

Europium-doped silicon clusters EuSi_n ($n = 3\text{--}11$) and their anions: structures, thermochemistry, electron affinities, and magnetic moments

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Abstract The structures, electron affinities, and dissociation energies of EuSi_n ($n = 3\text{--}11$) and their anions have been examined by means of four hybrid and pure density functional theory (DFT) methods. Basis sets used in this work are of segmented (SEG) Gaussian valence basis sets and relativistic small-core effective core potentials (ECP) with additional diffuse *2pdfg* functions, denoted aug-SEG/ECP for Eu atoms and aug-cc-pVTZ for Si atoms. The geometries are fully optimized with each DFT method independently. The ground-state structures for all of these species are found to be substitutional type, which can be regarded as being derived from the ground-state structure of Si_{n+1} (and/or Si_{n+1}^-) by replacing a Si atom with a Eu atom. The theoretical adiabatic electron affinities (AEAs) of EuSi_n predicted by the four DFT schemes are in excellent agreement with the experimental data, especially the AEAs of TPSSh and B2PLYP. The average absolute deviations from experiment are by 0.10, 0.06, 0.07, and 0.05 eV, and the largest deviations are 0.16, 0.12, 0.18, and 0.10 eV at the B3LYP, TPSSh, PBE, and B2PLYP levels, respectively. The AEA of EuSi_n ($n = 3\text{--}11$) is less than that of Si_n . With the increase in silicon cluster size, the AEA of EuSi_n may be close to that of Si_n , but cannot be larger than that of Si_n . The Eu atom acts as an electron donor, and the bonding between Eu and silicon clusters is ionic in nature. The bond between Eu and silicon clusters of neutral EuSi_n ($n = 3\text{--}11$) is stronger than that of the anions. The total magnetic moments of $\text{EuSi}_n/\text{EuSi}_n^-$ ($n = 3\text{--}11$) and the magnetic

moments on the Eu atom do not quench, and the total magnetic moments are contributed by Eu atom. The dissociation energies of Eu atom from EuSi_n and their anions have also been calculated to examine relative stabilities.

Keywords EuSi_n · Ground-state structure · Electron affinity · Dissociation energy

1 Introduction

Silicon clusters have been investigated both experimentally and theoretically because they are not only the most important material for the semiconductor industry but also building blocks for the fabrication of new nanostructures with controlled electronic properties, which can be manipulated by changing size, shape, and composition [1–10]. Bare silicon clusters are chemically reactive and unsuitable for building block of self-assembly materials because they much prefer sp^3 hybridization to sp^2 . Like carbon atoms, they can appear with sp , sp^2 , or sp^3 hybridization in compounds [11, 12]. However, a wide variety of experimental [13–15] and theoretical [16–18] research works elucidated that doping a suitable foreign atom inside silicon clusters can not only enhance the stability, but also influence profoundly the electron properties of these complexes. In particular, the examples of encapsulating a transition metal (TM) atom inside silicon clusters as building blocks of cluster-assembled materials with novel magnetic, electronic, and possibly optical properties are numerous. People hope that by inserting TM atom possessing unpaired d electrons and thus carrying a magnetic moment, the magnetic moment would be retained in a TM@Si_n cluster. However, the hybridization between silicon's sp orbitals and d orbitals of the encapsulated TM atom results in quenching the

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magnetic moment [19–21]. Instead, the electrons residing in the localized f orbitals of the rare-earth (RE) atom are to a large extent not interacting significantly with the silicon clusters and consequently give rise to often observed magnetic properties of the RE doping silicon clusters [22–24].

There have been some previous studies on silicon clusters. On the experimental aspect, Nakajima et al. [25–27] investigated first the geometric and the electronic structures of LnSi_n^- ($\text{Ln} = \text{Tb}, \text{Ho}, \text{Lu}, 6 \leq n \leq 20$) by means of photoelectron spectroscopy (PES) and a chemical-probe method. Then, Bowen et al. [22, 23] studied the structures and properties of LnSi_n^- ($\text{Ln} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Ho}, \text{Yb}$) by using PES. From the theoretical aspect, the structures and properties such as magnetic moments and stabilities of LnSi_n ($\text{Ln} = \text{La}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Ho}, \text{Yb}, \text{Lu}, n < 21$) clusters were studied by using density functional theory (DFT) with B3LYP, or GGA-PW91, or ZORA methods and LanL2DZ, or DNP, or TZP basis sets [28–37]. In addition to these, the structural and electronic properties of M@Si_6 ($\text{M} = \text{La}, \text{Ce}, \text{Pr}, \text{Gd}, \text{Ho}, \text{Yb}, \text{Lu}$) and their anions were reported by Wang et al. [38, 39]. The most stable geometry of Eu@Si_{20} , Sm@Si_{20} , Tm@Si_{20} , and Gd@Si_{20}^- clusters was predicted to be fullerene-like silicon structure and retain significant magnetic moments in their most stable geometry [24, 40].

Even though much effort has been made to research RE atom doping silicon clusters, there are still some problems in the process of determining the ground-state structures. First, the possibility of missing the lowest energy structure exists. This problem may be solved by an extensive search with a global optimization technique. For small sizes, this search can be performed, but as the cluster size increases, it becomes much more difficult because the search for the ground-state structure is dependent on the type of the calculation and on the optimization technique. That is, the search for the ground-state structure needs both accurate potential functions and an efficient optimization method. These conditions cannot be performed for larger size clusters. The second issue is that many isomers sometimes are nearly degenerate in energy resulting from very shallow potential energy surface of some species. Fortunately, the PES is generally sensitive to the structural change; therefore, a more reliable determination of the ground-state structure can be made by comparing the PES to predictions of theory for different isomers. There are two ways of comparison of the experimental PES with predictions of theory. One is the comparison of the first vertical detachment energy (VDE) and/or adiabatic electron affinity (AEA). And another is the comparing of the number of distinct peaks of simulated PES in the low bonding energy and their relative positions. The former is more quantitative than the latter. In this work, we have investigated the ground-state structures, AEAs, dissociation energies, relative stabilities, charge transfer, magnetic moments, and growth pattern of neutral

EuSi_n ($n = 3\text{--}11$) and their anions with four DFT methods, and with the aim of understanding how their properties differ from that of bare silicon clusters. The predicted AEAs are also compared with those measured previously by PES. The comparison with PES helps to discard wrong structures when the agreement with experiment is poor. Although the theoretical results of the ground-state structures and the properties such as AEAs, population, and magnetic moment have been already reported by Zhao et al. [30], our calculations will provide more accurate results. For instance, the ground-state structures of EuSi_n with $n = 5, 7, 9, 10$, and 11 reported in this paper are different from those reported previously [30].

