the lattice constants a = 2.3436 nm. As shown in Fig. 27, the boron framework of YB_{66} is basically made up of the giant icosahedron unit $B_{12}(B_{12})_{12}$ (Fig. 2) and a nonicosahedral cage. There are approximately 1584 boron atoms and 24 yttrium atoms in the unit cell. The majority of the boron atoms (1248) belong to eight $B_{12}(B_{12})$ giant icosahedra, and the rest (336) form eight nonicosahedral cages. The giant icosahedra are located in one orientation at the face-centered cubic lattice points. They also occur at the center of the cell and cell edges rotated by 90°. The nonicosahedral cages are situated at the centers of eight octants of the cubic unit cell. In Fig. 28, the arrangement of $B_{12}(B_{12})$ giant icosahedra on the (001) plane is projected along the c axis. In each giant icosahedron, four B_{12} icosahedra as well as the central B_{12} icosahedron are placed so as to have one of their respective mirror planes just on the (001) plane, and the remaining eight B_{12} icosahedra are laid above and below that plane; the (001) plane is also one of the mirror planes pertaining to the space group to which this crystal belongs. The two-dimensional icosahedral B_{12} network just on the structural mirror plane is presented in Fig. 29. Unlike the icosahedral

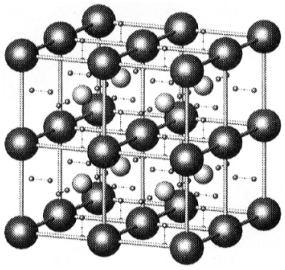


Fig. 27. Perspective drawing of the structure of YB_{66} (cubic, space group: Fm3c; a = 2.3436 nm). The largest circles stands for the $B_{12}(B_{12})_{13}$ giant icosahedron, the middle ones a nonicosahedral cage, and the smallest the Y atom.

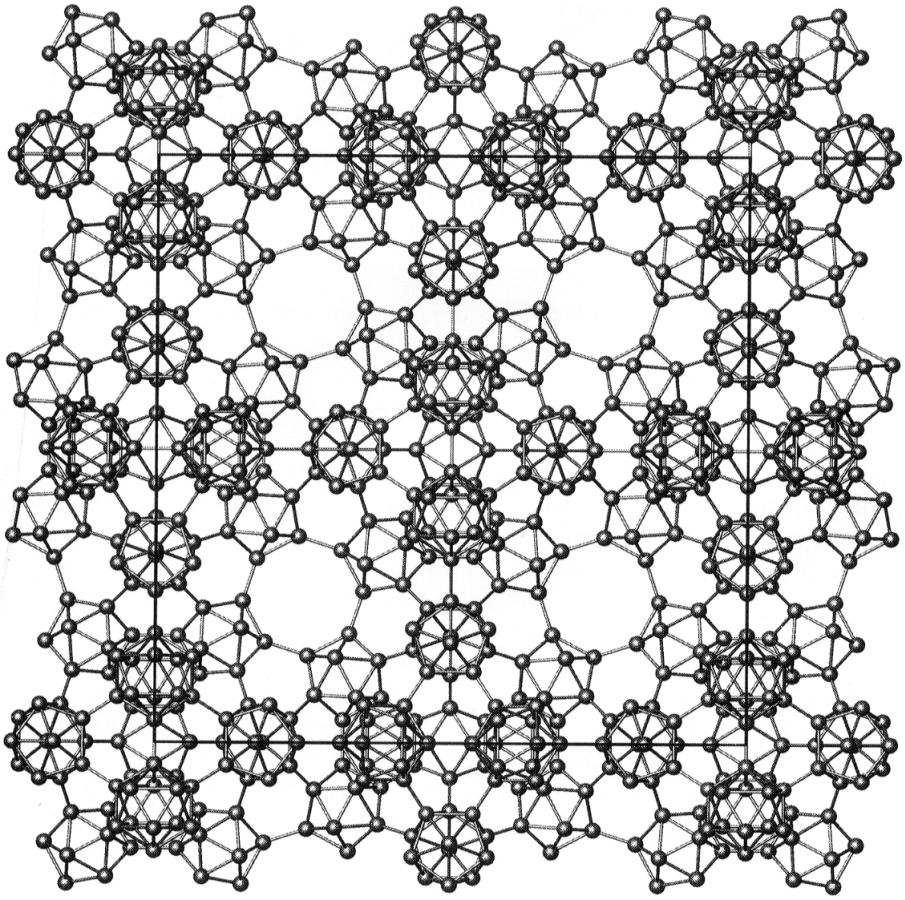


Fig. 28. The arrangement of $B_{12}(B_{12})_{13}$ giant icosahedra in the YB_{66} structure as seen along the <100> axes.

