

# Symmetry of STRUCTURE

an interdisciplinary Symposium

Abstracts

I.



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## Symmetry conservation and symmetry breaking in atomic structures

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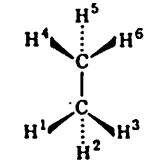
Symmetry will be used in its restricted sense as a repetition of a motif to compose a whole. The laws of repetition which we are considering are rotations, reflections and translations. These are called symmetry operations. The symmetry group of an object is the set of all symmetry operations which map the object onto itself. It is a group in the mathematical sense.

Atomic structures frequently exhibit symmetry. In crystals symmetry is realized in its highest perfection. We define a crystal to be an infinite, three-dimensional periodic object. In the first part of this lecture I will show that symmetry is imposed by some kind of "external forces". In the second part of this lecture I will show how symmetry breaks if the constraints imposed by the external forces are relaxed.

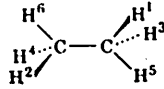
### 1. Conservation of symmetry

Symmetry can result from various sources. We will consider some cases:

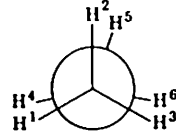
- i) Symmetry can result from a low energy equilibrium state between attractive and repulsive forces among the atoms, e.g. in the ethane molecule there exist two equilibrium states, the eclipsed and the staggered conformation. The staggered conformation is lower in energy thus the resulting symmetry group is  $D_{3d}$ . The eclipsed conformation has symmetry  $D_{3h}$  while intermediate states have  $D_3$  symmetry.



eclipsed

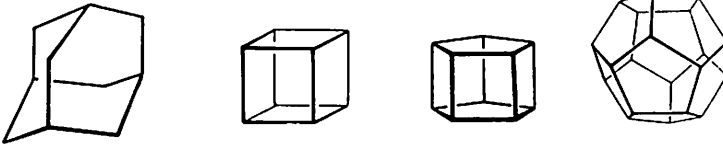


staggered

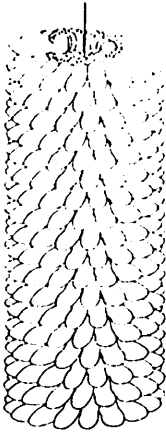


intermediate

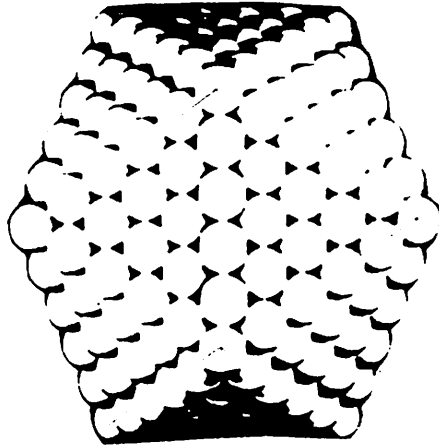
ii) Symmetry can result from the designed synthesis of a molecule. Recent examples are the successful syntheses of, among others, adamantane, cubane, pentaprismane, and dodecahedrane. All of them are highly symmetric molecules with symmetry group  $T_d$ ,  $O_h$ ,  $D_{5h}$ , and  $I_h$  respectively.



iii) In biological systems symmetry often results from economizing genetic information. In viruses the protein coats are built from identical subunits. Examples of this are the tobacco mosaic virus having a helical structure and the southern bean mosaic virus having icosahedral symmetry.

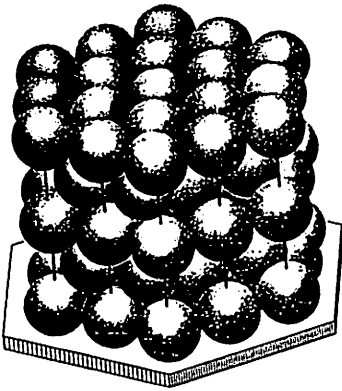


Model of the tobacco mosaic virus

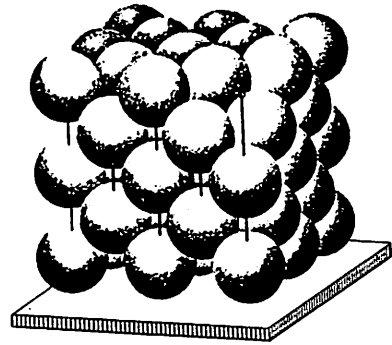


Model of the Adenovirus

iv) Symmetry can result from dense packing of equal atoms of spherical shape. Many elementary metals crystallize in cubic or hexagonal close packing with density 0.74. The corresponding crystals show symmetry groups  $Fm\bar{3}m$  for cubic and  $P6_3/mmc$  for hexagonal close packing.



