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## STRUCTURE OF THE AMORPHOUS METALLIC ALLOYS

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**Résumé.** — A la suite de nombreuses études effectuées dans ce domaine, il apparaît que les « métaux amorphes » constituent les premiers exemples expérimentaux de solides possédant une structure du type « assemblage compact désordonné de sphères dures ».

En passant en revue diverses études par R. X., on montrera d'abord comment le modèle de structure désordonnée compacte a été préféré au modèle microcristallisé pour décrire l'ordre local de la plupart des alliages amorphes. Différents modèles théoriques ont été récemment proposés pour rendre compte de ce type de structure : en particulier, nous comparerons le modèle de Bernal pour les liquides, construit à la main, aux modèles construits par ordinateur, soit par une méthode de type Monte-Carlo, soit par construction directe d'assemblages de sphères dures de tailles identiques — ou différentes.

**Abstract.** — As a conclusion of numerous studies on the subject, the amorphous metallic structure appears to be the first experimental example of a solid dense random packing of hard spheres.

In a first part, a brief report will be given on X-Ray studies showing how the random network model has been chosen for most of the amorphous metallic alloys, instead of the microcrystalline powder structure.

The second part will consist of a presentation and discussion of the various random models which have been recently proposed as a possible description of the short range order.

In particular, hand made packings of hard spheres formerly introduced by Bernal for liquids as well as Monte-Carlo Assemblies will be compared to more recent computer models simulating equal and non equal sized hard sphere packings.

The continuous random network model proposed by Polk and Turnbull to describe the amorphous Germanium structure has been one of the most successful result of the last conference on amorphous and liquid semi-conductors (Garmisch-Partenkirchen). Since it is now demonstrated that amorphous metallic alloys are also not microcrystalline a question is arising ! do microcrystals exist in the nature ? Obviously by microcrystals I mean crystals having a size smaller than 20 Å and containing no more than several hundred atoms.

The only chance to observe them has to be searched in pure metallic powders.

But even in this case the problem is not so easy.

The work of Kimoto [1] for example has been concerned with the observation of very thin layers of evaporated silver and minute grains of silver condensed in a low argon pressure.

The microdiffraction patterns of these films showed a large broadening of the diffraction lines which however allowed the identification of a f. c. c. structure.

But as the strong inelastic scattering of electrons

at low angles does not permit accurate intensity measurements of the elastic scattering, the f. c. c. structure of the grains was not questionable only for those having a 50 Å minimum size.

In recent theoretical studies Hoare [2] pointed out that the more stable structure for small aggregates of about 100 atoms is not necessarily the usual compact f. c. c. or h. c. p. packings.

Depending on the number of atoms and the shape of the aggregates, the minimum of free energy is often obtained with poly-tetrahedral arrangements which possess five fold symmetry axis (Fig. 1).

This result is experimentally confirmed by J. Farges and B. Raoult (private communication) by electron diffraction experiments on a condensed argon vapor in vacuum. By looking at the very beginning of the condensation directly in the gas jet they observe poly-tetrahedral aggregates which recrystallise in the f. c. c. system when their size reach an approximate value of 15 Å.

On the other hand thin films of pure metal such as Ag or Ni have been evaporated by Grundy [3] on to substrates held at nitrogen temperature. Diffraction pattern of these films have been performed *in situ*. They exhibit a non crystalline structure very similar

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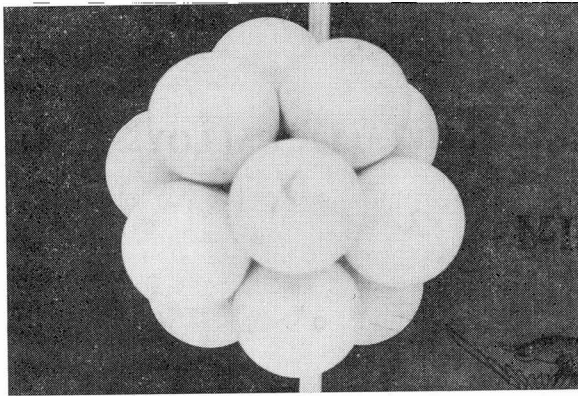


