

Noncrystalline Structures of Ultrathin Unsupported Nanowires

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Computer simulations suggest that ultrathin metal wires should develop exotic, noncrystalline stable atomic structures once their diameter decreases below a critical size of the order of a few atomic spacings. The new structures, whose details depend upon the material and the wire thickness, may be dominated by icosahedral packings. Helical, spiral-structured wires with multiatom pitches are also predicted. The phenomenon, analogous to the appearance of icosahedral and other noncrystalline shapes in small clusters, can be rationalized in terms of surface energy anisotropy and optimal packing. [S0031-9007(98)05930-4]

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The regular crystalline packing of atoms, which usually minimizes energy in a bulk solid, is known not to last indefinitely as physical size is decreased. For very small elemental clusters, for example, one expects a structural switch from bulklike to some new arrangement at some critical radius [1]. Such is the case, for example, of small (diameter $\sim 20\text{--}40$ Å) clusters of Ag [2] and other metals [3], and of rare gas clusters [4,5], which were observed to abandon single crystal structures in favor of an icosahedral shape below a critical size. Cluster calculations based on the Lennard-Jones (LJ) potential [5,6] confirm the stability of the icosahedral shape, implying a radical deviation from the bulk fcc morphology, for $N \lesssim 4000$. The driving force causing this morphological change at small size can generally be traced back to two very distinct sources: (i) electronic magic sizes, stabilized by filling of shells, as in atoms and nuclei; (ii) competition between optimal internal packing and minimal surface energy, the latter dominating for sufficiently small size. Here we shall address exclusively the phenomena caused by the second mechanism, which is important in a large class of cases. For example, very small icosahedral clusters, rather common in nature, are favored by their ability to expose an exceptional 100% of (111) faces, lowest in energy.

We address the same structural question for ultrathin nanowires. *A priori*, one could anticipate a weaker tendency to depart from the bulk structure than in clusters, because of the smaller relative surface/bulk ratio in the wires ($2/R$ against $3/R$, where R is the radius). However, we present here detailed optimization results, suggesting that new noncrystalline nanowire structures (which we propose, for convenience, to name “weird” wires) should in fact be rather readily realized in nature. As it turns out, the tendency for the wire structure to switch from crystalline to weird appears to be both general and stronger than anticipated. Moreover, there seems to be a variety of new structures, changing continuously and unpredictably from size to size, and from one substance to another. For our initial

analysis we have chosen to study elemental (unsupported) metal wires, whose fabrication should be within reach, thanks to the metal’s combined ductility and strength.

So far, we have considered Al and Pb as test cases. Both were assumed to be described by classical, empirical many-body interatomic potentials, of the “glue” type [7]. The glue parameters were previously optimized to model the properties of metallic Al [8] and Pb [9], respectively. Of course, such potentials are not meant to provide a quantitative description for metal wires of nearly atomic thickness, whose electronic structure may and will differ profoundly from that of the bulk metal. The structures thus generated should therefore be considered at this stage of mostly qualitative significance, while future *ab initio* studies will be called for to achieve quantitative accuracy, and to include electronic shell effects, expected to be very important at small radii. Nonetheless, the existence of stable weird wire structures, suggested by our energy optimizations with classical potentials, represents in our view a true, general, and parameter-independent phenomenon. For instance, it is found that even a hypothetical argon wire (as described by a Lennard-Jones potential) turns weird when sufficiently thin. We also note that the simplicity of the empirical potentials for metals has been at this initial stage quite instrumental, as it allowed a broad and thorough search for optimal structures, which would have been prohibitive had we adopted from the outset the more accurate *ab initio* approach.

For structural optimization, we adopted a molecular-dynamics-based “simulated annealing” methodology, using techniques previously employed to investigate pre-melting of thin wires [10]. We generally started with fcc (110)-oriented N -atom wires [in a few cases we also used (100) wires, with similar outcomes], with periodic boundary conditions (PBC) along the wire axis direction z . We first relaxed the atomic positions, to optimize the fcc wire structure. Starting from this structure, we simulated thermal annealing cycles, with T rising in steps

