Photoelectron spectroscopy of europium-silicon cluster anions, $EuSi_n^-$ $(3 \leqslant n \leqslant 17)$

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We report the photoelectron spectra of $EuSi_n^-$ cluster anions $(3 \leqslant n \leqslant 17)$. They reveal dramatic electronic rearrangements over the size range $n=10-12$. In particular, a marked increase in the adiabatic electron affinity of $EuSi_{12}$ (2.8 eV) compared to its stoichiometric neighbor, $EuSi_{11}$ (1.9 eV), is observed. We propose that a significant geometric reorganization due to the encapsulation of a europium atom occurs in this size range and is responsible for the detected changes in the electronic structure. In light of this interpretation, $EuSi_{12}$ is the smallest fully endohedral europium-silicon cluster. © *2008 American Institute of Physics*.
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I. INTRODUCTION

The importance of silicon in the semiconductor industry has stimulated significant interest in the properties of small silicon clusters.[1–5] It was observed that these clusters tend to form compact, diamondlike structures rather than the cages that are characteristic of its congener, carbon.[6] However, the first hints that silicon cages may be stabilized by the introduction of a dopant atom emerged from the early, pioneering experimental work of Beck who observed enhanced ion intensities of metal-silicon clusters, MSi_n^+, around $n=16$ when a transition metal atom (M=Mo, Cr, and W) was added to the cluster.[7] Then in a particularly important set of experiments, Hiura and Kanayama demonstrated that many transition metal atoms (M=Hf,Ta,W,Re,Ir, etc.) stabilize the silicon cages by sitting endohedrally within them, $M@Si_n$.[8] The prospect of exploiting these clusters as building blocks of cluster-assembled materials with novel magnetic, electronic, and possibly optical properties resulted in a flurry of papers that explored this possibility both theoretically[9–18] and experimentally.[8,19–23] The hope was that by inserting a transition metal (TM) atom possessing unpaired *d* electrons and thus carrying a magnetic moment, one could also retain that magnetic moment in a $TM@Si_n$ cluster. Furthermore, if these clusters resisted aggregation when placed near one another, one could envision interesting silicon-based magnetic materials that could serve as transition materials between the current semiconductor technology and the emerging field of spintronics.

While several clusters, most notably $TiSi_{16}$, were identified to resist aggregation when put in close proximity of one another,[17] there is convincing evidence which shows that silicon's *sp* orbitals interact strongly with the *d* orbitals of the endohedral TM atom, thereby quenching the latter's magnetic moment.[10,11,23] Since a nonzero magnetic moment arises from unpaired *d* electrons and because a cluster's stability relies heavily on its ability to attain a closed shell, it becomes clear why these two essential requirements for a magnetic cluster-assembled material are mutually exclusive when the same electrons are responsible for both magnetism and bonding. In order to lift this limitation Khanna and Jena proposed that *f*-block atoms instead of TM atoms be introduced endohedrally into the silicon cluster. Namely, the electrons residing in the more localized *f* orbitals of these elements are to a large extent not responsible for bonding and consequently give rise to often observed magnetic properties of the rare-earth containing compounds. Further supporting this idea are the relatively low oxidation numbers (from +2 to +4) that the *f*-block elements maintain in their compounds. These low oxidation numbers indicate a limited interaction of the valence *f* electrons with their environments.

Presently, only a very limited literature exists on rare-earth (RE) containing silicon clusters. Ohara *et al.* reported experimental photoelectron spectra and water reactivities of $TbSi_n^-$ $(6 \leqslant n \leqslant 16)$.[24,25] Kumar *et al.* theoretically studied encapsulated fullerenelike neutral and anionic clusters, $M@Si_{20}^{0/-}$ (M=La,Ac,Sm,Gd,Tm,Ce,Pa,Pu,Th,Np,Pm) and observed that $Pa@Si_{20}$, $Sm@Si_{20}$, $Pu@Si_{20}$, $Tm@Si_{20}$, and $Gd@Si_{20}^-$ retain significant magnetic moments in their most stable geometry.[26]

Here, we report our photoelectron spectroscopic (PES) studies of $EuSi_n^-$ $(3 \leqslant n \leqslant 17)$ mixed clusters. While the central goal of our ongoing work is to test whether $RE@Si_n^-$ clusters retain their magnetic moments,[27] in the present paper we focus on structural and electronic properties of this one system. The evolution of the photoelectron spectra of $EuSi_n^-$ clusters with size *n* reveals a major change in their electronic structure over the size range $n=10-12$. In light of the previously reported observation that Tb encapsulation occurs at $n=10$,[24,25] we conclude that europium starts encapsulating at $n=11$ and is likely fully endohedral by $n=12$.

