

No Evidence for Size-Dependent Icosahedral \rightarrow fcc Structural Transition in Rare-Gas Clusters

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A structural model for a 3000-atom Ar cluster has been developed whose simulated electron-diffraction pattern is in excellent agreement with hitherto unexplained experimental results [J. Farges *et al.*, J. Chem. Phys. **59**, 3454 (1973)]. Although the cluster size is intermediate with respect to the icosahedral and fcc crystalline regimes, the model does not involve a structural transition. It consists of a persisting multiply twinned core with dominant fivefold symmetry, surrounded by a faulted shell with defects that stimulate 3D fcc single crystal growth and prevent hcp stacking.

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In spite of considerable theoretical effort, the crystal structure of the heavier rare gases is not well understood [1]. The predicted structure is hcp, in clear contradiction with the observed fcc structure, although the significance of the calculated energy differences may be doubted in view of the calculation accuracy. This situation (even referred to as a “continuing scandal” [2]) was expected to change when it became possible, in the early 1970s, to produce, by adiabatic expansion, very small crystals or clusters of argon, in rather narrow size distributions around from some tens to thousands of atoms [3]. From electron diffraction experiments it became clear that these (solid) clusters had a structure that was completely different from the bulk crystalline fcc structure, involving noncrystalline fivefold symmetry in, e.g., multishell and polyicosahedral arrangements [4]. It was estimated that this behavior would persist up to sizes $N \approx 750$, to give way to the bulk crystal structure. On the other hand, calculations showed that the icosahedral structure remained more favorable up to some 10^4 atoms, when compared to fcc cuboctahedra of the same size; optimization of the external shape of the fcc crystals could bring down the crossover point to $N \approx 1500$ [5,6]. Subsequently, it was assumed [7] that beyond the crossover point a structural transition to fcc was to be expected, the details of which, when adequately simulated, could give a clue to the preference of the heavier rare gases for fcc over hcp. However, although the electron diffraction pattern at $N \approx 3000$ clearly showed features characteristic of an fcc structure, attempts to simulate these patterns with a variety of imperfect fcc crystals, involving (multiple) twinning and stacking faults, have been unsuccessful, at least suggesting that no “simple” icosahedral \rightarrow fcc transition had taken place. Consequently, it seemed appropriate to assume that the larger clusters (and even macroscopic crystals) consist of a noncrystalline core (identical with or similar to the smaller clusters), completely surrounded by fcc (single-) crystalline material. This requires the solution of two problems: (i) How can local arrangements with fivefold symmetry be embedded in a crystalline matrix? (ii) How can these arrangements stimulate the growth of

that matrix? The solution presented here is inspired by some observations on crystals of C_{60} that have been reported recently [8].

Although RT C_{60} crystals are fcc [9], the four $\langle 111 \rangle$ directions that should be equivalent in a perfect crystal are frequently found to give only three sharp x-ray reflections, e.g., $\bar{1}11$, $1\bar{1}1$, and $11\bar{1}$, and one diffuse, e.g., 111. Since this diffraction pattern is characteristic for *thin* crystals with $\{111\}$ facets (i.e., thin triangular or hexagonal platelets), the apparent inequivalency of $\langle 111 \rangle$ directions clearly results from (or gives rise to) anisotropy of $\langle 111 \rangle$ growth rates. Indeed, the observed diffuse streaking can be connected with the direction of slow growth (perpendicular to the large triangular or hexagonal faces), which, in turn, is apparently the direction of stacking disorder. Consequently, stacking disorder in one of the four $\langle 111 \rangle$ directions prevents stacking disorder in the other three directions (i.e., preserves the *ABCABC* stacking order). Moreover, the high growth rate in these directions suggests that the $(\bar{1}11)$ etc. faces are modified by the stacking faults in the $[111]$ direction in such a way that nucleation of new layers on these faces is much more probable than on the slow growing faces that are parallel to the stacking faults. This is in line with the explanation given by Hamilton and Seidensticker [10], and by Wagner (WHS model) [11] for their observation of dendritic growth, also involving thin triangular and hexagonal platelets, of Ge from the melt. These authors conclude that two closely spaced parallel twin planes, defining a twin *lamella* in an otherwise perfect fcc crystal, suffice to explain high growth rates in lateral directions of thin Ge crystals.