up to a maximum (typically about $0.75T_m$, where T_m is the bulk melting point) and then decreasing back to $T = 0$. The wire length was clamped by the PBCs, and its value kept constant during annealing, thus preventing surface-free-energy-driven contraction into a drop, which thermal diffusion would otherwise inevitably drive. Once back at $T = 0$, however, the length was finally allowed to adjust, and the wire structure further relaxed, before inspection of its energy and structure. The resulting annealed wire energy was almost invariably better than that of the fully relaxed original fcc structure. Its shape generally exhibited large irregularities and a z -dependent thickness, occasionally with sections showing a new regular structure, which initially triggered our curiosity. Simple annealing was generally unable to generate a fully regular wire. In a generality of cases where the spontaneous regular sections could be identified by visual inspection, new full-length entirely regular wires were produced with just that structure. In the new artificial wire, the total length and atom number were chosen such as to guarantee a proper matching through PBCs. After further relaxation we obtained the final wires, collectively depicted in Fig. 1. The wire radius R is defined by $S = \pi R^2$, where S is the area projected on the x - y plane by all of the atoms

(considered as spheres of diameter d , where d is the nearest-neighbor distance in the bulk crystal) included in a portion of the wire of length $2d\sqrt{2/3}$, corresponding to two (111) interplanar spacings.

Crystalline wires clearly prevail for R larger than a critical value R_c of the order of $3d$, depending on the system. For $R < R_c$, weird structures make their appearance. Their energies fall systematically *below* the extrapolated fcc line, consistent with simulations, showing an irreversible and exothermic spontaneous restructuring of the initially fcc wire. The structures found for Al and Pb bear certain resemblances, but are certainly not identical, although we have not attempted a complete search. A (simplified) visual illustration of some stable weird wire morphologies is offered in Fig. 1. These structures, though noncrystalline, are very regular. The thicker ones, about four atomic radii in diameter, are three-shell wires (A15, B6, B7), where a central string is surrounded by two successive coaxial cylindrical shells, mutually related by some kind of epitaxy. Several structures, including three-shell (A15, B6) and two-shell (A6, B4) cases and several composites (A8–A14), display pentagonal motives.

For better characterization, we have calculated angular correlation functions for all of our structures. These are

