REFERENCES AND NOTES

1. D. E. Brownlee, in *The Sea*, C. Emiliani, Ed. (Wiley, New York, 1981), vol. 7, pp. 733–762.
2. G. M. Raisbeck, F. Yiou, J. Klein, R. Middleton, D. E. Brownlee, *Lunar Planet. Sci.* **14**, 622 (1983); K. Nishiizumi, *Earth Planet. Sci. Lett.* **63**, 233 (1983).
3. P. W. Hodge, *Interplanetary Dust* (Gordon & Breech, New York, 1981).
4. A. Bauer, *Medd. Groenl.* **173** (no. 3), 1 (1968).
5. This expedition, initiated by C. Hammer and M. Maurette, included N. Reeh and H. H. Thomsen, Geological Survey of Greenland, as well as K. Rasmussen also from the Geophysics Institute of the University of Copenhagen.
6. P. Gudhamdsen, *Tech. Univ. Den. Lab. Electron Theory Lyngby Rep. 162* (1976).
7. N. S. Paterson, *The Physics of Glaciers* (Pergamon, New York, 1981).
8. N. Reeh, *Rep. Inst. Meteorol. Oceanogr. Rejks Univ. Utrecht*, in press.
9. C. Hammer and N. Reeh, unpublished data.
10. The modeling of the ice flow further indicated that it should be possible to investigate the past variations of this flux of cosmic debris over a time scale of about 10,000 years by sampling the sediments from the margin of the ice field (where the surface ice was formed about 10,000 years ago), up to an area about 80 km away from the margin, where the ablation just barely removes the "last-year" snow layer.
11. During our 10-day stay on the ice we observed a 15 to 20 cm ice retreat using sticks driven into the ice. Assuming a constant melt rate over the mid-June to mid-August melt season, this indicates an annual melt rate of 1 m per year. This rate is consistent with other stick method measurements at similar altitudes and latitudes in Greenland (A. Weidick, *Proc. 8th Int. Conf. Port Ocean Eng. Arct. Cond.*, in press.
12. We only discuss these blue lake samples. However, we also collected about 40 kg of sediments around the lake and our camp site some 50 km from Søndre Strømfjord, in particular on a 10-cm-thick pile of surface sediments that contained about 1 ton of sediment which looked similar to that investigated by D. De Kervain and P. Mercanton in 1912 [*Medd. Groenl.* **59**, 56 (1925)]. We were also provided with samples from the latitude of Jakobshavn by J. M. Gautier and J. M. Loubiere and the U.S. team of R. Scott.
13. These studies were conducted at Montpellier (G. Callot, Laboratoire de Sciences des Sols, Institut National de Recherches Agronomiques, and A. Dubois, Laboratoire de Paléontologie, Université de Montpellier), and at the University of Perpignan (F. Gadel and A. Monaco, Laboratoire de Sédimentologie Marine).
14. This work was done by C. Lafoy, Laboratoire de Séparation de Phases, Bureau de Recherches Géologiques et Minières, Orleans, France.
15. We acknowledge the work of C. Jelano, M. Wheelock, S. Taylor, B. Bates, and B. Doyle on analysis of the samples. We are also grateful to C. Lafoy for work on disaggregation of the cocoons and acknowledge the help of M. deAngelis, D. Donnov, and M. Pourchet (Laboratoire de Glaciologie, Grenoble, France) in preparation of the collection techniques used on the expeditions. The cost of the Blue Lake Expedition was mostly covered by a grant from Institut National d'Astronomie et de Geophysique, France; we also received financial help from Société Francaise de Production Audiovisuelles. The analytical work was supported by a grant from Programme Interdisciplinaire de Recherches sur l'Environment du Centre National de la Recherche Scientifique and NASA grant NSG9052.

