

Observation of quasimelting at the atomic level in Au nanoclusters

W. Krakow,* M. José-Yacamán, and J. L. Aragón

*Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, Delegación Alvaro Obregón,
01000 México, Distrito Federal México*

(Received 21 January 1994)

Experimental evidence is presented for the atomic origin of quasimelting of small Au clusters. Real-time high-resolution transmission electron microscopy, an *in situ* evaporation facility, and the choice of a controlled substrate clearly shows atomic motion adjacent to and on nanoclusters in the < 20 Å size range. We have been able to observe partial melting, atom sharing, absorption of small clusters, and shape adjustment. These phenomena are consistent with low-energy surface sputtering, energy minimization, and diffusive surface migration. Related to the transformation from icosahedral multiply twinned to single crystal observed under low voltage conditions, we propose a geometric model of the transformation which produces a continuum of low-energetic intermediate structures.

During the last several years the structure and stability of small metal clusters has been studied extensively by high-resolution transmission electron microscopy. The earliest studies showed evidence of multiply twinned large particles > 100 Å diameter and the visualization of atomic lattice planes.¹⁻⁴ Many of these studies required as part of the preparation procedure that the particles be encapsulated in an evaporated carbon film thus precluding observing atomic surface structures. In one study,⁵ evidence of the presence of surface migration was found where large amounts of metal were evaporated to form semicontinuous polycrystalline thin films. Although some atomic motion was observed by profile imaging, these films were prepared *ex situ* to the microscope and were in all likelihood contaminated, which precluded observing single atoms or their motion. One notable exception was the work of Marks and Smith,⁶ who were able to observe 2×1 reconstruction on (100) surfaces of gold, which was cleaned using the electron beam to etch away the hydrocarbons that contaminate the surface.

The structural instability of ultrafine metal particles of Au, which were not encapsulated, was first reported for clusters vapor deposited onto large silicon spheres.⁷ Although this work was performed in a lower voltage electron microscope operating at 120 keV (2.3 Å point resolution), dynamic changes in cluster shape were observed under intense electron-beam currents (about 1.3×10^5 e / Å² s. = 200 A/cm² on the specimen). Here the metal particles, which were attached to the periphery of the spherical silicon particles, were observed as projection images along the electron beam. The term "quasimolten state" was used to describe the unstable condition of particles < 50 Å in size.⁸ However, the physical role of atoms located on or near the small Au clusters and their relation to the total system was precluded by substrate interference. Hence, the origin of the structural instability remained in doubt. In a study by Mitome, Tanishiro, and Takayanagi⁹ the structures of small Au clusters of several tens of atoms as well as small particles 20–30 Å in size were observed in an ultrahigh-vacuum electron micro-

scope equipped with a heating stage and *in situ* evaporator. They stated that particle orientational fluctuations are caused by the heating due to electron irradiation. For most of their experiments, the specimen was maintained near room temperature with a temperature rise of perhaps 20°C and did not exceed 50°C at the beam currents employed. They further concluded that the fluctuating motion of small clusters at room temperature is intrinsic in nature owing to the lower melting point of surface atoms. However, owing to the interfering graphite support substrate, which often obscures single-atom imaging, it cannot be concluded that atoms migrating on the surface influence the configurational changes and which may dominate the transformational process in small clusters. It has been pointed out by Williams¹⁰ that inelastic losses might have an important effect. The ionization of the *M* shell appears to be important. However, the work of Ajayan and Marks⁸ showed that quasimelting can occur even at extremely low beam intensities suggesting that this might be a natural state of small particles when a situation with a weak interaction with the substrate is produced.

It is the purpose of this paper through the experimental observation of high-resolution microscopy video and still photographs, to show that the origin of quasimelting of small Au clusters and coalescence is related to the interaction of atoms coming to and going from small clusters. This interaction can take a cluster from an amorphous to a crystalline state or vice versa. This phenomena is also responsible for the orientational changes observed in somewhat larger clusters, which have undergone partial amorphization, cluster coalescence, and shape adjustment.

