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Stacking Principle and Magic Sizes of Transition Metal Nanoclusters Based on Generalized Wulff Construction

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Nanoclusters with extra stability at certain cluster sizes are known as magic clusters with exotic properties. The classic Wulff construction principle, which stipulates that the preferred structure of a cluster should minimize its total surface energy, is often invoked in determining the cluster magicity, resulting in close-shelled Mackay icosahedral clusters with odd-numbered magic sizes of 13, 55, 147, etc. Here we use transition metal clusters around size 55 as prototypical examples to demonstrate that, in the nanometer regime, the classic Wulff construction principle needs to be generalized to primarily emphasize the edge atom effect instead of the surface energy. Specifically, our detailed calculations show that nanoclusters with much shorter total edge lengths but substantially enlarged total surface areas are energetically much more stable. As a consequence, a large majority of the nanoclusters within the 3d-, 4d-, and 5d-transition metal series are found to be fcc or hcp crystal fragments with much lower edge energies, and the widely perceived magic size of 55 is shifted to its nearby even numbers.

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The electronic, magnetic, catalytic, optical, and mechanical properties of nanoclusters are often drastically different from their bulk counterparts due to their distinct geometric structures and quantum confinement effects and may lead to unique applications [1–4]. One class of nanoclusters, commonly known as “magic” clusters [5–8], has gained particular attention because of their extra stability. Such clusters are more abundant in typical fabrication processes (for example, in a cluster beam [7]), and may also exhibit highly desirable functionalities either individually or as building blocks in cluster assembled materials [2,9–11]. For a given nanocluster of a fixed size and specific elemental composition, it is of fundamental interest and practical importance to identify the dominant factors determining its preferred geometric structure and magicity, upon which the physical and chemical properties of the cluster can be reliably predicted and accurately tuned.

Two mechanisms have been frequently invoked in explaining the magicity of a given cluster: atomic shell closure [5] and electronic shell closure [6,8], or both [7]. The former is inherently rooted in the classic Wulff construction principle [12], which stipulates that the preferred structure of a given cluster should minimize its total surface energy, resulting in high symmetry close-shelled Mackay icosahedral (I_h) clusters [13] with odd-numbered magic sizes of 13, 55, 147, etc. [14–18]. Nevertheless, for such clusters of nanometer sizes, the validity of the classic Wulff construction principle has so far not been rigorously examined using state-of-the-art

theoretical and/or experimental approaches, especially concerning transition metal (TM) clusters with strongly directional d valence electrons.

In this Letter, we employ first-principles total energy calculations within density functional theory to demonstrate the need to generalize the classic Wulff construction principle by including the vital contribution of the edge atoms in the global energy minimization of the nanoclusters. Unlike the alkali or simple metal clusters, whose valence electrons are dominantly itinerant s electrons, the directional d orbitals within a TM cluster are more localized. Such localized d orbitals will be manifested in the form of unsaturated dangling bonds on the edge atoms, an aspect energetically undesirable. Furthermore, many of the surface atoms of a polyhedral nanocluster are actually located on the cluster edges, and such edge atoms can contribute substantially in determining the structure and the properties of the nanocluster. The present study, revealing the dominance of the edge atom effect instead of the surface energy in structural optimization of the TM nanoclusters, is particularly significant considering the crucial functional roles played by the edge atoms in nanoscale catalysis and many other related physical and chemical phenomena [19–23].

Our calculations were carried out using the density functional theory [24] within the spin-polarized generalized gradient approximation [25] as implemented in the VASP code [26]. The interaction of the valence electrons with the ionic core was described with the projector

augmented wave method [27]. The atomic positions were optimized with the energy convergence of 0.001 eV. In obtaining the ground state configurations of the TM_N clusters, we have considered many initial candidate configurations manually constructed or computationally generated via high temperature first-principles molecular dynamic simulations. We have also carried out selective checks on the most stable optimized structures using the particle swarm optimization (CALYPSO) code [28,29], as well as high temperature molecular dynamics simulations and vibrational frequency analysis, confirming that these structures are also dynamically stable.

