Size-Dependent Icosahedral-to-fcc Structure Change Confirmed in Unsupported Nanometer-Sized Copper Clusters

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Unsupported nanometer-sized copper particles in a molecular beam of inert carrier gas have been studied using electron diffraction. A distinct separation in the size distributions of fcc and icosahedral particles is observed: Icosahedra occur at sizes well below a diameter limit of 3.8 nm predicted for copper by molecular dynamics simulations, while fcc particles occur close to this limit or above. Molecular dynamics simulations have also provided information about particle temperature via thermal expansion and atomic dynamics. [S0031-9007(97)03846-5]

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The equilibrium structure of a nanometer-sized particle may differ from that same material's crystal structure in the bulk. Ultrafine particles with icosahedral and decahedral structures were first observed in gold [1] and have since been well documented in a range of materials, particularly metals which have been extensively studied because of their importance in heterogeneous catalysis [2]. These striking fivefold symmetry forms, which lack the translational symmetry of any lattice, have stimulated considerable interest. Their stability depends on a fine balance of surface and volume contributions to the total energy. The internal atomic arrangement deviates from the bulk crystal and hence incurs a penalty of internal strain. However, the structure does allow a more favorable arrangement of atoms at the surface and, providing the surface-to-volume ratio is large enough, a net energy gain to the particle. Theoretical work, whether applying macroscopic values of elastic constants and surface tension to the small objects [3] or modeling the interatomic potential and simulating the behavior of a number of atoms [4], predicts that for many elements the preferred atomic arrangement in a small particle is icosahedral rather than the crystal structure.

Observations of "big" decahedra and icosahedra are common, highlighting the fact that ultrafine metal particles, far larger than predicted critical sizes, occur routinely [2,5]. The existence of such particles suggests that the conditions under which their growth occurred have led to dimensions greater than thermodynamic equilibrium would allow. Kinetics, surface contamination, and contact with an external support are all clearly capable of influencing growing particles. However, the exact role that such factors play is difficult to quantify, and, as a result, verification of the critical sizes of *metal* particles has not been achieved.

For rare-gas clusters, on the other hand, a successful study has been carried out by Farges *et al.* [6]. Free clusters in a molecular beam were examined using electron diffraction, and the results were compared with molecular dynamics (MD) calculations of the structure and dynamics of the system at finite temperature, using the Lennard-Jones potential. In this way, a range of icosahedral structures were unambiguously identified at different cluster sizes [6].

A similar, molecular-beam, approach suitable for metal particles was pioneered by Stein *et al.* [7]. Unfortunately, the technique of producing a beam of metal particles adequate for diffraction work inevitably results in a much broader range of particle sizes, making it necessary to extract *both* size and structure-related information from the experimental diffraction data [8]. Furthermore, MD simulation of metals demands a sophisticated interaction potential, incorporating many-body effects, and was not available in this early work.

In the electron diffraction study of copper clusters presented here, these technical difficulties have finally been overcome, allowing a direct comparison to be made of critical size calculations and experimental observations. Following Stein, a molecular beam of copper particles has been produced using the inert-gas-aggregation technique (IGA). Hot metal vapor from an evaporation source mixes with helium gas at room temperature, causing cooling and supersaturation to occur, and leads to the nucleation and growth of ultrafine particles [9]. By pumping the mixture of gas and particles through a small nozzle in one end of the nucleation chamber, and then through two differential pumping stages, a collimated beam of small particles is produced in a high-vacuum diffraction chamber. The randomly oriented particles in the beam are then probed by high-energy electrons (100 kV), giving rise to a radially symmetric "powder" diffraction pattern. Measurement of the time-averaged intensity profile along a diameter of this pattern forms the basis of the experimental data collection here. In addition, samples of supported particles were obtained directly from the beam, by exposing electron microscope slides to the particle flux. These have been examined using transmission electron microscopy (TEM) and, in spite of contamination to the particles from exposure to

air, have contributed some information about the size distributions in the particle beams.

The conditions of particle production in these experiments were well suited to a study of small particle structure. Particles did not come in contact with a substrate and were studied only a few milliseconds after formation, eliminating concerns about contamination and external perturbations to the particle's surface. A strong correlation was found between particle size and the average residence time of particles in the chamber, suggesting that significant particle growth occurred while particles were drifting in a vapor-rich region towards the exit nozzle [10]. Furthermore, independent estimates of carrier gas and particle temperatures are in reasonable agreement, suggesting that the particles were thermalized with the surrounding carrier gas [11]. Under these conditions, it is reasonable to expect that particles have adopted configurations close to equilibrium. This contrasts with our own recent study of metastable structures in silver particles, in which the same source was used to produce quite a strong concentration gradient and rapid cooling, leading to growth dominated by kinetic factors [5].

