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IMAGING SMALL PARTICLES

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This paper reviews recent results on multiply twinned particles, emphasising the interplay between experimental electron microscopy and theoretical modelling of the internal and surface structures. A wide range of particle structures can be understood through the use of a modified Wulff construction. Inhomogeneous elasticity is also useful in understanding defects in small particles. With respect to the energy balance between multiply twinned particles and single crystals, it is important to include the weakening of the (111) surface bonding for Ag and Au evidenced by recent experimental results on the longitudinal surface phonon frequencies. Theoretical models need to be extended to the atomic level, and there remain a number of unsolved structural problems.

1. Introduction

The hardest area in electron microscopy of small particles is not the imaging, but rather the interpretation. For a long time much of the industrial emphasis has been on statistical information, for instance the particle size distribution of a heterogeneous catalyst, stimulating work at relatively low resolutions (~ 2 nm) when most of the information about the particle shape is lost. The data then fits into pseudo-continuum models of, for instance, Ostwald ripening. In this research we are matching the experimental information to the theories. Without denying the merit of this type of work, it does not exploit the full potential of an electron microscope as a tool for determining the atomic morphology and shape of the particles. Where the future of electron microscopy of small particles lies is in combining the experimental work with theories which match the sophistication and detail of the experimental data, i.e. letting the experiments rather than the theories lead.

This paper briefly reviews some of the work carried out in Cambridge by the author (in collaboration with Drs. V. Heine, A. Howie, D.J. Smith and E. Yoffe) on the structure of small, multiply twinned particles of silver and gold. Multiply twinned particles or MTPs, see references [1–10], are frequently found among small fcc particles. In addition to their possible role as growth nuclei and in heterogeneous catalysts, they are important as a means for refining our understanding of what controls the structure of small particles. In the work described herein much of the emphasis was on generating theories to understand the experimental results. Such a synergistic combination of experiment and theory has allowed some delineation of the factors controlling the particle morphologies, to the extent that atomistic surface effects may now be introduced into the models. However, there remain a number of unsolved structural problems.

2. Surface structure of decahedral MTPs [8]

One of the assumptions in work on MTPs has been that the experimentally observed particles have the equilibrium shape. In fact, growing particles by evaporation onto a substrate produces kinetic shapes, and the true equilibrium shapes are only obtained by annealing in equilibrium with the

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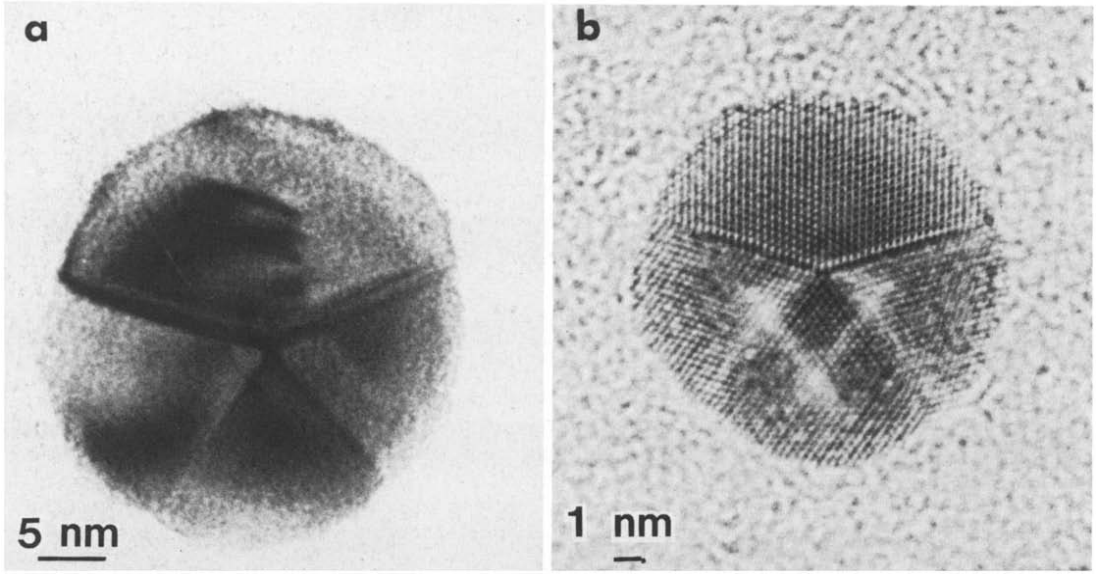

