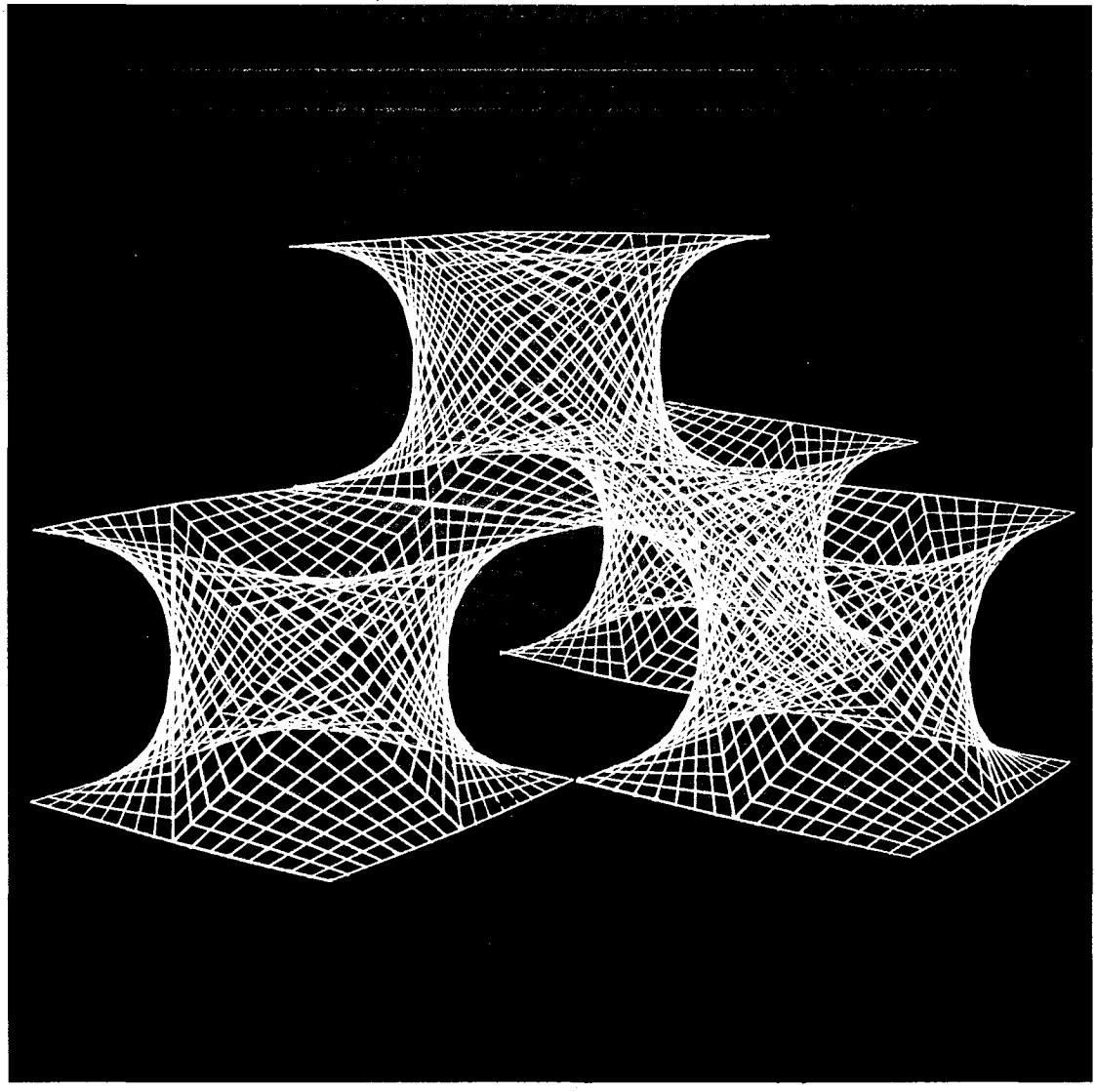
Symmetry: Culture and Science

ORDER / DISORDER
Proceedings, 4th Congress

The Quarterly of the
International Society for the
Interdisciplinary Study of Symmetry
(ISIS-Symmetry)

Volume 9, Numbers 2 - 4, 1998



Symmetry: Culture and Science
Vol. 9, Nos. 2-4, 257-268, 1998

ICOSAHEDRAL B_{12} ARRANGEMENTS IN YB_{66} AND $YB_{41}Si_{1.2}$

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Abstract: *Icosahedral* B_{12} *structures of boron-rich solids show unusual and fine appearances which originate in icosahedral structural entities, and are quite different from conventional atomic configurations which are widely seen in most of other inorganic compounds. This paper describes the structures of yttrium-containing boron-rich solids,* YB_{66} *and* $YB_{41}Si_{1.2}$*, which are unique even among icosahedral* B_{12} *crystals in that they are respectively constituted of the* B_{12}*-*$(B_{12})_{12}$ *giant-icosahedron and a similar giant structural unit,* B_{12}*-*$(B_{12})_8(B_{12}Si_3)_4$*. The* $(B_{12}Si_3)_4$ *polyhedral unit within the latter is an icosihexahedron (a polyhedron with 26 faces) discovered in the* $YB_{41}Si_{1.2}$ *compound. By describing the two giant structural units with a large circle, the complicated structures of these boron-rich compounds are presented in an understandable way. Comparison of packing densities of* B_{12} *icosahedra and the giant-icosahedra in these two compounds are made by defining some hypothetical diameters for the structural units.*

