

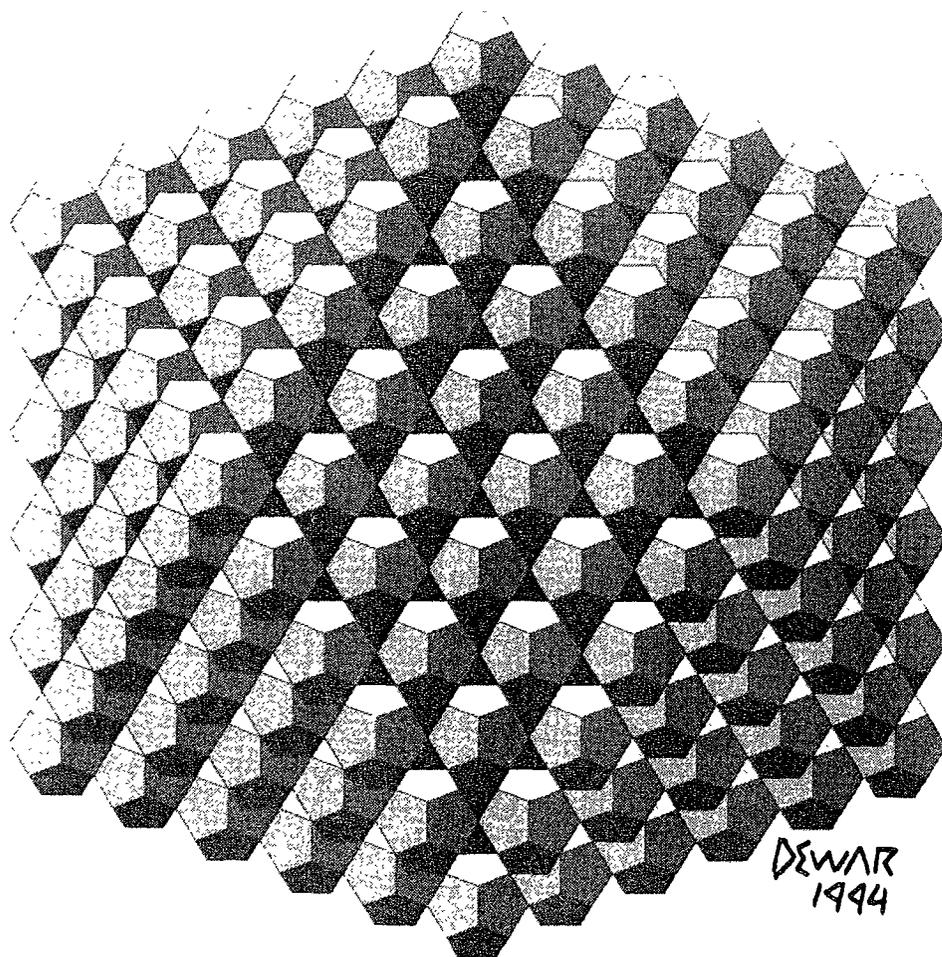
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ICOSAHEDRAL B₁₂ ARRANGEMENTS IN BORON-RICH SOLIDS

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1. Introduction

Although there are several interesting aspects in the field of boron-rich solids, most research scientists working with these materials are interested in their physical and chemical properties some of which are supposed to be of technological importance. In the present paper, however, we presents structural arrangements and symmetry of icosahedral B₁₂ structures in boron-rich solids. These topics are very interesting because of the unusual forms and beauty of the structures which are quite different from conventional atomic configurations.

Boron, borides and related compounds differ from conventional 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, etc.) which in many case are of possible technological importance giving rise to a growing interest in their physics and chemistry . Further, these materials are unique in that the boron atoms in their structures tend to gather to bond each other. With increase of boron concentration, the boron atoms form a pair, a (single, double and triple) zig-zag chain, a hexagonal network, B₆ octahedron, B₁₂ cubooctahedron and B₁₂ icosahedron.