Fig. 1. Images of decahedral MTPs showing the re-entrant surfaces at the twin boundaries, in (a) a large particle taken from ref. [8] and (b) a relatively small particle.

vapor [11]. In early work, annealing particles on amorphous carbon, decahedral particles were observed which were not simple pentagonal bipyramids. Instead they were substantially more rounded and showed clear evidence of notches at the twin boundaries (see fig. 1).

At first sight a re-entrant surface does not seem reasonable as an equilibrium surface feature. On further analysis its source becomes apparent. The equilibrium shape of a single crystal can be determined by a Wulff construction, e.g. refs. [12–14], which implies that the equilibrium shape of these particles should be amenable to a related analysis. Invoking the particle symmetry so that each single crystal segment is the same, minimising the surface energy of the total particle reduces to minimising one segment bounded by two "twin facets". From the symmetry, the energy per unit area of each twin facet is half that of a twin boundary. Treating each segment independently using a Wulff construction leads to the shape shown in fig. 2, in good agreement with the experimental results. The re-entrant surfaces arise naturally as being of lower energy than the alternative convex surfaces.

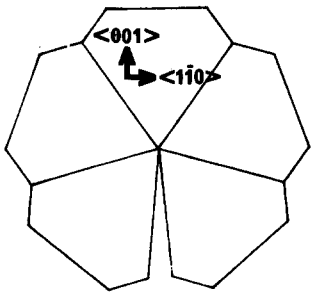

Fig. 2. Shape in a {110} projection of a decahedral MTP, taken from reference [8]. The correspondence to the shape shown in fig. 1 should be noted. Some additional rounding (facetting) of the Wulff shape would improve the fit.

3. Polyparticles and the modified Wulff construction [15,16]

Towards the end of the 1970's the high-resolution electron microscope in Cambridge started to produce images [17] and the author became involved in work in collaboration with Dr. D.J. Smith on the structure of particles in evaporated films. In addition to simple structures such as single crystals and MTPs, there were also a large number which could be described as partially coalesced particles or polyparticles, see for in-

