Correlated Orientations in Nanocrystal Fluctuations

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The dynamical behavior of small particles has been observed by high resolution electron microscopy. Spontaneous structural fluctuations, between various orientations, were observed and quantified. Clear transitions involving appearance and vanishing of twins were detected. Measurements of the angle change between succeeding configurations of the $\langle 111 \rangle$ atomic plane reveal the existence of several preferred angular changes. Twin related transformations give a good fit to the observed angular correlation, which excludes complete particle melting during the transition between successive configurations. It was also found that the particles rotate by a few degrees during this transformation. [S0031-9007(97)02816-0]

The structure of atomic clusters is interesting because they present a state of matter that is intermediate between single atoms and the bulk state. In ultrafine particles ($R < 10$ nm), new phenomena may be expected, especially due to the high ratio between surface area and volume.

Previous studies performed on small particles revealed a structure which is characterized by multiple twinned domains in many fcc metals [1–3].

High resolution electron microscopy (HREM) studies in ultrafine particles revealed instability in the particles structure [4] which was defined as quasimelting phenomenon. A comprehensive review on the structure and instability of small clusters has been presented by Marks [5]. Several models were proposed to explain the dynamical evolution in the cluster structure. These models can be divided into two categories. The first one relates the restructuring of the particle to a short but complete melting period, followed by recrystallization of a new structure [6–8]. The second approach suggests that due to the small energy barrier between the various particle configurations, there can be random fluctuations between the different structures without melting [9].

Previous study of lead particles reveals a definite range of particle size in which the structure is unstable, while in the solid state [10]. In this Letter, we report the first quantitative analysis of the fluctuations which occur in lead particles. This analysis reveals a definite angular correlation between successive structures.

The samples are lead particles embedded in an amorphous SiO matrix. The samples were prepared by successive evaporation of 10 nm of SiO, 5 nm of Pb, 10 nm of SiO on a copper grid covered by a thin film of carbon. The embedded case ensures better thermal coupling, which defines good thermodynamical variables and prevents oxidation, migration, and evaporation [11]. During deposition, the substrate was held at a temperature of 200 °C, causing the particles to coalesce in the liquid state, and resulting in an equilibrium spherical shape. The specimens were observed at room temperature in a HREM (JEOL 4000-EX) at 400 kV. The structure evolution of the particles was video recorded via a low level video CCD camera with a time resolution of 25 frames/sec. The records were examined frame by frame and processed (when necessary) using SEMPER image processing software [12]. The analysis was carried mainly in the Fourier space in order to determine the angular relationship between successive structures.

Our measurements on lead particles were focused on particles with a diameter range of 4 to 10 nm. Most of the particles, configurations ($>$90%) are characterized by the existence of twins. These twin structures are mainly single twin, micro twin, and multiple (3 to 5) twins. The particles fluctuate with time between the above configurations. The sequence of events is as follows: (i) crystalline structure visible (as $\langle 111 \rangle$ or $\langle 200 \rangle$ planes) in at least part of the particle, during a lifetime t: (ii) a fast transition of the particle configuration with transition time τ [faster than one video frame (0.04 sec)], either to new visible crystalline configuration with angular change θ, or to invisible crystalline structure. The probability for invisible crystalline structure is around 0.5. (iii) After a given waiting time, the crystalline structure reappears with new orientation and the sequence repeats itself. At room temperature the lifetime t of the stable configuration increases with the particle size, from about one frame time for particles with a diameter of 4 nm, up to long term stability for particles with a diameter larger than 10 nm. Accordingly, a careful analysis was performed on particles with a diameter D of 6–7 nm. In the following the particles are considered always crystalline, even when no lattice planes are visible; this is based on dark field
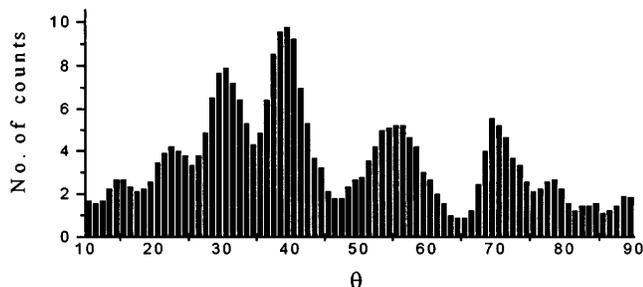
FIG. 1. Distribution of angle changes of the $\langle 111 \rangle$ planes (after triangle smoothing).

observations that do not reveal the typical liquid contrast [10] for similar periods [13].

