The Decmon-type Decahedral Motif In Metallic Nanoparticles

J.P. Palomares-Báez¹, J.L. Rodríguez-López,¹,† J.M. Montejano-Carrizales,² and M. José-Yacamán³

¹Advanced Materials Department, IPICYT, Camino Presa San José 2055 78216 San Luis Potosí, SLP, Mexico
²Instituto de Física, Universidad Autónoma de San Luis Potosí Alvaro Obregón 64, 78000 San Luis Potosí, SLP, Mexico and
³Department of Physics and Astronomy and International Center for Nanotechnology and Advanced Materials (ICNAM) University of Texas At San Antonio 78249-1644, San Antonio Texas, USA

Abstract

Structural and energy stability results for a new class of decahedral structural motif termed decmon (Montejano’s decahedra) are presented. After making proper truncations to the regular icosahedron, this structural motif presents exposed ⟨100⟩ and ⟨111⟩ facets, with an energy competition that makes the structures very stable. A structural transition as a function of the cluster size is also identified. An outline for a path transformation from the Mackay icosahedra (m-Iₖₚ) to the regular decahedra (s-Dₖₚ) symmetry structures, as well as experimental evidence of the decmon decahedral motif in metallic nanoparticles are presented.

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In the 1960’s, Shozo Ino was the first to report a very complete study on the structural phases for supported multi-twinned gold nanoparticles (NPs) - tetrahedra ($T_h$), truncated cuboctahedra ($co-O_h$), Mackay icosahedra ($m-I_h$), and regular decahedra ($s-D_h$) [1], by developing a theory that accounted for the specific surface, twin boundaries, elastic strain, and the adhesive energies to the substrate. This theory came after extensive studies of epitaxial growth of fcc metals on rocksalt faces by Ino [2] and Ino and Ogawa [3], where they proposed the *multi-twinned particle model with a nucleus of (001) orientation*, now known as the Ino decahedral ($i-D_h$) family. The Ino decahedron is a truncated decahedron with lower total surface-to-volume ratio that exposes higher energy $⟨100⟩$ facets parallel to the five-fold axis, and is energetically more stable than the simple (bi-pyramid) decahedra ($s-D_h$) but not with respect to other multi-twinned nanoparticles (MTNPs) like the $m-I_h$ in the small and intermediate size range ($\approx 10$ nm) [1].

This description was prevalent for around a decade or so, and although the thermodynamic processes of shape and morphology formation for fcc particles was well understood by then using of the Wulff construction [4] the more general problem of twinned nanoparticles was not. With the help of a modified Wulff construction for multi-twinned particles, Marks [5] proposed a modification to the Ino decahedra which allowed for nonconvex re-entrant facets at the twin boundaries of the decahedron. This structure is now known as the Marks Decahedron ($m-D_h$) and is energetically competitive with the $m-I_h$ in the small-size range, and even more stable than other multi-twinned particles such as the $s-D_h$, the $i-D_h$ and the $m-I_h$ structures in the medium and large size range.

Recently, Barnard and coworkers [6] have applied nonconvex re-entrant features to the regular Mackay-Icosahedron ($m-I_h$) to obtain the so-called Chui-Icosahedron ($c-I_h$), a modified icosahedron that, in the smallest re-entrant reconstruction, each particle contains 12 atoms fewer than the regular $m-I_h$ family members. This type of reconstruction had been observed in experiments with decahedral nanoparticles by Rodríguez-López et al. [7], and in many reports by molecular dynamics (MD) simulations [8] (see also inside Ref. 6).

