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# The fractal skeleton of the atomic structure of amorphous metals

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## Abstract

The atomic structure of pure amorphous Re and Re–Tb amorphous alloys was studied by the molecular dynamics method. Analysis of the atomic structure of amorphous metals was performed within the framework of percolation theory and fractal geometry. The structure of amorphous metals consists of dense and sparse areas. We established that the dense areas form the fractal skeleton of an amorphous material. The distribution of clusters by size, the probability of an atom belonging to the largest cluster, the fractal dimensionality of the percolation cluster and the concentration dependence of the percolation radius were calculated. Correlation between some physical properties of amorphous metals and their cluster structure was established.

## 1. Introduction

Why does an amorphous structure consist of dense and sparse areas while a crystalline one is homogeneous? The point is that distances between atoms of a crystalline structure are strictly determined (translation vectors  $a$ ,  $b$  in figure 1). Statistical dispersion of interatomic distances in an amorphous structure ( $r_1'$ ,  $r_1''$ ,  $r_1'''$  in figure 1) allows one to speak about a mean interatomic distance  $r_1$  only. Some atoms of amorphous structure are closer to each other than  $r_1$ , so they form clusters.

There are a large number of structural models for amorphous materials [1]. Many authors have tried to find a rule to construct an amorphous structure. Such rules are well-known for crystals (translation symmetry) and for quasicrystals (rotational symmetry). But in amorphous structures the laws of spatial atomic arrangement are unknown. There have been many cluster models in which the clusters are compact dense aggregates. We established that dense areas of amorphous structure are not compact. If we call the dense areas clusters, they extend up to the whole material volume and are porous and fractal.

In this work we used a new method to analyze the structure of amorphous metals based on the application of percolation theory and fractal geometry [2–4]. Percolation theory is based on lattice models. Percolation processes on regular lattices [5] and fully irregular lattices [6, 7] are already well studied. A regular lattice looks like a crystalline structure, while a fully irregular lattice looks like the irregular structure of a

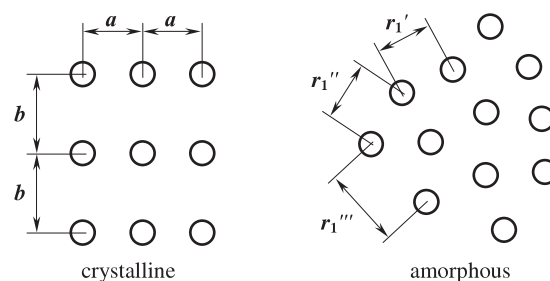
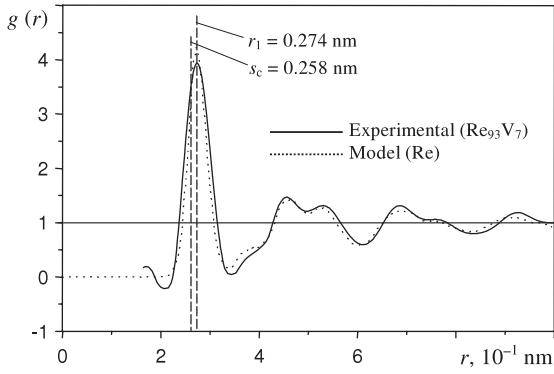


Figure 1. Interatomic distances in crystalline and amorphous solids.

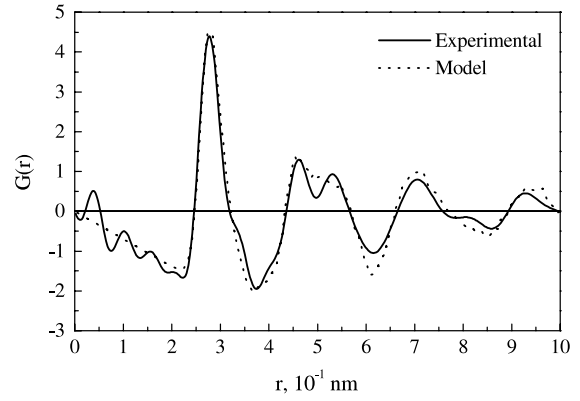
gas. Amorphous materials have no long-range order, unlike crystals, but they are not as disordered as a gas. They have short-range order. Amorphous structures are practically never studied by the percolation theory, so we expect the appearance of new regularities connected with the presence of short-range order only.

