

Structure of large argon clusters Ar_N , $10^3 < N < 10^5$: experiments and simulations

B.W. van de Waal^{a,*}, G. Torchet^{b,1}, M.-F. de Feraudy^b

^a Department of Physics TN5206, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

^b Laboratoire de Physique des Solides (UMR 8502, CNRS/PSI XI), Université Paris-Sud, F-91405, Orsay Cedex, France

Received 21 March 2000; in final form 6 September 2000

Abstract

Contrary to expectation, large argon clusters Ar_N , $10^3 < N < 10^5$, do not adopt the bulk fcc crystal structure. Rather they contain a mixture of fcc, hcp, and random close-packed regions, with no significant preference for fcc. This can be concluded from a simulation of observed electron diffraction patterns of large unsupported argon clusters with structural models. The new diffraction patterns exhibit features that have not been detected previously in experiments with smaller clusters; these features can unambiguously be attributed to hcp stacking. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The crystal structure of the classic rare gases, Ne, Ar, Kr, Xe, is *cubic*, rather than *hexagonal* close-packed (fcc rather than hcp) [1]. However, on the basis of *pair*-potentials of any realistic form, the observed higher stability of fcc cannot be understood, the difference in lattice energy being only 0.01%, with the *wrong* sign. Many efforts have been undertaken in the past 50 years to remedy this evident (if not embarrassing) shortcoming of the theory of intermolecular forces (known as the *rare gas solids* (RGS) problem). These efforts have concentrated on properly accounting for, e.g. thermal energy, entropy, zero-point effects, an-

harmonic vibrations, deviations from spherical symmetry of the atomic charge distribution (only fcc is centro-symmetric), and on non-additivity of pairwise interactions. With little success, however, the 0.01% level could not be overcome, even though, for example, three-body contributions to the lattice energy are substantial, but are virtually equal for the two modifications (for a review, see [2]; for an introduction to recent work, see, e.g. [3–5]).

A completely different approach would focus on the *growth* process, with special attention for the solid–liquid or solid–gas interface (low-index faces of fcc and hcp crystallites have different properties), and for growth-stimulating lattice defects (the different symmetries allow different types of defects). As is well known now, very small particles, consisting of up to some 1000 atoms (to many thousands in some metallic particles) may have structures that are completely different from the bulk crystalline structures, involving, for example, non-crystalline fivefold symmetry. Even when a

* Corresponding author. Fax: +31-53-489-1101.

E-mail addresses: b.w.vandewaal@tn.utwente.nl (B.W. van de Waal), gerard.torchet@sol.u-psud.fr (G. Torchet).

¹ Fax: +33-1-6915-6086.

convincing theoretical explanation for the fcc preference of the solid rare gases (except He) was available, it would only apply to the bulk and should be extended to the small size region to account properly for the finite size phenomena mentioned, and, in particular, be able to explain the size-dependent non-crystalline to crystalline structural transition that may be a crucial event in the growth history.

Alternatively, detailed knowledge (from experiment) of the structural evolution during growth could suggest an explanation for the fcc preference that would be rather insensitive to the precise form of the intermolecular interaction potential. In particular, starting with *clusters* of only a few atoms, produced in a supersonic beam, and examined by electron diffraction, structural information at regular intervals for sizes up to the ‘bulk’ size could be obtained.

Research on (among other species) argon clusters started in the early 1970s [6–8], with detailed results reported for Ar_N clusters up to $N \sim 1000$ [9,10]². These indicated that in this size range, the structure of the smaller clusters ($N < 750$) was indeed dominated by fivefold symmetry (e.g. structures, based on the icosahedron), incompatible with *any* crystal structure. From the observed evolution of diffraction patterns with cluster size, it was then expected that beyond $N \sim 1000$ the structure would become fcc (although not necessarily single crystalline). The details of the inferred structural transition remained unclear however, nor could they be predicted by computer simulations. Thus, the belief that the fcc preference of large crystals could originate in embryonal fivefold symmetry could not be given a solid basis.

It was then further assumed that the fcc preference could be connected with lattice defects other than multiple twinning (as in the icosahedron), in particular crossing stacking faults. These defects are only possible in fcc, not in hcp, and stimulate exclusively fcc growth; moreover they allow local fivefold symmetry, as observed in very small clusters. A model based on these ideas gave

excellent agreement with diffraction results for $N \sim 3000$ clusters [11].

Subsequently surrounding this model with new shells of atoms, in line with the proposed growth mechanism, indeed showed a *gradual* transition of the simulated diffraction patterns towards (nearly) perfect fcc.