2 Theoretical methods

The four different density functional forms used here are as follows: Becke's three-parameter hybrid exchange functional [41] with Lee, Yang, and Parr's (LYP) [42] correlation functional (B3LYP); the 1996 pure exchange and correlation functional of Perdew, Burke, and Ernzerhof [43, 44] (PBE); the 2003 hybrid functional of Tao, Perdew, Staroverov, and Scuseria [45, 46] (TPSSH); Becke's exchange and LYP correlation functional with Hartree–Fock exchange and perturbative second-order correlation part [47] (B2PLYP). The basis sets used for silicon are aug-cc-pVTZ [48]. For europium, the segmented (SEG) Gaussian ($14s13p10d8f6g$)/[$10s8p5d4f3g$] valence basis sets and relativistic small-core effective core potentials (ECP MWB28) [49] are denoted as SEG/ECP. Since diffuse functions are important for the anions, the Eu-segmented valence basis sets were augmented by $2pdfg$ diffuse functions with exponents 0.028 and 0.015 (p), 0.032 (d), and 0.05 (f, g) [50] denoted as aug-SEG/ECP.

At the B3LYP, the PBE and the TPSSH levels, harmonic frequency analysis for all EuSi_n ($n = 3\text{--}11$) and their anions was performed to guarantee that the optimized structures are local minima. These frequencies are then applied for the zero-point vibration energy (ZPVE) correction at 0 K (the B2PLYP ZPVE adopted that of B3LYP). All of calculations have been performed using the GAUSSIAN 09 program package [51].

To search for the ground-state structures, a large number of isomers need to be studied. Accordingly, in the optimization process of geometries, we considered a great number of isomers which can be classified into the following four types. One is the “substitutional structure,” which can be regarded as being derived from the ground-state structure of Si_{n+1} (and/or Si_{n+1}^-) by replacing a Si atom with a Eu atom. The second is the “attaching structure,” in which the Eu atom is attached to different positions on surface or edge or apex of the ground-state structure of Si_n (and/or

Si_n^-). The third type is the “evolving structure,” in which the Si atom is attached to various positions on surface or edge or apex of the lowest energetic structure of EuSi_n (and/or EuSi_n^-). The remaining geometries were designed by us and are named the “fourth type.” Starting with these structures, we obtained as many of the refined low-lying structures as possible with cc-pVTZ basis set for Si and SEG/ECP basis set for Eu. Then, we refined the energies of the selected low-energy isomers with aug-cc-pVTZ and aug-SEG/ECP basis sets for Si and Eu atom, respectively. In addition, the spin multiplicities of doublet, quartet, sextuplet, octuplet, and decuplet state were taken into account for neutral

EuSi_n with $n \leq 3$ and of singlet, triplet, quintuplet, septet, nonet, and eleven states were taken into account for their anions because the ground state of Si, Si_2 , and Si_3 is triplet. The results show that the ground states of neutral with the exception of EuSi are octuplet (the ground state of EuSi is decuplet), and nonet state for anion excluded EuSi^- which is eleven state (see Table 1, the total energies of EuSi_{1-3} and their anions are listed). Therefore, from $n = 4$, we only considered octuplet state for neutral and nonet for anion. Although we obtained many isomers for neutral and EuSi_n ($n = 3-11$) and their anions, we reported mainly the ground-state structures in this paper.

Table 1 Total energies (in Hartrees) of the EuSi_{1-3} and their anions

Species	Spin multiplicity	E(B3LYP)	E(TPSSh)	E(PBE)
EuSi	2	-999.6920411	-999.3999844	-999.6014731
	4	-999.8971676	-999.6184781	-999.6976147
	6	-999.9222241	-999.6414557	-999.7242963
	8	-999.9153494	-999.6343984	-999.7170941
	10	-999.9242218	-999.6436646	-999.7264711
EuSi ⁻	1	-999.5623591	-999.279092	-999.4505545
	3	-999.8523145	-999.5696502	-999.7065839
	5	-999.9601051	-999.6754507	-999.760178
	7	-999.9555906	-999.6723225	-999.7559231
	9	-999.9536104	-999.6707414	-999.7539923
EuSi ₂	11	-999.9654082	-999.6818376	-999.7664045
	2	-1289.2470326	-1288.9765237	-1288.9098343
	4	-1289.385971	-1289.1052747	-1289.0314408
	6	-1289.431754	-1289.1590327	-1289.0842422
	8	-1289.4771183	-1289.2004375	-1289.1266202
EuSi ₂ ⁻	10	-1289.444929	-1289.163109	-1289.0893617
	1	-1289.2003903	-1288.9143142	-1288.8615208
	3	-1289.2905317	-1288.9985059	-1289.0753053
	5	-1289.4715446	-1289.1951785	-1289.1224222
	7	-1289.5203567	-1289.2391257	-1289.1665492
EuSi ₃	9	-1289.5246681	-1289.2437534	-1289.1718432
	11	-1289.480403	-1289.2046765	-1289.1298792
	2	-1578.8113422	-1578.5593073	-1578.3265184
	4	-1578.9102176	-1578.6337488	-1578.4044519
	6	-1578.9728132	-1578.6938713	-1578.4620195
EuSi ₃ ⁻	8	-1579.0070426	-1578.7358089	-1578.5032516
	10	-1578.9818619	-1578.7038863	-1578.4719165
	1	-1578.7313658	-1578.4447876	-1578.2421328
	3	-1578.832322	-1578.708537	-1578.4770337
	5	-1579.0168632	-1578.7441853	-1578.5122817
	7	-1579.0583715	-1578.7819574	-1578.5505414
	9	-1579.0633684	-1578.7872699	-1578.5567073
	11	-1579.0269944	-1578.7551301	-1578.523183

