

# PHASE INSTABILITIES IN SMALL PARTICLES

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In this review we consider the existing theories for the structure of small particles and the nature of morphological instabilities as the size is reduced. The various electron microscopic observations confirming the stability of a new phase, the so called 'Multiply twinned structure', in small particles is discussed. A theoretical model is presented to calculate the free energy surfaces for a series of asymmetric and single crystal structures using a modified Curie–Wulff construction for the surface energy, and a disclination model for the elastic strain energy. Depending on the activation barrier heights and the Boltzmann occupancy factors for the various local minima on the energy surface, the idea of 'quasi-melting' is introduced and compared with the structural instabilities in molecular clusters seen recently by various authors using computer simulations. A phase diagram for small particles as a function of size and temperature is presented and the effect of statistical fluctuations on stability is discussed. Finally a phenomenological discussion relating the phase instabilities to various melting and related phase transitions is given.

**KEY WORDS:** Multiply twinned particles, quasi-melting, structural fluctuation.

## 1 INTRODUCTION

There has been for many years enormous interest in the study of material systems at very small sizes, primarily due to the difference in their physical and electronic properties compared to the bulk solid state. The lattice vibration spectrum in small particles differs drastically from the bulk, as demonstrated by Dickey and Paskin (1968), Burton (1970), Couchman and Karasz (1977), Matsubara, Iwase and Momokita (1977), Hasegawa, Hoshino and Watabe (1980) and many others. Khlyustikov and Buzdin (1987) suggested recently that the two dimensional nature of the phonon spectrum could explain the increase in superconducting transition temperatures in fine particles of tin. Kubo (1962) demonstrated that since the spacing of the quantized electronic states becomes large in small particles, especially at low temperatures, the electrical and thermal properties exhibited by them show large deviations from the bulk. He also noted that the electrons in a small particle are unique in that they do not obey Fermi statistics because the number of such electrons is so small. The effect of size on phase equilibria, leading to a depression in the thermodynamic melting point with decrease in particle size, has been pointed out over the years by Takagi (1954), Blackman and Sambles (1970), Couchman and Jesser (1977), Couchman and Ryan (1978), Borel (1981), Ross and Andres (1981), and a range in the melting transition has been predicted by Briant and Burton (1975), Eters and Kaelberer

(1977), Natanson, Amar and Berry (1983), Berry, Jellenik and Natanson (1984), Beck, Leitner and Berry (1988) and many others. Computer simulations on very small clusters containing a few hundred atoms have provided similar results implying inherent configurational instability and the possibilities of lower order phase transitions before the onset of the actual melting phenomena; see for example Hoare and Pal (1971, 1972) and Honeycutt and Anderson (1987). Electron microscopic, X-ray structure and theoretical analysis by Vermaak, Mays and Kulhmann-Wilsdorf (1968), Mays, Vermaak and Kulhmann-Wilsdorf (1968), Gordon, Cyrot-Lackmann and Desjonquers (1979), Woltersdorf, Nepijko and Pippel (1981), Heinemann, Osaka, Poppa and Avalos-Borja (1983), Marks, Heine and Smith (1984) and Marks (1985b) have indicated modifications in lattice parameters, contractions of the surface layer and the presence of residual stresses in small particles.

We shall in the following sections review the available information, both theoretical and experimental, on the evolution, growth and structure of small particles. A continuum theory approach will be used to evaluate parts of the energy surfaces populated by different structural configurations (phases) assumed by small particles. The question of phase instabilities seen in such systems will be discussed.

## 2 ATOMIC CLUSTERS

Studies of atomic clusters of a few atoms can be used as a precursor to treating bigger particles which can be experimentally observed. Using computer models (Monte Carlo or Molecular Dynamics Programs), searching for energy minima or using sphere packing studies, pair-potential or quantum mechanical calculations, workers such as Bernal (1960), Mackay (1962), McGinty (1971), Hoare and Pal (1972), Lee, Barker and Abraham (1973), Briant and Burton (1975), Eters and Kaelberer (1975, 1977), Farges, de Feraudy, Raoult and Torchet (1983, 1986), Jellenik, Beck and Berry (1986), Landman, Barnett, Cleveland, Scharf and Jortner (1987), Honeycutt and Anderson (1987) have proposed various novel structures for clusters. In a recent paper Halicioglu and Bauschlicher (1988) have reviewed the physics and properties of microclusters, outlining the progress as well as limitations of the present state of research. Most of the above studies indicate that below a few thousand atoms, clusters do not correspond to microcrystallites of fcc or hcp type close packed lattices, but form families of compact structures based upon packing of tetrahedra. Many structural sequences based on potential energy minimum criteria have also been proposed for clusters of very small sizes (e.g. Werfelmeier, 1937; Fukano and Wayman, 1969; Hoare and Pal, 1972). However it should be noted that depending on the programs involved and the nature of the ensemble chosen (canonical or micro-canonical), different results have been obtained for the stability of various structures. Many authors have observed that whenever the clusters contain certain 'magic number' of atoms (e.g. Mackay, 1962, Hoare and Pal, 1972), they form almost spherical shapes with nearly close packed surfaces which have exceptional stability. Such magic number clusters based on sphere packing arrangements have been observed experimentally by Kimota, Nishida (1977), Echt, Sattler and Recknagel

(1981) and others. These are generally structures with icosahedral symmetry which at larger sizes have been shown to relax to their conjugate structures, the dodecahedrons, or to fcc type close packed lattices. The literature on the subject of structures with icosahedral symmetry is rather overwhelming since the discovery of Schechtman, Blech, Gratias and Cahn (1984) of five fold symmetry in real bulk systems. The importance of this quasi-periodic symmetry (since the symmetry by itself cannot fill three dimensional space) has been reviewed in one of the many recent articles by Mort la Brecque (1988).

There have been extensive studies in the recent years of the electronic structure of atomic clusters using ab-initio approaches, see for example Kubo (1962), Messmer (1981), Rao, Khanna and Jena (1986), Landman *et al.* (1987). There has also been considerable effort trying to establish a shell structure for metallic clusters, which resembles the well established shell theories of atoms and nuclei used in quantum mechanical calculations; for a review of this field see De Heer, Knight, Chou and Cohen (1987). Clusters with magic number of atoms (magic number here corresponds to the shell structure and not sphere packing) have been observed experimentally by Ding and Hesslich (1983), Stephens and King (1983), Knight, Clemenger, de Heer, Saunders, Chou and Cohen (1984). In all this work the point should be stressed that the structures are only local minima on a configurational energy surface and we can only consider the relative probabilities of the occurrence of a particular morphology. One can consider a solid-like structure, which represents an apparent global minimum, and a liquid-like regime where more than one structure coexist. Similar ideas have been expressed by Berry *et al.* (1984) and Stillinger and Weber (1982). These authors considered the vibrational energy levels in clusters, with a deep narrow potential well with a sparse energy spectrum as solid-like and a broad shallow minimum with a high density of states as liquid-like structures. We shall return to the question of morphological potential energy surfaces for small particles in Section 4.

### 3 SMALL PARTICLES-STATICS

#### 3.1 *Structure and potential energy*

By small particles we shall mean particles having sizes between 1–1000 nm, thus differentiating them from atomic clusters. In industry this size range is important as it constitutes the useful range of most heterogeneous catalysts. The first observations of anomalous structures having five-fold rotational symmetry axes in material systems was by Melmed and Hayward (1959) during the vapor growth of metal whiskers for field emitter tips, and by Ogburn, Paretzkin and Peiser (1964) during the electro-deposition of copper dendrites. This was followed by detailed electron microscopic analyses during the late sixties by Ino (1966), Ogawa, Ino, Kato and Ota (1966), Ino and Ogawa (1967) and Allpress and Sanders (1967). These authors observed that during the vacuum deposition of fcc materials on non-metallic substrates the small particles formed were often non-crystallographic. These poly-tetrahedral structures were called multiply twinned particles or MTP's. A plethora of results obtained since

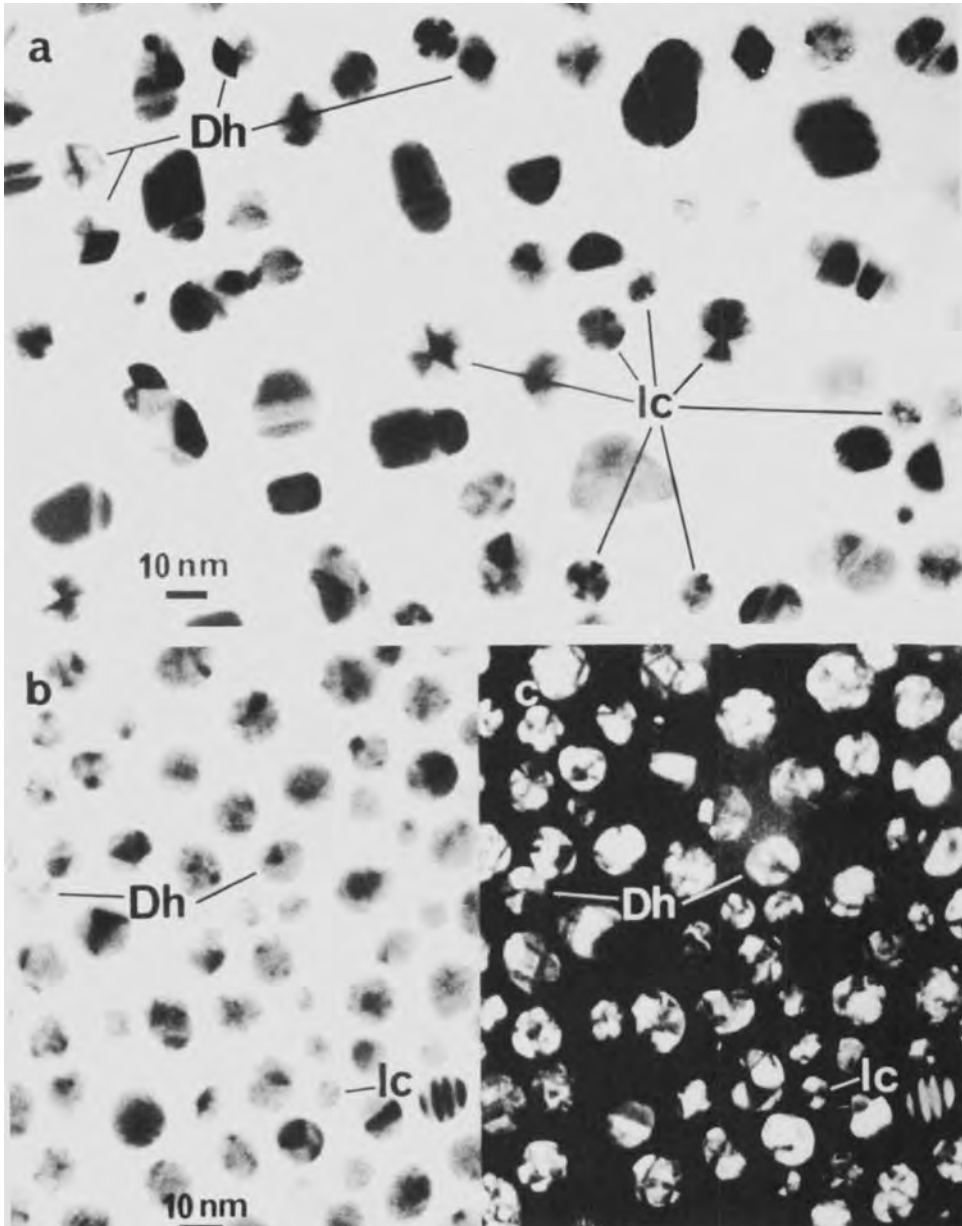
have confirmed that the preferred structure of ultrafine particles of a variety of materials are tetrahedral, icosahedral, cuboctahedral, pentagonal and their complex polyforms, many of them containing a multiplicity of internal twins. Table 1 shows a collection of some of the results published over the last twenty years on the anomalous structures of various materials prepared by different techniques.