Our experimental procedures involved the use of an *in situ* evaporator, which is compatible with an ultrahigh-vacuum transmission electron microscope operating in the low 10^{-10} -torr vacuum range. This evaporator has been adapted to fit a JEOL 4000 EX top-entry electron microscope with a point resolution of ≈ 1.7 Å operating at an accelerating voltage of 400 keV. The evaporator

was positioned perpendicular to the objective lens optical axis and tilting the specimen by a 25° angle allowed the evaporant to impinge on the specimen. Several evaporation experiments were performed at moderate vacuum levels in the 10^{-7} -torr range, which is the operating column vacuum of this instrument. The evaporator was equipped with two resistive heated filament evaporation sources and quartz-crystal thickness monitor. For Au, typical evaporation rates were $\approx 0.003 \text{ \AA/s}$, and total average coverages for each source evaporation were between 20 and 30 \AA . The deposited upon specimens were amorphous carbon films prepared by indirect carbon arc evaporation where only carbon, which is reflected from a baffle, is collected for the thin film. The estimated thickness of these films is between 50 and 100 \AA based upon their color against a white background (grayness). These films are relatively structureless and are suitable for single Au atom imaging. Microscope beam currents were between 10 and 20 A/cm^2 with the carbon support film becoming thinner over a period of minutes to hours. Usually during the thinning process, the film would become structureless and appear to have become graphitic with the graphite c axis perpendicular to the thin direction of the film. The whole deposition process from the inception of cluster formation to extended cluster sizes $> 50 \text{ \AA}$ in size were recorded continuously on a S-VHS video tape recorded at a rate of $\frac{1}{30} \text{ s}$ per frame from an intensified 525-line TV system coupled to the microscope. Electron optical magnifications were usually $800\,000\times$ for both TV rate recording and for still photography on plates to produce a higher image quality, which required 2–4-s exposure. Because no breaking of the vacuum environment was required during cluster formation, we were able to observe very small clusters which were free of contamination. Also, the propensity for coalescence when samples are exposed to the external environment was avoided, and thus the smallest clusters consisting of as little as a few atoms were observed in a microscope,

which had superior resolution to microscopes used in prior investigations.

Figure 1 shows a sequence of images of two nanoclusters in the 10–20- \AA size range which are undergoing continual structural transformations. The span of time for these 10 images covers approximately 8 s. Here the video time is listed by seconds as the first number and the frame number as the second, which ranges between 1 and 30. It is apparent from this sequence that the clusters are changing continuously between amorphous and crystalline states. Here atoms can be observed to move on and near clusters and can be tracked through several images, with some remaining stationary while others move or disappear entirely.

It is sometimes apparent that adatoms incorporate into a cluster [see arrow in 1(g)]. These atoms then rearrange and can produce clusters which have local energy minima that do not produce regular shapes or are noncrystalline in appearance. This type of effect has been observed for embedded atom calculations of the equilibrium shapes of platinum clusters between 5 and 60 atoms.¹¹ However, it should be noted that the cluster that we are observing is considerably larger in size than the ones calculated in Ref. 11. Therefore, their conclusions do not necessarily apply. The important point to note is that there are many structures possible with very similar energies in small particles. For example, the upper particle in 1(e) appears to be totally crystalline, while 2 s later in 1(g), the same particle is partially melted as evidenced by the small remaining crystalline region. The intervening frame 1(f) shows atomic features moving on the particle such that only a few atoms may have been responsible for the transformation. Further evidence of the importance of these reactions can be seen by the high-contrast atom images in 1(i) and 1(j) (see arrows). Here very strong dimerization or trimerization must have occurred to produce the much higher than single atom intensity such that the atoms are aligned along the direction of the electron beam. The



FIG. 1. Sequence of TV rate images of two Au clusters undergoing continual structural transformation from stable shapes to a quasimolten state. Single atom images appear as black dots. Time span of these images covers $\approx 8 \text{ s}$.

large size of this image feature indicates that it is behaving like free atoms, which are not in a crystalline lattice, which would restrict its image size to the lattice constant for a given projection.

Two examples of some crystalline shapes observed during *in situ* observation are shown in Figs. 2 and 3. Figure 2 is an example taken from a still picture of several clusters, one of which is a face-centered-cubic cluster viewed along a $\langle 100 \rangle$ direction. Here two crossed sets of $\{200\}$ lattice planes are visible across about $\frac{2}{3}$ of the particle, while the remainder of the particle appears structureless and in a quasimelted state. Here single atoms are evident in this noncrystalline region as well as in regions between other clusters and appear as diffuse black dots since the images were taken near a condition of Scherzer defocus of the microscope objective lens. It should be noted that the two small clusters in the field appear to be disordered. This is often the case for clusters $< 10 \text{ \AA}$ in size. We have found in other experiments on Au thin films that the melting phenomena occurs for about the outermost three layers near a film edge. Therefore, for these small clusters, the whole of the particle is within three layers from the surface as it is in a continuous quasimelted state. Figure 3 shows an example of a multiply twinned Au particle, which has an apparent fivefold symmetry for a portion of a sequence of exposures covering $\approx 5 \text{ s}$. Here the outermost atoms are moving on the cluster and it slowly transforms its shape into its bulk as their collective influence exerts itself. Some of the twinned regions disappear in the later frames 3(d)–3(f). It should be noted that the small particle to the left is in the critical size range where it is almost continuously quasimelted. Here a small degree of residual crystallinity is observed in frames 3(a) and 3(c). The observation of this type of surface melting behavior in thin films has been reported in medium-energy ion-scattering studies.¹²