14 March 1986; accepted 11 June 1986

Dynamic Atomic-Level Rearrangements in Small Gold Particles

David J. Smith, Amanda K. Petford-Long, L. R. Wallenberg, J.-O. Bovin

Small metal particles (<5 nanometers), which are widely used in catalysis, have physical and chemical properties that are markedly different from those of the bulk metal. The differences are related to crystal structure, and it is therefore significant that structural rearrangements in small particles have been observed in real time by using high-resolution electron microscopy. A detailed investigation at the atomic level has been made of the factors affecting the dynamic activity of small gold crystals that are supported on thin films of amorphous carbon, silicon, and germanium. The rate of activity depends mainly on the current density of the incident electron beam and the degree of contact of the particle with the substrate, but this rate decreases rapidly as the particle size is increased. The activity of the particles is very similar on either carbon or silicon, but it is generally less marked on germanium because of increased contact between the particle and the substrate. The electron beam effectively heats the particles, and it appears that their dynamic behavior depends on their thermal contact with the substrate.

DEVELOPMENTS IN INSTRUMENTATION for the high-resolution electron microscope (HREM) have facilitated the observation and recording of dynamic events at the atomic level directly within the microscope. Processes recorded include the motion of defects in gold foils (*1*), the annealing of defects in cadmium telluride (*2*), and atomic rearrangements on the surfaces of small gold particles and extended gold foils (*3–6*). Rapid structural rearrangements also occur in gold crystals smaller than about 5 nm (*4–7*), but to our knowledge, no detailed study of the various factors affecting these activities has been reported. In an attempt to understand these processes, and also because of the possible links and similarities between these electron beam–induced rearrangements and those that occur during thermal annealing treatments of small particles (*8*), we have carried out further systematic studies on small gold crystals.

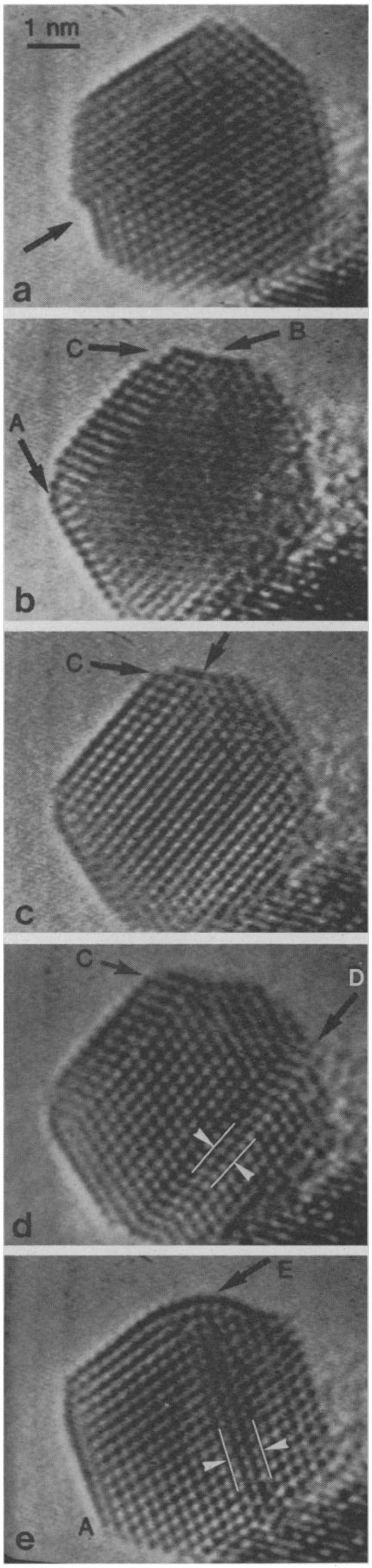
The small gold crystals were originally prepared as cluster complexes containing 55 gold atoms (*4*). Under electron irradiation, the attached ligands were evaporated, leaving the gold clusters randomly distributed on the supporting substrate. Further irradiation led to the development of bigger crystals, as documented previously (*4*), and our observations were then concentrated on those particles that were protruding over holes in the support film. For comparison purposes, the holey amorphous substrates were made of silicon and germanium as well as the traditional carbon. Samples were also prepared by direct evaporation of gold. Most of the observations were made with an HREM (JEM-4000EX) that was operated primarily at 400 kV, although some studies were also made at 200 and 350 kV. The microscope was equipped with a TV system (Gatan 622), fiber optically coupled to an yttrium-aluminum-garnet screen, and this was used both for image viewing and for video tape recording. Typical electron optical magnifications were 600,000 or 800,000 times, with electron current densities at the sample usually ~20 to 25 A/cm^2, although these values ranged from ~10 to ~80 A/cm^2 for those particular experiments designed to investigate the dependence on beam current density. Some of the videotapes were later processed with a digital video processing unit (Quantex DS-30) to reduce noise and to improve image contrast. Some observations were made with a 100-kV electron microscope (Philips 400ST) that was equipped with a specimen heating holder.

