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W. Y. Ching and Chun C. Lin

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STRUCTURAL MODELS FOR AMORPHOUS TRANSITION METAL BINARY ALLOYS*

W. Y. Ching

Department of Physics, University of Wisconsin, Madison, Wisconsin 53706 and Argonne National Laboratory, Argonne, Illinois 60439

and

Chun C. Lin

Department of Physics, University of Wisconsin Madison, Wisconsin 53706

ABSTRACT

A dense random packing of 445 hard spheres with two different diameters in a concentration ratio of 3:1 was hand-built to simulate the structure of amorphous transition metal-metalloid alloys. By introducing appropriate pair potentials of the Lennard-Jones type, the structure is dynamically relaxed by minimizing the total energy. The radial distribution functions (RDF) for amorphous $Fe_{0.75}P_{0.25}$, $Ni_{0.75}P_{0.25}$, $Co_{0.75}P_{0.25}$ are obtained and compared with the experimental data. The calculated RDF's are resolved into their partial components. The results indicate that such dynamically constructed models are capable of accounting for some subtle features in the RDF of amorphous transition metal-metalloid alloys.

INTRODUCTION

In order to study the electronic and magnetic properties of amorphous solids, it is necessary to have structural models of atoms which give the correct radial distribution functions (RDF) as determined from experimental measurements. The Dense Random

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Packing of Hard Spheres Model (DRPHS) has been used to represent the structure of amorphous transition metals.[1] For binary alloys involving transition elements, a model of dense random packing of spheres of two different sizes should be a promising one. Using computer calculations, Sadoc et al.[2] have studied the RDF of 300 spheres with various concentrations and diameter ratios. A major drawback of the hard-sphere model is that it only describes the repulsive part of the interaction potential neglecting the attractive part. A more realistic approach is to introduce a suitable pair potential and relax the structure as was done by Heimendahl,[3] and Rahman et al.[4] for the case of single-component atoms. In order to delineate the detailed differences in the structures of amorphous transition-metal-phosphorus alloys with different metallic constituents, we have constructed physical models, each with 445 atoms of which 75% represent the metallic atoms and 25% the phosphorus atoms. By using crystal-data information and experimentally measured RDF and density as guidelines, we select the appropriate parameters of the Lennard-Jones potentials and dynamically relaxed the structures to equilibrium. In this respect, our calculations are different from those of Refs. 3, 4, in which the RDF is studied as a function of the parameters. We obtain the RDF's of amorphous $Fe_{0.75}P_{0.25}$, $Ni_{0.75}P_{0.25}$, $Co_{0.75}P_{0.25}$ alloys and compared them with the experimental data. It is shown that such dynamically constructed models can explain several subtle features of the RDF's of alloys of different metallic constituents.

MODEL CONSTRUCTION

A round bottom Pyrex flask about 500 cm^3 in volume is cut into two halves near the middle. Steel balls of two different sizes are added to the hemispherical glass bowl one by one with no close contact allowed between the small balls. Slight occasional shaking is necessary for better close packing of the balls. When the bowl is full, the upper half of the flask is joined back to it by adhesive tape and the addition of steel balls is continued until the entire flask is about completely filled up. Hot liquid gelatin (algae-algae) is then poured into the flask solidifying at room temperature. After solidification is complete in about two hours time, the upper half portion of the flask is removed and a frozen structure of spherical dense random packing of two kinds of rigid spheres is obtained. The coordinates of the balls are measured and then removed one by one. The measurements are made with reference to a fixed point using long armed vernier calipers for easy reach of the balls. The recorded coordinates of the balls provide the initial configuration of the structural model for later computer relaxation. Since the structures are to be dynamically relaxed, it is not necessary to measure the coordinates very accurately nor is the choice of ratio of the radii of the spheres critical (1.40 in our case). One can equally well use a computer

generated model[2,15] as the initial configuration. In the present work, we find it more expedient to hand-build the initial structure rather than resorting to computers.