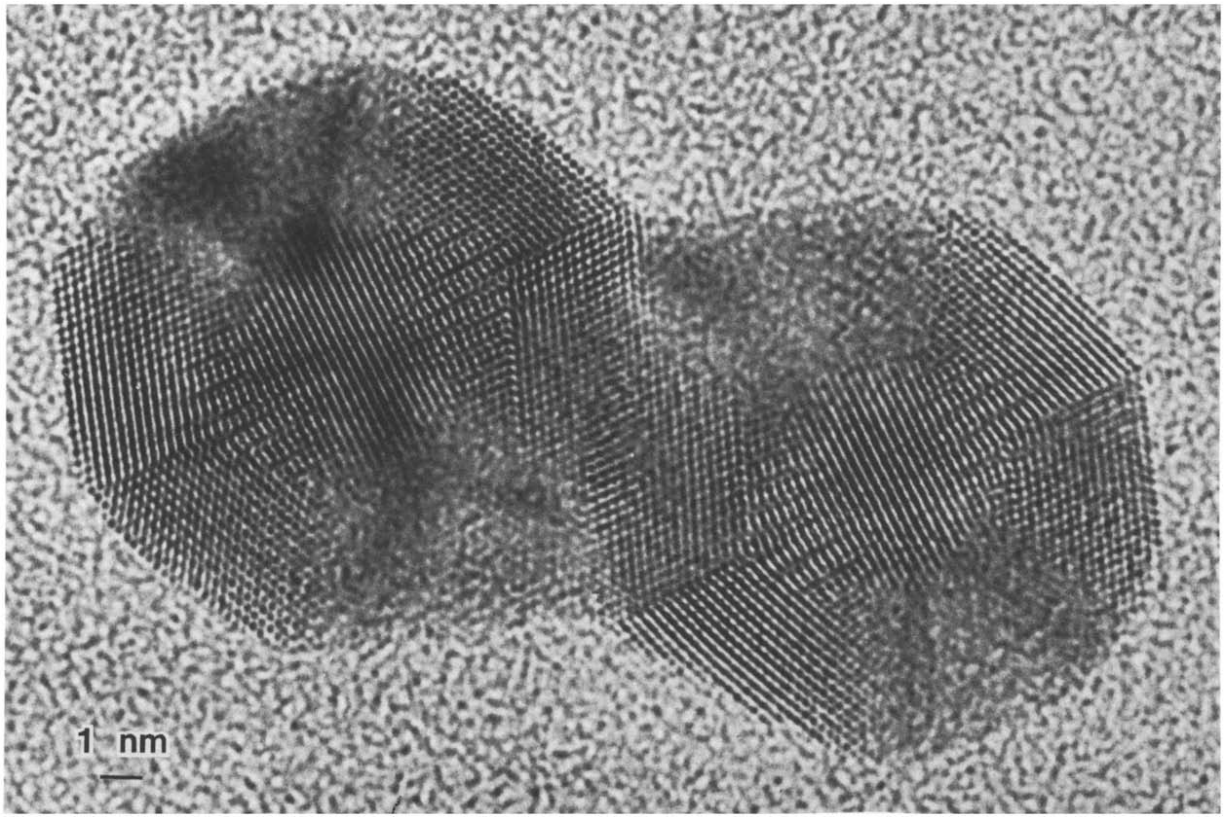

Fig. 3. High-resolution image of a poly-icosahedral MTP of silver.

stance fig. 3. Rather than the basic unit being a single crystal, it was instead a discrete particle, for instance an MTP; units such as MTPs retained their basic nature even when coalesced.

This experimental observation led to an extension of the approach used for the decahedral particles described in the previous section. A composite particle can be divided into different segments bounded by twin faces, with the twin boundary energy divided into two fractions $(1-\alpha)$ and α, where α is for the moment arbitrary, and the total particle volume similarly divided.

Having now separated the composite particle into individual single crystal units, the lowest surface energy shape for each unit (separately) will be a Wulff construction with the twin boundaries included as pseudo-surface facets. If a shape can be found such that each segment is a Wulff construction, and all the segments still assemble to a complete particle for a specific value of α and the volume partition (without any residual unsatisfied boundaries), this *may* be a local energy minimum. The possibility that such minima exist arises only with a three-dimensional model with anisotropic surface-energies rather than a two-dimensional or a liquid-like [18–20] model.

The above may be called a modified-Wulff construction. Mathematically it is difficult to prove that there are minima; it is straightforward to show that the shapes are energetically stationary points, but non-trivial to determine the sign of the second derivative. It is possible on physical grounds to argue that they are probably minima, but the "proof" is that they fit the experimental results. Because of the reflection symmetry of a twin boundary there is always one solution for an equal partition of the twin boundary energy. This is the solution used for the MTPs in the previous section.

More important there is also an assymmetrical solution which is quite common among experimental particles.

One of the more interesting predictions of the model is that asymmetric MTPs can be stable. The asymmetric Dh was first observed by Yagi et al. [21], and acts as an intermediary [16] between the symmetric MTPs and single crystals. An example taken from work by Matsui [22] is shown in fig. 4. The status of this particle as an intermediary has recently been confirmed by Iijima [23], who observed dynamic structure changes between single crystals and MTPs. It is now believed that very small clusters, typically only 20 atoms, have sufficient thermal energy, at room temperature, to be fluctuating in shape [24]. A very intense electron beam is known to heat small particles (on insulating supports), in some cases subliming the particles. Thus the structural changes observed by Iijima are manifestations of structural fluctuations of hot particles between modified Wulff shapes.