Figure 1 shows a typical low resolution electron microscope image showing the particle shapes that occur during the early stages of vacuum deposition of Ag onto rock salt. The basic structures of the two most commonly observed MTP's is shown in Figure 2 together with atomic resolution electron microscopy images. MTP's are non-crystallographic structures which to a first approximation are a collection of single crystal tetrahedra, twin related on their adjoining (111) faces. Five such units pack together with a  $D_{5h}$  point group symmetry to form a decahedral particle, and twenty units with an  $I_c$  symmetry form an icosahedron. Although these particles are assuming forms similar (in symmetry and packing) to those found in atomic clusters, they are highly distorted and defective (see for example Marks and Smith, 1983). It should be noted that when formed from perfect single crystal units the particle contains spatial discontinuities, thereby introducing inhomogeneous strains. Various defects other than twin boundaries, for instance partial dislocations, stacking faults, grain boundaries, notches at the twin boundary edges, re-entrant surfaces etc. also have been observed in MTP particles (see Smith and Marks, 1981; Marks, 1985c; Iijima and Ichihashi, 1987). The additional strain and twin energy associated with the formation of MTP's are balanced by a reduction of surface free energy. There has been conclusive experimental evidence for the presence of inhomogeneous strains in these particles shown by Marks (1985b). Various theoretical models, including homogeneous elasticity calculations by Ino (1969), structural modifications by Yang (1979), a Jahn-Teller or Pierls distortion by Bagley (1965), a dislocation model by Saito, Yatsuya, Mihama and Uyeda (1978), a disclination model by de Wit (1972), Howie and Marks (1985), Dundurs, Marks and Ajayan (1988), have been proposed.

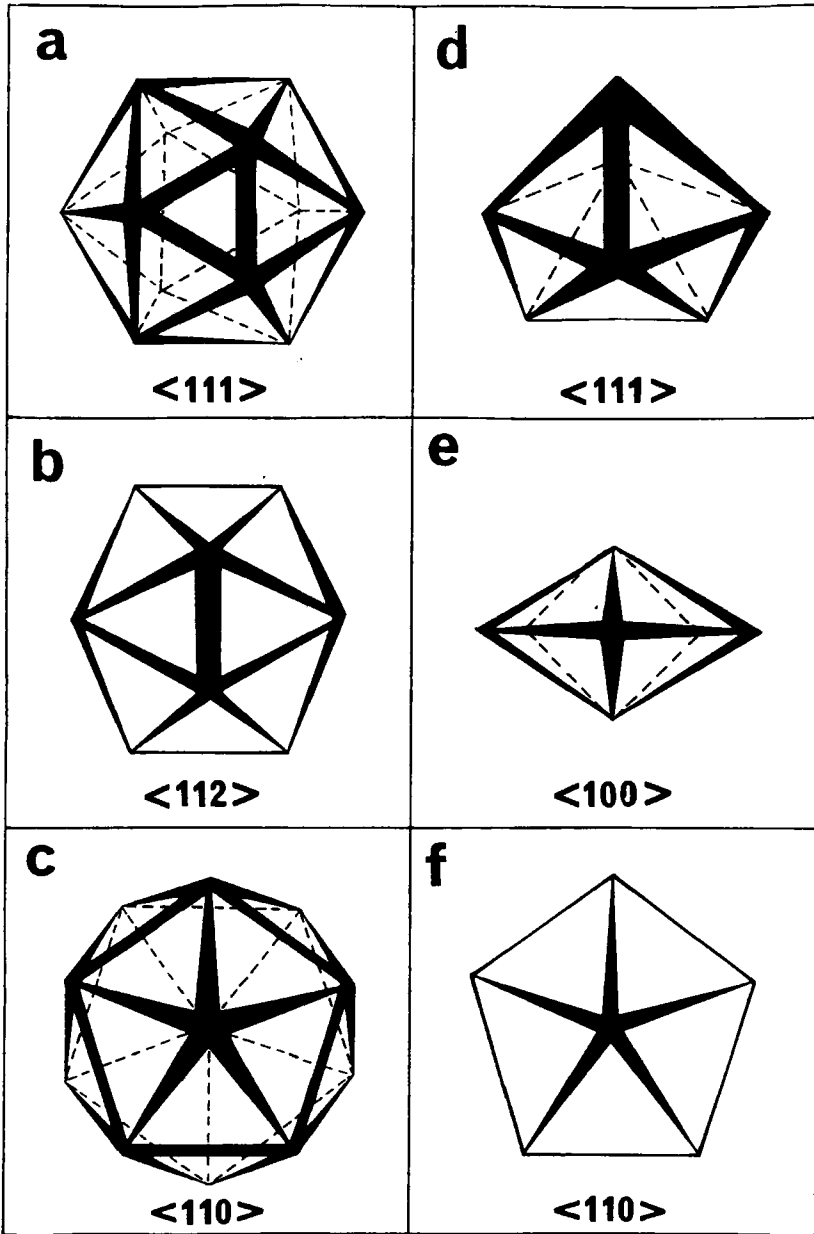
Fukano and Wayman (1969) and Hoare and Pal (1972) while considering the stability of clusters found MTP's to be among the more stable morphologies. The equilibrium surface morphologies of cluster size particles and their corresponding free energies have been analyzed in terms of semi-continuum approaches such as three-body interactions, packing corrections and capillary considerations by Griffin and Anders (1979), Martins, Car and Buttet (1981), Halicioglu and White (1981), Wang, Falicov and Searcy (1984), Marks (1985a) and many others. Gordon, Cyrot-Lackman and Desjonqueres (1979) calculated the cohesive energies of various size clusters with icosahedral and fcc type cuboctahedral geometries and found that for the same size but different geometries, the cohesive energy difference between clusters is extremely small (of the order of 500 cal/mole which is approximately 20 eV for a 25 Å radius particle) and co-existence of such structures is possible. The first real attempt to calculate the energetics of small particles and multiply twinned structures using continuum theories and macroscopic surface free energies was undertaken by Ino in 1969. He evaluated the free energies of various structures by including the cohesive energy, surface energy and adhesive energy associated with the particle-substrate bonding, elastic strain energy and the twin boundary energy associated

**Table 1** Some experimental results of observation of MTP structures in small particles of various material systems formed under different conditions. Here Dh, Ic, SC, CTP, LTP, and CCP stands for Decahedral MTP, Icosahedral MTP, Single crystal, Complex twinned particle, Lamellar twinned particle and Cubic close packed structure respectively.

<i>Authors (year)</i>	<i>Material</i>	<i>Substrate (if evaporated)</i>	<i>Size (Å)</i>	<i>Structure</i>
Melmed & Hayward (1959)	Ni	W, Fe, Pt	Whiskers	5-fold symmetry (pentagonal twins)
Ogburn <i>et al.</i> (1964)	Cu	Electro-deposition	Microns	Pseudo pentagonal twins
Schwoebel (1966)	Au	Au	< 1000	5-fold symmetric twins
Mihama & Yasuda (1966)	Au	NaCl	< 100	Twinned Particles
Allpress & Sanders (1967)	Au, Pd, Ni	Mica	50–200	Dh, Ic, SC, LTP
Ino & Ogawa (1967)	Au	NaCl, KCl	10–100	Dh, Ic
Kimoto & Nishida (1967)	Ag, Pd, Ni, Co	Evaporation in Ar gas	< 1200	Dh, Ic
Komoda (1968)	Au	NaCl, KCl	< 150	Dh, Ic
Ogawa <i>et al.</i> (1969)	Au	NaCl, KCl	20–100	Dh, Ic
Yagi <i>et al.</i> (1975)	Ag, Au	MgO, MoS <sub>2</sub>	20–500	Dh, Ic, SC
Gillet (1977)	Au	NaCl	30–250	Dh, Ic
Saito <i>et al.</i> (1978)	Ge	Evaporation in Ar gas	1000–5000	Dh, Twinned polyhedra
Heinemann <i>et al.</i> (1979)	Au	LiF, NaCl	50–200	Dh, Ic, SC
Marks & Smith (1981, 1983)	Au, Ag	KCl	100–1000	Dh, Ic, CTP, LTP
Matsumoto & Matsui (1983)	Diamond	Si	100–2micron	Dh, Ic twinned CCP
Hofmeister (1984)	Au	AgBr	100–1000	Dh, Ic, CTP
Marks (1985b, 1985c)	Au, Ag	NaCl	100–500	Dh, Ic
Matsui (1984)	Cubic Boron Nitride	Electron beam reduction	100–1000	Dh
Dhere <i>et al.</i> (1985)	Au	Colloidal	150–300	Twinned polyhedras
Dahmen & Westmacott (1986)	Ge precipitate	Al matrix	needles	Dh, CTP
Long <i>et al.</i> (1986)	Pt	Colloidal	5–30	Twinned Polyhedra
Wallenberg <i>et al.</i> (1986)	Pt	Colloidal	< 50	Structural instability
Wallenberg (1987)	Zn, Cd Rh, Pt	Various Techniques	10–100	Dh, Ic SC, Rafts
Curtis <i>et al.</i> (1987)	Cu	Colloidal	30–300	Dh, Ic, LTP
Iijima & Ichihashi (1987)	Au	Si/SiO <sub>2</sub>	< 50	Structural instability
Iijima (1987a)	Graphitized C clusters	Amorphous C	30–70	Truncated Ic
Iijima (1987b, 1987c)	Si, SiC	Gas evaporation	200–2000	Dh, CTP
Badzian <i>et al.</i> (1988)	Diamond	Si, Graphite	< 10 micron	Dh, SC, Ic Cuboids
Giorgio & Urban (1988)	Ag	Inert gas evaporation	30–100	Dh, 3-fold symmetry twins
Malm <i>et al.</i> (1988)	Ru	Micro-emulsion	10–50	Structural instability



**Figure 1** A typical ensemble of small particle structures found during the early stages of evaporation of Ag on to a NaCl substrate. Figure 1a and 1b show bright field and hollow-cone dark field images. Dh and Ic indicate decahedral and Icosahedral MTP's respectively.



**Figure 2** Figures 2a to 2c show the schematic of the structure of the icosahedral MTP in three major orientations. 2d and 2f show the structure of decahedral MTP's. 2g shows a high resolution electron microscopy (HREM) image of an Ic in a <110> orientation. Partial dislocations in the particle are arrowed. 2h Shows a HREM image of a Dh in <110> orientation.

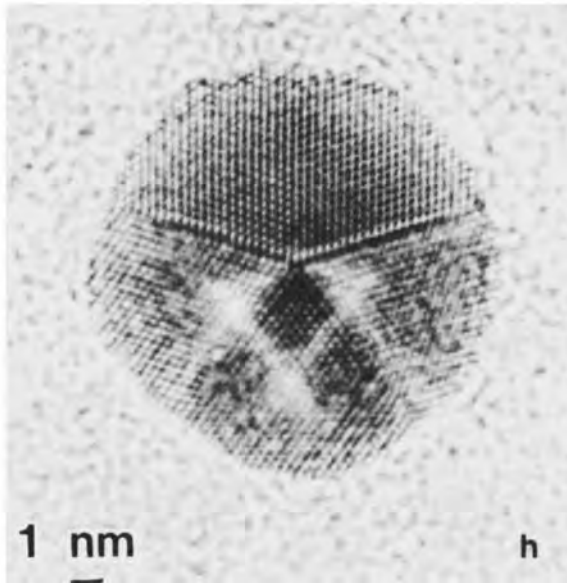
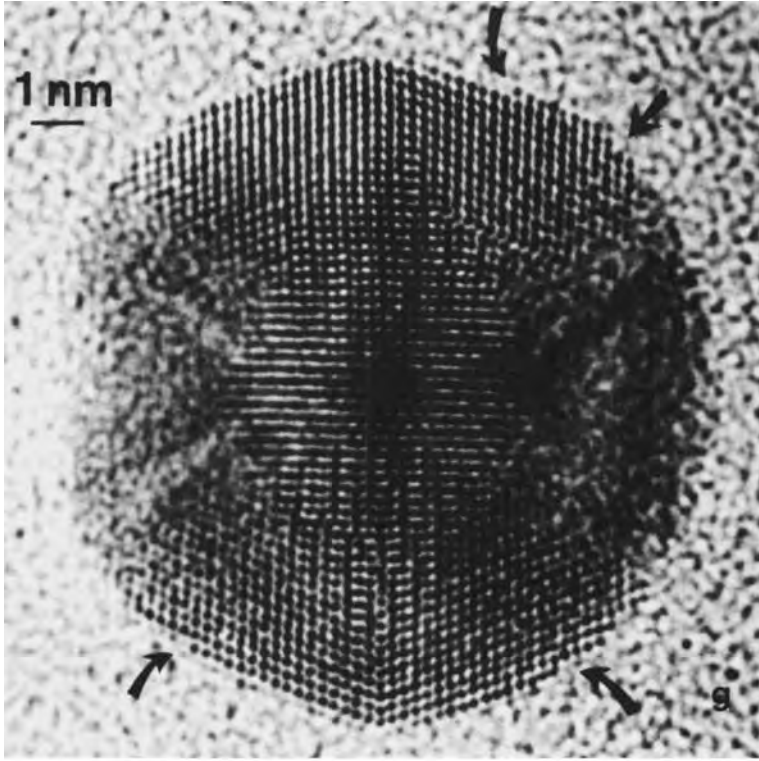


Figure 2 (continued)



with the multiple twins. He assumed the shapes of the single crystals and icosahedrons to be those given by the Curie–Wulff construction (see Herring, 1951; Linford, 1968; Rottman and Wortis, 1984) and pentagonal bi-pyramids to approximate and decahedrons. By evaluating the above energy balance he was able to show that for small sizes the icosahedral MTP was the most stable structure but the decahedrons were only quasi-stable with respect to a single crystal.