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II. EXPERIMENTAL METHODS

Anion PES is conducted by crossing a beam of mass-selected negative ions with a fixed-frequency photon beam and energy analyzing the resultant photodetached electrons. The photodetachment process is governed by the energy-conserving relationship, $h\nu$=EBE+EKE, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Our apparatus has been described previously elsewhere.[28] Briefly, the apparatus consists of an ion source, a linear time-of-flight mass analyzer, a Nd:YAG (yttrium aluminum garnet) photodetachment laser, and a magnetic bottle photoelectron spectrometer (MB-PES). The instrumental resolution of the MB-PES is ~35 meV at 1 eV EKE. The fourth (266 nm, 4.661 eV) harmonic of a Nd:YAG was used to photodetach the cluster anions of interest. Photoelectron spectra were calibrated against the well known atomic transitions of Cu^-.

Mixed europium-silicon cluster anions were generated in a two-laser-vaporization-source designed to mimic the arrangement first developed by Nakajima.[21] Briefly, two rotating rods are vertically mounted on opposing sides of a horizontal 3 mm diameter channel, through which a plume of helium gas expands. One of the two rods is positioned ~5 mm downstream from the other. This arrangement allows us to focus two independent laser beams onto the two rods and ablate them. By tuning the timing of the two laser pulses hitting the rods, one can control the amount of mixing between the two plasma bursts. Additionally, by adjusting the power of the two lasers one can in real-time dose an appropriate amount of each component to achieve the desired mixed cluster compositions.

For this particular set of experiments, a silicon rod (1/4 in. DIA, 3N5 purity purchased from ESPI) was positioned downstream and ablated with 532 nm laser light from a Nd:YAG laser. To act as a europium "rod," we wrapped a thin sheet of europium (25×25 mm, 0.010 in. thick foil, 3*N* purity purchased from Alfa Aesar) around an aluminum rod. The rod was ablated by a mixture of 1064 and 532 nm light from a second Nd:YAG laser that lacked the dichroic mirrors to separate the two harmonics. To improve the stability of the mixed cluster intensities, we employed a power attenuator for the latter laser beam. The enhanced peak-to-peak stability of this "dopant" laser beam is crucial to ensure the long-term stability of the mixed cluster compositions, in particular, when low stoichiometric ratios of one component (i.e., dopant) are required. For optimal mixing the laser pulse hitting the silicon rod was delayed by ~5 μs relative to the one ablating the europium. An ultrahigh purity helium gas plume produced by a general-purpose pulsed valve at a backing pressure of ~15 atm was correctly timed to flush the created plasma mix down a ~7 cm long condensation channel. The rapidly expanding supersonic gas confined within the channel cooled the plasma and generated the clusters.

III. RESULTS

A mass spectrum of Eu–Si mixed cluster anions with the source optimized for generating silicon cluster anions with a single europium atom is shown in Fig. 1(a). The magnified portion of the spectrum, shown in Fig. 1(b) reveals the expected doublet isotope pattern (^{151}Eu: 48%, ^{153}Eu: 52%) superimposed with the silicon isotope distribution for $EuSi_n^-$ clusters. Aside from the known intense, "magic" peak for Si_{10}^-, no particularly magic cluster compositions among the mixed Eu–Si cluster anions were observed.

