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# Structural evolution of Pd-79 cluster before melting

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**Abstract**

The melting of Pd-79 has been studied by molecular dynamics simulation method. It is found that Pd-79 cluster shows abnormal structural evolution before melting, i.e., the structure evolves alternately amongst ideal FCC, FCC with some surface point defects and amorphous when the temperature ranges from 581 K to 641 K. Considering the structural sensitivity to temperature, the Pd-79 cluster may be applied in thermally sensitive devices.


*Keywords:* Pd clusters; Molecular dynamics; Melting

The melting process of small nanoclusters is different from the bulk materials due to large surface to volume ratio, which has been studied theoretically [1,2] and experimentally [3,4]. To study the melting process in more detail, one needs to use the computer simulation method, such as molecular dynamics (MD) simulation or Monte Carlo (MC) methods, where these methods can give accurate information at atomic level. Westergren and Nordholm [5] studied the melting of Pd-13, Pd-55 and Pd-147 clusters by calculating the density of states of Pd clusters by MC simulation; Miao et al. [6] found (by MD simulation) that the melting temperature of Pd cluster is lower than that of Pd nanowire in the comparable size; Sankaranarayanan et al. [7] simulated the melting of Pd–Pt nanoclusters and found that the Pt–Pd clusters exhibited a two-stage melting: surface melting of the external Pd atoms followed by homogeneous melting of the Pt core. Pan et al. [8] showed (MD simulation) that the cubooctahedron Pd-309 cluster melts around 1040 K, but the icosahedron Pd-309 nanocluster melts around 1070 K. Inspired by these works, we have simulated the melting process of isolated Pd clusters in different sizes (Pd-79, 135, 321, 531, 767, 1157, 1601, 2123, 3043), and found that only the Pd-79 cluster shows abnormal structure evolution before melting, which will be reported in this letter.

The molecular dynamics simulation package, MATERIALS EXPLORER [9], was used to study the Pd-79 cluster in NVT ensemble. The potential function employed was the Rosato–Guillope–Legrand (RGL) potential [10–12], which has the following form

$$\Phi = \sum_i (E_{\mathrm{b}}^i + E_{\mathrm{r}}^i) \tag{1}$$

where

$$E_{\mathrm{r}}^i = \sum_j A \cdot \exp\left[-p\left(\frac{r_{ij}}{r_0}-1\right)\right]$$
$$A = \frac{q}{p-q}\cdot\frac{E_{\mathrm{c}}}{Z} \tag{2}$$

and

$$E_{\mathrm{b}}^i = -\sqrt{\rho_i}$$
$$\rho_i = \sum_{j=i} \xi^2 \cdot \exp\left[-2q\left(\frac{r_{ij}}{r_0}-1\right)\right] \tag{3}$$
$$\xi = \frac{p}{p-q}\cdot\frac{E_{\mathrm{c}}}{\sqrt{Z}}$$

$E_{\mathrm{r}}^i$ is the two body term and $E_{\mathrm{b}}^i$ is the many-body term. $p$ and $q$ are dimensionless parameters, $E_{\mathrm{c}}$ the cohesive energy, $Z$ the number of nearest neighbor atoms and $r_0$ the nearest neighbor

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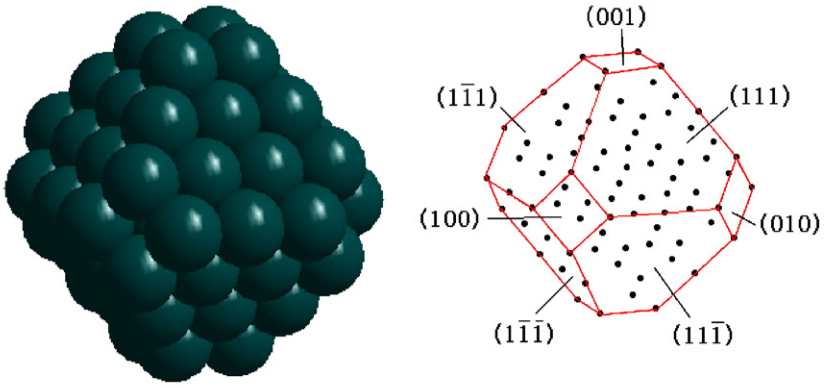


Fig. 1. The initial atomic configuration of truncated octahedral Pd-79 cluster.

distance. It should be mentioned that RGL potential is one type of EAM potential, and this potential has been well applied for FCC metals such as Ni, Cu, Rh, Pd, Ag, etc [10–12].