Despite the success of the modified Wulff construction, it is important to point out that it does not explain all the morphologies found in small particles. One example is shown in fig. 5, a somewhat distorted decahedral MTP.

4. Strains [7,9,25–27]

One of the interesting features of MTPs is that they contain large inhomogeneous strains, typically between 2 and 6%, which produce substantial dark field contrast [27]. These strains are large compared to the yield strains of many materials, so they should nucleate dislocations. However, in a number of experiments by dark field techniques [1,2,28,29] there was no evidence for any dislocations. One of our earliest observations was of partial dislocations in the icosahedral MTPs, see for instance fig. 6. Why were these not observed in the dark field work? In an already strained particle there will be strain cancellation, eliminating most of dark field contrast. The phase information due to the shifts of the atomic columns at the stacking fault associated with the dislocation is lost in dark

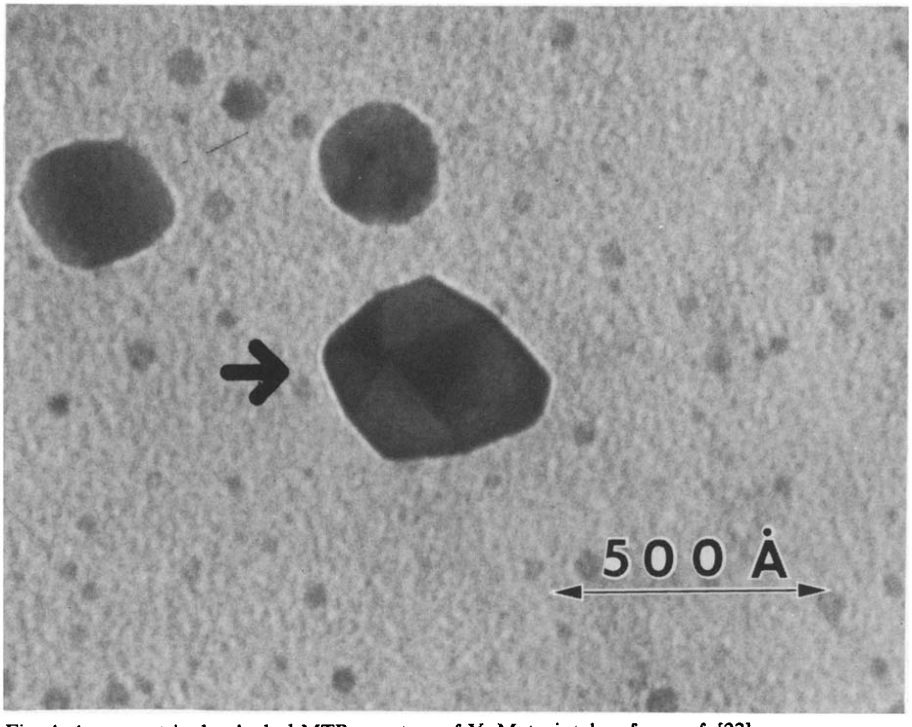

Fig. 4. Assymmetric decahedral MTP, courtesy of Y. Matsui, taken from ref. [22].