FIG. 1. — One atom with 12 neighbours arranged in a polytetrahedral manner. Note the five ball rings. There is an infinite number of similar configurations because the 12 balls in hard contact with the central ball are not in hard contact between each others.

to that we are dealing with in amorphous metallic alloys. In this case the crystallisation takes place at 100 K. So, at room temperature pure metal films are always crystallised with grain sizes of at least 50 Å.

The only way to obtain very small crystals consists of separating them from each others into a neutral matrix.

This can be achieved by evaporating Pt and C together, which have the same evaporation temperature and do not form intermediate compounds. Thick films of about 1 µm can be obtained with 80 at. % of C and 20 at. % of Pt.

Despite the high concentration of C, X-rays and electron experiments give informations almost only on the Pt atom distribution regarding the very small weight of C.

The pattern is made of large and monotoneous rings (Fig. 2-a) [4].

By annealing the film at 200 °C a first transformation occurs. Definite small f. c. c. crystals precipitate whose size is 20 Å.

The crystal growth is stopped at this stage even after several days of annealing (Fig. 2-b).

A new transformation takes place at 300 °C which gives rise to large crystals of 200 Å in size (Fig. 2-c). These Pt crystals are embedded in a still amorphous C matrix. A careful X. R. study of the as deposited films shows that a f. c. c. or h. c. p. structure may be consistent with the observed diagram, with crystals having a size as small as 8-10 Å (Fig. 3).

The crystalline structure becomes obvious when the grain size reaches 15 Å. The (200) peak of the f. c. c. diagram appears clearly on the right side of the (111) line and also a splitting of the 2nd peak as it is theoretically expected for such a grain size.

This case is up to now the only amorphous alloy the structure of which can be accounted for by a microcrystalline model. Nevertheless one can argue that 2 phases are present in the film (small Pt crystals and amorphous C) and thus no alloy has been formed.

Since a decade a great number of amorphous alloys have been prepared either by « splat cooling », evaporation in vacuum, or electrodeposition techniques [5-6].

They always contain a transition metal as Fe, Co, Ni, Pd, Pt, from 60 to 90 at. % and a non metallic element as B, P, Si, C.

The amorphous composition range is lying around the eutectic concentration and the equilibrium phase diagram indicates that one should have at room temperature a mixture of 2 phases : almost the pure metal and an intermediate compound such as  $A_3B$  or  $A_2B$  (where A is the metal and B the non metallic element).

A very important remark has to be made at this point : all these amorphous alloys exhibit almost the same diffraction diagram (Fig. 4). A first intense peak is followed by large rings with decreasing intensities. Moreover, a special feature of the second ring must be emphasized : a shoulder is more or less visible on its high angle side depending on the kind of alloy. Sometimes it disappears completely but in other cases this shoulder is well accentuated. Several alloys exhibit exactly the same diagram such as Ni-P, Co-P, Pd-Si, in spite of their different compositional elements.

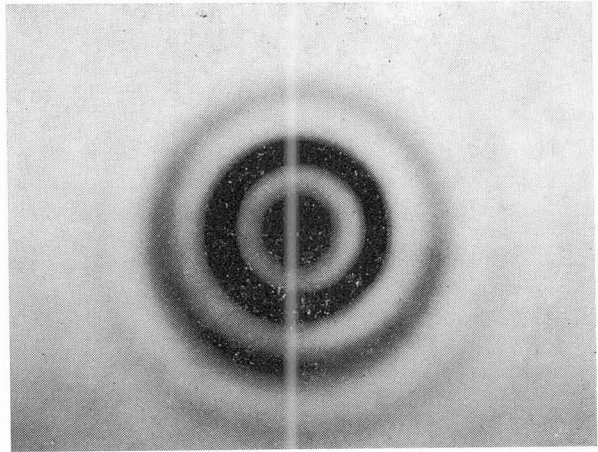
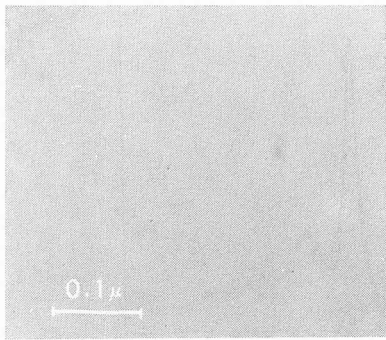
In order to characterise the diagram let us compare it to 2 limit cases i. e. : interference functions of a pure molten metal and a calculated one for a 13 atoms f. c. c. aggregate (Fig. 5).