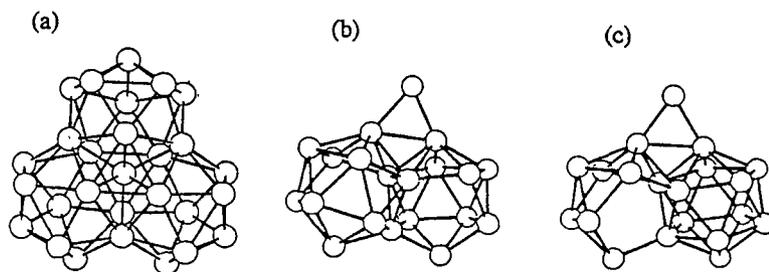
2. B₁₂ icosahedron and its derivatives

Although a great many icosahedral B₁₂ compounds have so far been published, they can be classified into eight types (Table 1) according to the mode of icosahedral B₁₂ arrangement (Higashi, 1986). It is not possible to utilize fivefold rotation symmetry in a two- or three-dimensional periodic network, and thus three dimensional arrangements of B₁₂ icosahedra form open although rigid three dimensional frameworks. Except α -rhombohedral boron, therefor, icosahedral B₁₂ crystals need additional structural entities such as B₂₈, B₂₂ and B₂₀ units, and isolated boron atoms to fill openings within the B₁₂ frameworks.

Table I Classification of icosahedral B₁₂ crystals

Structure type	Structural Formula	Reference
α -rhom. boron	B ₁₂	(Decker & Kasper, 1959)
β -rhom. boron	(B ₁₂) ₄ ·(B ₂₈) ₂ B	(Hughes et al., 1963)
α -tet. boron	(B ₁₂) ₂ B ₂ /(B ₁₂) ₂ ·C·B	(Hoard et al., 1958) / (Will & Kossobutzki, 1976)
β -tet. boron / α -AlB ₁₂	(B ₁₂) ₂ B ₂₂ B _x / (B ₁₂) ₂ B ₂₀ ·Al _{3.33}	(Vlasse et al., 1979) / (Higashi et al., 1977)
AlC ₄ B ₂₄	(B ₁₂) ₂ C ₈ ·B ₄ Al _{2.1} ·C·B	(Will, 1969)
YB ₆₆	(B ₁₂) ₁₃ B ₄₂ ·Y ₃	(Decker & Kasper, 1959)
AlMgB ₁₄	B ₁₂ B ₂ ·AlMg	(Matkovich & Economy, 1970) (Higashi & Ito, 1983)
γ -AlB ₁₂	(B ₁₂) ₄ (B ₂₀) ₂ ·Al _{6.66}	(Hughes et al., 1977) (Higashi, 1983)

In Fig. 1, B₂₈ and B₂₀ units are presented. The B₂₂ unit can be made up of B₂₀ unit by filling two vacant sites with two B atoms. In addition to occurrence of these icosahedral derivatives, there are successive stages in the evolution of the basic unit (B₇, B₁₂, B₈₄, and B₁₂(B₁₂)₁₂) of boron framework in some boron-rich solids (Fig. 2).

Fig. 1.(a) B₂₈, (b) B₂₀-(C₂), and (c) B₂₀-(C_s)

As shown in Fig 2, B₇ is a half-icosahedron with an additional B atom. B₈₄ unit is a basic structural unit of the β -rhombohedral boron structure. This unit consists of one central B₁₂ icosahedron and surrounding twelve B₆ half-icosahedra. (In the β -rhombohedral boron structure, the twelve half-icosahedra belong to six icosahedra and six B₂₈ units which are directly linked to the central icosahedron.) B₁₂(B₁₂)₁₂ unit is a basic structural unit of YB₆₆, and made up of a

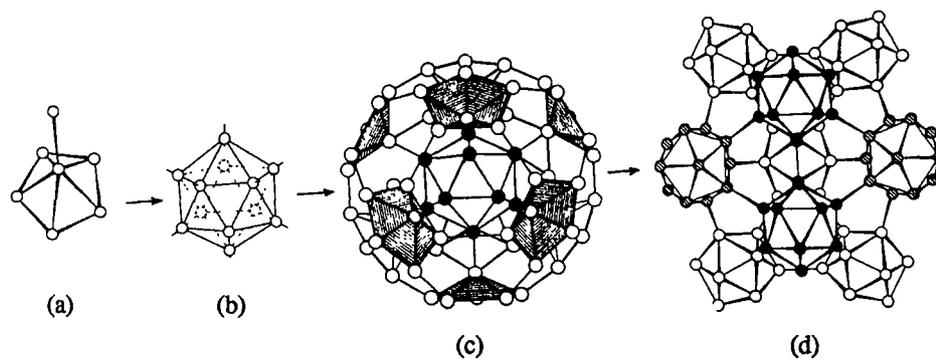


Fig. 2. Evolution of the basic unit of the boron framework in some boron-rich phases: (a) B₇, (b) B₁₂, (c) B₈₄, (d) B₁₂(B₁₂)₁₂ (From Naslain, 1977).