More than 300 transitions between succeeding configurations were analyzed in order to find the distribution of the angular change θ between the $\langle 111 \rangle$ atomic planes of succeeding configurations (Fig. 1). The θ distribution reveals the existence of strong preferential angular changes. The angular correlation between succeeding configurations points out to the transformation mechanism. The three well defined peaks, at 31°, 39°, and 70° are clearly attributed to twin related changes in the same plane as can be seen in Fig. 2. The 70° angle is equal to the angle between two $\langle 111 \rangle$ planes in a FCC lattice. The 39° angle is related to the angle between two $\langle 111 \rangle$ planes after one twinning. The 31° angle is equal to the angle between two $\langle 111 \rangle$ planes after two successive twinnings in the same plane. An additional clear peak is located at 56°. This peak is related to a twinning plane nearly perpendicular to the incident electron beam. For a full stereoscopic analysis see Renou and Penisson [14]. Further angles are expected for three dimensions, twin related transitions.

In Figs. 3 and 4 one can see two sets of successive frames, showing typical transitions, occurring only for a fraction of the particle. These cases clearly show that the transition mechanism involves the appearance, movement, and vanishing of twin boundaries.

Investigating the special transitions in which a clear twin appears or vanishes, while the rest of the particle
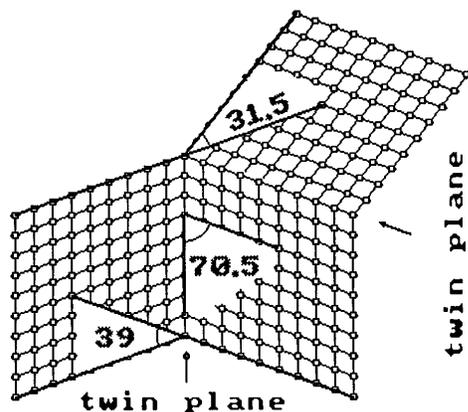

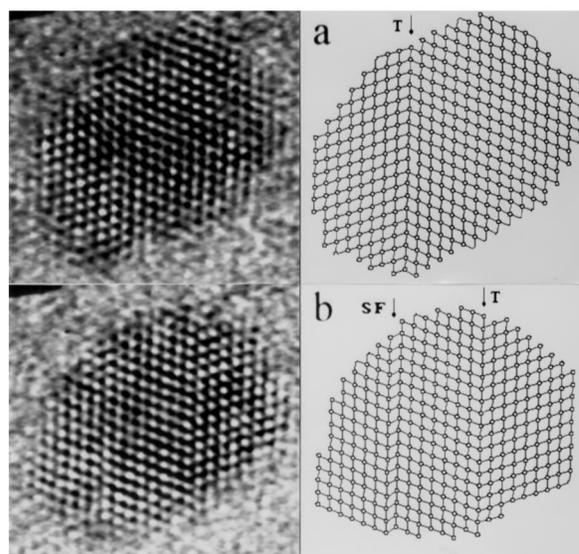FIG. 2. Typical angles in a twinned structure.

FIG. 3. Configuration transition, involving vanishing of a twin (T) on the left side, leaving a stalking fault (SF), and appearance of twin on the right side. (The first configuration was stable for 1.5 sec, the second configuration was stable for 6.5 sec, the transition time is less than 0.04 sec.)