In our study, we first choose Ru nanoclusters of sizes around 55 atoms as prototypical examples. The preferred bulk structure of Ru is hcp, but it becomes a fcc-like crystal fragment for the Ru nanoclusters in the studied size range. Furthermore, we reveal the nonmagic nature of the I_h - Ru_{55} cluster and identify the nearby even-numbered cluster of Ru_{56} to be magic. We then extend our investigation to the 3 series of TM clusters around nd - TM_{55} ($n = 3, 4$, and 5), including fcc, hcp, and bcc elements. Most strikingly, we find that all these clusters prefer the fcc- or hcp-crystal-fragment (FCCCF or HCPCF) structures, except for the earliest and the latest TM elements in the periodic table. These structures have lower symmetries compared with the I_h configuration, but each with significantly reduced edge length, thereby compensating the energy increase associated with the larger surface area. Consequently, the widely assumed I_h magic clusters of size 55 actually possess much less relative stability than their nearby even-numbered clusters within the new configurations. The exceptions of the earliest and latest TM_{55} clusters can be attributed to the negligible numbers of d -type dangling bonds on the edge atoms.

Figure 1 displays 4 representative low energy Ru_{55} candidate structures optimized from various initial configurations. The 2 low symmetry structures in Figs. 1(a) and 1(b) are found to be much lower in energy than the high symmetry I_h structure shown in Fig. 1(d), by 3.120 and 2.691 eV, respectively. Each of the 2 more stable FCCCF structures contains 4 layers of atoms stacked in the A-B-C-A sequence, distributed as A(13)-B(15)-C(14)-A(13), and A(12)-B(16)-C(16)-A(11) in Figs. 1(a) and 1(b), respectively, with the number of atoms in a given layer listed in the parentheses. These two structures are constructed by having 5 (FCCCF-1a) and 3 (FCCCF-2a) fewer inner atoms than the I_h structure, resulting in enlarged fcc(111) facets in each case, as well as slightly reduced average bond length R , by $\sim 1\%$. The 3-layered HCPCF configuration constructed as A(18)-B(19)-A(18) (Fig. 1(c)) is also lower in energy than the I_h structure (Fig. 1(d)). We also note that, starting with these stable structures, other alternative configurations can be generated, and these structures are also more stable than the I_h structure (see Supplemental Material, S1 and S2 [30]).

Before we focus our attention on the edge effects within the context of the generalized Wulff construction principle,

FIG. 1 (color online). Geometric structures and relative energies of the 4 representative low energy configurations of Ru_{55} . The relative energies in (a)-(c) are measured from that of the I_h structure in (d), given by $\Delta E = E(\text{TM}_{55}) - E(\text{TM}_{55}(I_h))$.

we first rule out the possibility that these low symmetry FCCCF and HCPCF Ru_{55} structures are stabilized via the usual electronic or geometric closed-shell mechanism. The former can be ruled out by the observation that there is no significant energy gap between the highest occupied and lowest unoccupied molecular orbitals for either the FCCCF or HCPCF structure, the latter by the fact that these structures deviate severely from perfectly closed-shell configurations. Exclusion of other possible mechanisms, such as strong relativistic effects [31–34] that stabilize the s orbitals and destabilize the d orbitals, and enhanced s - d hybridization [33], is presented in the Supplemental Material S3 [30].

To assess the relative importance of the edge atoms, we can qualitatively separate the total energy of a given polyhedral cluster of size N into 3 terms:

$$E_{\text{Tot}} = E_{\text{Bulk}} + E_{\text{Surf}} + E_{\text{Edge}}, \quad (1)$$

where E_{Bulk} represents the leading-order, bulk contribution to the cluster energy from the N atoms, E_{Surf} and E_{Edge} are the total surface and edge energies needed to create the mini-facets on the clusters and the edges defined by the intersections of adjacent facets, respectively. For simplicity, the vertex atoms of a cluster are counted as part of the edge atoms. Within these definitions, the first term is negative definite, while the other two terms are always positive. As a zeroth-order approximation, we have $E_{\text{Bulk}} = -Ne_1$, representing the total energy of N atoms inside an infinite bulk crystal of chemical potential e_1 . At this level of accuracy, the first term is identical for all 4 structures shown in Fig. 1.

Nevertheless, as shown in Figs. 2(a) and 2(b), each of the 3 more stable FCCCF or HCPCF structures actually have

FIG. 2 (color online). Relative energies and atomic arrangements of the 4 structures of Ru_{55} , with configurations 1, 2, 3, and 4 corresponding to the structures shown in Figs. 1(a)–1(d), respectively. (a), the relative energies measured from that of the I_h structure, ΔE . (b), the numbers of the inner atoms in the clusters, N_{inner} . (c), the total numbers of triangularly shaped mini-facets defined by the 3 adjacent atoms on the surfaces of the clusters, N_{surf} . (d), the total numbers of the atomic bonds defined on the edges, N_{edge} .