Another related structure has been observed by Ascencio et al. [9] by means of high resolution transmission electron microscopy (HRTEM) characterization. They observed images with a contrast similar to the icosahedral or the truncated decahedra in gold nanoparticle samples. However, they also observed pseudo-square faces of type $⟨100⟩$ together with triangular faces $⟨111⟩$; therefore they proposed a new structure termed the *truncated icosahedron*
Thus, non-crystallographic atomic arrangements, such as icosahedral (m-I\textsubscript{h}) and decahedral (s-D\textsubscript{h}) symmetries and some variations of them have been widely established, both from atomistic simulations \cite{10} and first-principle calculations \cite{11} in the small-size range (1-2 nm) or experimentally \cite{12,13,14}, and even other MTNPs like the bi-m-I\textsubscript{h} \cite{5,15} have been observed; these non-crystallographic symmetry structures are lower in energy than the fcc pristine structures, such as the truncated octahedra (t-O\textsubscript{h}) and the cubo-octahedra (co-O\textsubscript{h}). A plausible explanation for this fact is that the observed MTNPs are in metastable states but with a lower free energy barrier from the liquid to the m-I\textsubscript{h} phase compared to the barrier from the liquid to the fcc crystalline phase \cite{16}.

In this letter we present two new sub-families that result from particular truncations made to the regular icosahedron. This type of truncation exposes facets $\langle 100 \rangle$ and $\langle 111 \rangle$—in addition to the external $\langle 111 \rangle$ facets in the regular icosahedron—that improve the energy stability of these new kind of decahedral nanoparticles compared with the icosahedron near that size.

FIGURE 1 HERE

In Fig. 1(a), we present a sample of a HRTEM image of a gold nanoparticle, where a central pentagonal pyramid arrangement can be observed, as well as some $\langle 111 \rangle$ and $\langle 100 \rangle$ arrays. After these intriguing experimental observations, we introduce a model to reproduce the images observed. The model shown in Figs. 1(b) and 1(c), is formed by a central pentagonal pyramid of triangular faces, where each one of these faces is connected to $\langle 100 \rangle$-type array and each vertex to $\langle 111 \rangle$-type array and these two arrays are join together into couples. This model is a pyramid termed the decmon (Montejano’s decahedron) motif, and it presents a decagonal base along with a pentagonal pyramid at the top.

The model proposed in Fig. 1 is only the top view of the particle and full particles could adopt one of the four different shapes seen in Fig. 2. These truncated icosahedra come from particular truncations made to the regular icosahedron, and the truncations are made drawing out (first) one pentagonal cap to a given $\nu$ order icosahedron (the order $\nu$ is defined as the number of atoms in one edge, including both vertices), resulting a single truncated icosahedron ($^{q=1}_{\nu} $st-I\textsubscript{h}$, where $q$ is termed the order of the truncation made to the m-I\textsubscript{h}, and the following relation $\nu = p + q$ holds). If a second truncation is made to a single truncated icosahedron, the top cap to be eliminated is different from the one discussed above; now the
top cap of the $^q$st-$I_h^\nu$ is formed by all the atoms of the decmon motif, but the number of atoms in both top caps is the same, whether the cap has been truncated or not. With this fact in mind, successive truncations can be made either in the $^q$st-$I_h^\nu$ or in the $^q$dt-$I_h^\nu$. There are single (Figs. 2(d)–2(e)) and double (Figs. 2(g)–2(k)) truncations made to the $\nu = 11$ and 10 order icosahedra, respectively. All these structures form a new set of nanoparticle sub-families members with decahedral symmetry, the so-called decmon family.

FIGURE 2 HERE

Experimental results on gold NPs are shown in Figs. 2(a)–2(c), where a central five-fold pyramid with some $\langle 100 \rangle$ and $\langle 111 \rangle$ atomic arrays is observed. These intriguing HRTEM image contrasts are compared with simulations using representative members of the decmon family (see the third column in Fig. 2). From these results, the model that best resembles the experimental contrast is in Fig. 2(f), which comes from the single truncated icosahedron proposed by Ascencio et al. [9]. Models are shown for the $^q$st-$I_h^{11}$ in Figs. 2(d)–2(f); the double truncated icosahedra family is shown in two types ($^q$dt-$I_h^{11}$ in Figs. 2(g)–2(h) and $^q$dt-$I_h^{10}$ in Figs. 2(j)–2(k), where $\nu$ is the order of the icosahedron which they came from). Finally, in Figs. 2(j)–2(l), the regular decmon structure (dm-$D_h$) is also shown.

