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CHARACTERIZATION OF THE LOCAL ORDER
IN AMORPHOUS MODEL STRUCTURES

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АННОТАЦИЯ

Сравнивались ближние порядки различных структурных моделей: модели со случайной плотнейшей упаковкой, модели, основанной на неупорядоченной системе молекулярных единиц, и квазикристаллической модели. Сравнивались полиэдры, определенные первыми соседями металлоидных атомов двухкомпонентной системы Бенетта, с дырками Берналя и моделей более упорядоченных систем. Показано, что в случае координационных чисел от 6 до 9 чаще всего встречающимся полиэдром является тригональная призма.

KIVONAT

Különböző szerkezeti modellek, nevezetesen a véletlen szoros illeszkedésü modell, a molekuláris egységek rendezetlen rendszerére alapozott modell és a kvázikristályos modell közeli rendjét hasonlitottuk össze. Egy két komponensü Bennett szerkezet metalloid atomjainak első szomszédai által meghatározott poliédereket hasonlitottuk össze a Bernal lyukakkal és rendezettebb modellek állitásával. Megmutattuk, hogy 6 és 9 közötti koordinációs számok esetén a leggyakoribb poliéder a háromszög alapu hasáb.

ABSTRACT

The local orders of dense random packing, random packing of molecular units and quasicrystalline models are compared. The polyhedra formed by the nearest neighbours of the metalloid atoms in a two component Bennett structure are compared with the Bernal holes and the predictions of more ordered models. Trigonal prisms are shown to be the most frequent polyhedra for coordination numbers from 6 to 9.

INTRODUCTION

Metallic glasses are characterized by the structural randomness that is by the lack of translational symmetry. Because of this the information obtainable from scattering experiments is restricted to correlation functions. The detailed geometry of the structure cannot be studied experimentally. An indirect way is, however, the study of structural models. Having the "atom-coordinates" of a model cluster the pair correlation functions as well as any directly unmeasurable quantities can be calculated.

Although the most prominent feature of metallic glasses is the structural randomness, they exhibit a rather well-defined short range order up to a distance of about 15-20 $\overset{o}{A}$. This short range order is determined by geometrical contraints as well as by the chemical bonds. Till now numerous models have been proposed to describe the idealized homogeneous structure of metallic glasses. Classification of these structural models is possible on the basis of the kind and degree of order and disorder they assumed.

(i) Very strong chemical and topological short range order is assumed by the quasicrystalline (QC) models [1,2]. Its principal assumption is that the short range order of the glassy state is identical to that of a crystalline intermetallic compound produced
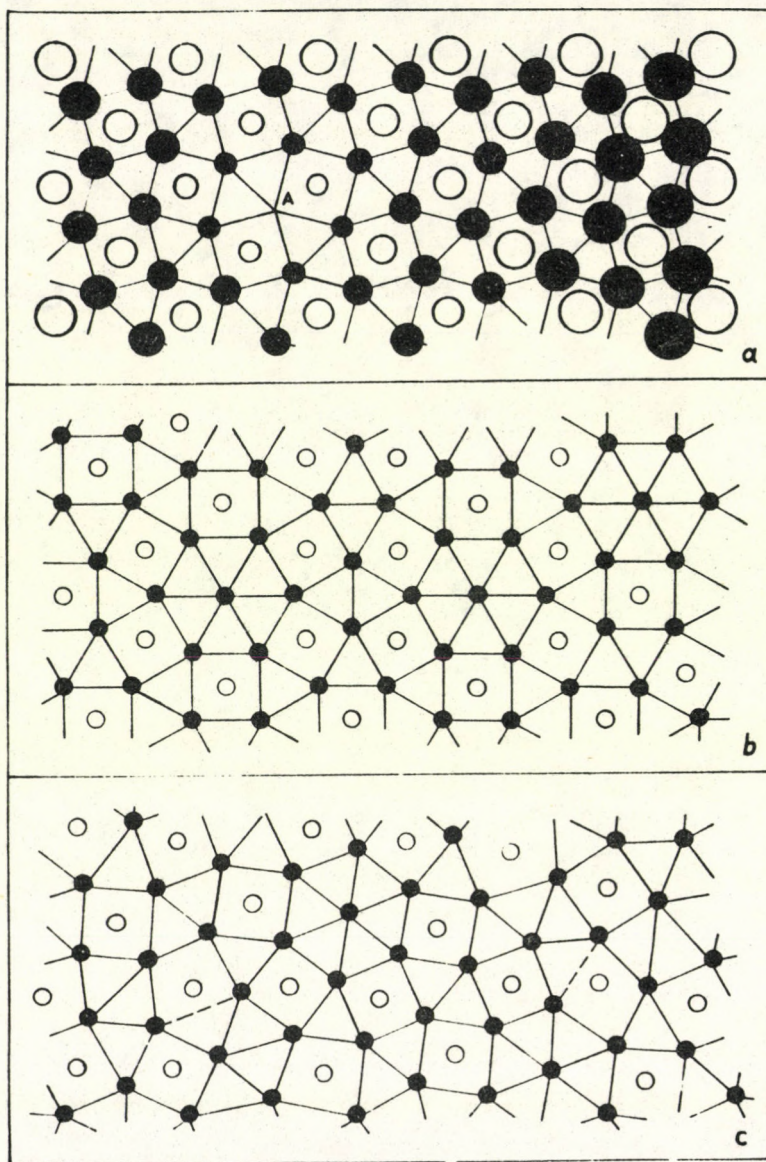
Fig. 1. *Two dimensional representation of a/ quasicrystalline /QC/; b/ random packing of molecular units /RPMU, one "molecule" consists of a square capped with four triangles/ and c/ dense random packing /DRP/ models. Open and closed circles represent metalloid and metal atoms, respectively. In Fig. a atom A is the origin, the measure of the circles indicate the area where the probability of finding the atom is significant. In Fig. c the dashed lines indicate arbitrariness of defining nearest neighbour polyhedra.*

