The development of metallic behaviour in clusters

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A review is presented of theoretical models for describing and rationalizing the development of metallic properties in clusters, as a function of cluster size. Clusters, which span a wide size range, can be approached from the bulk solid (infinite cluster) limit—via quasi-continuum models derived from condensed matter physics—and from the small molecule limit—via discrete quantum mechanical models. Smooth and oscillatory cluster size effects are described and their origins rationalized. The competition between electronic and geometric shell stability effects, and the importance of the cluster temperature and its physical state, are discussed. The archetypical metal to non-metal transition observed in mercury clusters, as a function of size, is considered and the possibility of forming metallic clusters from non-metallic elements is investigated.

Keywords: clusters; metallic particles; electronic shells; jellium model; geometric shells; mercury clusters

1. Introduction

There is considerable experimental and theoretical interest in the study of elemental clusters in the gas phase and in the solid state (Haberland 1995; Martin 1996*a*). Clusters are of fundamental interest both due to their own intrinsic properties and because of the central position that they occupy between molecular and condensed matter science. One of the most compelling reasons for studying clusters is that they span a wide range of particle sizes, from the molecular (with quantized states) to the microcrystalline (where states are quasi-continuous). Clusters constitute a new type of material (nano-particles) which may have properties which are distinct from those of discrete molecules or bulk matter. The study of the evolution of the geometric and electronic structures of clusters and their chemical and physical properties is also of great interest. One fundamental question which has arisen is: 'how large must a cluster be before its properties resemble those of the bulk element?' (Jortner 1992). The answer to this question depends critically on which properties are being considered and on the nature of the component atoms. Finally, the high ratio of surface to interior atoms in clusters means that there are many common features between clusters and bulk surfaces.

In this paper, I will concentrate on the change in electronic properties of clusters with cluster size, with particular emphasis on the development of metallic properties and the transition from non-metal- to metal-like behaviour. Particularly interesting, in this respect, is the fundamental question: 'how many atoms maketh metal?' posed by Edwards & Sienko (1983). Although this seems like a simple question, it is beset

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Table 1. *Approximate diameters (d) and fractions of surface atoms (F_S) for N-atom spherical sodium clusters*

size	N	$d(N)$ nm^{-1}	$F_S(N)$
small	$\leqslant 10^2$	$\leqslant 1.9$	$\geqslant 0.86$
medium	10^2–10^4	1.9–8.6	0.86–0.19
large	$> 10^4$	> 8.6	$\leqslant 0.19$

with problems. First of all (as has become apparent in the course of this meeting), we encounter the problem that, even in bulk matter, it is often difficult to locate and define (either experimentally or theoretically) the metal to non-metal transition point at finite temperatures. Other problems which arise due to the finite nature of the clusters themselves are: (i) it is presently impossible to measure the electrical conductivity of isolated gas phase clusters directly; (ii) it is difficult to generate intense size-selected cluster beams; (iii) surface-supported clusters may be perturbed by the substrate; (iv) the concept of temperature is not well defined for finite particles; and (v) there is no such thing as a true first-order phase transition for finite clusters (Mott 1961; Berry 1996), though transitions do become sharper for larger clusters.

Since clusters in a molecular beam are generally not in thermodynamic equilibrium, many researchers prefer to avoid applying terminology which has thermodynamic connotations (i.e. which imply well-defined phases in equilibrium). Berry (1996) has shown, however, that clusters can exist in a number of *'phase-like forms'*, some of which, such as the liquid- or solid-like forms, have similar properties to the bulk phases, while others are unique for clusters—having no bulk counterparts. Strictly speaking, rather than describing clusters as metallic or non-metallic, these states should be described as metal- and non-metal-like. For convenience, I shall use the terms derived from bulk condensed matter—while acknowledging the differences between the meaning of the terminology for clusters and bulk materials.

2. Size effects in clusters

(*a*) *Cluster sizes*

In this paper, I shall refer to three cluster size regimes: small clusters (less than 100 atoms); medium-sized clusters (100–10 000 atoms); and large clusters (greater than 10 000 atoms). Assuming that the cluster is approximately spherical, it is easily shown that the diameter of a cluster of N atoms is given by

$$d(N) = 2r_{\mathrm{WS}} \times N^{1/3}, \tag{2.1}$$

where r_{WS} is the Wigner–Seitz radius of the element under consideration (i.e. the radius of a sphere whose volume is equal to the volume per atom in the solid). Table 1 gives the ranges of diameters for the three cluster size regimes, taking as an example clusters of sodium atoms (with $r_{\mathrm{WS}} = 0.2$ nm). As will become evident, many properties of clusters depend on the fraction of atoms (F_S) which lie on the surface of the cluster, of nuclearity N. For *pseudo*-spherical clusters, this quantity is given by

$$F_S(N) = 4N^{-1/3}. \tag{2.2}$$

Ranges of F_S values, for the three cluster size regimes, are also given in table 1, from which it is apparent that clusters with as many as 10 000 atoms still have nearly 20% of their atoms on the surface. In fact, F_S only drops below 0.01 (i.e. less than 1% of atoms are on the surface) for $N > 6.4 \times 10^7$ atoms (corresponding to a diameter of approximately 0.16 μm for sodium clusters).

(*b*) *Cluster size effects*

The variation of various cluster properties with size can be gathered together under the heading of cluster size effects (CSEs). Probably the first person to ask a question relating to a CSE was Lord Kelvin who asked: 'does the melting temperature of a small particle depend on its size?' (Thomson 1871). With regard to this question, Pawlow (1909) showed that the melting temperature of a metallic particle should decrease as the particles get smaller. Although Pawlow observed a slight depression of melting point for small particles, the first accurate experiments (studying gold clusters under a transmission electron microscope) were performed by Buffat & Borel (1976). They confirmed Pawlow's prediction and measured melting temperatures as low as 300 K for the smallest clusters (the bulk melting temperature of gold is 1338 K).

Lord Kelvin's question is a specific example of the more general CSE problem: 'how large must a cluster be before its properties resemble those of the bulk element?' The answer to this question, as Jortner (1992) has pointed out, is that 'the critical size for which the properties of the bulk matter will be reached depends on the nature of the experimental observable'. Particularly important is whether the cluster property is related to the volume or surface area of the cluster. Reviews of the size-dependent behaviour of a variety of cluster properties have been presented by Jortner (1992), Müller *et al.* (1994) and Echt (1996).