Later Marks (1984c) and Howie and Marks (1984) worked out semi-quantitative results for the stability of various structures which showed that both MTP's were stable compared to normal structures. In their model the equilibrium shapes of the MTP's were modified forms of the Curie–Wulff polyhedrons, incorporating extra point values for the twin boundaries in the construction. The surface energy was evaluated using a dimensionless energy parameter depending only on the shape and not on the volume of the particle, found by minimizing the surface energy integral with the constraint that volume remains a constant and the different segments match along the adjoining twin boundaries. The surface energies were assumed to be anisotropic and a strong faceting model, with only the low index (100) and (111) facets decorating the surface, was used in comparison to a liquid-like isotropic model. This is justified by experimental observations where high index facets are absent in small particles, since the high index faces act as nucleation sites and are eliminated in an atom-by-atom growth process. Experimental values for the surface anisotropies of small particles can be found in the works of Heyraud and Metois (1980), Menon and Martin (1986) and Flueli and Borel (1988) etc. but results are far from conclusive and information at low temperatures is almost non-existent. The spatial misfit formed when the tetrahedral segments are put together was taken care of in the above model by introducing a  $7.5^\circ$  wedge disclination and the strain energies were calculated using inhomogeneous two-dimensional elasticity. Disclinations are defects which are readily observed in frustrated configurations such as amorphous materials and in configurations involving interactions between spatially incompatible structures at the molecular scale, see for a discussion Kleman (1983). They are usually related to symmetries of rotation, similar to dislocations which are related to symmetries of translation in a crystalline lattice, and like dislocations are sources of internal strains (de Wit, 1971; Harris and Scriven, 1971).

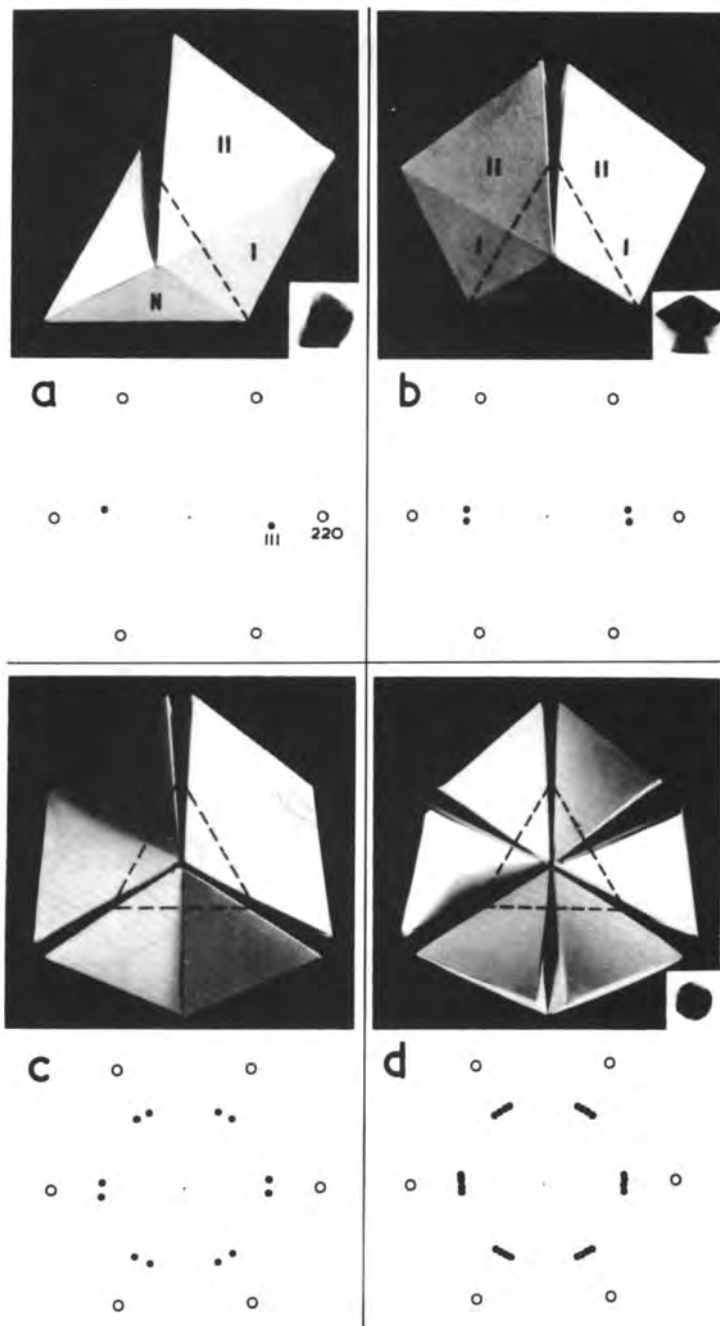
### 3.2 *MTP's-Growth and Twinning*

A point that should be raised here is whether MTP's are thermodynamic forms or kinetic shapes, forming and disappearing as growth artifacts. Attempts were made right from the early sixties to explain the formation of micro-twins in evaporated fcc metal films; see Matthews and Allinson (1963). They proposed that in the event of a thickness gradient in the evaporated film, the nuclei that were formed at the thin end of the deposit were misaligned with respect to each other. As a result of this, in the early stages of growth, it was more probable for neighboring nuclei to have lattices which are nearer to a twin relationship than a parallel alignment. If these nuclei coalesce, one of them could easily rotate and become exactly a twin of the other. As the probability of misalignment increased with decrease in nuclei size, it

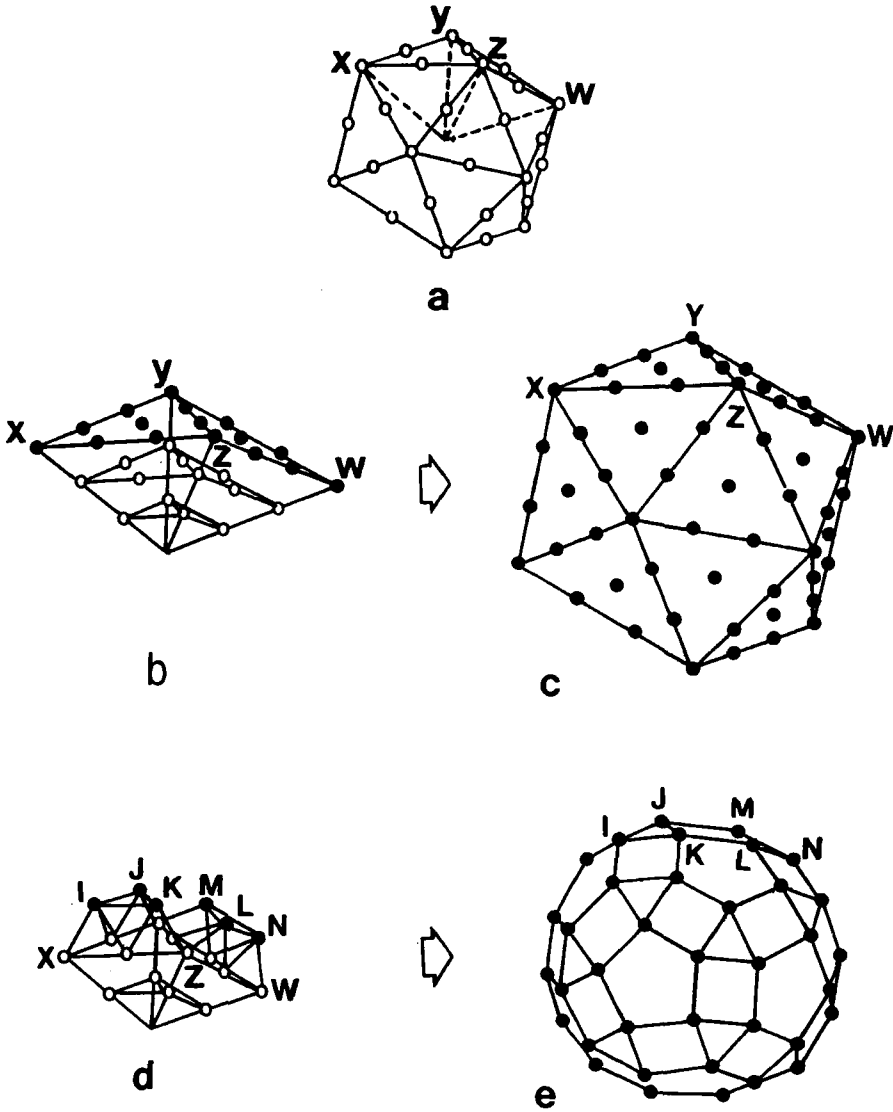
was found that the volume of twins found was smaller compared to the bulk. It was proposed that after coalescence of many nuclei, the twins could spread over the (111) facet of the larger nuclei as a step would move over a growing crystal.

The problem still remained to explain the twin formation in individual nuclei or a small particle before coalescence took place. A model for the growth and twinning in MTP's during crystal growth was proposed by Allpress and Sanders in 1967. They considered that the most stable arrangement of three atoms on a substrate is a triangular array lying fixed on the substrate. Depending on the relative bonding energies between the metal-substrate atoms and metal-metal atoms a fourth atom can either form a planar or tetrahedral configuration. In the former case, where the substrate surface is in a high energy configuration (kinked and rough), continued growth could produce planar layers of atoms (forming raft-like or lamellar structures). But in most practical cases, especially during epitaxial vapor depositions where the substrates are smooth, discrete tetrahedra are formed as nuclei. These could further grow into 3-dimensional clusters, and by packing considerations expose the low-index faces (where atoms are in high coordination positions) on the surface. Renucleation of a layer of atoms on such surfaces is then accompanied by a large probability of faulting. Thus primary twins could be introduced on to these faces, and could be followed by formation of successive secondary and tertiary twins, finally resulting in pentagonal and icosahedral particles with multiple twins. If the metal-metal interaction is very strong, highly faulted crystallites could result at early stages of growth, but could undergo rearrangements into low energy and ideal tetrahedral structures which then grow into MTP's by the same mechanism. This mechanism of growth by successive twinning is illustrated in Figure 3. The authors also suggested that larger crystals could be formed by particle coalescence, either retaining their original structures or, due to high atom mobility and liquid-like coalescence of clusters, reforming into new and rather perfect structures after coalescence.

Gillet in 1979 proposed another model for the formation of MTP's. He suggested that the decahedral and icosahedral particles are characterized by pentagonal crowns of atoms around their 5-fold axes. Growth then involves a layer-by-layer process around the existing nuclei, leading to pentagonal symmetry. Farges, de Feraudy, Raoult and Torchet (1983, 1984) in a similar model proposed two growth mechanisms for the growth of a multilayer icosahedra. They suggested that the growth of an extra layer of atoms on an existing collection of twenty tetrahedra, which constitutes an icosahedral nucleus could proceed either by the formation of an extra fcc layer by the adatoms taking up the normal fcc positions, or by the formation of an extra layer corresponding to a twin. The sequence of the two growth mechanisms is given in Figure 4. Depending on the potential energy criteria the authors conclude that the latter arrangement becomes unstable with respect to the former for icosahedra having more than three layers. In a different structural model, Bagley (1965), Yang (1979) etc. proposed that the icosahedrons and decahedrons, rather than being collections of discrete crystallites in twin orientation with each other, are actually structures with distorted body-centered orthorhombic and rhombohedral point group symmetries respectively. Although they were able to show this from a purely geometric point of view, no account was given for the energetics and kinetics of growth and transformation. Recently Iijima (1987c) put forward an argument, similar to the Gillet model,



**Figure 3** Photographs of models of multiply twinned crystals, with diffraction patterns from the crystals below them. a) A twin I grows on the face N of a crystal sitting on the substrate. b) Secondary twin II grows on one face of I and the crystal appears pentagonal when viewed from above. c) Shows another possibility of twinning on another face of the original crystal N. d) Structure produced when tertiary twins are formed on the uppermost faces of the crystal shown in c.



