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Structural analysis of a binary metallic glass model.

II. A study of Pd$_{1-x}$Si$_x$ alloys (+)

F. Lançon (*), L. Billard and A. Chamberod
Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, Section de Physique du Solide, 85X, 38041 Grenoble Cedex, France

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Abstract. — We analyse several amorphous Pd$_{1-x}$Si$_x$ alloys obtained by simulation. The metalloid atoms environments can be studied in the same way as that described in the first paper of this series. The main part of this paper is devoted to the evolution of the density as a function of the concentration. In order to interpret the values obtained by the simulation, we develop two models : the first one assumes a complete disorder; the second one, which is shown to be better, assumes a tendency to a local ordering : Si atoms are assumed to have only Pd neighbours.

1. Introduction.
In a previous paper [1], that will be noted as I in the following, we have proposed a simulated amorphous model to describe the Pd$_{80}$Si$_{20}$ alloy. This was obtained by relaxation of initial packings under a system of three Johnson potentials corresponding to the three types of pairs.

It is clear that this work is not limited to the 80-20 concentrations and can be done for any hypothetical Pd$_{1-x}$Si$_x$ amorphous alloy. In this second paper, we will give some details about them, but we will also be especially interested in the concentration dependence of the density, which has been the subject of several studies [2-4].

2. Construction of the models.
As in I, the starting configurations are constructed either by a substitutional or an interstitial method. The state is then fully relaxed. Then, it is subject to a cycle of compressions and relaxations, followed by a cycle of dilatations and relaxations, and finally a full relaxation is done.

As concerning the interstitial method, we do not introduce Si atoms in the tetrahedral interstitial sites, which limits the concentration of Si to about 27 pct : we thus consider alloys in which the concentration $x$ varies by steps of 5 pct between 0 and 25 pct. This constraint does not exist in the substitutional method, so that it is possible, in principle, to have models with $x$ in the full range : 0 to 100 pct. Naturally, we do not claim that we have simulated an amorphous Si alloy containing Pd impurities, using the Johnson pair potential ! This must be considered as a formal way to study the behaviour of a bimetallic alloy ; nevertheless, for the sake of simplicity, we will speak of Pd and Si atoms in the whole range of concentrations.

3. Local structures.
As in I, one obtains partial pair correlation functions showing the interesting property that they have a deep minimum, being in fact nearly zero, at 1.26 times $r_{PdPd}$ and $r_{PdSi}$, thus leading to the natural definition of neighbouring pairs Pd-Pd and Pd-Si as those pairs which have a length less than this critical value. By analogy, but now, arbitrarily, Si-Si neighbouring pairs are considered as those pairs having a length less...
than 1.26 \(r_{\text{SiSi}}\). We have plotted in figure 1 the mean numbers of Pd and Si neighbours for Pd and Si atoms. As previously quoted [5], we obtain a nearly constant value of 8.5 for the Pd neighbours of Si atoms, revealing thus a kind of ordering. This is also clearly shown on figure 2, where we have represented the histograms for the numbers of neighbours of the two types of atoms. Although the distributions of Pd around Si, Si around Pd, and Si around Si show a more or less binomial behaviour, with a mean varying with \(x\) as shown in figure 1, the histogram of Pd around Si shows a very different behaviour; it varies only very slightly with \(x\), and Si atoms are almost completely belonging to two classes: those having 8 and those having 9 Pd neighbours. This is possibly because the depth of the Si-Si potential has been taken as much less than that of the Pd-Si one, correlated with the fact that \(r_{\text{SiSi}} > r_{\text{PdSi}}\). The Si-Si potential leads to practically no correlations between Si atoms and this is also revealed by a partial Si-Si pair correlation functions showing practically no structure, as previously described in I.

As for the Pd\(_{80}\)Si\(_{20}\) alloy, a full analysis in terms of polyhedra defined by the radical planes method can be done. We can also analyse the Bernal environments, and their generalization, deltahedra, around all Si atoms. As it was the case in the Pd\(_{80}\)Si\(_{20}\) alloy, we observe that trigonal prisms and Archimedean anti-prisms are the more frequent deltahedra. Their relative proportions are shown in figure 3 as a function of the alloy concentration.

We will now be interested in the concentration dependence of the density, where simple hypotheses can be done, leading to an interpretation of it.