(*c*) *Scaling laws*

In the large cluster regime, many cluster properties (G), such as ionization energy (IP), electron affinity (EA), melting temperature (T_{m}) and cohesive or binding energy (E_{b}) show a regular variation with cluster size. By adopting a spherical cluster model, in which the N-atom cluster is approximated by a sphere of radius R, this smooth CSE behaviour can be described by simple scaling laws (Jortner 1992), either in powers of the cluster radius

$$G(R) = G(\infty) + aR^{-\alpha} \tag{2.3}$$

or the nuclearity

$$G(N) = G(\infty) + bN^{-\beta}, \tag{2.4}$$

where $G(\infty)$ is the value of property G in the bulk. Since many properties depend on the ratio of surface to bulk (volume) atoms in a cluster, and since $N_{\mathrm{s}}/N_{\mathrm{v}} \propto N^{-1/3}$ (or $1/R$), the exponents in (2.3) and (2.4) are generally $\alpha = 1$ and $\beta = \frac{1}{3}$.

(*d*) *Clusters as liquid drops*

Ionization energies and electron affinities of large and medium clusters of metallic elements have been predicted to follow such power laws. According to the liquid drop model (LDM)—a classical electrostatic model in which the cluster is approximated by a uniform conducting sphere—the IP of a cluster of radius R is given by (Bréchignac 1994)

$$IP = W + \tfrac{3}{8}(e^2/R), \tag{2.5}$$

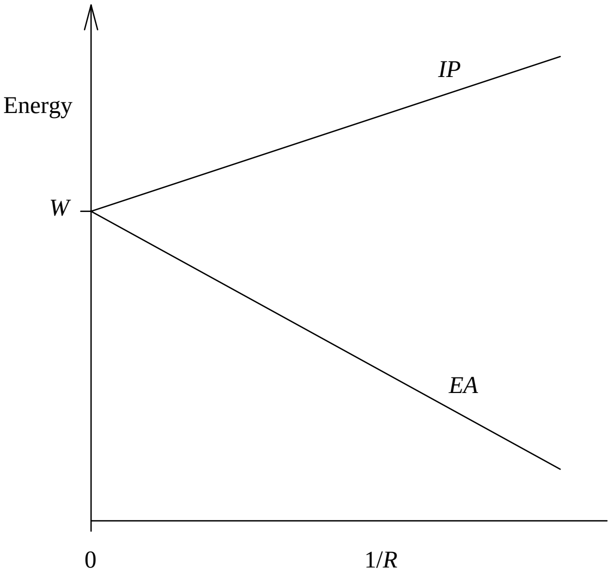

Figure 1. Dependence of cluster *IP* and *EA* on cluster radius (R) as predicted by the LDM.

where e is the charge on the electron and W is the workfunction of the bulk metal. The EA is given by

$$EA = W - \tfrac{5}{8}(e^2/R). \tag{2.6}$$

As $1/R \rightarrow 0$ ($N \rightarrow \infty$), the IP and EA both tend towards the bulk workfunction, W. These trends are shown in figure 1.

By studying the photodetachment energies of a wide range of neutral and anionic metal clusters, Kappes (1988) showed that the LDM correctly predicts the trends of decreasing IP and increasing EA with increasing cluster size. For small clusters (large values of $1/R$), however, there are large deviations from the LDM predictions. In fact, large deviations (usually observed as oscillations about the smooth CSE trend representing the power law) are observed for many properties in the medium and (especially) the small cluster size regimes. Such deviations, which have been discussed in detail by Jortner (1992), arise due to *quantum size effects* (QSEs, such as those caused by electronic shell closings) and *surface effects* (geometric shell closings), which are discussed below. A schematic representation (adapted from Jortner 1992) of a cluster property (G), which exhibits smooth CSE (liquid drop) behaviour at high nuclearity and quantum size and surface effect oscillations at low nuclearity, is shown in figure 2.

Returning to the question of how big a cluster must be before it resembles the bulk solid closely, I will adopt Jortner's criterion (1992) that we can describe a cluster property as bulk-like when $G(N)$ is within 1% of the bulk value. With this definition, N_{c} is of the order 10^6 for the cohesive energies of alkali metal clusters and 10^5–10^6 for the IP and EA of metal clusters. These values are to be expected for properties which depend on the fraction of atoms on the cluster surface—and which therefore exhibit a $1/R$ ($N^{-1/3}$) dependence on cluster size—since, as discussed above, the fraction of surface atoms drops below 1% of the total at $N \sim 10^6$. It should be noted, however (Edwards & Sienko 1983; Harrison & Edwards 1985; Benfield 1994), that magnetic resonance (NMR and ESR) studies indicate that the onset of spin

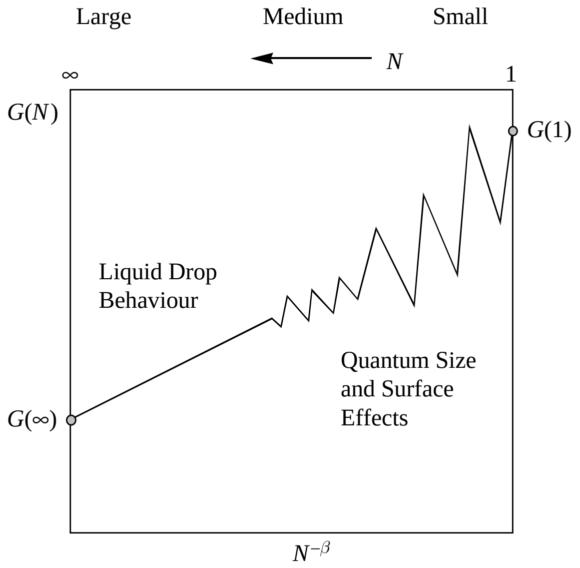

Figure 2. Schematic representation of the variation of cluster property G with cluster nuclearity N.

delocalization occurs at lower nuclearities than electron (charge) delocalization as spin delocalization does not depend on the formation of free carriers.

3. Clusters as small metallic particles

One way of analysing metal clusters, conceptually, is by starting from a macroscopic crystal of bulk metal and reducing the size of the crystal to the micron scale (*'microcrystallites'*) and ultimately to the nanometre scale. In this way, clusters can be regarded as small metallic particles or as very finely divided metals (Edwards 1986, 1992). Metallic particles in the micron to nanometre size range are traditionally regarded as colloids but, as Edwards (1992) has pointed out, the distinction between colloids and large clusters is largely a matter of semantics.