1. INTRODUCTION

Boron, borides and related compounds differ from conventional solids in that it is impossible to interpret their structural features in terms of conventional rule of valence.

As a result, these materials manifest a number of unique properties which in many cases are of potential technological importance giving rise to a growing interest in their physical and chemical properties. In a previous paper (Higashi et al. 1995), we have presented structural arrangements of icosahedral B_{12} structures of some boron-rich solids. That is because they show unusual and fine structures that have originated in icosahedral structural entities, and are quite different from conventional atomic configurations which are widely seen in most of other inorganic compounds.

Although a great number of icosahedral B_{12} crystals have thus far been reported, they can be classified into eight types according to the modes of icosahedral B_{12} arrangements (Higashi 1986). It is impossible to utilize five-fold rotation symmetry in a two- or three-dimensional periodic network, and thus three dimensional arrangements of B_{12} icosahedra form open although rigid three dimensional networks in real boron-rich solids. Except α-rhombohedral boron, therefore, icosahedral B_{12} structures need additional boron polyhedral units, such as B_{28}, B_{22}, and B_{20} and isolated boron atoms to fill the openings within the icosahedral B_{12} frameworks.

In the present paper, we describe the structures of yttrium-containing boron-rich compounds YB_{66} and $YB_{41}Si_{1\,2}$, which are unique even among icosahedral B_{12} crystals in that they are respectively constituted of so-called giant-icosahedron $B_{12}{\cdot}(B_{12})_{12}$ and a similar giant structural entity $B_{12}{\cdot}(B_{12})_8(B_{12}Si_3)_4$.

2. DESCRIPTION OF STRUCTURES

2.1 Structural units

An icosahedral polyhedron shows various outer appearances according to the direction along which it is seen. Therefore, to facilitate understanding the structural figures in this paper, the projections of icosahedron along the two-fold (a), three-fold (b), and five-fold axes are presented in Figure 1. The projection (d) in Figure 1 shows a directional nature of the linkage between boron icosahedra; it is mostly effected approximately along the five-fold axis. In Figure 2, a new structural unit $B_{12}Si_3$ is projected along the a, b and c axes of the $YB_{41}Si_{1\,2}$ structure in which the $B_{12}Si_3$ unit occupies an important position as a structural unit. As in the icosahedron, this unit has a mirror plane or bisecting plane, on which three Si sites are located.

The B_{12}·$(B_{12})_{12}$ giant-icosahedron and the similar structural unit $B_{12}(B_{12})_8(B_{12}Si_3)_4$ are projected along their two-fold axes in Figure 3 and Figure 4, respectively. In each figure, the central icosahedron was surrounded with twelve icosahedra (Figure 3) or eight icosahedra plus four $B_{12}Si_3$ units (Figure 4), showing that the mirror plane or bisecting plane of the unit is just on the projection plane.