**Figure 4** Growth mechanisms producing a multilayer icosahedron. a) An icosahedral nucleus having two complete layers (55 atoms). b) The external face of one of the tetrahedra is covered with a third layer of regular fcc layer, and c) the corresponding 3-layer icosahedron when completely covered. d) The same tetrahedra covered with a third layer in twin fault position, and e) the corresponding structure (rhombicosidodecahedron) when full layer is formed over the structure shown in d.

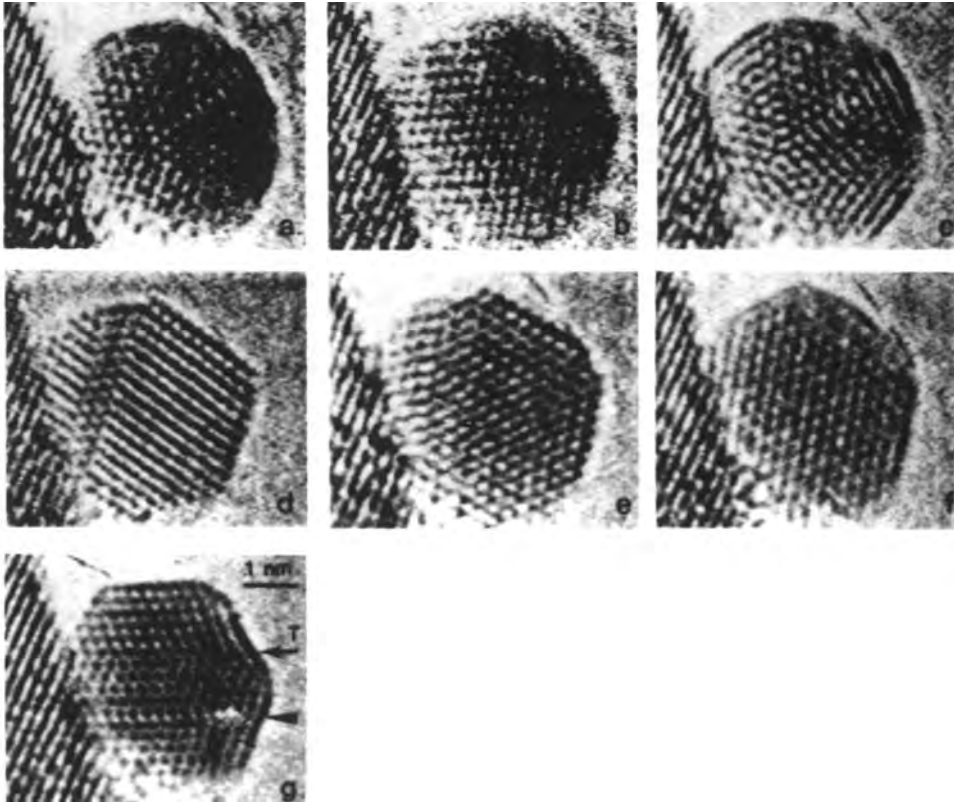
for the growth of decahedral MTP's in fine particles of Si, by considering the crystallization from liquid droplets. He assumed that a liquid droplet is formed and an embryo of the decahedral MTP is nucleated on the surface of the droplet, which subsequently grows along the pentagonal symmetry axes into a compact decahedral MTP. A question of importance is whether the structures are crystallo-

graphically inter-related, and suggestions by Mackay (1962), and Marks (1980), imply that thermal vibrational modes can induce structural transformations between various existing single crystals and MTP's, although experimental observations to support this have not yet been presented.

A classic paper is the one by Yagi, Takayanagi, Kobayashi and Honjo (1975), which demonstrate most of the above models experimentally. This was the first ever proof for the different growth mechanisms that were proposed by various authors, thus clarifying many of the existing controversies regarding the way structures evolve during the atom-by-atom growth phenomena. They observed in-situ inside the electron microscope, the ab-initio nucleation and growth of Au and Ag MTP's, coalescence and reformation into compound MTP's, and their formation from successive twinning starting from epitaxial single crystal particles. These experiments prove that MTP's have to have at least the thermodynamic stability of the local minima on the energy surface. Apart from ideal pentagonal and icosahedral MTP structures, compound and asymmetric structures (see Matsui, 1984; Marks, 1985c) are also found in most systems which are quite stable up to large particle sizes.

#### 4 SMALL-PARTICLE DYNAMICS

So far we have been concentrating on the static structure of small particles. But is such a simple static analysis adequate? Recent electron microscopy observations using real time video recordings by Iijima and Ichihashi (1986), Smith, Petford-Long, Wallenberg and Bovin (1986) and Wallenberg, Smith, Petford-Long and Smith (1986) have indicated that particles smaller than 50 Å in size, under an intense electron beam, exhibit structural instability and fluctuate between various MTP and single crystal shapes with frequencies greater than 50 Hz. It has also been observed by Malm, Bovin, Petford-Long, Smith, Schmid and Klein (1988) that in material systems that do not readily form MTP structures, for example ruthenium, the fluctuations take place between close packed structures of hcp, ccp and bcc with similar frequencies. A similar type of phase transition between ordered crystalline lattice and a chaotic cloud of ions have been observed recently by Blumel, Chen, Peik, Quint, Schleich, Shen and Walther (1988) in a trapped ion source of laser cooled ions. A typical sequence of a structural transformation during the electron beam irradiation of a small particle of gold, taken from single frames of a real time video recording, is shown in Figure 5. These observations are commensurate with the configurational instabilities in clusters predicted by Hoare and Pal and others, except that the phenomena is now extended to larger systems. It should be noted that the particles are quite stable under low electron beam fluxes, which means that there exists a critical activation energy barrier between the stable structure and the instability region. Systematic experiments monitoring the exact evolution sequence in shapes have yet to be done in order to understand the nature of such transformations. The effect of the substrate interaction could be vital in deciding the value of this activation barrier, as discussed by Blaisten-Barojas, Garzon and Avalos-Borja (1987) in the wetting transitions and morphologies of clusters as a function of the



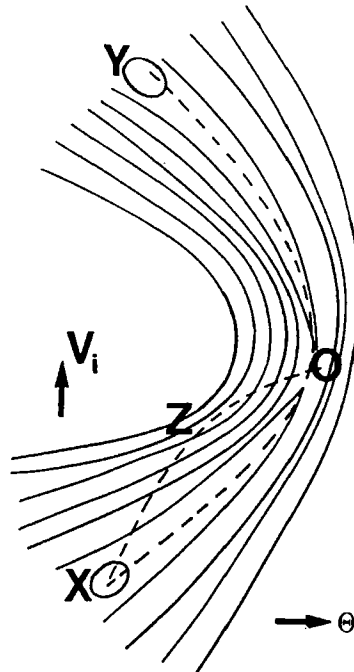
**Figure 5** Shows the structural changes observed in a 3.5 nm gold crystal supported on amorphous silicon, as seen in single frame exposures from a real time video recording. The shapes change as follows: a) Icosahedral. b) Single crystal; 1.8 sec. c) Icosahedral; 4.2 sec. d) Stacking fault; 6.0 sec. e) Twin plane; 6.2 sec. f) Single crystal; 9.6 sec. g) Stacking fault (arrowed) and a twin plane, T; 20 seconds.

substrate strength, and by Ino (1969) in the values of adhesive energies chosen in the calculation of the energies of MTP's.

So far the theories had only given information about the structure of individual particles, based on the potential energy arising from the bonding of atoms and electronic contributions. Even this was rather limited to the idealized structures involved and the size ranges that could be treated by ab-initio theories. The theoretical models of growth and kinetics were treated qualitatively in order to match experimental results. Although the approximate stability of MTP's with respect to a single crystal particle was demonstrated in the models described in the previous section, it should be obvious that in order to understand the nature of phase equilibria between the various asymmetric shapes and the structural fluctuations one needs to compute the free energy surfaces and the activation energy barriers existing between the different local minima. Marks (1984a) proposed how a modified form of the Wulff construction could be applied to the general problem of surface morphologies in

twinned particles. By considering an anisotropic surface energy for a small particle and using a two variable approach, the volume fractions of the different segments that formed the twinned particle and for arbitrary values of the partition fraction of the twin boundaries between the adjacent segments, a hypothetical potential energy surface was constructed for the twinned particle. The basic procedure involved a constrained minimization of the surface and twin boundary energy at constant volume. Such a potential energy surface is shown in Figure 6. The various allowed solutions of the partition fraction represented the various local minima on the potential energy surface. At higher temperatures when the surface of the particle becomes more isotropic, the restraint action of the twin boundaries will be lifted and the minima will be converted to saddle points, suggestive of a 'phase change' in twinning. But the discussion was qualitative and lacked quantitative figures for energy values as functions of temperature, anisotropy and particle shape.

In order to understand how the energy surface of a small particle populates the infinitum number of structural configurations we took a slice, one line along the  $n$ -dimensional energy surface, corresponding to a series of asymmetric decahedral multiply twinned particles. The movement of an eccentric disclination from one end

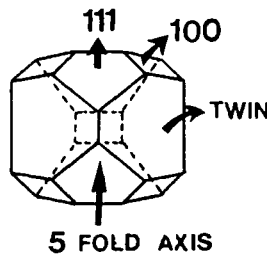
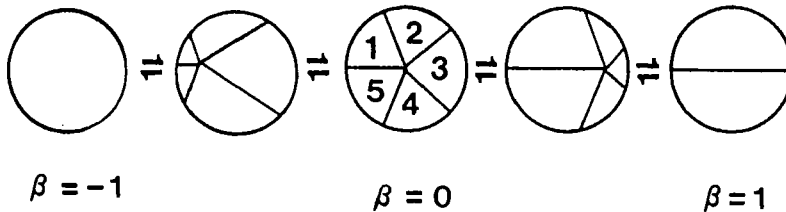


**Figure 6** Hypothetical potential energy surface for a twinned particle. Energy contours correspond to non-equilibrium values of the relative volumes of the tetrahedra,  $V_i$ , and the relative fraction of the twin boundary energy shared by two adjacent single crystal segments,  $\theta$ , all other variables being minimized.  $X$  and  $Y$  represent single crystals and  $O$  is a constrained minima, a Wulff-polyhedron for the twinned particle.  $OX$  and  $OY$  are low energy paths but the motion of the particle is constrained by the geometry of the twin boundary and hence to the path  $OZX$ .

to the other, as shown in Figure 7 describes the evolution in shapes starting with a single crystal and ending in a bi-crystal or a particle with one twin boundary. The model assumed for the calculation of surface energies of individual particle shapes is similar to the one by Howie and Marks (1984) and can be found in Dundurs, Marks and Ajayan (1988) and Ajayan and Marks (1988). The various forms of the elastic energies were calculated using an inhomogeneous 2-D elasticity model for the disclination, the position of which inside the particle defining the shape of the particle.

Figure 8 shows the potential energy surfaces for a 25 Å particle as a function of the particle shape parameter, for three different values of surface anisotropy ratio ( $\gamma_{100}/\gamma_{111}$ ). An obvious result from this is that the stability of the particle is dependent on the surface anisotropy. Even before introducing the temperature dependence of the system one can predict that the energy variations, and hence the thermodynamic stability, decrease as the surface energy becomes more isotropic. The potential energy surfaces were converted into free energy surfaces (shown in Figure 9) by evaluating the defect and surface entropies. This was done using the perturbation theory of Huntington, Shirn and Wajda (1955) for the entropy contribution from the disclination and the experimental values of surface entropy given by Kirchner and Chadwick (1970). A schematic of the free energy calculations is given in Table 2. The same effect of decreasing the anisotropy is observed by increasing the temperature, an expected result.

The instability should not be confused with the onset of melting, since the difference in the maximum activation energy for transition between any of the structural forms



**Figure 7** (a) shows the evolution of a series of single crystal ( $\beta = -1$ ), asymmetric decahedral MTP's ( $0 > \beta > +/ - 1$ ), symmetric MTP ( $\beta = 0$ ) and a bicrystal ( $\beta = 1$ ) as a disclination moves from one end of the particle to the other. The shape parameter,  $\beta$ , is defined as the fractional distance of the disclination from the center of the particle. Figure (b) shows the basic Curie-Wulff polyhedron, which forms a segment of the decahedral particle, used in the calculation.