The energies obtained with aug-SEG/ECP basis sets. The geometries for EuSi_2 and its anion are *triangle*. The geometries are *planar rhombus* for EuSi_3 with the exception of four spin multiplicities, which are *triangular pyramid*. For anion EuSi_3^- , the geometries are *planar rhombus* when spin multiplicities are 1, 7, and 9 and *triangular pyramid* when spin multiplicities are 3, 5, and 11

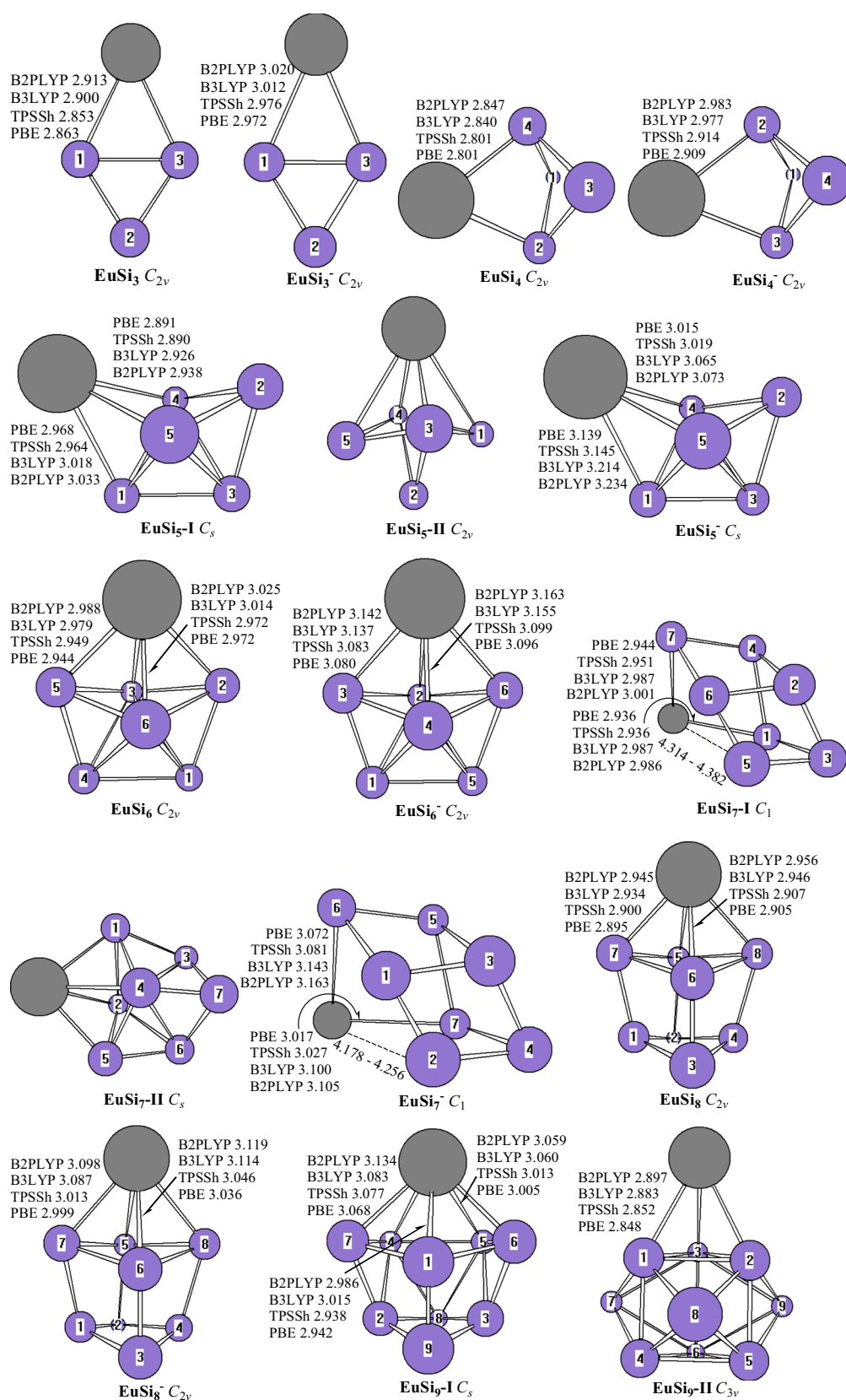


Fig. 1 The geometries for neutral EuSi_n ($n = 3-11$) and their anions in which only silicon atoms are numbered. The Eu-Si bond lengths are shown in Å