Starting with a metal crystal and gradually reducing its size, one anticipates that, at some point, a metal to non-metal (MNM) transition must occur, since an isolated atom surely cannot be described as a metal. Perenboom *et al.* (1981) elegantly expressed this as follows: 'when the number of atoms contained in a grain of solid matter is steadily reduced, it is plausible that in the course of this process a stage is realized when the particle does not behave like a smaller copy of the corresponding bulk solid anymore'. Experimental and theoretical studies of clusters in this size regime have been reviewed by Edwards & Sienko (1983), Kubo *et al.* (1984), Harrison & Edwards (1985) and Edwards (1986, 1990, 1992).

The consequences, as regards electronic structure and properties, of conceptually going from a crystal of bulk metal to smaller and smaller metallic particles were discussed by Fröhlich (1937) and Kubo (1962). The Fröhlich–Kubo approach is based on the recognition that, in the limit of a bulk metal, electron energy levels are quasi-continuous and the electronic structure of the metal is well described by band theory. As the size of the metallic particle is reduced, however, the electronic energy levels become discrete—there are now a finite number of electronic states and the energy

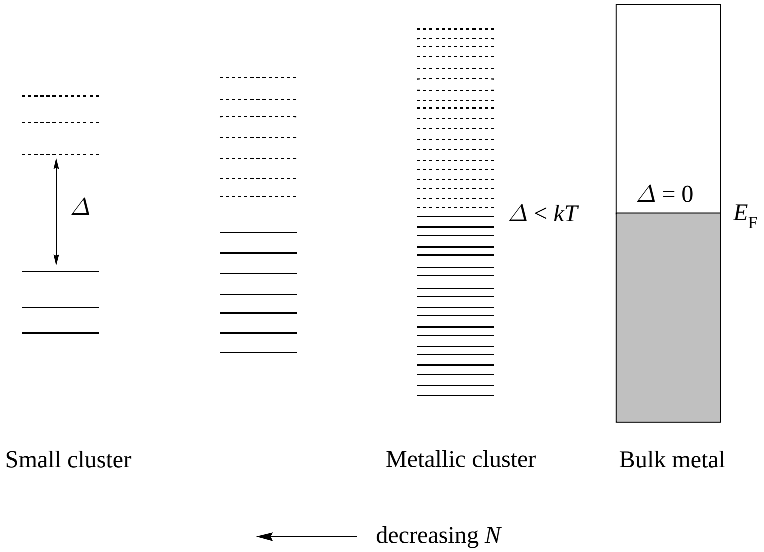

Figure 3. Discretization of electronic energy levels with decreasing metallic particle size (N). Filled levels (at 0 K) are indictated by full lines and empty levels by dashed lines.

spacing between adjacent levels, for an N-atom particle is of the order E_{F}/N, where E_{F} is the Fermi energy of the bulk metal. The next step is to consider how the energy level spacing might be related to metallic or non-metallic behaviour (at non-zero temperature). As DiCenzo & Wertheim (1994) have said: 'metallic properties presuppose the existence of a partially occupied band with level spacing sufficiently small near the Fermi level so that a small external potential (or thermal activation) can create electron-hole pairs, allowing a flow of current. This is a statement of the Kubo criterion or condition for a finite metallic particle (large cluster) to exhibit metallic conduction

$$\mathit{\Delta} \approx E_{\mathrm{F}}/N \leqslant kT, \tag{3.1}$$

where $\mathit{\Delta}$ is the band gap or electronic energy level spacing at the Fermi level (defined as the highest occupied orbital in a finite particle). Smaller particles will have larger $\mathit{\Delta}$ values and hence will require higher temperatures for metallic conduction. This transition from metallic to non-metallic behaviour, upon decreasing the size of a metallic particle, is shown schematically in figure 3. The discretization of electronic energy levels, which leads to the suppression of metallic behaviour when $\mathit{\Delta} > kT$, is responsible for the QSEs discussed above.

Harrison & Edwards (1985) have predicted the temperatures at which sodium clusters ($E_{\mathrm{F}}(\mathrm{Na}) = 3.24\,\mathrm{eV}$) of different sizes will be metallic—according to Kubo's criterion. Thus, a cluster with a diameter d of 10 nm ($N \approx 16\,000$) should behave as a metallic particle at $T > 5\,\mathrm{K}$, while a smaller cluster (e.g. $d \approx 5$ nm; $N \approx 2000$) will be metallic at higher temperatures (50 K). For $N > 125$ atoms ($d > 2$ nm), sodium clusters should exhibit metallic conductivity at room temperature.

The Fröhlich–Kubo principle can be extended to transition metal particles, which are characterized by narrow d bands and consequently high densities of electronic states. This leads to much narrower energy spacings between electron energy levels so that room temperature metallic conductivity should occur at smaller cluster sizes ($N > 40$) than for the s-valent alkali metals, such as sodium.

4. Quantum mechanics of metal clusters

In the previous section, it was shown how metal clusters can be approached from the infinite limit of bulk crystals by decreasing particle size, thereby introducing the discretization of electronic energy levels. In this section it will be demonstrated that the same point can be reached by using quantum mechanical techniques, normally applied to small molecules, to describe the electrons in small clusters and noting the changes that occur as the cluster size increases.

(*a*) *The jellium model*

In a seminal experiment, Knight *et al.* (1984) found a number of intense peaks in the mass spectra of alkali metal clusters. The nuclearities correponding to these peaks were termed *magic numbers* and were attributed to the enhanced stability of a cluster (corresponding to an intense peak) as compared with its immediate neighbours. The quantum mechanical *jellium* model was adapted from nuclear structure theory to account for these magic numbers and the non-LDM behaviour of the *IP* and *EA* of small alkali metal clusters. Agreement with experiment was subsequently improved by allowing for ellipsoidal distortions of the clusters, for electron counts corresponding to incomplete jellium subshells (Clemenger 1985).

In the jellium model, the cluster is modelled by a uniformly positively charged sphere filled with an electron gas. The Schrödinger equation is solved for an electron constrained to move within the cluster sphere under the influence of an attractive mean-field potential. This may be an empirical potential or effective potentials may be evaluated from density functional theory or at the Hartree–Fock MO level. Magic numbers arise due to the complete filling of jellium levels or subshells (1s, 1p, 1d, 2s, 1f, etc.). It should be noted that the principal quantum number, n in the jellium model, because of its origin in nuclear physics, is distinct to that used in the definition of atomic orbitals (n_{at}). The two are related by

$$n = n_{\mathrm{at}} - \ell, \tag{4.1}$$

where ℓ is the angular momentum quantum number. Thus, the number of radial nodes in a jellium wave function is given by $n - 1$ (compared with $n_{\mathrm{at}} - \ell - 1$ for atomic orbitals).