The images shown in Fig. 1 provide a graphic representation of the structural changes that occurred in the small gold crystals. Each image is a photograph of the monitor screen showing two to four averaged frames from a video tape recording, and the total elapsed time of the sequence is only 20 seconds. The images show the particle, supported on a thin film of amorphous silicon, near to a [110] orientation; they were taken at close to the optimum defocus (an amount out of focus at which one can directly interpret the image), so that the atomic columns appear black.

The sequence of images shown in Fig. 2 is

D. J. Smith, Center for Solid State Science and Department of Physics, Arizona State University, Tempe, AZ 85287.
A. K. Petford-Long, Center for Solid State Science, Arizona State University, Tempe, AZ 85287.
L. R. Wallenberg and J.-O. Bovin, Inorganic Chemistry 2, Chemical Center, University of Lund, S-22100 Lund, Sweden.

Fig. 1. Series of high-resolution electron micrographs showing some of the structural rearrangements of a small gold crystal (diameter, 4.8 nm), supported on an amorphous silicon substrate, during 20-second time span. Imaging conditions: 400 kV; 40 A/cm^2; electron-optical magnification, ×800,000. (a) The particle contains one twin plane (indicated by arrow) with a notch. (b) Four seconds later, the twin plane is displaced. Atomic columns are in an anomalous position at A, the notch is at B, and there are two missing atom columns at C. (c) The crystal is rotated slightly away from the well-aligned condition, so the two-dimensional lattice structure is not readily visible. The twin plane is still discernible (arrow) if one tilts the image and looks along the various lattice directions. A column of atoms has hopped away from the site at C. (d) The twin is again clearly visible with good contrast but with a pronounced notch. A stacking fault appears at D; there are no missing columns at C. (e) The upper twin is still visible. The stacking fault visible in (d) has disappeared, and another stacking fault (arrow) parallel to the other set of {111} planes has appeared. An anomalous surface structure appears at A, and there is severe lattice distortion at E.



of another gold crystal on an amorphous silicon support. This sequence was recorded under imaging conditions identical to those in Fig. 1 except that the overall particle "diameter" was considerably smaller ($\sim$3.5 nm compared with $\sim$5.0 nm). In this case, the structural changes occurred more rapidly, and it was difficult to obtain good contrast photographs from the monitor since many individual frames showed a blurred image of the particle because of its motion. The contrast in Fig. 2, a and c, suggests that the particle has an icosahedral multiply twinned shape (*9*), whereas in Fig. 2, b and f, it appears to be a single crystal, and in Fig. 2, d, e, and g, it contains, respectively, a stacking fault, a twin plane, and both a stacking fault and a twin plane. Depending on size and contact with the support, the particles were often observed to rotate on the substrate, and it was difficult in some cases to be certain whether a structural change had really occurred or whether the change observed in the image of the particle was simply a result of rotation.

In the very small crystals (diameter, <2 nm), motion was extremely rapid, making it unclear whether rotations or shape changes were taking place. Such particles would behave like pulsating liquid globules that could momentarily "freeze" in a particular shape and then "melt" into motion several fractions of a second later. A good example of a gold crystal on an amorphous carbon support is shown in Fig. 3. Similar behavior was also seen in larger particles that had minimal contact with the support, such as the gold crystal (diameter, $\sim$4 nm) on amorphous silicon shown in Fig. 4. Single-frame images cannot convey the fascinating dynamic behavior of these rearrangements. The two twin planes meet at an angle in Fig. 4b, and Fig. 4c shows the decahedral multiply twinned shape, with pronounced reentrant notches at the separate twin boundaries. This latter configuration is expected because of minimization of the surface free energy (*10*).

