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LOW-DIMENSIONAL SYSTEMS  
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# Formation of an Icosahedral Structure during Crystallization of Nickel Nanoclusters

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**Abstract**—The crystallization of nickel nanoclusters is investigated using a molecular dynamics simulation with tight-binding potentials. The formation of a cluster structure depends on the cooling conditions. Slow cooling results in the formation of a face-centered cubic structure, whereas fast cooling, according to the data obtained in 40% of the simulation experiments, leads to the formation of an icosahedral structure. The molecular dynamics simulation experiments demonstrate the possibility of controlling the formation of a structure of nickel nanoclusters during crystallization. © 2004 MAIK “Nauka/Interperiodica”.

## 1. INTRODUCTION

Investigation of the properties of small-sized metallic particles containing from several hundreds to several thousands of atoms is of great research interest due to their possible use as catalysts or surface nanostructures [1–4]. The properties of such particles are intermediate between those exhibited by molecules and crystalline solids. This makes them especially attractive for use in various fields of engineering. In this respect, the understanding of the mechanisms of formation of nanoclusters from a liquid or gas phase is particularly important for the controlled growth of low-dimensional structures with specified parameters. Elucidation of the internal structure of free clusters can play a key role in explaining their physical and chemical features.

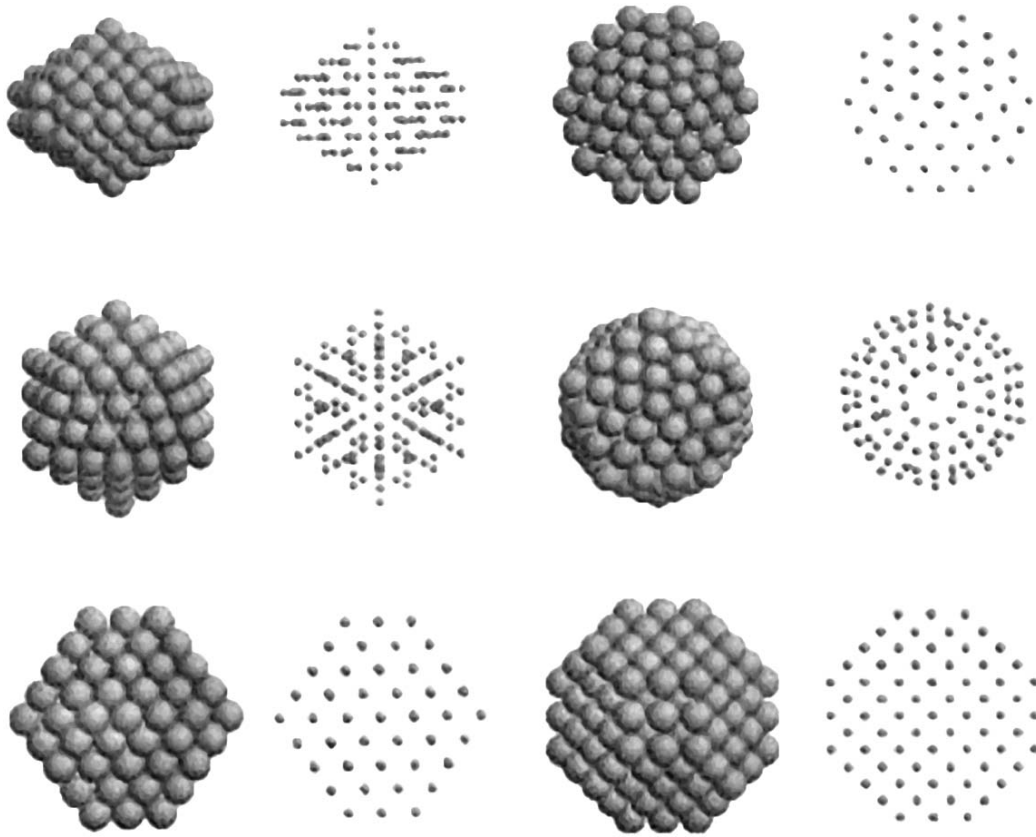
The structure of metallic nanoclusters and, in particular, the size dependence of their properties have been intensively studied using experimental and theoretical methods over the course of more than 30 years. Computer simulations have demonstrated that, compared to conventional bulk materials, nanoclusters are characterized by several structural modifications. For example, nanoclusters of metals with a face-centered cubic lattice can exist in face-centered cubic, hexagonal closely packed, icosahedral, and decahedral modifications [5–11]. Some of these modifications are presented in Fig. 1. Metallic clusters with different symmetries were experimentally observed by Martin [7] with the use of an electron microscope. It should be noted that, in bulk face-centered cubic materials, the formation of other structures is suppressed kinetically, whereas nanoclusters of these materials can be obtained in different structural modifications with a great variety of physical and chemical properties.