A regular icosahedron of order $\nu$ is a cluster with a central site and $\nu - 1$ concentric icosahedra shells; observed perpendicularly to the five-fold symmetry axis, it has pentagonal pyramids at the top and the bottom. This picture contrasts with Fig. 2(d) where the st-$I_h$ has a decmon pyramid (similar to Figs. 1(b)), at the top and a pentagonal one at the bottom. Furthermore, when the top caps of two opposite vertices are eliminated from an icosahedron, the double truncated icosahedron is obtained (dt-$I_h$), shown in Figs. 2(g) and 2(j), with a decmon pyramid at each side.

For the single truncation case in a $\nu$-order icosahedron, there are $\nu - 1$ single possible truncations; the shape for any $^q$st-$I_h^\nu$ is a decmon pyramid on one side and a pentagonal one in the opposite vertex. Once all the possible truncations have been made, a fully single truncated icosahedron is obtained with a structure which is an irregular decahedron.

Regarding the double truncations permissible in a $\nu$-order icosahedron, there are $[\nu - 1]/2$ ($[\nu - 1]/2$) for $\nu$ (even or odd). The shape for any dt-$I_h$ is formed by two opposite decmon pyramids joined by 10 trapezoidal lateral faces. However, the final shape for the fully $^q$dt-$I_h^\nu$ does depend on whether the order ($\nu$) of the icosahedron is odd (Fig. 2(g)) or even (Fig. 2(j)).
The *decmon* type polyhedron, Figs. 2(m)–2(n), is a structure that results from reflecting the decmon pyramid with respect to the base, being thus a symmetric polyhedron with respect to the equator, contrasting with the $^5$dt-I$_h^{1,1}$ (Figs. 2(g)–2(h)), which, despite looking similar, represent very different structural models.

As previously discussed, the decmon (dm-D$_h$) structural motif results from a particular truncation made to the regular icosahedron, being very different from the one known as the Chui truncation [6]. This is a very efficient way to optimize the energy stability of metallic NPs, as can be observed in Fig. 3, where we use as energy reference the cohesive energy per atom for the icosahedral family [19].

**FIGURE 3 HERE**

First, as seen in Fig. 1(b) the $(p, q)$ indexes define a given st-I$_h$, we can vary $p$ as a function of the number of atoms ($N$) and $q$ can be kept constant, or viceversa. But we can also vary $(p, q)$ as a function of the number of atoms ($N$). Keeping $q$ constant in all the size range, it should be observed that the first truncation ($q = 1$, blue triangles) made to all the cluster sizes, begins with a positive high slope in the small-size region. After a given cluster size (around $d = 4.1$ nm), this truncation improves their stability significantly making it even more stable than the icosahedra near $d = 5.3$ nm ($N \approx 5000$ atoms). This change in the curvature is size dependent and is only observed up to the truncation $q = 3$ (not shown). After that, successive truncations only increase monotonically the energy stability of the $^q$st-I$_h$. This abrupt change in the curvature of the stability has been identified as a surface reconstruction in the st-I$_h$ [21].

Now, if successive truncations are made to a given icosahedron; e.g. $\nu = 15$, with $N = 10179$ atoms, and a particle diameter of $d \approx 9.3$ the indexes $(p, q)$ would be changing (keeping the relation $p + q = \nu$) and what is obtained is a transformation path from the m-I$_h$ to the s-D$_h$ symmetry structures (green ▽ in Fig. 3, where each point represents cohesive energy per atom for a different $^q$st-I$_h$ structure, but all of them come from the same m-I$_h^{\nu=15}$). The first truncation slightly improves its energy, the next four truncations take the particle below the icosahedral energy reference, and then the next five truncations or structures are more stable than those icosahedra around the respective st-I$_h$ size cluster, reaching a maximum in $\nu - q = 5 = p$. If truncations are made until they are exhausted, an irregular decahedron is obtained, which after relaxation turns into either a *structure with the same energy for a perfect decahedra* (here shown the complete s-D$_h$ family with red circles),
or a *surface reconstructed* decahedra, *e.g.*, last truncation for st-I$_h^{\nu=15}$ (○ in purple).