MODEL RELAXATION

We used the Lennard-Jones potential of the form

$$V(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}] \qquad (1)$$

to describe the interactions between atomic pairs. The parameter σ is related to the equilibrium separation σ' by $\sigma = 0.89089\sigma'$ and ε is the potential depth at the equilibrium distance σ'. The Lennard-Jones potential is best suited for systems of closed-shell atoms and molecules;[6] the validity of its application to the metallic species is less apparent. Our justification here is that we are using it to provide an attractive component to a steep repulsive barrier. This feature indeed can be reasonably well mimicked by a judicious choice of the two parameters in Eq. (1). Generally the value of σ should be chosen so as to reflect the closest distance of approach. Minor adjustments can be made to give better RDF's. As a first step we use the crystalline data as a guide.[7] In the Fe_3P crystal because not all the Fe atoms (or P atoms) are equivalent, the difference in distances between "nearest Fe-Fe neighbors" (or "nearest P-P neighbors") ranges over a few tenths of an Å. Thus we take their average values as σ'_{Fe-Fe} (and σ'_{P-P}). The same criterion can be used to determine σ'_{Fe-P} yielding 2.34 Å. However, if this value of σ'_{Fe-P} is used in conjunction with $\sigma'_{Fe-Fe} = 2.72$ Å, the leading structure (at $r \simeq 2.61$ Å) in the calculated RDF would show two sub-peaks as opposed to a single peak at 2.61 Å observed experimentally. Since the first sub-peak corresponds to the Fe-P pairs the second to the Fe-Fe pairs, this discrepancy can be resolved if we slightly increase σ'_{Fe-P} and decrease σ'_{Fe-Fe} so that the density of the model is close to the experimental measured value. The values of σ'_{Fe-P} and σ'_{Fe-Fe} which we adopt are included in Table I. The parameters for the Ni-P alloy are obtained in the same way from the Ni_3P crystal data. For the case of Co, we are not able to find crystalline Co_3P reported in the literature, thus we have to resort to the experimental data of the amorphous Co alloy to guide our selection of the parameters. We notice that the first major peak of the experimental RDF for the amorphous Co alloy occurs at a slightly larger distance than the Ni alloy whereas the density of the Co alloy is appreciably larger than that of the Ni alloy. Accordingly we choose σ_{Co-Co} to be slightly larger than σ_{Ni-Ni} and σ_{Co-P} smaller than σ_{Ni-P}.

TABLE I. Lennard-Jones Potential Parameters for the Amorphous Transition-Metals-Phosphorus Alloys.

	σ'_{M-M}(Å)	σ'_{M-P}(Å)	σ'_{P-P}(Å)	ε_{M-M}(eV)	ε_{M-P}(eV)	ε_{P-P}(eV)
$Fe_{0.75}P_{0.25}$	2.67	2.46	3.53	0.479	0.683	0.138
$Ni_{0.75}P_{0.25}$	2.60	2.34	3.55	0.500	0.723	0.134
$Co_{0.75}P_{0.25}$	2.61	2.37	3.54	0.502	0.695	0.136

The values of σ'_{P-P} deserve some comments. They are much larger than the nearest-neighbor distances in, say, the pure phosphorus crystal, and do not correspond to the onset distance of the repulsive potential between two P atoms. The nearest-neighbor distance between two P atoms in M_3P (M standing for Fe, Co, or Ni) is dictated primarily by the constraint of the 3:1 composition and, to some extent, the M-P interaction, but has little to do with the direct interaction between two P atoms. Since we use a pairwise-interaction description, the composition constraint and the influence of the M atoms on the P-P distances are all folded in σ'_{P-P}, resulting in an effective repulsive barrier which has a much larger onset distance than does the true barrier. For the same reason, the σ'_{M-M} and σ'_{M-P} values do not correspond to the true atom-atom interaction parameters. Thus the usual relation $\sigma'_{AB} \simeq \frac{1}{2}(\sigma'_{AA} + \sigma'_{BB})$ does not hold here.

To find the ε parameters, we start with the pure crystals (FCC structure) of Fe, Co, and Ni. From the nearest-neighbor distance and the cohesive energy,[8] we can derive a "true" Lennard-Jones potential for an M-M pair. The σ'-values for these "true" potentials are found to be slightly lower than the corresponding σ'_{M-M} values exhibited in Table I. We can think of the effect of alloying on the Lennard-Jones potential as a shift of the steep repulsive component to a larger distance while retaining the same attractive behavior. Thus the ε_{M-M} value for an amorphous alloy is taken as the value of the "true" Lennard-Jones potential at the interatomic distance equal to σ'_{M-M} of the amorphous alloy. Likewise we derive a "true" Lennard-Jones potential for a P-P pair and obtain ε_{P-P} for the alloy. As to the ε parameter for M-P interaction, we use the rule of geometrical means between M-M and P-P.