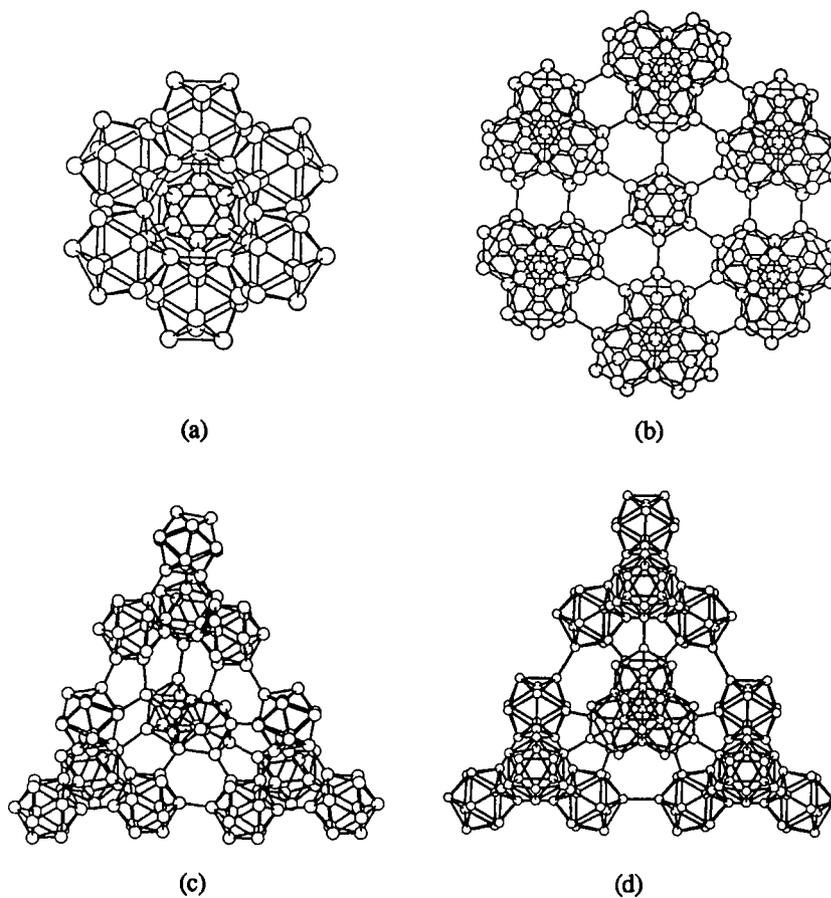


Fig. 3. Features of the linkages, (a) B₁₂-6B₁₂, (b) B₁₂-6B₂₈, (c) B₂₀-9B₁₂, (d) B₂₈-9B₁₂

central B_{12} icosahedron and surrounding twelve B_{12} icosahedra. All the linkages between neighboring icosahedra within the giant $B_{12}(B_{12})_{12}$ unit are formed along the fivefold axes of icosahedra. Construction of any structural unit greater than $B_{12}(B_{12})_{12}$ by linking B_{12} icosahedra through their fivefold axes seems to be impossible, since five-fold rotation symmetry can not be utilized in constructing three dimensional periodic space. Therefore, in the YB_{66} structure (Cubic; Space group, $Fm\bar{3}c$; $a = 23.44 \text{ \AA}$) the giant $B_{12}(B_{12})_{12}$ unit is situated at the lattice point of the face-centered cubic unit cell, resulting in the occurrence of large openings, which are filled with Y atoms and irregularly shaped B_{42} units having considerable number of vacant sites.

In Fig. 3, features of the linkages, $B_{12}-6B_{12}$ (β -rhombohedral boron), $B_{12}-6B_{28}$ (β -rhombohedral boron), $B_{28}-9B_{12}$ (β -rhombohedral boron), and $B_{20}-9B_{12}$ (α - AlB_{12}), are presented. The beauty of the structures of icosahedral B_{12} crystals is in that all the linkages between the structural units are effected along their fivefold axes of icosahedra or similar axes of the icosahedral derivatives, neatly constructing infinite three dimensional rigid frameworks.

