Magic Numbers in Metallo-Inorganic Clusters: Chromium Encapsulated in Silicon Cages

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A systematic theoretical study of the equilibrium geometries and total energies of Cr encapsulated in Si clusters reveals that Cr@Si_{12} is more stable than its neighbors. The origin of this enhanced stability is consistent with the 18-electron sum rule commonly used in the synthesis of stable chemical complexes, and may provide a criterion for a systematic search of magic numbers in metalloinorganic clusters. The $6\mu_B$ magnetic moment of the caged Cr atom, the largest among the $3d$ transition metal atoms, is completely quenched. This effect of caging on the properties of transition metal atoms may lead to the synthesis of novel cluster based materials.

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One of the biggest challenges in the synthesis of cluster-assembled materials has been to find clusters that are likely to retain their structural integrity during self-assembly [1]. While it is possible to coat the clusters with organic ligands to prevent them from coalescing, the coating can affect the intrinsic properties of the clusters. It was suggested earlier [2] that magic clusters that interact weakly can serve as suitable building blocks. The criteria for magicity, however, differ depending on the chemistry that binds the clusters. For example, clusters of free electron metal atoms containing 2, 8, 20, 40, . . . valence electrons are considered to be magic [3] as these electrons are just enough, in a jellium model, to fill successive electronic shells. This criterion has been used in the design and synthesis of many magic clusters composed primarily of metallic elements. Among these, clusters based on Al_{13} skeleton have attracted the most attention. In particular $Al_{13}X$, where X is an alkali atom has been found to have all the properties of magic clusters [4]. Although the stability of $Al_{13}X$ and the ionic bond between $Al_{13}{}^-$ and X^+ are ideal for the synthesis of a metastable cluster-assembled solid, it is yet to be reduced into practice.

The only clusters that have been used to synthesize a cluster-assembled solid thus far are carbon fullerenes. However, general rules that govern the magicity of covalently bonded clusters, similar to those for metallic clusters, have not yet been developed. Recently [5], an experiment on endohedral complexes involving metal atoms and Si_n clusters has demonstrated that clusters such as $Si_{12}W$ are magic. Assuming that each Si contributes 1 electron and W contributes 6 electrons, the authors argued that the stability of $Si_{12}W$ could be a consequence of the 18-electron rule used in chemistry. We recall that the rare-gas atoms such as argon which are stable and chemically inert satisfy the octet rule with outer electron configuration of 2, 8, and 18. This rule of stability also has been found to apply to organometallic complexes [6], such as Cr-(benzene)$_x$ clusters. For example, Cr-(benzene)$_2$ is 30 times more stable than Cr-(benzene)$_1$. Note that since each benzene (C_6H_6) molecule and Cr atom donate six valence electrons, the total number of valence electrons in Cr-(benzene)$_2$ is 18. Thus, its enhanced stability is consistent with the octet rule.

In this Letter, we examine the validity of the 18-electron rule in the design of magic clusters involving metalloinorganic systems. We focus on Si clusters encapsulating a Cr atom which is isovalent with W. Note that both Si and C belong to the same column of the periodic table. However Si, unlike C, does not prefer to form sp^2 hybridization. Consequently, Si clusters do not form fullerenelike cage structures. It has been shown recently [5,7] that encapsulating a metal atom inside silicon clusters may stabilize the endohedral complex. These complexes can then form the building blocks for cluster-assembled materials. Previous electronic devices have relied on the fact that an electron has a charge, but that it also has a spin has not been exploited until recently in device engineering. It is, therefore, useful to study what happens to the magnetic moment of a transition metal atom once it is encapsulated inside a Si cage cluster. This is particularly relevant for chromium which has an atomic configuration of $3d^5 4s^1$ and the highest magnetic moment of all the $3d$ transition metal atoms, namely $6\mu_B$. In addition, doping metal atoms into Si clusters may induce additional states in the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap, and hence affect their optical properties.