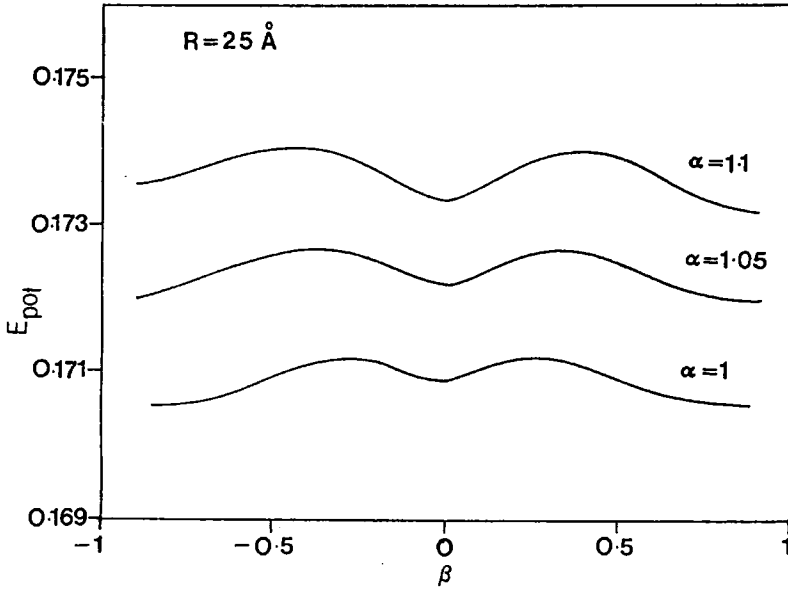


Figure 8 Shows the variation of the total potential energy with particle shape, evaluated for three values of the surface anisotropy ratio,  $\alpha$ . The energy units are arbitrary.

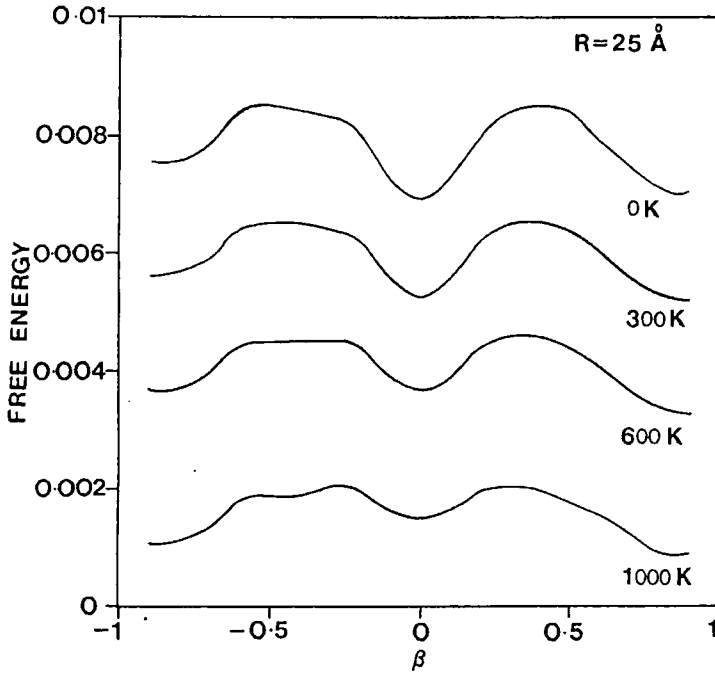


Figure 9 Shows the free energy surfaces, obtained after adding the entropy contributions to the potential energy surfaces of Figure 8, as a function of the particle shapes at different temperatures.

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**Table 2** Shows the schematic of the calculations used in the determination of the free energy surfaces in small particles as a function of size, shape and temperature. Here  $\gamma$  = surface specific energy,  $\omega$  = angle of the wedge disclination,  $\mu$  = shear modulus,  $\kappa = (3 - \nu)/(1 + \nu)$  where  $\nu$  is the Poisson's ratio.  $r_1$  and  $r_2$  are the conjugate coordinates of the disclination system,  $a$  = particle radius,  $\beta$  is the shape parameter,  $\epsilon_D = \omega/2\pi$ ,  $V$  = volume of the particle,  $A$  = surface area,  $g$  = surface stress tensor (taken to be 1),  $\eta$  = Gruneisen constant,  $dV$  = dilatation in atomic volumes,  $k$  = Boltzmann constant and  $H$  and  $S$  denote enthalpy and entropy respectively.

## I. Potential Energy

### 1. Surface energy (Wulff's theorem)

#### a. Dimensionless energy parameter:

$$E_w = \int (\gamma_A/\gamma_{111}) V^{-2/3} dA$$

#### b. Surface energy = $E_w \gamma_{111} V^{2/3}$

### 2. Elasticity of the disclination (2-D)

#### a. Airy stress function (using slab analogy: Ref. Dundurs *et al.*, 1988, *Phil. Mag.*, **57**, 605):

$$\phi = [\omega\mu/\pi(k+1)][r_1^2 \log(r_1/\beta r_2) + 0.5(1 - \beta^2)(a^2 - r^2)]$$

#### b. Strain energy of disclination:

$$W_D = 0.25\epsilon_D^2 \mu V(1 - \beta^2)^2/(1 - \nu)$$

#### c. Surface stress energy:

$$W_{\text{Stress}} = 0.5\epsilon_D g \gamma_{111} E_w V^{2/3}(1 - \beta^2)$$

## II. Entropy

### 1. Entropy of defect (Vibrational):

#### a. Temperature dependence of elastic stored energy:

$$\begin{aligned} S_{E1} &= -dW/dT = -(dW/d\mu)(d\mu/dT) \\ &= 0.25\epsilon_D^2 V(1 - \beta^2)^2(d\mu/dT)/(1 - \nu) \end{aligned}$$

#### b. Dilatation due to stresses (Gruneisen relation):

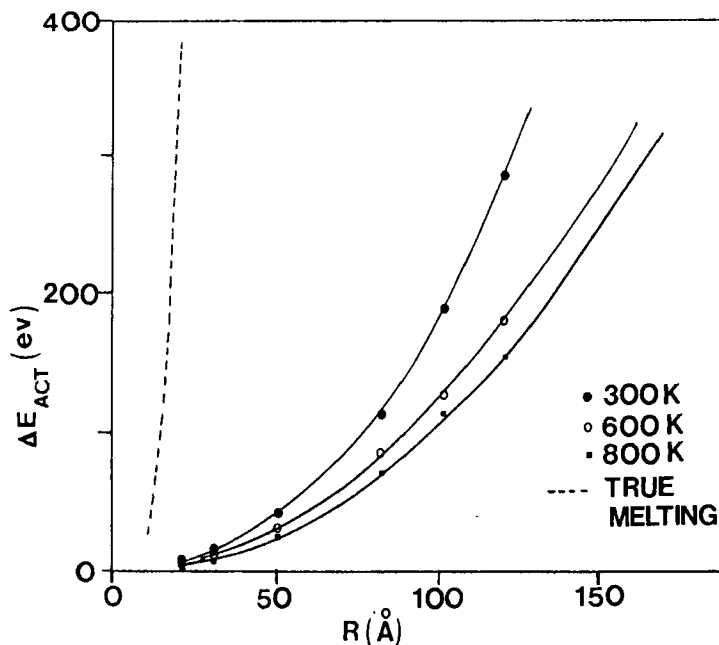
$$S_{\text{Dilat}} = -3\eta dV/k$$

### 2. Entropy due to surface anisotropy:

$$S_{\text{Anis}} = E_w \gamma_{111}^S V^{2/3}$$

$$\text{where } \gamma_{111}^S = -(d\gamma_{111}^H/dT)$$

that we have considered, both at room temperature and higher temperatures, is orders of magnitude less than that for melting (Couchman and Ryan, 1978; Borel, 1980), see Figure 10. This basic difference in the two instabilities will be discussed at a later stage in the paper. Another interesting result from these calculations is the fact that the maximum activation barrier between the different shapes at room temperature is very small, about ten electron volts for a 25 Å particle. This value is taken over the entire energy surface, and the energy barrier between two neighboring configurations during a structural fluctuation sequence should be orders of magnitude smaller. Even the maximum energy barrier corresponds to only about 0.0005 eV per atom, a value much lower than  $kT$  at room temperature. Given the classical degrees of freedom for at least those atoms residing in the first few surface shells, the particle can undergo structural rearrangement with rather high probabilities. By analogy with



**Figure 10** Shows the maximum activation energy barriers over the entire free energy surface as a function of the particle size, at different temperatures. The dotted line corresponds to the activation energy barriers for the thermodynamic melting of small particles (taken from Borel, 1981; Couchman and Ryan, 1984) and is seen to be orders of magnitude larger.

quantum mechanics one could say that as the energy differences (fluctuation energy) are becoming smaller the uncertainties in finding the particle in a particular configuration is increasing.

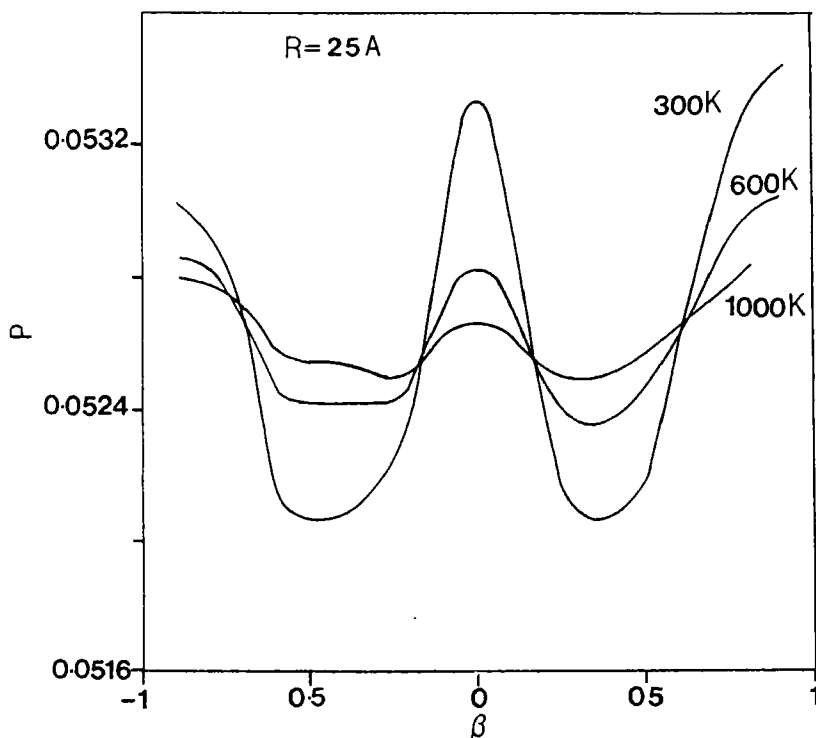
## 5 “QUASI-MELTING”

The configurational instability suggested by the free energy curves of small particles, to distinguish it from thermodynamic melting, shall be called “quasi-melting”. This is the same type of phenomena found in small clusters by computer calculations, and experimentally observed in small particles when a certain amount of energy is provided by an external source. Following authors such as Stillinger and Weber (1983), Berry, Jellenik and Natanson (1984), Honeycutt and Anderson (1987), we shall treat this coexistence region of a ‘group of inherent structures of similar energy’ as a separate phase occupying a region of the configurational space. This raises questions about the possibility and nature of a phase transition, but we shall discuss this later.

It should be quite clear by now that when one talks about the ‘structure’ of a small particle one is only considering the most probable statistical occupancy of the various local minima that populate the shallow energy surface. In order to semi-quantify the idea of “quasi-melting” we chose to define an index,  $I$ , which is the ratio

of the Boltzmann probability factor of the minimum to the maximum value on the energy surface for a particular size of the particle at a certain temperature. This follows directly from the free energies involved and is shown in Figure 11. As the temperature is raised the probability distributions flatten out and the particle escapes into a quasi-molten state. For a given value of the index, say 0.98, 98% of the particle shapes have equal probability of existing on the energy surface, or, in other words, the configurational space has expanded 98% with respect to the occupancy of a single solid-like crystalline structure. The value of this index is quite arbitrary, but nevertheless expresses the extent to which the particle becomes unstable.