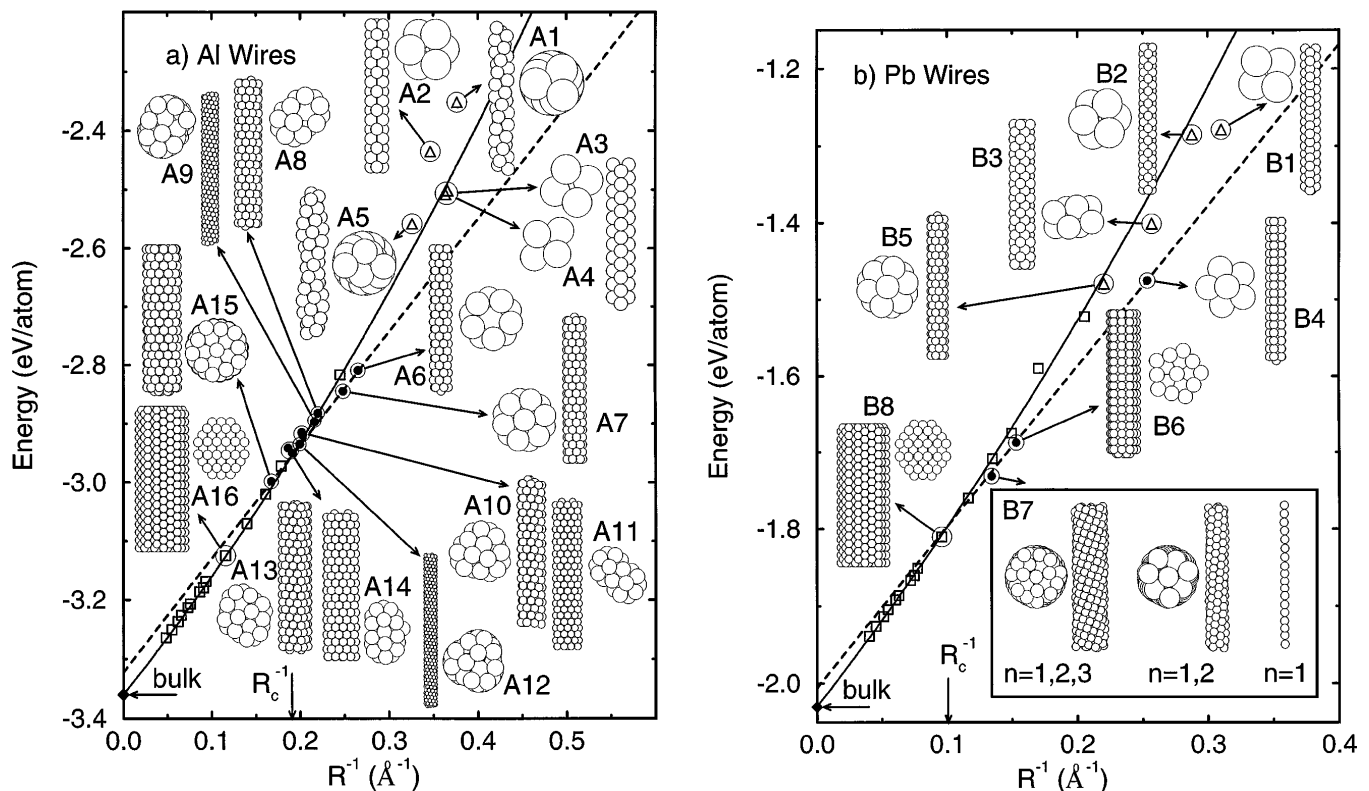


FIG. 1. Total energy per atom E vs inverse wire radius $1/R$ for the relaxed structures obtained by optimization for (a) Al and (b) Pb wires. A selection of morphologies is shown. fcc wires are represented by open squares and weird wires by full circles. Very thin wires which do not belong to either class have been marked with open triangles. Solid lines represent a fit to fcc wires using Eq. (1), and dashed lines represent a fit to weird wires using Eq. (2). Weird structures become favored for $R < R_c$. (b) Inset: structure of the helical Pb wire B7: complete wire ($n = 1, 2, 3$), with outer shell removed ($n = 1, 2$), and inner strand ($n = 1$). Note how the outer shell exhibits a nearly square atomic structure, while that of the second shell is nearly triangular. Also note the different helical pitches of these two shells.

defined by considering all of the angles formed by bonds ij and ik , where i runs on all of the atoms closest to the wire axis, and j and k on their neighbors. The cutoff distance used to define the neighbors is 3.3 \AA for Al and 3.5 \AA for Pb. Results for a selection of cases are shown in Fig. 2. Wires A16 and B8 exhibit peaks at 60° , 90° , 120° , and 180° , typical of regular fcc structure. In contrast, the pattern of the pentagonal wire A6 has only three peaks near 63° , 117° , and 180° , the signature of icosahedral packing. Strong icosahedral features can also be observed on A11 and A15. A local icosahedral geometry has recently been found in a Na neck studied by first principles molecular dynamics [11]. Occasionally, we find structures such as A10 exhibiting a broad distribution, indicating a marginal case. In the thinnest wires (probably less meaningful than the others), we also observe triangular and tetrahedral packings. Pb wires also exhibit pentagonal motifs (B4, B6), but angles show no icosahedral packing: This different behavior is discussed below.

Some wires, such as A1, A5, A9, A12, B7, are truly weird, possessing chiral, or helical, arrangements with long periods. In these cases we also checked for stability against a discrete change of pitch, although we could not generally rule out the possibility of a continuously changing (incommensurate) pitch.

The detailed internal structure of a beautiful weird wire, the three-shell helical B7 of Pb, is illustrated in Fig. 1(b) (inset). The center ($n = 1$) consists of a single, nearly straight atomic chain, or strand. The surrounding shells, $n = 2, 3$, can be seen as being made up of m_n identical strands, each helically wound with a linear pitch λ_n in a cylinder of radius r_n . Choosing conventionally the strand direction closest to the wire axis z , we follow each strand and determine the number M_n of periodically repeated cells and the corresponding number of turns N_n required for that strand to connect back to itself. Hence, $\lambda_n = M_n c / N_n$, where $c = 60.83 \text{ \AA}$ is our cell length. For

wire B7 we find $m_2 = 7$, $r_2 = 3.3 \text{ \AA}$, $M_2 = 7$, $N_2 = 2$, $\lambda_2 = (7/2)c$, and $m_3 = 11$, $r_3 = 6.0 \text{ \AA}$, $M_3 = 11$, $N_3 = 7$, $\lambda_3 = (11/7)c$. Strikingly, the two consecutive shells are not simply commensurate, which implies in this case an overall coincidence length of $(7 \times 11)c$, or 4684 \AA .