by annealing. Disorder is introduced only by defining a probability
distribution of finding an atom at a given place around its equi-
librium crystalline position. Two features of this model should be
emphasized:

a) As no kind of topological disorder is introduced in the
model, not only the short range order but even the long range
crystalline symmetry is preserved in the glassy state.

b) In each case a single crystalline phase is assumed as the
basis of the glassy structure. Thus abrupt structural changes are
expected as a function of composition where the structure of the
crystalline products formed during heat treatments changes.

(ii) The importance of the metal-metalloid bonds is emphasized
by the random packing of molecular units (RPMU) model by P.H.
Gaskell in a completely different way [3,4]. The basis of this
model is the observation that trigonal prism formed by metal atoms
is the almost universal nearest neighbour environment in transi-
tion metal rich borides, phosphides, carbides and silicides such as
Pd_3Si, Fe_3P and Pd_6P. Assuming similar bonds in the crystalline
and the glassy state, a metalloid atom with its six metal neigh-
bours can be used as a building molecule of the amorphous struc-
ture. These elements, however, can be connected randomly without
refering to the topology of any of the crystalline compounds. Com-
paring with the QC model two basic differences can be found:

a) Topological disorder is explicitly included, so only the
short range order around the metalloid atoms is similar both in
the crystalline and the glassy state.

b) As trigonal prisms are the general building elements of a
number of crystalline compounds, RPMU model predicts only minor
differences between the structure of different transition metal -
metalloid metallic glasses.

(iii) Dense random packing (DRP) models form the broadest
class of structural models [5-10] including hard and soft sphere
packings, models refined by energetic relaxation, Monte Carlo and
molecular dynamics calculations. Although there are several dif-
ferences between these models, their basic idea is common: The
arrangement of the atoms is essentially random, but a sufficiently
dense aggregate of hard or soft spheres cannot be built without
clear-cut short range ordering. This short range order is dicta-

ted by geometrical constraints and - taking into consideration
the chemistry of the system - by the pair potentials and the
exclusion of metalloid-metalloid hard contacts.

As one of the most useful concepts to understand the struc-
ture of metallic glasses, the model by Polk [6] should be men-
tioned separately. He assumed that the transition metal atoms form
a DRPHS structure and the metalloids fill the largest holes pre-
sent in that skeleton. Although the hole-statistics given by
Bernal [5] has been reevaluated [11,12] and the quantitative va-
lidity of the Polk model has been questioned [13,14], this model
is the easiest way to the qualitative understanding of the metal-
lic glass structure.

RESULTS

In this paper the short range order of different structural
models is compared in terms of the polyhedra formed by the nearest
neighbours of a metalloid atom. A conventional two component
Bennett structure has been constructed using the global criterion
and not allowing metalloid metalloid hard contacts. The diameter
ratio of the metal and metalloid atoms is 1:0.76.

The spheres within a distance of 1.15 times the sum of the
radii - $1.15(r_1+r_2)$ - were taken into consideration as nearest
neighbours when constructing the polyhedra. As this cut-off dis-
tance is arbitrary and spheres near to this value can occur, only
those metalloid atoms were taken into consideration, which had no
neighbours within an $0.15(r_1+r_2)$ long distance interval around the
cut-off at $1.15(r_1+r_2)$.

Finally, 50 polyhedra formed by the nearest neighbours of a
"metalloid atom" have been folded from carton paper. As all the
polyhedra are more or less distorted, having them in hand was a
great help in their identification. In principle the polyhedra
have only triangular faces because the probability of finding four
or more coplanar points in a random array of points is zero. If,
however, the angle between the planes of two neighbouring triangles
is small - less than 20-30° - these triangles are regarded as
forming a distorted square.