## 2. X-ray diffraction study and computer simulation technique

There are no stable one-component amorphous metals that would be the best object for studying the density percolation. Fortunately there are some amorphous alloys, such as the Re–V system, where the atomic radii of both components are almost equal: 0.274 and 0.272 nm. Besides, we can use alloys of this system containing practically only Re, for example



**Figure 2.** X-ray diffraction data confirm the amorphous Re model. The experimental RDF<sub>E</sub> and model RDF<sub>M</sub> practically coincide.



**Figure 3.** Reduced distribution functions  $G(r)$  of  $\text{Re}_{82}\text{Tb}_{18}$  amorphous alloy.

$\text{Re}_{93}\text{V}_7$ . We obtained the experimental radial distribution function  $\text{RDF}_E$  for amorphous alloy  $\text{Re}_{93}\text{V}_7$  using the x-ray diffraction method.

Unfortunately, the RDF contains only limited structural information. To know the atomic arrangement in the structure, we constructed a computer model of amorphous Re [8–10] and Re–Tb amorphous alloys [3] using the molecular dynamics method.

For the description of interatomic interaction in these systems we used the model potential represented as a polynomial of the fourth power [11]:

$$U(r) = \begin{cases} C_1(r - r_k)^4 + C_2(r - r_k)^3 + C_3(r - r_k)^2 & \text{at } r \leq r_k \\ 0 & \text{at } r > r_k. \end{cases} \quad (1)$$

Here  $r_k$  is a cut-off radius of the potential. Coefficients  $C_1$ ,  $C_2$ ,  $C_3$  were found as a solution of the system of three linear equations which connect the potential energy, its first and second derivatives with parameters for crystalline analogues:

$$\begin{aligned} \varphi(a) &= -AE_a \\ \varphi'(a) &= 0 \\ \varphi''(a) &= \frac{18Kv_a}{a^2}, \end{aligned} \quad (2)$$

where  $\varphi(r)$  is the potential energy of a crystal calculated per atom as a sum of pair potentials defined by the formula (1),  $E_a$  is the atomization energy,  $A$  is a coefficient of order unity,  $a$  is the equilibrium interatomic distance,  $K$  is the bulk modulus and  $v_a$  is the volume per atom. Introduction of the coefficient  $A$  is caused by the fact that potential energy in the amorphous and crystalline states is not equal. The value of  $A$  was chosen so that coincidence of the model and experimental RDF would be achieved.

Simulation was carried out in a cube with periodical boundary conditions containing  $10^4$  atoms. In these systems the temperature was rapidly decreased at a rate of  $10^{10} \text{ K s}^{-1}$ . In the resulting relaxation a dense random packing of atoms formed.