Apparently, to obtain high growth rates (and to prevent stacking disorder) in *all* $\langle 111 \rangle$ directions, a second twin lamella must be introduced in the crystal, *not* parallel to the first, which modifies the slow growing face in the same way as the fast growing faces. Since then the two lamellae must cross, it is likely that the atomic arrangement in a small part of the crystal, i.e., in the crossing region, must deviate significantly from the ideal fcc arrangement. It is this deviating arrangement that can model the structure

of medium sized (i.e., the size region where a structural transition would be expected) argon clusters.

A model for the atomic arrangement in the crossing region is shown in Fig. 1. The faces of the (nano) crystal that are perpendicular to the page are modified by the lamellae to exhibit grooves and ridges. The preferred nucleation in the grooves (which would explain the increased growth rate, according to the WHS model) is clearly connected with the extra bond that can be made. If a new atom (upper thin arrow; the "double" bond denotes two single bonds inclined $\pm 30^\circ$ to the page) would sit in a hcp stacking fault position, this extra bond could not be made, which explains the absence of stacking disorder in the fast growth directions. As indicated by the pentagons, the central region is far from fcc crystalline, but contains (at least) two axes of approximate local fivefold symmetry, i.e., the same feature that is dominant in small Ar clusters. A spherical fragment, containing some 3000 atoms, was cut out and allowed to relax, employing a two-body Lennard-Jones potential [Fig. 2(a)] [12]. The simulated electron diffraction pattern [$s^3I(s)$, rather than $I(s)$; no free atoms assumed; cf. Ref. [6] for calculational details], Fig. 3(b),

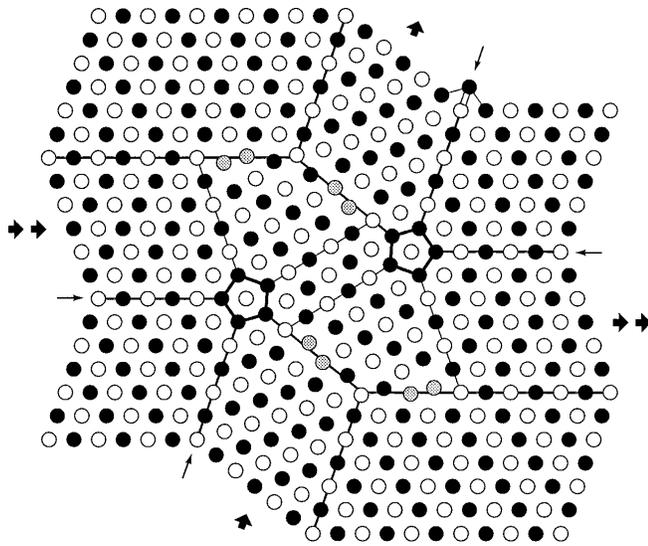


FIG. 1. [110] view of atomic positions in {111} faceted nanocrystal of Ar with two crossing twin lamellae (bold arrows). The view is down close packed rows in close packed planes, with atoms at $z = 0$ (plane of the page), ± 1 , etc. (black dots), and at $z = \pm \frac{1}{2}$, $\pm \frac{3}{2}$, etc. (white dots; atoms not to scale; numbers in units of the effective hard sphere diameter); light shading denotes uncertain positions near incoherent domain boundaries. Thin arrows mark reentrant corners or grooves (perpendicular to the page), with preferred nucleation sites where new atoms can make four bonds, rather than three (upper thin arrow; the "double" bond denotes two single bonds to atoms at $z = \pm \frac{1}{2}$; new atom is at $z = 0$); such atoms will be in correct registry (fcc, rather than hcp) with both domains defining the groove. Local fivefold symmetry, resulting from the crossing, is highlighted by bold pentagons; domain boundaries are shown in thin lines; the heavier lines run along the lamellae.