Note the small angle scattering on the 13 atom curve due to a size effect. We have to keep in mind the height of the first peak on each curve which are respectively 1.5 and 2 times the form factor value at this angle.

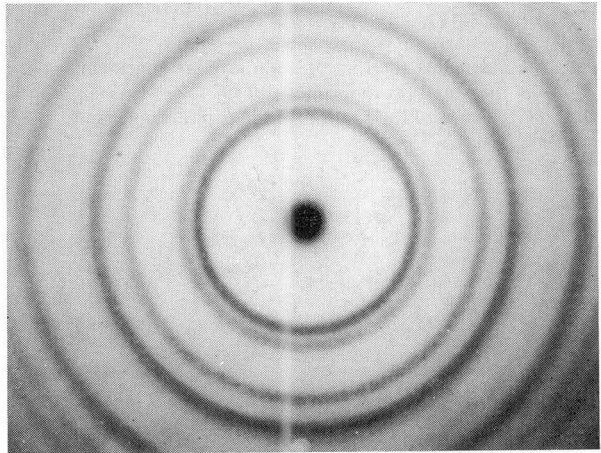
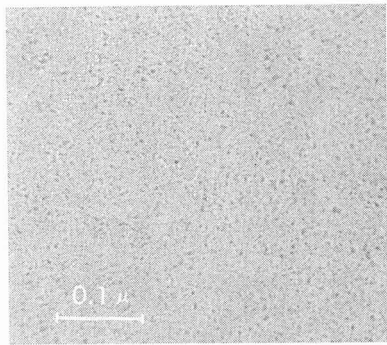
The corresponding reduced atomic distribution function obtained by Fourier transform of these curves indicates what kind of information can be obtained from radial distribution functions (RDF) : size of grains, distances between pairs of atoms inside the grains ( $\sqrt{2}\sigma$  ;  $\sqrt{3}\sigma$  ;  $2\sigma$  where  $\sigma$  is the atom diameter). In a liquid no extra distances are observed but the first neighbour distance and its multiple. Moreover there is no size effect and the disorder yields a vanishing of the successive RDF oscillations.

Now, let us look at the amorphous Ni-P diagram (Fig. 6). In this case the height of the first peak is 4 times the form factor value at this  $K$  value. A splitting of the second peak is clearly visible. If one derives an hypothetic grain size from the half height width of the first peak one finds 20 Å. Thus, one should expect for this size a 200 line on the right side of the first peak and a reversed intensity splitting on the second ring. The reduced atomic distribution function indicates the features of the short range order. As in the liquid state the second neighbours are absent i. e. the first distances between 2 close packed layers.