Thermodynamically equilibrium modifications of metallic clusters have been thoroughly studied in the

framework of different theoretical models. The results of theoretical calculations performed by Iijima and Ichihashi [12] and K. Mannien and M. Mannien [13] indicate that, for some metals with a face-centered cubic lattice (such as gold and nickel), the icosahedral structure is metastable even in the case of small-sized clusters (containing less than 100 atoms), which is inconsistent with experimental observations. Furthermore, an increase in the cluster size is accompanied by a decrease in the stability of the icosahedral structure [12]. However, direct observations with the use of an electron microscope [7–10] have revealed that clusters containing even several thousands of atoms can exhibit icosahedral or decahedral morphology. These experiments have demonstrated that the formation of an icosahedral structure of a cluster is most likely governed by the kinetic rather than thermodynamic factors [14].

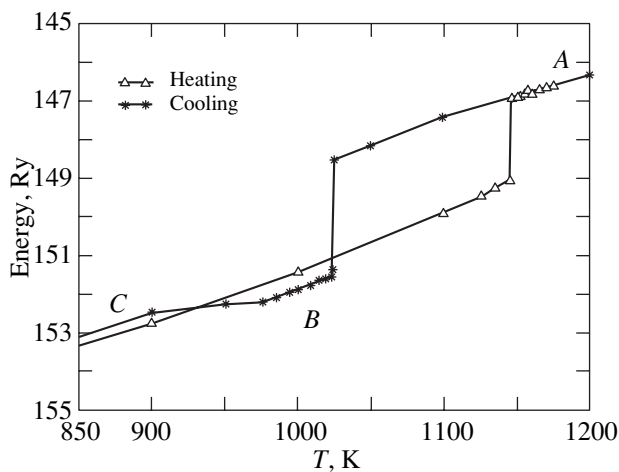
## 2. SIMULATION TECHNIQUE

In order to investigate how the kinetic factors affect the formation of a structure of nickel nanoclusters, we carried out a molecular dynamics simulation of heating of nickel nanoparticles with subsequent cooling to the formation of a crystal phase. The computer simulation was performed with the use of the tight-binding potentials proposed by Cleri and Rosato [15]. In the simulation experiment, a face-centered cubic nickel cluster consisting of 555 atoms was used as an initial structure. With the aim of completely destroying the long-range order in the nickel cluster, it was smoothly heated to a temperature of 1800 K, which is considerably higher than the melting temperature of nickel clusters ( $T_{\text{melt}} = 1145$  K). During the simulation experiment, the temperature was determined from the mean kinetic energy of the atoms. The cluster was held at  $T = 1800$  K for a



**Fig. 1.** Decahedral (upper row), icosahedral (middle row), and face-centered cubic (lower row) structures of the nanoclusters [1]. Each structure is drawn in two projections: the lateral view (first and second columns) and the top view (third and fourth columns).

long time, more precisely, for 200 ps ( $1.0 \times 10^5 \Delta t$  where  $\Delta t = 2$  fs is the time step in the molecular dynamics simulation experiment). Then, the cluster was cooled to a temperature of 300 K. The cooling and heating curves are depicted in Fig. 2, which shows the temperature dependence of the potential energy of the nickel nano-