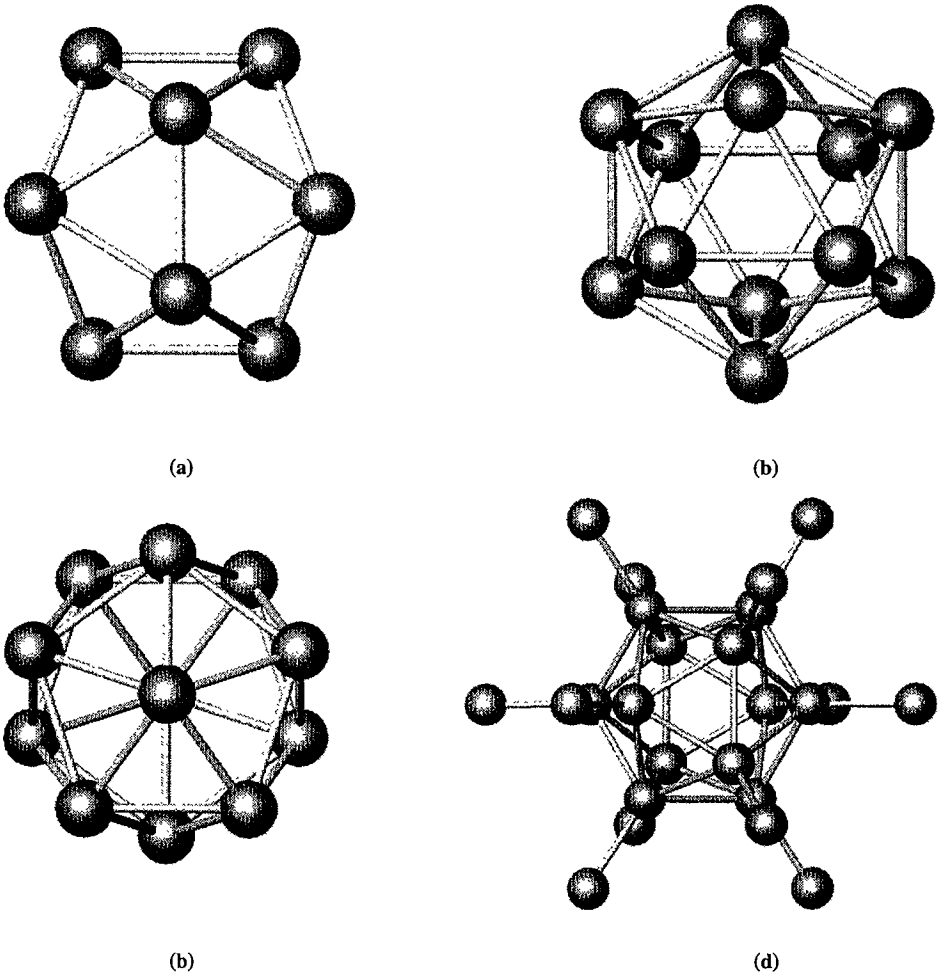

Figure 1: The icosahedral B_{12} unit as seen along the two-fold axis (a), three-fold axis (b), and five-fold axis (c). Figure (d) demonstrates a directional nature of linkages between the B_{12} icosahedron and neighboring boron structural units; the linkages are almost always effected along its five-fold axes.

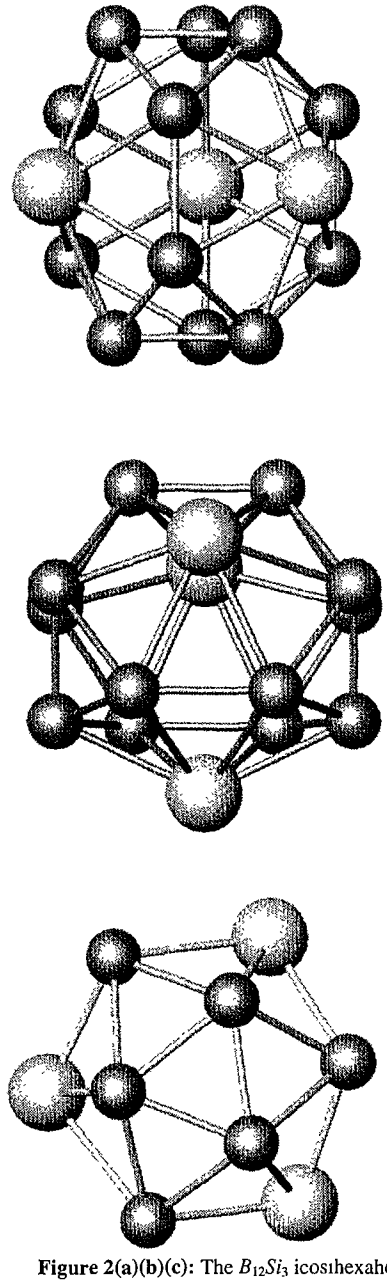

Figure 2(a)(b)(c): The $B_{12}Si_3$ icosihexahedron (a polyhedron with 26 faces) projected along the a axis (a), b axis (b) and c axis (c) of the $YB_{41}Si_{12}$ structure in which the $B_{12}Si_3$ unit occupies an important position as a structural unit

2.2 Structure of YB_{66}

The YB_{66} compound belongs to the face-centered cubic system (space group: Fm3c) with the lattice constant $a = 2.34364(6)$ *nm* (Richards and Kasper, 1969). The structure of this compound is basically constructed with the B_{12}-$(B_{12})_{12}$ giant-icosahedron (Figure 3), which is located in one orientation at the face-centered cubic lattice-point (Figure 5). It also occurs at the centers of the cell and the cell edges rotated by 90° (Figure 5). In consequence, there are eight B_{12}-$(B_{12})_{12}$ units (1248 boron atoms) in one unit cell. The relatively large hole at the center of each octant is filled with an irregularly shaped boron cluster consisting of 42 atoms, and smaller holes are filled with Y atoms. (In this paper, descriptions of the boron clusters and the distribution of Y atoms are omitted.)