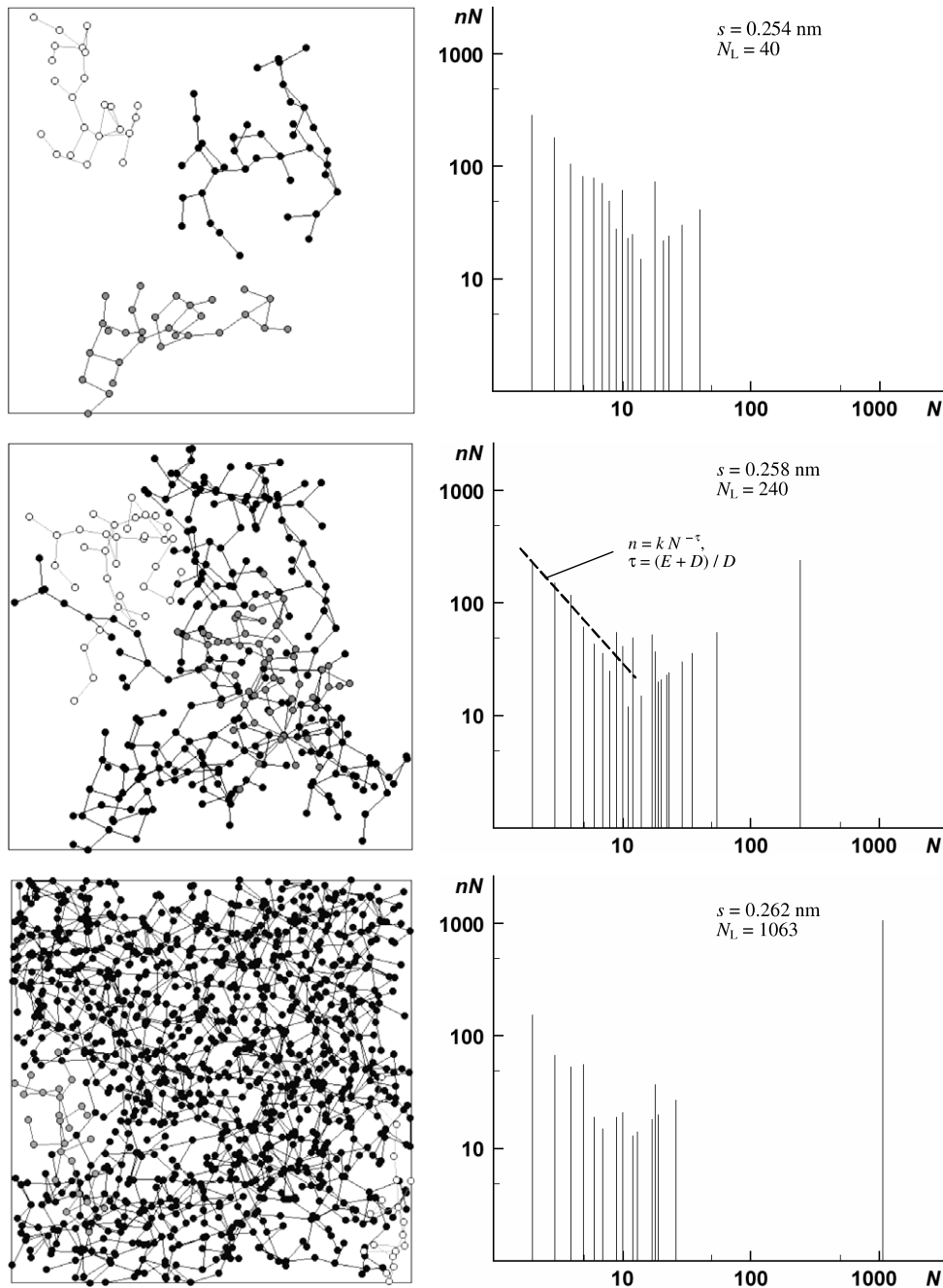
For the model of pure amorphous Re the radial distribution function  $\text{RDF}_M$  was calculated. Comparing RDFs we can see

that  $\text{RDF}_M$  and  $\text{RDF}_E$  practically coincide (figure 2). The reduced RDF  $G(r)$  calculated for the model of  $\text{Re}_{82}\text{Tb}_{18}$  amorphous alloy is in good agreement with the  $G(R)$  function obtained from the x-ray diffraction experiment [12] (figure 3). For the models of the  $\text{Re}_{100-x}\text{Tb}_x$  ( $x = 36, 53, 71$  and  $89$  at.%) amorphous alloys the positions and shape of the first peaks and the positions of the following peaks on the RDFs also agree with the experiment. The atomic arrangement obtained was the object of further study in the framework of the percolation theory.

### 3. Percolation in a one-component amorphous metal

We consider the cluster as a group of atoms that are at a distance from each other not exceeding a formal parameter  $s$ . If we change  $s$  for the same structure, the number, form and size of the clusters also change. When  $s < (0.6\text{--}0.7) r_1$ , there are no clusters in the structure, but if  $s > (1.1\text{--}1.4) r_1$  there is just one infinite cluster, containing all the atoms of the system. The clusters at intermediate  $s$  values are more interesting. Increasing  $s$  increases the number and size of the clusters (figure 4). The figure shows projections of the three greatest clusters to a main cube face (left-hand figures) and the cluster distributions by size (right-hand figures). The number of atoms in the largest cluster  $N_L$  is also shown. When the value of  $s = s_c = (0.94 \pm 0.01) r_1$  the percolation transition takes place, i.e. a large cluster forms which connects the opposite faces of the cube [5]. It is a geometrical phase transition [2, 9]. The cluster distribution by size shows the percolation transition with greater accuracy. Here we can see how the largest cluster (right-most vertical line) step by step comes off the dense quasi-continuous spectrum.