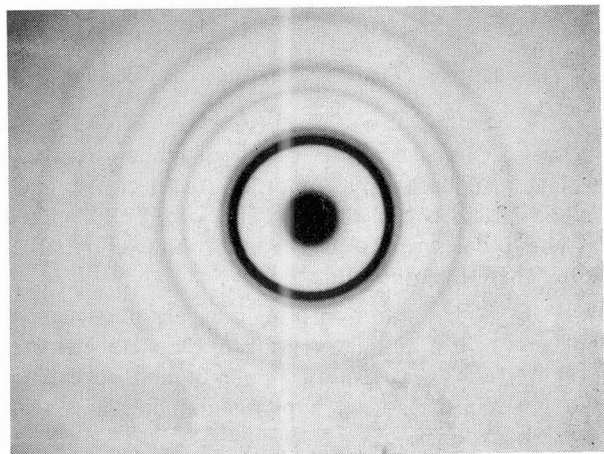
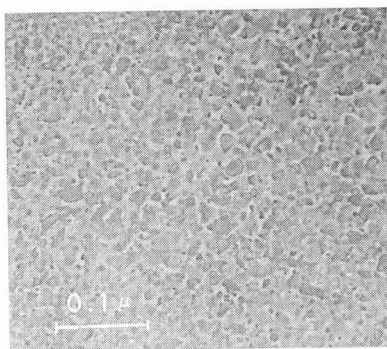
Nevertheless the splitting of the 2nd ring indicates that the structure of amorphous Ni-P has a greater degree of short range order than that observed in molten metals.



A as deposited



B annealed at 200 °C



C annealed at 300 °C.

FIG. 2. — Evaporated Pt-C film

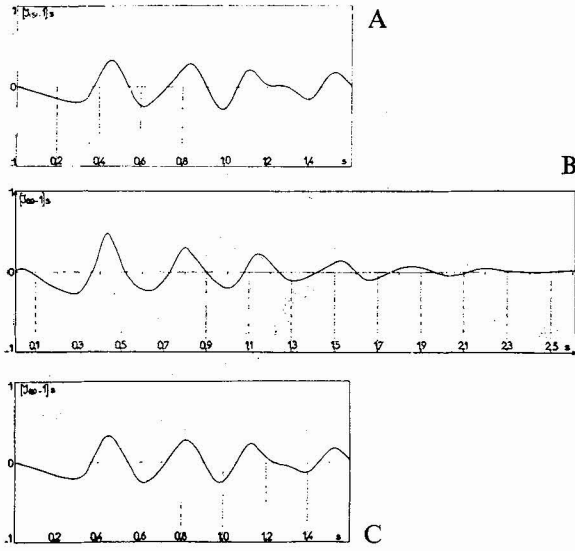


FIG. 3. — Reduced interference functions :

$$(I(s) - 1) S \text{ where } S = \frac{2 \sin \theta}{\lambda}$$

- A calculated for 13 atoms in f. c. c. arrangement
- B measured for amorphous Pt-C
- C calculated for 13 atoms in h. c. p. arrangement.

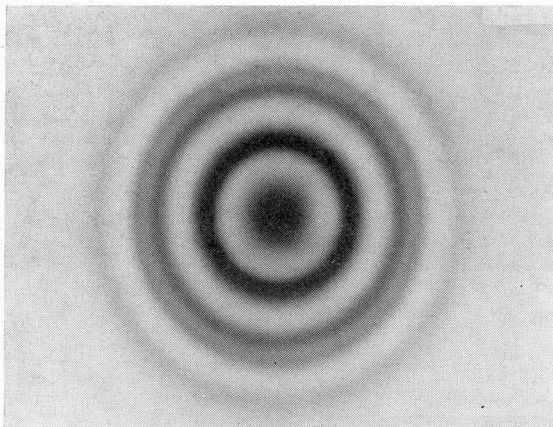


FIG. 4. — Microdiffraction of an amorphous  $\text{Co}_{85}\text{P}_{15}$  alloy. This diagram is similar to many other alloy diagrams.

Now let us give a brief review of numerous works which have been done in order to select the good hypothesis between those which can be proposed as possible description of the amorphous alloy structure. These hypothesis are :

- 1) A solid solution of the non metallic element in f. c. c. or h. c. p. microcrystals of the metal element. Staking faults and strains should be able to explain the non consistency of experimental diagrams with theoretical ones.
- 2) A 2 phase system with intermediate compound and almost pure metal microcrystals. This hypothesis is of course suggested by the equilibrium diagram.
- 3) A continuous disordered structure similar to a glass.