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HEXA-PLEXUS

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●SIX-SCRUMMED PENTAGRAMS

A structure as shown in Figure 1 is constructed with six pentagons intersecting each other. The structure consists of 30 pieces as shown in Figure 2.

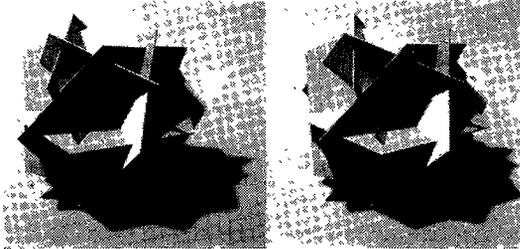


Fig. 1 SIX-SCRUMMED PENTAGRAMS

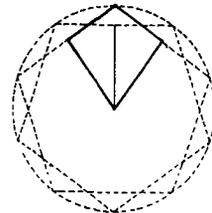


Fig. 2 A piece of SIX-SCRUMMED PENTAGRAMS

If the pentagon is replaced with a pentagonal frame as shown in Figure 3, the structure is as shown in Figure 4. The pentagonal frame in Figure 3 is formed in accordance with the golden section τ . The frames support each other at a contact point.

When the frame has a width w , and a thickness d , the length of one side of the pentagon is:

$$l = 4 (\sqrt{\tau + 2} w + d / \tau) \quad (\tau : \text{The golden section})$$

Figure 6 shows a work formed in this manner. Six pentagonal frames having certain thickness engage with each other. The work, made by assembling 30 pieces in Figure 5, can be a puzzle.

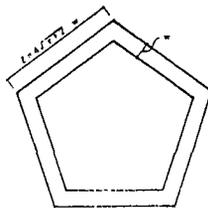


Fig. 3. A piece of SIX-SCRUMMED PENTAGONAL FRAMES

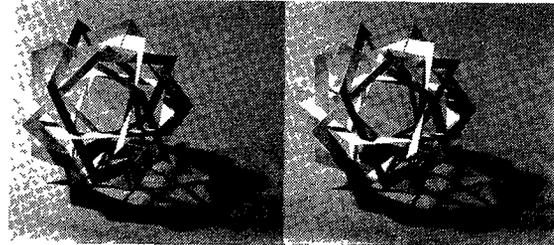


Fig. 4 SIX-SCRUMMED PENTAGONAL FRAMES



Fig. 5 A piece of SIX-SCRUMMED THICK PENTAGONAL FRAMES

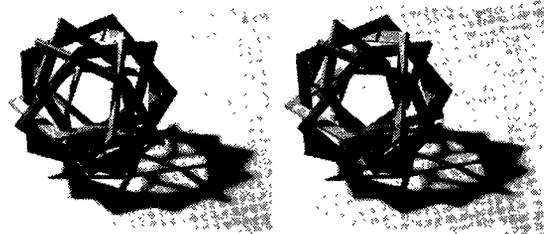


Fig. 6. SIX-SCRUMMED THICK PENTAGONAL FRAMES

●SIX-SCRUMMED FINGERS

If the pentagons are replaced with pentagonal frames made of columnal bars each having a radius r , the length of one side of the pentagon is:

$$l = 4\sqrt{\tau+2} \left(1 + \frac{\sqrt{17\tau+18}}{3\tau+1}\right) r$$

The completed work seems like scrummed people or naturally crossed fingers (Figure 7). Figure 8 is an developed view of a joint part of a finger.