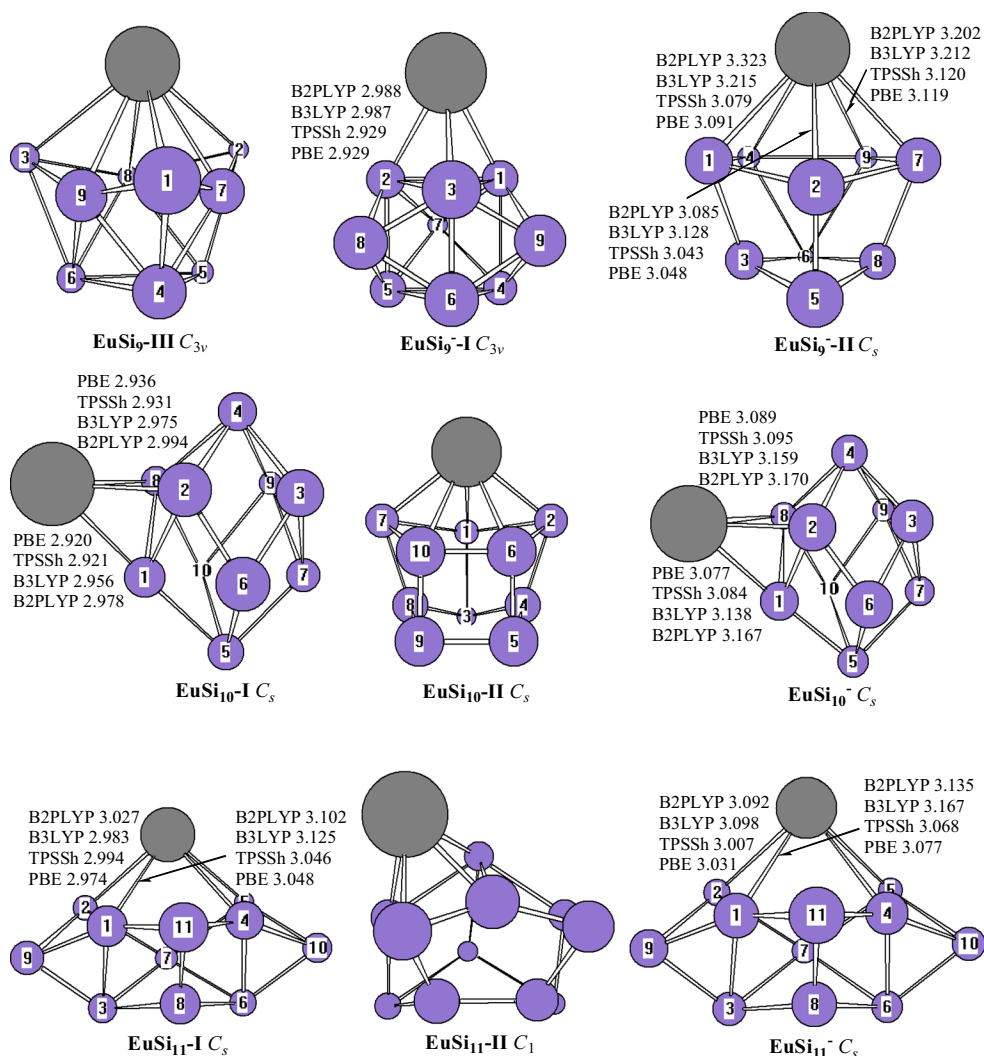


Fig. 1 continued

3 Results and discussion

The geometries optimized with all of these methods for EuSi_n ($n = 3$ – 11) clusters and their anions are shown in Fig. 1.

3.1 Lowest energy structures and isomers of EuSi_n and their anions

The lowest energy structure for EuSi_3 is predicted to be a *planar rhombus* with C_{2v} symmetry and $^8\text{A}_2$ ground state, which is the same as the results reported by Zhao et al. [30]. Similar to CaSi_3 [52], it can be viewed as being derived from not only the ground-state Si_4 structure [1, 2, 4, 5] by replacing a Si atom with a Eu atom but also the ground-state Si_3 structure [1, 2, 4] by attaching a Eu atom. For anion EuSi_3^- , the lowest energy structure is also a *planar*

rhombus, but $^9\text{A}_2$ ground state. The equivalent Eu–Si bond lengths are by 0.11 Å longer than its neutral counterparts.

Zhao et al. [30] reported that the lowest energy structure of EuSi_4 is C_{2v} symmetry. Our results are also C_{2v} symmetry with $^8\text{A}_2$ ground state. It can be viewed as being derived from the *trigonal bipyramid* of Si_5 [1, 2, 4] by replacing a Si atom with a Eu atom. For anion EuSi_4^- , the lowest energy structure of $^9\text{A}_2$ ground state can also be viewed as being derived from the *trigonal bipyramid* of Si_5 and/or Si_5^- [1, 2, 4, 6] by replacing a Si atom with an Eu atom. A pair of equal Eu–Si bond lengths is by 0.11–0.14 Å longer than its neutral counterparts.

The lowest energy structure of EuSi_5 (shown in Fig. 1 EuSi_5 -I) of ^8A ground state belongs to not only “substitutional structure” but also “attaching structure” (for Si_6 , *tetragonal bipyramid*, *face-capped trigonal bipyramid*, and *edge-capped trigonal bipyramid* compete with each other

Table 2 The adiabatic electron affinity (AEA) with zero-point corrected for EuSi_n and Si_n clusters

Species	Methods	EAs	Species	Methods	EAs
EuSi ₃	B3LYP	1.53	Si ₃	B3LYP	2.23
	TPSSh	1.40		TPSSh	2.23
	PBE	1.45		PBE	2.21
	B2PLYP	1.42		B2PLYP	2.20
	Expt.	1.45 ± 0.05 ^a		Expt.	2.29 ± 0.02 ^b
EuSi ₄	B3LYP	1.74	Si ₄	B3LYP	2.09
	TPSSh	1.58		TPSSh	2.21
	PBE	1.63		PBE	2.18
	B2PLYP	1.70		B2PLYP	2.01
	Expt.	1.60 ± 0.05 ^a		Expt.	2.13 ± 0.01 ^b
EuSi ₅	B3LYP	1.77	Si ₅	B3LYP	2.36
	TPSSh	1.59		TPSSh	2.52
	PBE	1.69		PBE	2.40
	B2PLYP	1.67		B2PLYP	2.32
	Expt.	1.70 ± 0.05 ^a		Expt.	2.40 ± 0.25 ^c
EuSi ₆	B3LYP	1.69	Si ₆	B3LYP	2.07
	TPSSh	1.48		TPSSh	2.14
	PBE	1.63		PBE	2.04
	B2PLYP	1.57		B2PLYP	1.95
	Expt.	1.55 ± 0.05 ^a		Expt.	2.08 ± 0.14 ^d
EuSi ₇	B3LYP	1.79	Si ₇	B3LYP	1.92
	TPSSh	1.64		TPSSh	1.92
	PBE	1.74		PBE	1.88
	B2PLYP	1.68		B2PLYP	1.77
	Expt.	1.70 ± 0.05 ^a		Expt.	1.85 ± 0.02 ^b
EuSi ₈	B3LYP	1.90	Si ₈	B3LYP	2.47
	TPSSh	1.70		TPSSh	2.46
	PBE	1.86		PBE	2.40
	B2PLYP	1.77		B2PLYP	2.33
	Expt.	1.75 ± 0.05 ^a		Expt.	2.36 ± 0.10 ^d
EuSi ₉	B3LYP	2.24	Si ₉	B3LYP	2.10
	TPSSh	2.17		TPSSh	2.11
	PBE	2.29		PBE	2.16
	B2PLYP	2.12		B2PLYP	2.06
	Expt.	2.20 ± 0.10 ^a		Expt.	2.31 ± 0.25 ^e
EuSi ₁₀	B3LYP	2.05	Si ₁₀	B3LYP	2.25
	TPSSh	1.88		TPSSh	2.30
	PBE	1.95		PBE	2.24
	B2PLYP	1.95		B2PLYP	2.14
	Expt.	2.00 ± 0.10 ^a		Expt.	2.29 ± 0.05 ^d
EuSi ₁₁	B3LYP	2.06	Si ₁₁	B3LYP	2.57
	TPSSh	1.95		TPSSh	2.55
	PBE	2.08		PBE	2.52

for the ground-state structure, see Refs. [1, 2, 4–6]). Our result differs from the outcome reported by Zhao et al. [30]. Zhao et al. [30] presented that the lowest energy structure

