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# INVESTIGATION OF THE STABLE STRUCTURES OF $Ni_x$ , $Fe_x$ , $Ni_{x-y}P_y$ , $Ni_{x-y}B_y$ , $Fe_{x-y}P_y$ , AND $Fe_{x-y}B_y$ ( $x=13, y < 13$ ) MICROCLUSTERS

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**ABSTRACT.** Computer simulation of the structure of  $Ni_x$ ,  $Fe_x$ ,  $Ni_{x-y}P_y$ ,  $Ni_{x-y}B_y$ ,  $Fe_{x-y}P_y$ ,  $Fe_{x-y}B_y$  clusters has been carried out by molecular dynamics simulation using empirical potentials of interaction. Results indicate that the symmetry of the clusters changes with increasing of number of metalloid atoms ( $y$ ). A surprising result is that when the Stillinger-Weber potential is used the great majority of the Morse minima are not supported.

## INTRODUCTION

The investigation of physical and chemical properties of small particles becomes more and more interesting lately. It is because there are wide possibilities for application of these particles in catalysis, laser technology, biology, etc. Some recent works concerning metal clusters [1,2], inert gases [3,4] and covalent crystals [5,6] made it possible to understand many structural and electronic properties of small clusters. Inert gases clusters are formed mainly as icosahedral structures with the number of atoms of 13,55,... For simple metals clusters the stable structures are related with the number of atoms of 8,20,... Obviously, this can be explained by the model of so called spherical shells.

There are many works concerning cluster physics. Nevertheless, the number of investigated objects remains limited. For example, metal-metalloid systems (which are very important from practical point of view) have not been investigated yet in the form of clusters. The exposure of stable configurations of these systems will make it possible to understand the processes of growth of metal-metalloid systems and their chemical activity. Since at present there exists an opportunity to get the clusters of required size and composition, so the information about the stable configurations may be used to regulate the physical

properties.

This article concerns the investigation of structure of small cluster systems Ni-P, Ni-B, Fe-P and Fe-B and also structural changes influenced by the clusters composition changes. Section II offers the basic method of investigation, section III gives the results and their discussion, section IV presents the main conclusions.

#### METHOD OF CALCULATION

Molecular dynamics simulation was used to define stable geometrical configurations of small clusters of Ni-P, Ni-B, Fe-P, Fe-B. In the calculations empirical potentials of interatomic interaction were used.

Stillinger-Weber potentials [7] and Morse potentials [8] were used for Ni-P. Morse potentials [9-11] were used for the other systems.

Stillinger-Weber potentials are given by

$$V(r) = \begin{cases} A\epsilon [(\alpha r/\sigma)^{-p} - (\alpha r/\sigma)^{-q}] [\exp(\alpha r/\sigma - a)^{-1}] & \\ 0, & \alpha r/\sigma > a \end{cases}$$

The parameters chosen were  $p=12$ ,  $q=0$ ,  $a=1.652194$ ,  $\sigma=2.2183$  Å, and  $\epsilon=0.08$  eV. For the case of Ni-Ni,  $A=1.0 \times 8.805977$ ,  $\alpha=1.0$ , for Ni-P,  $A=1.5 \times 8.805977$ ,  $\alpha=2.49/2.2 (=1.1318)$ , and for P-P,  $A=0.5 \times 8.805977$ ,  $\alpha=2.49/2.2 (=1.1318)$ .

Morse potential is given by

$$V(r) = \epsilon \{ \exp[-2\alpha(r/r_0 - 1)] - 2 \exp[-\alpha(r/r_0 - 1)] \} f(r/r_0)$$

$$f(z) = \begin{cases} 1 & z < 1 \\ 3z^4 - 8z^3 + 6z^2 & 1 < z < r_c/r_0 \\ 0 & z > r_c/r_0 \end{cases}$$

$$x = r/r_0; \quad z = (x - r_c/r_0) / (1 - r_c/r_0); \quad \alpha = 3.76; \quad r_c/r_0 = 1.4$$

The parameters for Morse potentials in the investigated system are shown in Table 1.