4. The atomic density.

We have shown in I that the radical plane method (or the Voronoi analysis) leads to the analysis of the whole structure as an assembly of tetrahedra. Thus, any A\(_1\) - B\(_2\) amorphous alloy can be seen as made of tetrahedra, the vertices of which are atoms A or B. There exists thus five types of tetrahedra: AAAA, AAAB, AABB, ABBB, BBBB. We propose a model resting on the following approximation: the edges of the tetrahedra have lengths corresponding to the nature of the atoms which are at their ends, \(a\) for edges AA, \(b\) for edges BB, and \(c\) for edges AB. In the case of the system Pd\(_{1-x}\)Si\(_{x}\), we take \(a, b, c\) as proportional to the potential parameters given by:

\[
\begin{align*}
r_{\text{PdPd}} &= 2.83 \, \text{Å}, & r_{\text{PdSi}} &= 2.42 \, \text{Å}, & r_{\text{SiSi}} &= 2.75 \, \text{Å}. \\
a &= k r_{\text{PdPd}} \\
b &= k r_{\text{SiSi}} \\
c &= k r_{\text{PdSi}}
\end{align*}
\]

where \(k\) is a proportionality factor which will be adjusted to reproduce the density of the monoatomic (\(x = 0\) or 1) model. It will appear in fact that \(k\) is very close to 1.
If we denote $x, \beta (x = 0, 1, 2, 3, 4$ and $\beta = 4 - x)$ the tetrahedra having $x$ A atoms and $\beta$ B atoms as vertices, and $N_{\alpha \beta}$ and $M_{\alpha \beta}$ the mean numbers of them which can be found around A and B atoms respectively, we find that the mean atomic volume $V$ is given by

$$4V = (1 - x)\sum N_{\alpha \beta} V_{\alpha \beta} + x\sum M_{\alpha \beta} V_{\alpha \beta},$$  (3)

where the summation is made over $\alpha$ from 0 to 4, with $\beta = 4 - \alpha$. The factor 4 in front of $V$ is due to the fact that, when we sum the tetrahedron volumes around each atom over all the atoms, each tetrahedron is counted 4 times.

The volumes $V_{\alpha \beta}$ of each type of tetrahedra can be easily calculated as:

1. $V_40 = a^3 \sqrt{2/12}$
2. $V_{31} = a^2 \sqrt{3(c^2 - a^2)/12}$
3. $V_{22} = ab \sqrt{4(c^2 - (a^2 + b^2))/12}$
4. $V_{13} = a^2 \sqrt{3(c^2 - b^2)/12}$
5. $V_{04} = b^3 \sqrt{2/12}.$

The mean numbers $N_{\alpha \beta}$ and $M_{\alpha \beta}$ are not independent parameters because, each tetrahedron having a definite geometry, we must express that the sum of all the solid angles $\Psi_{\alpha \beta}$ at the vertex A for $\alpha \beta$ tetrahedra must be equal to $4\pi$, and, in the same manner, the sum of all the solid angles $\phi_{\alpha \beta}$ at the vertex B for $\alpha \beta$ tetrahedra is equal to $4\pi$:

$$4\pi = \sum N_{\alpha \beta} \Psi_{\alpha \beta},$$

$$4\pi = \sum M_{\alpha \beta} \phi_{\alpha \beta}. $$  (5)

The individual solid angle $\Psi$ and $\phi$ can be calculated:

$$\Psi_{40} = 3 \arccos(1/3) - \pi$$
$$\Psi_{31} = \arccos((2c^2 - a^2)/(4c^2 - a^2)) + 2\arcsin(\sqrt{3(4c^2 - a^2)}/4c^2 - a^2) - \pi$$
$$\Psi_{22} = \arccos((4c^2 - 2b^2 - a^2)/(4c^2 - a^2)) + 2\arcsin(\sqrt{3(4c^2 - a^2)}/4c^2 - a^2) - \pi$$
$$\Psi_{13} = 3 \arccos((2c^2 - 2b^2)/(4c^2 - b^2)) - \pi$$  (6a)

and naturally $\Psi_{04}$ is undefined (and $N_{04} \equiv 0$) because there is no BBBB tetrahedron having an A vertex.

In the same way, for tetrahedra around B vertices:

$$\phi_{04} = 3 \arccos(1/3) - \pi$$
$$\phi_{13} = 3 \arccos((2c^2 - a^2)/(4c^2 - a^2)) - \pi$$
$$\phi_{22} = \arccos((4c^2 - 2a^2 - b^2)/(4c^2 - b^2)) + 2\arcsin(\sqrt{3(4c^2 - b^2)}/4c^2 - b^2) - \pi$$
$$\phi_{31} = \arccos((2c^2 - b^2)/(4c^2 - b^2)) + 2\arcsin(\sqrt{3(4c^2 - b^2)}/4c^2 - b^2) - \pi$$  (6b)

and naturally $\phi_{40}$ is undefined (and $M_{40} \equiv 0$) because there is no AAAA tetrahedron having a B vertex.