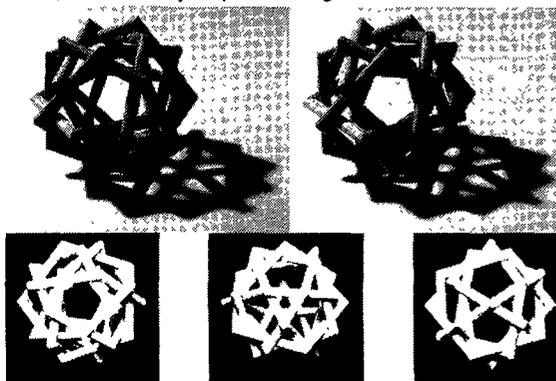


Fig. 7 SIX SCRUMMED FINGERS

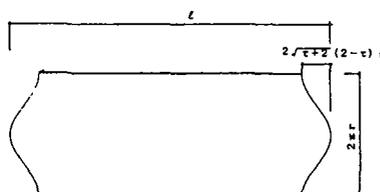


Fig.8. An develop view of a piece of SIX-SCRUMMED FINGERS

There are heterogeneities of these six-fold constructions, distinguished between clockwise and counterclockwise directions. However, the pentagon can not be distinguished. The element has no play, and if we are careless about the ratio, the structure should be loose. Precise assembling is required. Once completed, the work has a stable and rigid structure. If we were classicists with an old sense of beauty, we would be satisfied with such a limited formative art, and be absorbed in making the plan minutely. However, it does not satisfy me, because all of them are self-concluded and there is no chance to expand to infinity. The nature would avoid such an uncomfortable formation.

●HEXA-PLEXUS

A pentagon could not be distinguished between clockwise and counterclockwise direction, indeed. Using a kind of spiral star structure (Figure 9) instead of a pentagon, we can easily distinguish them. I have invented the structure expanded into unlimited plane, called "STAR CAGE 五勾(GO-MAGARI)" (1990). It stands by itself as a five-fold planar structure.

To make a six-fold structure with the spiral star structure, we can see the planes, which are constructed with "GO-MAGARI", quasi-periodically intersect one another (Figure 11, 12). The spiral star structures support each other at straight lines.

The regular dodecahedral, or regular icosahedral symmetry and size of the structure is defined based on the straight lines.

There are four solid-heterogeneity. Like "GO-MAGARI", this three-dimensional structure will be expanded into unlimited quasi-crystallized network. This reminds me of plexus — tissues of brain, I call this system a "HEXA-PLEXUS".

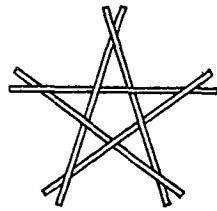


Fig. 9. SPIRAL PENTAGRAM

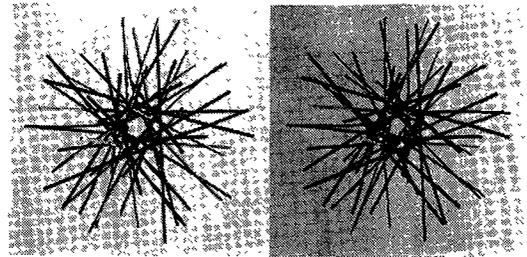


Fig. 11. An unit of HEXA-PLEXUS

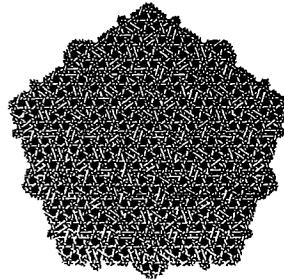


Fig. 10. STAR CAGE 六勾 (MU-MAGARI)

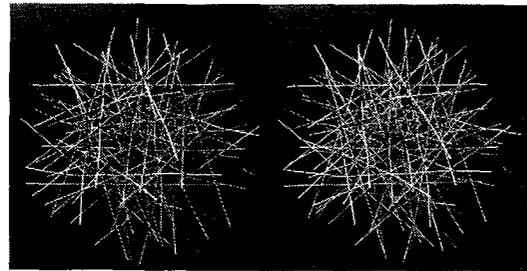


Fig. 12. HEXA-PLEXUS

I presented a solid structure called "STAR CAGE 六勾 (MU-MAGARI)" in 1993 (Figure 13). This quasi-periodical model was made by innumerable rods. Note that a "Penrose Weaving", presented by someone else, has a similar structure as "MU-MAGARI". Like "MU-MAGARI", "HEXA-PLEXUS" will also provide a new vision for quasi-periodical models