In the size region shown in Fig 3, $p = 5$ for the two path truncations made from the m-I$_h$ to the s-D$_h$ structures (< from $\nu = 15$ and ○ from $\nu = 16$ icosahedrons, respectively), and is constant over a given size range, *i.e.* it is dependent on the cluster size. Therefore, and very interestingly, there are (size dependent) constants $p_1 < p_2 < \ldots$, a fact that is related to a delicate competition between energy release strain from the appearance of $\langle 100 \rangle$ vs. $\langle 111 \rangle$ facets in these single truncated icosahedra. All these facts are discussed in more detail in a forthcoming paper [21].

Figure 4 shows how these decmon subfamilies (st-I$_h$, dt-I$_h$, and dm-D$_h$) compete among themselves, where the cohesive energy for gold NPs is plotted as a function of the cluster size (upper $x$-axis) or as a function of the relative particle diameter (lower $x$-axis). We choose to plot representative truncations for each subfamily, *i.e.*, the 5th truncation for the st-I$_h$ (green diamonds), the 2nd truncation for the dt-I$_h$ (blue triangles), the maxima for all the path truncations from the m-I$_h$ to the s-D$_h$ symmetries (black solid diamond) and in the inset, the energetically non-competitive dm-D$_h$ structure family (brown ×). For energy reference, the cohesive energies per atom for the icosahedral (m-I$_h$, black solid circles) as well as the regular decahedral family (s-D$_h$, red solid circles) are plotted.

FIGURE 4 HERE

It can be concluded from this figure, that up to a given truncation, these single truncations made to the regular icosahedron improve its energy stability on the resulting st-I$_h$, but that double truncations do not improve the energy of the NPs, as seen for the dt-I$_h$ and dm-D$_h$. However, the *decmon* structural motif that results from this particular truncation made to the regular icosahedron is a very efficient way to optimize the energy stability of metallic NPs.

In conclusion, we have introduced the *decmon* decahedral motif for metallic NPs, which identifies a new family of decahedral structures, that after proper truncations made to the icosahedron present exposed $\langle 100 \rangle$ and $\langle 111 \rangle$ facets, with an energy competition that makes the structures very favorable. Other outlined aspects worthy of mention, are the finding of structural transitions as a function of the cluster size, the appearance and competition of surface reconstruction with faceting, and the outlined path transformation from the m-I$_h$ to the s-D$_h$ symmetry structures. Also, we have presented experimental evidence of the decmon decahedral motif in metallic nanoparticles.
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† Corresponding author: jldrzd@ipicyt.edu.mx

[1] S. Ino, J. Phys. Soc. Jpn. 27, 941 (1969).
[2] S. Ino, J. Phys. Soc. Jpn. 21, 346 (1966).
[3] S. Ino and S. Ogawa, J. Phys. Soc. Jpn. 22, 1365 (1967).
[4] G. Wulff, Z. Kristallogr. 34, 449 (1901).
[5] L.D. Marks, J. Cryst. Growth 61, 556 (1983).
[6] A.S. Barnard, G. Opletal, I.K. Snook, and S.P. Russo, J. Phys. Chem. C 112, 14852 (2008).
[7] J.L. Rodríguez López et al., Phys. Rev. Lett. 92, 196102 (2004).
[8] Y.H. Chui, R.J. Rees, I.K. Snook, B. OMalley, and S.P. Russo, J. Chem. Phys. 125, 114703 (2006); Y.H. Chui, G. Grochola, I.K. Snook, and S.P. Russo, Phys. Rev. B 75, 033404 (2007).
[9] J.A. Ascencio, M. Pérez, and M. José-Yacamán, Surf. Sci. 447, 73 (2000).
[10] C.L. Cleveland et al., Phys. Rev. Lett. 79, 1873 (1997).
[11] F. Baletto et al., J. Chem. Phys. 116, 3856 (2002).
[12] L.D. Marks, Rep. Prog. Phys. 57, 603 (1994).
[13] T.P. Martin, Phys. Rep. 273, 199 (1996).
[14] K. Koga, T. Ikeshoji, and K. Sagawara, Phys. Rev. Lett. 92, 115701 (2004).
[15] K. Koga, Phys. Rev. Lett. 96, 115501 (2006).
[16] H.-s. Nam et al., Phys. Rev. B 71, 233401 (2005).
[17] A. Gomez-Rodríguez and L.M. Beltrán Del Río Caballero, Rev. LatinAm. Met. Mat. 21, 46 (2001).
[18] Because of the discrete numbers of atoms do not coincide in most cases among different structures, and therefore we can not operate differences directly, the values for $\Delta E$ in Figs. 3
and 4 have been obtained applying an interpolation made to the m-Ih reference values.