To examine the relative stability of metal atoms encapsulated inside Si clusters and the effect of caging on its electronic and magnetic properties, we have carried out self-consistent calculations of Si_nCr ($n = 11, 12, 13, 14$) clusters. Note that if each Si atom could be assumed to donate one valence electron, consistent with a sp^2 bonding scheme, the number of such electrons in $Si_{12}Cr$ should be 18. Consequently, $Si_{12}Cr$ could be more stable than $Si_{11}Cr$ or $Si_{13}Cr$. Since the clusters are at finite temperatures, their stability should be governed by the free energy that requires a knowledge of the entropy. In practice, however, clusters are sufficiently cold and the calculated ground state energies have been found to explain well the relative stability of different clusters. We have computed the total energies, equilibrium geometries, electronic structure, ionization potentials (IP), and electron affinities (EA) using all

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electron density functional theory with generalized gradient approximation for exchange and correlation. No symmetry constraint was used in the optimization procedure. Several interesting results have emerged: (i) While Cr occupies endohedral position in all these clusters, the structure of $Si_{12}Cr$ is the most symmetric with the geometry of a hexagonal bi-prism. (ii) $Si_{12}Cr$ exhibits maximum relative stability among the clusters studied with a binding energy of 4.18 eV measured against dissociation into a Cr atom and a Si_{12} cluster. (iii) While magic clusters composed of metallic elements are characterized by high IP and low EA, magic $Si_{12}Cr$ cluster exhibits no such trend. On the contrary, the IP continues to decrease from $Si_{11}Cr$ to $Si_{14}Cr$ while the adiabatic EA of $Si_{12}Cr$ is higher than those of its neighbors. (iv) The properties of Si_nCr clusters are very different from those of Si_{n+1} as well implying that substitution of a metal atom in the place of Si atom has a significant effect on the stability and electronic properties. (v) Perhaps the most interesting result of this study is that all these clusters have singlet spin multiplicities; i.e., the entire $6\mu_B$ magnetic moment of Cr is completely quenched. In the following, we provide a brief description of our theoretical procedure and a discussion of our results.

The calculations are carried out using the density functional theory [8] and generalized gradient approximation (GGA) for exchange and correlation [9]. The atomic wave functions are represented by Gaussian bases, and the cluster wave function is constructed by a linear combination of atomic orbitals. The total energies and the forces at the atomic sites are computed and the cluster atoms are allowed to relax along the path of steepest descent without any symmetry restriction. The actual calculations were carried out using the NRLMOL set of codes developed by Pederson and co-workers [10] with a $6s$, $5p$, and $3d$ basis set for Si and $7s$, $5p$, and $4d$ basis for Cr [11]. Several initial configurations were used in order to prevent getting trapped in local minima of the potential energy surface.

It should be emphasized that finding global minima structures of clusters becomes an increasingly challenging task as cluster size increases. This becomes particularly difficult when clusters possess several nearly degenerate structures and/or large energy barriers separate them. In spite of the extensive search for geometries of Si clusters carried out in the last two decades [12], one continues to discover lower and lower energy structures. Unfortunately, there are very few experimental techniques that can determine cluster structure and often the properties are sensitive to cluster size. Thus, if clusters are to be used for synthesizing materials, one must understand how sensitive their tailored properties are to size and topology. We find that the magnetic moment of endohedral Cr is quenched independent of the size or the geometry of the cluster.

In Fig. 1 we plot the equilibrium geometries of pure Si_n clusters for $n = 11$, 12, 13, and 14 and compare them with Si_nCr clusters. The geometries of pure Si_n optimized here at the GGA level of theory agree with those obtained earlier [13] using the local density approximation (LDA) with the only exception that the interatomic distances are slightly enlarged. These structures are different from those of carbon clusters [14] and do not show any evidence of forming compact fullerenelike cages. However, as a Cr atom is allowed to interact with all these clusters, it occupies an interior site with the Si_n atoms forming a cagelike structure around it. In particular, the structure of $Si_{12}Cr$ is the most symmetric of all the ones studied. Here Cr atom is sandwiched between two hexagonal planes of Si atoms. This structure is analogous to the Cr-bis benzene complex [5] where the Cr atom is sandwiched between two benzene molecules with a D_{6h} geometry.

