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Stability and magnetic properties of T2Sin (T=Cr,Mn,1≤n≤8) clusters

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Stability and magnetic properties of T_2Si_n ($T=Cr,Mn, 1\leq n\leq 8$) clusters

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First-principles studies on the geometry, electronic structure, and magnetic properties of neutral and anionic Cr_2Si_n and Mn_2Si_n ($1\leq n\leq 8$) have been carried out within a gradient corrected density-functional framework. We find that Cr_2Si_n clusters containing up to five Si atoms and Mn_2Si_n clusters containing up to eight Si atoms are all marked by finite local spin moments at the transition-metal site that order ferromagnetically or antiferromagnetically depending on the size and the charged state. Our studies of the variation in the binding energy upon addition of successive Si atoms and the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital indicate Mn_2Si_4 to be a potential motif for generating magnetic cluster-assembled material. While the individual Mn_2Si_4 motif has a ground state with antiferromagnetically coupled local moments, the studies on the assembly of two basic motifs show that it favors a ferromagnetic state. It is hoped that the present work will motivate examination of such assemblies in the recently developed cluster beam deposition experiments.

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I. INTRODUCTION

The current microelectronics industry relies heavily on the semiconducting material silicon. As the pace of technology carries us to smaller electronic devices, the ultimate length scale is expected to reach the dimension of clusters that are on the order of nanometer. At this length scale, the properties of clusters are not only fundamentally altered from the bulk behavior, but they can be modified by changing their size and/or composition atom by atom.[1] Thus, attaining an atomic level control over the synthesis and properties of silicon-based clusters and assembling them to create new cluster-assembled materials will have technological implications. The biggest challenge is to find clusters that have interesting properties and yet are stable enough to retain their identity during their assembly to form cluster-assembled materials. The resulting materials will then carry the imprints of the building blocks, thus providing an unprecedented opportunity to design materials with desirable traits.[2] The discovery of fullerides based on carbon cages of differing sizes[3] along with the recent works on As_7K_3, $As_{11}K_3$, and As_2Te_2 systems[4,5] has provided us several examples that cluster-based materials can indeed be synthesized in the bulk phase. It will be remarkable if these successes could be extended to metal-silicon systems. It will be even more interesting if the new clusters could be magnetic because of the recent interest in magnetic semiconductors and spintronics devices with novel functionalities.[6] The present work explores this later possibility.

Like carbon, silicon also belongs to the group IV of the Periodic Table. However, unlike carbon, it prefers sp_3 bonding, favors tetrahedral coordination, and does not form graphitic sheets or fullerene cages. The structure of silicon clusters has been the subject of intense research over the past 20 years. It is now known that, in contrast to bulk Si, small clusters often have compact structures with Si sites of varying coordination. In particular, it has been suggested that silicon cages with low coordinated Si sites could be further stabilized by introducing metal atoms. This has generated considerable interest in studies of silicon cages with endohedral metal atoms.[7–15] Theoretical calculations by Jackson *et al.*[7] showed that $Zr@Si_{20}$ is indeed a very stable cluster. Subsequent theoretical calculations by Han and Shi[8] on MSi_{15} ($M=Cr,Mo,W$) and by Kumar and Kawazoe[9] and Kumar *et al.*[10] on MSi_{16} ($M=Hf,Zr$) and $Ti@Si_{16}$ reported these to be stable species. The theoretical suggestions were experimentally confirmed by Hiura *et al.*,[11] who demonstrated that clusters such as WSi_{12} are indeed very stable. Assuming that each silicon atom contributes 1 electron and the tungsten atom contributes 6 electrons, the authors suggested that the enhanced stability of WSi_{12} could be a consequence of the 18-electron rule, well known in chemistry. These findings ignited a flurry of theoretical activity. Khanna *et al.*[12] performed calculations on silicon cages containing a chromium atom and Zheng *et al.*[16] substantiated their findings via photodetachment experiments on $CrSi_{12}$. In an effort to develop simple rules for the stability of metal-silicon species, Reveles and Khanna[13] carried out a systematic study of the electronic structure and stability of MSi_{12} ($M=Sc,Ti,V,Cr,Mn,Fe,Co,Ni$) clusters and showed that the observed trends in the binding energy of various metal atoms to the cage could be rationalized within an 18-electron sum rule. As each Si is coordinated to three other silicon atoms and to the central metal atom, one can assume that each Si contributes one electron to the nearly free electron gas inside the silicon cage. Clusters where the total number of electrons coming from the silicon sites coordinated to the metal and those coming from the valence pool of the transition-metal atom is 18 exhibit enhanced stability. Later studies by Reveles and Khanna[14] on neutral, anionic, and cationic MSi_{15}, MSi_{16}, and MSi_{17} ($M=Sc$, Ti, and V) species showed enhanced stability for a sum of 20 electrons, in agreement with experiments. As to going from free stable motifs to cluster materials, recent theoretical studies[15] have