The analysis of the percolation cluster shows that its mass dimensionality is lower than topological one, i.e. it is a fractal object [5, 13]. The number of atoms located inside a sphere of radius  $R$  is  $N = kR^D$  (figure 5(a)), where  $D$  is fractal dimensionality. We have approximated the dependence  $\ln N = f(\ln R)$  by a linear dependence using the least squares technique. Averaging  $D$  by 30 realizations of the 10000-atom structure we obtained  $D = 2.5 \pm 0.2$ . This coincides with the classical value for lattice models  $D = 2.55$ . We



**Figure 4.** Influence of increasing formal parameter  $s$  on the cluster structure of the amorphous Re model. Projections of the three largest clusters (black circles, largest; gray, the second largest; white, the third largest) (on the left-hand side) and cluster distribution by size (on the right-hand side);  $N$  is the number of atoms in a cluster and  $nN$  is the total number of atoms within the  $N$ -atom clusters.

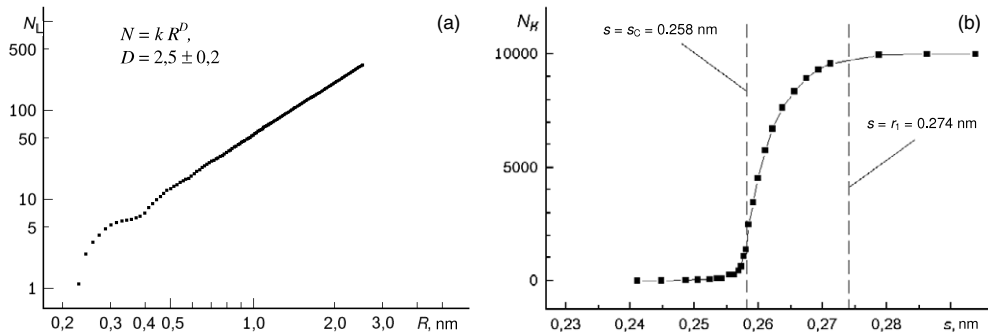
also obtained the fractal dimensionality in another way—using cluster distribution by size (figure 4). This gives practically the same value for  $D$ .

The number  $N_L$  of atoms within the largest cluster depends on  $s$  as a diffuse step (figure 5(b)). Such a step is typical for the temperature dependence of an order parameter. So percolation is really a geometrical phase transition. We suppose that ‘diffusion’ of the step is connected to the degree of disarray of the structure. An additional computer experiment on structure annealing shows that the ‘diffusion’ decreases (the step becomes sharper) after annealing. Besides, this ‘diffusion’ is correlated to the half-width of the first RDF peak.

#### 4. Percolation in binary amorphous alloys

Atomic clusters in the models of Re–Tb amorphous alloys were defined as follows: a cluster is a group of atoms of one type (terbium) which are in direct contact with each other, i.e. they are the nearest neighbors. The percolation radius  $r_c$  (the parameter which determines whether an atom belongs to the cluster) was chosen to be equal to the distance to the first minimum of the partial RDF  $g_{Tb-Tb}(r)$ :  $r_c = 0.4329 \text{ nm} = 1.22d_{Tb}$ .

We show in figure 6 the partial structure of the subsystem of Tb atoms (the projection on the  $XY$  plane) for several



**Figure 5.** Number  $N_L$  of atoms: (a) of the largest cluster which are within the sphere (radius  $R$  changes from the mean interatomic distance  $r_1$  to half of the cube linear size); (b) within the largest cluster, depending on  $s$  as a ‘diffuse step’.

compositions and the corresponding size distribution of clusters  $N - nN$ , where  $N$  is the number of atoms in the cluster and  $n$  is the number of clusters having the size  $N$ . The largest cluster is shown with links between neighboring atoms.