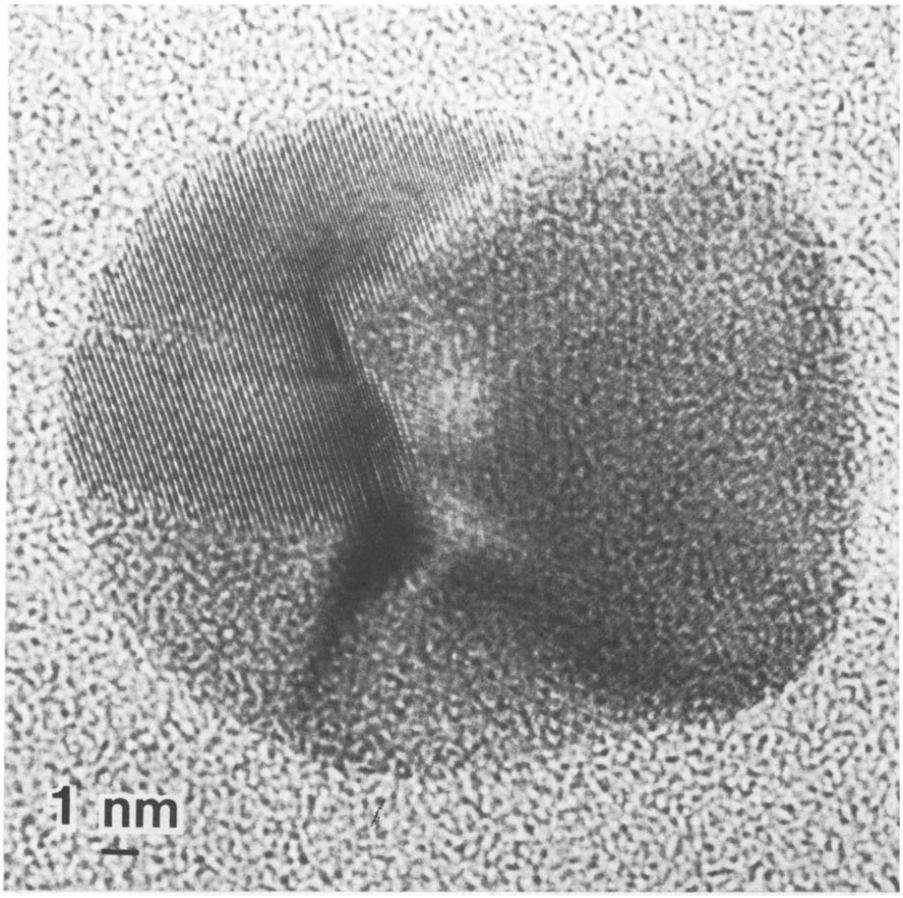

Fig. 5. High-resolution image of a highly distorted decahedral MTP.

field imaging (one diffracted spot only), but retained in a lattice image.

At the same time as the HREM work, there was also work on the strain fields within the particles using inhomogeneous isotropic elasticity [9]. This suggested that there were two possible mechanisms for the stress relief; climb of a Frank partial dislocation along a twin boundary or glide of a Shockley partial. On energetic grounds one might expect the Shockley mechanism since the core energy of a Shockley partial is substantially smaller than that of a Frank partial. However, the experimental results rule out the Shockley mechanism, in particular an experimental image which clearly showed a Frank loop nucleating at the free surface (fig. 7). Further analysis combined the experimental [7] and theoretical [9] work in a model with a Frank loop climbing about 1/3 of the way into the particle, then dissociating into a stair-rod and a Shockley partial, with the Shockley subsequently gliding across the particle.

However, there is still room for further analysis. Modelling the initial activation energy of a dislocation loop at a surface requires knowledge of the atomic energy of the loop and that of any residual surface steps. For instance, continuum models suggest that a surface step could be unstable compared to a very small dislocation loop, which is surely wrong.