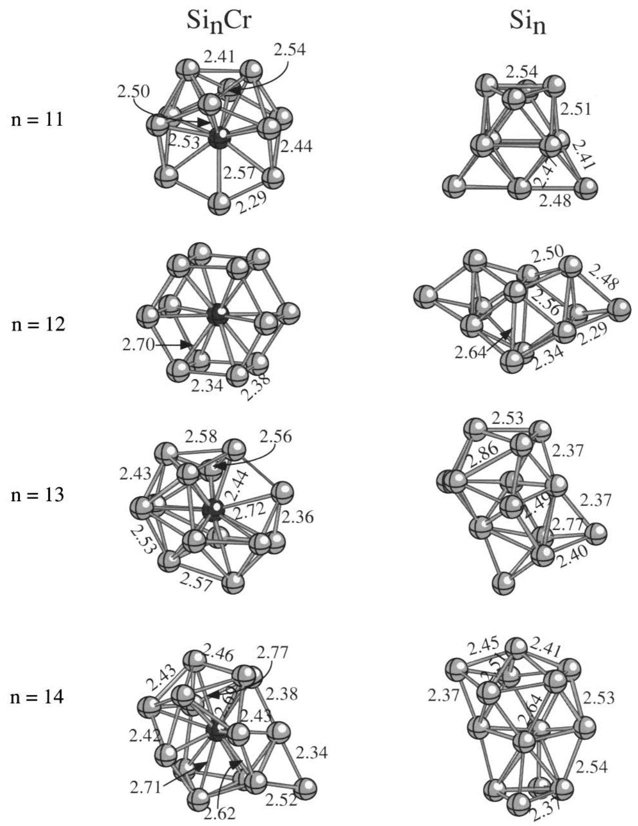

FIG. 1. The ground state geometries of neutral Si_nCr and Si_n clusters. All bond lengths are in Å.

We first consider the evolution of the energetics of pure Si_n clusters. We have calculated the binding energy (BE), the vertical ionization potential (VIP), the vertical detachment energy (VDE), adiabatic electron affinity (AEA), gap between the highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO), and energy (Δ) gained in adding a Si atom to a Si_n cluster. Similar calculations have also been performed for Si_nCr clusters. These energies are defined by

$$\mathrm{BE} = -[E(\mathrm{Si}_n\mathrm{Cr}_x) - nE(\mathrm{Si}) - xE(\mathrm{Cr})], \qquad (1)$$

$$\mathrm{VIP} = E(\mathrm{Si}_n\mathrm{Cr}_x{}^{+}) - E(\mathrm{Si}_n\mathrm{Cr}_x), \qquad (2)$$

$$\mathrm{VDE} = -[E(\mathrm{Si}_n\mathrm{Cr}_x{}^{-}) - E(\mathrm{Si}_n\mathrm{Cr}_x)], \qquad (3)$$

$$\Delta = -[E(\mathrm{Si}_{n+1}\mathrm{Cr}_x) - E(\mathrm{Si}_n\mathrm{Cr}_x) - E(\mathrm{Si})]. \qquad (4)$$

TABLE I. Binding energy (BE), vertical ionization potential (VIP), HOMO-LUMO gap, vertical detachment energy (VDE) from doublet anion to singlet neutral, adiabatic electron affinity (AEA), and energy gain, Δ in Si_n clusters.

Cluster	BE (eV)	VIP (eV)	HOMO-LUMO gap (eV)	VDE (eV)	AEA (eV)	Δ (eV)
Si_{11}	40.91	7.00	1.74	1.93	1.78	···
Si_{12}	44.96	7.43	2.23	2.96	2.27	4.05
Si_{13}	48.55	7.28	1.00	3.26	3.01	3.59
Si_{14}	52.91	7.22	1.79	2.42	2.22	4.36

Note that VDE yields the energy difference between anion and neutral both at the anion ground state geometry while AEA yields the energy difference between the ground states of the anion and the neutral. For pure Si_n clusters, the energetics in Eqs. (1)–(4) are derived by putting $x = 0$, i.e., no Cr and for $\mathrm{Si}_n\mathrm{Cr}$ clusters, we take $n = 1$. The results for pure Si_n clusters are given in Table I. Note that as expected, the BE increases with cluster size, but the energy gain Δ in Si_{13} cluster is lower than that of Si_{12} or Si_{14}. This is accompanied by a minimum in the HOMO-LUMO gap and a maximum in the VDE. However, the VIP shows no anomalous behavior. It can be concluded, based on the trend in Δ, that Si_{13} is relatively less stable than Si_{12} or Si_{14}.

