

## Short-range order of dense-random-packing models of metallic glasses

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Numerical calculations have been performed pertaining to the structure of binary transition-metal-metalloid glasses as a function of concentration and ratio of the atomic radii. A dense-random-packing-of-hard-spheres model as well as a relaxed model have been employed. To obtain information about the short-range order in the model structures, the average coordination numbers and probability distributions of coordination numbers have been studied in particular. It is shown that the short-range order predicted by the two models is nearly the same. The discrepancy with chemical ordering observed in some experiments is ascribed to the use of spherically symmetric interatomic potentials in the model calculations.

### I. INTRODUCTION

A first approximation to models of atomic arrangements in metallic glasses is based on structures formed by the dense random packing of hard spheres.<sup>1</sup> These rigid spheres, depicting atoms, are packed together in a cluster which is dense because it contains no internal holes large enough to accommodate another sphere, and is random because it lacks long-range order. There are various ways of constructing such a cluster. We have used a so-called global algorithm in which a new sphere is added to an initial cluster according to the following recipe: A list is made of all possible sites for new spheres, which are required to touch at least three spheres already present; the new sphere is then placed on the site nearest to the origin. For the construction of a model for an alloy, different atoms are represented by hard spheres of different radii, chosen to be the radii of the atoms in the related crystalline compound. The probability of adding a new sphere of a certain type is equal to the corresponding atomic concentration.

Given the atomic positions as derived from this model, one evaluates the following physically important properties: the pair-correlation functions, total radial-distribution function, packing fraction, density, average coordination numbers, and the probability distributions of coordination numbers. Comparing these quantities with the measured ones, we find reasonable agreement for the radial-distribution functions, but too low a density. The agreement between the calculated and measured radial-distribution functions can be improved substantially by introducing a relaxation of the structure.<sup>2,3</sup> Relaxation also narrows the

gap between the calculated and the measured densities. In a relaxation procedure interatomic potentials of the Lennard-Jones- or Morse-type are introduced, and the total potential energy is calculated. Starting with atomic positions provided by a dense-random-packing model, the atomic positions are shifted by small amounts to obtain an atomic configuration of minimal energy.

The average coordination numbers and probability distributions of coordination numbers supply information on the short-range order in metallic glasses. In this paper we show that neither the dense-random-packing model nor the relaxed model reproduces the specific kind of chemical order present in metallic glasses consisting of a transition-metal host to which has been added approximately 20 at. % of a metalloid.<sup>4,5</sup> In order to improve the agreement between theory and experiment, it is necessary to use potentials of non-spherical symmetry, of which three-body forces are an example.

### II. DESCRIPTION OF THE MODELS

This paper focusses on models of binary transition-metal-metalloid (TM-M) glasses. These alloys are found in rather narrow composition ranges, almost universally centered at 78–80 at. % TM. Therefore, we have constructed dense-random-packing structures with six values of the concentration  $c$  of the metalloid atoms in the range between 0.05 and 0.30. In addition to the concentration, the ratio  $R$  of the radii of the metalloid and transition-metal atoms is an important parameter. In order to simulate different kinds of metallic glasses, we varied  $R$  from 0.4 to 1.0 in steps of one-tenth.

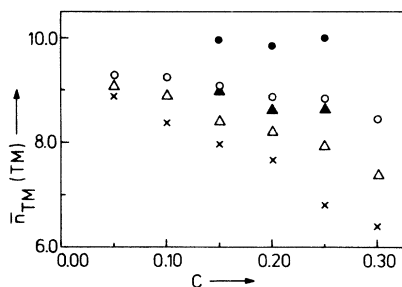


FIG. 1. Average number of transition-metal atoms surrounding a transition-metal atom as a function of the metalloid concentration  $c$  and the ratio of the radii  $R = r_M/r_{TM}$ . The values of  $R$  are:  $\circ$  0.5,  $\triangle$  0.7,  $\times$  1.0 dense random packing of hard spheres (DRPHS), and  $\bullet$  0.52,  $\blacktriangle$  0.72 (relaxed).

Most clusters contained 1500 transition-metal atoms, but we performed additional calculations on smaller clusters to investigate the influence of inhomogeneity and anisotropy,<sup>2</sup> which are quantities depending on the cluster size. It was found that the values of the average coordination numbers changed, the forms of the probability distributions remained essentially the same,<sup>6</sup> and, more importantly, the trends as a function of  $c$  and  $R$  were not affected. Since we are mainly interested in trends, cluster size is not a significant parameter in our problem.