The experimental verification (or, as it turned out: falsification) of this scenario is the subject of this Letter.

2. Experimental

Unsupported argon clusters were prepared by free jet expansion of pure argon gas through a conic nozzle into a supersonic beam. This beam is crossed by a 50 keV electron beam, producing Debye–Scherrer diffraction patterns $s^3I(s)$ (rather than $I(s)$; see [12,13] for instrumental details). Relevant experimental parameters are the stagnation-pressure p_0 (40 bar) and -temperature T_0 (173 K), and the nozzle diameter d (0.2 mm) (figures in parentheses apply to the largest cluster, $N \sim 80000$). A reliable size estimation, applying the Scherrer method, is not possible since the clusters appear to be polycrystalline and may have an unusually high hcp/fcc ratio. We came to an estimate of $N \sim 80000$ by noting that the slope of the straight line $\log N$ vs $\log p_0$ in the range $10^3 < N < 10^5$ is the same as in the size range $10^2 < N < 10^3$. Here the sizes are accurately known from model fitting and mass spectroscopic data. Since the large-size N s (to be used in the log/log plot) were calculated with the Scherrer formula (applied to the well-defined 220 maximum), it was not surprising to find the equally sloping lines to be parallel shifted one from the other. The large-size Scherrer results were then multiplied by 3.0 to make the two lines continuous. That the Scherrer result may be off by this large factor could be expected, since peak widths are strongly affected by stacking faults, as will be discussed below. The cluster temperature was estimated by extrapolating a Wilson plot ($\ln(I_{\text{obs}}/I_{\text{calc}})$ vs s^2) to $N \rightarrow \infty$ (to eliminate surface mobility). This gives an rms thermal atomic displacement $\langle u^2 \rangle^{1/2} \approx 0.24 \text{ \AA}$ in the clusters interior. From this value we estimate

² The quoted cluster sizes are to be understood as estimated mean sizes of a distribution.

the cluster temperature to be 35 ± 4 K. This temperature agrees well with that of the smaller clusters (the cluster temperature appears to be size independent) [9,10], and also with that predicted by Klots [14] for an evaporative ensemble.

Two diffraction patterns are shown in Fig. 1: that of an $N \sim 3000$ atoms cluster, and that of an $N \sim 80000$ atoms cluster; they are rather similar, despite the large difference in cluster size; in particular the expected splitting of the first peak in fcc (1 1 1)/(2 0 0), that should be resolved at this size, is *not* observed. Also, the transformation from one pattern into the other, with increasing cluster size, is quite gradual. The patterns may be compared with the calculated patterns for $N \sim 20000$ spherical clusters ($R \sim 50$ Å), that are three- and two-dimensionally perfectly crystalline, viz fcc or

hcp, and randomly stacked, respectively, cf. Fig. 2 (for details of the pattern calculations, see [15]).

3. Analysis

Figs. 1 and 2 suggest that the structure is close to fcc, albeit that the peaks are too broad for the inferred size. All observed peaks in the $N \sim 3000$ trace can be indexed fcc, whereas typical hcp peaks like hcp(102) and hcp(103) are missing. To a lesser extent this also applies to the $N \sim 80000$ trace. Thus, in a first attempt to solve the structure, it was supposed to be monocrystalline fcc, with an (as yet) unknown number of (parallel) stacking faults. Two kinds of stacking faults have been considered: *growth faults* (or twin faults):