From many observations similar to those

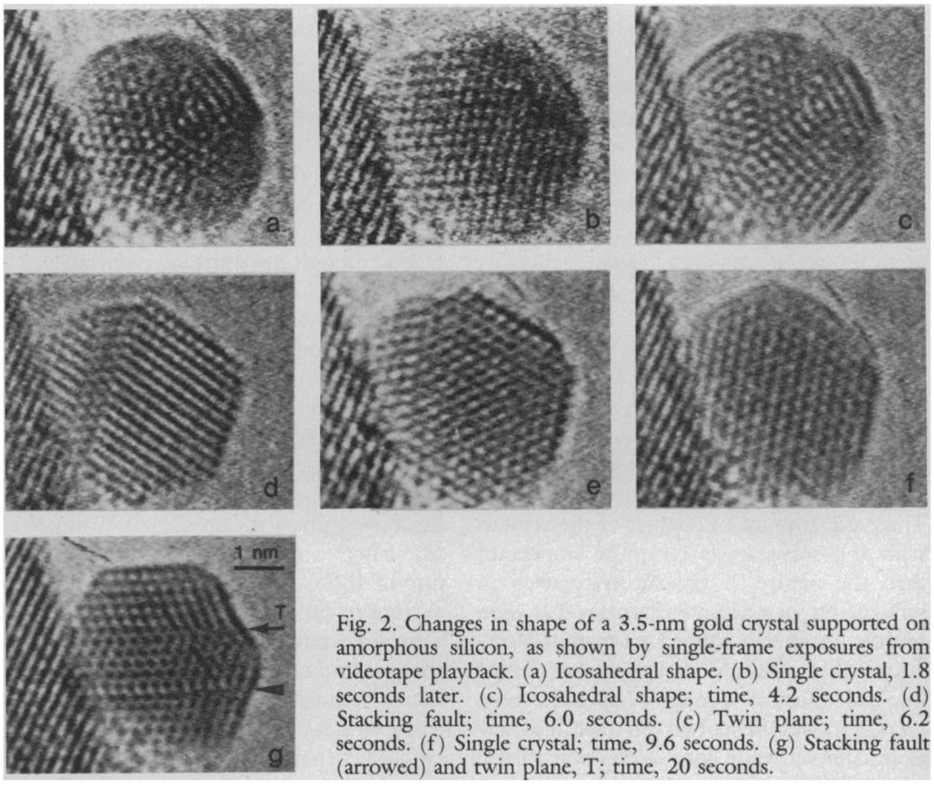


Fig. 2. Changes in shape of a 3.5-nm gold crystal supported on amorphous silicon, as shown by single-frame exposures from videotape playback. (a) Icosahedral shape. (b) Single crystal, 1.8 seconds later. (c) Icosahedral shape; time, 4.2 seconds. (d) Stacking fault; time, 6.0 seconds. (e) Twin plane; time, 6.2 seconds. (f) Single crystal; time, 9.6 seconds. (g) Stacking fault (arrowed) and twin plane, T; time, 20 seconds.

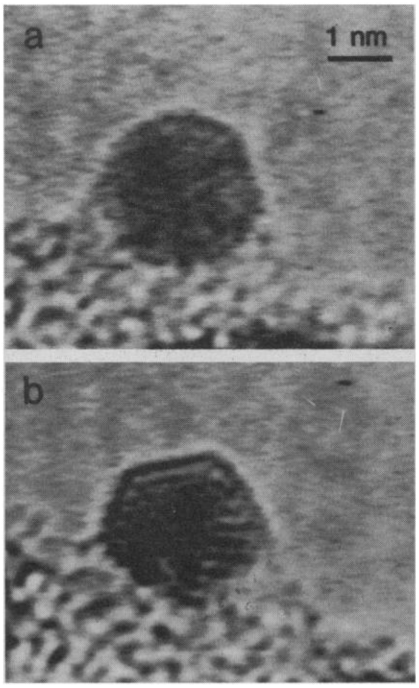


Fig. 3. Single-frame videotape images of a small, rapidly pulsating gold crystal (diameter, 2.5 nm) on an amorphous carbon substrate. (a) No lattice structure visible because of rapidity of motion or structural arrangement. (b) Crystal temporarily "frozen" in place, showing structure with one twin plane.