The jellium model ignores the positions of the atomic nuclei (or ionic cores since the valence electrons are assumed to be delocalized). This assumption is valid if the valence electrons are weakly bound (as in the alkali metals) and the clusters are molten. Since the melting points of clusters decrease as clusters get smaller (Pawlow 1909), and as alkali metals have low melting temperatures anyway, under the experimental conditions pertaining to cluster creation and detection, alkali clusters may indeed be molten. Experiments by Honea *et al.* (1990), who generated lower temperature clusters and used near-threshold ionization (to ensure that the ionization process does not induce cluster heating and/or fragmentation), demonstrated that magic numbers (jellium electronic effects) are not observed for cold solid-like clusters.

(*b*) *Electronic shells and supershells*

Martin *et al.* (1990, 1991*a*) measured the mass spectra of sodium clusters with up to 25 000 atoms and observed two series of periodic oscillations in intensity which are approximately evenly spaced when plotted against $N^{1/3}$. For $N < 2000$, the oscillations have a small period. The magic numbers correspond to dips in mass spectral (MS) intensity since, in these experiments, near-threshold ionization is used

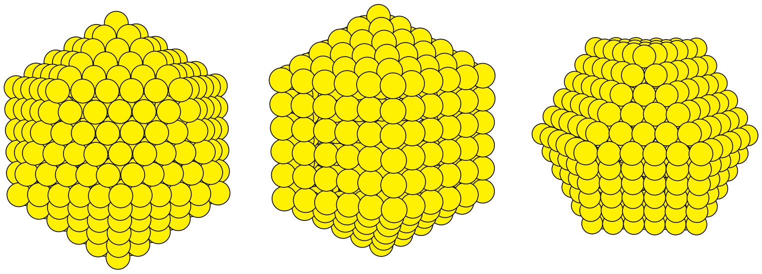

Figure 4. Five shell polyhedral clusters with (from left to right) icosahedral, decahedral and cuboctahedral geometries.

to produce the cations which are actually detected and the more stable clusters tend to have higher *IP*s and smaller ionization cross-sections. The magic numbers in this size regime have been attributed to the filling of *electronic shells* which occur due to the bunching together of jellium electronic energy levels (subshells). Classical and quantum mechanical arguments have been used to show that, at high energies, jellium levels with the same value of the *quasi*-quantum number $(3n+\ell)$ are approximately degenerate (Bjørnholm 1994; Koch 1996). In addition to oscillations due to electronic shell structure, longer period intensity variations are observed in the region $N < 2000$. This beat mode is due to the merging of electronic shells into dense band-like blocks or *supershells* (Bjørnholm 1994).

5. Polyhedral clusters

(*a*) *Geometric shells*

For sodium clusters with $N > 2000$ (Martin *et al.* 1991*a*), a new periodicity in MS intensity is observed, which has a longer period than that arising from supershell structure. The magic numbers (which may be dips or peaks in MS intensity, depending upon experimental conditions) are due to the filling of concentric polyhedral shells of atoms. Filled *geometric shells* (Näher *et al.* 1993; Martin 1996*b*) impart stability to the cluster by maximizing the average coordination number, $\bar{Z}$, and thereby reducing the cluster surface energy. For alkali metal clusters, the magic numbers are close to those expected for filling K polyhedral geometric shells, based on 12-vertex polyhedra, such as the icosahedron, decahedron or FCC-like cuboctahedron

$$N(K) = \tfrac{1}{3}(10K^3 + 15K^2 + 11K + 3). \tag{5.1}$$

Five shell polyhedral clusters ($K = 5$, $N = 561$) with these geometries are shown in figure 4.

By analysing the fine structure in the MS intensity plots (Martin 1996*b*), it is possible to distinguish between icosahedral, decahedral and cuboctahedral growth as they differ in the secondary magic numbers associated with geometric subshells—arising from the covering of individual faces or groups of faces of a polyhedron without giving rise to a complete polyhedral shell. Similar arguments have been used to show that calcium clusters (at least as far as $N = 5000$) grow as icosahedra (Martin *et al.* 1991*b*).

(*b*) *Competition between electronic and geometric shell structure*

It has been said that, under experimental conditions, the atoms (nuclei) in small clusters are mobile, so that the cluster can be regarded as a spherical liquid-like droplet. Quantization of the electrons' motions leads to jellium electronic structure. As the clusters get larger, the jellium levels bunch into electronic shells and supershells and eventually into bands where the level spacing is quasi-continuous (i.e. level spacing $\Delta \ll kT$). This is clearly just the opposite process to that (*vide supra*) of taking a metallic particle and decreasing it's size until the electronic energy levels become discretized.

It is reasonable to suppose that, when the level spacing Δ is small compared with kT, the pattern of experimental MS intensities will no longer be governed by electronic shell filling, since there will be no preference for a certain electron count over any other. If the temperature is below the melting temperature (T_{m}) of the cluster (which rises with increasing cluster size) the clusters are solid like and the clusters grow as nano-crystallites. Structures and stabilities are governed by crystal growth effects (such as the minimization of surface energies) and geometric, rather than electronic shell structure is observed (Martin 1996*b*).

The size at which the transition from electronic to geometric shell structure occurs depends on a number of factors, such as the density of electronic states (DOS), atomic electron configuration, cluster melting temperature and the temperature of the cluster. Thus, clusters of the transition metals, where the valence d orbitals give rise to narrow bands, with a high DOS, have MS characteristic of geometric shell structure even for clusters of tens of atoms (Pellarin *et al.* 1994). Geometric shell structure (octahedral clusters with local FCC-like structure) is also seen for Al and In clusters (with occupied valence p as well as s orbitals) of even a few hundred atoms (Martin *et al.* 1992; Martin 1996*b*).

Geometric shell structure is observed for small alkaline earth clusters (e.g. Mg, Ca and Ba; Rayane *et al.* 1989; Martin *et al.* 1992; Martin 1996*b*) because these elements have formally closed shell $[(n\mathrm{s})^2(n\mathrm{p})^0]$ electronic configurations. Clusters of closed shell atoms, such as the noble gases (He, Ne, Ar, etc.) are weakly bound by van der Waals forces and adopt geometric shell structures so as to minimize their surface energies. For larger alkaline earth clusters, such as the Ca clusters with up to 5000 atoms studied by Martin *et al.* (1992), the s and p bands must overlap, thereby making the clusters metallic. However, at these nuclearities, electronic shell structure is not manifest in the MS because the level spacings are already small enough to wash out any electronic preferences and geometric shell structure is again observed.