Since the systems that we have considered are small the effect of statistical fluctuations are immense and the question arises whether equilibrium thermodynamics is valid in this range. It should be noted that our results in the regime of "quasi-melting" are only extrapolations and any attempt to define the system in terms of thermodynamic variables should be treated with caution. For particles with such small sizes the equilibrium thermodynamic variables have meaning only when the particle is coupled with a reservoir (see Kittel, 1988). It looks promising to relate the phenomena to situations in which irreversible thermodynamics (see Nicolis and Prigogine, 1977; Prigogine, 1980) plays a major role in self-organization and evolution of dissipative structures, where non-equilibrium may be a source of order, as seen in



**Figure 11** The Boltzmann probability factors,  $P$ , for various shapes in a 25 Å particle, shown at three different temperatures.

many physical and biological systems. In these situations when the system passes through a region of the configurational space where the energy is finely distributed between the many 'eigenstates' (by analogy with quantum mechanics), the system may leave the thermodynamic branch and, aided by macroscopic fluctuations, internal or imposed externally, may undergo bifurcations into an altogether new structure. This may introduce an extra entropic term, similar to a communal entropy during melting, of the order of a small fraction of  $R \ln 2$  as discussed by Stishov, Makarenko, Ivanov and Nikolaenko (1973), and Tallon (1980). This new entropy term could more than offset the activation barriers, thus stabilizing the quasi-molten state. A major difference between the two is that whereas the dissipative structures the bifurcations are localized both in time and space (microscopic patterns are evolved in macroscopic systems), quasi-melting should be a phenomena localized only in time.

Such ideas mentioned in the above paragraph can only be expressed qualitatively and work remains to be done. A rough idea is obtained when one plots the relative fluctuations in energy, with respect to a mean energy level, in configurational space as a function of temperature for different particle sizes. Figure 12 shows that at higher temperatures the relative energy fluctuations in a 10 Å particle become more than those for a 25 Å particle, whereas the energy barriers are much lower for the former.

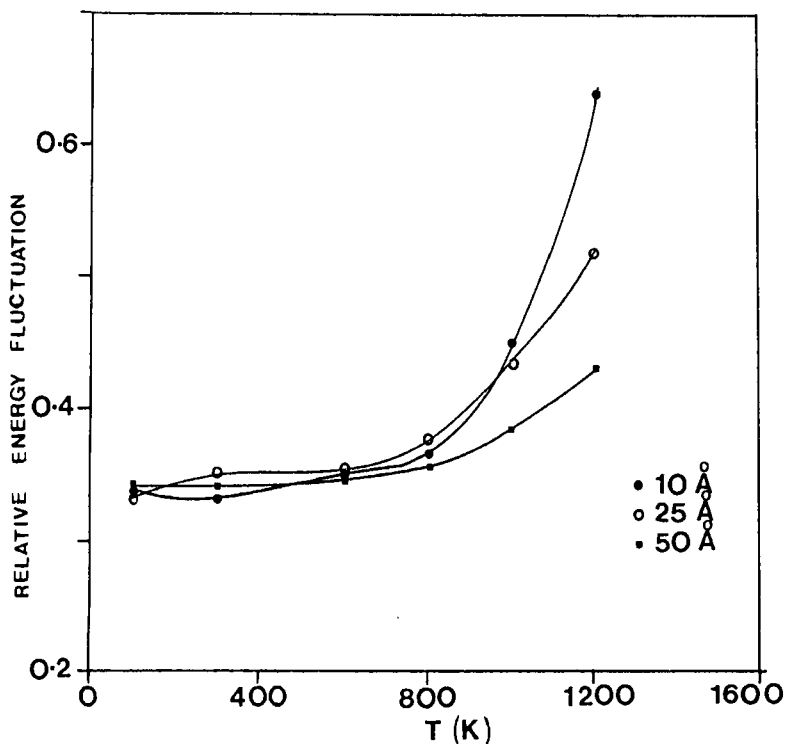
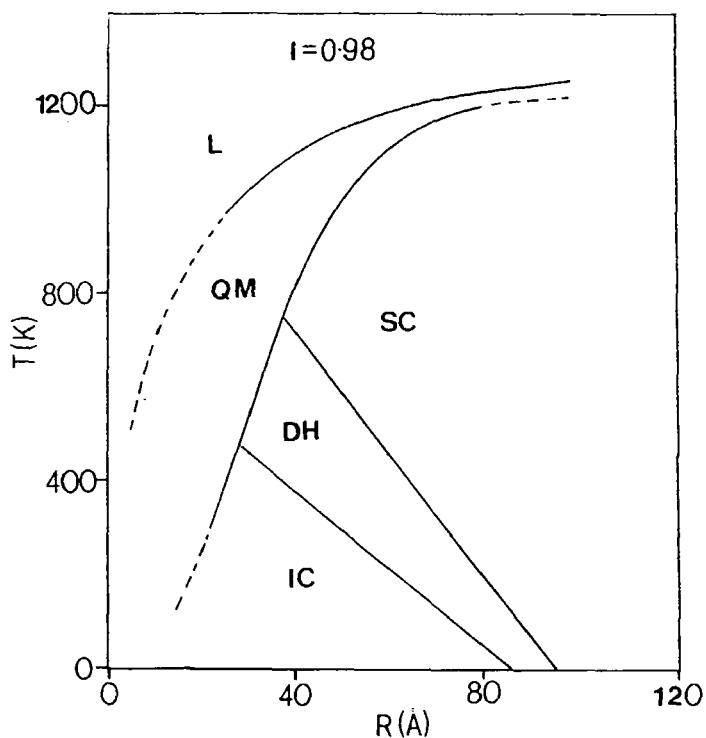


Figure 12 The relative fluctuations in energy, about the mean energy level, plotted as a function of temperature for three different particle sizes.

This indicates that with decreasing particle size the system exhibits an increasing tendency for fluctuation dependent non-equilibrium processes.

## 6 PHASE DIAGRAM

From the data of the free energies, the index of quasi-melting at different temperatures and sizes and the data for size dependent melting given by Borel (1980), a phase diagram can be constructed for small particles, as shown in Figure 13. The phase boundaries are semi-quantitative and far from rigorous. However, they indicate the stability regimes for the different important phases that are observed in many materials at smaller particle sizes. They also describe a new phase, a coexistence region of many structures which are energetically unstable or rather metastable. In real situations this region should be modified to take care of the substrate-particle interaction, the energy supplied by the external observant etc. The latter point, the fluxional nature of clusters, has been discussed in a recent article by Halicioglu (1988). Similar type of phase diagrams have been proposed before dealing with the instability



**Figure 13** Phase diagram for small particles. Part of the liquidus line has been taken from values obtained by Borel (1981) and Couchman and Ryan (1984). Dotted lines are extrapolated. QM stands for quasi-melting, IC for icosahedral structure, Dh for decahedral structure and SC for single crystal. The boundary of the QM phase corresponds to a value 0.98 for index of quasi-melting.

of the crystalline phase, see for example Wautelet, Laude and Antoniadis (1986) for thin films and wires, and Marks (1986) for polymorphs during thin film growth.

The phase diagram is important in predicting the nucleation and growth patterns in material systems as a function of temperature. The values used in the calculation are for gold but the general trend in the phase boundaries should not vary appreciably with other materials. A unique feature in the phase diagram is that we have a new phase (by phase we only mean a coexistence region of different structures of similar energy states and not the usual thermodynamic Gibbsian definition of the state of matter). There are interesting ramifications of the phase diagram of small particle growth. As nucleation proceeds by atom addition, the nuclei formed remain highly unstable not only against evaporation of the nascent atoms to decrease the free energy, but also due to the inherent structural instability. The latter instability remains even after the formation of a stable nucleus until the activation energy barriers becomes large and a single solid like structure is stabilized. This could be the first precursor of a crystalline solid state. It does not mean that this will be the final crystal structure of the infinite lattice. It only means that a particle with a strong global minima on the energy surface is formed for the first time.

The phase diagram could also predict the nature of epitaxy in different systems. For example, at higher temperatures where the quasi-molten phase is contiguous with the single crystal phase we would expect good epitaxial growth. Experimental observations by Ino (1966), Ino and Ogawa (1967), Roos and Vermaak (1972), Heinemann *et al.* (1979, 1983), see Table 1, for noble metals on alkali halide substrates and palladium on MgO suggest that our predications of the phase boundaries are consistent within limits with experimental results. The phase diagram may also be valuable in the field of catalysis since shape and structure of particles influence the catalytic activity (see for example, Yacaman, Fuentes and Domenguez, 1981; Freund, Lynch and Szymanski, 1986). The variability found in many supported catalyst systems could be due to the meta-stable structure-sensitive catalytic states (Spencer, 1986) and their corresponding reactivity. The onset of quasi-melting in small particles could be related to the 'Huttig' temperature used in catalysis at small particle sizes, which is suggestive of a soft transition between an equilibrated metal surface and a metastable metal surface of a small particle catalyst due to an appreciable change in the mobility of the surface atoms.

Computer simulations by Honeycutt and Anderson (1987) and others predict that for large clusters (up to a few thousand atoms), the stable shape is icosahedral type clusters at lower temperatures, but fcc or tetrahedral at higher temperatures. Farges *et al.* (1987) suggest that the transition of the icosahedral structure to fcc type lattice, at larger sizes, could be due to addition of incomplete layers onto the icosahedral shell in order to avoid strains and compressions, inside the particle, which increase as the number of the icosahedral shells are increased. Our phase diagram also shows the icosahedral structure as a low temperature phase and the decahedron with a narrow range of stability. For better quantitative results, which should include the effect of substrate and so on, the phase boundaries have to be tested and refined with carefully monitored experiments. An important point that should be stressed here is that the energy surfaces for small particles are strongly surface energy limited (similar

to an increased manifestation of surface tension effect in liquids when they are constrained to a capillary), and do not vary much with different crystal structures. This is also borne out by the fact that the surface profiles of small particles, when seen without strong substrate interaction (e.g. amorphous substrates), appear mostly rounded and close to spherical.

## 7 DISCUSSION

The results from our theoretical calculations lead us to believe that same type of structural fluctuations observed for atomic clusters can be extended to larger systems. The various anomalous properties observed at smaller sizes can be attributed to the fact that in that regime many new metastable and unstable phases appear, due to the fine distribution of energy levels and driven by external or non-equilibrium statistical forces. The environment could play an important role in deciding the exact structural configuration of these low-dimensional systems, and any generalization of results on the properties of these materials should be treated very carefully.

The question of the nature of the phase transitions at very small particle sizes is a curious one, and has yet to be resolved. Although melting itself is a complicated as well as a controversial phenomena, the relationship between the two is worth examining. The simplest and probably the most successful model of melting is based on lattice instability, propounded over the years by Lindemann (1910), Herzfeld and Goepfert-Mayer (1934), Born (1939) etc., and recently reviewed by Boyer (1985), has been used by authors like Takagi (1954), Buffat and Borel (1976), Couchman and Ryan (1978), Hasegawa, Hoshino and Watabe (1980) to calculate the depression in melting point in lower dimensional systems. It appears from these works that there is no unique way of defining the melting point in small particles. Moreover, work on small clusters predicts that there exists a range in the melting transition and the energy change in the vicinity of this range is a slowly varying function of temperature. The boundary of quasi-melting could be treated as an extension of this regime and hence the phase transition associated with it should be weaker compared to the melting transition in the corresponding real crystal. The Lindemann criteria in melting may be extended to a lower critical temperature for the instability range (from quasi-melting to melting) in small particles. Quasi-melting could set in when the atomic vibration exceeds a certain fraction of the Lindemann's criteria (say,  $T_{q.m}/T_m$ ), with the actual melting taking place at the value given by the above criteria. This lower limit of instability could be due to the lower average coordination of atoms in a small particle resulting in a higher entropy and the lack of long range order which stabilizes the infinite crystalline lattice. Authors such as Eters and Kaelberer (1977), Lee, Barker and Abraham (1976) and Briant and Burton (1975) have provided inconclusive results for the nature and order of the structural phase transitions in clusters containing a few atoms. Statistical mechanical predictions suggest that sharp phase transitions cannot exist in small finite systems. This is also suggested by the fact that the activation energies involved during quasi-melting are much smaller than those for melting. The fact remains that the order of the



solid-liquid phase transition is controversial. It would be interesting to see the analogy between quasi-melting and displacive transformations (Boyer and Hardy, 1981; a similar analogy is discussed by Boyer (1985) in the case of melting). Here, above the transition temperature the parameter that defines the lattice undergoes a change from a static to a dynamically fluctuating one. The potential energy surface in the latter shows a distinct double well structure of a low and high symmetry crystal lattice where as in the former the energy surface consists of many weak well local minima with no preferred structure after the transition. The instabilities in the shape of a small particle was explained in terms of molecular motions associated with a redistribution in the vacancy concentration in different parts of the crystal, by Searcy (1984). A dynamic equilibrium is established when the vacancies are so distributed that the molecular fluxes between various regions of different binding energies are equalized. Tholen (1981) suggested that structural changes in small particles could result from vibrational amplitudes during a martensitic type of transformation. He associated such a shear transformation with the passage of supersonic dislocations through the particle.