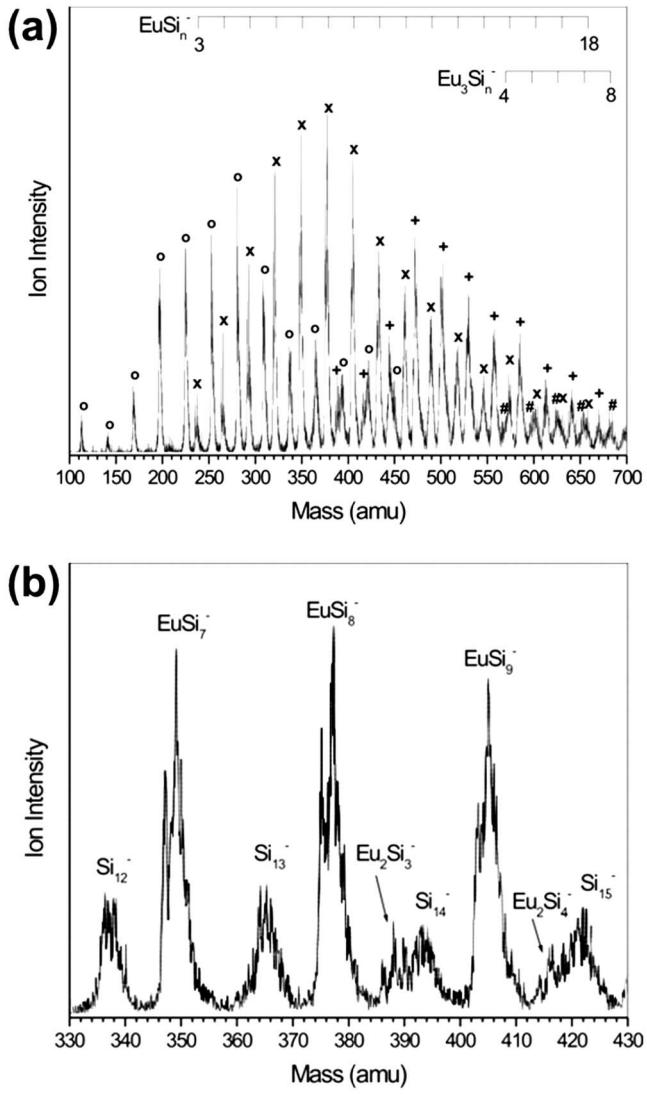

FIG. 1. (a) Typical mass spectrum of Eu–Si mixed cluster anions obtained when the source was optimized for generating silicon clusters doped with a single europium atom. (○) Si_n^-, (×) $EuSi_n^-$, (+) $Eu_2Si_n^-$, and (#) $Eu_3Si_n^-$. (b) Magnified portion of the same mass spectrum confirms the expected isotope pattern for $EuSi_n^-$ clusters.

The photoelectron spectra of $EuSi_n^-$ clusters ($3 \leqslant n \leqslant 17$) are presented in Fig. 2. The raw data were smoothed by taking a moving average of five neighboring data points. Due to the partial overlap of the $EuSi_n^-$ series with the $Eu_3Si_n^-$ series (see Fig. 1), special care was taken to keep the conditions and therefore compositions stable. Nevertheless, for the larger clusters ($n \geqslant 12$) small peaks at low EBEs that changed in intensity between runs were sometimes observed. By recording the spectra of corresponding $Eu_3Si_n^-$ cluster anions such peaks were identified, and in cases where pure compositions were impossible to obtain ($n \geqslant 15$), they were removed by subtracting the appropriate fraction of the $Eu_3Si_n^-$ spectrum. Assuming similar photodetachment cross