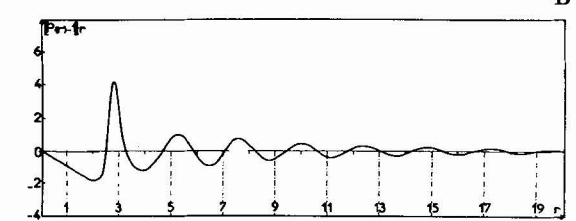
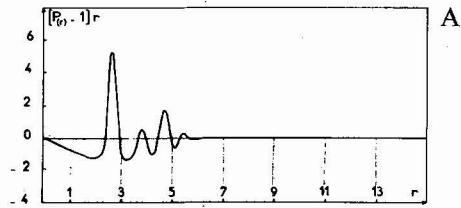
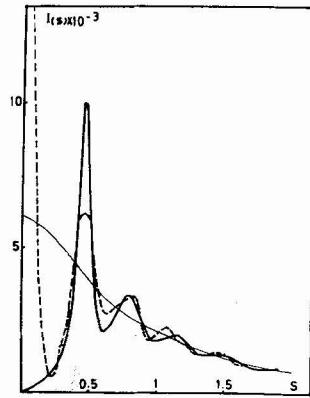


FIG. 5. — Upper figure : comparison between 2 diffraction patterns of :

- full line : molten gold.
- dotted line : a powder of microcrystals of 13 atoms in f. c. c. arrangement.

Lower figure : reduced atomic distribution functions.

- A) 13 atoms microcrystal powder    B) Molten gold.

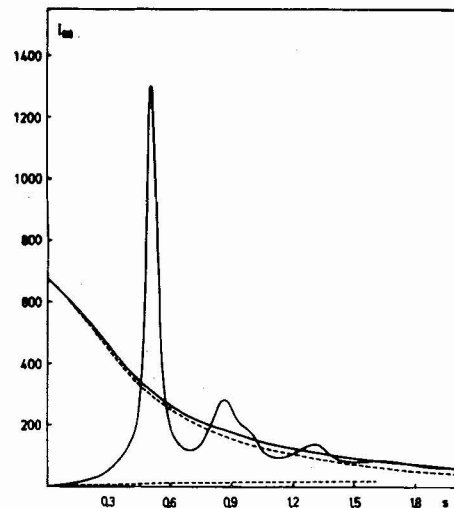


FIG. 6. — Diffraction pattern for  $\text{Co}_{85}\text{P}_{15}$  and related alloys.



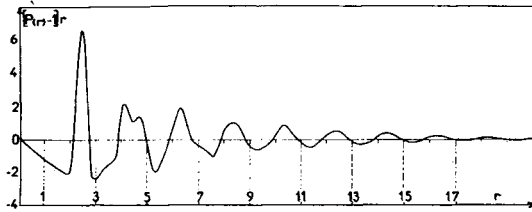


FIG. 7. — Reduced atomic distribution function for  $\text{Co}_{85}\text{P}_{15}$  and related alloys. Note the splitted second peak. This splitting is absent on a liquid metal ADF.

Before careful X-Ray studies took place, several authors as Graham in 1965 [7], Albert *et al.* in 1967 [8] have been thinking to a crystalline solid solution explanation. On the other hand, Goldenstein *et al.* [9] and Schlesinger *et al.* [10] proposed a liquid like structure but did not give any details on it. Precise X-Ray measurements followed by Fourier transform yielding RDF have been done by Dixmier *et al.* [11], Maitrepierre [12] and Cargill [13].

In a first attempt all these authors demonstrate that no crystalline structure either f. c. c., h. c. p. or any other system can account for the observed experimental diagram (Fig. 8-9).