Trajectories of particles in real space are found by means of integration of Newton equation. In this article algorithm [12] for integration of movement equation was used. The initial conditions  $R(t=0)$  and particles velocity  $V(t=0)$  were chosen at will, so that it had no influence on the final result.

The potential  $V(R)$  determines the surface in 3N-dimensional space. This surface is characterized by the existence of the number of minima that correspond to various stable and metastable structures. The evolution of clusters geometry with final temperature looks like trajectories on

constant energy surface in 6N-dimensional phase space. The projection of this trajectory on 3N-dimensional configurational space will pass through all possible minima of potential energy, corresponding to possible structures. Each point of this configurational space can be connected to local (or global) minimum. Mathematically this procedure is performed by means of steepest descent minimization.

TABLE 1. The parameters for Morse potentials

	metal		metal		metalloid	
	metal		metalloid		metalloid	
	r(Å)	ε(eV)	r(Å)	ε(eV)	r(Å)	ε(eV)
Fe-B	2.585	0.32	2.057	0.342	3.515	0.015
Ni-B	2.532	0.52	2.015	0.55	2.28	0.015
Fe-P	2.620	0.51	2.253	0.848	3.406	0.194
Ni-P	2.53	0.19	2.24	0.32	2.10	0.06

Molecular dynamics simulation determines the positions  $\{R_i\}$  and  $\{V_i\}$  at each time step. The steepest descent minimization method allows one to find the instant position of local minimum, where the interatomic forces and velocities are equal to zero.

## RESULTS AND DISCUSSIONS

$Ni_{12}P_7(y=0-7)$ .  $Ni_{13}(y=0)$  cluster in the most stable condition is realised in icosahedral structure. While using Stillinger-Weber potential for  $Ni_{12}P$  cluster the atom of phosphorus is "pushed out" on the cluster surface. Note that the 6 axes of the fifth order five disappear. The remaining axis of the fifth order pass through the centre of the atom of phosphorus and through the centre of the cluster. In Morse potential case  $Ni_{12}P$  (M) the atom of phosphorus is located in the centre of the cluster.

In Stillinger-Weber cluster  $Ni_{11}P_2$  the atoms of phosphorus form P-P pair which is located on the cluster surface. While in this cluster the axis of the second order can be observed (see Fig. 1.1), in the cluster  $Ni_{11}P_2$  (Morse) the second atom of phosphorus is located on the axis of the fifth order.

When  $y=3$  in Stillinger Weber cluster  $Ni_{10}P_3$  the atoms of phosphorus form an equilateral triangle that is located on the cluster surface nearest to the centre. The cluster possesses only the axis of the third order (see Fig.1.2). The Morse cluster  $Ni_{10}P_3$  possesses the axis of the second order (see Fig. 2.1).

The study of the structure of the cluster  $Ni_9P_4$  shows that in this Stillinger-Weber cluster the atoms of phosphorus

form tetrahedra, one atom of which enters the volume of the cluster and the axis of symmetry of the third order is observed (Fig. 1.3). In  $Ni_9P_4$  (Morse) the cluster composed of atoms of phosphorus also possesses the geometry of tetrahedra and, consequently, the axis of the third order (Fig. 2.2).

In Stillinger-Weber Ni P case one can observe the axis of the second order, and in Morse  $Ni_8P_5$  and Morse  $Ni_7P_6$  - planes of symmetry.