The molecular dynamics calculations in this study were performed using effective medium theory to describe the interaction of copper atoms [12]. Initial configurations were generated from purely geometrical structures and allowed to relax, at finite temperature, until stable forms were obtained. These structures then evolved, at constant temperature, while being monitored to record atomic movements for a few tens of picoseconds. Finally, a quench to 0 K was applied, which determined the static atomic arrangement of the cluster.

Diffraction patterns for a series of five sets of nucleation conditions are shown in Fig. 1, the experimental conditions are summarized in Table I. Profiles are displayed in order of increasing residence time in the source chamber. The average particle size (determined by microscopy) correlates well with this parameter, which is inversely proportional to carrier gas throughput [13].

The degree of change in the series of profiles presented in Fig. 1 is a clear indication of the structural changes taking place in the beam. Profile 5 exhibits distinct peaks of intensity which are indexed as Bragg reflections of the fcc copper lattice. Moving forward, profiles show increasingly broad diffraction features leading, finally, to the distinctly asymmetrical maximum at $s \approx 5\ \mathrm{nm}^{-1}$ and a weak band of scattered intensity between 7.5 and 9.5 nm^{-1}, in profile 1.

Interpretation of these measurements requires care and is discussed in some detail in [14]. The diffraction profiles arise from a mixture of structures and particle sizes in the beam. Our analysis optimizes a linear combination of basis diffraction patterns, calculated using fcc, icosahedral, and decahedral structure models of different sizes, to provide a fit to the experimental data. It is impractical to use molecular dynamics to calculate model structures for each basis pattern used in the fitting process. However, a small number of fully relaxed structures were essential in interpreting the outcomes of fitting, using purely geometrical models. Relaxation in clusters causes subtle, but systematic, changes to occur in the corresponding diffraction profile. When fitted with profiles based on geometric forms, artifacts occur which can be removed only by careful analysis of the inadequacies in the basic geometric models used.

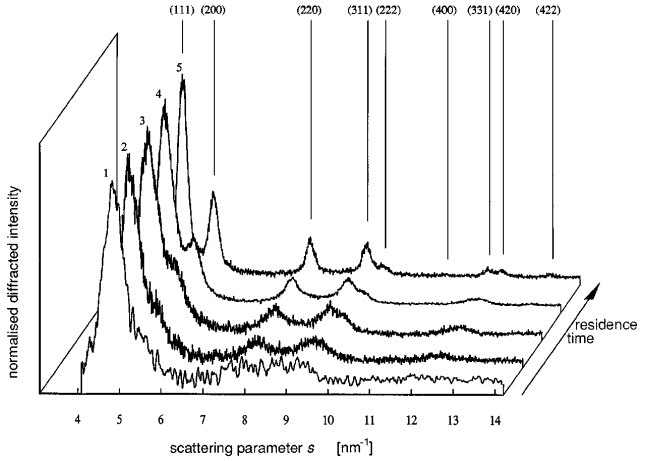

FIG. 1. Diffraction profiles obtained under the conditions described in Table I. The horizontal axis represents the scattering parameter s, where $s = 2\sin\theta/\lambda$, θ is the scattering angle, and λ the electron wavelength. Scattering from carrier gas has been removed, and all profiles are normalized to constant height at the principal maximum. In the case of profile 1, a simple smoothing routine has also been used to reduce statistical fluctuations. The positions and Miller indices of the fcc Bragg reflections for bulk copper at 300 K are shown above profile 5.