remains in the same configuration, reveals additional small rotation of the stable part. A histogram of this small angle rotation between successive frames is shown in Fig. 5. The average angle change is 2.1°, while during the stable periods, the particles exhibit only very small rotations between successive frames (average of 0.25°). This phenomenon of small rotation during transformation can explain the rather broad shape of the peaks in Fig. 1.
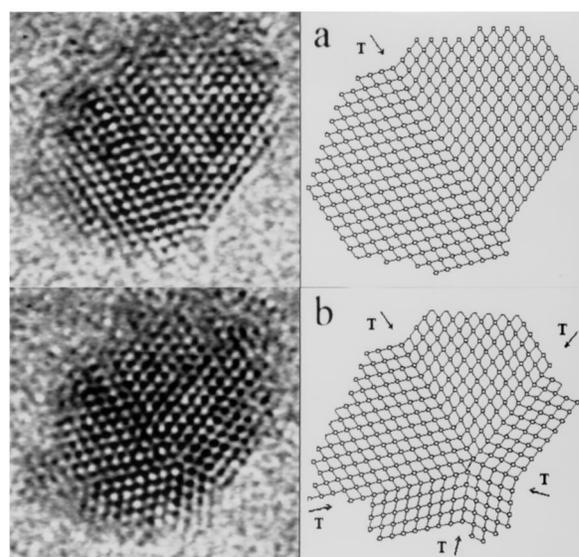

FIG. 4. Configuration transition, between single twin structure and a five-fold structure, by introducing four additional twins (marked with arrows). (The first configuration was stable for 7 sec; the second configuration was stable for 0.5 sec; the transition time is less than 0.04 sec.)
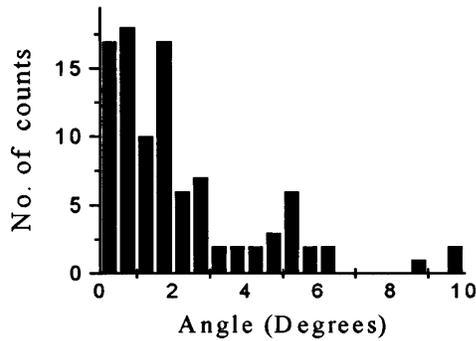
FIG. 5.   Distribution of small angle rotation during configuration transition.

The exact mechanism that occurs during the fast transition is not observable experimentally. In most cases the initial and final configurations are the only detected images. However, our results show clearly that a complete melting of the particle followed by recrystallization is excluded, due to the fact that any memory from the previous orientation would then be lost. Moreover, it was found that the angular correlation between succeeding configurations corresponds to angles between twinned domains.

Therefore the present data is compatible with only a few mechanisms which are now briefly discussed.

In the framework of the "melting" models only partial melting is possible and could occur via one of the two following mechanisms: (i) Partial melt of the particle occurs, followed by recrystallization epitaxialy on the still crystalline part. During crystal regrowth the twin position is equally probable as the starting position, especially if the liquid solid front is a $\langle 111 \rangle$ plane. The number of atoms involved in this transformation is a given volume fraction of the particle and should vary as $\sim D^3$. (ii) A thin wave of "liquid" material along the $\langle 111 \rangle$ planes propagates through the particle, and recrystallization occurs on the trailing part of this wave. The melted part is thin enough, few $\langle 111 \rangle$ atomic planes, to induce a recrystallization on the $\langle 111 \rangle$ planes, thus producing either a twinned or the original orientation. That mechanism involves a number of atoms which is proportional to a cross section of the particle and should vary as $\sim D^2$.

In the framework of the solid-solid transition via random fluctuations, transformation could occur through the classical propagation of successive $\frac{1}{6} \langle 122 \rangle$ dislocations. This process involves the propagation of defects lines containing a number of atoms varying as $\sim D$.

At this point none of these different possibilities could be eliminated based on the experimental facts. However, there are significant differences in the dependence on the particles diameter of the total number of atoms involved to initiate the transformation. Therefore it is likely that some of this mechanisms could be selected. Work is in progress in that direction.

In conclusion, the results here bring completely new insight in a long standing problem concerning the instability phenomenon of small metallic particles, by the following:

(1) There exist two time scales in the system, a long one during which the structure is crystalline and stable, and a short one during which the structure undergoes a fast transition.

(2) After transition a memory effect of the original crystalline orientation is observed. This memory effect is not compatible with complete melting of the cluster.

Further quantitative measurements of the dependence of the fluctuations frequency on the temperature and the particles size are necessary in order to establish the transformation mechanism.

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