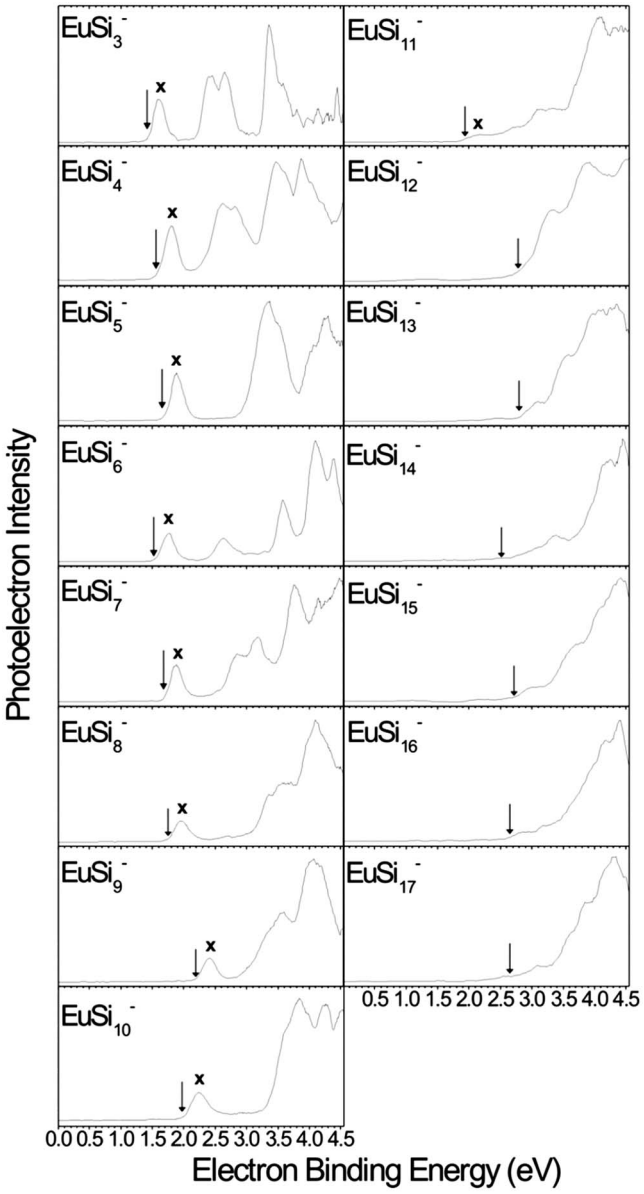

FIG. 2. Photoelectron spectra of $EuSi_n^-$ ($3 \leqslant n \leqslant 17$) clusters recorded with 4.661 eV photons. The arrows indicate the threshold energy used to estimate the adiabatic electron affinities of the corresponding $EuSi_n$ neutral clusters. Features marked with an X are proposed to signal a surface-bound europium atom. Consequently, its disappearance indicates the complete encapsulation of the guest atom.

sections between the two series, the amount of $Eu_3Si_n^-$ impurities in the spectra of $EuSi_n^-$ never exceeded 10%.

IV. DISCUSSION

In general, peaks in the photoelectron spectra correspond to transitions from the ground electronic state of the anion to the ground and excited electronic states of the neutral. Consequently, anion PES provides information about the electronic structure of the resulting neutral as well as the energetic relationship between an anion and its neutral counterpart. Structural changes associated with a change in charge state often lead to broadening of peaks in the spectrum, since more states of the neutral's vibrational manifold can then be accessed from the ground electronic state of the anion. Since the adiabatic electron affinity (EA_a) corresponds to the energy difference between the lowest vibrational level of the ground electronic state of the neutral and the lowest vibrational level of the ground electronic state of the anion, one can estimate its value from the threshold energy of the lowest EBE peak in the photoelectron spectrum. Due to the finite temperature of the clusters, a range of rovibrational levels in their electronic ground state is populated that lead to additional broadening of the peaks. In order to account for this effect ~0.1 eV is usually added to the threshold energies to obtain the clusters' adiabatic electron affinity. The values of EA_a for the $EuSi_n$ clusters obtained in such a manner are listed in Table I and are plotted as a function of the number of Si atoms in Fig. 3.

TABLE I. Adiabatic electron affinities (EA_a) of $EuSi_n$ clusters inferred from the photoelectron spectra of $EuSi_n^-$ clusters (Fig. 2). All units are in eV.

n ($EuSi_n$)	EA_a (eV)
3	1.45 ± 0.05
4	1.60 ± 0.05
5	1.70 ± 0.05
6	1.55 ± 0.05
7	1.70 ± 0.05
8	1.75 ± 0.05
9	2.2 ± 0.1
10	2.0 ± 0.1
11	1.9 ± 0.1
12	2.8 ± 0.2
13	2.8 ± 0.2
14	2.5 ± 0.3
15	2.7 ± 0.3
16	2.6 ± 0.3
17	2.6 ± 0.5

The plot shows a large increase in the EA_a value of the $EuSi_{12}$ cluster compared to that of $EuSi_{11}$ (2.8 ± 0.2 versus 1.9 ± 0.1 eV). We interpret this drastic increase in electron affinity as reflecting the full encapsulation of a europium atom. This is consistent with the conclusions of the earlier study on $TbSi_n^-$ clusters that found a similarly large increase in the electron affinity of $TbSi_{10}$ compared to $TbSi_9$ (3.60 and 2.20 eV, respectively)[24,25] and explained it in terms of encapsulation of the Tb atom. Note also that the general appearance of the photoelectron spectra of $EuSi_n^-$ dramati-

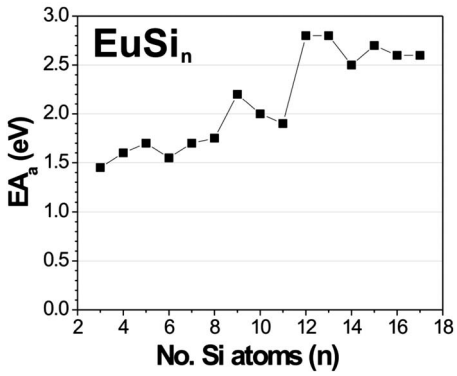

FIG. 3. Adiabatic electron affinities (EA_a) of $EuSi_n$ clusters as a function of the number of silicon atoms n.

cally changes over the size range $n=10-12$. In particular, the lowest binding energy peak prominent in spectra of $EuSi_{n\leqslant 10}^-$ (marked X in Fig. 2) suddenly diminishes in intensity for $n=11$ and entirely disappears by $n=12$. We attribute these major electronic redistributions to significant geometric rearrangements that occur upon addition of extra silicon atoms to $EuSi_{10}$ cluster. The encapsulation of the europium atom would represent just such a significant structural change. The diminishing, yet not completely vanished feature, X in the photoelectron spectrum of $EuSi_{11}^-$ may therefore signal that the europium atom is on the brink of full encapsulation at that cluster size. In light of the proposed interpretation, the low binding energy feature, X in the photoelectron spectra of $EuSi_n^-$ clusters may serve as a marker of a surface-bound europium atom.