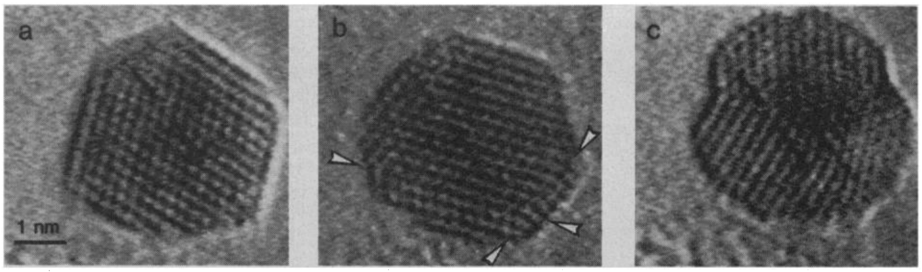


Fig. 4. Structural rearrangements of a 3.7-nm gold crystal supported on amorphous silicon. Pronounced faceting of {100} and {111} surfaces is visible in (a). A twin plane is indicated in (b), and a decahedral shape with reentrant notches is visible in (c).

shown in Figs. 1 through 4, a number of generalizations about the gold particle behavior can be made. For example, the activity decreased rapidly as the particle size increased, and it was rare for crystals larger than $\sim$8 nm to show any structural rearrangements [although atom hopping (*5*) and atom clouds above certain crystal faces (*6*) were still visible]. No significant differences in behavior between crystals supported on either amorphous carbon or amorphous silicon substrates were observed, although the motion and activity on the amorphous germanium was generally, though not always, markedly less for particles of equivalent size. Often it appeared that the gold particles were being enveloped by the amorphous germanium substrate, resulting in contact between much of the particle surface and the substrate. For carbon or silicon supports, the particles invariably had minimal contact with the substrate surface. Thus, the amount of contact of the crystals with the substrate is far more important than the nature of the substrate itself in influencing their activity. Particles that were resting on convex-shaped or rounded surfaces of the substrate were much more mobile than those on concave shapes. In some cases, particles were observed to shift slowly along the substrate into depressions; once they were located in such positions a drastic curtailment of their activity was observed.

The behavior documented here has been observed in other microscopes at 200 kV (*4*) and 120 kV (*7*). The threshold for exit surface sputtering in gold is around 400 kV (*11*), and direct "knock-on" from the bulk occurs at even higher voltages. This dynamic activity of the particles at lower voltages implies that an explanation for the motion of the particles and their rearrangements in terms of atomic displacement mechanisms is unlikely.

The observations suggest that the quasi-fluid behavior of the gold particles is explicable in terms of local heating of the particles by the electron beam, with more substrate contact providing greater opportunity for heat dissipation and thereby reducing the dynamic behavior. The TV system attached to the microscope was not equipped with an image intensifier, so the electron current densities at the sample could not be varied over a wide range. At 1 million times magnification and 60 to 80 A/cm^2, the rate of activity noticeably increased after a short period (presumably as the particle warmed up). At 500,000 times magnification and 10 A/cm^2, when the crystal lattice structure was just visible on the monitor, it was still possible to tell that the motion was considerably, though not entirely, reduced.

Since small metal particles are extensively used to catalyze chemical reactions at elevated temperatures, it was interesting to study the behavior of the gold crystals as the substrate was heated. We expected the structural rearrangement to occur for increasingly larger particle sizes and for lower current densities as the temperature was increased. Moreover, given the studies of Wang *et al.* (*8*), where a threshold annealing temperature of 480°C was established for structural alterations in small platinum particles, it seemed reasonable to expect that structural changes in the smallest gold particles would occur spontaneously at sufficiently high temperatures. Observations were made with evaporated particles on an amorphous carbon substrate in the heating holder of the 100-kV microscope. The resolving power of this machine is limited to $\sim$0.35 to 0.40 nm, which excluded the possibility of lattice plane or atomic resolution, and some thermal drift prevented satisfactory image recording. Nevertheless, at a substrate temperature of $\sim$470°C, some particle motion was visible on a TV monitor, even when the electron current density at the sample was kept to a low level ($\sim$1 A/cm^2). At a temperature of 520°C, many particles were moving rapidly, and several appeared to change shape.