In Figure 6, the arrangement of giant-icosahedra in the YB_{66} structure is presented by replacing the B_{12} icosahedral unit with a large circle. (In Figure 5, the B_{12} unit is depicted with twelve small circles.) The linkages between neighboring giant-icosahedra are formed by the inter-icosahedral B_{12}-B_{12} bonds approximately along the fivefold axes (Figure 1(d), Figure 5). The opening at the center of each octant of the unit cell is filled with the irregularly shaped cluster mentioned above.

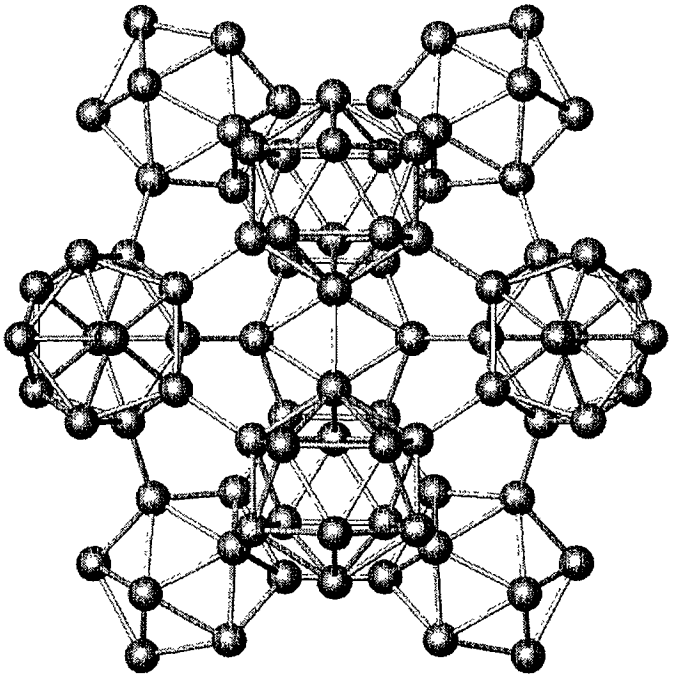

Figure 3: The $B_{12}'(B_{12})_{12}$ giant-icosahedron as seen along its two-fold axis.

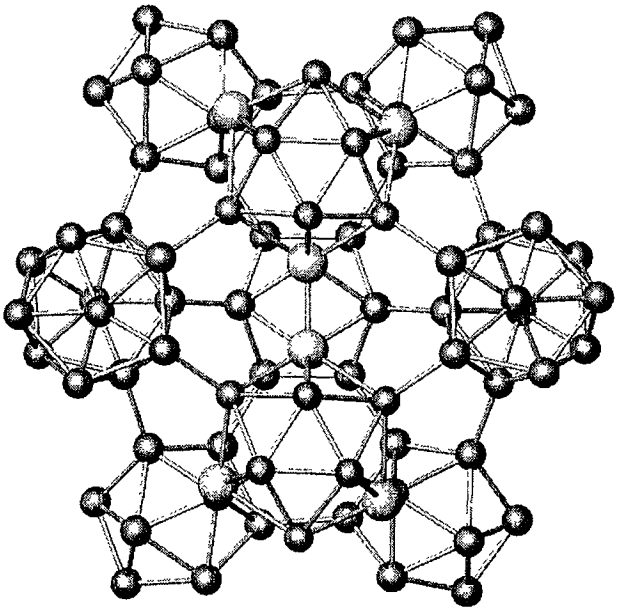

Figure 4: The $B_{12}'(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedron as seen along its two-fold axis.