B_{12} networks so far described, the present network is unusual in that it consists of triangles, squares, and pentagons of B_{12} icosahedra in equal frequency. After the code of kagomé net 3636 (PEASON, 1972), this type of network might be called as "345 (or 345345)" net. The four-fold symmetry axis (pertaining to the structure) is situated at the center of each square in parallel with the <100> axes. Being forced to create pentagons, the B_{12}-B_{12} bond directions are significantly deviated from the five-fold axis directions. The feature of the bent bond is more clearly seen in Fig. 30, where a section of the icosahedral B_{12} network in Fig. 29 is presented; the icosahedra at both ends of the section are those which are centered at the positions 0,0,0 and 1,0,0 in Fig. 29. It would be interesting here to compare

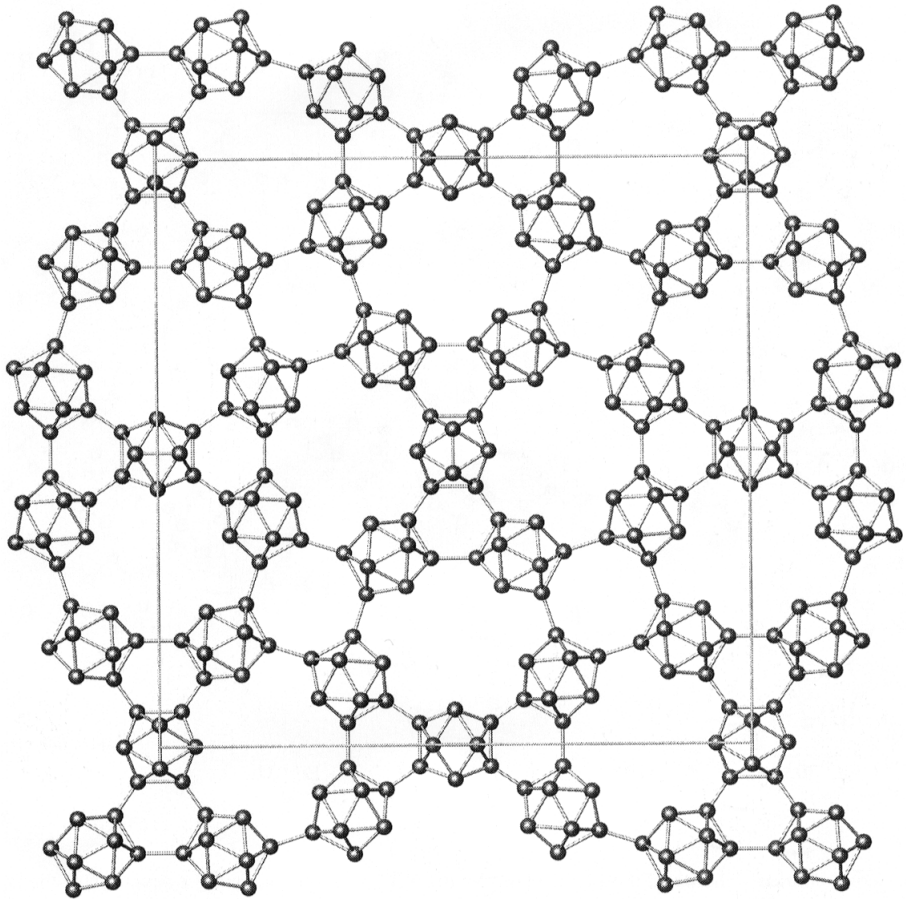


Fig. 29. Icosahedral B_{12} network in the YB_{66} structure extending on the {100} planes, showing the "345" type network.

the icosahedral B_{12} network (Fig. 29) and its section (Fig. 30) with those observed in the related compound $YB_{41}Si_{1.2}$ (HIGASHI *et al.*, 1997). The $YB_{41}Si_{1.2}$ compound is crystallized in the orthorhombic structure (space group, Pbam) with the lattice constants a = 1.67 nm, b = 1.767 nm, c = 0.9511 nm. It is composed of the B_{12} icosahedron and the $B_{12}Si_3$ polyhedral unit. The icosahedral B_{12} network lying just on the (001) plane (which is a mirror plane of crystal structure) is presented in Fig. 31. In this network similar sections to that of YB_{66} (Fig. 30) is seen in the <110> directions, although the curved icosahedral B_{12} chains are disconnected once every translation in this direction (Fig. 32).