An extension of the work on small particles has involved correlating the electronic instabilities when an electron beam in the microscope induces excitations inside a small particle which provide the activation energy needed for it to quasi-melt. Most of the proposed mechanisms involve electronic excitations produced by the incident electrons, for example plasmon excitation, a coulomb explosion (Howie, 1986), localized melting and recrystallization due to secondary auger electrons (Williams, 1987). However a small particle is stable against ionization, especially at lower temperatures, due to the large gaps in the energy levels as suggested by Kubo (1962). Another question is whether the effect of temperature rise in a small particle is responsible for the instability. Calculations have indicated (Iijima, 1985; Dundurs, Marks and Ajayan, 1988) that the particle does not get thermally heated in the process of electron irradiation and remain canonical with the substrate. Buxbaum and Marks, (1987) proposed that the particle may be sensing an equivalent 'electronic temperature' which is localized in time and space. What thermodynamics or the phase diagram predict is the equilibrium structure and the position of the particle on a morphological energy surface. As the energy distribution becomes dense, statistical and non-equilibrium forces assume importance. Quasi-melting will give the probability that a particle can jump the potential wells on the energy surface. The exact route for the energy gain and phase transformation still remains unanswered.

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#### *References*

- Ajayan, P. M. and L. D. Marks (1988). Quasimelting and Phases of small particles. *Phys. Rev. Lett.*, **60**, 585.  
Allpress, J. G. and J. V. Sanders (1967). The structure and orientation of crystals in deposits of metals on Mica. *Surf. Sci.*, **7**, 1.

- Bagley, B. G. (1965). A dense packing of hard spheres with five-fold symmetry. *Nature*, **208**, 674.
- Badzian, A. R., T. Badzian, R. Roy, R. Messier and K. E. Spear (1988). Crystallization of Diamond crystals and Films by microwave assisted CVD-II. *Mat. Res. Bull.*, **23**, 531.
- Beck, T. L., D. M. Leitner and R. S. Berry (1988). Melting and Phase space transitions in small clusters: Spectral characteristics, dimensions and K entropy. *J. Chem. Phys.*, **89**, 1681.
- Bernal, J. D. (1960). Geometry of the structure of monatomic liquids. *Nature*, **185**, 68.
- Berry, R. Stephen., Julius Jellenik and Grigory Natanson (1984). Melting of clusters and melting. *Phys. Rev. A.*, **30**, 919.
- Blackman, M. and J. R. Sambles (1970). Melting of very small particles during evaporation at constant temperature. *Nature*, **226**, 38.
- Blaisten-Barojas, E., I. L. Garzon and M. Avalos-Borja (1987). Melting and freezing of Lennard-Jones clusters on a surface. *Phys. Rev.*, **B36**, 8447.
- Blumel, R., J. M. Chen, E. Peik, W. Quint, W. Schleich, Y. R. Shen and H. Walther (1988). Phase transitions of stored laser-cooled ions. *Nature*, **334**, 309.
- Borel, J. P. (1981). Thermodynamic size effect and the structure of metallic clusters. *Surf. Sci.*, **106**, 1.
- Born, M. (1939). Thermodynamics of crystals and melting. *J. Chem. Phys.*, **7**, 591.
- Boyer, L. L. and J. R. Hardy (1981). Theoretical study of the structural phase transition in  $\text{RbCaF}_3$ . *Phys. Rev. B*, **24**, 2577.
- Boyer, L. L. (1985). Theory of melting based on lattice instability. *Phase Transitions*, **5**, 1.
- Briant, C. L. and J. J. Burton (1975). Molecular dynamic study of the structure and thermodynamic properties of argon micro-clusters. *J. Chem. Phys.*, **63**, 2045.
- Buffat, Ph. and J. P. Borel (1976). Size effect on the melting temperature of small particles. *Phys. Rev.*, **A13**, 2287.
- Burton, J. J. (1970). Configuration, energy, and heat capacity of small spherical clusters of atoms. *J. Chem. Phys.*, **52**, 345.
- Buxbaum, A. and L. D. Marks (1986). The electronic temperature in TEM. Proc. XIth Int. Cong. on Electron Microscopy, Kyoto, 1441.
- Couchman, P. R. and F. E. Karasz (1977). The effect of particle size on debye temperature. *Phys. Lett.*, **62A**, 59.
- Couchman, P. R. and W. A. Jesser (1977). Thermodynamic theory of size dependence of melting temperature in metals. *Nature*, **269**, 481.
- Couchman, P. R. and C. L. Ryan (1978). The Lindemann hypothesis and the size-dependence of melting temperature. *Phil. Mag.*, **37**, 369.
- Curtis, A. C., D. G. Duff, P. P. Edwards, D. A. Jefferson, B. F. G. Johnson and A. I. Kirkland (1988). The preparation and structure characterization of an unprotected copper solution. *J. Phys. Chem.*, **92**, 2270.
- Dahmen, U. and K. H. Westmacott (1986). Observations of pentagonally twinned precipitate needles of germanium in aluminum. *Science*, **233**, 875.
- de Heer, W. A., W. D. Knight, M. Y. Chou and M. L. Cohen (1987). Electronic shell structures and metal clusters. *Solid state Physics* (ed: Ehrenreich, H. and D. Turnbull), **40**, 93.
- de Wit, R. (1971). Relation between dislocation and disclinations. *J. Appl. Phys.*, **42**, 3304.
- de Wit, R. (1972). Partial disclinations. *J. Phys. C: Solid state Phys.*, **5**, 529.
- Dhere, A. G., R. J. De Angelis, P. J. Reucroft and J. Bentley (1985). Twinned colloidal gold particles. *Ultramicroscopy*, **18**, 415.
- Dickey, J. M. and A. Paskin (1968). Phonon spectrum changes in small particles and their implications for superconductivity. *Phys. Rev. Lett.*, **21**, 1441.
- Ding, A. and J. Hesslich (1983). The abundance of Ar and Kr microclusters generated by supersonic expansion. *Chem. Phys. Lett.*, **94**, 54.
- Dundurs, J., L. D. Marks and P. M. Ajayan (1988). Structural fluctuations in small particles. *Phil. Mag.*, **57**, 605.
- Echt, O., K. Sattler and E. Recknagel (1981). Magic numbers for sphere packings: Experimental verification in free Xenon clusters. *Phys. Rev. Lett.*, **47**, 1121.
- Etters, R. D. and J. Kaelberer (1975). Thermodynamic properties of small aggregates of rare-gas atoms. *Phys. Rev. A*, **11**, 1068.
- Etters, R. D. and Jaya Kaelberer (1977). On the character of melting transition in small atomic aggregates. *J. Chem. Phys.*, **66**, 5112.
- Farges, J., M. F. de Feraudy, B. Raoult and G. Torchet (1983). Noncrystalline structure of argon clusters. *J. Chem. Phys.*, **78**, 5067.
- Farges, J., M. F. de Feraudy, B. Raoult and G. Torchet (1984). Surface arrangements on multilayer icosahedra. *Dynamics of surfaces*, B. Pullman *et al.* (eds.), 425.

- Farges, J., M. F. de Feraudy, B. Raoult and G. Torchet (1986). Noncrystalline structure of Argon clusters, II-multilayer icosahedral structure of  $Ar_N$  clusters  $50 < N < 750$ . *J. Chem. Phys.*, **84**, 3491.
- Farges, J., M. F. de Feraudy, B. Raoult and G. Torchet (1987). From five-fold to crystalline symmetry in large clusters. *Large Finite Systems*, J. Jortner *et al.* (eds.), 113.
- Flueli, M. and J. P. Borel (1988). Surface energy anisotropy measurements on small cuboctahedron of gold observed by HREM. *J. Cryst. Growth*, **91**, 67.
- Freund, E., J. Lynch and R. Szamanski (1986). Small particles in the field of industrial supported catalysts. *Ultramicroscopy*, **20**, 107.
- Fukano, Y. and C. M. Wayman (1969). Shapes of nuclei of evaporated fcc metals. *J. Appl. Phys.*, **40**, 1656.
- Gillet, M. (1977). Structure of small metallic particle. *Surf. Sci.*, **67**, 139.
- Giorgio, S. and J. Urban (1988). Fivefold and threefold symmetries in silver clusters. *Appl. Phys. Lett.*, **52**, 1467.
- Gordon, M. B., F. Cyrot-Lackmann and M. C. Desjonqueres (1979). Relaxation and stability of small transition metal particles. *Surf. Sci.*, **80**, 159.
- Griffin, G. L. and R. P. Andres (1979). Microscopic capillary approximation : free energies of small clusters. *J. Chem. Phys.*, **71**, 2522.
- Halicoglu, T. and P. J. White (1981). Structures of microclusters: an atomistic approach with three body interactions. *Surf. Sci.*, **106**, 45.
- Halicoglu, T. (1988). Fluxional nature of gas-phase clusters. *Surf. Sci.*, **197**, L233.
- Halicoglu, T. and C. W. Bauschlicher (1988). Physics of microclusters. *Rep. Prog. Phys.*, **51**, 883.
- Harris, W. F. and L. E. Scriven (1971). Intrinsic disclinations as dislocation sources and sinks in surface crystals. *J. Appl. Phys.*, **42**, 3309.
- Hasegawa, M., K. Hoshino and M. Watabe (1980). A theory of melting in metallic small particles. *J. Phys. F: Metal Phys.*, **10**, 619.
- Heinemann, K., M. J. Yacaman, C. Y. Yang and H. Poppa (1979). The structure of small vapor deposited particles. I. experimental study of single crystals and particles with pentagonal profiles. *J. Crystal Growth*, **47**, 177.
- Heinemann, K., T. Osaka, H. Poppa and M. Avalos-Borja (1983). In-situ TEM studies of Pd on MgO. *J. Catalysis*, **83**, 61.
- Herring, C. (1951). Some theorems on the free energies of crystal surfaces. *Phys. Rev.*, **82**, 87.
- Herzfeld, K. F. and M. Goeppert-Mayer (1934). On the theory of fusion. *Phys. Rev.*, **46**, 995.
- Heyraud, J. C. and J. J. Metois (1980). Equilibrium shape of gold crystallites on a graphite cleavage surface: Surface energies and interfacial energy. *Acta Met.*, **28**, 1789.
- Hoare, M. R. and P. Pal (1971). Physical cluster mechanics: statics and energy surfaces for monatomic systems. *Advan. Phys.*, **20**, 161.
- Hoare, M. R. and P. Pal (1972). Statistics and stability of small assemblies of atoms. *J. Crystal Growth*, **17**, 77.
- Hofmeister, H. (1984). Habit and Internal structure of multiply twinned gold particles on silver bromide films. *Thin Solid Films*, **116**, 151.
- Honeycutt, J. D. and H. C. Anderson (1987). Molecular dynamics study of melting and freezing of small Lennard-Jones cluster. *J. Chem. Phys.*, **91**, 4950.
- Howie, A. and L. D. Marks (1984). Elastic strains and energy balance for multiply twinned particles. *Phil. Mag.*, **49**, 95.
- Howie, A. (1986). Coulomb explosion in metals? *Nature*, **320**, 684.
- Huntington, H. B., G. A. Shirn and E. S. Wajda (1955). Calculation of entropies of lattice defects. *Phys. Rev.*, **99**, 1085.
- Iijima, S. (1985). Electron microscopy of small particles. *J. Electron Microsc.*, **34**, 249.
- Iijima, S. and T. Ichihashi (1986). Structural instability of ultrafine particles of metals. *Phys. Rev. Lett.*, **56**, 616.
- Iijima, S. and T. Ichihashi (1987). Grain boundary migration in small gold particles. *Surf. Sci. Lett.*, **192**, L872.
- Iijima, S. (1987a). The 60-carbon cluster has been revealed! *J. Phys. Chem.*, **91**, 3446.
- Iijima, S. (1987b). Fine particles of silicon. I. Crystal growth of spherical particles of Si. *Jap. J. Appl. Phys.*, **26**, 357.
- Iijima, S. (1987c). Fine particles of Silicon. II. Decahedral Multiply Twinned Particles. *Jap. J. Appl. Phys.*, **26**, 365.
- Ino, S. (1966). Epitaxial growth of metals on rocksalt faces cleaved in vacuum II (Orientation and structure of gold particles formed in ultrahigh vacuum). *J. Phys. Soc. Japan*, **21**, 346.
- Ino, S. and S. Ogawa (1967). Multiply twinned particles at early stages of gold film formation on alkali halide crystals. *J. Phys. Soc. Japan*, **22**, 1365.