Table 2 continued

Species	Methods	EAs	Species	Methods	EAs
	B2PLYP	1.99		B2PLYP	2.40
	Expt.	1.90 ± 0.10 ^a		Expt.	2.59 ± 0.16 ^d

Presented in eV. For Si_n ($n = 3–11$) clusters, the ground-state structures confirmed by theoretical and experimental schemes are *equilateral triangle* for Si_3 , *rhombus* for Si_4 , *trigonal bipyramid* for Si_5 , *tetragonal bipyramid* or *face-capped trigonal bipyramid* for Si_6 , and *pentagonal bipyramid* for Si_7 . Many calculations showed that the lowest energy geometry of Si_8 , Si_9 , Si_{10} , and Si_{11} is *distorted bicapped octahedron*, *bicapped pentagonal bipyramid*, *tetracapped trigonal prism*, and *distorted tricapped tetragonal antiprism*, respectively (see Refs. [1–5, 52]). For anions Si_n^- ($n = 3–11$), the ground-state geometries resemble those of corresponding neutral with the exception of Si_8^- and Si_9^- . The anion Si_8^- is C_{3v} symmetry (see Ref. [2]). The anion Si_9^- is *distorted tricapped trigonal prism* with C_s symmetry (see Ref. [6])

^a Ref. [23]

^b Ref. [55]

^c Ref. [56]

^d Ref. [10]

^e Ref. [9]

of EuSi_5 was C_{2v} symmetry. The C_{2v} -symmetry structures (shown in Fig. 1 EuSi_5 -II) we obtained possess two electronic states. One is 8B_1 state, and another is 8A_2 state. The 8B_1 isomer is less stable than that of EuSi_5 -I by 0.81, 1.08, and 0.93 eV in energy at the B3LYP, the TPSSh, and the B2PLYP levels, respectively. The 8A_2 isomers are a saddle point on the potential surface due to having an imaginary 48i, 49i, and 50i frequency with b_2 mode at the B3LYP, the TPSSh, and the PBE levels, respectively. They undergo Jahn–Teller distortion to give the ground-state structures. For anion EuSi_5^- , the lowest energy structure is also C_s symmetry, but $^9A''$ ground state.

The lowest energy structure of EuSi_6 is predicted to be C_{2v} symmetry with 8A_2 ground state, which are the same as in previous study of Zhao et al. [30]. Similar to CaSi_6 [52], it belongs to “substitutional structure.” For anion EuSi_6^- , the lowest energy geometry of 9A_2 ground state keeps the frame of the corresponding neutral unchanged.

The C_1 symmetry EuSi_7 -I structure of octuplet state is predicted to be the ground state for neutral EuSi_7 . It can be viewed as being derived from the *distorted bicapped octahedron* of Si_8 [2, 3, 6, 7] by replacing a Si atom with a Eu atom, analogous to CaSi_7 [52]. This result is different from previous study of Zhao et al. [30]. The geometry reported in Ref. [30] is similar to EuSi_7 -I (see Fig. 1) with C_s symmetry and $^8A'$ state. It can be viewed as attaching a Si atom to the face of the ground state of EuSi_6 , that is, “evolving structure.” Energetically, it is higher than that of EuSi_7 -I by 0.57, 0.43, 0.38, and 0.62 eV at the B3LYP, the PBE, the TPSSh, and the B2PLYP levels of theory, respectively. For

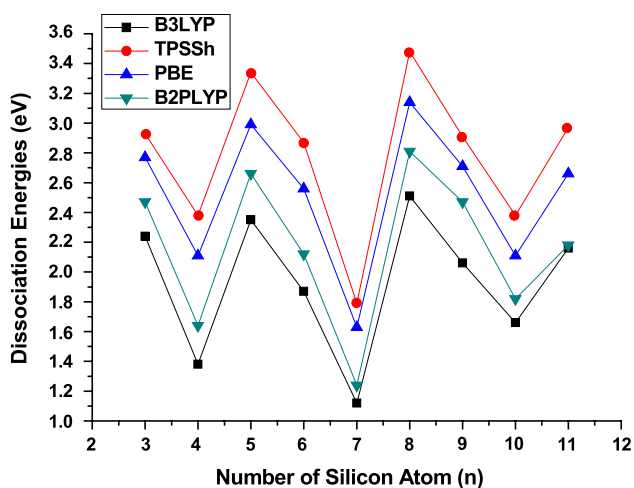


Fig. 2 Dissociation energy (eV) with ZPVE corrections for the reaction $\text{EuSi}_n \rightarrow \text{Eu} + \text{Si}_n$ versus the number of atoms n for EuSi_n clusters

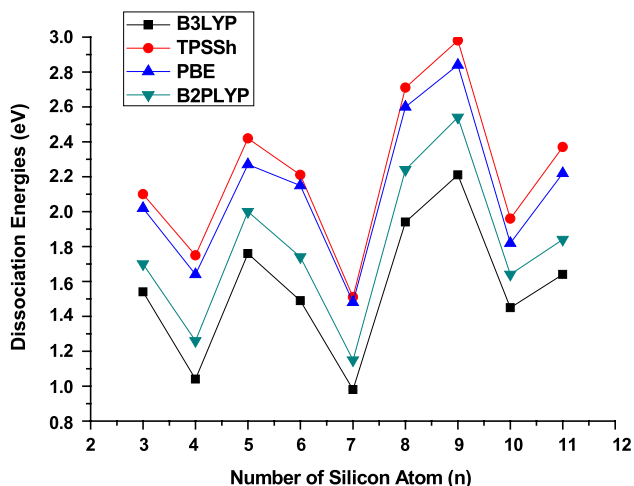


Fig. 3 Dissociation energy (eV) with ZPVE corrections for the reaction $\text{EuSi}_n^- \rightarrow \text{Eu} + \text{Si}_n^-$ versus the number of atoms n for EuSi_n^- clusters

anion EuSi_7^- , the framework of lowest energy structure of nonet ground state is unchanged compared to its neutral. The Eu–Si bond lengths of the anion are longer than its neutral counterparts by 0.08–0.16 Å.