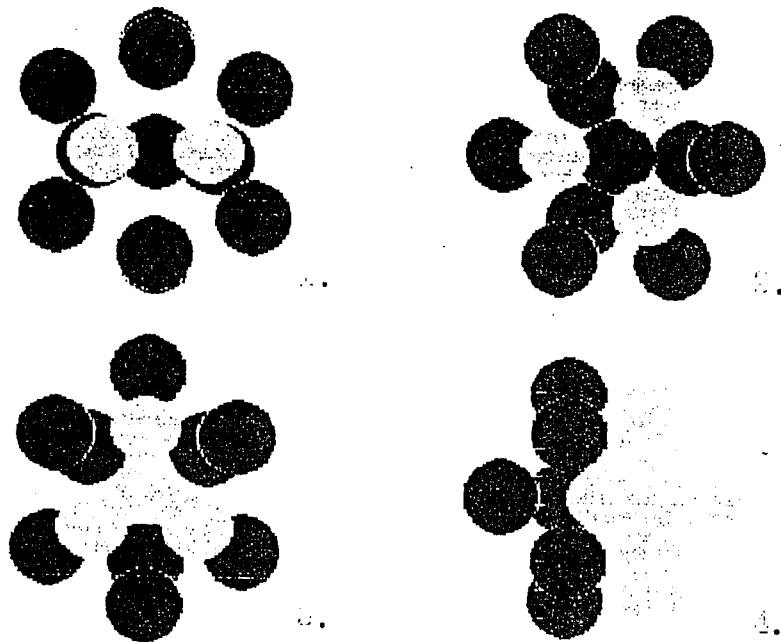


Fig. 1. The Stillinger-Weber clusters (1)  $Ni_{11}P_2$ , (2)  $Ni_{10}P_3$ , (3)  $Ni_9P_4$ , (4)  $Ni_6P_7$ .

In Stillinger-Weber  $Ni_6P_7$  the atoms of phosphorus form pentagonal bipyramid (Fig. 1.4). Note that the increase rise of concentration of the atoms of phosphorus in Stillinger-Weber cluster  $Ni_{13-y}P_y$  more distinctly distinguishes the isolation of Ni and P atoms, i.e. phosphorus and nickel clusters form "independent" structures.

$Ni_{13-y}P_y$ ,  $Ni_{13-y}B_y$ ,  $Fe_{13-y}P_y$ ,  $Fe_{13-y}B_y$ . This section represents the results of calculation using Morse potential.

When  $y=1$  in the clusters  $Ni_{12}P$  and  $Fe_{12}P$  the atoms of phosphorus are located in the centre of the cluster. Quite a different picture can be found in  $Ni_{12}B$  and  $Fe_{12}B$ . The boron is "pushed out" to the surface, from the 6 axes of the fifth

order only one remains and it pass through that atom and the centre of the cluster.

If the number of metalloid atoms is increased ( $y=2$ ) the process will go in such a way: the atoms of boron in  $Ni_{11}B_2$  and  $Fe_{11}B_2$  will form pairs B-B, that are located on the surface, like we had it in Stillinger-Weber cluster  $Ni_{11}P_2$  case (Fig. 1.1); the atoms of phosphorus in  $Ni_{11}P_2$  and  $Fe_{11}P_2$  are located on the axis of the fifth order.

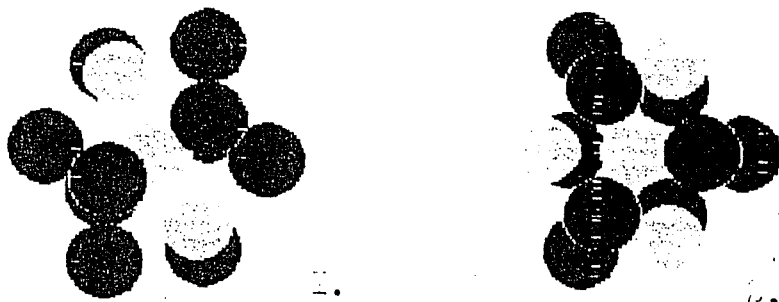


Fig. 2. The Morse clusters (1)  $Ni_{10}P_3$ , (2)  $Ni_9P_4$ .

When  $y=3$  in  $Ni_{10}P_3$ ,  $Fe_{10}P_3$  the axis of symmetry is of the second order (Fig. 2.1). In  $Ni_{10}B_3$  and  $Fe_{10}B_3$  the cluster seems to be the syntheses of two structures with the axes of symmetry of different orders - the fourth and the fifth. Fig. 3.1 and 3.2 show the cluster  $Ni_{10}B_3$  ( $Fe_{10}B_3$ ) from two opposite views.