The energetics in $\mathrm{Si}_n\mathrm{Cr}$ clusters derived from Eqs. (1)–(4) are summarized in Table II. We note that the binding energies once again increase with size as expected. However, the systematics in energy gain, as well as HOMO-LUMO gap and AEA are very different. For example, 4.65 eV of energy is gained in adding a Si atom to $\mathrm{Si}_{11}\mathrm{Cr}$ while only 3.60 and 4.08 eV energies are gained in adding a Si atom to $\mathrm{Si}_{12}\mathrm{Cr}$ and $\mathrm{Si}_{13}\mathrm{Cr}$, respectively. This clearly demonstrates that $\mathrm{Si}_{12}\mathrm{Cr}$ is relatively the most stable cluster studied here. This is even more apparent when one asks the following question: Given a Si_n cluster, is it energetically more favorable to form Si_{n+1} or $\mathrm{Si}_n\mathrm{Cr}$ cluster? From the energetics given in Tables I and II, it is seen that only in the case of Si_{12} does one gain more energy by forming $\mathrm{Si}_{12}\mathrm{Cr}$ rather than Si_{13}. This clearly indicates that $\mathrm{Si}_{12}\mathrm{Cr}$ cluster is magic from both points of view. This is consistent with the experimental observation of Hiura *et al.* [5] that $\mathrm{Si}_{12}\mathrm{W}$ is magic. Although these authors as well as Kumar and Kawazoe [7] have calculated several caged structures for metal encapsulated Si clusters, to demonstrate that a particular cluster is magic, clusters in the neighboring sizes have to be studied. Our study is the first one in this regard.

The magicity of $\mathrm{Si}_{12}\mathrm{Cr}$ is different from the magicity of metal clusters. Note that magic clusters composed of metallic elements are characterized not only by higher binding energy, but also by large VIP and low AEA. We see from Table II that $\mathrm{Si}_{12}\mathrm{Cr}$ does not follow this trend. The VIP decreases steadily from 7.64 eV in $\mathrm{Si}_{11}\mathrm{Cr}$ to 7.08 eV in $\mathrm{Si}_{14}\mathrm{Cr}$. In addition, the AEA of $\mathrm{Si}_{12}\mathrm{Cr}$ is the highest in the series. Had it been a metallic cluster, it would have been the lowest.

It is also interesting to note that with the exception of Si_{13} and $\mathrm{Si}_{13}\mathrm{Cr}$, the HOMO-LUMO gaps are consistently lowered in adding Cr to a Si_n cluster. This lowering is especially large in $\mathrm{Si}_{12}\mathrm{Cr}$ where the HOMO-LUMO gap is lowered by 1.3 eV in adding a Cr atom to Si_{12}. An analysis of the electronic states indicates that the HOMO has almost 70% contribution from the Cr $4p$ states while the LUMO has around 70% contribution from Cr d states. The gap is therefore controlled by the mixing between Cr and Si states and therefore is governed by the location of the $4p$ and $3d$ states of the transition metal. In this context, it should be possible to change the gap by replacing Cr by other transition metal atoms. No significant changes occur in the VIP and VDE between Si_{12} and $\mathrm{Si}_{12}\mathrm{Cr}$. Metallic clusters do not behave in this way. Thus, the signature of magicity in clusters with covalent bonding is different from that in clusters with metallic bonding.

To further examine the stability of $\mathrm{Si}_{12}\mathrm{Cr}$ we have analyzed the difference and total electron charge density distribution. In Fig. 2(a) we plot the difference charge density surface corresponding to 0.015 a.u. which depicts the charge transfer as atoms are allowed to interact. The red corresponds to regions with excess electrons while the green signifies electron deficit region. Note that electrons are removed from the vicinity of the atoms and piled up in the interstitial space including that along the bonds. The total charge density contours are shown in Fig. 2(b) as

TABLE II. Binding energy (BE), vertical ionization potential (VIP), HOMO-LUMO gap, vertical detachment energy (VDE) from doublet anion to singlet neutral, adiabatic electron affinity (AEA), and energy gain, Δ in $\mathrm{Si}_n\mathrm{Cr}$ clusters.

Cluster	BE (eV)	VIP (eV)	HOMO-LUMO gap (eV)	VDE (eV)	AEA (eV)	Δ (eV)
$\mathrm{Si}_{11}\mathrm{Cr}$	44.49	7.64	1.38	2.86	2.75	···
$\mathrm{Si}_{12}\mathrm{Cr}$	49.14	7.50	0.94	3.11	3.11	4.65
$\mathrm{Si}_{13}\mathrm{Cr}$	52.74	7.40	0.98	3.20	3.02	3.60
$\mathrm{Si}_{14}\mathrm{Cr}$	56.82	7.08	1.00	3.16	3.00	4.08