Moreover, the $M_{\alpha \beta}$ are not independent of the $N_{\alpha \beta}$ because all $\alpha \beta$ tetrahedra can be obtained, either in counting them around A atoms, or in counting them around B atoms. Thus, we have the three relations:

$$\frac{(1 - x)N_{\alpha \beta}}{\alpha} = \frac{xM_{\alpha \beta}}{\beta} \quad \alpha = 1, 2, 3 \quad (\beta = 4 - \alpha).$$  (7)

Thus it appears that relations (5) and (7) (together with $M_{40} = N_{04} = 0$) leave three free parameters among the $N_{\alpha \beta}$ and $M_{\alpha \beta}$ and we must make some hypotheses about the repartition of the different types of tetrahedra in order to define them completely. Then, we will be able to calculate the mean volume $V$ by (3), and deduce the atomic density $\rho_0$ as

$$\rho_0 = 1/V.$$

In the monoatomic case, only one kind of tetrahedra exists and the proportionality factor $k$ (cf. (2)) has been found to be $k = 1.0069$.

4.1 THE POSTULATE OF DISORDER. — We first try the hypothesis that the neighbours of a given atom are randomly distributed around it. This means that the population of the different types of tetrahedra can be written as:

$$N_{40} = (1 - y_A)N; \quad M_{40} = 0$$
$$N_{31} = 3(1 - y_A)^2 y_B N; \quad M_{31} = (1 - y_B)^3 M$$
$$N_{22} = 3(1 - y_A)^2 y_B^2 N; \quad M_{22} = 3(1 - y_B)^2 y_B M$$
$$N_{13} = y_A^3 N; \quad M_{13} = 3(1 - y_B)^2 y_B M$$
$$N_{04} = 0; \quad M_{04} = y_B^3 M$$  (9)

where $y_A$ and $y_B$ are local concentrations of B atoms around A and B respectively, whereas $N$ and $M$ are the total mean numbers of tetrahedra around A and B, respectively ($N = \sum N_{\alpha \beta}, M = \sum M_{\alpha \beta}$).

Turning now to (7), it will be easily seen that only two of these equations are independent, and give

$$y_A = y_B,$$

that we will note $y$,

and

$$x = \frac{y}{(M/N) + y \{1 - (M/N)\}}.$$  (11)

Then, equations (5) can be put in the more explicit form:

$$N \{(1 - y)^3 \Psi_{40} + 3y(1 - y)^2 \Psi_{31} + 3y^2(1 - y) \Psi_{22} + y^3 \Psi_{13}\} = 4\pi$$
$$M \{(1 - y)^3 \phi_{31} + 3y(1 - y)^2 \phi_{22} + 3y^2(1 - y) \phi_{13} + y^3 \phi_{04}\} = 4\pi.$$  (12)

From (12), we can obtain $M/N$ as a function of $y$ and, putting it in (11), obtain an implicit equation for the local concentration $y$ as a function of the mean concentration $x$. Solving it as $y = y(x)$, and turning back to (12), we obtain $N(x)$ and $M(x)$, so that finally $N_{3\!p}$ and $M_{3\!p}$, as given by (9), can be calculated as functions of $x$.

Finally, we compute $\rho_0(x)$ by means of (8) and (3). The results of this hypothesis are shown in figure 4a, where we have also plotted $\rho_\text{Pd}$ the palladium atomic density, which is merely given as:

$$\rho_\text{Pd}(x) = (1 - x) \rho_0(x). \quad (13)$$

A careful examination of these results (see curve a) in figure 4c shows that the predictions of the model, concerning $\rho_0$ in particular, are lower than the values obtained by simulation, which is not satisfactory. Indeed, the self-consistency of the model requires a good agreement in the whole range of concentrations, and we will now try another postulate.

4.2 THE POSTULATE OF ORDER. — In fact, we have shown that several local informations tend to prove a kind of ordering: for example, we have noticed the singular distribution of Pd around Si atoms. Another result can be given: in the preceding section, where complete disorder has been postulated, we have found that the local concentration of Si atoms around Pd or around Si was the same (Eq. (10)). For instance, for $x = 0.20$, the calculation provides the value $y = 0.154$. However, in I, we have analysed the environments of Pd and Si from the point of view of the radical plane method. From table II of I, it can be calculated that we have $y_A = 0.158$ in fair agreement with the above value of $y$, but $y_B$ is much lower, being obtained as $y_B = 0.08$. This leads us to make the simplifying assumption of strong ordering: $y_B = 0$, that means that we postulate that no Si can be neighbour of another Si atom. In other words, only AAAA or AAAB tetrahedra can exist, i.e. we take

$$M_{22} = M_{13} = M_{04} = 0. \quad (14)$$

Naturally, this is impossible for high values of $x$, and we will give the limiting concentration above which this happens.

