crystallographers, physicists and photographic scientists, whose names are too numerous to be mentioned here, for informative suggestions and valuable discussions.

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Self-Crystallizing Molecular Models

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It is shown that the structure of a molecular crystal corresponds to a minimum of electrostatic energy between the molecules when the molecules have simple shapes and sufficiently strong electric multipoles. In these cases the crystal structure can be reproduced with molecular models, which are made of magnets so as to simulate magnetically the electric forces between actual molecules. When their shapes and magnetization are adequately patterned after given molecules, the 'crystals', into which these models are assembled, show the crystal structures actually given by the molecules. Photographs of several types of such 'crystals' are shown.

The purpose of this paper is to show that the structure of a molecular crystal is governed by electrostatic forces between the molecules when the molecules have simple shapes and sufficiently strong electric multipoles. Molecular models devised by the author (Kihara, 1960) are used for this purpose.

The models are made of magnets so as to simulate magnetically the electric forces between actual molecules. When their shapes and magnetization are adequately patterned after given molecules, the 'crystals', into which these models are assembled, show the crystal structures actually given by the molecules.

An approximate choice of such molecular models is the following (Fig. 1):

Type I. Fifteen octupolar spheres, each of which is composed of eight magnets in the symmetry $\bar{4}3m$ (T_d).

Type II. Fourteen quadrupolar spheres, each of which is composed of two hemispherical magnets.

Type III. Fourteen quadrupolar spindle-shaped models.

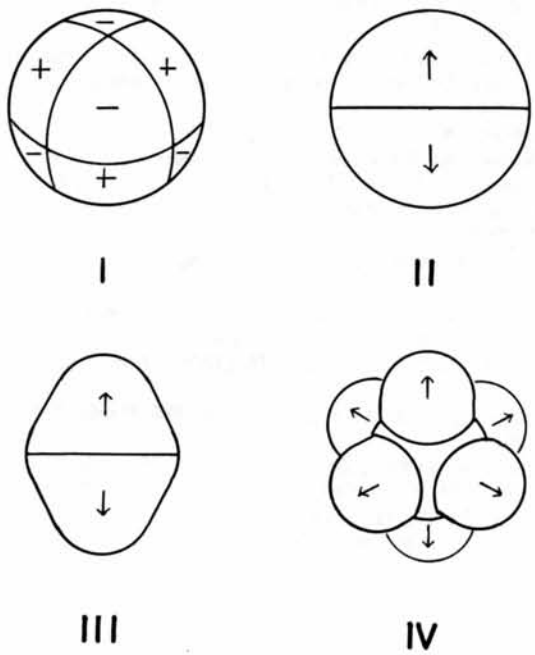

Fig. 1. Typical molecular models for crystallization.

Type IV. Eight hexadecapolar octahedron-like models, each of which is composed of six hemispheroidal magnets attached to a non-magnetic roundish cube in the symmetry $m3m$ (O_h).

Type I

The crystalline structures of molecules with perfect spherical symmetry are closest-packing. Thus neon, argon, krypton, and xenon crystallize into the face-centered cubic lattice. Furthermore, almost spherical molecules such as methane CH_4 and adamantane (sym-tricyclodecane) $(CH_2)_6(CH)_4$ crystallize into the face-centered cubic lattice of the space group $F\bar{4}3m$ (T_d^2) (*cf.* Wyckoff, 1953, Fig. XVD2).

Silicon tetrafluoride SiF_4 and hexamethylenetetramine $(CH_2)_6N_4$ are both nearly spherical ilke methane and adamantane (Fig. 2). Their crystal structure, however, is body-centered cubic $I\bar{4}3m$ (T_d^3), all the molecules being in the same orientation (Wyckoff, 1953, Fig. XVD1). These molecules have

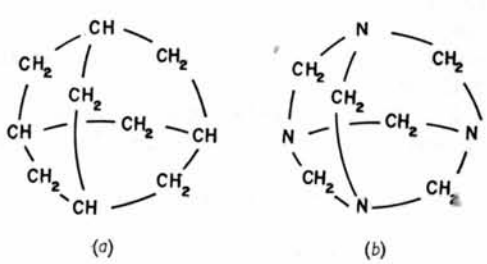

Fig. 2. Nearly spherical molecules, whose crystal structures are different: (*a*) adamantane, (*b*) hexamethylenetetramine.