The temperature of the cluster in relation to its melting temperature (T_{m}) is of critical importance in deciding whether electronic or geometric effects prevail. For $T > T_{\mathrm{m}}$, the cluster will be liquid like and will resemble a spherical liquid drop. Geometric shell structure is observed to disappear upon cluster melting (Martin *et al.* 1994) since spherical clusters are not regular polyhedra and so there is no inherent stability associated with any given nuclearity. Indeed, Martin *et al.* (1994) have used the dissappearance of MS features related to geometric shell structure as a measure of T_{m} for clusters. In certain cases (e.g. Na (Pedersen *et al.* 1991), Al (Baguenard *et al.* 1994; Lermé *et al.* 1996)), melting clusters actually results in a transition from geometric to electronic shell structure. Lermé *et al.* (1996) have shown that gallium clusters exhibit electronic shell structure even up to 5000 atoms, indicating that they are presumably liquid like over a wider range of temperatures than aluminium clusters. This is consistent with the lower melting temperature of elemental Ga (303 K) compared to Al (933 K) and the wide liquid range of Ga. Finally, Ellert *et al.* (1995) investigated the temperature dependent optical spectra of small Na clusters ($N = 4$, 7, 11) and showed that, while at low temperatures ($T \sim 35$ K), discrete lines are observed (corresponding to transitions between electronic states of solid-like clusters), at high temperatures ($T > 380\,\mathrm{K}$), broad surface plasmon-type peaks are observed, consistent with liquid-like clusters exhibiting collective electronic excitations (Broglia 1994).

There has been some debate as to whether electronic shell closings actually require the cluster to be liquid like. Calculations by Mansikka-aho *et al.* (1994) have shown that, due to their high symmetry, solid-like icosahedral Na clusters exhibit electronic shell structure, which is similar to jellium predictions, up to 1000 atoms. Pavloff & Creagh (1993) have demonstrated, however, that the electronic supershell structure, observed by Pedersen *et al.* (1991) for sodium clusters, are inconsistent with solid icosahedral structures. Finally, Mansikka-aho *et al.* (1994) and Manninen (1996) have illustrated that the structure of the cluster surface (i.e. its roughness, softness and how facetted it is) determines the details of the cluster's electronic structure. (The states near the Fermi level, which are responsible for electronic control of cluster stability, are most strongly affected by the nature and structure of the surface.)

Thus, it appears that electronic shell structure is manifest by hot liquid-like clusters, whereas geometric shell structure is exhibited by colder solid-like clusters and that the transition from electronic to geometric structures can be accomplished by lowering the cluster temperature or increasing the cluster nuclearity. Wales and coworkers (Doye & Wales 1996; Wales *et al.* 1996) have studied the effect of varying the range of the interatomic forces on the geometric structures and melting temperatures of clusters, with particular emphasis on the relative stabilities of amorphous, liquid-like structures and the more highly symmetric solid-like geometries.

(*c*) *The approach to bulk structure*

In the size regime where geometric shell effects determine cluster structure and stability (i.e. where clusters are solid like), a variety of cluster geometries are observed (or inferred from experiment). As mentioned above, many clusters of metallic elements are found to form icosahedral clusters. The icosahedron, with it's six 5-fold symmetry axes, is incompatible with translational symmetry and therefore involves non-crystalline packing of atoms. Since bulk metals are crystalline, generally adopting FCC, HCP or BCC packing, elements adopting non-crystalline icosahedral or decahedral cluster geometries must undergo a structural phase transition as a function of increasing cluster size. This leads to the important question: 'at what size do metal clusters adopt the structure of the bulk metal?'

There is, as yet, very little direct experimental evidence identifying a critical nuclearity for such a structural phase transition in the gas phase. According to MS experiments (Martin *et al.* 1991*b*; Martin 1996*b*), calcium clusters remain icosahedral (rather than adopting the fcc structure of bulk Ca) up to at least 5000 atoms, while sodium clusters are icosahedral up to tens of thousands of atoms. Aluminium clusters, by contrast, adopt octahedral geometries, based on FCC packing (as in the bulk) for clusters as small as hundreds of atoms (Martin *et al.* 1992). Similar results have been observed for indium (Martin 1996*b*). Considering transition metals, there is MS evidence (Pellarin *et al.* 1994) that cobalt and nickel clusters, of tens or hundreds of atoms have icosahedral shell structures. The situation for iron is more complicated, with possible evidence for magic numbers associated with BCC-like 14-vertex rhombic dodecahedral clusters in addition to cuboctahedral or icosahedral geometries.

Many simulations have been performed for small- and medium-sized metal clusters based on geometric shells, using empirical pair and many-body potential energy functions. Wales *et al.* (1996) have used model pair potentials of the Lennard–Jones and Morse types and a number of many-body potentials to investigate the effect of the range and anisotropy of the potential on the preferred geometric shell structure (icosahedral versus decahedral versus cuboctahedral, etc.) adopted by metal clusters. Calculations using empirical $2+3$-body potential energy functions (Murrell & Mottram 1990; Johnston & Fang 1992) indicate that calcium clusters should become FCC like at around 32 000 atoms (Hearn & Johnston 1997), while iron clusters are predicted to become BCC like at approximately 2000 atoms (Besley *et al.* 1995).

In most of these model calculations, the predicted lowest energy structures are icosahedral for small shell clusters. As can be seen from table 1, small clusters have high surface/bulk ratios and therefore unfavourable surface energies. The surface energy of a cluster can be reduced by adopting non-crystalline highly coordinated icosahedral or decahedral geometries. Inspection of figure 4 reveals that, while FCC-like cuboctahedral clusters have eight close-packed (111)-like faces (i.e. faces which are equivalent to the (111) surfaces of an FCC crystal) and six non-close-packed (100)-like faces, icosahedral clusters have 20 pseudo-close-packed (111)-like faces. There is, however, an inherent elastic strain in the icosahedral structure, arising from the fact that the tangential (surface) bonds are 6% longer than the radial bonds in such structures. Although the icosahedron can be constructed from 20 fused tetrahedra, these tetrahedra are not regular, i.e. there is a frustration involved in packing regular tetrahedra (Nelson & Spaepen 1989). In conclusion, non-crystalline icosahedral and decahedral geometries are preferred for small and medium sized clusters (with a high proportion of surface atom) as these structures minimize surface energy. As the clusters get larger, the elastic strain (a bulk phenomenon) gets larger. The balance between the two effects therefore depends on the ratio of surface/bulk atoms, which varies as $N^{-1/3}$, which explains why at a certain critical nuclearity there must be a transition from non-crystalline (low surface energy, high strain) to bulk-like crystalline (strain-free, higher surface energy) structures (Doye & Wales 1996; Hearn & Johnston 1997).