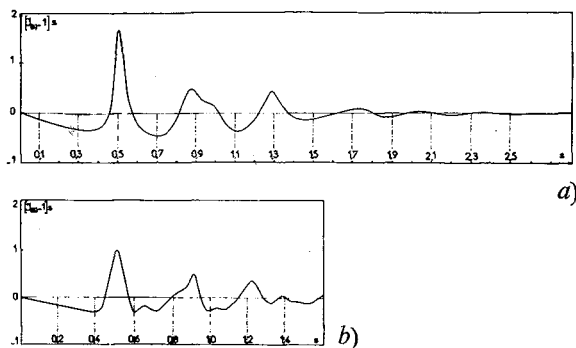


FIG. 8. —  $(I(s) - 1) S$  for:

- a) measured amorphous  $\text{Co}_{85}\text{P}_{15}$   
 b) calculated for 106 atoms in h. c. p. arrangement.

Moreover stacking faults have been introduced in the calculated model by Cargill as well as the effect of strain distribution [13]. These 2 attempts have failed in finding a good agreement between a distorted crystalline model and the experimental  $I(k)$ .

By applying a Gaussian broadening function to the atomic distances of crystalline models Maitrepierre has shown [12] that a quasi crystalline model based on intermediate compounds structure fitted the experimental RDF much better than a quasi crystalline model based on the metal f. c. c. lattice.

This result emphasized the role played by special bonds between metallic and non metallic elements.

But as far as the displacement of each atom is in this technique not correlated with the other atom displacements one cannot accept a quasi crystalline approach as a model.

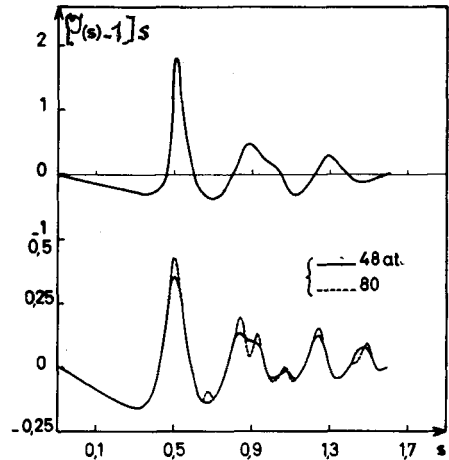


FIG. 9. — Amorphous Ni-P alloy is not a microcrystalline powder of  $\text{Ni}_3\text{P}$ .

- upper : amorphous Ni-P  
 below : calculated curves for :  
 — crystalline  $\text{Ni}_3\text{P}$  :  
 — full line : crystals of 48 atoms  
 — dotted line : crystals of 80 atoms.

A similar remark can be made regarding the first approach of Dixmier-Doi-Guinier [11] using Wilson theory for calculating X-Ray diffraction pattern by piling random layers. Although they succeed to recalculate the experimental  $I(k)$  by piling several close packed planes whose dimensions range from 5.5 to 11 Å this attempt remains at last a qualitative representation of the short range order but certainly not a model that one can put on a table. Moreover as pointed out by Cargill [13] the parameters used to fit the experimental curve are inconsistent with the expected atomic size for the constitutive elements of the sample.

Summarizing these attempt one can say that all approaches starting from lattice based models have failed. Moreover these results actually demonstrated the glassy character of the materials. Thus the next approach must be a continuous random network model.

The first continuous random model which has been built is that of Bernal [14] for liquid metals.

Irregular packings of equal sized balls have been constructed by stacking together steel ball bearings. The balls were fixed to each others by means of wax. Then, Bernal and Mason measured the sphere center coordinates one by one. From this model a radial distribution function was obtained by Scott [15] which was very similar to those obtained from X-Rays and neutron experiments on molten metals i. e. a large peak for the first neighbours and other periodic decreasing oscillations.

Perfecting their techniques by expanding the constructed model (the so called «expanded ball and spoke reconstruction technique») Bernal, Finney *et al.* obtained a 8 000 particle model yielding a more accurate RDF [16] (Fig. 10-a).