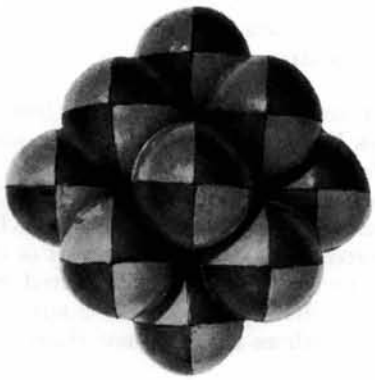

Fig. 3. The body-centered cubic assembly of octupolar spheres.

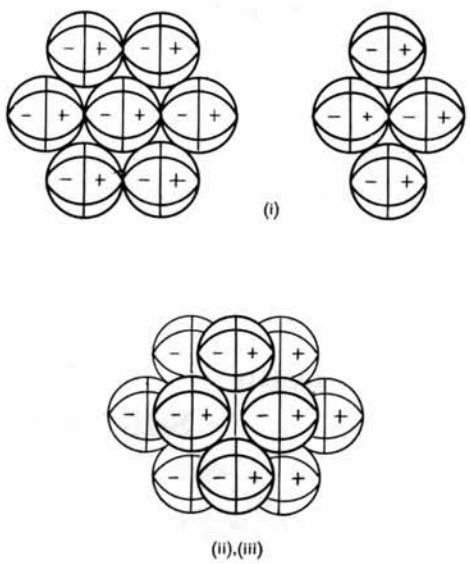

Fig. 4. Steps in the assembling of models of type I.

strong electric octupoles; and it is possible that the octupolar interaction makes the energy of the body-centered lattice lower than the closest-packing face-centered lattice. In fact, the models of type I can be assembled into this body-centered structure as shown in Fig. 3.

A crystal formed by the present molecular models is quite stable against gravitation and other disturbances. It is preferable, however, to assemble the models step by step as shown in Fig. 4: (i) Collect seven molecules on a desk into such a pattern that all the octupoles are in the same orientation; on the other side, collect furthermore four molecules in the same orientation as before. (ii) Put the four-molecule system on the seven-molecule system. Then the two systems attract each other, and small gaps appear automatically in proper positions. (iii) Turn the whole system upside down, and put four more molecules on in the same way.

Type II

The crystal structure of carbon dioxide CO_2, β-hexachlorocyclohexane $C_6H_6Cl_6$, and β-hexabromocyclohexane $C_6H_6Br_6$ is face-centered cubic in the arrangement of molecular centers (Wyckoff, 1948, 1953, Figs. IV32 and XVA9). It is constituted by four simple cubic Bravais lattices, on each of which molecules are respectively in one of the four body-diagonal orientations, the space group being $Pa3$ (T_h^6).

The models of type II, which form the same crystal structure (Fig. 5), show that the stability of this structure is based on the strong electric quadrupoles which these molecules possess. (The spherical shape is an idealization of the shapes of these molecules; prolate and oblate spheroids will be closer to reality, *cf.* Figs. 6 and 7.)

Preferable steps of assembling are the following (Fig. 8): (i) Make, on a desk, two three-molecule systems which are congruent without reflection. (ii) Hold an additional molecule above the center of one system with the molecular axis kept in the vertical direction. Then the three underlying molecules make a slight inclination, as a result of which the vertically held molecule is attracted and a stable four-molecule system is formed. (iii) Put the four-molecule system on the three-molecule system. Then the whole system automatically takes the configuration in which the upper system is rotated by 60° with respect to the lower system. (iv) Put three molecules in vertical orientation around the upper system. (v) Turn the whole upside down on the palm of one hand, and put four more molecules on in the same manner.

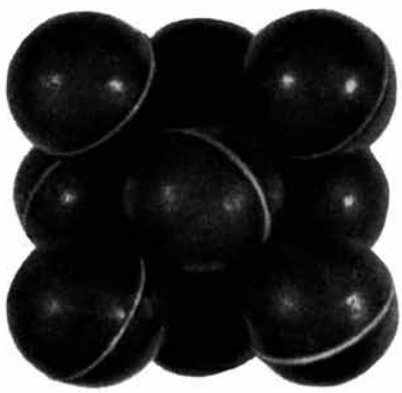

Fig. 5. The face-centered cubic assembly of quadrupolar spheres.