These preliminary, low-resolution results provide a crucial link between particle rearrangements that are beam-induced and those that occur naturally at elevated temperatures. Moreover, rearrangements in small crystals of platinum, rhodium, cadmium, and zinc have also been observed under high current density conditions (*12*). HREM observations could therefore represent a valuable alternative method for duplicating and characterizing the behavior of small metal particles, in particular those structural changes that occur during the annealing treatment. Further studies on other metals might assist in establishing the real structure of catalyst particles, particularly their surfaces, and might also help to elucidate the perplexing changes in physical and chemical properties that occur in small particles.

REFERENCES AND NOTES

1. H. Hashimoto *et al.*, *Jpn. J. Appl. Phys.* **19**, L1 (1980).
2. R. Sinclair *et al.*, *Nature (London)* **298**, 127 (1982).
3. D. J. Smith and L. D. Marks, *Mater. Res. Soc. Symp. Proc.* **41**, 129 (1985).
4. R. Wallenberg, J.-O. Bovin, G. Schmid, *Surf. Sci.* **156**, 256 (1985).
5. R. Wallenberg, J.-O. Bovin, D. J. Smith, *Naturwissenschaften* **72**, 539 (1985).
6. J.-O. Bovin, R. Wallenberg, D. J. Smith, *Nature (London)* **317**, 47 (1985).
7. S. Iijima and T. Ichihashi, *Phys. Rev. Lett.* **56**, 616 (1986).
8. T. Wang, C. Lee, L. D. Schmidt, *Surf. Sci.* **163**, 181 (1985).
9. L. D. Marks and D. J. Smith, *J. Cryst. Growth* **54**, 426 (1981).

10. L. D. Marks, *Philos. Mag.* A49, 81 (1984).
11. D. Cherns, M. W. Finnis, M. D. Matthews, *ibid.* 35, 693 (1977).
12. J.-O. Bovin, L. R. Wallenberg, A. K. Petford, D. J. Smith, in preparation.
13. Supported by the Swedish Natural Science Research Council (E-CG-3914-110), the National Swedish Board for Technical Development (DNR-84-3515), the National Science Foundation(DMR-830871), and the Arizona State University Research Fund. The Arizona State University National Facility for High Resolution Electron Microscopy is supported by grant DMR-8306501 from the National Science Foundation.

27 January 1986; accepted 29 May 1986

Observations of Pentagonally Twinned Precipitate Needles of Germanium in Aluminum

U. DAHMEN AND K. H. WESTMACOTT

Unusual pentagonally twinned precipitates were observed in a high-resolution transmission electron microscopy study of needle-shaped germanium particles in aluminum. Although commonly found in small particles formed on substrates, such twinning has not been seen in precipitates grown in the solid state. The morphologies and orientation relationships are consistent with symmetry principles.

THE MORPHOLOGY OF A PRECIPITATE forming in a solid matrix is determined by many factors. Strain energy, interfacial energy, formation temperature, and prior history are among the most important. The fundamental processes underlying a precipitation reaction have been treated by many different approaches, for example, thermodynamic, mechanistic, kinetic, and elastic continuum methods, all of which illuminate various aspects of the problem. It has recently become clear that considerable understanding of a precipitation process might be deduced from an analysis of the precipitate morphology and orientation relationship in terms of crystal symmetry operations (*1–3*). In this report we consider a striking example of a precipitate morphology found in an aluminum-germanium alloy and discuss the results of a preliminary analysis on the basis of symmetry considerations.