The polyhedra can be compared with the predictions of other models: they should be identical with the Bernal holes in terms of the Polk model; RPMU model emphasizes trigonal prismatic coordination; QC model predicts a local order identical with that of a crystalline intermetallic compound.

The following polyhedra have been identified in the course of increasing coordination number Z:

Z = 5: Only one "metalloid atom" has five nearest neighbours forming a distorted half octahedron.

Z = 6: All the 12 polyhedra have distorted intermediate shapes between trigonal prism and octahedron.

Z = 7: 22 smaller spheres have 7 nearest neighbours. The most frequent polyhedra are trigonal prism capped on one square face with a half octahedron, pentagonal bipiramid and some intermediate shapes between them. Distorted cube with one missing vertex and some unidentified polyhedra occur as well.

Z = 8: Among the 12 polyhedra with 8 vertices trigonal prisms capped on two square faces with half octahedra are the most frequent. Some polyhedra have shapes between cube and square antiprism, one polyhedron is a cube with a missing vertex and with an additional "atom" above one of the edges. The surrounding of one of the "metalloids" consists of two trigonal prisms connected at a square face. Tetragonal dodecahedra have not been found.

Z = 9: Two polyhedra with unidentified shape.

Z = 10: One unidentified polyhedron.

The topology of the polyhedra could be described in terms of a set of numbers giving the number of vertices where 3, 4, 5 etc. edges meet. This characterization, however, is rather insensitive. For example, among the 12 polyhedra with Z = 8 11 is described by (0,4,4) regardless of the great variety of their shapes.

DISCUSSION

The most interesting point in this study is the comparison of the Bernal holes - the surrounding of the metalloid atoms according to the Polk model - and the polyhedra formed by the nearest neighbours of a metalloid atom in a two component system. Unfortunately only a qualitative comparison is possible because of the arbitrary

definitions. Moreover, the structure is sensitive to the diameter ratio of the smaller and the larger balls, but the Polk model predicts the same structure for every metallic glass.

The polyhedra found are more distorted than expected. (Perhaps relaxation results in more regular polyhedra.) Although there is a considerable correspondance between them and the Bernal holes (especially in the case of trigonal prisms), a number of unexpected polyhedra has been found and tetragonal dodecahedron does not occur. Many polyhedra would be divided into two or more parts and would be counted as more separate smaller polyhedra when making a hole statistics. These results indicate that the increase of the intersticies to accomodate the metalloid atoms requires the reconstruction of the metal skeleton even if its space-filling remains almost unchanged.

The fact that trigonal prisms are the dominant surroundings of the metalloid atoms raises the question whether there is any basic difference between the structures built by the RPMU and DRP algorithms especially after energetic relaxation. It is interesting to note that trigonal prisms occur not only for $Z = 6$ and $Z = 9$ but also for $Z = 7$ and $Z = 8$. Similar local orders can also be found in some crystalline metal-metalloid intermetallic compounds. If the metalloid is very small, the coordination number is 6. If, however, the diameter of the metalloid atoms increases in comparison with the metal atoms, the edges of one or more square faces increase and the next neighbours come closer to the metalloid atom. For example, $Z = 6$ in Fe_3C and $Z = 9$ in Ni_3P. A typical intermediate case is Pd_3Si where the six atoms forming the trigonal prism around a Si atom are at distances between 2.35 Å and 2.48 Å, the next two atoms are at 2.56 Å but the nineth neighbour would be at 3.04 Å, i.e. the coordination number is $Z = 8$.

REFERENCES

[1] P.L.Maitrepierre, J.Appl.Phys. 40, 4826 (1969)

[2] T.Kemény, I.Vincze, B.Fogarassy and S.Arajs, Phys.Rev.B. 20, 476 (1979)

[3] P.H.Gaskell, J.Non-Cryst.Sol. 32, 207 (1979)

[4] P.H.Gaskell, J.Phys.C: Sol.State Phys. 12, 4337 (1979)

[5] J.D.Bernal, Nature 185, 68 (1960)

[6] D.E.Polk, Scripta Met. $\underline{4}$, 117 (1970)

[7] J.L.Finney, Nature $\underline{266}$, 309 (1977)

[8] C.H.Bennett, J.Appl.Phys. $\underline{43}$, 2727 (1972)

[9] D.S.Boudreaux, Phys.Rev.B. $\underline{18}$, 4039 (1978)

[10] L. von Heimendahl, J.Phys.F: Metal Phys. $\underline{9}$, 161 (1979)

[11] E.J.W.Whittaker, J.Non-Cryst.Sol. $\underline{28}$, 293 (1978)

[12] R.Yamamoto and M.Doyama, J.Phys.F: Metal Phys. $\underline{9}$, 617 (1979)

[13] S.R.Nagel, Scripta Met. $\underline{12}$, 43 (1978)

[14] R.Yamamoto, T.Mihara and M.Doyama, phys.stat.sol.(a) $\underline{50}$, 165 (1978)

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