Fig. 6. The face-centered cubic assembly of quadrupolar prolate spheroids representing carbon dioxide.

Fig. 7. The face-centered cubic assembly of quadrupolar oblate spheroids representing hexachlorocyclohexane.

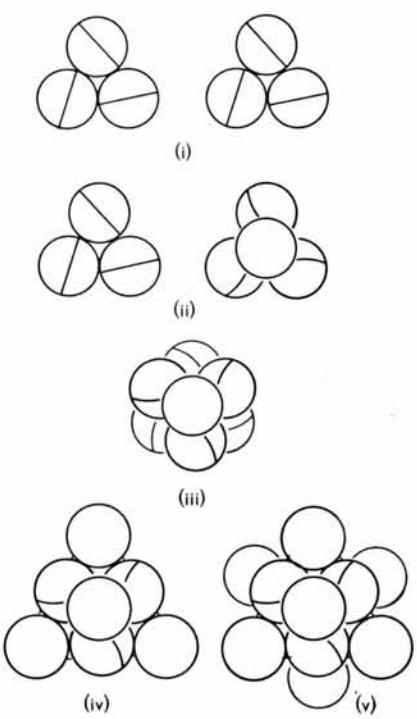

Fig. 8. Steps in the assembling of models of type II.

Type III

The most stable two-dimensional arrangement of the models of type III is shown in Fig. 9. Several structures can be formed when such arrangements are piled up in layers.

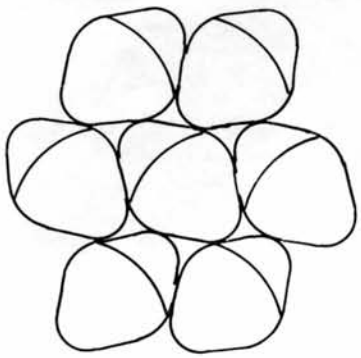

Fig. 9. The most stable two-dimensional arrangement of type III.

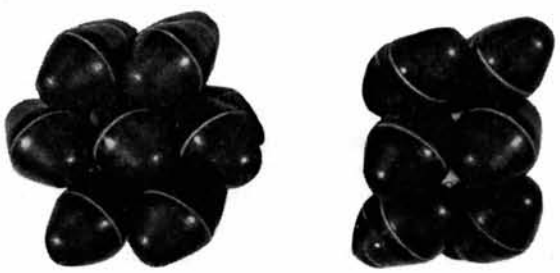

Fig. 10. The structure $P2_1/c$ (C_{2h}^5) of the spindle-shaped models (a front view and side view).

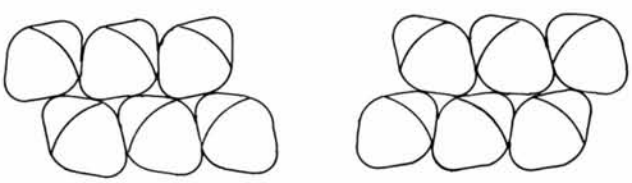

Fig. 11. Two systems which together form the orthorhombic structure of Fig. 12.

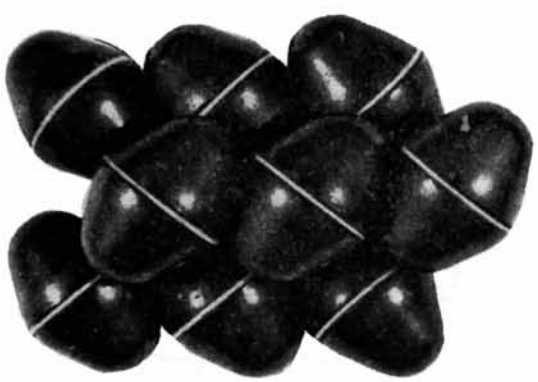

Fig. 12. The structure $Pnnm$ (D_{2h}^{12}) of the spindle-shaped models.

Fig. 13. The structure $P4_2/mnm$ (D_{4h}^{14}) of the spindle-shaped models.