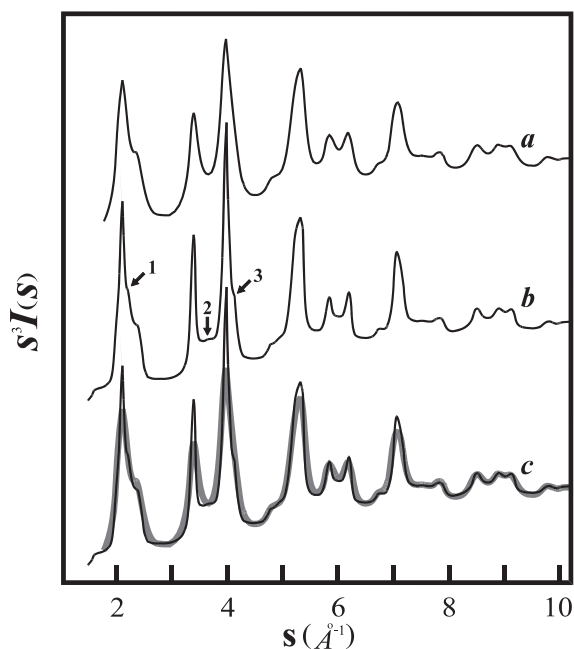


Fig. 1. Experimental diffraction patterns $s^3I(s)$ vs s ($s = (4\pi/\lambda) \sin \frac{1}{2}\theta$). (a) $p_0 = 20$ bar, $T_0 = 300$ K, $N \sim 3000$; (b) $p_0 = 40$ bar, $T_0 = 173$ K, $N \sim 80000$ (N : estimated average cluster size); (c) superposition of both patterns. The most striking difference between the two traces is in the enhanced 'tapering' of the first three peaks. Minor differences are marked by numbered arrows. Features 1 and 2 are in the hcp(101) and hcp(103) positions; feature 3 is in the fcc(222) position. Note the *absence* of resolved splitting of the first peak in fcc(111)/(200) and the *absence* of hcp(102) at 2.8 \AA^{-1} (cf. Fig. 4).

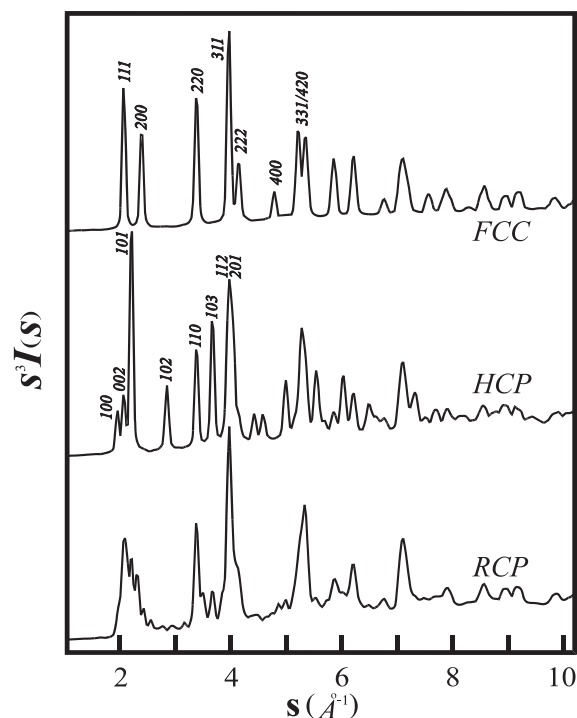


Fig. 2. Calculated diffraction patterns of 20000-atom model clusters with different stackings of close-packed layers: fcc, hcp, and rcp. Whereas the fcc structure has four (equivalent) stacking directions, the hcp and rcp structures have only one (accounting for the increased number of diffraction peaks). Most features of the fcc pattern (except the (1 1 1)/(2 0 0)-splitting of the first peak) can be distinguished in the rcp pattern, whereas many details of the hcp pattern are lost (notably hcp(102), and, to a lesser extent, hcp(103)).

... $\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow$... , and *deformation faults*: ... $\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow$... ³. The concentrations of these defects, β and α respectively, can be estimated from peak-broadening (PB), peak-asymmetry (PA), and peak-position shifts (PS) [17]. Although in favorable cases β can be determined from PA alone, this feature is ill defined and difficult to measure. Since PB gives only a value for $(1.5\alpha + \beta)$, the accuracy of β depends not only on the accuracy of the PB measurement, but also on the accuracy of α . α in turn can be derived from careful measurements of peak shifts with respect to unfaulted crystals of the same size. However, the results of applying this procedure turned out to be rather disappointing, leading to unphysical values for α and β : $\alpha = 0.25$ (at least one order of magnitude too large, for the underlying theory to be valid), and $\beta < 0$ [18].

Despite the similarity of the two experimental traces of Fig. 1, a close examination reveals distinct features in the large-cluster trace not present in the small-cluster trace (see figure caption for details)⁴. The differences cannot be accounted for by a difference in size only. The small but significant features that are only visible in the large-cluster trace allow the conclusion that the cluster is not (polycrystalline) fcc, but may contain an appreciable amount of hcp (or even *random*) stacking as well. This possibility was not considered earlier, because characteristic hcp peaks (like hcp(1 0 2) and hcp(1 0 3)) were not observed.