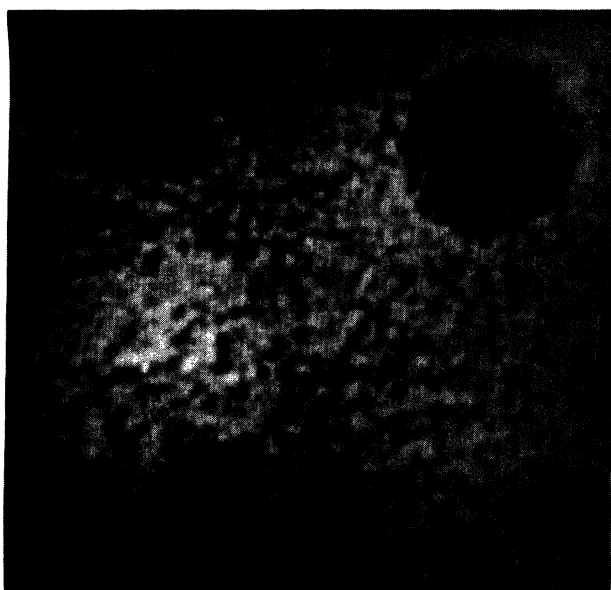


FIG. 2. Example of a face-centered-cubic particle, which is partially quasimolten. The remaining particles are disordered since they are in a quasimolten state.

Under the low-voltage conditions of the experiment of Iijima and Ichihashi,⁷ where the electron beam plays a less important role, it is observed that the particle fluctuates between multiply twinned and crystalline with no evidence of an amorphous state. This can be explained without the interaction with atoms in the surface if a low-energy barrier exists between initial, intermediate, and final states. There are numerous simulations shown that there is a small difference in energy between a multiply twinned icosahedron and a cuboctahedron. In addition, we shall describe a continuous path connecting both structures with a very low energy cost. A single icosahedron can be transformed into a cuboctahedron by means of the transformation defined by the following variable set of vectors:¹³ $v_1(\theta) = 1/\sqrt{2}(\cos\theta, -\sin\theta, 0)$, $v_2(\theta) = 1/\sqrt{2}(\cos\theta, -\sin\theta, 0)$, $v_3(\theta) = 1/\sqrt{2}(0, \cos\theta, -\sin\theta)$, $v_4(\theta) = 1/\sqrt{2}(0, \cos\theta, \sin\theta)$, $v_5(\theta) = 1/\sqrt{2}(-\sin\theta, 0, \cos\theta)$, $v_6(\theta) = 1/\sqrt{2}(\sin\theta, 0, \cos\theta)$. At $\theta = 31.7174^\circ$, these vectors point to six vertices of an icosahedron oriented along the twofold axis, at $\theta = 45^\circ$ the vectors point to six vertices of a cuboctahedron, and there exists a continuum of intermediate structures (all having cubic symmetry) when $31.7174^\circ < \theta \leq 45^\circ$. Now, all the vertices of an icosahedral multiply twinned particle of N atoms¹⁴ can be expressed as linear integer combinations of the six vectors $\{v_1, v_2, \dots, v_6\}$ pointing to the vertices of a regular icosahedron: $x_k' = \sum_{i=1}^6 m_i^{(k)} v_i$, for integers $m_i^{(k)}$ and $k = 1, 2, \dots, N$. Consequently, one finds the set $(m_1^{(k)}, m_2^{(k)}, \dots, m_6^{(k)})$ for each vertex x_k of the icosahedral particle, this can be transformed onto a cuboctahedron through a continuation of intermediate structures by sampling θ between 31.7174° and 45° in the expression $x_k = m_i^{(k)} v_i(\theta)$, for $k = 1, 2, \dots, N$. This evolution was carried out for several magic-number icosahedral particles and at different steps of the evolution binding energies were calculated using a 6-12 Lennard-Jones potential^{15,16} as is detailed elsewhere. Results for $N = 13, 55, 147, 309$, and 561 are shown in Fig. 4. Note that in the proposed path, a low-energetic barrier exists between those structures, and intermediate forms are possible. The icosahedral and cuboctahedral structures are only extreme points of a continuum of low-energetic intermediate structures. Indeed there is now supporting evidence in many studies using high-resolution electron microscopy that such intermediate structures exists.