When a seven-molecule system as shown in Fig. 9 is put on another *congruent* seven-molecule system, a monoclinic structure is obtained (Fig. 10). The structure is $P2_1/c$ (C_{2h}^5) to which many crystals of organic compounds belong, *e.g.*

dicyanoacetylene	$C_2(CN)_2$	(Wyckoff, 1951, Fig. XIIIC81)
p-dichlorobenzene	*p*-$C_6H_4Cl_2$	
p-dibromobenzene	*p*-$C_6H_4Br_2$	(Wyckoff, 1953, Fig. XIVA1)
p-dinitrobenzene	*p*-$C_6H_4(NO_2)_2$	(Wyckoff, 1953, Fig. XIVA14)
p-benzoquinone	*p*-$C_6H_4O_2$	(Wyckoff, 1953, Fig. XIVA3).

When the two systems shown in Fig. 11 are piled up, the orthorhombic structure $Pnnm$ (D_{2h}^{12}) is formed as shown in Fig. 12. This structure is taken by ethylene C_2H_4 if the complication caused by the position of hydrogen atoms is neglected (*cf.* Dows, 1962; Wyckoff, 1951, Fig. XIIIC12) and perhaps also by acetylene C_2H_2 at lower temperatures.

These two structures can be transformed to tetragonal $P4_2/mnm$ (D_{4h}^{14}), which is shown in Fig. 13.

Type IV

The models of type IV can be assembled into three structures:

- $P\bar{3}1m$ (D_{3d}^1) with three hexagonal Bravais lattices (Fig. 14),
- $P\bar{3}1c$ (D_{3d}^2) with two hexagonal Bravais lattices (Fig. 15),
- $R\bar{3}$ (C_{3i}^2) with one rhombohedral Bravais lattice (Fig. 16).

The first structure, to which uranium hexachloride UCl_6 belongs (*cf.* Wyckoff, 1948, Fig. VF3), can be obtained in the following way: (i) Make, on a desk,

a ring as shown in Fig. 17 with six molecules in the same orientation. (ii) Let a molecule approach the central hole, then the molecule is attracted and sinks half-way. (iii) Turn the whole upside down on the palm of one hand and put one more molecule into the central hollow.

The third structure $R\bar{3}$ (C_{3i}^2), to which wolfram hexachloride WCl_6 belongs (*cf.* Wyckoff, 1948, Fig. VF2), can be formed in the following way: (i) Make two three-molecule systems as shown in Fig. 18, in which molecules are all in the same orientation. (ii) Put one system on the other, then a stable six-molecule system is formed. (iii) Put two more molecules on the top and bottom of the system.

The author wishes to thank Prof. I. Nitta for his suggestions as regards improvement of the manuscript.

Fig. 14. The structure $P\bar{3}1m$ (D_{3d}^1) of the molecular models of type IV.

Fig. 15. The structure $P\bar{3}1c$ (D_{3d}^2) of the molecular models of type IV.

Fig. 16. The structure $R\bar{3}$ (C_{3i}^2) of the molecular models of type IV.

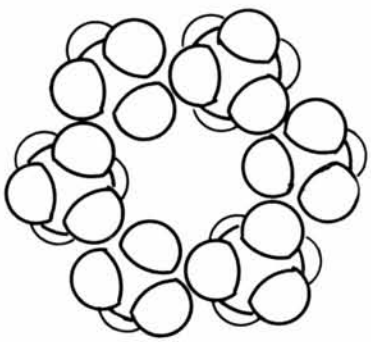

Fig. 17. Step (i) in assembling the model shown in Fig. 14.

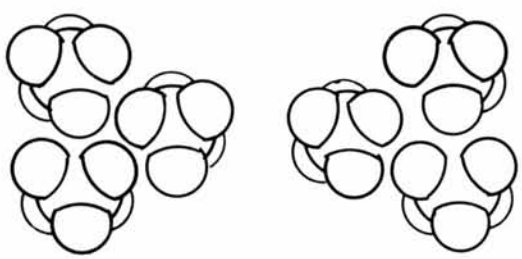

Fig. 18. Step (i) in assembling the model shown in Fig. 16.

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