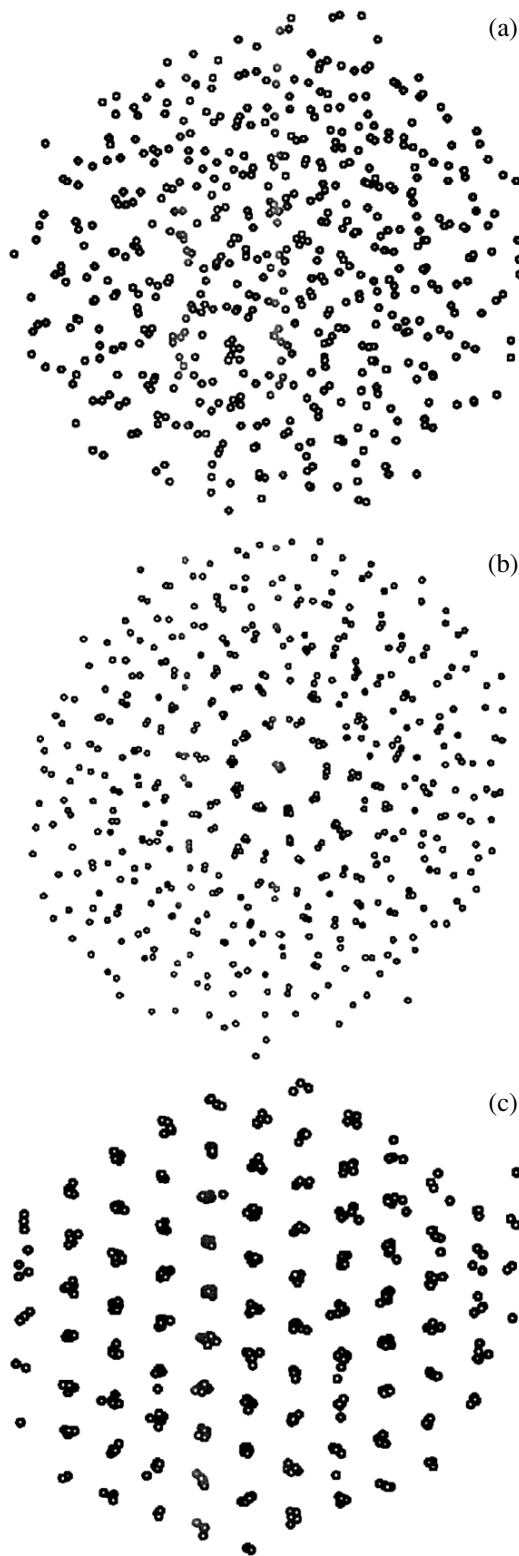
**Fig. 2.** Dependence of the potential energy  $E_p$  of the nickel nanocluster ( $N = 555$ ) on the absolute temperature  $T$ .

cluster. The melting and crystallization points of the cluster were determined from the jumps in the potential energy as a function of temperature. The temperature was stabilized by two methods: (i) with the use of a Nose thermostat and (ii) according to the Anderson method. When simulating a constant temperature, the best results were obtained using the Nose thermostat. In this case, the total energy is represented as the sum of the kinetic and potential energies of the particles and the kinetic and potential energies of the thermal reservoir  $s$ :

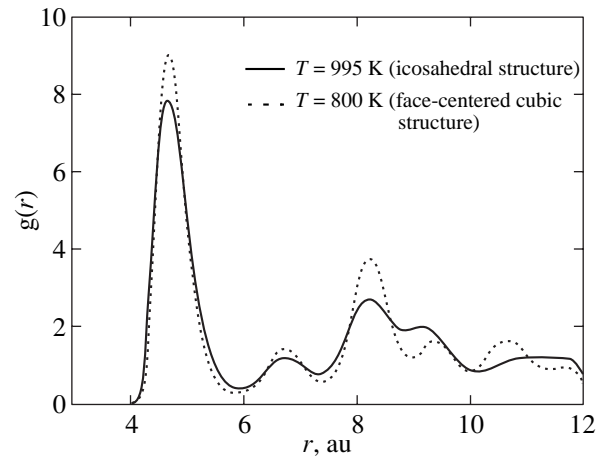
$$H = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2 + \Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) + \left( \frac{d \ln s}{dt} \right)^2 \frac{Q}{2} + (3N + 1) k_B T_0 \ln s, \quad (1)$$

where  $Q$  is an adjustable parameter. The smooth variation in the temperature at a specified rate was simulated using the Anderson method:

$$H = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2 + \Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) + \frac{W}{2} \dot{V}^2 + P_0 V, \quad (2)$$



**Fig. 3.** Nickel cluster configurations corresponding to portions A, B, and C in the crystallization curve depicted in Fig. 2: (a) the nanocluster in a molten state,  $T = 1200$  K; (b) the nanocluster immediately after crystallization,  $T = 995$  K; and (c) the nanocluster after complete structural transformation,  $T = 800$  K.