The aluminum-rich end of the aluminum-germanium phase diagram is particularly simple. A decreasing solubility with decreasing temperature gives it characteristics typical of age-hardening systems. In dilute alloys (1.14 atom percent in the present work) a quench from near the solidus temperature (450°C) followed by an aging treatment below 320°C leads directly to the precipitation of the pure germanium equilibrium phase. However, in contrast to its metallurgical simplicity, the precipitation process is by no means facile. This is a consequence of large disparities in the crystal structures and atomic volumes of the parent and product phases (aluminum and germanium have face-centered cubic and diamond cubic crystal structures, respectively, and atomic volumes of 16.6 Å^3 and 22.6 Å^3, respectively). In the absence of excess vacancies that fulfill both structural and volume accommodation roles in the transformation (*4*), germanium precipitates cannot readily nucleate and grow in the aluminum matrix. This effect manifests itself in a variety of morphologies (*5*), which presumably reflect variations in local vacancy concentration.

Transmission electron microscopy (TEM) micrographs show mainly needle-shaped germanium precipitates; when the foil is viewed along an <001> zone axis, it is apparent that these needles lie along the three crystallographically equivalent <100> directions of the aluminum matrix. As shown elsewhere (*3*), <100> is an invariant line direction in this alloy system, thus constituting a favorable direction for needle growth. The length of the needles typically ranges from 100 to 500 nm. Until recently, their cross-sectional shape was unknown. In the course of the present study, high-resolution images of many needle cross sections have shown that the needle axis is always parallel to a <110> direction of the germanium precipitate (*3, 5*). However, at least three major orientation relationships were found within the confines of <110> Ge ‖ <100> Al. All precipitates contained twins along the needle axis, and often complex, multiply twinned particles were observed.

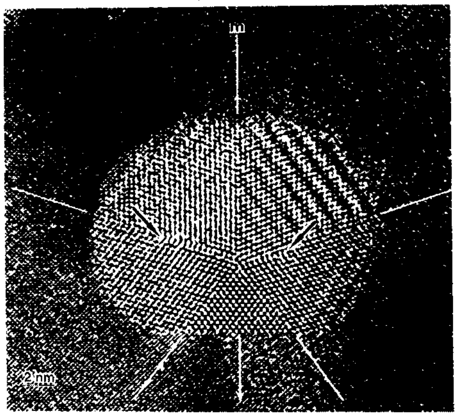


Fig. 1. High-resolution micrograph of a pentagonally twinned germanium precipitate in an aluminum matrix with the beam direction along <110> Ge and <100> Al. The specimen was water-quenched from 450°C and aged for 1 hour at 240°C.

An interesting and unusual example of a multiply twinned germanium particle is shown in the image in Fig. 1, which was taken on the 1-MeV JEOL atomic resolution microscope. Five wedge-shaped sections radiate from a common center of a precipitate that is roughly circular in cross section. The five sections meet along planar twin boundaries indicated by lines drawn on the image. The {111} twin planes in the diamond cubic structure of germanium enclose an angle of 70.5°. Five such sections are therefore insufficient to fill a complete circle. The closure failure of 7.5° is taken up by two extra lattice planes inserted radially and ending at the arrow marks. A slight relative rotation between adjacent segments results from these extra planes, and these defects are perhaps more appropriately described as wedge disclinations (*6*). Note the step in the left boundary at the end of the extra plane and the stacking fault from there to the center. The particle appears to have pentagonal symmetry, but closer inspection reveals that the facet on the lower segment and the notch between the upper two segments are not compatible with a fivefold rotation axis. It is also apparent that the center of the fivefold star is not at the centroid of the particle. However, the particle does possess mirror symmetry with respect to the twin plane marked *m* and with respect to the image plane, as well as a twofold rotation axis along the intersection of the two mirror planes. Hence the morphological symmetry of this precipitation is *mm2*, one of the three orthorhombic point groups. This symmetry describes its entire substructure, including the two extra half planes, as well as the shape.

Inspection of the lattice fringe directions in the aluminum matrix indicates that the {110} mirror plane in the matrix is parallel to the mirror plane marked *m* in the particle. The other mirror plane and the twofold axis are parallel to a {001} mirror plane and a <110> diad in the matrix, respectively, so that *mm2* also represents the symmetry that the particle and matrix have in common,

---

National Center for Electron Microscopy, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.