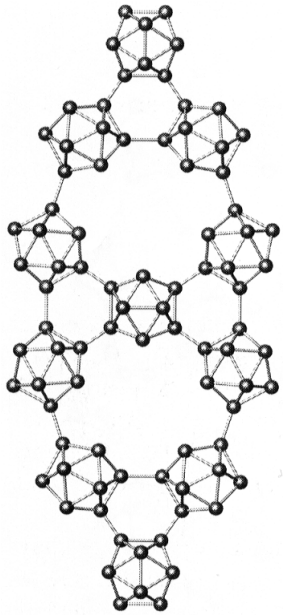


Fig. 30.

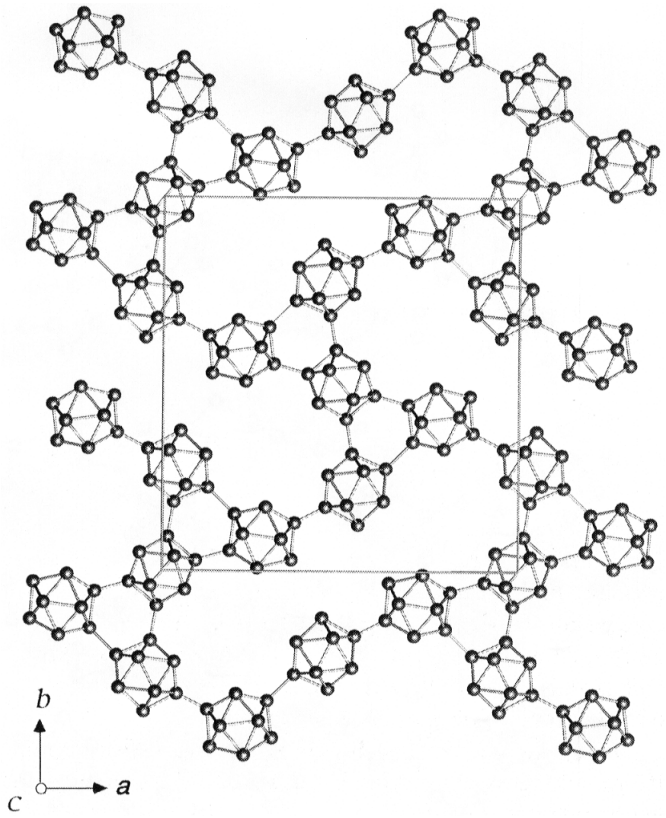


Fig. 31.

Fig. 30. Icosahedral B_{12} chains on the {100} planes in the YB_{66} structure, showing a deviation of the B_{12}-B_{12} linkage from the five-fold axis of the icosahedron.

Fig. 31. Icosahedral B_{12} network in the $YB_{41}Si_{1.2}$ structure extending on the (001) plane, showing disconnections of the B_{12}-B_{12} bonds within the "345" type network.

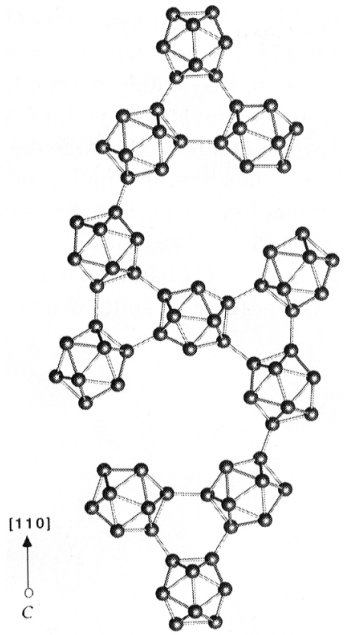


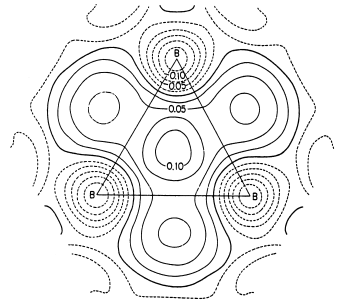
Fig. 32. Icosahedral B_{12} chains on the (001) plane of the $YB_{41}Si_{1.2}$ structure, showing a disconnection of the B_{12}-B_{12} bond every translation along the [110] direction.