One problem with studying naked metal clusters (such as those created in cluster molecular beams) is that 'they cannot be isolated and handled on a preperative scale like normal chemical compounds' (Schmid 1994). To enable the investigation of approximately uniformly sized clusters, it is necessary to protect them with a ligand shell, as this avoids coalescence at high cluster densities. Electron microsopy and scanning tunneling microscopy studies of colloidal metal particles (clusters with diameters ranging from nanometre to micrometre dimensions) have shown that platinum and palladium colloids grow as FCC single crystals, even for particles with diameters as small as 40 Å (Edwards 1992; Schmid 1992, 1994). Gold and silver colloids, by contrast, are often found to consist of icosahedral and decahedral particles. However, while smaller decahedral silver particles ($d \sim 40$ Å) appear to be true decahedra (with non-FCC packing), the larger particles ($d \sim 200$ Å) appear to consist of FCC-packed regions which are multiply twinned into an overall decahedral structure. The reason for this change is that, as decahedral particles grow, the inherent (bulk) elastic strain in the structure eventually overcomes the low surface energy term. The formation of defects and dislocations enables local regions of FCC packing to be formed, leading to the observed multiply twinned structure.

The smaller ligand-stabilized colloidal clusters reported by Schmid and co-workers (Schmid 1992; Schmid *et al.* 1996) have cuboctahedral (FCC-like) geometries (e.g.

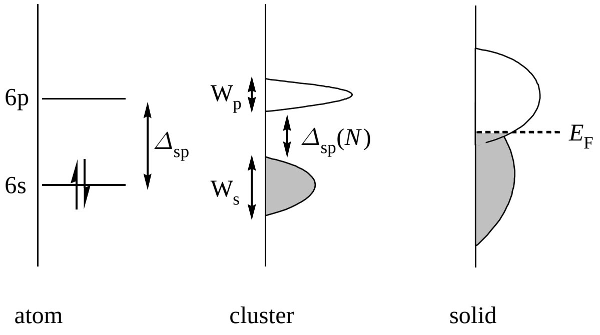

Figure 5. Band formation and overlap on going from atomic to bulk mercury via mercury clusters. Occupied bands are indicated by shading. (Note that band hybridization and overlap will occur well before the bulk limit is reached.)

Au_{55}, Pt_{309} and Pd_{561}), though there is continuing discussion as to the exact nuclearities of these species (Edwards 1992). EXAFS measurements of nearest-neighbour coordination numbers have been compared with analytically derived mean coordination numbers (Benfield 1992) to estimate the size of certain ligand-stabilized metal particles (Fairbanks *et al.* 1990). Mulder *et al.* (1996) have found, using ^{197}Au Mössbauer spectroscopy, that both the surface atoms and the inner atoms of Au_{55} clusters are influenced by the ligands and that the central atom charge densities are not the same as those in the bulk metal. By contrast, in Pt_{309} clusters (in which ^{197}Au is produced by neutron activation), the inner shell atoms have the same charge density as in the bulk metal. Finally, it is interesting to speculate as to what extent the differences in observed geometries of colloidal particles (where there is a greater preponderance of cuboctahedral structures) and gas phase clusters (where icosahedral structures are found) may be due to structure changes induced by the coordination of ligands to the surfaces of the colloidal particles.

6. The metal to non-metal phase transition in mercury clusters

Some of the most elegant experiments concerning MNM transitions in clusters have been performed on mercury clusters by Rademann and co-workers (Rademann *et al.* 1987), who interpreted the variation of the *IP* of mercury clusters, as a function of cluster size, in terms of a gradual transition from van der Waals to metallic bonding in the region $N = 13$–70 atoms. For $N < 13$, the approximate straight line of $IP(N)$ versus $1/R$ extrapolates to $IP(\infty) \approx 6.5$ eV. This extrapolated value is significantly higher than the bulk work function of Hg (4.49 eV) and reflects a different type of bonding in these small clusters. For $N > 13$, $IP(N)$ decreases more rapidly and converges on the LDM straight line at $N \approx 140$. In the bulk limit, the *IP* of the large Hg clusters extrapolate to a value very close to the bulk work function. Other experiments, such as the size-dependence of the 5d–6p autoionization spectrum (Bréchignac *et al.* 1988) and the appearance of the surface plasmon mode (Rademann *et al.* 1992; Haberland *et al.* 1993), provide supporting evidence for a non-metal to metal (NM → M) transition in this size regime.

(*a*) *Theory of bonding in mercury clusters*

The closed shell electronic configuration, $(6s)^2(6p)^0$, of the free Hg atom causes small mercury clusters to be non-metallic and held together by weak van der Waals dispersion forces (as is the case for closed shell noble gas clusters). As the cluster grows, the atomic 6s and 6p levels broaden into bands, as shown in figure 5. A NM → M phase transition occurs at a critical nuclearity N_c due to 6s–6p band overlap, though there is probably a transition to a semiconducting (covalently bonded) state (due to s–p band hybridization, prior to band overlap) before the metallic state is reached (Pastor & Bennemann 1994). For a cluster, the s and p band widths are related to the mean coordination number of the atoms ($\bar{Z}$) as follows:

$$(W_s, W_p) \propto \bar{Z}^{1/2}, \tag{6.1}$$

where the square root dependence on $\bar{Z}$ comes from a tight binding analysis (Pastor & Bennemann 1994). The MNM transition therefore occurs at a critical mean coordination number ($\bar{Z}_c$) and hence a critical nuclearity (N_c), rather than a critical density (ρ_c). Analytical formulae for calculating mean coordination numbers have been presented by Benfield (1992) and Fritsche & Benfield (1993). By making the analogy with expanded liquid mercury, where a MNM transition occurs at $\rho_c = 5.75$ g cm^{-3}, corresponding to $\bar{Z}_c \sim 6$–7 (Freyland & Hensel 1985; Hensel 1990), Tománek *et al.* (1983) predicted a MNM transition for Hg$_N$ clusters in the range $20 \leqslant N_c \leqslant 50$. Pastor & Bennemann (1994), using a tight binding model, obtained a change in bonding from van der Waals to covalent at around $N = 13$, with a transition to metallic bonding at around $N = 80$, in good agreement with experiment.