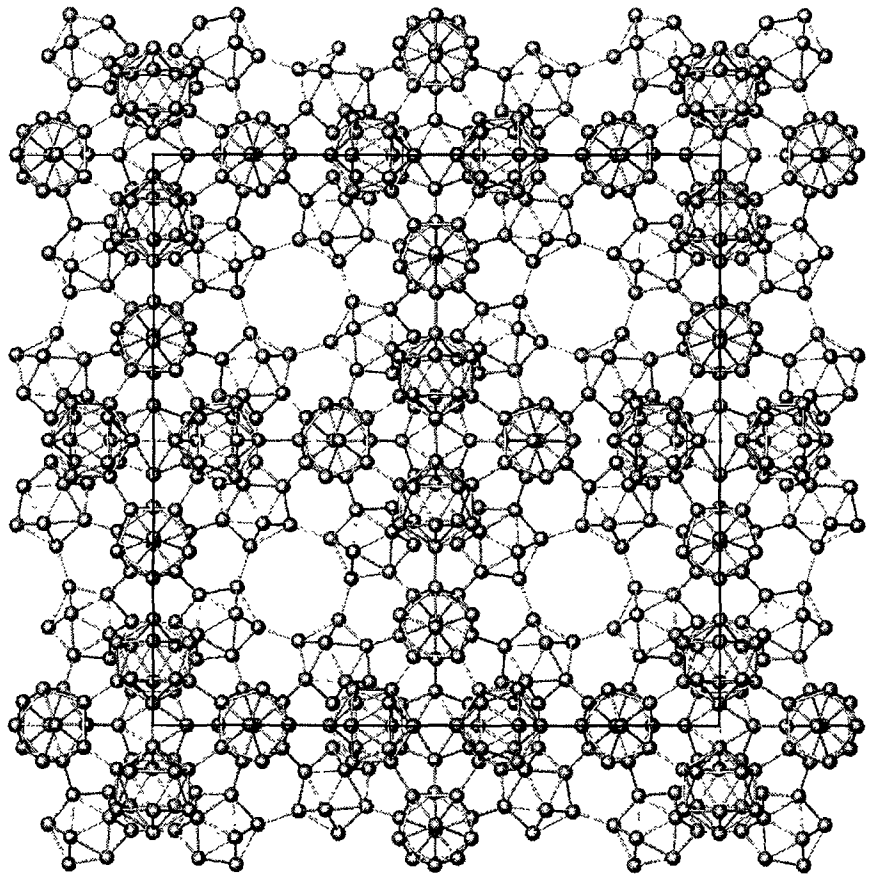

Figure 5: Arrangement of the B_{12}-$(B_{12})_{12}$ giant-icosahedron (or B_{12} icosahedron) in the YB_{66} structure. In this figure, boron atoms are depicted with a small circle.

2.3 Structure of $YB_{41}Si_{1.2}$

$YB_{41}Si_{1.2}$ is a new compound with a new structure-type, which have recently been prepared and the structure determined (Tanaka et al. 1997, Higashi et al. 1997). The structure of this compound is made up of the B_{12} icosahedron and $B_{12}Si_3$ icosihexahedron (a polyhedron with 26 faces) (Figure 2). The crystal belongs to the orthorhombic system (space group: *Pbam*) with the lattice constants a = 1.6674(1), b = 1.7667(1), and c = 0.9511(7) *nm*. By analogy with the YB_{66}-structure, the complicated boron-framework can be interpreted by use of the B_{12}-$(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedron (Figure 4), which corresponds to the B_{12}-$(B_{12})_{12}$ giant-icosahedron in YB_{66}.

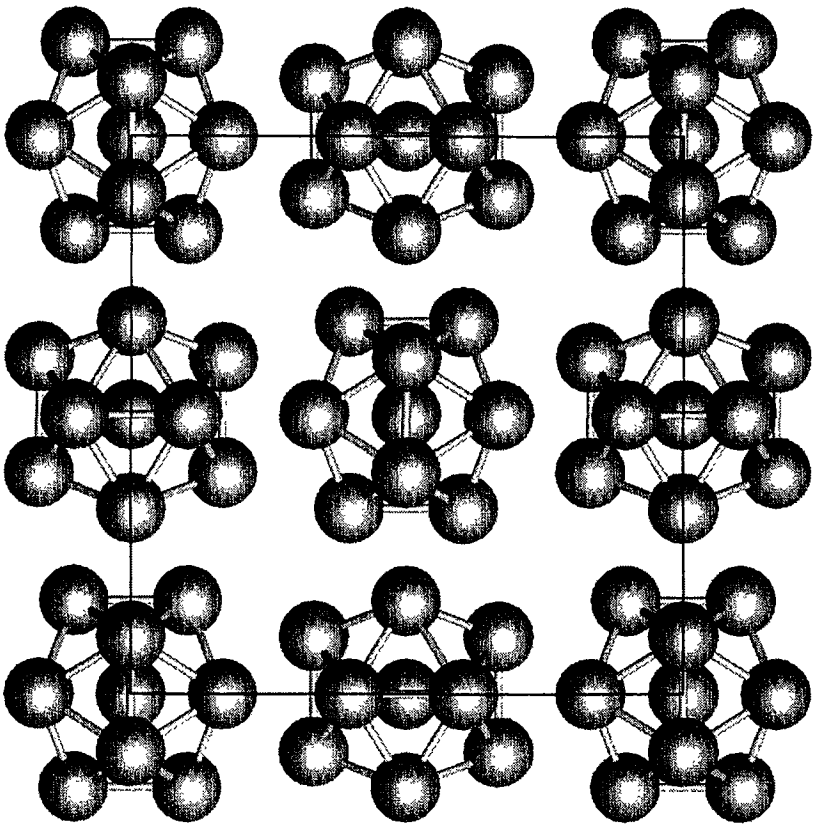

Figure 6: Arrangement of the $B_{12}(B_{12})_{12}$ giant-icosahedron (or B_{12} icosahedron) as seen along the a axis of the YB_{66} structure. In this figure, each icosahedron is depicteded with a large circle.

