

## Possible Sphere Packings of Quasicrystal

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The atomic structure of the recently discovered new alloy phase called the quasicrystal is regarded as a three-dimensional Penrose lattice which is composed of two kinds of rhombohedral unit cells proposed by Mackay (1981). Various ways of atomic decoration of the two unit cells are examined on the basis of the sphere packing concept for the two-layered unit cell structure. Some discussion is given of the relation between the obtained structures and the experimental facts.

### INTRODUCTION

Since the first discovery by Shechtman et al. (1984) of a new phase with the icosahedral symmetry in quenched Al-Mn (or Fe, Cr) alloy, this novel phase has become widely known as the "quasicrystal" after Levine and Steinhardt (1984), in which the structure of the "icosahedral phase" was interpreted by a new concept of ordered structure. The same concept had earlier been proposed by Mackay (1981, 1982) as the "quasi-lattice", which is the non-periodic structure filled with two or more definite unit cells. Characteristic features of the quasicrystal are that the structure possesses a perfect bond-orientational order and that it can have a rotational symmetry which cannot be allowed in crystals, such as the 5-fold symmetry existing in the icosahedral phase. The two dimensional quasi-lattice has been derived already in early 1970's by Penrose and is known as the Penrose tiling or the Penrose pattern (see, Gardner: 1977). An infinite Penrose tiling can be constructed by the so-called deflation method, where a pattern is successively divided into similar figures to increase infinitely the number of unit figures. Mackay (1981, 1982) suggested that the three dimensional version of the Penrose tiling will be constructed by two rhombohedral unit cells, prolate and oblate rhombohedra shown in Fig. 1, and the 3D-Penrose lattice will have a symmetry of the icosahedron. Recently, Ogawa (1985) found out a rather complicated deflation

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rule for these rhombohedral unit cells, and thus an infinite 3-D Penrose lattice has been completed.

Although there are still divergent views (e.g., Pauling: 1985), it is being recognized widely that the observed icosahedral phase possesses the 3-D Penrose structure. However, even if the unit cells are the two rhombohedra shown in Fig. 1, there still remains an important problem how these cells are decorated with atoms. In this paper, we discuss the possible atomic arrangements of the cells from the point of view of the sphere packing concept.

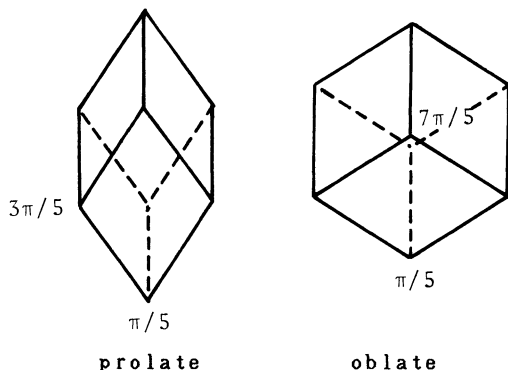


Fig. 1. Two types of rhombohedral unit cells composing 3-D Penrose lattice. Solid angles of vertices are given.

### EXPERIMENTAL FACTS

So far, four kinds of alloys have been reported to form the quasicrystalline phase by a quenching procedure. The first one is  $\text{Al}_{100-x}\text{X}_x$  ( $x=10-22$ ) alloy where X is either of, or a combination of, Mn, Fe, Cr, V, Si, Ru, Pt and Pd (Shechtman et al.: 1984, Bancel et al.: 1985). The others are  $\text{Pd}_{60}\text{U}_{20}\text{Si}_{20}$  (Poon et al.: 1985),  $\text{Mg}_{49}(\text{Al}, \text{Zn}, \text{Cu})_{32}$  (Mukhopadhyay et al.: 1985) and  $(\text{Ti}, \text{V})_2\text{Ni}$  (Zhang et al.: 1985). The atomic size ratios of these alloy systems are as follows: Al(1.00): Mn(0.85): Fe(0.90): Cr(0.80): V(0.82): Si(0.96): Ru(0.93): Pt(0.97): Pd(0.96); Pd(1.0): U(1.0): Si(0.85); Mg(1.00): Al(0.90): Zn(0.83): Cu(0.80); Ti(1.00): V(0.91): Ni(0.86). Here, the atomic sizes are defined by the Goldschmidt atomic radius which corresponds to the nearest neighbor distance for the close-packed structure, except for Al-Mn, -Cr, -V and -Si alloys where the atomic sizes are determined from the lattice parameter change with alloying. It is found that in all cases the size ratios of atoms composing quasicrystals range between 0.8 and 1.0. This fact clearly indicates that the atomic sizes of constituent elements play an important role in the formation of the quasicrystal. This is quite natural considering the fact that some special size requirement must be fulfilled for the metallic packing into the definite forms of rhombohedra shown in Fig. 1.

In the powder X-ray diffraction spectra of quasicrystalline alloys, we obtain two strong diffraction peaks indexed as (100000) and (110000) (Bancel et al.: 1984, Kimura et al.: 1985).

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The lattice spacings of these peaks,  $d_{100000}$  and  $d_{110000}$ , are slightly larger than 0.2 nm; so that they correspond to the spacings of closest-packed atomic layers. (110000) type plane is parallel to the rhombic faces of the two rhombohedra composing the quasicrystal. However, the  $d_{110000}$  cannot correspond directly to the spacing between parallel faces either of the two rhombohedral unit cells, because if so the atoms are to be located only at vertices of the cells, which results in unrealistically short interatomic distance for a short diagonal pair of atoms in the oblate unit cell. Therefore, the rhombohedral unit cells must be composed of a multiple atomic layer. In the following, as a simplest case we discuss the two-layered structure and consider possible sphere packings of the quasicrystal.