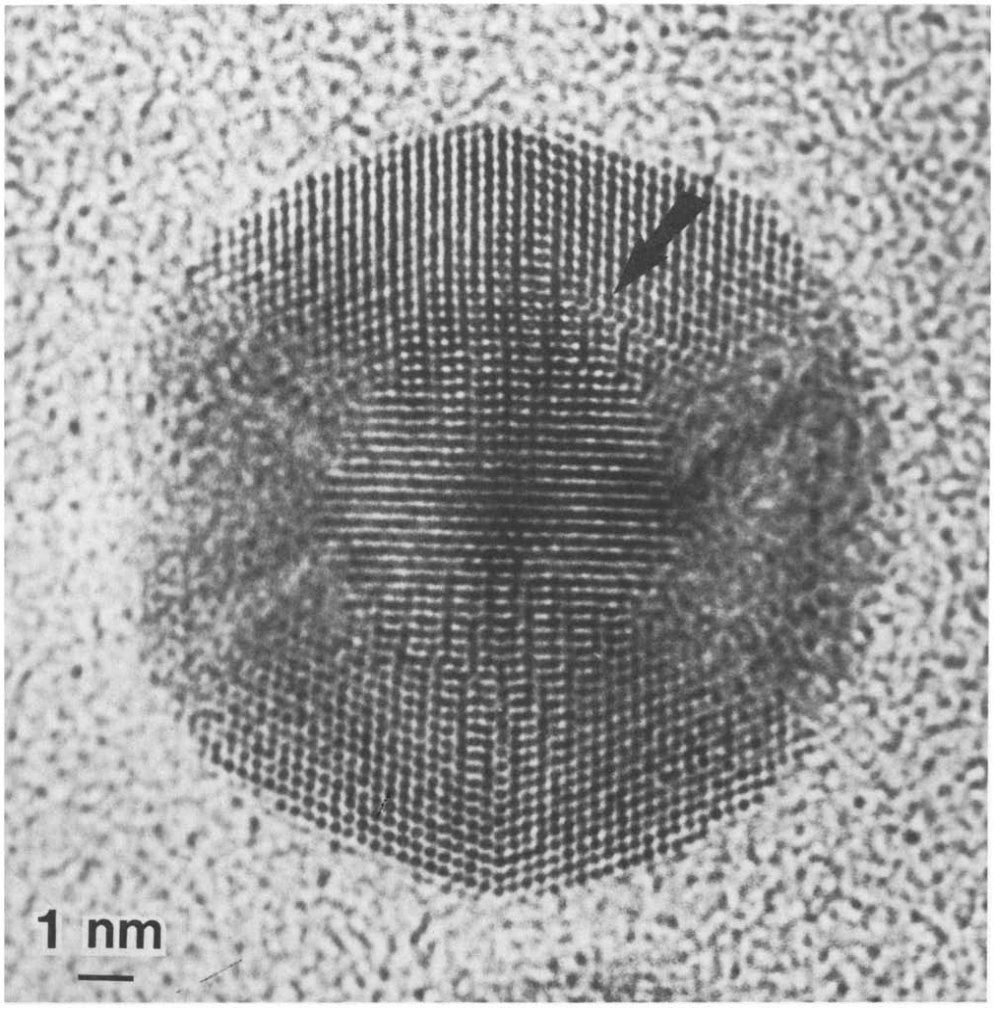

Fig. 6. High-resolution image of an icosahedral MTP showing a partial dislocation (arrowed). The strongest indication of the defect is the associated stacking fault.

5. MTP energies, surface stresses and surface science [9,30–33]

What can now be said concerning the energies of MTPs relative to single crystals? All the parameters are known except one, namely the energy associated with expanding the surface, the surface stress contribution. In addition to the energy stored in distorting the bulk, there is a surface correction which can be either positive or negative. If left to its own devices the surface would contract; this would oppose the internal strains and therefore increase the energy required to form an MTP. If, like solid argon, the surface wants to expand, this reduces the energy. Assuming that the surface stress term is proportional to the surface free energy (see ref. [9]), the numbers for the relative stability of MTPs versus single crystals seem reasonable: typically an MTP of radius 10nm is more stable than a single crystal, as indicated in table 1.

However, there is relatively little variation from element to element, which does not fit the experimental evidence: MTPs occur profusely in Ag and Au, but comparatively rarely in the other fcc or fcc-like (e.g. diamond) materials (see ref. [10]). Why are Ag and Au so different?