In figure 6(a) the subsystem of Tb atoms for 10% Tb is shown. Black circles represent atoms in the largest cluster in the model. White circles represent the rest of the Tb atoms. The Re atoms are not shown. It is seen that at 10% Tb a great number of small clusters exist, all the clusters are friable and extensive, and there are no compact ones.

Then we increased the concentration of the Tb atoms by just 3% (figure 6(b)). At concentration of 13% Tb one large cluster is formed which connects two opposite sides of the basic cube. Thus, near this concentration a percolation cluster is formed and percolation transition takes place. To check the presence of percolation the thin boundary layer was considered near each side of the cube. Percolation was registered only when the same cluster had at least two atoms in boundary layers belonging to opposite sides of the cube. The shape of the size distribution of clusters changes when changing the concentration of the Tb atoms. At 13% Tb one large cluster is distinguished, the number of small clusters rapidly decreases.

Then we increased the concentration of the Tb atoms by 2%. In figure 6(c) the subsystem of the Tb atoms for 15% Tb is represented. At this concentration almost all the atoms belong to the largest cluster. With increasing concentration of Tb atoms the number of small clusters rapidly decreases. The small clusters associate with the largest cluster. The large and then the small pores in it disappear, and the cluster becomes compact.

The dependence of probability  $P(x)$  that an atom belongs to the largest cluster with increasing concentration of Tb atoms is shown in figure 7. It has a shape which is characteristic of geometrical phase transitions and represents a diffuse step. The value of  $P(x)$  was determined as the ratio of the number of the Tb atoms in the largest cluster to the total number of the Tb atoms in the system.

As is known from percolation theory, the percolation cluster is a fractal object [5, 13]. Fractal properties of the percolation cluster are connected with its scale invariance (self-similarity): the cluster has pores of all sizes, from the atomic diameter up to the size of the basic cube, as can be seen in figure 6(b). The value of fractal dimensionality of

the percolation cluster is  $D = 2.5$ ; it was averaged over 10 realizations of the model (figure 8). It is close to the theoretical value  $D = 2.55$  for well-known lattice percolation problems [2, 11].

### 5. Concentration dependence of the percolation radius

Different physical interactions can have different characteristic radii. Therefore, in the general case, the percolation radius  $r_c$  is not constant. At any concentration of terbium atoms  $x > 0$  we can find the value  $r_c$  at which this composition will be situated on the percolation threshold. To investigate the dependence  $r_c(x)$  models of  $\text{Re}_{100-x}\text{Tb}_x$  ( $x = 1, 2, 3, 5, 10, 13, 15, 18, 36, 53, 71$  and 100 at.%) amorphous alloys were constructed. The results were averaged over 10 realizations for every composition.