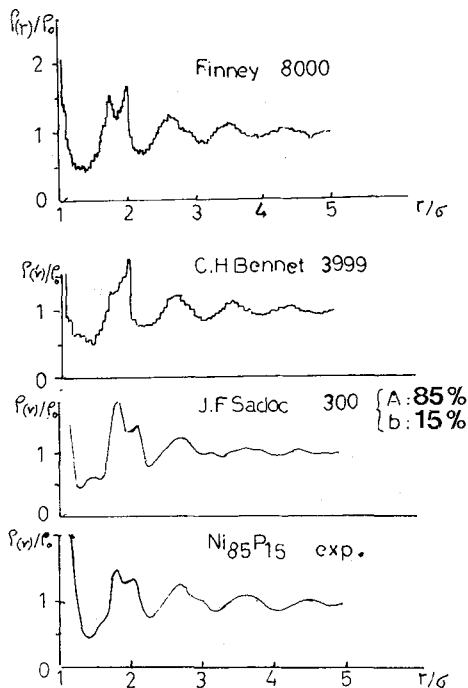


FIG. 10. — Calculated radial distribution functions from various models compared to Ni<sub>85</sub>P<sub>15</sub> RDF's.

For the first time a splitting of the second RDF peak was observed which however do not exist on liquid metal RDF.

On the other hand Finney has shown that a very similar RDF should be obtained by using a Monte-Carlo method of simulating the liquid state.

Just remembering that the Monte-Carlo method consists of performing on atoms of a given lattice a large number of random displacements ; each atom displacement is related to all other atom positions through an intermolecular potential function of the Lennard-Jones type. The computer calculates after each displacement the energy and virial of the system and the minimum energy is obtained by performing a great number of configurations.

This technique has been used for melting simulation of metals and the calculation of their liquid thermodynamic properties [17].

The thermodynamic of liquid argon for example is well represented by using the following parameter values in the potential formula

$$\varphi(r) = 4 \epsilon_n \left| \left( \frac{\sigma_n}{r} \right)^n - \left( \frac{\sigma_n}{r} \right)^6 \right|$$

$\sigma$  : atom diameter = 3.4 Å

$\epsilon$  : 119.8 K.

The repulsive part of the potential  $(\sigma_n/r)^n$  is found to be adequate when  $n$  is equal to 12.

By hardening the core of the potential Finney brings the interaction between particles towards the hard spheres repulsive potential which corresponds to  $n \geq 75$  for the repulsive exponent value. RDF

resulting from such calculations exhibit a splitting of the second peak like hand made model RDF's.

The Finney's model has been proposed by Cargill [18] and also Polk [19] as a possible description of the amorphous metallic structure. Polk suggests that the non metal element is supposed to fill the big holes of the dense packing. Indeed the DRPHS'RDF exhibit a splitted second peak as the observed Ni-P RDF. But the splitting is reversed on the experimental function (Fig. 10). Moreover the special bonds between metal and non metal are not taken into account. A more recent approach deals with computer simulated models of hard spheres.

Two different methods have been used simultaneously by Bennett [20] and Sadoc [21].

The 2 methods start with a little seed of 3 hard spheres in contact. Then spheres will be added one by one at a surface site obeying certain rules.

In Bennett's method the computer calculates for each aggregate the «pockets» being defined as a point lying from each of 3 particles center and at least  $\sigma$  away from all other particle center.

Sadoc's method of calculation has the same goal i. e. realize a packing as dense as possible with tetrahedra.

Here one sphere A is put in contact with 2 others B and C then rotated about the BC axis until A arrives in contact with an other 3rd sphere. Then a new C sphere is chosen, etc.

Bennett's rule for choosing the place of a new sphere to be added is a follows :

2 criteria were investigated, one in which the new particle is added at the site closest to the center of the original seed cluster (global criterion) and one in which the new particle is added at the site most nearly coplanar with its 3 defining neighbours.

Sadoc's rule for doing the same : the B sphere is chosen among those which have the smallest coordination number.