The difference between the minimum sizes of the silicon clusters required for encapsulation of europium and terbium (12 and 10, respectively) implies that the two dopant atoms are of dissimilar size. While the metallic radius of europium (2.0 Å) is known to be unusually large among the RE elements (1.75–1.85 Å),[29] it is difficult to rationalize its use for determining the dopant's size in a predominantly silicon-based system that is likely not metallic. On the other hand employing effective ionic radii as a more appropriate measure of the RE's size in these systems reveals that in their most common oxidation state the atoms are comparable in size [e.g., Eu(III): 1.21 Å versus Tb(III): 1.18 Å][30] and would thus be expected to fit the same sized silicon cage. It is only when these elements adopt different oxidation states that their radii differ significantly. For example, if europium were to assume a lower oxidation state, such as +2 that is often found in europium-containing compounds,[31–35] aqueous solutions,[34–37] and small clusters,[38,39] its radius would be as large as 1.39 Å, thereby possibly explaining the larger minimum number of silicon atoms required for encapsulation of a single europium versus terbium atom.

The overall dissimilar appearance of $TbSi_n^-$ photoelectron spectra[24,25] compared to those of $EuSi_n^-$ implies a substantial influence by the chemical nature of the RE dopant on the electronic properties of the RE silicon clusters. This is consistent with the idea that the two elements are in different oxidation states and therefore interact differently with their environments. Although offering a qualitative explanation for the observed dissimilarities in photoelectron spectra, the underlying question (from the point of view of *f* electrons' participation in bonding and their impact on a cluster's magnetism) is how large are the oxidation numbers in which the endohedral RE elements are found. For example, a low oxidation number would indicate only limited involvement of *f* electrons, raising the prospect of magnetic $RE@Si_n^-$ clusters. On the other hand, high oxidation numbers would parallel the situation found in $TM@Si_n^-$ clusters, where most *d* electrons are known to interact with the surrounding cage, thereby quenching the guest atom's magnetic moment. Our present data set indicates only that the europium atom is likely in a lower oxidation state than terbium, yet does not specify what that value is. However, hints that the REs indeed favor the low oxidation numbers in $RE@Si_n^-$ clusters are emerging from our developing studies of several other $RE@Si_n^-$ systems. They namely show slightly shifted, but otherwise identical photoelectron spectra to those of $TbSi_n^-$ clusters in cases where the REs are known to take on only the +3 oxidation state in their compounds as terbium does. These results seem to imply that the majority of *f* electrons, in fact, do not form chemical bonds between the RE atoms and their silicon cluster environment. Interestingly, considerable work on endohedral RE carbon fullerenes has reached a similar verdict and has furthermore shown that they, consequently, retain substantial magnetic moments.[39] Together, these findings suggest that $RE@Si_n$ clusters, in which the RE's *f* electrons to a large extent appear not to interact significantly with the silicon cage, may retain their magnetic moments. Further support from theoretical calculations is needed to validate this speculation.

V. CONCLUSION

The photoelectron spectra of $EuSi_n^-$ clusters ($3\leqslant n\leqslant 17$) reveal dramatic electronic rearrangements over the size range $n=10-12$. In addition, a sharp increase in the adiabatic electron affinity of $EuSi_{12}$ (2.8 eV) compared to that of $EuSi_{11}$ (1.9 eV) is observed. We propose that significant geometric rearrangements due to the encapsulation of a europium atom occur in this size range. $EuSi_{12}$ is consequently the smallest fully endohedral europium-silicon cluster. The stark differences between the photoelectron spectra of $EuSi_n^-$ and $TbSi_n^-$ cluster series are attributed to the different oxidation states that the dopant atoms adopt in these clusters [Eu(II) and Tb(III), respectively]. Consequently, the larger size of the Eu(II) center compared to Tb(III) (1.39 and 1.18 Å, respectively)[30] explains the observed dissimilarity between the minimum number of silicon atoms required to fully encapsulate a single europium and terbium atom (12 and 10, respectively) in $RE@Si_n^-$ clusters.[24,25]

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