The extension of an earlier proposed 3000-atom cluster model to larger sizes, as described above, cannot account for these changes. In particular, increasing its size to 10 000 atoms results in a noticeable splitting of the first peak [21]. The same applies to other models of the same size, based on

crossing stacking faults and ‘stair-rod’ dislocations [21]. Also, polycrystalline models, consisting of relaxed conglomerates of up to 27 fcc crystallites in random orientations could not account for the non-splitting of the first peak, although other features of the 3000-atom trace were reproduced rather well [21]. It was then concluded that the persistent non-splitting of the first peak could be attributed only to a significant hcp/fcc ratio in the large clusters, in spite of the clear absence of a hcp peak at 2.8 \AA^{-1} . We were encouraged to do so by the appearance of the simulated random close packing (rcp) trace of Fig. 2, where the splitting of the first peak is unresolved and hcp(1 0 2) is absent.

However, no satisfactory results could be obtained with all close-packed planes parallel (as in rcp), whereas different stacking directions lead to complicated crossings. As a compromise, a polycrystalline model was constructed by gluing a large cube from eight equal-sized smaller cubes, and cutting a sphere out of the large cube. Relaxation of the sphere (28 178 atoms) under a Lennard–Jones potential⁵ improved the atomic scale fit in the grain-boundary regions (Fig. 3 shows a cross-section of this cluster). This resulted in considerable smoothing of the diffraction function as compared to that of the individual crystallites. The eight crystallites (small cubes) were constructed from eight *different* stacks of 40 close-packed layers⁶, by cutting out equal-sized cubes in arbitrary

³ A stacking arrangement of close-packed layers can be conveniently represented by a sequence of arrows [16]: \uparrow denotes a translation operator $A \rightarrow B \rightarrow C \rightarrow A$; and \downarrow denotes the inverse operator $A \rightarrow C \rightarrow B \rightarrow A$; thus, the fcc stacking is characterized by the sequence ... $\uparrow\uparrow\uparrow\uparrow\uparrow$..., the hcp stacking by ... $\uparrow\downarrow\downarrow\uparrow\downarrow$...

⁴ A shoulder on the first peak (feature 1) has also been observed by Kovalenko et al. [19], in relatively small nitrogen clusters (ca 6000 molecules) in their α -phase (fcc), and by Reinhard et al. in Ag clusters [20], although it was attributed to rhombohedral distortion of fcc tetrahedra in multishell icosahedra (cf. [21]).

⁵ Lennard–Jones potential in reduced units (dimer nuclear distance, dimer bond energy): $V(r) = r^{-12} - 2r^{-6}$. Correct scaling is assured by dividing s by 3.822.

⁶ The stacking *order* in a particular stack i of 40 close-packed layers was characterized by a sequence of 40 arrows (cf. Footnote 3). The sequence of arrows in turn was derived from a sequence of 40 random numbers (<1) as follows: the $(n+1)$ th arrow will have the same (opposite) direction as the n th arrow when the $(n+1)$ th random number is smaller (larger) than r_i . Here r_i is a number, $0 < r_i < 1$, assigned to the i th stack, governing its degree of stacking (dis-)order. In this way, the overall character of the complete cluster can be manipulated routinely with the choice of r_i values (the use of random numbers ensures that two stacks with the same r value are similar, but not identical). The reported results were obtained with $r_i = 0.13i - 0.04$ ($1 < i < 8$). Thus, the first cube is nearly perfect hcp, the eighth cube is fcc, and the other cubes have intermediate structures. The rcp curve of Fig. 2 was obtained with $r = 0.5$ (single crystallite, rather than eight).

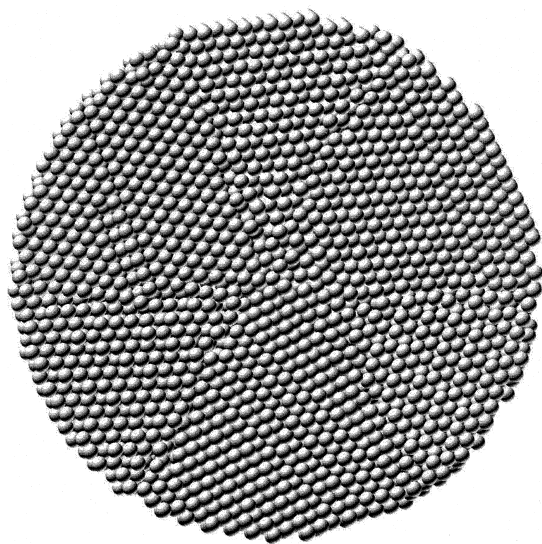


Fig. 3. A special cross-section of the 28 178-atom model cluster, showing six out of eight domains (the missing domains being entirely above and below the page) as equal 60° -sectors of a circular area. Note the different stacking directions, as well as the different degrees of stacking disorder in the domains.

spatial orientations with respect to the stacks. This was done to assure that the eight cubes have different degrees of stacking *disorder*, and different stacking *directions* when glued together.