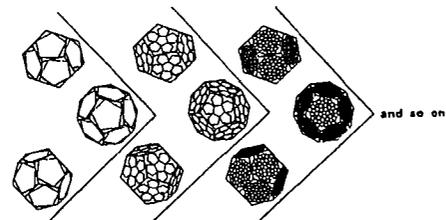
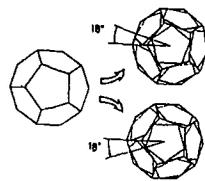
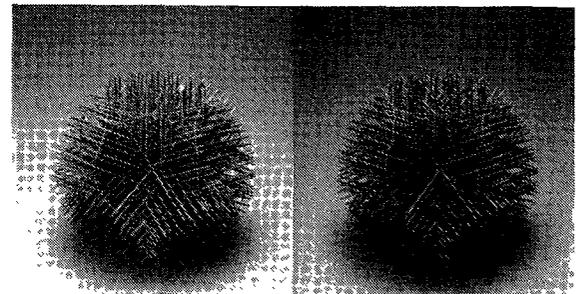
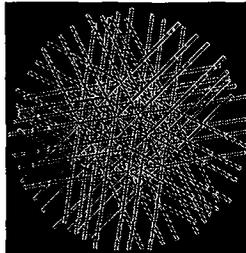


Fig. 13. STAR CAGE 六勾 (MU-MAGARI)

●PLEIADES

I made a small work called "昴 (subaru) = pleiades", with six pentagrams (Figure 14). Like the Great Bear, the pleiades have been popular since old times

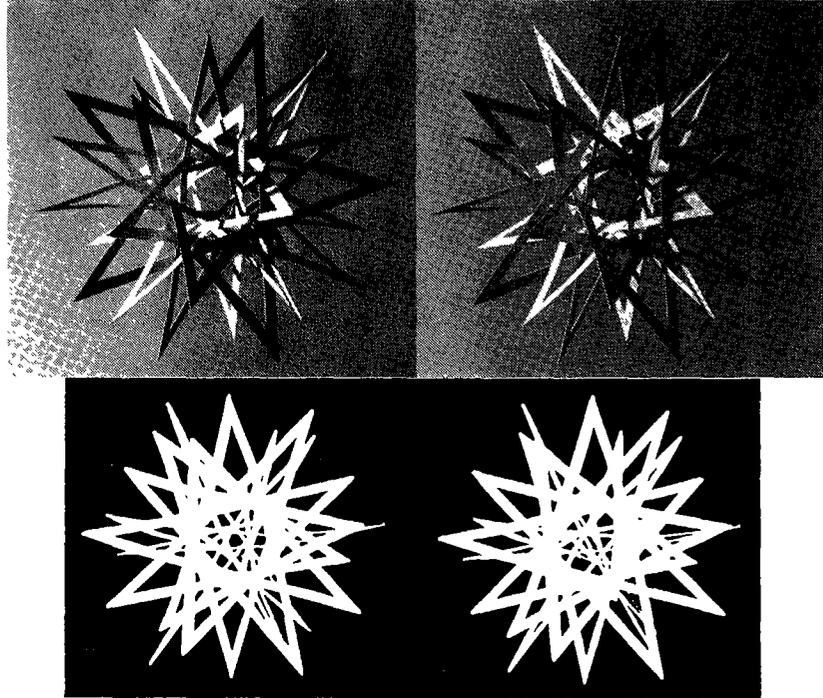


Fig 14 PLEIADES

●DECA-PLEXUS

The "Poly-link" by A. Holden (Figure 10) is constructed with ten triangle frames. It can be transformed like our "HEXA-PLEXUS". It must be a ten-fold structure like Figure 16. So it might be called DECA-PLEXUS

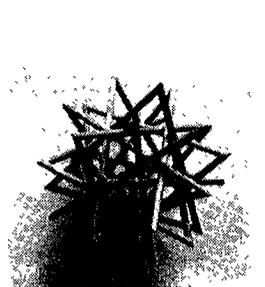


Fig 15 The POLY-LINK by A. Holden

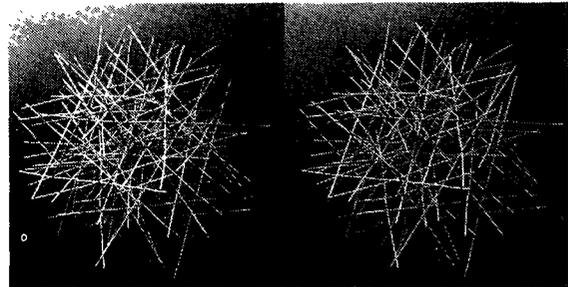


Fig. 16 DECA-PLEXUS

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