The lowest energy structure of EuSi_8 is predicted to be C_{2v} symmetry with 8A_2 ground state, which are the same as previous study of Zhao et al. [30]. It can be viewed as being derived from the *bicapped pentagonal bipyramid* of Si_9 [2, 3, 7] by replacing a Si atom with a Eu atom, analogous to CaSi_8 [52]. For anion EuSi_8^- , the geometry of 9A_2 ground state is unchanged compared to its neutral. The Eu–Si bond lengths of the anion are by 0.10–0.17 Å longer than its neutral counterparts.

Table 3 Natural population analysis (NPA) valence configurations and charge of Eu atom (in a.u.) calculated with the TPSSh scheme for the lowest energy EuSi_n ($n = 3\text{--}11$) clusters and their anions

Species	Electron configuration	Charge
EuSi_3	$[\text{Core}]6s^{0.36}4f^{6.99}5d^{0.49}6p^{0.07}$	1.11
EuSi_4	$[\text{Core}]6s^{0.22}4f^{6.99}5d^{0.59}6p^{0.06}$	1.16
EuSi_5	$[\text{Core}]6s^{0.25}4f^{6.99}5d^{0.54}6p^{0.06}$	1.18
EuSi_6	$[\text{Core}]6s^{0.17}4f^{6.99}5d^{0.70}6p^{0.09}$	1.06
EuSi_7	$[\text{Core}]6s^{0.29}4f^{6.99}5d^{0.48}6p^{0.08}$	1.17
EuSi_8	$[\text{Core}]6s^{0.15}4f^{6.99}5d^{0.77}6p^{0.11}$	1.02
EuSi_9	$[\text{Core}]6s^{0.14}4f^{6.98}5d^{0.75}6p^{0.13}$	1.02
EuSi_{10}	$[\text{Core}]6s^{0.31}4f^{6.99}5d^{0.37}6p^{0.05}$	1.29
EuSi_{11}	$[\text{Core}]6s^{0.18}4f^{6.98}5d^{0.65}6p^{0.14}$	1.06
EuSi_3^-	$[\text{Core}]6s^{0.98}4f^{6.99}5d^{0.32}6p^{0.31}$	0.40
EuSi_4^-	$[\text{Core}]6s^{0.85}4f^{6.99}5d^{0.34}6p^{0.28}$	0.55
EuSi_5^-	$[\text{Core}]6s^{0.93}4f^{6.99}5d^{0.29}6p^{0.29}$	0.50
EuSi_6^-	$[\text{Core}]6s^{0.86}4f^{6.99}5d^{0.41}6p^{0.33}$	0.42
EuSi_7^-	$[\text{Core}]6s^{0.88}4f^{6.99}5d^{0.26}6p^{0.27}$	0.60
EuSi_8^-	$[\text{Core}]6s^{0.78}4f^{6.99}5d^{0.44}6p^{0.31}$	0.50
EuSi_9^-	$[\text{Core}]6s^{0.65}4f^{6.99}5d^{0.45}6p^{0.17}$	0.77
EuSi_{10}^-	$[\text{Core}]6s^{0.93}4f^{6.99}5d^{0.17}6p^{0.24}$	0.67
EuSi_{11}^-	$[\text{Core}]6s^{0.49}4f^{6.98}5d^{0.61}6p^{0.23}$	0.68

Two isomers for neutral EuSi_9 are reported. Both $\text{EuSi}_9\text{-I}$ and $\text{EuSi}_9\text{-II}$ can be viewed as being derived from the *tetracapped trigonal prism* of Si_{10} [2, 3, 6, 7] by replacing a Si atom located at different position with a Eu atom. Energetically, the $\text{EuSi}_9\text{-I}$ structure of $^8A''$ ground state is more stable than the $\text{EuSi}_9\text{-II}$ isomer of 8A_2 state by 0.12, 0.04, 0.08, and 0.14 eV at the B3LYP, the TPSSh, the PBE, and the B2PLYP levels, respectively. Our results are different from previous study [30]. The geometry reported by Zhao et al. [30] is similar to C_{3v} symmetry $\text{EuSi}_9\text{-III}$ of 8A_2 state. Energetically, it is less stable than that of $\text{EuSi}_9\text{-I}$ by 0.22, 0.13, and 0.21 eV at the B3LYP, the TPSSh, and the PBE levels, respectively. For anion EuSi_9^- , two isomers are also presented. The C_{3v} symmetry $\text{EuSi}_9\text{-I}$ structure of 9A_2 state is predicted to be the ground state. Energetically, it is more stable than the C_s symmetry $\text{EuSi}_9\text{-II}$ structure of $^9A''$ electronic state by 0.36, 0.46, 0.41, and 0.34 eV at the B3LYP, the TPSSh, the PBE, and the B2PLYP levels, respectively. It is note that although both the ground-state structures of EuSi_9 and its anion belong to substitutional type, the substitutional sites are not identical.