In the Sadoc's model small spheres can be added at random in a given proportion with a special rule

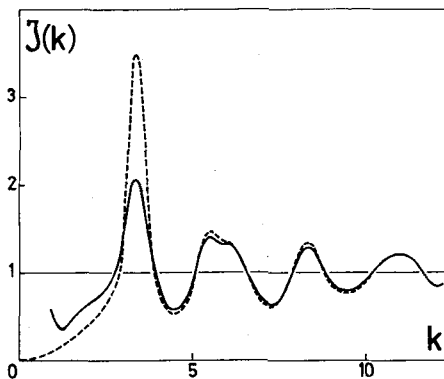


FIG. 11. — Interference functions :  
— full line : calculated for a theoretical model of Sadoc's type : 2 different ball sizes  $\sigma_A = 2.50$   $\sigma_B = 2.24$  with 15 % of B balls.  
— dotted line : experimental interference function for Ni<sub>85</sub>P<sub>15</sub>.

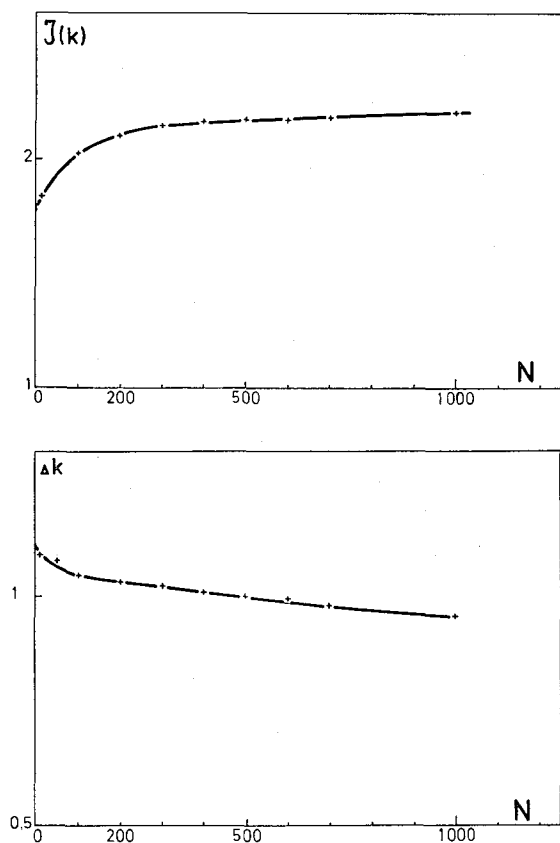


FIG. 12. — Variation of the 1st ring height and width of  $I(k)$  with increasing number of balls in the models.

regarding their environment. When a small sphere is added at the surface site no other small sphere is allowed to be in contact with it.

Thus a chemical affinity between metal and non metal atoms are simulated.

Results are gathered in figure 10. The Sadoc's distribution function is smoothed by using a gaussian peak instead of a Dirac's peak for each distance. One can see that the Sadoc's atomic distribution function is more consistent with the experimental function than the other model ADF'S, considering the 2nd peak.

The interference function has been calculated for each model in the Sadoc's study. The splitting of the 2nd peak has been shown to be dependent on the concentration of small sphere and also the diameter ratio of large and small spheres.

The best fit with experimental Ni-P  $I(k)$  has been obtained with a 15 % of small spheres and 10 % of diameter difference ratio (Fig. 11). The remaining discrepancy regarding the height of the first peak is due to the small size of the model. Indeed the high and half height of the 1st peak are varying with the number of atoms in the model as shown on figure 12.

**Conclusion.** — The dense random packing of non equal sized spheres has been shown to be able to account for the local order in a serie of amorphous metallic alloys exhibiting the so called « shoulder interference function ».

But a great number of theoretical disordered models can be proposed depending on the criteria which have been used in constructing them. More experimental studies are needed such as neutron diffraction in order to provide precise informations in particular on the non metallic element coordinence and the statistic of the various polyhedra which characterize a given disordered compact structure.

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