The phenomena of classical liquid-like coalescence during island growth has been observed for the last several years,^{15,17,18} although it is not until recently that quasimelting has been associated with cluster coalescence.¹⁹ These preliminary results at elevated temperatures did not capture the merger of clusters at the atomic level but did report on the rotational and shape transforms which we have also found accompany coalescence. In order to show the atomic motion, Fig. 5 is a sequence of single-frame TV images covering a 20-s time interval. Here the time intervals are not equal owing to the observation of different events which sometimes occur in one frame time. The initial picture 5(a) shows a 20- \AA twinned cluster in proximity to a considerably larger cluster at the left side of the image field. The next frame 5(b) shows an



FIG. 3. Example of a multiply twinned particle transforming over a 5-s time interval along with a smaller quasimolten particle.

atom between the clusters and shortly thereafter the small cluster is changing its shape while moving slightly and coming to within a few Å of the larger cluster. In frame 5(e), more intense atomic motion is occurring between the two clusters and merging has started. By frame 5(i), only four TV frames later, the twin structure has transformed into a single orientation which has now partially merged with the larger cluster and assumed its orientation. Within a period of a few seconds the edges of the smaller merged particle, which were somewhat ill defined, become sharply faceted to minimize surface energy as shown in 5(k). The subsequent images show a slow but steady rounding of the facets, which appears to be more like the classical ideas of diffusion-controlled coalescence. However, it is the interval prior to this which can be identified with single atom hopping and rapid structural arrangements. It is during this stage that particles have been observed to undergo a rapid fluctuation in crystal orientation and diffraction contrast effects were noticeable. In the case presented here, the smaller particle is absorbed into the larger as expected; however, when the particles are more nearly equal in size, a grain boundary results between the two grains of the coalesced cluster. The boundary will assume a local energy minimum coincidence site lattice structure which is dependent upon the relative orientation of the particle and on their size; since above a size of around 100 Å, the cluster orientations remain stationary and coincidence does not necessarily occur.

We have reported upon the atomic nature of quasimelting being viewed *in situ* in an ultrahigh resolu-

tion electron microscope. While thermal effects appear to have a minimal effect, the electron beam plays an important role in energetically promoting the movement of atoms on or near clusters. It is also the case that the electron beam acts as a means of eliminating contamination buildup. In our case, the *in situ* evaporation coupled with this cleaning action serves to sustain the interactions of atoms and clusters. This is generally not true for specimens prepared *ex situ* where they are usually

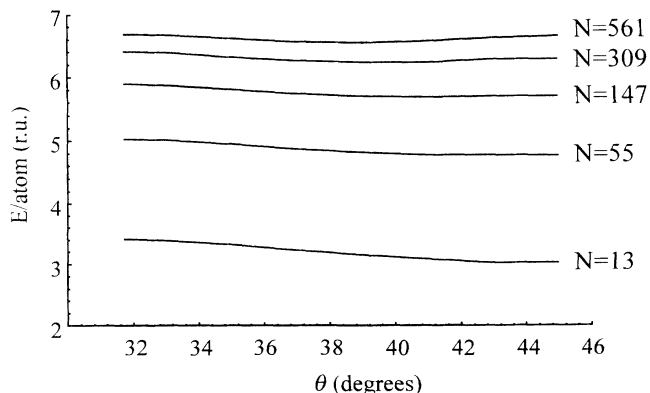


FIG. 4. Energy per atom (in reduced units) at different steps of the transformation from icosahedral multiply twinned particle to cuboctahedral for different size particles using a 6-12 Lennard-Jones potential. Icosahedral particle is at $\theta = 31.7174^\circ$, and cuboctahedral particle at $\theta = 45^\circ$.