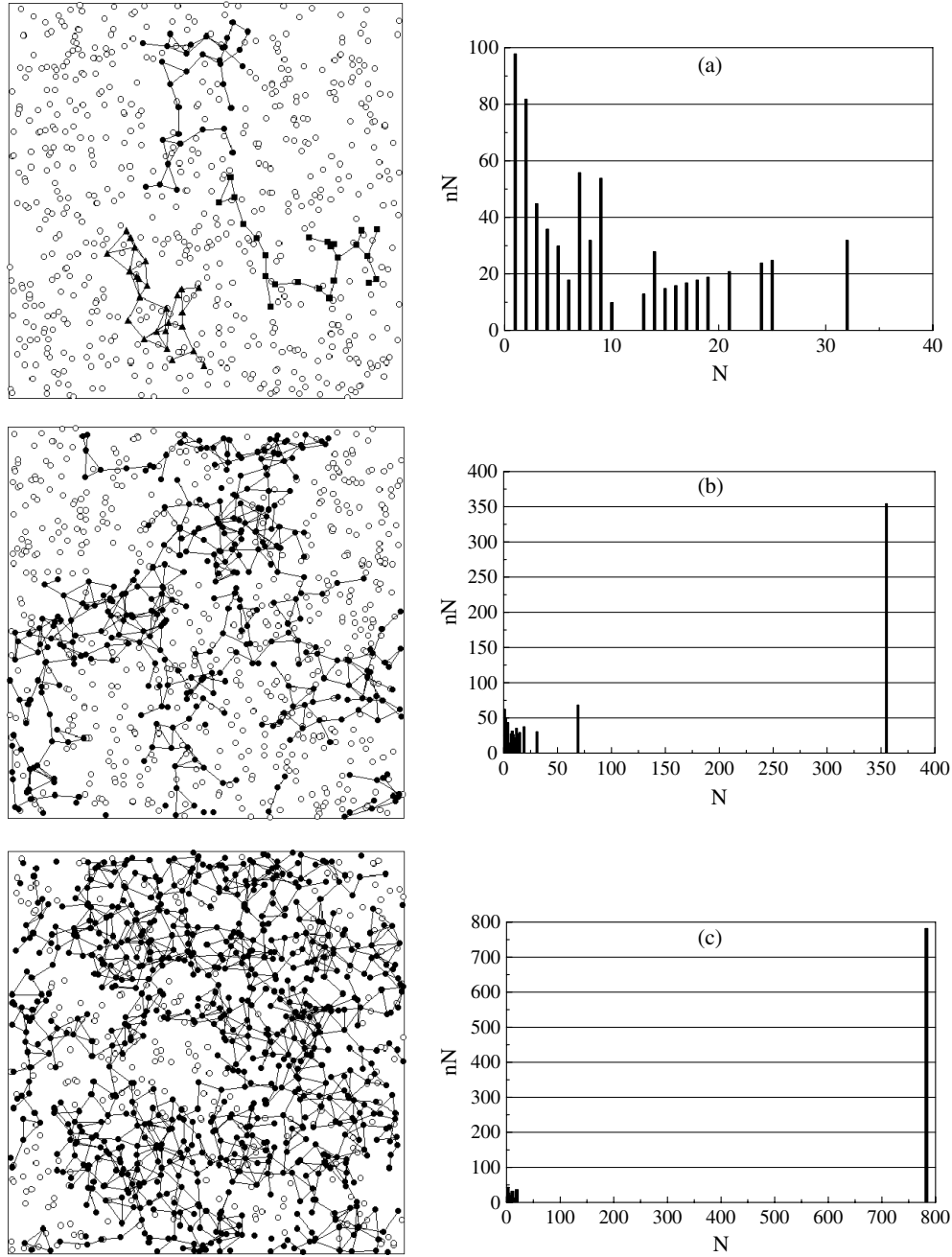
In order to analyze the influence of short-range order on concentration dependence of the percolation radius we also calculated concentration dependence of the percolation radius for the model of a random arrangement of atoms which is uniform over all the simulation volume. This problem of random sites is completely equivalent to that known from the percolation problem of spheres in the literature [14]. The sizes of the cube and the number of Tb atoms were given according to the compositions indicated above. The results of calculation were also averaged over 10 realizations for every composition.

In figure 9 the concentration dependence of the percolation radius is given, i.e. at each concentration of Tb atoms a value of the percolation radius was found at which the percolation cluster was formed for the first time. In other words, this cluster is on the percolation threshold. Such dependence is calculated for the models of Re–Tb amorphous alloys (black circles) and for a random distribution of atoms (white circles).

The percolation radius depends on the concentration of Tb atoms and the volume of the simulation cube  $V$ . But volume of the cube  $V$ , in its turn, also depends on the number of Tb atoms. For a random arrangement of atoms the following equality must be fulfilled because of scale invariance of the problem:

$$\frac{r_c}{\sqrt[3]{V}} = \frac{A}{\sqrt[3]{x}}, \tag{3}$$

where  $A$  is constant.



**Figure 6.** Projection of the subsystem of Tb atoms for  $\text{Re}_{100-x}\text{Tb}_x$  ((a)  $x = 10$ , (b)  $x = 13$ , (c)  $x = 15$  at.%) amorphous alloys on the  $XY$  plane and the size distribution of clusters.  $N$  is the number of atoms in a cluster,  $n$  is the number of clusters with the size  $N$ .