fewer highly coordinated inner atoms, and should, therefore, be reflected by lower average values of e_1 than the I_h structure (while maintaining a constant N). This observation as a first-order correction will make the subsequent discussions concerning E_{surf} and E_{edge} more compelling. We can now estimate E_{surf} by the total surface area times the energy per unit area, and E_{edge} by the total edge length times the energy per unit length. First, as indicated in Fig. 2(c), each of the 3 more stable structures possesses a larger total surface area than the I_h structure. Furthermore, because the I_h structure contains 20 fcc(111) or hcp(0001) mini-facets, while the mini-facets on the 3 new cluster structures are either also fcc(111)-like, or bcc(100)-like with higher energy per unit area, showing that each new structure corresponds to a higher E_{surf} than the I_h structure. Based on these analyses, we must attribute the overall energy reductions associated with the 3 FCCCF or HPCPF structures to dramatic lowerings in the 3rd term, E_{edge} . Here we note that, in the present study, the relative importance of the surface and edge energies of a given nanocluster has been discussed only qualitatively, primarily due to the constraint that the actual surface energy for a given facet or the edge energy for a given ridge cannot be precisely and independently obtained for such nanoscale systems. Nevertheless, for a given structural model of a specific cluster, both the total surface area and total edge length can be and have been quantitatively determined. Furthermore, only the total edge length correlates directly with the total cluster energy (Figs. 2(a) and 2(d)), whereas such a close correlation is lacking between the total surface area and the total cluster energy (Figs. 2(a) and 2(c)), thereby establishing that the edge atom effect is the dominant factor at such nanometer cluster sizes.

Now that we have invalidated the I_h structure to be the stable structure for Ru_{55} , it is natural to search for the

existence of potential new magic cluster sizes around TM_{55} . In these searching efforts, the newly generalized Wulff construction principle, stipulating minimization of edge lengths, turns out to serve as a highly instrumental guide. In doing so, we have systematically investigated the magicity of Ru_N clusters ($N = 53 \sim 58$) by comparing the average binding energy per atom, $E_b(N)$, for a given cluster of size N adopting the lowest energy configuration. We found that, within this size range, the most stable configuration is consistently the FCCCF form (see more details in the Supplemental Material S4 [30]). The results are plotted in Fig. 3(a), together with the second-order difference, $\Delta^2 E_b(N)$. Both plots establish $N = 56$ as the new magic number. The even- rather than odd-numbered nature is inherently tied to the inversion symmetry of the 4-layered FCCCF form. As detailed later, the even magic number 56 is also commonly adopted by many other TM clusters in the central regions of the 3d, 4d, and 5d elements, as selectively represented in Figs. 3(b) and 3(c) for Rh and Nb, respectively. Furthermore, for TM clusters that still prefer the I_h structure such as Ag, the number 55 is preserved to be a magic cluster size (see Fig. 3(d)). In particular, for Ag clusters, the preserved magic number 55 and our newly predicted magic number of 58 have both been observed experimentally [34].

Next, we show that the generalized Wulff construction principle established here for the case of Ru_{55} is also applicable to most of the 3d-, 4d-, and 5d-TM elements in the periodic table, merely leaving the earliest and the latest elements as exceptions and these TM_{55} adopt the I_h structure (see Supplemental Material S5 [30]). Collectively, the findings presented above not only firmly establish the vital importance of the edge atoms in stabilizing the structures of many of the nd - TM_{55} clusters, but also convincingly exclude the relativistic effect [32–35] and s - d hybridization [33] as the likely dominant factors (see Supplemental Material, S3 and S5 [30]). Furthermore, as detailed in Supplemental Material S6 [30], these main

FIG. 3 (color online). Average binding energy per atom, $E_b(N) = -[E(\text{TM}_N) - N \times E(\text{TM}_{\text{atom}})]/N$, and its second-order difference, $\Delta^2 E_b(N) = E_b(N+1) + E_b(N-1) - 2E_b(N)$, for different TM_N clusters. In each panel, the data represented by the stars are for the binding energies, $E_b(N)$, while the circles represent the second-order derivatives, $\Delta^2 E_b(N)$, respectively.

findings stay valid when different exchange-correlation functionals are adopted.