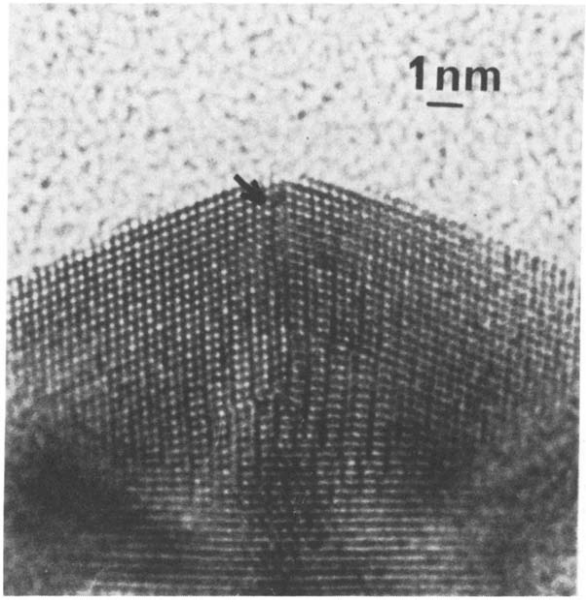

Fig. 7. High-resolution electron micrograph of a icosahedral MTP showing evidence for a small dislocation loop near the surface in the region indicated, taken from ref. [9].

The answer to this has come from some recent work on gold surfaces [30–32], theoretical analysis [33] and data on the longitudinal surface phonon frequencies [34–36] for Ag and Au (111) surfaces. The electron microscope work indicates that Au surfaces tend to expand, particularly the (110) [30] and (111) [31,32] surfaces. On theoretical grounds [33], Au surfaces behave rather like solid argon surfaces; gold is strongly influenced by a full d-shell, as in the full-shell inert gases, so the surfaces tend to expand. (The full explanation is substantially more complicated [33].) Finally, the longitudinal surface phonons on Ag and Au (111) [34–36] are anomalously low in frequency, with approximately a 25% reduction [36] in the strength of the Au surface bonds.

Table 1
Cross-over radii for single crystals relative to MTPs, taken from ref. [9]

	Ag	Al	Au	Cu	Ni
R_1 (nm)	4.7	Negative	5.6	2.0	Negative
R_2 (nm)	8.8	3.68	9.9	7.3	5.6
R_3 (nm)	9.2	6.39	10.3	7.8	6.5

For a particle of volume $\frac{4}{3}\pi R^3$, the energies of the different particles are for
$R < R_1$, single crystal > decahedral MTP;
$R < R_2$, single crystal > icosahedral MTP;
$R < R_3$, decahedral MTP > icosahedral MTP.
MTP formation in Ag and Au is clearly favored, but not enough to explain the experimental data.

Taking this into account, it is apparent that the energy required to stretch Au and Ag surfaces will be particularly small, explaining why MTPs are so common. It also opens up avenues for understanding how environmental conditions may affect particle morphologies. Chemisorbed gases can effect this surface strain cost (and also the surface energy anisotropy [8]), and thereby swing the energy balance either towards or away from MTP formation.

6. Discussion

This work has emphasised the extent to which one needs to develop theoretical models to go with the electron microscopical work. The modified Wulff construction has proved to be exceedingly powerful in understanding the surface morphologies, similarly elasticity calculations for the defect structures. However, real surfaces are atomistic. Including such atomistic effects can lead to substantial changes in the surface structure, for instance packing corrections which make (111) surfaces preferential to (100) surfaces [37]. There may also be insufficient room for many of the vicinal surfaces on a small particle [38,39]. Models like the Wulff construction with atomic details included would appear to be promising topics for future work.

There are also problems with the elasticity analyses. For the decahedral particles there is only a two-dimensional solution, and for the icosahedral particles only an average solution [9]. For defects more complicated models are required, perhaps again an atomistic analysis.

Looking towards the future, perhaps the most important work will in some respects lie outside of electron microscopy. Techniques such as multiple dark field [1,2], STEM imaging (e.g. refs. [40]) or microanalysis (e.g. [41]) and HREM structure [15] or surface imaging [30–32] have now been developed. The important questions lie in small-particle

physics with electron microscopy as one of many techniques. The future lies in the interpretation of the images, rather than in obtaining them.

7. Conclusions

The combination of high-resolution electron microscopy with detailed theoretical modelling has led to some progress in understanding small particles. A wide range of particle structures can be understood, but not all. Inhomogeneous elasticity calculations are powerful in understanding defects such as dislocations within these particles. A full analysis should include the variation of surface free energies with surface adsorbates and changes in the surface bonding as monitored by the surface phonon frequencies. However, there is still much work to be carried out.

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