The $\text{EuSi}_{10}\text{-I}$ structure of $^8A''$ ground state can be viewed as being derived from the *distorted tricapped tetragonal antiprism* of Si_{11} [3] by replacing a Si atom with a Eu atom. This result is different from previous study of Zhao et al. [30]. The geometry reported by Zhao et al. [30] is similar to $\text{EuSi}_{10}\text{-II}$ (see Fig. 1) with C_s symmetry and $^8A''$ state. It is higher in energy than that of $\text{EuSi}_{10}\text{-I}$ by 0.81, 0.98,

Table 4 Magnetic moment (μ_B) of $6s$, $4f$, $5d$, $6p$ states for Eu atom, total magnetic moment (μ_B) of Eu atom, and total magnetic moment of the ground-state structure of EuSi_n ($n = 3\text{--}11$) and their anions calculated with the TPSSh scheme

Species	Eu moment					Molecule (μ_B)
	$6s$	$4f$	$5d$	$6p$	Total	
EuSi_3	0.04	6.97	0.11	0.01	7.13	7
EuSi_4	0.02	6.97	0.13	0.00	7.12	7
EuSi_5	0.02	6.97	0.01	0.00	7.00	7
EuSi_6	0.01	6.97	0.11	0.01	7.10	7
EuSi_7	0.03	6.97	0.08	0.00	7.08	7
EuSi_8	0.01	6.96	0.11	0.01	7.09	7
EuSi_9	0.00	6.96	0.09	0.00	7.05	7
EuSi_{10}	0.03	6.97	0.07	0.01	7.08	7
EuSi_{11}	0.01	6.96	0.08	0.00	7.05	7
EuSi_3^-	0.64	6.98	0.09	0.22	7.93	8
EuSi_4^-	0.62	6.97	0.08	0.20	7.87	8
EuSi_5^-	0.69	6.98	0.05	0.21	7.93	8
EuSi_6^-	0.68	6.97	0.07	0.23	7.95	8
EuSi_7^-	0.60	6.97	0.06	0.19	7.82	8
EuSi_8^-	0.61	6.97	0.07	0.21	7.86	8
EuSi_9^-	0.52	6.97	0.09	0.09	7.67	8
EuSi_{10}^-	0.67	6.98	0.03	0.18	7.86	8
EuSi_{11}^-	0.29	6.95	0.13	0.09	7.46	8

and 1.12 eV at the B3LYP, the PBE, and the TPSSh levels, respectively. Compared to neutral, the anionic geometry of the ^9A ground state is unchanged. The Eu–Si bond lengths of the anion are longer than its neutral counterparts by 0.15–0.20 Å.

The $\text{EuSi}_{11}\text{-I}$ structure of ^8A ground state can be viewed as being derived from the *hexacapped trigonal prism* of Si_{12} [8] by replacing a Si atom with a Eu atom. Our results differ from ones reported previously [30]. The geometry reported previously [30] is similar to $\text{EuSi}_{11}\text{-II}$ (see Fig. 1). It is higher in energy than that of $\text{EuSi}_{11}\text{-I}$ by 0.39, 0.41, and 0.43 eV at the B3LYP, the PBE, and the TPSSh levels, respectively. For anion EuSi_{11}^- , the structure of ^9A ground state is unchanged compared to its neutral.

From described above, we can conclude that the lowest energy structure of EuSi_n ($n = 3\text{--}11$) can be viewed as being derived from the ground-state structure of Si_{n+1} (and/or Si_{n+1}^-) by replacing a Si atom with a Eu atom, that is, “substitutional structure.” This result is similar to that of CaSi_n [52], but not for MgSi_n [53] and KSi_n [54]. The reason may be explained that although the electron configurations ([core] $6s^24f^75d^0$) of Eu include $4f$ orbitals, the electrons residing in the f orbitals are to a large extent not responsible for bonding in EuSi_n clusters (see below). Consequently, the electron configurations ([core] $6s^25d^0$) of Eu are similar to those of Ca ([core] $4s^23d^0$), but not K ([core] $4s^13d^0$) and Mg ([core] $3s^23p^0$). In terms of predicting the Eu–Si bond lengths, the B3LYP and B2PLYP bond distances are nearly identical, while the PBE and TPSSh

bond lengths are nearly identical. The bond distances of B3LYP and B2PLYP are averagely larger than those of PBE and TPSSh by 0.04 Å. The Eu–Si bond lengths are slightly longer than or nearly close to corresponding Ca–Si bonds of CaSi_n . These indicate that the modification of calcium–silicon-based materials via doping Eu atom would be easily implemented. For anion, the lowest energy geometries of EuSi_n^- ($n = 3\text{--}11$) with the exception of $n = 9$ are unchanged compared to corresponding neutrals. The Eu–Si bond lengths of the anions are averagely longer than its neutral counterparts by 0.12 Å.

3.2 Electron affinities

The adiabatic electron affinities (AEAs) [defined as the difference of total energies in the manner $\text{AEA} = E(\text{optimized neutral}) - E(\text{optimized anion})$] of EuSi_n and Si_n clusters with $n = 3\text{--}11$ are evaluated. These values and their experimental ones are listed in Table 2. From Table 2, we can see that (1) the theoretical AEAs of EuSi_n predicted by the four schemes are in excellent agreement with the experimental values (taken from Ref. [22]), especially the AEAs of TPSSh and B2PLYP. The average absolute deviations from experiment are by 0.10, 0.06, 0.07, and 0.05 eV at the B3LYP, the TPSSh, the PBE, and the B2PLYP levels, respectively. The largest deviations are 0.16 eV (the B3LYP), 0.12 eV (the TPSSh), 0.18 eV (the PBE), and 0.10 eV (the B2PLYP). (2) The theoretical AEAs of Si_n are also in excellent agreement with available experimental

results. The average absolute deviations from experiment are by 0.07, 0.08, 0.07, and 0.12 eV at the B3LYP, the TPSSh, the PBE, and the B2PLYP levels, respectively. The largest deviations with the exception of Si_9 are 0.11, 0.10, 0.10, and 0.19 eV, respectively. Though the largest deviations are that of Si_9 , which are off by 0.21 eV (the B3LYP), 0.20 eV (the TPSSh), 0.15 eV (the PBE), and 0.25 eV (the B2PLYP), they fall within the experimental error bars of ± 0.25 eV [9]. (3) The AEAs of EuSi_n are less than those of Si_n . The reason can be explained that when a Eu atom is attached to Si_n cluster, the charge transfer from Eu atom to silicon cluster (see below) results in the decrease in the AEAs of Si_n clusters. With the increase in silicon cluster size, the average charge obtained by each silicon atom would become less and less. As a result, the AEAs of EuSi_n can be close to the AEAs of Si_n , but cannot be larger than the AEAs of Si_n . In light of this point of view, we inferred that the experimental value of 2.8 ± 0.2 eV [22] of EuSi_{12} may be inaccurate because it is larger than the experimental value of 2.66 ± 0.20 eV [57, 58] of Si_{12} . We hope that this prediction will provide strong motivation for further experimental studies of EuSi_{12} and its anion.