If the next atom of metal is replaced by metalloid in the cluster  $Ni_9P_4$ , the axis is of symmetry of the third order (Fig. 2.2); in  $Ni_9B_4$  and  $Fe_9B_4$  (Fig. 3.3) the axis of symmetry is of the fourth order which is absent in icosahedral structures possessing point groups of symmetry 532. That means that the structural changes which appeared with the changes in the clusters composition may be non-trivial.

If  $y$  is increased ( $y=5,6$ ) in  $Ni_{13-y}P_y(M)$  and  $Fe_{13-y}P_y$  there are only the planes of symmetry. Note that in  $Fe_8P_5$  the cluster of atoms of Fe represents two squares that have the angle of  $45^\circ$  between their diagonals.

In  $Ni_8B_5$  ( $Fe_8B_5$ ) and  $Ni_7B_6$  ( $Fe_7B_6$ ) (Fig. 3.4) there are the elements of cubical cell (their "genesis").

The above mentioned results show that the behaviour of clusters  $Ni_{13-y}B_y$  and  $Fe_{13-y}B_y$  is the same, which is due to the used potentials.

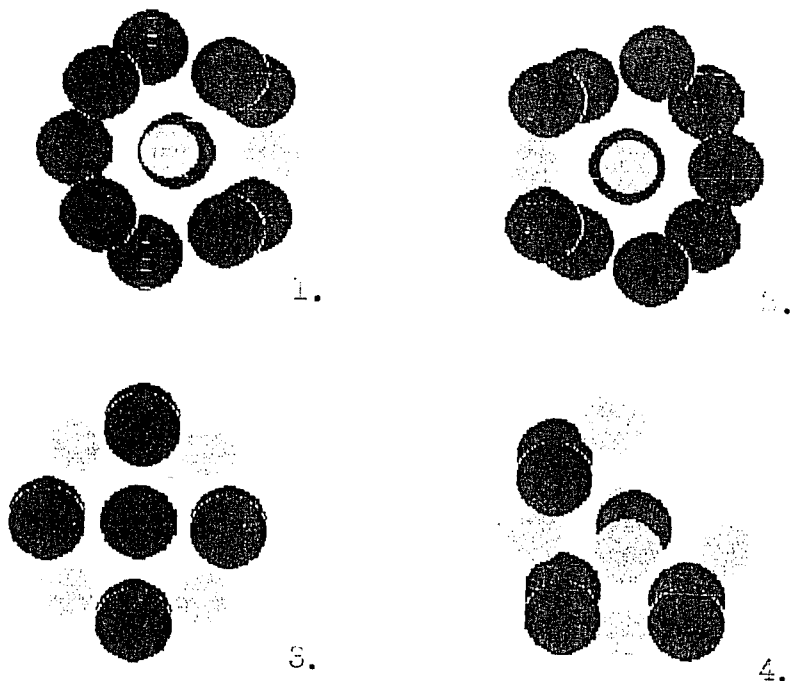


Fig. 3. (1) and (2)  $\text{Fe}_{10}\text{B}_3$ , (3)  $\text{Fe}_9\text{B}_4$ , (4)  $\text{Fe}_7\text{B}_6$ .

### CONCLUSIONS

1. The empirical potentials of interatomic interaction which have some common features in small ensembles lead to quite different basic results.
2. In the clusters Ni-B and Fe-B the atoms of metalloid are located in the surface of the clusters, while in Ni-P and Fe-P the atoms of metalloid are also introduced into "the volume" of the clusters.
3. The structures of the clusters  $\text{Ni}_{13-y}\text{B}_y$  and  $\text{Fe}_{13-y}\text{B}_y$  is the same while the configurations of  $\text{Ni}_{13-y}\text{P}_y$  and  $\text{Fe}_{13-y}\text{P}_y$  are different.
4. For the clusters  $\text{Ni}_{13-y}\text{B}_y$  and  $\text{Fe}_{13-y}\text{B}_y$  non-trivial transitions between the structures with different symmetry types were discovered.

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