How should we understand these new morphologies? The basic explanation is clearly related to surface energy. In the weird wires, contrary to fcc wires, the ‘‘bulk’’ packing is not very good, but the surface packing is excellent. Unlike crystalline wires (which must by necessity possess different crystallographic facets), the weird wires in fact display a *single*, optimal surface structure. This feature is also a characteristic of, e.g., icosahedral clusters, and represents the winning ingredient at very small radii.

Quantitatively, we can write the crystalline wire energy per atom as

$$E_c(R) = -E_{\text{coh}} + \frac{2\Omega_c}{R} \bar{\gamma} + \frac{\Omega_c}{\pi R^2} 8\bar{\mu}, \quad (1)$$

where E_{coh} is the bulk cohesive energy, $\Omega_c = \pi R^2 L / N$ (L is the wire length) is the average atomic volume, $\bar{\gamma}$ is the surface energy (averaged on the different facets), and $\bar{\mu}$ is the average edge energy per unit length (there are eight edges in our geometry). $\bar{\gamma}$ can be written as $\bar{\gamma} = \gamma_{111}[\alpha_{111} + \alpha_{100}f_{100} + \alpha_{110}f_{110}]$, where γ_{111} is the close-packed surface energy, α_{ijk} is the fraction of exposed area relative to $\langle ij k \rangle$ facets, and $f_{ijk} = \gamma_{ijk} / \gamma_{111}$. Moreover, $8\bar{\mu} = 4\mu_1 + 4\mu_2$, where μ_1 and μ_2 are the edge energies relative to the $\langle 111 \rangle$ - $\langle 100 \rangle$ and $\langle 111 \rangle$ - $\langle 110 \rangle$ edge, respectively. The weird wire energy, on the other hand, is much simpler:

$$E_w(R) = -E_{\text{coh}} + \Delta + \frac{2\Omega_w}{R} \gamma_{111}, \quad (2)$$

reflecting (i) a single smooth closed-packed surface and (ii) no edges. This surface gain is countered by bad packing, causing a bulk energy increase Δ and an average atomic volume Ω_w (defined as for the crystalline wires)

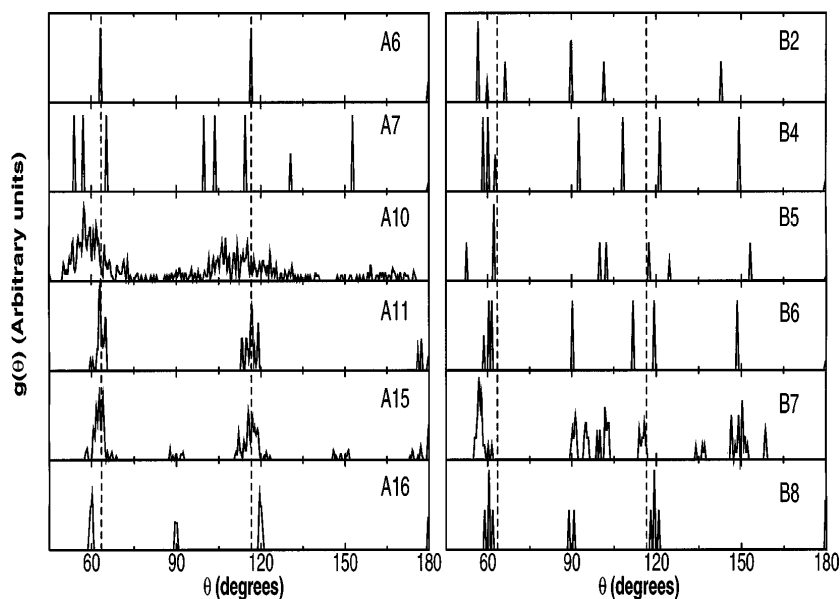


FIG. 2. Angular correlation functions, restricted to corner atoms located at or near the wire axis. Al wires are on the left panel and Pb wires on the right panel. Dashed lines correspond to perfect icosahedral angles (63.4° , 116.6° , and 180°). A16 and B8 represent a nearly perfect fcc packing, and A6 is a nice example of icosahedral order.