Figure 7 shows the arrangement of the $B_{12}(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedra as seen along the c axis. In this figure, five B_{12} icosahedra within the giant icosahedron, which are projected along their respective two-fold axis (as seen in Figure 1(a)), are placing their bisecting plane on the crystallographic mirror plane at $z = 0$. On the other hand, the $B_{12}Si_3$ units, involved in the giant icosahedron, are having their bisecting plane on the mirror plane at $z = 0.5$. The two large openings being bisected respectively with the (100) and (010) planes are filed with icosahedral B_{12} pairs shown in the Figure 8. It is of interest to note that the intericosahedral bond of B_{12}-B_{12} pair is quite different from the conventional B_{12}-B_{12} bond which is formed approximately along the five-fold axis; the bond of icosahedral pair is effected by putting one edge of each icosahedron in parallel to each other, forming an approximately square plane which lies on a plane bisecting both icosahedra.

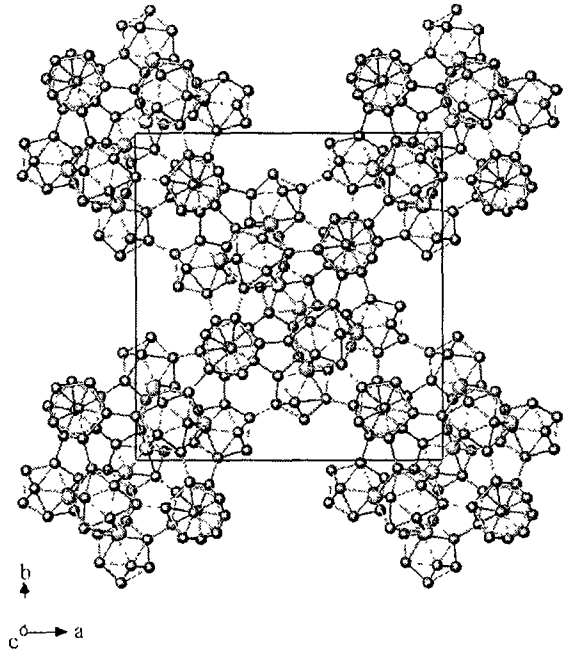

Figure 7: Arrangement of the $B_{12}'(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedron as seen along the c axis of the $YB_{41}Si_{12}$ structure. In this figure, as in Figure 5, the boron atoms are described with a small circle, and the silicon atoms with a little larger circle.

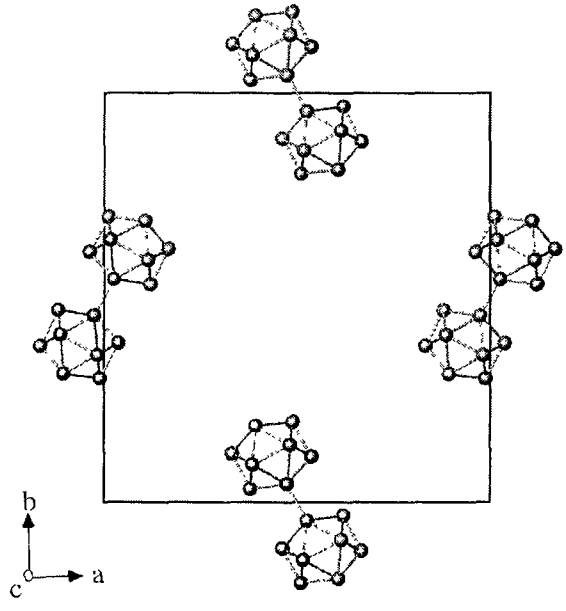

Figure 8: The B_{12}-B_{12} pair which occupies a large hole within the $B_{12}'(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedral network (see Figure 7).

In Figure 9, as in the case of the YB_{66}, the arrangement of the B_{12}-$(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedra in the $YB_{41}Si_{1.2}$ structure is presented by replacing the B_{12} and $B_{12}Si_3$ units with large circles. As seen from the unit cell indicated with a rectangle drawn in thick line, the arrangement of the giant-icosahedra is crystallographically quite different from that in YB_{66}. The sequences of the giant units are, however, similar to that in YB_{66}.