We now discuss in more detail the underlying mechanisms defining the different structures. For a given row of the TM elements, we can qualitatively rationalize the trend in their stable structures by contrasting their different edge effects. Similarly, for the earliest element(s), there are only one or two d electrons per atom, and an edge atom essentially has no unsaturated d bond; accordingly, the energetically undesirable edge effect is minimal. For the latest element(s), the d orbitals are far below the Fermi level(s), and an edge atom essentially has no unsaturated d bond. Therefore, clusters of the earliest and latest elements indeed prefer the high symmetry I_h structure. In contrast, for elements located in the central region, each edge atom has multiple d orbitals, some of which staying as dangling bonds, and such energetically highly undesirable local electronic configurations serve as the primary driving force for the I_h to FCCCF or HCPCF structural transition. These qualitative pictures can be further validated by plotting the charge density distributions of the representative clusters shown in Fig. 4, which displays the energy windows of the charge plotted (upper panels) and the corresponding charge distributions projected onto the high symmetry plane bisecting the I_h cluster (lower panels). If we compare the charge distributions within a comparable energy window below the Fermi level, the contrasts are dramatic, depicting no unsaturated directional bond around the edges of Y_{55} (Fig. 4(a)) or Ag_{55} (Fig. 4(c)), and strongly directional dangling bonds around the edges of Ru_{55} (Fig. 4(b)). As a closer comparison, we have also plotted the charge distribution of Ag_{55} within an energy window that is far below the Fermi level and, therefore, contains the d orbitals (Fig. 4(d)), depicting negligible dangling bond nature if compared with Fig. 4(b).

Similar to the cases around Ru_{55} the generalized Wulff construction principle may lead to magic-sized clusters that are different from $N = 55$ (Fig. 3(a)), especially for clusters consisting of the central nd elements ($n = 3, 4$, and 5) in the periodic table. Indeed, we found that the earliest and latest elements preferring the I_h structure still preserve 55 as the magic size, while the central elements consistently adopt new magic cluster sizes of some even numbers near 55. Three additional representative examples from the 4d elements are shown in Fig. 3. The first example is Rh, an fcc crystal in bulk form, and the new magic sizes are 56 and 60, which have nearly degenerate stabilities. The 2nd is a bcc element, Nb, again with 56 as the magic size. Note again that these even-numbered magic clusters are the natural outcomes of the symmetry restrictions obeyed by the corresponding even-layered FCCCF or HCPCF configurations. The last one is Ag, preserving I_h - Ag_{55} as the magic cluster due to the atomic closed-shell configuration, and the nearby magic size 58 due to electronic closed shell is also distinctively observed (Fig. 3(d)).

We now discuss the validity of the established generalized Wulff construction principle to clusters around other atomic closed shells and make further comparisons between the present theoretical predictions and the experimental observations. We note that the new principle can also be applied to I_h -TM₁₃ and I_h -TM₁₄₇ (Supplemental Material S7 [30]). There is presently still no systematic experimental investigation surrounding the TM₅₅ clusters; nevertheless, scattered experimental support of the present theoretical findings do exist: first, it was observed experimentally that the ionization potential of Nb_{55} is clearly lower than that of its neighboring even-numbered clusters, Nb_{54} and Nb_{56} [36], indicating that the former cluster is less stable than the latter two; second, the magic numbers of 55 and 58 for

FIG. 4 (color online). Densities of states around the Fermi levels contributed by the edge atoms (upper panels) and projected charge contours of all the electrons within selected energy windows (lower panels), for 3 representative 4d TM₅₅ clusters. The projection plane bisects the I_h -TM₅₅ cluster, and the contours are drawn between 0.0 and 0.02 e/Å³.

the Ag clusters have also been experimentally observed [34]; third, the energetically favorable structure of Ru_{55} possesses a negligible magnetic moment, consistent with experimental observations [37], whereas the I_h - Ru_{55} structure would produce a much larger magnetic moment of $\sim 10 \mu\text{B}$ [38]. The even-numbered magic clusters around TM_{55} predicted here are thus amenable to existing experimental tests and, more importantly, are also expected to stimulate future systematic investigations. As a final note, we expect that the generalized Wulff construction established here could also play an instrumental role in future materials design involving nanoclusters consisting of other elements with strong directional-covalent bonding.

In summary, the present study has shown unambiguously the need to generalize the classic Wulff construction principle in determining the structure and magicity of various d -electron-dominated nanoclusters. We also emphasize that, on an actual operational level, the classic Wulff construction typically stipulates minimization of the total surface area, whereas the generalized Wulff construction principle established here stipulates minimization of the total edge length. As a new principle of fundamental importance, the generalized Wulff construction is also expected to play an instrumental role in the future design of novel nanostructures with desirable functionalities for potential applications in nanocatalysis, nanomagnetism, and related areas.

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