Here the M-M and P-P values are taken from the respective "true" Lennard-Jones potentials at the distance σ'_{M-P} appropriate for the amorphous alloy. The ϵ parameters for the three amorphous alloys are summarized in Table I. Several trial calculations with slight variations of σ' (and hence ϵ) were carried out. The parameters listed in Table I give the best overall agreement with the experimentally measured density and RDF.

With the appropriate Lennard-Jones potentials obtained for each atomic pair, the hand-built structure is then relaxed by computer using a process analogous to the molecular dynamics technique. Starting from the outer edge of the cluster, each particle, one at a time, is displaced along a random direction for a certain specified distance. If the new position results in a lowering of the total energy as calculated by summing the pair potentials, the particle is moved to that new position, otherwise it is not moved. The process is repeated in an iterative fashion until there is virtually no change in the calculated RDF. The resulting configuration is taken as the equilibrium structure. To achieve fast convergence, the displacements start from typically 0.05 Å and are gradually decreased to 0.005 Å as the iteration process proceeds. In computing the total energy by summing the pair potentials, it is not sufficient to consider only nearest neighbors. In the present calculation, we consider all the atoms which are less than 6 Å from the one under displacement. Thus the movement of a particle affects the positions of the atoms well beyond the nearest-neighbor distance; in this sense, the relaxation process is truly dynamical.

RESULTS AND DISCUSSION

The experimentally determined RDF for a multicomponent system is a weighted sum of the partial number densities $\rho_{ij}(r)$, i.e.,

$$\text{RDF} = 4\pi r^2\rho(r) = 4\pi r^2[w_{11}\rho_{11}(r) + 2w_{12}\rho_{12}(r) + w_{22}\rho_{22}(r)]. \quad (2)$$

The weighting factors w_{ij} in general depend on the composition and the scattering factors of the atomic species.[1-11] To a good approximation, the scattering factor for each type of atom can be replaced by its atomic number. In our calculation, we obtained the following weighting factors: $w_{11} = 0.9379$, $w_{12} = 0.5411$, $w_{22} = 0.1041$ for $Fe_{0.75}P_{0.25}$; $w_{11} = 0.9599$, $w_{12} = 0.5142$, $w_{22} = 0.0918$ for $Ni_{0.75}P_{0.25}$; $w_{11} = 0.9492$, $w_{12} = 0.5273$, $w_{22} = .0977$ for $Co_{0.75}P_{0.25}$. The very small weighting factor for the P-P pairs make their contributions to the RDF practically negligible.

In Fig. 1(a)-(c) we display the calculated RDF for the three amorphous alloys $M_{0.75}P_{0.25}$ along with the experimental results for