was compared with the observed pattern, Fig. 3 (exp), for argon clusters of estimated size $N \approx 3000$. The striking agreement suggests that the model adequately describes the "transition" from one regime to another: from *mainly* pentagonal to *mainly* fcc crystalline [there are no traces of typical hcp lines, cf. Fig. 3(d)]. If there was some kind of size-dependent structural transition involved, the experimental curve should be compared with a weighted sum of simulations *b*, *c*, and *e*; despite considerable efforts, including smaller and larger sizes as well, attempts in this direction have remained unsuccessful [13]. The main obstacle is the 111/200 splitting of the first peak in the fcc

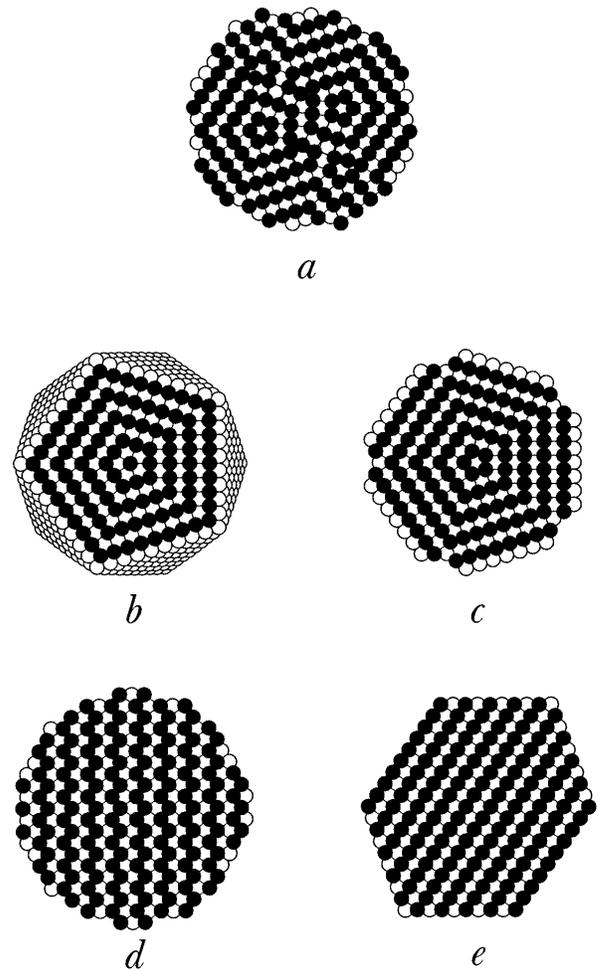


FIG. 2. Cross sections of different models for 3000-atom Ar clusters. (a) present model; (b) nine-shell icosahedron; (c) [7,7,2] Marks' decahedron; (d) hcp spherical cluster; (e) fcc nine-shell {100}/{111} faceted cuboctahedron ([12]; see, e.g., Ref. [6] for nomenclature). Shading and view as in Fig. 1; the cuts are through the clusters' centroids, except in the icosahedron, where it is perpendicular to one of the six fivefold axes, at $\frac{1}{4}$ of its height. Close packed planes are horizontal, perpendicular to the page, in the single crystal clusters (d) and (e), and in at least two domains in the multiply twinned clusters (a), (b), and (c). The local arrangement near the fivefold axes in (a) is identical to the internal structure of decahedron (c).