Hexagonal close packing

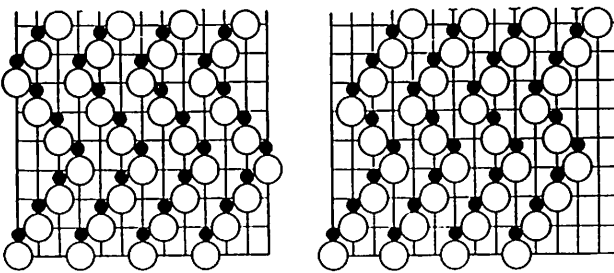


cubic close packing

We consider crystals as built up from small atomic aggregates. These building blocks, for simplicity, we take to be the content of a fundamental domain of a crystal. In a crystal each building block is surrounded in exactly the same way by all the neighbouring building blocks. Crystallization is considered as a higher level aggregation of identical building blocks. A fundamental law of crystallography states, that such an aggregate is crystalline if every building block is surrounded in exactly the same way within the first two neighbourhoods. Remarkably, in most cases it is sufficient to require a congruent first neighbourhood in order to establish periodicity. Thus symmetry results from the local requirement that every building block is surrounded in a congruent way within the first neighbourhood.

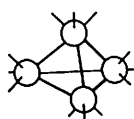
## 2. Breaking of symmetry

Of particular interest are the few exceptional cases where a congruent surrounding in the second neighbourhood is absolutely required to establish periodicity. If the constraint of congruent surroundings is partly relaxed then a break in symmetry could result. Examples are the frequent occurrence of polytypes which show a one-dimensional disorder.

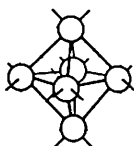


Polytypes of SiC

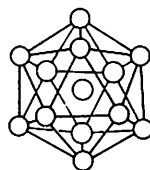
Thus, symmetry is not an intrinsic property of nature. If the constraint imposed by some external forces is relaxed then, in general, symmetry breaks. Particular interesting cases of symmetry breaking occur when non-spherical building blocks are densely packed. In metals, for example, we often encounter building blocks of icosahedral symmetry as a result of locally dense packing of atoms. The maximum number of atoms that can be placed in contact with a central atom is 12. At equilibrium the resulting aggregate shows icosahedral symmetry,  $I_h$ . For example such aggregates can be observed as gold clusters.



$M_4$



$M_6$



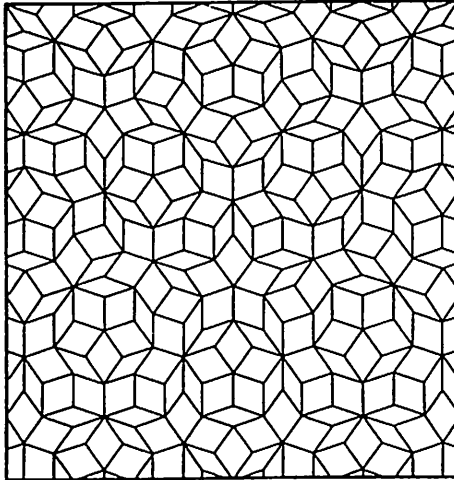
$M_{13}$

We may place another 20 atoms at the largest interstitial sites which occur above the triangular faces of the icosahedron to obtain a locally dense packing of atoms. Further shells cannot be packed as dense as that. An infinite non-periodic packing with density 0.734 has been described.

A classical result of crystallography states, that five-fold rotation is not consistent with periodicity in three dimensions. Since the icosahedron has five-fold rotation axes it is not possible to pack icosahedra densely in a crystal. Hence, in order to obtain a denser packing of equal atoms, at some embryonal state of crystal growth a rearrangement into a cubic or

hexagonal closed packing has to occur. This means that the local symmetry is broken in order to obtain a higher global symmetry.

If the central atom of such an icosahedral aggregate is slightly smaller and has a relative radius of 0.902 then the twelve surrounding atoms are in contact with its neighbours. This situation may occur in binary alloys having two kinds of atoms of different radii. More stable icosahedral aggregates result which do not rearrange so easily. Trying to pack such building blocks densely could result in aperiodic quasi-crystals. In quasi-crystals the local symmetry is retained at the expense of global symmetry. Examples are the quasi-crystals of Al/Mn/Si alloys.



Penrose tiling as a model for quasicrystals