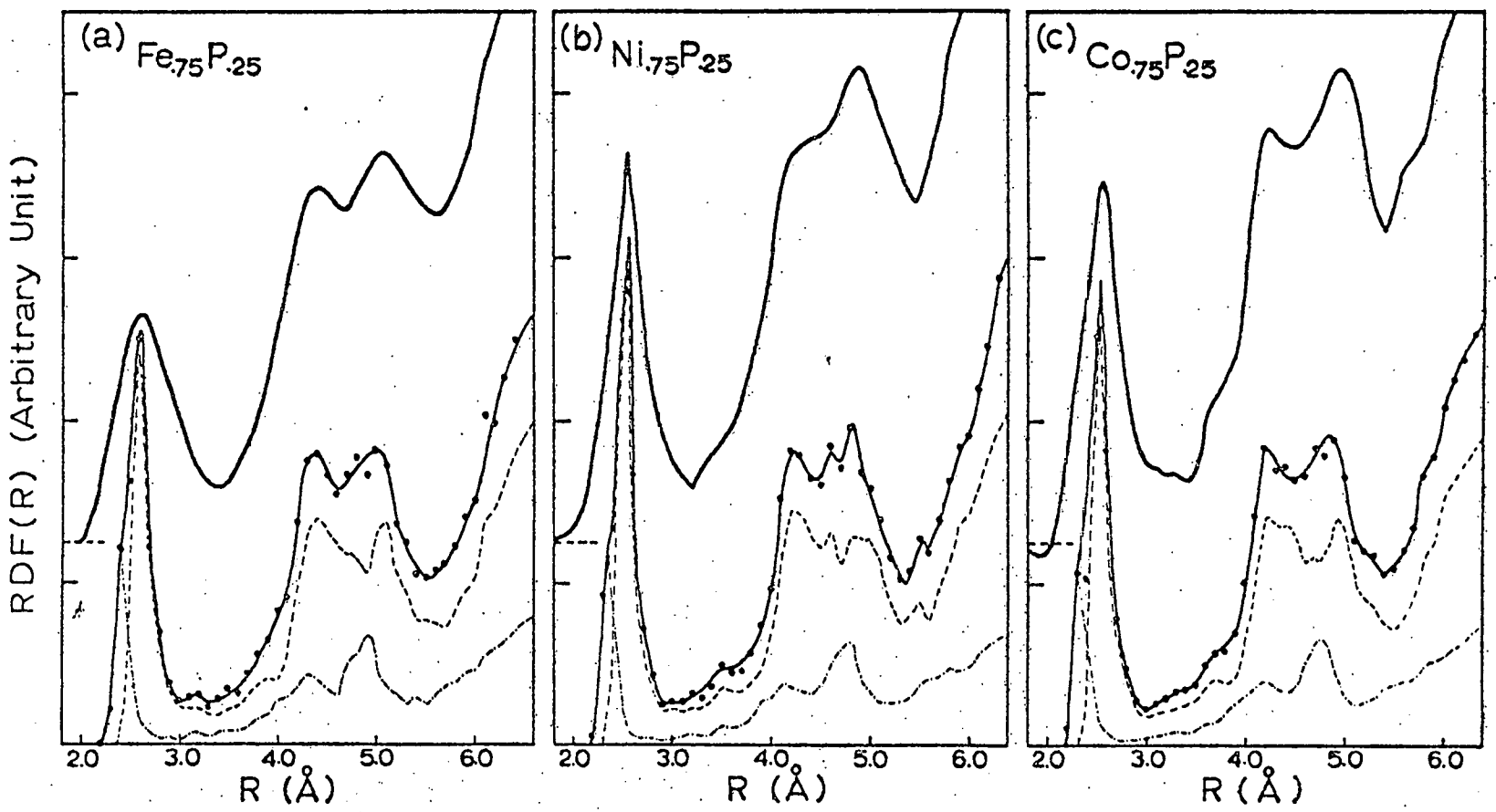

Fig. 1. Radial distribution functions for the amorphous M-P alloys for M = Fe, Ni, and Co in (a), (b), and (c) respectively. The solid curves are the experimental data for $Fe_{0.784}P_{0.216}$, $Ni_{0.77}P_{0.23}$, and $Co_{0.78}P_{0.22}$ (Refs. 9-11). The dots (connected by a line) are the theoretical points for $M_{0.75}P_{0.25}$. The dash and dash-dot curves are the weighted partial components (theoretical) of RDF for M-M and M-P respectively. The weighted contributions from P-P are negligible.

$Fe_{0.784}P_{0.216}$, $Co_{0.78}P_{0.22}$, and $Ni_{0.77}P_{0.23}$.[9,10,11] The calculated RDF's are resolved into their metal-metal, metal-P weighted components. Because of the limited number of atoms in our model, the RDF's are only calculated up to 6.2 Å. It can be seen that all the RDF's calculated agree with their experimental counterparts rather well with regards to the peak position and shape. Of special interest are the following subtle features:

(1) In the experimental curves, the first-nearest-neighbor peak is broadest for the Fe alloy and narrowest for the Ni one; this order is also found in the theoretical RDF's. The calculated peaks are much sharper than the experimental ones because the theoretical calculation does not allow for thermal broadening.

(2) Experimentally $Fe_{0.785}P_{0.216}$ has a more smooth RDF and its double-peak structure is more pronounced whereas the first sub-peak is quite weak for $Ni_{0.77}P_{0.23}$, with the Co alloy having intermediate behaviors. This trend is barely reproduced in the calculated curves although the first calculated sub-peak of the Ni alloy appears to be too strong.

(3) The slopes of the double peak (on both sides) are quite different for different alloys. The calculated curves, to some extent, show similar features.

(4) The position of the second minimum is also well reproduced.