7. Metallic clusters of non-metallic elements?

Many semiconducting elements have significantly reduced resistivity upon melting and some, such as silicon and germanium, actually become metallic (Enderby & Barnes 1990). This metallic conductivity (which is essentially due to band overlap) is associated with an *increase* in density on melting (Ubbelohde 1978) and is consistent with the fact that these elements also become metallic at high pressures (Minomura & Drickamer 1962). The increase in density of these covalently bonded network solids on melting is due to the increase in mean coordination number ($\bar{Z}$) and decrease in average network ring size which accompany the collapse of the open network (Štich *et al.* 1991).

Recent polarizability measurements by Schäfer *et al.* (1995) indicate that Si clusters, in the region of $N \approx 36$, may have metallic cores. This is consistent with Car–Parinello calculations by Röthlisberger *et al.* (1994) and empirical many-body potential studies by Li *et al.* (1992) which predict clusters with dense highly coordinated cores in this size regime. The calculations of Li *et al.* (1992) indicate that, up to at least 100 atoms, Si clusters may adopt structures based on simple cubic or BCC packing rather than bulk-like diamond structures. In fact, for Si$_{27}$, the preferred geometry appears to be a $3 \times 3 \times 3$ cube with simple cubic packing.

There is therefore a genuine possibility of clusters which have insulating exteriors (crusts) and metallic cores—as shown schematically in figure 6. This coexistence of metallic and non-metallic regions is analogous to the coexistence of liquid- and solid-like regions which has been postulated, on the basis of molecular dynamics simulations, for noble gas and metal clusters (Berry 1993, 1996; Wales & Berry 1994). Coexistence, which is a finite-size effect, generally results in solid-like (rigid) cores, and liquid-like (mobile) exteriors. Interestingly, Berry (1996) has suggested that elements which are denser in the liquid phase than in the solid (such as Si and Ge) may give rise to clusters in which this situation is reversed, i.e. where the core is

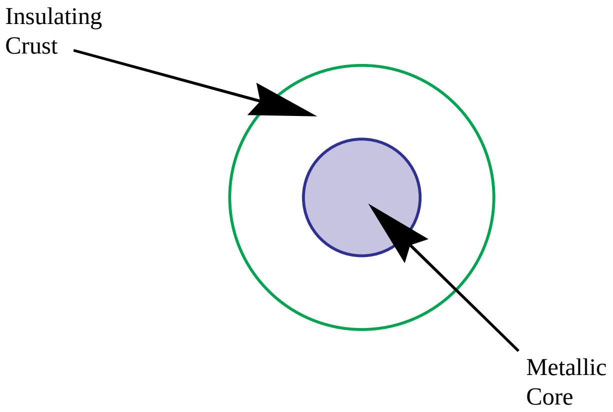

Figure 6. Schematic of a cluster with a metallic core and an insulating crust.

molten and the outer regions of the cluster form a solid crust. Since molten Si and Ge are metallic, it is interesting to speculate on whether, in the experiment of Schäfer *et al.*, the cores of the clusters are metallic because they are solid like but dense, or because they are actually molten. The answer will depend on the experimental conditions under which the clusters are generated and studied and, in particular, the cluster temperature.

8. Conclusions

In this paper, I have demonstrated how models derived from condensed matter physics and molecular quantum mechanics can be applied to the study of the electronic structures of clusters. Cluster size effects have been analysed and split into smooth (liquid drop like) trends and, at smaller nuclearities, oscillatory patterns due to discretization (quantum size effects) and surface structure (surface effects). The problem of the non-metal to metal transitions which must occur, as a function of size, for clusters of elements which are metallic in the bulk limit, has been addressed—as has the question of how the physical state (liquid or solid like) of the cluster influences its electronic structure and, in particular, whether cluster stability is determined by electronic or geometric (packing) effects. The metallization of mercury clusters due to s–p band overlap has been described and the possibility of having clusters of non-metallic elements which are, at least partially, metallic has been discussed.

I thank Professor Peter Edwards for many fruitful discussions and acknowledge the great depth and breadth of his knowledge and understanding, especially in the field of metal to non-metal transitions. I am grateful to Mrs L. D. Lloyd and Mr N. T. Wilson for help in producing the manuscript.

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Discussion

C. N. R. RAO (*Indian Institute of Science, Bangalore, India*). In the case of gold, silver and many transition metals, clusters of 1 nm diameter and below exhibit a continuous metal–non-metal transition in measurements of electron binding energy, density of occupied and unoccupied states, and tunnelling conductance. I am referring to clusters on solid substrates.