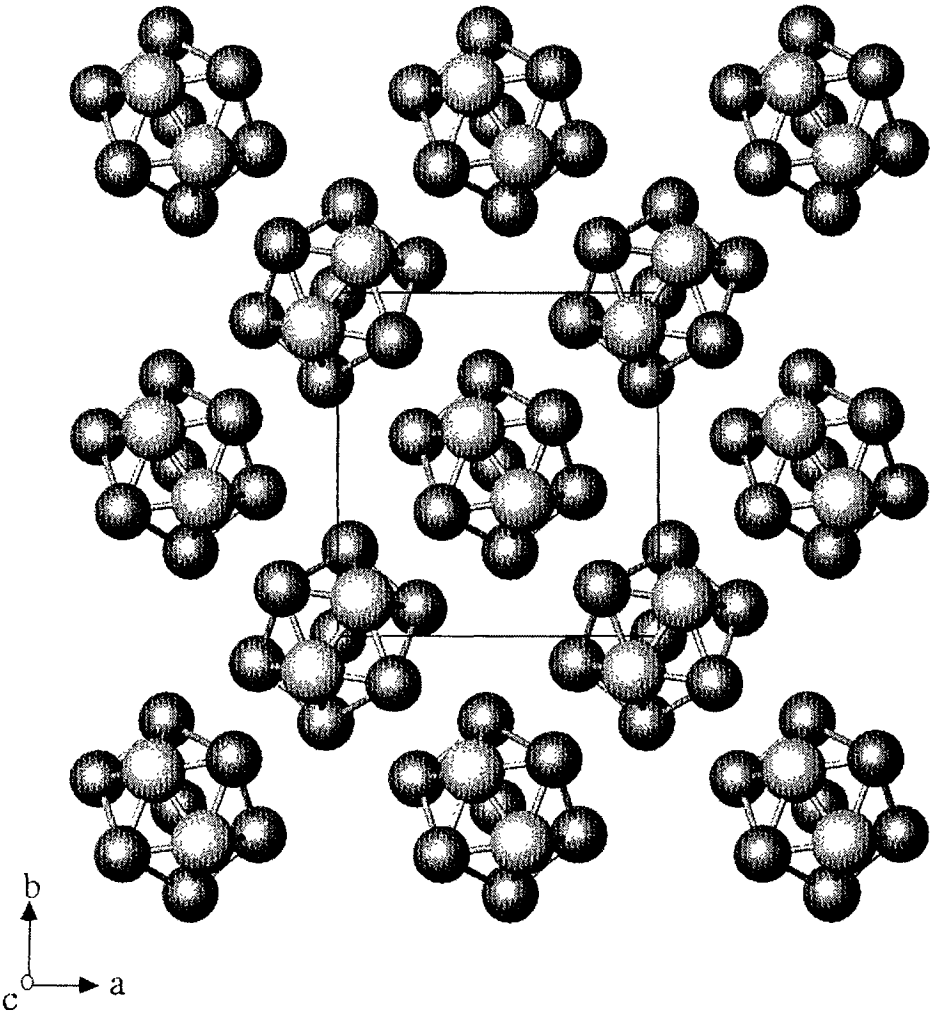

Figure 9: Arrangement of the B_{12}-$(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedron as seen along the c axis of the $YB_{41}Si_{1.2}$ structure In this figure, each B_{12} icosahedron or the $B_{12}Si_3$ unit is depicted with a large circle. (The larger ones are the $B_{12}Si_3$ unit.)

Arrangement of the $B_{12}{\cdot}(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedron as seen approximately along the $[\overline{1}10]$ axis of the $YB_{41}Si_{1\,2}$ structure is presented in Figure 10. In this figure, as in Figure 9, each icosahedron or the $B_{12}Si_3$ unit is depicted with a large circle. There are giant-icosahedral chains running along the c axis, in which each giant-icosahedron is connected to neighboring ones by sharing the $B_{12}Si_3$-$B_{12}Si_3$ giant icosahedral edges. Unlike the case that the linkages between $B_{12}{\cdot}(B_{12})_{12}$ giant icosahedra in the YB_{66} structure are always effected through intericosahedral B_{12}-B_{12} bonds along five-fold axes of B_{12} icosdahedra, the linkages formed by sharing the $B_{12}Si_3$-$B_{12}Si_3$ edges necessarily result in a dense giant-icosahedral framework in the $YB_{41}Si_{1\,2}$ structure.

