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COMPUTER SIMULATION OF THE STRUCTURE OF AMORPHOUS METALLIC CLUSTERS DEPOSITED ON VARIOUS SURFACES

M.A. Popescu

Institute of Physics and Technology of Materials, Bucharest, P.O. Box MG.7, Roumanie.

Abstract.—The structure of the supported 13-atom metallic cluster was simulated by computer. Various substrate configurations and interaction forces were considered. While in free space the icosahedral-like structure is more stable, the interaction with the support shifts the equilibrium structure towards a crystalline one. The crystalline nucleus exhibits the orientation (100)/(100), (111)/(111) and (111)/(110).

1. Introduction. — The first stages of the atomic deposition on various substrates (crystalline or amorphous) are still a challenging problem for the physics of thin solid films. The atomic scale structure in very small particles is not yet completely understood /1/.

On the other hand there is a continuous interest in the field of heterogeneous catalysis for the dependence of the activity on the particle size of the metallic clusters in supported catalysts /2/. The most active catalysts usually have particle sizes below 40-50 Å, which roughly correspond to clusters of fewer than a thousand of atoms.

Cyrot-Lackmann et al /3/ have studied the stability of small transition metal particles and the electronic structure of their surfaces and succeeded to explain the variation of activity of the metallic-catalysts with the level of catalyst dispersion.

Due to energetical consequence of the high ratio surface atoms/bulk atoms the atomic configuration in clusters must depend on the cluster size. Burton /4/ was the first to show that for a Lennard-Jones interaction potential there exists very dense low-energy structures for clusters of 13 and 55 atoms.

Recent experimental observations /5/ seems to give support to the theoretical results according to which the stablest configuration of small clusters is an icosahedral-like arrangement of atoms with five-fold symmetry axes.

In this paper we performed a computer simulation of the structure of a small metallic cluster (13 atoms) taking into account the interaction with the support.

2. Method. — The simulation of the structure of small metallic cluster was carried out using a Monte-Carlo procedure for the search of the configuration of minimum energy /6/ when a Lennard-Jones potential is acting between the atoms. The interaction potential was taken as:

\[ V_C(r) = \frac{A}{r^{12}} - \frac{A}{r^{6}}; \quad A = C \cdot r_0 \]

where \( C \) is a constant and \( r_0 \) is the equilibrium distance between two nearest atoms in the crystalline lattice of nickel \((r_0=2.48 \text{ Å})\). Of course, the peculiar choice of the metal does not affect the general conclusions. The constant \( C \) was chosen so as to have a minimum of \( V_C \) at \( r_0 \).

Starting from the initial (random) set of coordinates, the total interaction energy of the cluster \( (E_C) \) was computed. Then every atom (taken in a random sequence) was
shifted by a small distance, the cluster energy for the new position was calculated and the new position of the shifted atom was retained only when $E_c$ decreased. Using atom displacements of a mean step gradually diminishing from $0.2 \, \AA$ to $0.02 \, \AA$, the final configuration of the cluster was practically attained after $\sim 1000$ moves/atom. An IBM 370/135 computer was used for this simulation.

Firstly we simulated the structure of a 13-atom cluster (the minimum size corresponding to a metallic atom and its first order coordination). Secondly we simulated the simultaneous deposition of 13 atoms on a surface, taking into account the interaction potential with various deposition planes. The interaction potential with the substrate, $V_s$, was chosen as $V_s = kV_C$, the constant $k$ accounting for various strength of interaction between metal atoms and the support.

3. Results. - Starting from the coordinates of a f.c.c. nucleus with 13 atoms (a cubooctahedron) an energy relaxation was performed using the above described method.

In figure 1 it is shown the result of the computation. The total energy ($E_c$) of the cluster can be reduced by an atomic rearrangement leading in the final stablest form to a perfect icosahedron which have six five-fold symmetry axes and an energy lower by 8.8 %. The main feature of the transition cubooctahedron-icosahedron, reflected in the distribution of the pair distances inside the cluster, is the disappear-
stable configuration of minimum energy. Two levels of interaction with the support were assumed: \( V_S = V_C \) and \( V_S = 10 \ V_C \).

In figure 2 are shown the results.

![Figure 2](image_url)

**Fig.2.** The distribution of the distances and of the coordination numbers in a 13-atom cluster supported on a homogeneous plane.

When \( V_S = 0 \) the metallic cluster takes an icosahedral (non-crystalline) structure. When \( V_S = V_C \) there is a tendency to leave the icosahedral structure and to move towards a crystalline cluster. Some distances in the pair distribution function (PDF) appear in the region around \( \sim 3.50 \ \text{Å} \) where a peak in the f.c.c. cluster is prominent. At higher interactions (\( V_S = 10 \ V_C \)) the stablest configuration of the cluster is, clearly, that of an ordered, crystalline configuration. Close inspection of the cluster reveals an orientation with the atomic plane (111) along the supporting plane.

In other simulation experiments we considered deposition substrates defined by the following crystallographic planes: (100), (110) and (111). 18 atoms were used in defining every crystallographic plane.

The first interatomic distance was scaled to \( r_0 = 2.48 \ \text{Å} \).

In order to smooth the configurational fluctuations of the final relaxed cluster, seven simulation experiments were performed, starting every time from different random coordinates. The cumulated PDF was calculated. Two cases of interaction clustering atoms - crystallographic plane were considered: \( V_S = V_C \) and \( V_S = 5V_C \).

The results are shown in figure 3a and 3b. For \( V_S = V_C \), as can be easily seen, the deposition on (100) crystal face induces a more crystalline configuration of the cluster. When the cluster is attached to the plane (111) the icosahedral structure of the free cluster is better preserved. This is probably a consequence of the fit between the atomic configuration in the plane (111) and the atomic configuration on the small triangular faces of the icosahedron surface.

For higher interaction forces atom 7 substrate (\( V_S = 5V_C \)) this trend becomes more apparent. A well developed crystalline ordering is obtained when the deposition plane is (100) and, to a smaller extent, when the plane is (110). A careful analysis of the cluster configuration when supported on various crystallographic planes allows to conclude that the deposited cluster is oriented with the plane (100) along the substrate surface when the substrate exhibits a (100) plane. The cluster develops a (111) plane along the substrate when supported on a (111) plane.
4. Conclusions. - Computer simulation of the structure of a small cluster of atoms with Lennard-Jones interaction (which approximates the interaction between metallic atoms) gave interesting results. While for the free cluster of atoms the stabilest atomic configuration is an icosahedral (non-crystalline) one, for the supported cluster the crystalline configuration becomes more advantageous from the energetical point of view. The crystalline ordering is dependent on the type of substrate and on the ratio between the interaction strength within the cluster and the interaction clustering atoms-substrate (VS/VC).

References
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