In this approximation, only $M_{31}$, $N_{31}$ and $N_{40}$ are non-zero. Equation (5) gives at once:

$$M_{31} = 4 \pi/\phi_{31}, \quad (15)$$

whereas, from (7), one has

$$N_{31} = \left\{ 3 x/(1 - x) \right\} \left\{ 4 \pi/\phi_{31} \right\}. \quad (16)$$

The normalization condition (5) for tetrahedra around A atoms gives the value

$$N_{40} = \frac{4 \pi}{\Psi_{40}} \left\{ 1 - \frac{3 x}{1 - x} \frac{\Psi_{31}}{\phi_{31}} \right\}, \quad (17)$$

which shows that $N_{40} \leqslant 0$ for $x \geqslant x_{\text{lim}}$ given by

$$x_{\text{lim}} = \frac{\phi_{31}}{\phi_{31} + 3 \Psi_{31}}, \quad (18)$$

the numerical value of which is 0.3742: beyond this limiting concentration our postulate cannot be maintained because there are necessarily Si-Si pairs.

Then, the mean volume per atom is easily seen to be a linear function of $x$:

$$V(x) = \frac{\pi V_{40}}{\Psi_{40}} + x \left\{ 4 \frac{\pi V_{31}}{\phi_{31}} - \frac{\pi V_{40}}{\Psi_{40}} \left( 1 + 3 \frac{\Psi_{31}}{\phi_{31}} \right) \right\}. \quad (19)$$

Let us note that it is possible to show that this expression coincides with the development of $V(x)$ in the disordered case approximation a) to first order in $x$.

Explicit numerical values in (\AA)$^3$ are:

$$V = 15.54 - 10.11 x \quad (20)$$

for $x < 0.3742$.

The corresponding densities $\rho_0$ and $\rho_m$ are shown in figure 4b. The more detailed figure 4c in the region of low values for $x$ shows clearly, even though at low concentrations it is rather difficult to distinguish...
between the two approximations, that the second one is better than the first one: we have a very good agreement with the values obtained through the simulation, and this confirms once that there is a kind of ordering in this series of simulated Pd$_{1-x}$Si$_x$ alloys.

5. Conclusion.

In this second paper, we have extended to a full range of concentrations the results given in I concerning the amorphous Pd$_{80}$Si$_{20}$ alloy: several samples have been constructed by a simulation procedure, which can be analysed in terms of energies, densities, or partial pair correlation functions and their relationship to detailed local structures. In particular, it has been shown that Si atoms have a strong tendency to have 8 or 9 Pd atoms around them. This was also confirmed by a model for the atomic density where the hypothesis of no Si-Si neighbouring pairs has lead to a very good agreement with the numerical values obtained through the simulation procedure.

We now conclude for this series of papers (I and this one): we have simulated Pd$_{1-x}$Si$_x$ amorphous alloys by an assembly of soft spheres, relaxed in a simple system of pair potentials. We have shown that the starting configurations have little importance on the resulting relaxed state: in particular, after a cycle of relaxation corresponding to a mechanical annealing, one obtains a reproducible state. The pair correlation functions are in good agreement with known experimental results. The investigation of local structure has been attacked from several points of view, which reveals that the used Si-Si potential has a weak influence on the correlations between the Si atoms. These atoms show a strong tendency to be in an environment constituted essentially by 8 or 9 Pd atoms. This kind of ordering, where Si-Si pairs are excluded, has been used to propose a model for the concentration dependence of the atomic density: the mean volume per atom has been shown to vary linearly with the concentrations, in very good agreement with that is observed in the simulated samples, and we expressed it in terms of the parameters $r_{PdPd}$ and $r_{PdSi}$. Thus it appears that even with very simplified forms of the interactions between atoms, and without any a priori assumptions concerning the structure, one can obtain a model which can be considered as very reasonable for this type of alloys. From a more theoretical point of view, we have also described a method which can characterize the environment of any Si atom in the Pd$_{1-x}$Si$_x$ system, and we can hope that it will be useful for a better knowledge of the microscopic structure of these materials.

References