**Fig. 4.** Radial distribution function  $g(r)$  of the nickel nanocluster ( $N = 555$ ) for portions B and C in the crystallization curve depicted in Fig. 2.

where  $W$  is an adjustable parameter. This approach makes it possible to determine more exactly the melting and crystallization temperatures of simulated particles as compared to the method used by Qi *et al.* [16], according to which it was necessary to perform additional calculations (specifically of the maximum of the heat capacity) when determining these temperatures.

### 3. RESULTS AND DISCUSSION

It can be seen from Fig. 2 that, during cooling below the melting temperature, the simulated system tends to transform into an icosahedral structure (portion B in the cooling curve). However, the nickel nanocluster in this temperature range is in a very unstable state and undergoes transformation into a face-centered cubic structure with a further smooth decrease in the temperature. In order to analyze the crystallization of the nickel nanocluster, we consider the cluster configurations (Fig. 3), which correspond to the portions A, B, and C in the crystallization curve depicted in Fig. 2 (at temperatures  $T = 1200$ ,  $995$ , and  $800$  K, respectively), and the radial distribution function (Fig. 4), which is calculated for the portions B and C in this curve. To avoid errors in determining the cluster structure due to side effects associated with thermal noise, the nanocluster was kept at the aforementioned temperatures for approximately 400 ps with the aim of attaining an equilibrium configuration.

At a temperature of  $1200$  K (which is higher than the crystallization temperature  $T_{\text{cryst}} = 1025$  K), the nanocluster exists in a molten state and its particles strongly fluctuate, even though the cluster shape, as a whole, remains nearly spherical (Fig. 3a). An abrupt decrease in the potential energy (Fig. 2) indicates that the cluster at  $T = 995$  K occurs already in a crystalline state (Figs. 3b, 4). In this case, the nanocluster has a facet structure with a pronounced fivefold symmetry, which

corresponds to an icosahedral configuration. With a further smooth decrease in the temperature, the nickel nanocluster undergoes a structural transformation with the formation of a face-centered cubic structure involving stacking faults (Fig. 3c). The formation of an icosahedral configuration upon fast cooling was observed in 40% of the simulation experiments. In other cases, the final face-centered cubic configuration of the nickel nanocluster is formed without a metastable icosahedral structure. In our simulation experiments performed with nickel, we did not reveal the formation of an icosahedral structure first on the cluster surface and then deep in the cluster core, as was observed for gold in [14].

The result obtained is in agreement with the classical theory of nucleation [17–19], according to which the final face-centered cubic structure of a cluster formed in the course of crystallization is energetically more stable than the icosahedral structure. However, numerous molecular dynamics simulations have demonstrated that, at  $T = 0$  K, it is this icosahedral configuration that is energetically more favorable, at least for clusters containing from two to three thousands of atoms [13]. It should be noted that the metastable icosahedral structure (portion *B* in the cooling curve in Fig. 2) can be stabilized by instantaneous cooling to lower temperatures, for example, to temperatures in the range 600–700 K.

#### 4. CONCLUSIONS

Thus, the structural properties of nickel nanoparticles were investigated using a molecular dynamics simulation of their melting and crystallization in terms of tight-binding potentials. The simulation experiments demonstrated the possibility of controlling the formation of a structure of nickel nanoclusters. The results obtained in the computer simulation allowed us to conclude that, after the onset of crystallization, the formation of a cluster structure strongly depends on the cooling conditions. Slow cooling leads to the formation of only a face-centered cubic structure, whereas fast cooling results in the formation of a metastable icosahedral structure, as was observed in 40% of the simulation experiments.

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