[19] All the calculations were performed using the semi-empirical embedded atom method (EAM) as coded in the XMD algorithm [20]. The clusters were quenched at a rate of $5 \times 10^{12}$ K/s for 35 ps.

[20] Jon Rifkin, University of Connecticut, http://www.ims.uconn.edu/centers/simul.

[21] J.P. Palomares Báez, J.L. Rodríguez López, J.M. Montejano Carrizales, and M. José Yacamán, 
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FIG. 1: (a) Experimental image that shows a contrast following the pyramidal decmon-type decahedral growth pattern. The Montejano’s Decahedral (decmon) motif shown in side and top views, a decahedral atop motif that is shared by the single (st-Ih) and double (dt-Ih) truncated icosahedra, as well as the decmon subfamily (dm-Dh). Indexes \((p, q)\) are shown for this model.
FIG. 2: From (a)-(c), the HRTEM experimental images show a contrast following the pyramidal decmon-type decahedral growth pattern, contrasting them with simulations of HRTEM (E = 200 kV, Cs = 0.5 mm at optimal defocus Sherzer) [17]; the best fitting can be seen in (f). A comparison of representative members of the Montejano’s decahedra family is shown for $^5$st-$I_h^{11}$ (d-e), the $^5$dt-$I_h^{11}$ (g-h) and $^3$dt-$I_h^{10}$ (j-k), and the regular dm-$D_h$ (m-n). Models are colored to show structural differences among them.
FIG. 3: Color on-line. Different truncations made to the regular icosahedra are shown, plotting energy difference vs. mean diameter of the particle ($d \propto N^{1/3}$), where icosahedra energy is used as reference [18]. Blue line reflects how the first truncation ($q = 1$, blue solid triangles) affects the energy of the particles, stabilizing it after a given cluster size. Big circles shown in the reference line ($\Delta E = 0$) correspond to Mackay $I_h$ of order $\nu = 15$ and 16. From these clusters, successive single truncations (green triangle and purple circle) make the structures metastable until a maximum stability (black diamonds) is obtained. From these maximum points, there is a steady decay towards the regular $s-D_h$ (red circles) and other closely related decahedral structures; i.e., a surface reconstructed decahedron ($\circ$). These truncation paths offer evidence of a structural transformation from the $m-I_h$ to the $s-D_h$ symmetry structures.
FIG. 4: Color on-line. Energy competition between the different sub-families that show the decmon decahedral motif, plotting the energy difference vs. mean diameter of the particle \((d \propto N^{1/3})\), where icosahedra energy is used as reference \([18]\). For reference, the curves for regular s-D\(_h\) (red circles), and the maximum obtained with the single truncations (black solid diamonds) are plotted. Green diamonds correspond to \(^5\)st-I\(_h\) and blue triangles is for the \(^2\)dt-I\(_h\). The decmon (dm-D\(_h\)) structure does not compete in energy with these \(^9\)st-I\(_h\) and \(^9\)dt-I\(_h\) structures, that is shown in the inset (brown \(\times\) symbol).