examined the possibility of a cluster-assembled material of $Ti@Si_{16}$ units. Their results show that a solid where the $Ti@Si_{16}$ cages bind weakly together, such as fullerite, is stable. While the cluster studies mentioned above have identified numerous stable species, the magnetic moment on the transition-metal atom in the cage was completely quenched.

One way to stabilize the magnetic moment on the transition-metal atom is to introduce multiple transition-metal atoms in the hope that the coupling between the transition-metal atoms may stabilize the moment. In this paper, we explore this possibility through comprehensive investigation of the transition metal–silicon clusters, T_2Si_n ($T=\mathrm{Cr},\mathrm{Mn}, 1\leq n\leq 8$), containing two transition elements. We have chosen Cr and Mn as the isolated atoms have high spin moments of $6.0\mu_B$ and $5.0\mu_B$, respectively. Isolated Cr_2 and Mn_2 dimers are known to have antiferromagnetically aligned local spin moments. It is then interesting to examine if, along with stabilizing the atomic moments, the silicon clusters could also alter the magnetic coupling. One of the experimental methods used to probe the magnetic moment is negative-ion photodetachment spectroscopy. Here, the clusters generated in beams are crossed with a photon and the energy of the resulting electrons measured. For a cluster with spin multiplicity M, the spectrum of the emitted electrons exhibits peaks at energies corresponding to the difference between the ground state of the anion and the neutral of multiplicity $M\pm 1$. These energies thus carry an imprint of the geometry and the spin state of the cluster. In previous papers, we showed how the combination of the theory and experiment can allow experimental determination of the spin magnetic moment.[17,18] Keeping this in mind, we have carried out calculations on both neutral and anion clusters with a view that the theoretical predictions may stimulate experimental investigations.

In Sec. II, we describe the theoretical approach, while Sec. III presents the results and a discussion of results. Section IV is dedicated to final conclusions.

II. THEORETICAL APPROACH

We have performed density-functional calculations using an all electron linear combination of atomic orbitals–molecular orbital approach. The exchange-correlation contributions were included within using generalized gradient approximation (GGA) functionals proposed by Perdew *et al.*[19] In the scheme we used, the atomic wave functions are built from Gaussian bases. The ground states were determined by calculating the forces at the atomic sites and the atoms were allowed to relax along the path of steepest descent until the forces dropped below a threshold value of 0.05 eV/Å. No symmetry restrictions were imposed. Since the current calculations are carried out at 0 K, the cluster can get trapped in local minima of the potential-energy surface. Consequently, several magnetic and geometrical starting configurations were used to identify the ground state and higher-energy isomers. The actual calculations were based on the Naval Research Laboratory Molecular Orbital Library (NRLMOL) set of codes developed by Pederson and co-workers.[20–22] We used a 6*s*, 5*p*, and 3*d* basis set for the Si atoms and a 7*s*, 5*p*, and 4*d* basis set for the Mn and Cr atoms. In all cases the basis set was complemented with a diffuse orbital. For the calculation of the local magnetic moments, we have integrated the spin density of states in a sphere of 1.17 Å for the Si atoms and 1.18 Å for the Cr and Mn ones. The total magnetic moments are unambiguously defined as the difference between the numbers of spin-up and spin-down electrons occupying the molecular orbitals of the cluster.