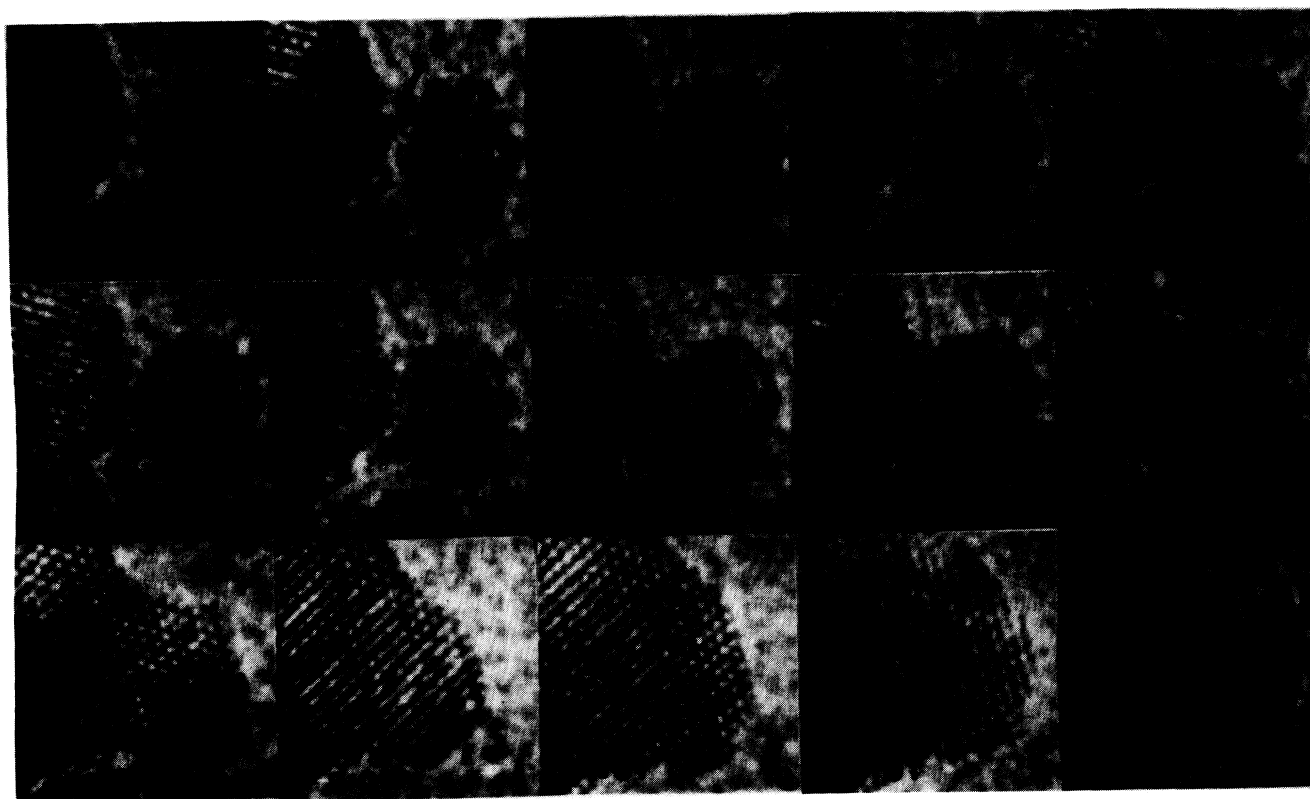


FIG. 5. Sequence of images showing coalescence of two clusters at the atomic resolution level. Small black dots are atoms between the clusters. The total time interval of the exposures covers ≈ 20 s.

covered with many layers of contamination before experiments are possible. The additional supply of atoms impinging on the surface in our experiments also provides a sustained level of atoms available for atomic level interactions, which would not be available otherwise.

In summary, we found a number of results about small gold particles. First, it should be pointed out that the transition between crystalline and the amorphous state shown in Fig. 1 has not been reported before. In prior work, Flueli²⁰ reported an observation of a particle in a steady state with a crystalline portion and an amorphous portion. However, no oscillations were reported. This can be interpreted in terms of the periodic "melting" predicted by Williams.¹⁰ This phenomenon is related to an M shell ionization losses. The vacancies produced will undergo Auger decay. According to Williams, for a standard flux of electrons at 400 keV about 100–200 times per second, a 2-keV Auger electron will transverse the cluster. Since this energy couples into atomic motion more rapidly than heat can be conducted out of the particle (into the support), this will produce a rapid increase on the temperature. This will produce a transient state in which melting is possible followed by a very rapid recrystallization. In this model it is possible to explain a partial amorphization of the cluster probably stabilized somehow by the substrate.

The most acute objection to this model comes from the fact that during pulsations, atomic resolution in the im-

ages is maintained. It is well known that this occurs only in a very limited set of conditions. Particularly critical is the cluster orientation with respect to the electron beam; it is very difficult to visualize how a particle can have a transient melting state and still keep its overall orientation with $<0.1^\circ$ with respect to the electron beam. Even more troublesome is the fact that particles can move along the substrate during quasimelting with atomic resolution observed all the time. It is clear that more theoretical insight is necessary in order to fully understand the quasimelting phenomenon.