slightly larger than Ω_c . The crystalline-weird transition will take place at

$$\frac{1}{R_c} = \frac{1}{R_{c0}} \left[\sqrt{1 + \left(\frac{\Omega_c \delta}{R_{c0} \Delta} \right)^2} - \frac{\Omega_c \delta}{R_{c0} \Delta} \right], \quad (3)$$

where $R_{c0} = \sqrt{8\Omega_c \bar{\mu} / \pi \Delta}$, and $\delta = \bar{\gamma} - (\Omega_w / \Omega_c) \gamma_{111}$ is an effective surface energy difference taking into account the different atomic volumes that can be either positive or negative, depending on the material. From separate calculations, we know *a priori* all parameters, except for Δ and $\bar{\mu}$. The geometries of the sections of fcc wires are adequately represented by $\alpha_{111} = 0.55$, $\alpha_{100} = 0.25$, and $\alpha_{110} = 0.20$. For Al (Pb), $\Omega_c = 16.1$ (27.9) \AA^3 , $\Omega_w / \Omega_c = 1.10$ (1.00), $\gamma_{111} = 54.3$ (37.5) $\text{meV}/\text{\AA}^2$, $f_{100} = 1.08$ (1.01), $f_{110} = 1.19$ (1.11), $\bar{\gamma} = 57.5$ (38.5) $\text{meV}/\text{\AA}^2$.

Figure 1 shows the resulting plots for Eqs. (1), obtained with $\bar{\mu}$ as a fit parameter, and (2), with Δ as the sole parameter. The accord with energies obtained by simulations is quite good, yielding $\Delta = 37$ (24) meV , $\bar{\mu} = 35$ (25) $\text{meV}/\text{\AA}$, and $R_c = 5.3$ (9.8) \AA . These values of Δ are in good agreement with the $T = 0$ energy difference between the glassy metal (obtained by simulated quenching of the liquid) and the fcc solid, namely, 51 (29) meV . The weird wire interior is therefore close to a glass. The edge energies are also reasonable, since they should be close to half the step value, or about $\gamma d/4$, which is 39 (33) $\text{meV}/\text{\AA}$. We conclude that Eq. (3) should have predictive power for other materials, provided the glass, the surface, and the edge energies can be estimated.

This physics also explains the diversity of behavior between the two metals Al and Pb, both fcc in bulk. The surface anisotropy of Pb is much smaller than that of Al. All stable Al wires display an outer shell which is triangular—like a curved (111) surface—to a very good degree. In Pb, conversely, weird wires tend to possess a roughly square outer layer, which can be explained with the exceptionally low γ_{100} [12]. For instance, the pentagonal (nonicosahedral) structure B4 with (100)-like lateral faces is preferred over A6 (icosahedral), similar but with (111)-like lateral faces. In the helical wire B7, the presence of a relative tilt angle between third-shell and second-shell strands, $\theta_3 - \theta_2 = \tan^{-1}(2\pi r_3/\lambda_3) - \tan^{-1}(2\pi r_2/\lambda_2) \approx 16.0^\circ$, appears to realize a good approximate coincidence of the third (outer) shell atoms with the hollow sites of the second shell, which in turn has a roughly triangular packing (inset). This provides an amusing case of what might be considered “curved surface epitaxy” between two otherwise incompatible 2D lattices.

Finally, we compare wires with clusters. The non-fcc wire structures we just found for Pb are plentiful. Conversely, the same potential is known to stabilize only fcc crystalline clusters and to destabilize icosahedra, in agreement with experimental indications [13], down to the lowest size (13 atoms) [9]. Hence, the tendency of wires to abandon the bulk fcc structure is much stronger than could have been expected, in particular, stronger than in

clusters. The reason is most likely related to the well-known fact that icosahedral shapes require (111) faces to be stretched in order to form a space filling structure [3]. Owing to the high tensile surface stress of the metal, this circumstance can disfavor icosahedral clusters against fcc structures, when the surface energy anisotropy is small, as in Pb. On the other hand, this negative factor is absent in wires, which are open, and thus can fully adjust along z . A second difference is that icosahedral clusters have edges, while most weird wires have none. In both respects, therefore, wires are not necessarily just a two-dimensional version of clusters, and new phenomena can arise.

Could such unsupported metal nanowires be fabricated, and their possibly weird structure eventually be detected? Wires of over a thousand angstroms length can be pulled by a scanning tunneling microscope tip [14]. They can be expected to possess, at least in some sections, the ultra-small radii which we have addressed here. Weird structures could be sought in field ionization or transmission electron microscopy images. Also, the electronic structure of a wire is, in principle, a strong function of its atomic structure. Further study might reveal a measurable imprint of its weird shape, if present. More work in these directions is currently planned.

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