### SIMPLE SPHERE PACKING

We further assume for the moment that every face of the two rhombohedral unit cells possesses an identical and symmetric configuration, so that quasicrystalline packings can be achieved without any matching rule. This is in contrast to the unit cell structures proposed by Elser et al. (1985). We also assume that the ratio of the composing spheres is between 0.75 and 1.0.

One can classify the way of packing into two types; one is the edge-center type and the other is the face-center type. In the former, the spheres in the oblate rhombohedron are located at every vertex and every edge-center, while in the latter they are at every vertex and every face-center. In the prolate rhombohedron, there exists a large open space inside the cell and hence more spheres can be accommodated in it. (The volume ratio of the prolate and oblate rhombohedra is the golden mean  $\tau$ .) In both the edge-center type and the face-center type, a sphere can be positioned at the body-center. In the edge-center type, however, the densest packing can be obtained when two spheres are positioned in the form of dumbbell along the long diagonal of the prolate rhombohedron. Thus, there are five kinds of positions, the vertex position (v), the edge-center position (ec), the face-center position (fc), the body center position (bc) and the dumbbell position (d), shown in Fig.2. In the case of face-center type, there are two slightly different ways of sphere

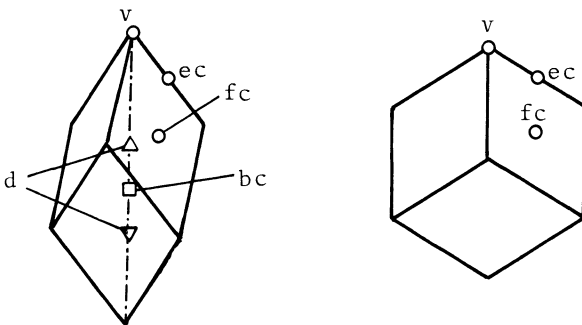


Fig. 2. Five kinds of position in rhombohedral unit cells.

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Table 1. Sphere diameter (upper line), percentages of site number (lower line) for various positions, the numbers of spheres in prolate and oblate cells (m and n) and the packing fraction ( $\eta$ ) for five types of packing.

Packing type	Positions					m : n	$\eta$
	v	ec	fc	bc	d		
Edge-center type	I	0.902 19.10	1.000 57.30			1.177 23.61	6 : 4 0.674
	II	0.902 21.65	1.000 64.96		1.000 13.38		5 : 4 0.510
	III	0.902 18.24	1.000 54.71	0.902 15.79	1.000 11.27		6.4 : 4 0.584
Face-center type	I	1.000 21.65		1.000 64.96	0.902 13.38		5 : 4 0.521
	II	1.049 21.65		0.951 64.96	0.951 13.38		5 : 4 0.499

packing: In one case the sphere diameters at the v-position and the fc-position are the same, and in the other case those at fc-position and the bc-position are the same. Thus, we have four types of packing which will be denoted as edge-center I (dumbbell edge-center type), edge-center II (body-centered edge-center type), face-center I and face-center II. The diameter of the sphere at each position in the above various types of packing is listed in the upper line for each type in Tab. 1, where the unit of length is taken such that the short diagonal of the rhombic face is 2.00. In the lower line for each type is given the percentage of number of sites at each position in the three-dimensional Penrose lattice, where the number ratio of the prolate cells and the oblate cells is  $\tau$ . m and n in the table indicate the number of spheres in the prolate and oblate cells, respectively. Numerals in the last column of the table show the calculated values of the packing fraction  $\eta$ , which is defined by the volume fraction in the space occupied by the spheres. (The values for the fcc, bcc and simple cubic structures are 0.740, 0.680 and 0.524, respectively.)

So far we have assumed the identical face structure. If we violate this rule, we can obtain denser packing in some types of packings. For the body-centered edge-center type, there is a large space at the face center position, and hence when two prolate cells are in contact face to face, we can put another sphere at the common face-center. After calculating the probability of the existence of these coupled prolate cells for Ogawa's 3-D Penrose lattice (Ogawa: 1985), we obtain a new type of packing given in Tab. 1 as the edge-center III type.

DISCUSSION

Experimentally, single phase quasicrystals have been

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obtained as a composition Al-(20-22)at%Mn for binary alloy (Kimura et al.: 1985, Masumoto et al.: 1985) and Pd<sub>60</sub>U<sub>20</sub>Si<sub>20</sub> for ternary alloy (Poon et al.: 1985). We should note that as far as the composition is concerned, Al-Mn quasicrystal is roughly consistent with any of the packing types in Tab. 1, if Mn atoms occupy the v-position and Al atoms the other positions. Also, for Pd-U-Si quasicrystal, the composition agrees very roughly with the edge-center I type packing.

For Al-Mn quasicrystals, the lattice spacings and the density have been obtained experimentally. From the requirements that the packing density should be consistent with the above experimental results and that Mn atom is smaller than Al atom, we are almost automatically led to the conclusion that the Al-Mn quasicrystal has the edge-center II type structure, as already discussed in detail in a previous paper (Kimura et al.: 1986). This conclusion, however, has been obtained under the assumption of the perfect 3-D Penrose lattice. There remains a possibility that the real structure is a highly defective one based on other type of packing, especially the closest packed structure of the edge-center I type. Incidentally, Hiraga et al. (1985) suggested two alternative structure models of the edge-center I type and a face-center type for Al-Mn quasicrystal, based on high resolution electron microscopy.

We have so far considered only the two-layered unit cell structure. There is, of course, a possibility that the unit cells in real quasicrystals consist of three or more layered unit cells. It seems, however, more reasonable to consider that the unit cells of the Penrose lattice in nature has a simpler atomic structure as discussed in this paper to achieve a continued growth of the phase with a long range bond orientational order.

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