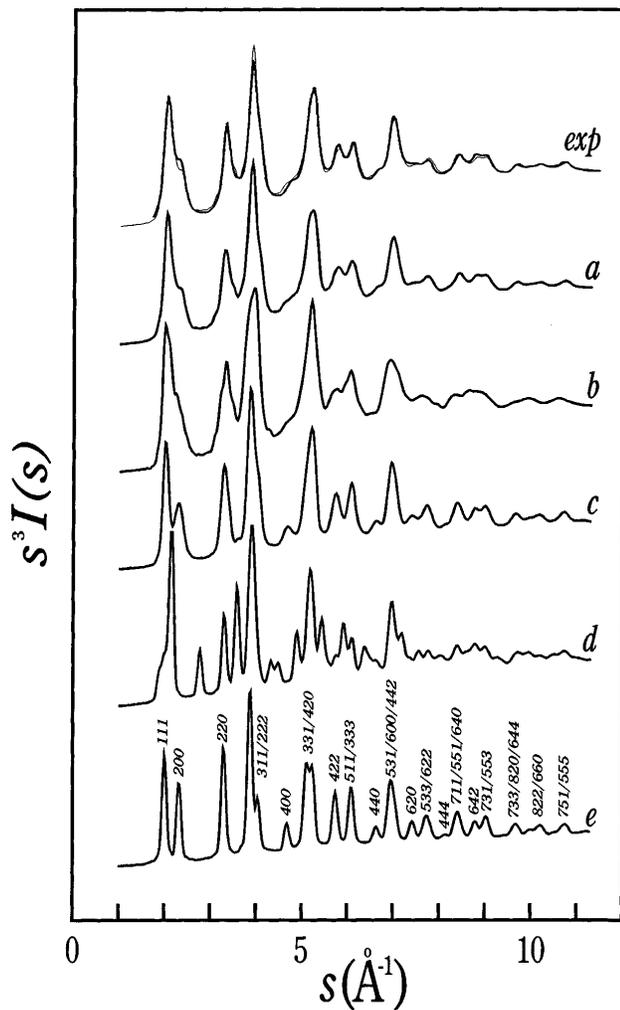


FIG. 3. Calculated electron diffraction patterns for the model structures of Fig. 2, compared with the observed pattern ("exp," reproduced from Ref. [3], with permission; the simulated pattern *a* has also been superimposed over the observed pattern: thin line). Indexing of the fcc pattern *e* is for reference [$s = (4\pi/\lambda) \sin \frac{1}{2} \Theta$].

pattern *e*, which, although size dependent, is already present in 250-atom clusters [6]. The splitting does not occur in icosahedral patterns (b), but the icosahedral contribution to the mixture must be so large to suppress the splitting that the fcc lines in the observed pattern beyond $s \approx 7 \text{ \AA}^{-1}$ (e.g., 533, 551, 642, 553) are suppressed as well. We conclude therefore that there is no evidence for a structural transition, but that the gradual evolution of the diffraction function towards an fcc pattern can be explained by further growth of a cluster like our model, Fig. 2(a), along the lines described above. Since the thickness of the crossing twin lamellae remains unchanged in the growth process, the effects of (multiple) twinning on the diffraction pattern will gradually disappear.

The proposed model is only one of many possible in the same spirit. Thus the twin layer thickness may be varied, more crossings can be introduced, conceivably involving a third lamella, not parallel to the two already present, obviously resulting in a complicated arrangement, but with *icosahedra*, rather than *decahedra*. It appears, however, that the result of Fig. 3(a) cannot be further improved with a single cluster model.

Crossing of twin lamellae is not possible in a hcp crystal. Moreover, stacking faults in one direction stimulate fcc growth in other directions, as explained. This could be the origin for the preference for fcc over hcp in rare gas solids, and also in C_{60} , at least in isolated clusters [14]. The present model presupposes the growth and intergrowth of multishell multiply twinned particles, as indeed is observed in small clusters. The growth history of *these* particles is not fully understood, however, but may be connected with the finite size of the freezing droplets. Obviously, such a size effect cannot be operative in the bulk liquid.

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- [12] All clusters shown have been relaxed before calculating their diffraction functions, Fig. 3. Although the cohesive energy is sensitive to the external shape of the cluster (sphere, faceted), the diffraction function is not. Also, the growth properties of the cross-twinning model, Fig. 1, do not depend critically on the external shape of the nanocrystal. If only surface sites that are at least fourfold coordinated are occupied in a growth process, the

spherical fragment a will eventually develop in a nearly perfect fcc single crystal. The number of atoms, and the minimized cohesive energy (in units of ϵ) per atom, are, respectively, a : 2942, 7.43, b : 2869, 7.54; c : 2622, 7.52; d : 2927, 7.51; e : 2869, 7.51.

[13] Even a good fit would not imply a structural transition in each individual particle. It would allow the view that the *smaller* droplets in the expansion solidify predominantly

as multiple twins (including decahedra and icosahedra), whereas the *larger* droplets tend to crystallize in fcc nanocrystals.

[14] Since cross twinning is energetically unfavorable [12]; this would imply that the fcc preference is kinetically in origin (i.e., not the cohesive energy, but the growth rate is the deciding factor).