The simulated diffraction pattern (Fig. 4) is seen to be in good agreement with the experimental curve. The non-splitting of the first peak in the observed patterns can now be attributed to the mixing in of the hcp(101) peak and not, as had been assumed previously, to lattice defects in an otherwise perfect fcc structure. Likewise, the observed sharpening (with size) of the second and third diffraction peaks, along with the broadening of the plateau between them, can be ascribed to the mixing in of hcp(110), (103) and (112)/(201) maxima.

Although all observed peaks are in fcc positions it is the *shape* of the peaks that reveals that the cluster has probably as much hcp as fcc character. This is more surprising since none of the characteristic hcp peaks, like hcp(102), is observable. It is this observation that practically rules out the possibility of a *mixture* of various pure crystalline structures (including pure fcc and pure hcp) in a

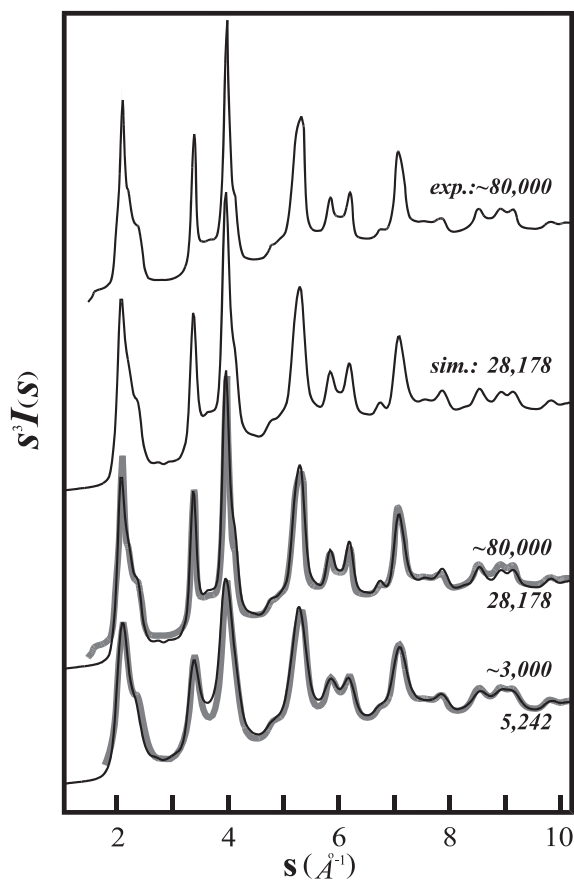


Fig. 4. Comparison of simulated (28 178 atoms) and observed ($\sim 80\,000$ atoms) diffraction patterns. Both traces are also superimposed, to facilitate comparison (shaded: observed; black: simulated). A 5242-atom fragment was extracted from the interior of the 28 178-atom model, and relaxed. Its calculated diffraction pattern is compared with the observed pattern Fig. 1a in the lower trace. The two calculated patterns differ in the same way as the two observed patterns of Fig. 1. Apparently, a wide range of cluster sizes can be simulated by a single structural model.

broad cluster mass distribution: the observed non-splitting of the first peak cannot be reproduced by pure fcc model structures with more than a few *hundreds* of atoms; when the non-splitting is ascribed to the presence of hcp clusters in the beam, these should be in the same size range as the fcc clusters (to make their hcp(101) peak fill the fcc(111)/(200) gap); however, since the hcp(102) peak becomes already prominent at a size $N \sim 100$, increases rapidly with size, and is

situated at a scattering angle where the pure fcc trace is virtually flat, the hcp(102) peak will show up in all fcc/hcp mixtures that *do* reproduce the non-splitting of the first peak. Other mixtures, including decahedra and icosahedra, give similar problems, and are, especially in the case of icosahedra, inappropriate to reproduce high-angle detail. None of the weighted averages we examined gave a simulated pattern competitive with that of Fig. 4. Finally, it should be remembered, in this connection, that many interatomic distances, involved in the fourier transformation to the diffraction function, correspond to atoms on *different* sides of grain boundaries between different crystalline domains in the same cluster. As is apparent from a comparison of the superposition of the diffraction patterns of isolated domains with that of the connected domains, these ‘intergrain-distances’ are crucial to the appearance of the pattern. In fact they are able to *suppress* peaks originating from single crystalline domains that would show up in the simulated patterns of a cluster *distribution*, but that are not observed.