The analysis of the diffraction profiles of Fig. 1 is summarized in Figs. 2 and 3, and Table II. The fitting procedure has been applied repeatedly to all profiles, yielding distinct size distributions of cuboctahedra, icosahedra, and decahedra at each application. Because of the inherent noise in the experimental data, and the stochastic nature of the algorithm, repeated fitting gives a range of values. The mean size, $\bar{D}_i$, for a given structural family i has been averaged over the fits to obtain the values $\langle \bar{D}_i \rangle$ shown in Figs. 2(a) (icosahedra) and 2(b) (cuboctahedra). The full range of individual values are indicated by vertical bars, and the regions of instability at 0 K predicted by MD are shaded [15]. The relative contribution to the total diffracted intensity from each structure type is given in Table II. Figure 3 shows the difference $\langle \bar{D}_{\mathrm{cubo}} - \bar{D}_{\mathrm{ico}} \rangle$ which highlights the size dependence of the small particle structure. This figure shows that the average diameter of icosahedral particles is systematically smaller than that for fcc particles in the same sample. Furthermore, the size distributions for icosahedra and fcc particles (not shown) are generally well separated with little overlap.

Although the diameters of the icosahedral particles lie comfortably below the critical size for stability at 0 K,

TABLE I. Source conditions for the data in Fig. 1. T_v is the temperature of the evaporation source, p_g the inert gas pressure in the nucleation chamber, and Q_g the gas throughput in the nucleation chamber (The geometry of the source was changed slightly in profile 1 increasing the pumping speed in the nucleation chamber.)

Profile	1	2	3	4	5
T_v (K)	1974 ± 2	1977 ± 2	1968 ± 2	1911 ± 2	1916 ± 2
p_g (mbar)	4.6 ± 0.1	4.2 ± 0.1	3.8 ± 0.1	3.1 ± 0.1	1.4 ± 0.1
Q_g (cm^3/min)	350 ± 2	149 ± 2	130 ± 2	108 ± 2	43 ± 2
p_v (mbar)	6.6 ± 0.4	6.6 ± 0.4	6.6 ± 0.4	1.6 ± 0.1	1.6 ± 0.1

predicted by MD, the size of fcc particles also tends to fall below the line of critical stability, suggesting either a systematic error in the estimate of particle sizes or that the predicted critical diameter may be slightly too high. We believe both factors may be contributing to the discord.

TEM has provided apparent particle size distributions for a number of supported samples taken from the beam. While TEM observations cannot distinguish between different structures, these measurements can be compared directly with total size distributions obtained by fitting. We find the average fit diameter is systematically smaller, by about 1 nm, than that obtained by microscopy (see Table II). The result is not surprising. Contributions to the diffraction pattern from a small particle are characteristic of domains of coherent structure in that particle, rather than its size. Any regions of imperfection in a particle will therefore make it appear smaller in our analysis.

The second concern is that the finite temperature of particles under observation may lower the critical size. This has been suggested in studies mapping out a phase diagram for small metal particle structures on the basis of high resolution electron microscope observations of gold [16]. Unfortunately, MD cannot at present provide a similar basis for estimating critical sizes at finite temperature; this would require too much simulation time. Also, near critical size, the differences in the total energy of icosahedra and cuboctahedra are not strongly size dependent so that the diameter limit determined from MD calculations can not be taken too literally [15].

Particle temperature has been estimated in two ways from the diffraction profiles. Profile 5, as already stated, can be indexed according to fcc structure. Scaling of that pattern shows that the lattice is dilated by 0.3 ± 0.1% (compared to Cu at room temperature). According to bulk parameters [17], at a temperature of 500 K a lattice expansion of 0.364% is expected, and a full MD simulation of a copper crystal at 500 K shows a lattice expansion of 0.385%. Our results also suggest that, in fcc copper particles (diameter = 4.0 ± 0.5 nm), any size-related lattice contraction must be less than the experimental uncertainty of ±0.1% and this, too, is supported by MD simulation.

Finite-temperature MD simulations have been used to estimate particle temperature through the thermal agitation of atoms. Rapid fluctuation of interatomic distances causes the intensity of a diffraction profile to fall off with increasing scattering angle. Usually, a simple model of random motion is assumed which leads to a Gaussian,