A second interesting result is the fact that we have confirmed the earlier proposal of Miki-Yoshida, Tehuacanero, and Yacamán,¹⁹ who used a low-resolution microscope and a heating stage and, although they were not able to attain atomic resolution, they predicted quasimelting precedes coalescence. They observed that in many cases particles come in contact and separate several times without coalescence. This contradicts the classical mechanism of Pashley¹⁷ consisting of a diffusion driven coalescence in which a neck is formed once the particles come into contact and atoms diffuse from one crystal to another. The idea that the neck then grows by subsequent atom diffusion until a new single particle is formed does not seem to hold in our case. As shown by our results, the contact between particles is not enough to start the coalescence. In many cases, the contact is broken and particles separate again. In addition, the coales-

cence seems to happen so fast that a neck cannot be observed in many cases (within the experimental video recording capabilities). The coalescence mechanism seems to be more complicated than anticipated.

This work was partially supported by a grant to W. K. from the Consejo Nacional de Ciencia y Tecnología (CONACYT). The authors are indebted to Samuel Tehuacanero for technical help.

*Present address: Mountainside Trail, Peekskill, NY 10566.

¹T. Komoda, Jpn. J. Appl. Phys. **7**, 27 (1968).

²D. J. Smith and L. D. Marks, Philos. Mag. **44**, 735 (1981).

³L. D. Marks and D. J. Smith, J. Cryst. Growth **54**, 425 (1981).

⁴D. J. Smith and L. D. Marks, J. Cryst. Growth **54**, 433 (1981).

⁵D. J. Smith and L. D. Marks, Ultramicrosc. **16**, 101 (1985).

⁶L. Marks and D. Smith, Nature **303**, 316 (1983).

⁷S. Iijima and T. Ichihashi, Phys. Rev. Lett. **56**, 616 (1986).

⁸S. Ajayan and L. Marks, Phys. Rev. Lett. **60**, 585 (1988).

⁹M. Mitome, Y. Tanishiro, and K. Takayanagi, Z Phys. D **12**, 45 (1989).

¹⁰H. Williams, Appl. Phys. Lett. **50**, 1760 (1987).

¹¹A. Sachdev, R. I. Masel, and J. B. Adams, J Catal. **136**, 320 (1992).

¹²J. W. M. Frenken, *Endeavor News Series* (Pergamon, London, 1991), Vol. 14, pp. 2–7.

¹³M. Torres, G. Pastor, I. Jiménez, and J. Fayos, Philos. Mag. Lett. **59**, 181 (1989); Phys. Status Solidi B **154**, 439 (1989).

¹⁴A. L. Mackay, Acta Crystallogr. **15**, 916 (1962).

¹⁵H. Terrones, BSc thesis, UIA México, 1987.

¹⁶D. Romeu, Int. J. Mod. Phys. B **2**, 77 (1988); **2**, 265 (1988).

¹⁷D. W. Pashley, Adv. Phys. **14**, 327 (1965).

¹⁸M. Flueli, Surf. Sci. **202**, 343 (1988).

¹⁹M. Miki-Yoshida, S. Tehuacanero, and M. José-Yacamán, Surf. Sci. Lett. **274**, L569 (1992).

²⁰M. Flueli, Ph.D. thesis, EPL Lausanne, Switzerland, thesis **796**, 1989.