4. Discussion and conclusion

The fact that the observed diffraction function of a 80 000-atom cluster of argon (or, better: a model cluster, that reproduces this function) seems to indicate that there is no significant preference for either fcc or hcp, contrasts with the known preference for fcc in the bulk, and with the generally accepted view that the cluster structure approaches the bulk structure with increasing size. The reason for this discrepancy may be in the way the clusters are made, i.e. in vacuum, possibly not in equilibrium with the liquid (although the clusters are believed to be initially liquid-like). The timescale of the process of solidification could prevent full annealing, or weaken the relative importance of kinetic effects in the growth process, as proposed earlier [11]. Also, the apparently significant (energy) difference between the two modes, fcc and hcp, of stacking in the bulk, is too small to play a decisive role in the cluster solidification process.

Agreement between observed and simulated diffraction patterns does not necessarily imply the correctness of the model in detail however. Indeed, the construction from eight fused cubes is rather arbitrary, and is only a poor reflection of what can be expected to be really the case: an unknown number of domains, with different spatial orientations, are connected to each other by twinning, rather than by amorphous regions. Modeling of three-dimensional twinning in the size region of interest is still beyond our capacities, however, as is the modeling and relaxation of clusters with the size they should actually have ($\sim 10^5$ atoms). Finally, we realize that the observed traces are only averages over many clusters, possibly different in size and structure. Our confidence in the adequacy of a single structural model derives from its capacity to reproduce virtually every detail in the observations. Moreover, we were not able to improve the agreement by averaging over a distribution of clusters including individual clusters significantly different from our model.

The height of the first peak is too small (cf. Fig. 4); this could be remedied by increasing the number of crystallites (decreasing the long-range order). Thus, further models with 9, 16, and 27 crystallites have been constructed and relaxed. The increased intensity of the first peak had to be paid for, however, by losing much detail in the peak shapes. The latter effect is due to the increased total grain-boundary surface, which tends to affect the stacking within the crystallites in the relaxation process. Obviously, this is an artefact of our way of modeling a polycrystalline cluster; when the different crystalline domains would be connected by twin-planes (as they probably are), this effect would play no role.

The question of the coherence of the domains is relevant in connection with the growth process: with no coherence at all (as in our model), the crystallites could have their origin in (virtually) simultaneous nucleations in different regions inside the initially liquid droplets; coherence, on the other hand, would suggest a single nucleation. As has been proposed earlier, coherence could also be brought about by simultaneous nucleations on the droplets surface; however, the corresponding simulation results [21] were not as close to the

observed diffraction patterns as in the present study. The effect of amorphous grain boundaries is well illustrated by the lower trace of Fig. 4: a 5242-atom spherical fragment was taken out of the 28 178-atom model cluster, and relaxed again. All details that could be indicative of a large hcp content are lost, most probably as a result of the larger fraction of atoms in the grain boundaries; also the relative height of the first peak has increased. The similarity with the observed ~ 3000 atom trace is rather surprising, taking into account that the smaller cluster was not *constructed* to simulate this trace.

The close agreement between simulations and observations (and, for that matter, the *disagreement* found for many other models [21]) permits the following conclusions:

- (1) Argon clusters do not adopt the bulk crystal structure as their size increases. Consequently, argon cluster research can no longer be expected to contribute to a solution of the RGS problem.
- (2) No preference for fcc over hcp is apparent. Large argon cluster diffraction patterns can only be simulated assuming hcp and fcc stackings to be present in approximately equal amounts.
- (3) Although (close) agreement between observed and simulated Debye–Scherrer diffraction patterns does not rule out the possibility of a different structure, the observed sensitivity of the simulated patterns to the model parameters at least strongly supports conclusions (1) and (2).
- (4) Clusters with only *one* stacking direction cannot reproduce the observed patterns. Also, no distribution over sizes and structures, leading to a satisfactory simulation of the diffraction pattern, could be found. Consequently, the clusters are believed not to be single crystalline, but composed of a number of domains with internal structures ranging from pure fcc to pure hcp.

Finally, we note that the present result was unexpected only in view of the *bulk* crystal structure. By contrast, from the viewpoint of crystal structure prediction, the reported *cluster* structure would appear the more plausible, in view of the virtually equal contributions of fcc and hcp arrangements.

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