The initial structure of Pd-79 cluster was cut from an ideal FCC Pd bulk crystal, where the shape was truncated octahedron (Fig. 1), surrounded by {100} and {111} crystal planes. The free boundary condition was applied, and the time step was 2 fs. To find the most stable structure, we used the relaxation method, i.e., the temperature was fixed in every process, and the structures relaxed to thermodynamics equilibrium after simulation. The temperature ranged from 300 K to 900 K. From 300 K to 500 K and 750 K to 900 K, the temperature varied in steps of 10 K; from 500 K to 570 K and 680 K to 750 K, varied in steps of 5 K; and from 570 K to 680 K, varied in steps of 1 K. In each fixed temperature, the total simulating steps reached 500,000 (1000 ps ). The simulation information was recorded for every 10 steps.

Fig. 2 shows the mean energy per atom during the temperature increasing from 300 K to 900 K. The energy curve can be divided into three intervals. In the first interval, corresponding to the temperature from 300 K to 581 K, the Pd-79 keeps the initial crystal structure (FCC) and truncated octahedron shape. The mean energy per atom increases linearly with the increase of temperature except for that at 525 K, where a surface atom moves from {111} to {100} surface plane (Fig. 3). In the second interval, the temperature ranges from 581 K to 541 K, and the structure evolves between FCC and amorphous (or liquid-like state, see Fig. 4), which will be explained in detail in the following paragraphs. In the third interval, the temperature is higher than 541 K, and the structure of Pd-79 is in liquid state.

The second interval in Fig. 2 is enlarged in Fig. 5, where the energy increases or decreases with the increase of the temperature alternately. The simulated points can be classified in three groups: the points in the first group still have a linear relation with temperature, where the fitted line is the extension of that in the first interval (300 K–581 K). The cluster in the first group is still in ideal FCC structure and truncated octahedron shape at the temperatures 583, 584, 586, 587, 588, 589, 590, 592, 593, 596, 598, 599, 601, 602, 606, 607, 609, 613, 619, 623 and 640 (K). The points in the second group have higher energy than the first group, where

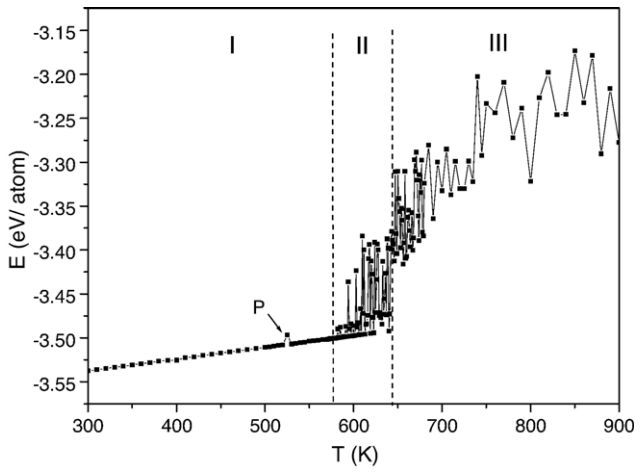


Fig. 2. The mean energy per atom during the increase of temperature.

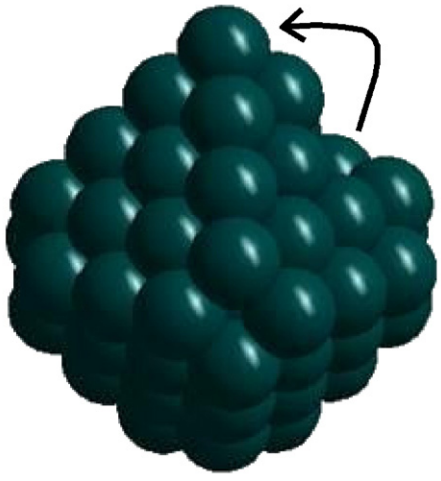

Fig. 3. A surface atom in {111}plane of Pd-79 cluster moves to {100} surface.