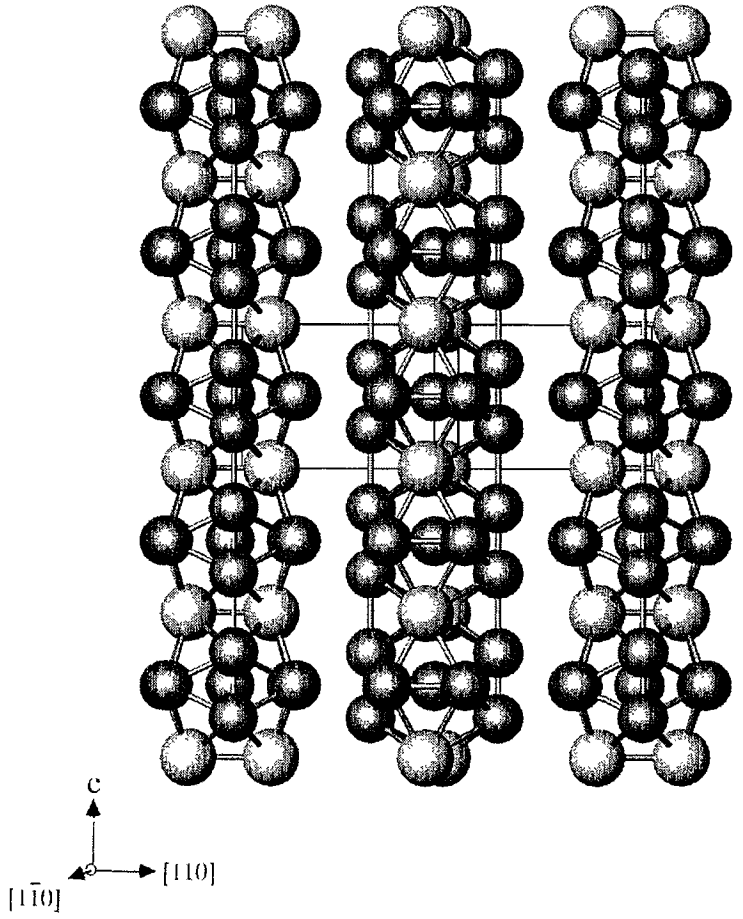

Figure 10: Arrangement of the $B_{12}{\cdot}(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedron as seen approximately along the $[\overline{1}10]$ axis of the $YB_{41}Si_{1\,2}$ structure. In this figure, as in Figure 9, each B_{12} icosahedron or the $B_{12}Si_3$ unit is depicted with a large circle. (The larger one is the $B_{12}Si_3$ unit) There are giant-icosahedral chains running along the c axis, in which each giant-icosahedron is connected to neighboring ones by sharing the icosahedral $B_{12}Si_3$-$B_{12}Si_3$ edges.

2.4 Packing densities of structural units

Packing densities of structural units in the YB_{66} and the $YB_{41}Si_{1.2}$ structures are compared in Table 1. Calculations of packing densities were made assuming that the structural units are spheres with hypothetical diameters. The diameter of each unit was estimated by examining distances between the centers of directly connected structural units. The B_{12} icosahedron is thus proved to have almost the same size in both crystals; the estimated diameter of B_{12} icosahedron is 0.5 *nm*. The diameters of the $B_{12}Si_3$ unit and the $B_{12}{\cdot}(B_{12})_{12}$ giant icosahedron were estimated to be 0.53 *nm* and 1.17 *nm*, respectively. As to the $B_{12}{\cdot}(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedron, the diameter can not be defined owing to its edge sharing with neighboring ones.

Units / Compounds [a]	B_{12}		$B_{12}+B_{12}Si_3$		$B_{12}\cdot(B_{12})_{12}$	
	n	d(%)	n	d(%)	n	d(%)
YB_{66}	104	53			8	52
$YB_{42}Si_{1.2}$ [b]	20	47	20 + 4	58		

[a] *n* is the number of the units contained in a cell, and *d* is volume fraction of the unit/units.

[b] As to $YB_{41}Si_{1.2}$, packing densities of B_{12} ($n = 20$) and B_{12} plus $B_{12}Si_3$ ($n = 24$) were calculated.

Table 1: Packing densities of structural units in YB_{66} and $YB_{42}Si_{1.2}$

The packing densities (52%) of $B_{12}{\cdot}(B_{12})_{12}$ unit in the YB_{66} structure is the same as that of spheres with equal size in the simple cubic close-packed arrangement, because the $B_{12}{\cdot}(B_{12})_{12}$ unit is located at the corner of each octant of the cubic structure of YB_{66}, and the hypothetical diameter of the unit is equal to the edge length of the octant. It is noteworthy, however, that the packing densities of B_{12} icosahedral units in the YB_{66} structure is almost equal to that of the $B_{12}{\cdot}(B_{12})_{12}$ unit. As to $YB_{41}Si_{1.2}$ structure, the packing density of B_{12} unit (47%) is smaller than that in the YB_{66} structure, while the packing density of B_{12} plus $B_{12}Si_3$ (58%) is larger.

3. CONCLUSIONS

Icosahedral arrangements in the YB_{66} and the $YB_{41}Si_{12}$ structures are presented and unique features in both structures compared. Although the B_{12} icosahedron is the fundamental structural unit of both compounds, the complicated structures are explained in an understandable way by using the $B_{12}{\cdot}(B_{12})_{12}$ and $B_{12}{\cdot}(B_{12})_8(B_{12}Si_3)_4$ giant-icosahedral units for description of the YB_{66} and the $YB_{41}Si_{12}$ structures, respectively.

Spherical diameters were assumed for the structural units, and packing densities of B_{12} and $B_{12}{\cdot}(B_{12})_{12}$ in YB_{66}, and of B_{12} and B_{12} plus $(B_{12}Si_3)$ in $YB_{41}Si_{12}$ were estimated; the obtained values were 53, 52, 47, 58%, respectively.

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