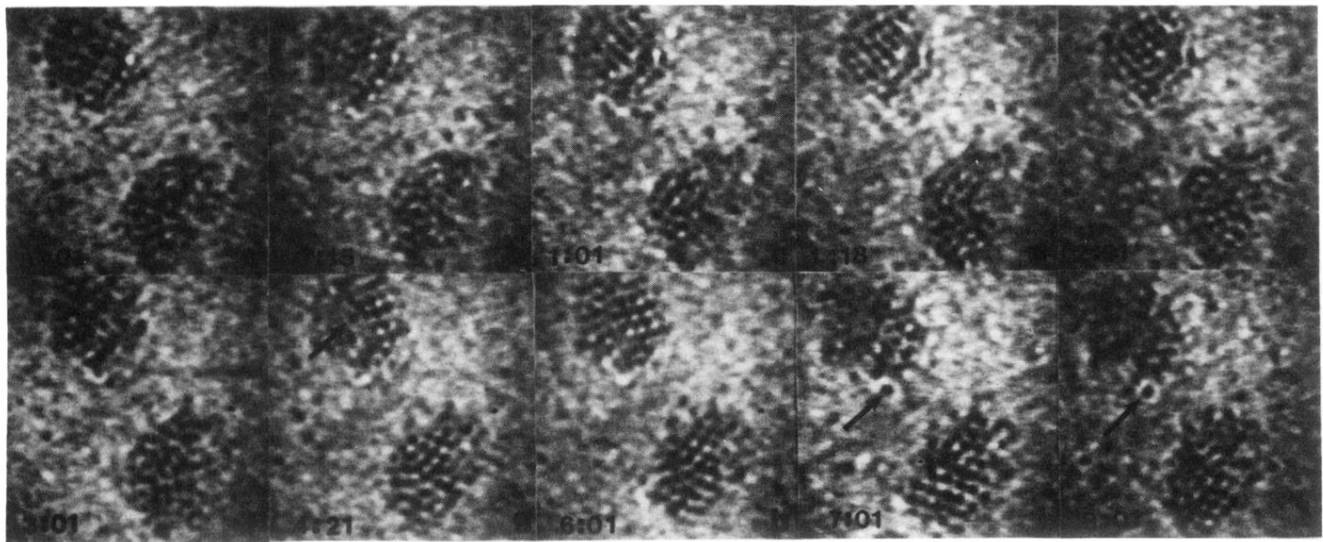


FIG. 1. Sequence of TV rate images of two Au clusters undergoing continual structural transformation from stable shapes to a quasimolten state. Single atom images appear as black dots. Time span of these images covers ≈ 8 s.

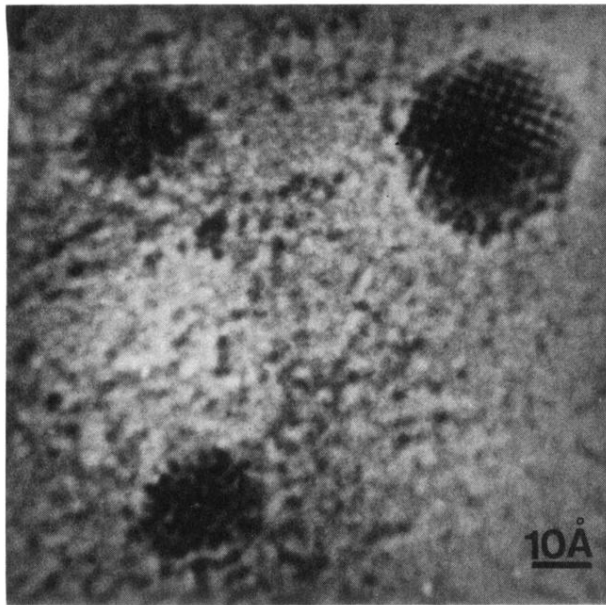


FIG. 2. Example of a face-centered-cubic particle, which is partially quasimolten. The remaining particles are disordered since they are in a quasimolten state.