It is expedient to consider another dimensionless parameter which does not depend on the number of atoms It is expressed by the formula

$$B_c = \frac{4}{3}\pi Cr_c^3, \quad (4)$$

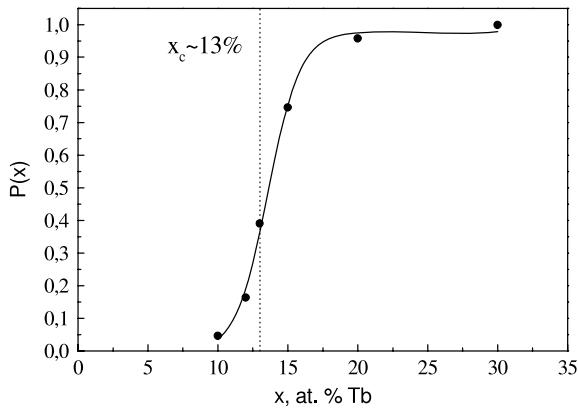
where  $C$  is the volume atomic concentration.

In figure 10 we present the concentration dependence of the parameter  $B_c$ . It is known that for a random arrangement of atoms (for the problem of spheres) the value of  $B_c$  is constant and equal to  $2.7 \pm 0.1$  [14, 15]. It is seen from figure 10 that for  $x = 13$ –100 at.% Tb the value of  $B_c$  does not depend on

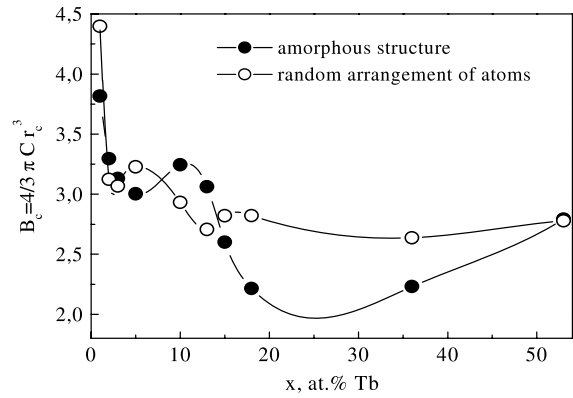
the concentration of Tb atoms and its average value is  $B_c = 2.75$ . At low concentrations ( $x = 1$ –10 at.%) considerable deviations from the mean value are observed due to the scale effect connected with the small size of the system [14, 15].

For an amorphous structure statistically significant deviations from the  $r_c(x)$  and  $B_c(x)$  curves for a random distribution of atoms are observed in figures 9 and 10. These deviations are connected with the presence of short-range order in the amorphous structure. The decreasing curves for the amorphous structure at  $x = 15$ –53 at.% Tb are connected with the proximity of the percolation radius to the first maximum of the partial RDF  $g_{\text{Ta-Tb}}(r)$ . At distances  $r \approx r_c$  a large

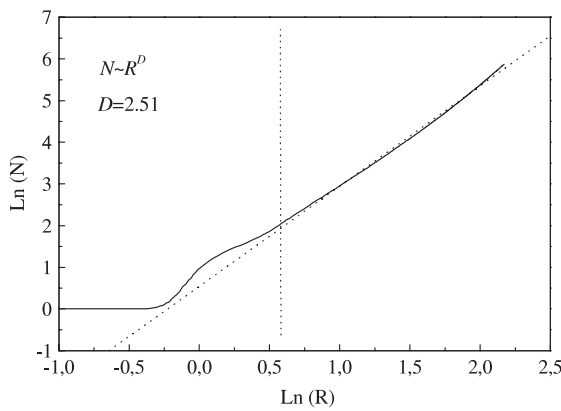




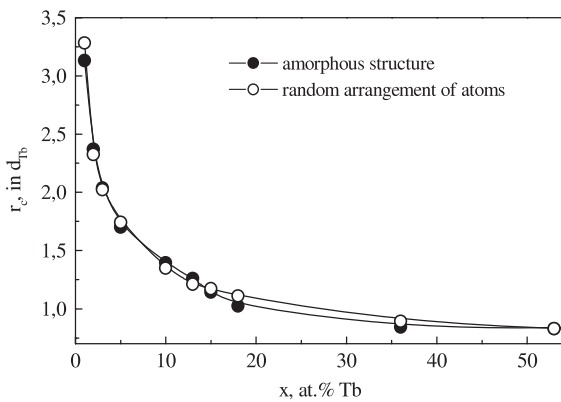
**Figure 7.** Dependence of the probability of an atom belonging to the largest cluster on composition of the Re–Tb amorphous alloys.