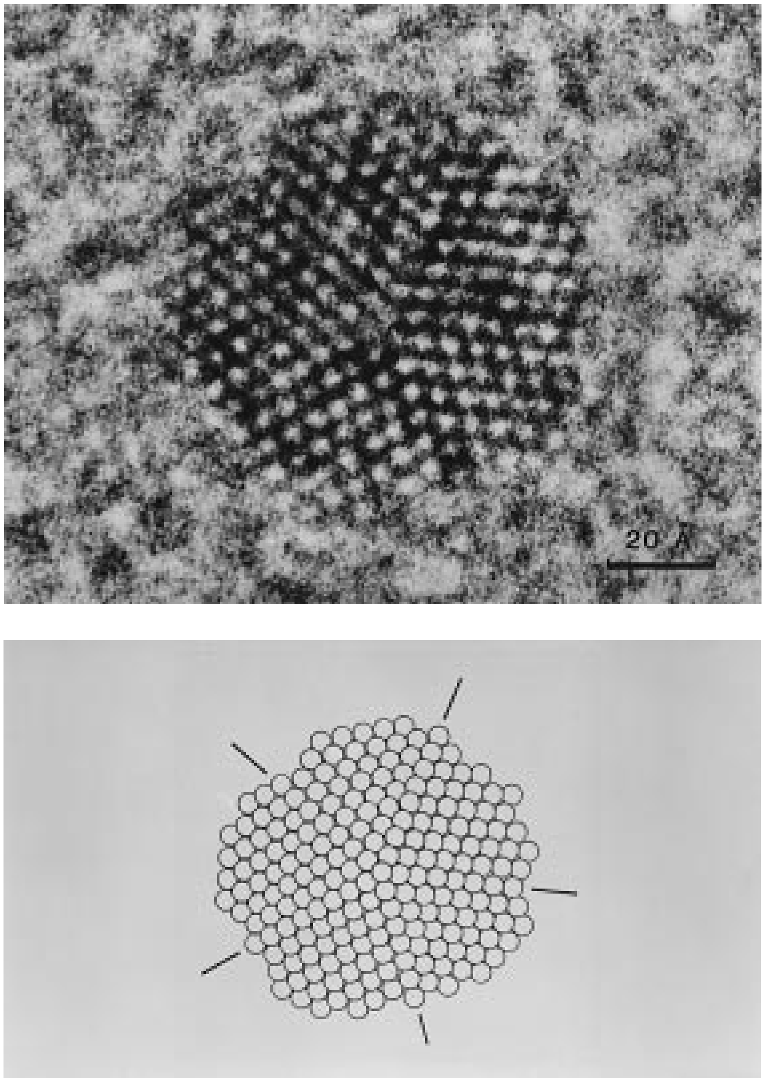
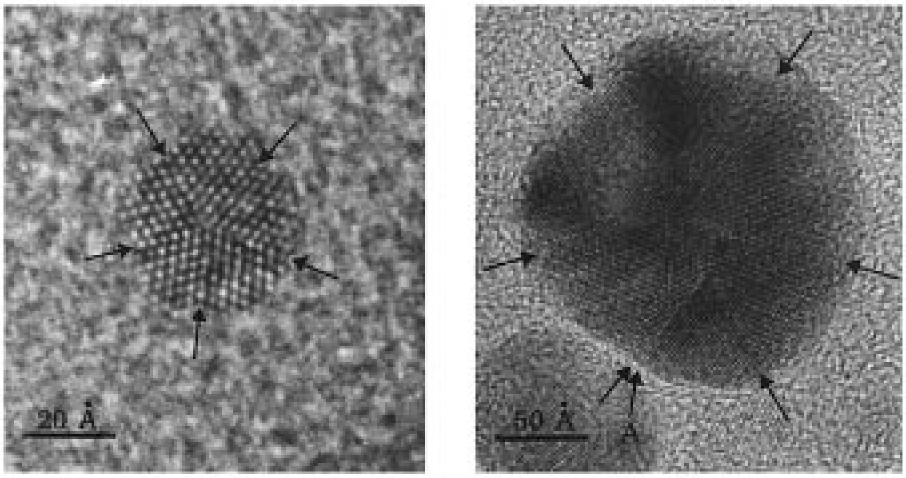


Figure 7. High-resolution electron microscope image of a perfect decahedral single nanocrystal of silver, having diameter *ca.* 40 Å with atoms imaged as white dots, together with the derived crystal packing for the cluster containing 1011 silver atoms.

R. L. Johnston. Yes, this is definitely so, and is consisitent with the Fröhlich–Kubo approach, mentioned above, and the general trend for phase transitions to become continuous in reduced dimensions. Of course, since experiments are carried out at temperatures above 0 K, there will be thermal populations of 'virtual' states when $kT > \Delta$ and this, along with possible cluster–substrate interactions, will serve to blur the transition further.

P. P. Edwards (*School of Chemistry, University of Birmingham, UK*). Can I make two comments in relation to the elusive 'size-induced metal–non-metal transition'?

(1) In the case of colloidal particles of silver, one sees an undoubted change in the crystal structure of these particles as they go below diameters of *ca.* 100 Å. Very small silver particles appear to be perfectly decahedral, with no evidence of either



(*a*) (*b*)

Figure 8. (*a*) Perfect decahedral nanocrystal of silver viewed down the five-fold axis. The boundaries between individual regions in the crystal are arrowed. (*b*) A larger silver particle, with a residual five-fold axis, but with seven individual components.

strain contrast or discontinuities between the individual regions (figure 7). It seems reasonable that the core of such a particle cannot have an FCC structure. As the particle size increases, however, a fundamental change in microstructure takes place, as shown in figure 8.

By the time this size regime has been reached in Ag particles (or nano-particles), the structural mismatch imposed by the non-FCC nucleus of the particle is therefore incompatible with the normal FCC packing by which further growth may proceed, and dislocations and defects must be introduced. In essence, this changeover in structure type could be taken as an indicator of a size-induced metal–non-metal transition. However, in colloidal Pt (and probably Pd), we apparently see no fundamental change in structure type as the particles become smaller and smaller (see Edwards 1992 and references therein).

(2) I completely agree with the view that the onset of electron and spin delocalization in both macroscopic and microscopic systems is of crucial importance. In both situations, one sees the onset of substantial changes in, for example, NMR and ESR properties, before significant changes are observed in transport and other measurements. I believe the same will hold for high energy spectroscopic probes, as discussed by other speakers at this meeting (e.g. Professor Rademann, Professor Palmer and Professor Dowben).

R. L. Johnston. (1) I completely agree with the first part of Professor Edwards's comment. The non-crystalline (icosahedral and decahedral) structures of colloidal particles in this size regime are also consistent with gas phase cluster edperiments, for a number of metallic elements (see, for example, Martin 1996*b*) and with calculations (Wales *et al.* 1996; Hearn & Johnston 1997). These structures are preferred for low nuclearities because they have smaller surface energies than cuboctahedral FCC-like particles, but as they grow, the greater bulk strain inherent in these geometries eventually destabilizes them relative to the bulk structure (Doye & Wales 1996).

As regards his second point, however, I would not view the change in structure type as being indicative of a size-induced metal–non-metal transition, since I believe that clusters and particles with non-crystalline (icosahedral and decahedral type) geometries are probably metallic at nuclearities well below those at which the crystalline (FCC, BCC, etc.) structures are preferred. This is especially likely in the case of transition metal clusters (such as those of cobalt and nickel), which are icosahedral up to several hundreds of atoms (Pellarin *et al.* 1994), but which have high densities of electronic states and thus may be expected (using the Fröhlich–Kubo criterion) to be metallic. Calculations of band gaps for sodium clusters also predict metal-like conductivity for clusters of thousands of atoms (Harrison & Edwards 1985), while mass spectral data indicate clusters in these size regime adopt icosahedral geometries (Martin *et al.* 1991*a*).

(2) I agree.

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