New sites for transition-metal atoms are selected as described in the Introduction, but the criterion for choosing new metalloid atom sites must be changed. Selecting positions nearest to the origin results in an inhomogeneous distribution of metalloid atoms, especially when they are small compared to the transition-metal atoms. The concentration in the center of the cluster would become too high, while in the outermost regions it would become too low. This is circumvented by discarding all possible sites within a certain distance from the origin where the concentration is already equal to  $c$ . Besides this modification we also incorporated the usual metalloid-metalloid avoidance.<sup>7</sup>

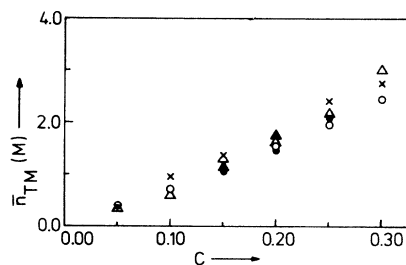


FIG. 2. Average number of metalloid atoms surrounding a transition-metal atom. Symbols as in Fig. 1.

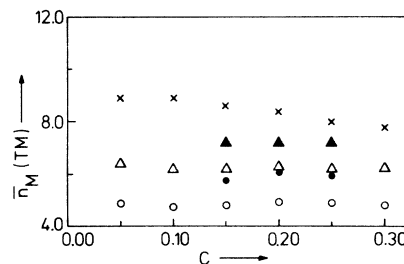


FIG. 3. Average number of transition-metal atoms surrounding a metalloid atom. Symbols as in Fig. 1.

The calculations using a relaxed model are described elsewhere.<sup>3</sup> The values of  $R$  were adjusted to the cases of Fe-B and Fe-P metallic glasses and were chosen to be 0.52 and 0.72.

### III. AVERAGE COORDINATION NUMBERS

The average coordination number  $\bar{n}_A(B)$  denotes the average number of atoms of type  $B$  in the nearest-neighbor shell of an atom of type  $A$ . The concentration dependence of some of these numbers is shown in Figs. 1–3; numbers for other values of  $R$  do not show any deviant behavior. Within the statistical errors of the models the coordination numbers are linear functions of concentration in the whole range from  $c = 0.0$  to  $c = 0.3$ . In other words, the effect of a metalloid atom on the transition-metal matrix is independent of the presence of other metalloid atoms. The explanation of this feature is rather simple. By construction a metalloid atom is surrounded only by transition-metal atoms, and the atomic configuration of these transition-metal atoms is typical for the binary alloy. An atom situated in the second-neighbor shell contacts three transition-metal atoms but cannot make a distinction between a metalloid or a transition-metal atom in the center, because a configuration of three transition-metal atoms is not typical for a binary alloy. Conclusion: there are no long-range forces to indicate which kind of atoms reside in the second-neighbor shell; hence, the screening of metalloid atoms is very effective.

There is a notable difference in the surroundings of small ( $R = 0.4$ – $0.6$ ) and large ( $R = 0.9$ – $1.0$ ) metalloid atoms. In the case of small metalloid atoms,  $\bar{n}_{TM}(TM)$  decreases only slowly as a function of  $c$ , indicating that the configuration of the transition-metal atoms is similar to that of the amorphous transition metal. Thus, small metalloid atoms are placed in voids of the transition-metal matrix, which is also confirmed by the increase of the packing fraction (Fig. 4). A perfect fit of the metalloid atoms in the voids would result

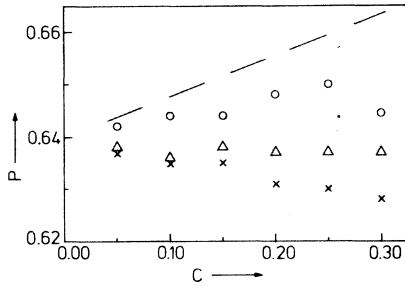


FIG. 4. Packing fraction  $P$  as a function of the metalloid concentration  $c$  and the ratio of the radii  $R = r_M/r_{TM}$ . Symbols as in Fig. 1. The dashed line indicates the maximal values of  $P$  that can be obtained when  $R = 0.5$ .

in a packing fraction of the form  $P(c) = P(0)(1 + cR^3)$ . This line is drawn in Fig. 4 for  $R = 0.5$  and shows that the holes are not large enough, even for such small metalloid atoms.

In the case of large metalloid atoms  $\bar{n}_{TM}(TM) + \bar{n}_{TM}(M)$  is independent of concentration, indicating that the total number of atoms surrounding a transition-metal atom does not change: metalloid atoms simply replace transition-metal atoms. The decrease of the packing fraction and of  $\bar{n}_M(TM)$  reveals that the system becomes less dense. The prohibition of neighboring metalloid atoms introduces rather large (but smaller than the size of a transition-metal atom) voids near metalloid atoms.

#### IV. PROBABILITY DISTRIBUTIONS

So far, we only considered average coordination numbers allowing us to draw some conclusions on the environment of atoms. However, it is far more elucidating to consider probability distribu-

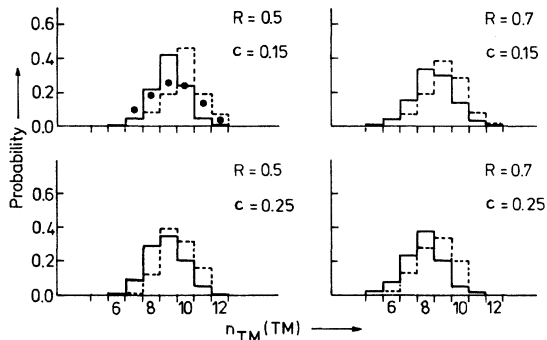


FIG. 5. Probability distributions of the number of transition-metal atoms surrounding a transition-metal atom. Solid lines indicate DRPHS results, and dashed lines indicate results obtained from a relaxed model. The dots represent a binomial distribution corresponding to the DRPHS results.