**Figure 10.** Dependence of the parameter  $B_c$  on the concentration of Tb atoms.



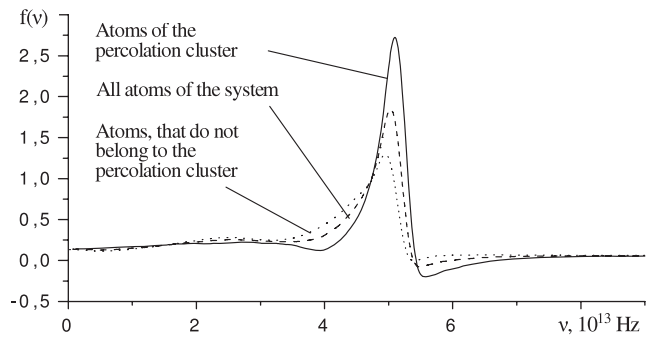
**Figure 8.** Calculation of fractal dimensionality of the percolation cluster.  $R$  is the radius of the sphere,  $N$  is the number of atoms of the percolation cluster in a sphere of radius  $R$ .



**Figure 9.** Dependence of the percolation radius on the concentration of Tb atoms.

number of Tb atoms exist, and this facilitates formation of the percolation cluster.

Thus,  $B_c$  and  $r_c$  are structure sensitive parameters and their dependence on the concentration of Tb atoms correlates with RDF. The values of fractal dimensionality averaged over all compositions for the amorphous structure and for random



**Figure 11.** Phonon spectra of the amorphous Re model.

arrangement of atoms coincide ( $\bar{D} = 2.5$ ) and are close to the theoretical value  $D = 2.55$  for three-dimensional lattice problems. This agrees with the fact that critical exponents  $\beta$  and  $\nu$  are determined by properties of the system with an infinite increase in its size and, thus, they cannot be sensitive to the structure of short-range order. The obtained result confirms the assumption [14] that the critical exponents for continuous percolation have the same values as for the lattice problems, since they do not depend on the geometry of a lattice.

## 6. Percolation in amorphous metals and their physical properties

A percolation cluster is a region of major compression in an atomic structure. So it plays the role of the skeleton of amorphous metals. The fractal skeleton can be displayed by studying some mechanical properties. For example, we have calculated the phonon spectrum of the model structure by Fourier transformation of the autocorrelation velocity function (figure 11). A partial phonon spectrum for the percolation cluster is sharper and more intense than for the atoms that do not belong to the percolation cluster.

The density defects of Egami and Vitek [16], which were determined for a 10% density level, were local. We have shown that if we determine the defects for a density level of 6% ( $r_1 - 0.94r_1 = 0.06r_1$ ) the defects should be continuous and form a percolation skeleton.

We also expect that a percolation cluster influences the magnetic, electrical and optical properties of an amorphous material. To feel the fractal nature, any external influence must be comparable in linear size with the critical percolation radius [17].

The proposed percolation model for binary amorphous alloys can be useful for a description of the magnetic properties of amorphous alloys in which the atoms having their own magnetic moment (Tb) are randomly distributed in the paramagnetic matrix (Re).

In Re–Tb amorphous alloys in the wide compositional region a maximum in the temperature dependence of the dynamic magnetic susceptibility  $\chi(T)$  and the irreversibility of magnetization  $M(T)$  is observed [18]. This is evidence of the spin-glass phase transition. The transition temperature  $T_f$  increases with increasing concentration of magnetic ions. The transition is observed only in alloys containing more than 13% of magnetic atoms, i.e. the magnetic ordering is observed only above the percolation threshold in the system.

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