9. Concluding Remarks

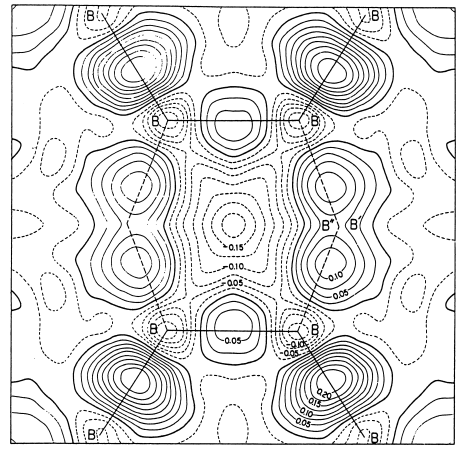
The icosahedral B_{12} crystals can be classified into eight types according to the mode of B_{12} arrangement (HIGASHI, 1986). The two-dimensional icosahedral B_{12} networks described in the present paper are therefore related to the structures of most of icosahedral B_{12} crystals. They are all plane networks (neither wavy nor puckered) extending on or parallel to the typical crystallographic planes such as (100), (010), (001), (110), (101), and (111) planes. It is of interest to point out that most of the icosahedral networks show 3^6 and 3636 (kagomé) type nets (PEASON, 1972).

When the icosahedral B_{12} networks are viewed down perpendicularly, they display different features of individual icosahedral B_{12} units, depending on the structural nature of the crystal plane on which (or parallel to which) they are extending. On the (111) plane of the α- or β-rhombohedral boron structure, the icosahedral B_{12} unit precisely shows its three-fold rotation-inversion symmetry, reflecting the same symmetry element along the [111] axis of the structures (Figs. 6, 9 and 11). (The icosahedral B_{12} network of Fig. 12 is not on the (111) plane but just in between the {111} planes.) On the other hand, the icosahedral B_{12} networks on the {100} planes of both structures show almost perfect two-fold or mirror symmetry of B_{12} icosahedra (Figs. 7 and 13). In the cubic, tetragonal, and orthorhombic structures, the icosahedral B_{12} units in the icosahedral B_{12} networks display

roughly or almost exactly its two-fold or mirror symmetry (Figs. 15, 18, 19, 23, 26, 29 and 31); only one exception is seen in Fig. 22 in which the icosahedral B_{12} unit is arranged so as to have one of its five-fold axes approximately perpendicularly to the icosahedral B_{12} network. In the crystals belonging to above orthogonal crystal systems, the icosahedral B_{12}-B_{12} linkages are necessarily deviated to a certain extent from the five-fold axis. This tendency is significant as for the crystals having smaller unit cell size (α-tetragonal boron and $AlMgB_{14}$: Figs. 16 and 24, respectively), as well as for the YB_{66} structure in which the icosahedral B_{12} network has the "345 (or 345345)" arrangement. As for the structure of $AlB_{24}C_4$, owing to the presence of C-B-C chains as a structural entity, the deviation of icosahedral B_{12}-B_{12} linkages is not notable in spite of its relatively small unit cell size.



(a)



(b)

Fig. 33. Average difference electron densities through (a) the triangular face and (b) the bisecting plane of the icosahedron in α-AlB_{12}.

It would be interesting to refer to the strong chemical bond within the structures of icosahedral B_{12} crystals, which is necessarily responsible for their extremely high hardness (2,000–3,000 kg/mm^2) and high-melting points (higher than 2,000°C). Features of bonding electron density distributions of the B_{12} icosahedron (three-centered bond) and the B_{12}-B_{12} inter-icosahedral two-centered bond are presented in Fig. 33 (ITO *et al.*, 1979). The difference electron density maps in the figure, obtained from a precision X-ray diffraction work, are reflecting the symmetry of icosaheron.

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