All these interesting features which distinguish the structures of the amorphous transition-metal alloys of different metallic constituents must arise from the slightly different interactions existing between different atoms. The fact that these features are well reproduced by the calculated RDF's adds further justifications for using the Lennard-Jones potential to calculate pair distributions.

From the partial components of RDF, it can be seen that the first major peak is dominated by the contribution from the M-M pairs while the M-P pairs contribute to the asymmetry of the peak. The present results give a larger M-P distance than previously suggested.[1] For the double peak, the first sub-peak is mainly due to the M-M pairs, whereas the second one has considerable contributions from the M-P pairs as well. In constructing these models we assume that there is no contact between two P atoms. In fact the P atoms are kept rather far apart by choosing large σ_{P-P} values. It should be interesting for further study to ascertain whether a closer contact between the P atoms is acceptable. Because of the very small weighting factor for the P-P pairs, the calculated RDF is insensitive to the choice of σ_{P-P}.

We have also calculated the density of the constructed models as a function of distance from the centroid of the model. The results are shown in Fig. 2. The average densities are in good agreement with the corresponding experimental values.[1,9]

As remarked earlier, the position of the first peak in the RDF is associated with the M-M pair distance. Although the Co alloy shows its first peak at a larger distance than the Ni alloy, yet the former has a higher density than the latter. This observation is suggestive of a substantial difference in the short-range interaction between these two alloys.

In conclusion we have presented a simple dynamical scheme for constructing structural models for amorphous magnetic alloys. Such models are useful for studying the electronic and magnetic properties of these alloys.

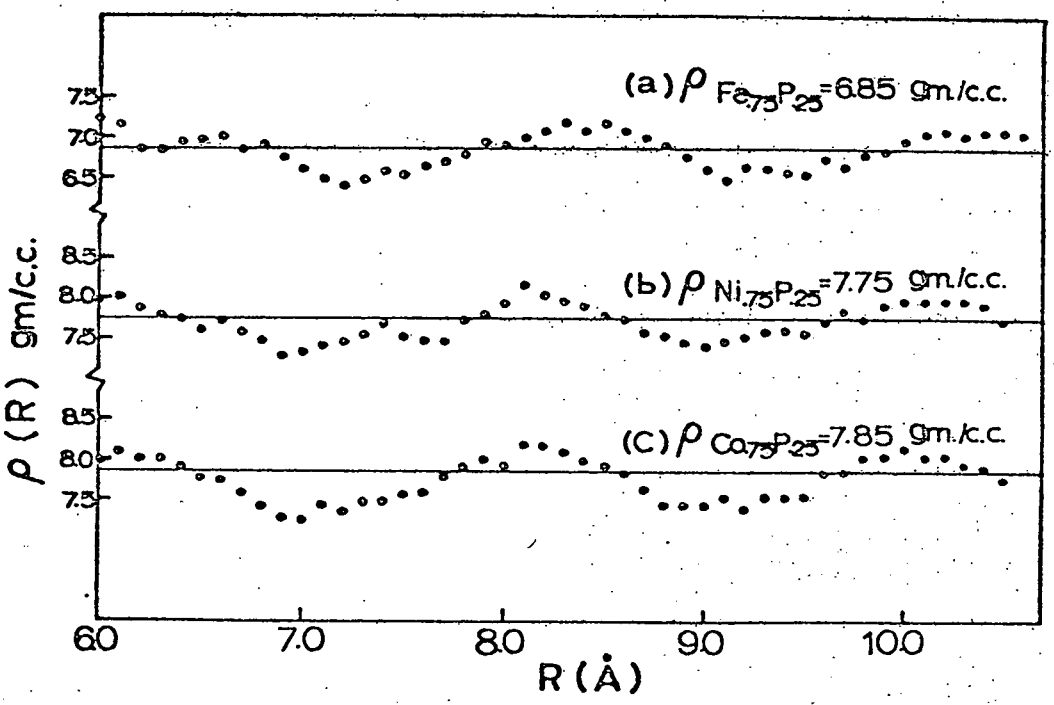

Fig. 2. Density (theoretical) of the amorphous alloys as a function of distance from the centroid of the model for (a) $Fe_{0.75}P_{0.25}$, (b) $Ni_{0.75}P_{0.25}$, and (c) $Co_{0.75}P_{0.25}$. The straight lines are the estimated average densities.

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