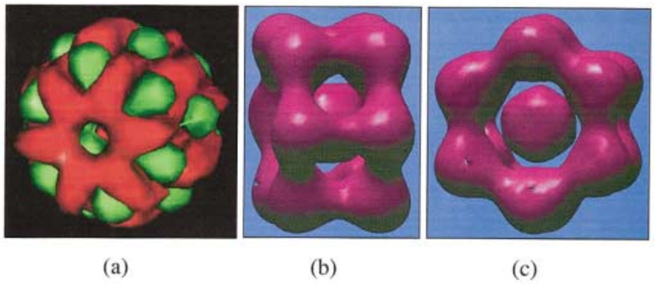

FIG. 2 (color). The electron charge density distribution in the $Si_{12}Cr$ cluster. (a) Difference charge density surface corresponding to 0.015 a.u. depicting the difference between the total charge density in $Si_{12}Cr$ and that obtained by a superposition of atomic charge densities. The red corresponds to regions with excess electrons, while the green corresponds to electron deficit regions. (b) Constant charge density surface viewed from the side of the hexagonal plane. (c) The same surface viewed from the top. The charge density at the surface is 0.0055 a.u.

viewed from the top with Si atoms forming squares and in Fig. 2(c) from the side of the hexagonal plane. Note that the bonding between Si atoms is clearly covalent while the charge distribution around the caged Cr is nearly spherical. Cr site gains around $2.6e^-$ while each of the Si atoms lose between $(0.20-0.24)e^-$, indicating that the former behaves like a superatom.

What we find most interesting is the effect of caging on the magnetic moment of Cr. The $3d$-transition atoms Sc, Ti, V, Cr, Mn, Fe, Co, and Ni have magnetic moments of $1\mu_B$, $2\mu_B$, $3\mu_B$, $6\mu_B$, $5\mu_B$, $4\mu_B$, $3\mu_B$, and $2\mu_B$, respectively. Note that Cr has the highest magnetic moment. When these atoms are deposited on metallic substrates, the trend in the moments remains the same although their magnitudes are somewhat reduced [15]. When supported on an organic molecule such as benzene, the magnetic moments for Sc, Ti, and V are enhanced by $2\mu_B$ while for Mn, Fe, Co, and Ni they are reduced by $2\mu_B$ from their free atom value [16]. The magnetic moment of Cr remains unchanged, namely at $6\mu_B$. In the case of Si_nCr clusters, the magnetic moment of Cr is completely quenched. This results from strong hybridization between Cr $3d$ and $3s$ $3p$ states of Si. The effect of Si caging on the magnetic moments of transition metal atoms can have significant implications in spintronics applications.

Since Si_nCr clusters are nonmagnetic, Stern-Gerlach experiments where one relies on the deflection of a cluster in the gradient magnetic field are not very useful as probes. The lack of magnetism of these clusters can, however, be inferred by comparing calculated photodetachment spectra with experiment [17]. When a cluster anion is photodetached by using a fixed frequency laser, the spin multiplicity of the resulting neutral can be $M' = M \pm 1$ where M is the spin multiplicity of the anion. The ground states of all Si_nCr^- clusters are in a doublet state (i.e., $M = 2$). The neutral clusters following the photodetachment can, therefore, be either in singlet or triplet states. For $Si_{12}Cr^-$ clusters, we find two vertical transitions at 3.11 and 3.72 eV resulting from the doublet → singlet and doublet → triplet transitions, respectively. Note that photodetachment spectra are usually broad if the anions and neutrals have very different ground state geometries. From Table II we expect the photodetachment peaks to be relatively narrow, especially for $Si_{12}Cr$ where the VDE and AEA have nearly identical values. Preliminary experimental results performed in Bowen's group [18] show a sharp peak at 3.10 eV for $Cr@Si_{12}$. This agreement validates our prediction that caged $Cr@Si_{12}$ is nonmagnetic.

In summary, we have calculated the energetics of neutral and anionic Si_nCr clusters corresponding to their equilibrium geometries. The results reveal that Cr atom is caged inside Si clusters. In particular, $Si_{12}Cr$ is found to be a very stable cluster. Although its stability is consistent with the 18-electron rule, we note that Si is fourfold coordinated only in $Si_{12}Cr$ cluster. Thus, it is not entirely clear if the enhanced stability of $Si_{12}Cr$ is due to 18-electron rule or due to fourfold coordination of Si. One way to answer this question would be to examine clusters involving other transition metal doped Si clusters. For example, the number of Si atoms needed to make $M@Si_n$ magic according to the 18-electron rule should be $n = 15$, 14, 13, 12, 11, 10, 9, and 8 for $M =$ Sc, Ti, V, Cr, Mn, Fe, Co, and Ni, respectively. These studies are currently in progress.

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