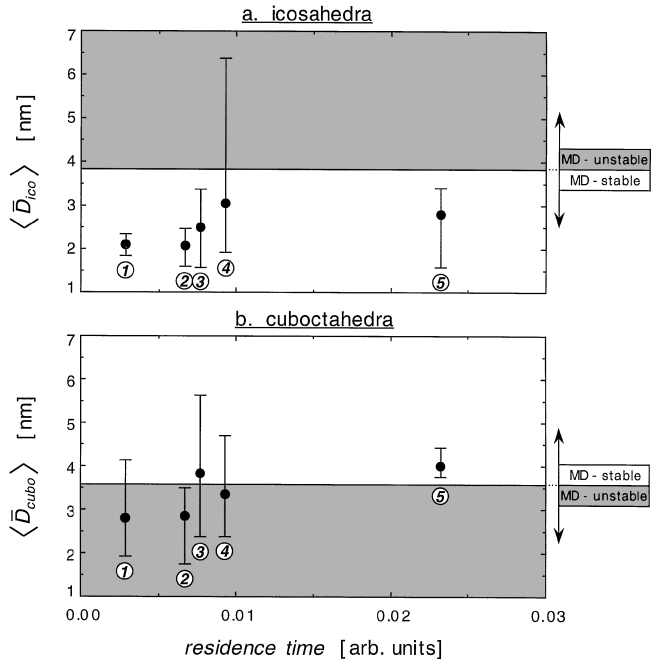

FIG. 2. Average diameters for icosahedra (a) and cuboctahedra (b) after fitting the profiles in Fig. 1. Vertical bars show the full range of values obtained by repeated fitting. The predicted regions of instability, taken from [15], are shown in gray.

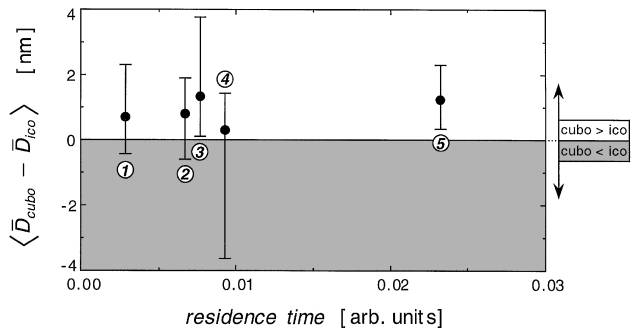

FIG. 3. The size effect is shown clearly by the difference in average diameters at each fit $\langle \bar{D}_{\mathrm{cubo}} - \bar{D}_{\mathrm{ico}} \rangle$, and the region where values would contradict the predicted structural size effect is shown in gray. Vertical bars show the full range of $\bar{D}_{\mathrm{cubo}} - \bar{D}_{\mathrm{ico}}$ values obtained during fitting.

TABLE II. Relative abundances of each of the three structural components used to fit the experimental data. D_{av} is the average diameter for the sample, obtained from the fitted distributions; D_{TEM} is the average diameter obtained by microscopy.

Profile	1	2	3	4	5
fcc (%)	1 ± 1	2 ± 2	1 ± 1	14 ± 7	58 ± 25
Icosahedra (%)	98 ± 2	81 ± 15	27 ± 16	66 ± 23	31 ± 24
Decahedra (%)	1 ± 1	17 ± 17	72 ± 16	19 ± 19	11 ± 11
D_{av} (nm)	2.1 ± 0.3	2.1 ± 0.3	2.3 ± 0.4	2.8 ± 0.8	3.6 ± 1.2
D_{TEM} (nm)	···	3.1 ± 0.2	3.4 ± 0.1	3.6 ± 0.1	···

Debye-Waller (DW), envelope on the diffracted intensity [18]. Using MD simulations, however, "time-averaged" diffraction profiles can be calculated at constant temperature, showing the effects of temperature directly on the diffraction pattern. We have compared profiles from rigid relaxed models, to which a DW factor has been applied, with MD averaged profiles. In spite of pronounced shell-related inhomogeneities present in MD simulations, we found that a DW factor calculated at 500 K gave adequate overall agreement; in all but a number of small details relating to specific diffraction features, the profiles match well. We have incorporated a DW factor for Cu at 500 K in all the basis profiles used in this study.

In conclusion, this diffraction study of unsupported ultrafine particles is in good agreement with earlier MD predictions of a size-related structural change at a diameter of 3.8 nm in copper. Our results show that icosahedral structure dominates at small particle sizes and fcc structure appears at larger sizes. The structural change occurs because of competition between surface and bulk energy components: The icosahedral structure minimizes surface energy whereas the fcc structure minimizes bulk energy. At 3.8 nm, a Cu cluster consists of roughly 2500 atoms, of which about 30% are at the surface. To put this in some perspective, the series of materials, Au, Ag, Cu, Ni, and Al, have been compared in several studies [3], and, although the exact values differ, a distinct order and range of critical sizes emerge (as listed here, Au having the largest critical diameter). For Ag, a critical size is expected only marginally greater than copper which agrees well with previous observations of free Ag clusters [8].

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