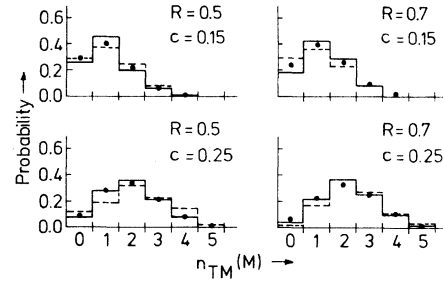


FIG. 6. Probability distribution of the number of metalloid atoms surrounding a transition-metal atom. Symbols as in Fig. 5.

tions of coordination numbers, for these contain more detailed information on the occupation of the nearest-neighbor shell. These are shown in Figs. 5–7, where both dense-random-packing results (solid lines) and results of the relaxed model (dashed lines) are displayed. The dots represent binomial distributions whose averages are derived from the dense-random-packing model.

There is a striking difference between the occupation numbers of transition-metal atoms and those of metalloid atoms. The probability distributions of both  $n_{TM}(TM)$  and  $n_M(TM)$  always have a width smaller than the corresponding binomial distribution, which indicates some correlation between the positions of the transition-metal atoms. This feature may be illustrated by comparing the results with the numbers obtained for an fcc structure. Suppose all atoms are placed on an fcc lattice, so that the total number of neighbors will always be 12. In this case the probability distribution of  $n_A(B)$  will be binomial for any pair of atoms  $A$  or  $B$ . In our models, however, the atoms are not placed on ideal close-packed fcc positions; as a consequence, the repulsion of the atomic cores introduces some correlation, for it gives rise to a lower probability of a high number of transition-metal neighbors.

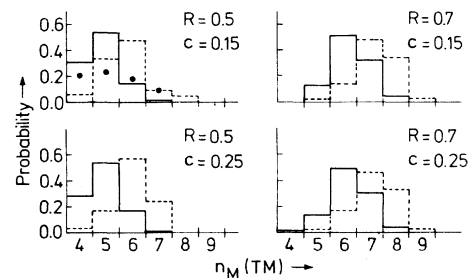


FIG. 7. Probability distributions of the number of transition-metal atoms surrounding a metalloid atom. Symbols as in Fig. 5.

The probability distribution of  $n_{TM}(M)$  shows a totally different behavior since it is always binomial. This feature is achieved only when the binomial distributions are evaluated using a maximum value of  $n_{TM}(M)$  of 6 instead of 12, which is justified by the repulsion of metalloid atoms. We should remark that these values may be replaced by, for example, 7 and 14, respectively, without any significant effect. We conclude that, apart from the prescribed metalloid-metalloid avoidance, there is no additional correlation between the metalloid atoms.

#### V. CONCLUSIONS

In Secs. I–IV we have discussed average coordination numbers and probability distributions of coordination numbers in order to clarify the nature of the short-range order prevailing in two models of metallic glasses. The dense-random-packing model and the relaxed model predict the same chemical ordering, because trends as a function of  $c$  and  $R$  of average coordination numbers and shapes of probability distributions are the same for both models. This resemblance is a consequence of the relaxation procedure preserving the spherical symmetry of the interatomic forces.

In our models there are only two interactions accounting for short-range order: the repulsion between the atomic cores and that between the metalloid atoms. The spherical symmetry of these interactions is revealed by the Gaussian shape of the probability distributions. However,

there exists some experimental evidence for directional bonds playing an important role in metallic glasses. The analysis of iron hyperfine field distributions for the amorphous  $Fe_{1-c}B_c$  system suggests the presence of compoundlike short-range order.<sup>4</sup> For example, in the case of  $Fe_{0.75}B_{0.25}$  one finds only iron atoms with 2, 3, and 4 boron neighbors, appearing with equal probabilities. This is contradictory to the predictions of both the dense-random-packing model and the relaxed model (Fig. 6). The presence of directional bonds thus changes the shapes of the probability distributions significantly, and hence we conclude that chemical bonds are not simulated in the models under consideration. Consequently, if one wishes to incorporate short-range order, it is necessary to introduce many-body potentials to obtain preferred bonding directions. The resulting numerical procedures are then far more complicated.

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<sup>6</sup>See also Fig. 6 of C. H. Bennet, *J. Appl. Phys.* **43**, 2727 (1972).

<sup>7</sup>D. S. Boudreaux and J. M. Gregor, *Proceedings of the 2nd International Conference on Rapidly Quenched Metals*, edited by N. J. Grant and B. C. Giessen (MIT, Cambridge, Mass., 1976).