- Ino, S. (1969). Stability of multiply-twinned particles. *J. Phys. Soc. Japan*, **27**, 941.
- Jellenik, J., T. L. Beck and R. S. Berry (1986). Solid-liquid phase changes in simulated iso-energetic Ar<sub>13</sub>. *J. Chem. Phys.*, **84**, 2783.
- Khlyustikov, I. N. and A. I. Buzdin (1987). Twinning-plane superconductivity. *Adv. Phys.*, **36**, 271.
- Kimoto, K. and I. Nishida (1967). Multiply twinned particles of FCC metals produced by condensation in Argon at low pressures. *J. Phys. Soc. Japan*, **22**, 940.
- Kimoto, K. and I. Nishida (1977). A study of lithium clusters by means of a mass analyzer. *J. Phys. Soc. Japan*, **42**, 2071.
- Kirchner, H. O. K. and G. A. Chadwick (1970). Surface entropies of Cadmium and Zinc. *Phil. Mag.*, **22**, 449.
- Kittel, C. (1988). Temperature fluctuation: an oxymoron. *Physics Today*, May, 93.
- Kleman, M. (1983). Points, Lines and Walls. Wiley publication, chap. 10.
- Knight, W. D., K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou and M. L. Cohen. Electronic shell structure and abundance of sodium clusters. *Phys. Rev. Lett.*, **52**, 2141.
- Komoda, T. (1968). Study on the structure of evaporated gold particles by means of high resolution electron microscopy. *Jap. J. Appl. Phys.*, **7**, 27.
- Kubo, R. (1962). Electronic properties of metallic fine particles. *J. Phys. Soc. Japan*, **17**, 975.
- Landman, U., R. N. Barnett, C. L. Cleveland, D. Scharf and J. Jortner (1987). Electron excitation dynamics, and solvation in small clusters. *J. Phys. Chem.*, **91**, 4890.
- Lee, J. K., J. A. Barker and F. F. Abraham (1973). Theory and Monte Carlo simulation of physical clusters in imperfect vapor. *J. Chem. Phys.*, **58**, 3166.
- Lindemann, Von F. A. (1910). Über die Berechnung Molekularer Eigenfrequenzen-Concerning the calculation of molecular fundamental frequencies. *Z. Physik*, **11**, 609.
- Linford, R. G. (1973). 'Surface thermodynamics of solids' in Solid State Surface Science, Vol. II (ed: Green, M., Marcel Dekker, New York), 1.
- Long, N. J., R. F. Marzke, M. Mckelvy and W. S. Glaunsinger (1986). Characterization of Pt Microcrystals using HREM. *Ultramicroscopy*, **20**, 15.
- Mackay, A. L. (1962). A dense non-crystallographic packing of equal spheres. *Acta. Cryst.*, **15**, 916.
- Malm, Jan-Olle, Jan-Olov Bovin, A. Petford-Long, D. J. Smith, G. Schmid and N. Klein (1988). Real-time atomic-resolution imaging of polymorphic changes in ruthenium clusters. *Angew. Chem.*, **27**, 555.
- Marks, L. D. (1980). The structure of small silver particles. PHD dissertation, University of Cambridge, England.
- Marks, L. D. and D. J. Smith (1981). High resolution studies of small particles of gold and silver, I. multiply twinned particles. *J. Cryst. Growth*, **54**, 425.
- Marks, L. D. and D. J. Smith (1983). HREM and STEM of defects in multiply twinned particles. *J. Microscopy*, **130**, 249.
- Marks, L. D. (1984a). Modified Wulff constructions for twinned particles. *J. Cryst. Growth*, **61**, 556.
- Marks, L. D., V. Heine and D. J. Smith (1984). Direct observation of elastic and plastic deformations at Au(111) surfaces. *Phys. Rev. Lett.*, **52**, 656.
- Marks, L. D. (1984b). Surface structure and energetics of multiply twinned particles. *Phil. Mag.*, **49**, 81.
- Marks, L. D. (1985a). Particle size effects of Wulff constructions. *Surf. Sci.*, **150**, 358.
- Marks, L. D. (1985b). Inhomogeneous strains in small particles. *Surf. Sci.*, **150**, 302.
- Marks, L. D. (1985c). Imaging small particles. *Ultramicroscopy*, **18**, 445.
- Marks, L. D. (1986). Solid-like growth. *Thin solid films*, **136**, 309.
- Martins, J. L., R. Car and J. Buttet (1981). Variational spherical model of small metallic particles. *Surf. Sci.*, **106**, 265.
- Matthews, J. W. and D. L. Allinson (1963). A mechanism for the formation of twins in evaporated fcc metal films. *Phil. Mag.*, **8**, 1283.
- Matsubara, T., Y. Iwase and A. Momokita (1977). Theory of anharmonic lattice vibration in metallic fine particles. *Progress in Theoretical Physics*, **58**, 1102.
- Matsui, Y. (1984). Small Particles of cubic Boron Nitride prepared by electron irradiation of hexagonal Boron Nitride in TEM. *J. Cryst. Growth*, **66**, 243.
- Matsumoto, S. and Y. Matsui (1983). Electron microscopic observation of diamond particles grown from the vapor phase. *J. Mat. Sci.*, **18**, 1785.
- Mays, C. W., J. S. Vermaak and D. Kulhmann-Wilsdorf (1968). On surface stress and surface tension II. *Surf. Sci.*, **12**, 134.
- McGinty, D. J. (1971). Vapor phase homogeneous nucleation and thermodynamic properties of argon clusters. *J. Chem. Phys.*, **55**, 580.
- Melmed, A. J. and D. O. Hayward (1959). On the occurrence of five-fold rotational symmetry in metal whiskers. *J. Chem. Phys.*, **31**, 545.

- Menon, S. K. and P. L. Martin (1986). Determination of the anisotropy of surface free energy of fine metal particles. *Ultramicroscopy*, **20**, 93.
- Messmer, R. P. (1981). Theoretical treatment of the electronic structure of small particles. *Surf. Sci.*, **106**, 225.
- Mihama, K. and Y. Yasuda (1966). Initial stage of epitaxial growth of evaporated gold films on Sodium Chloride. *J. Phys. Soc. Japan*, **21**, 1166.
- Mort La Brecque (1987). Opening the door to forbidden symmetries. *Mosaic*, **18**, 3.
- Natanson, G., Francois Amar and R. Stephen Berry (1983). Melting and surface tension in microclusters. *J. Chem. Phys.*, **78**, 399.
- Nicolis, G. and I. Prigogine (1977). 'Self-Organization in non-equilibrium structures'. Wiley-Interscience publication (John Wiley and Sons, New York).
- Oberli, L., R. Monot, H. J. Mathieu, D. Landolt and J. Buttet (1981). Auger and X-ray photoelectron spectroscopy of small Au particles. *Surf. Sci.*, **106**, 301.
- Ogawa, S., S. Ino, T. Kato and H. Ota (1966). Epitaxial growth of FCC metals on Alkali halide crystals cleaved in UHV. *J. Phys. Soc. Japan*, **21**, 1963.
- Ogburn, F., B. Paretkin and H. S. Peiser (1964). Pseudopentagonal twins in electrodeposited copper dendrites. *Acta Cryst.*, **17**, 774.
- Prigogine, I. (1980). From being to becoming: time and complexity in the physical sciences. W. H. Freeman and company, San Francisco.
- Rao, B. K., S. N. Khanna and P. Jena (1986). Ab initio studies of the electronic structure of micro-clusters. *Ultramicroscopy*, **20**, 51.
- Roos, J. R. and J. S. Vermaak (1972). On the growth process of Au and Ag on various air- and vacuum-cleaved alkali halid crystals. *J. Cryst. Growth*, **13/14**, 217.
- Ross, J. and R. P. Andres (1981). Melting temperature of small cluster. *Surf. Sci.*, **106**, 11.
- Rottman, C. and M. Wortis (1984). Statistical mechanics of equilibrium crystal shapes: Interfacial phase diagrams and phase transitions. *Physics Reports*, **103**, 59.
- Saito, Y., S. Yatsuya, K. Mihama and R. Uyeda (1979). Multiply twinned particles of Germanium. *Jap. J. Appl. Phys.*, **17**, 1149.
- Schwoebel, R. L. (1966). Anomalous growth of gold from vapor phase. *J. Appl. Phys.*, **37**, 2515.
- Searcy, A. W. (1984). The influence of molecular motions on the stabilities and shapes of solid particles. *J. Chem. Phys.*, **81**, 2489.
- Shechtman, D., I. Blech, D. Gratias and J. W. Cahn (1984). Metallic Phase with long range orientational order and no transnational symmetry. *Phys. Rev. Lett.*, **53**, 1951.
- Smith, D. J. and L. D. Marks (1981). High resolution studies of small particles of gold and silver, II. Single crystals, lamellar twins and polyparticles. *J. Cryst. Growth*, **54**, 433.
- Smith, D. J., A. K. Petford-Long, L. R. Wallenberg and J. O. Bovin (1986). Dynamic atomic-level rearrangements in small gold particles. *Science*, **233**, 872.
- Solliard, C. (1981). Structure and strain of the crystalline lattice of small gold and platinum particles. *Surf. Sci.*, **106**, 58.
- Spencer, M. S. (1986). Stable and metastable metal surfaces in heterogeneous catalysis. *Nature*, **323**, 685.
- Stephens, P. W. and J. G. King (1983). Experimental investigation of small helium clusters: magic numbers and the onset of condensation. *Phys. Rev. Lett.*, **51**, 1538.
- Stillinger, F. H. and T. A. Weber (1982). Hidden structure in liquid. *Phys. Rev. A*, **25**, 978.
- Stishov, S. M., I. N. Makarenko, V. A. Ivanov and A. M. Nikolaenko (1973). On the entropy of melting. *Phys. Lett.*, **45A**, 18.
- Takagi, M. (1954). Electron-diffraction study of liquid-solid transition of thin metal films. *J. Phys. Soc. Japan*, **9**, 359.
- Tallon, J. L. (1980). The entropy change on melting of simple substances. *Phys. Lett.*, **76A**, 139.
- Tholen, A. R. (1981). Vibrations and Martensitic transformation in small cobalt particles. *Surf. Sci.*, **106**, 70.
- Vermaak, J. S., C. W. Mays and D. Kulhmann-Wilsdorf (1968). On surface stress and surface tension I. *Surf. Sci.*, **12**, 128.
- Wallenberg, L. R., J. O. Bovin, A. K. Petford-Long and D. J. Smith (1986). Atomic-resolution study of structural rearrangements in small platinum crystals. *Ultramicroscopy*, **20**, 71.
- Wallenberg, L. R. (1987). Atomic imaging in real time of small metal clusters: a high resolution electron microscopy study. PHD dissertation, LUND University, Lund, Sweden.
- Wang, S. W., L. M. Falicov and A. W. Searcy (1984). The equilibrium shapes of small particles. *Surf. Sci.*, **143**, 609.
- Wautelet, M., L. D. Laude and C. Antoniadis (1986). Phase diagrams of thin films and wires. *Mat. Chem. and Phys.*, **14**, 57.

- Werfelmeier, W. (1937). Ein geometrisches modell des atomkerns. *Z. Physik*, **107**, 332.
- Williams, P. (1987). Motion of small gold clusters in the electron microscope. *Appl. Phys. Lett.*, **50**, 1760.
- Woltersdorf, J. A. S. Nepijko and E. Pippel (1981). Dependence of the lattice parameters of small particles on the size of the nuclei. *Surf. Sci.*, **106**, 64.
- Yacaman, M. J., S. Fuentes and J. M. Dominguez (1981). The effect of shape and crystal structure of small particles on their catalytic activity. *Surf. Sci.*, **106**, 472
- Yacaman, M. J., K. Heinemann, C. Y. Yang and H. Poppa (1979). The structure of small vapor deposited particles. II. experimental study of particles with hexagonal profile. *J. Cryst. Growth*, **47**, 187.
- Yagi, K., K. Takayanagi, K. Kobayashi and G. Honjo (1975). In situ observation of growth processes of multiply twinned particles. *J. Crystal Growth*, **28**, 117.
- Yang, C. Y. (1979). Crystallography of decahedral and Icosahedral particles. *J. Crystal Growth*, **47**, 274.