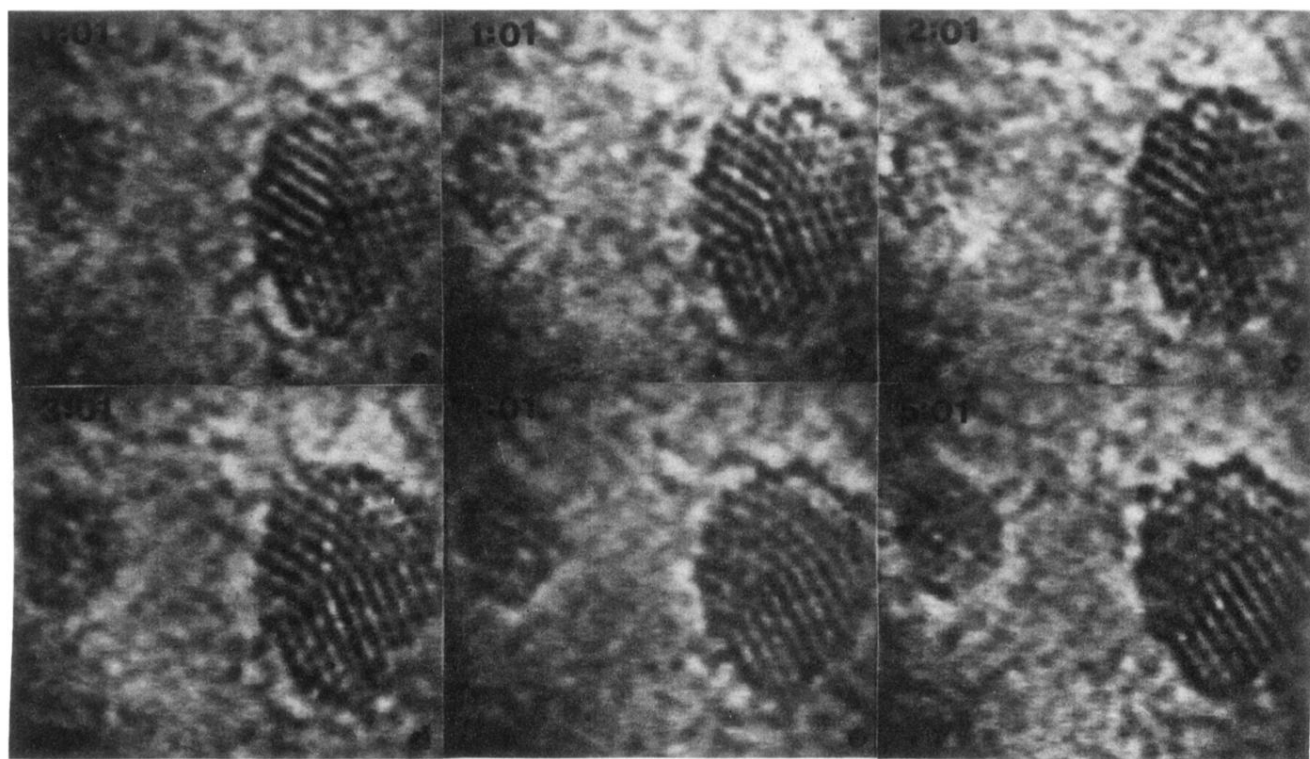


FIG. 3. Example of a multiply twinned particle transforming over a 5-s time interval along with a smaller quasimolten particle.

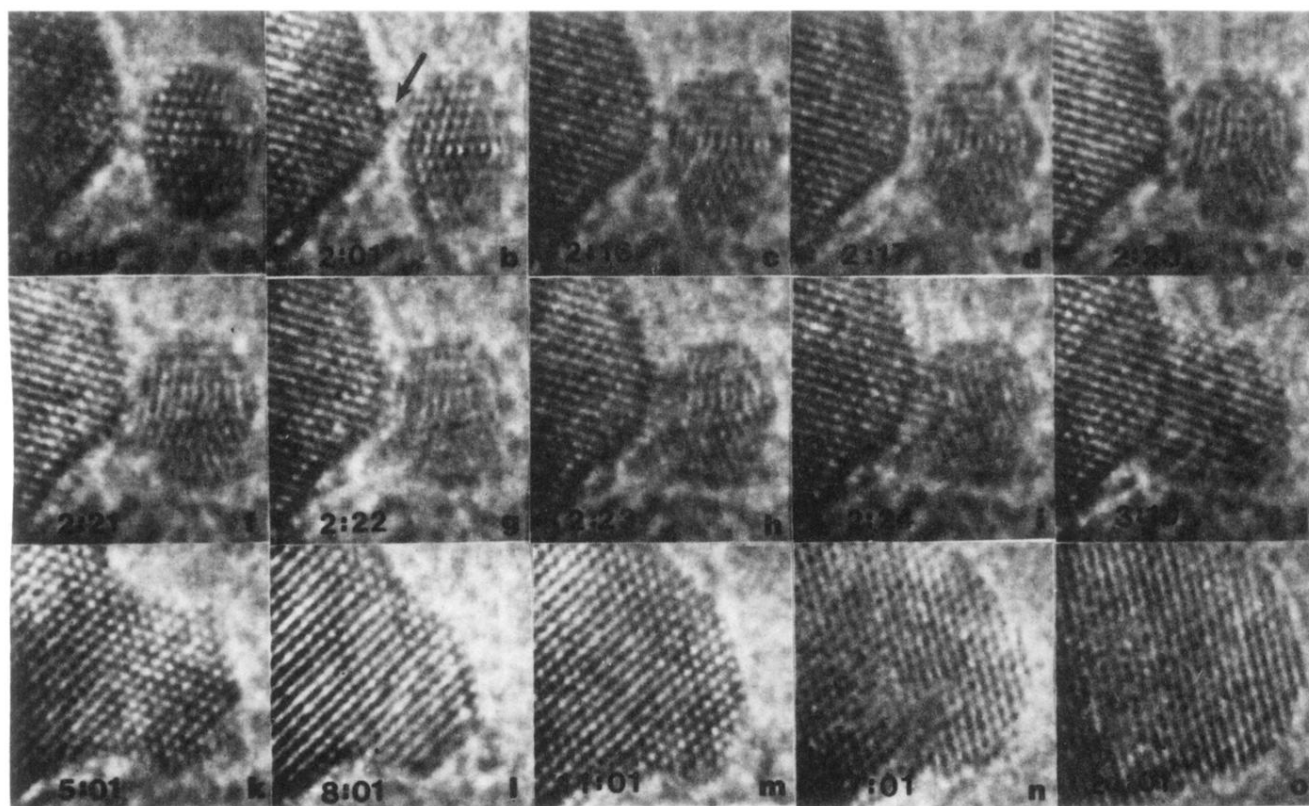


FIG. 5. Sequence of images showing coalescence of two clusters at the atomic resolution level. Small black dots are atoms between the clusters. The total time interval of the exposures covers ≈ 20 s.