A very good agreement of AEA with experiment is a necessary condition for predicting the ground-state structure. This means that if the ground-state structure is accurate, then the theoretical AEA will be in good agreement with experimental value. But a good agreement with the experiment is not necessarily to say that the geometry is the ground-state structure. Therefore, even though the geometries reported in Ref. [30] are not the ground-state structures for $n = 5$ and 7, they also obtained the very good agreement of AEA with experiment.

3.3 Dissociation energies

The dissociation energies (DEs) (defined as the energies required in the reactions $\text{EuSi}_n \rightarrow \text{Eu} + \text{Si}_n$ for neutral EuSi_n and $\text{EuSi}_n^- \rightarrow \text{Eu} + \text{Si}_n^-$ for anion EuSi_n^-) of EuSi_n and their anions are calculated and sketched in Figs. 2 and 3, respectively. The stability of bonding a Eu atom to silicon clusters can be found from the DEs. The higher values of the DEs indicate that the cluster bonding of a Eu atom is stable. A better way of comparing the local relative stability of various size clusters is by means of the incremental binding energies. From Figs. 2 and 3, we can see that (1) the DE curves for the four methods are parallel. The orders of DE predicted by the four methods are TPSSh > PBE > B2PLYP > B3LYP. (2) The EuSi_n for $n = 4, 7$, and 10 is less stable than for $n = 5$ and 8 because the DEs are local minimal values for $n = 4, 7$, and 10 and local maximal values for $n = 5$ and 8. This also indicates that Si_4 , Si_7 , and Si_{10} are more stable and Si_5 and Si_8 less stable for Si_n cluster. (3) The EuSi_n^- anion with $n = 4$ and

7 is less stable than with $n = 2$ and 9. (4) The DEs of neutral are larger than those of their anions. The reason will be explained in Sect. 3.4.

3.4 Charge transfer and magnetic moment

To further understand the interaction between the silicon clusters and the Eu atom, natural population analysis (NPA) is performed with the TPSSh method. The NPA valence configurations and charge of Eu atom are listed in Table 3. The magnetic moments of 6s, 4f, 5d, and 6p state for Eu atom, total magnetic moments of Eu atom, and total magnetic moments of the ground-state of EuSi_n ($n = 3-11$) and their anions are listed in Table 4. From Table 3, we can see that (1) the valence configuration is $6s^{0.14-0.36}4f^{6.9}8-6.995d^{0.37-0.77}6p^{0.05-0.14}$ for Eu in EuSi_n ($n = 3-11$) species. Obviously, the 4f shell of Eu in the clusters is nearly unchanged (the configuration of free Eu atom is [core]6s²4f⁷5d⁰6p⁰), which reproduced the conclusion reported by Zhao et al. [30]. The charge transfer takes place mainly from 6s to 5d orbitals, leading to hybridization between the 6s and 5d orbitals. (2) The calculated charges of the Eu atom in EuSi_n ($n = 3-11$) species are 1.02–1.29 *e*, which indicates Eu atom acts as an electron donor analogous to the results reported in Ref. [30], and the bonding between Eu atom and silicon clusters is ionic in nature. (3) In the cases of anion EuSi_n^- ($n = 3-11$), the majority of the extra electron's charge was found to be localized on the silicon clusters. Compared with neutral EuSi_n ($n = 3-11$), averaged charges of 0.55 *e* go back to Eu atom from silicon clusters. As a result, the bonds between Eu and silicon clusters are weakened. So the DEs of Eu atom from the ground-state structure of the anions EuSi_n^- are smaller than those of their neutral. From Table 3, we can see that the total magnetic moments of $\text{EuSi}_n/\text{EuSi}_n^-$ ($n = 3-11$) and the magnetic moments on the Eu atom do not quench and the total magnetic moments are contributed by Eu atom.

4 Conclusions

Carefully selected DFT methods applied with aug-SEG/ECP basis set for lanthanide atoms are capable of reliably predicting the available structures, AEAs, and other properties for the EuSi_n clusters. The ground-state structures for all of these species are found to be substitutional structure, which can be regarded as being derived from the ground-state structure of Si_{n+1} (and/or Si_{n+1}^-) by replacing a Si atom with a Eu atom. The bond distances predicted by the B3LYP and the B2PLYP are larger than those predicted by PBE and the TPSSh. The theoretical AEAs of EuSi_n predicted by the four DFT schemes are in excellent agreement with the experimental data, especially the TPSSh

and B2PLYP AEAs. The average absolute deviations from experiment are by 0.10, 0.06, 0.07, and 0.05 eV, and the largest deviations are 0.16, 0.12, 0.18, and 0.10 eV at the B3LYP, the TPSSh, the PBE, and the B2PLYP levels, respectively. The AEA of EuSi_n ($n = 3-11$) is less than that of Si_n . With the increase in silicon cluster size, the AEA of EuSi_n may be close to that of Si_n , but cannot be larger than that of Si_n . The EuSi_n for $n = 4, 7$, and 10 is less stable than for $n = 5$ and 8 , and the EuSi_n^- anion with $n = 4$ and 7 is less stable than with $n = 2$ and 9 . Eu atom acts as an electron donor, and the bonding between Eu and silicon clusters is ionic in nature. The bond between Eu and silicon clusters of neutral EuSi_n ($n = 3-11$) is stronger than that of their anions. The total magnetic moments of $\text{EuSi}_n/\text{EuSi}_n^-$ ($n = 3-11$) and the magnetic moments on the Eu atom do not quench, and the total magnetic moments are contributed by Eu atom.

We hope that our theoretical predictions will provide strong motivation for further experimental and theoretical studies of other lanthanide atom-doped silicon clusters and their anions.

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