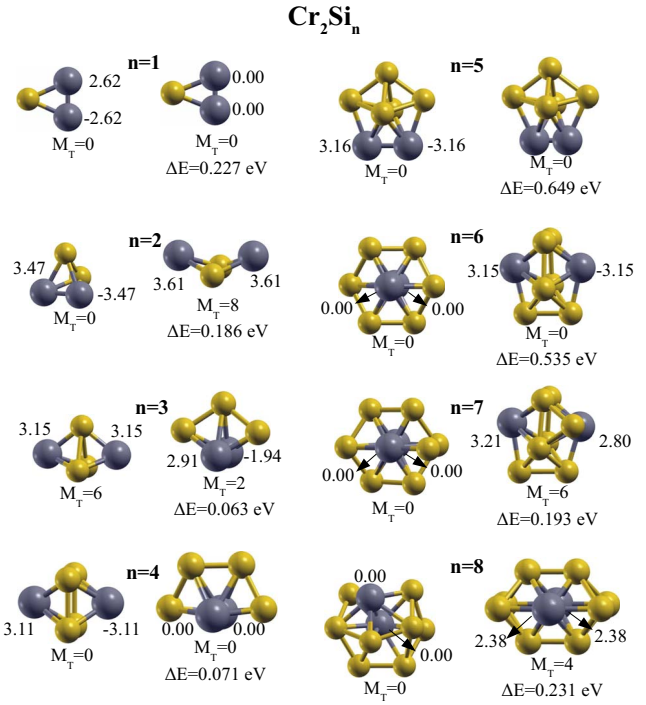

FIG. 1. (Color online) Equilibrium geometries, total spin moment M_T (in μ_B), and local spin moment at the transition-metal atoms (in μ_B, marked beside each site) of the neutral Cr_2Si_n clusters for the ground state and the lowest higher-energy isomer of the cluster. For the isomer the increment of energy with respect to the ground state, ΔE, is also listed. The gray (yellow) balls represent chromium (silicon) atoms.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the equilibrium geometries, the total spin moment M_T, and the local spin moment at the transition-metal atoms of the neutral chromium-silicon clusters for the ground state and the lowest higher-energy isomer of the cluster. We have also listed the energy ΔE of the higher-energy isomer with respect to the ground state. Note that the clusters generally exhibit compact structures. The local coordination of the silicon atoms varies from three to six. Starting from a free Cr_2 with antiferromagnetically aligned local moments of $3.12\mu_B$ each, the addition of silicon preserves the local magnetic moments until reaching the size of six or more than six Si atoms, at which the local spin moment is completely quenched. At smaller sizes, the local moment is preserved; however, the local spin moments are antiferromagnetically coupled except for Cr_2Si_3, which has a ferromagnetic ground state with a total spin magnetic mo-

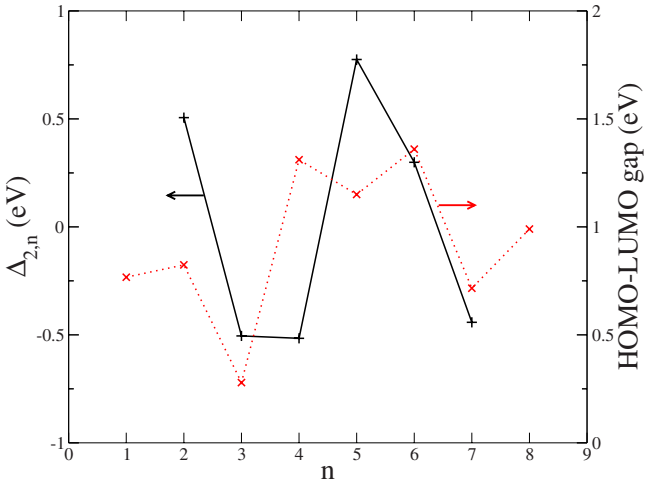

FIG. 2. (Color online) $\Delta_{2,n}$ (as defined in the text) and HOMO-LUMO gaps for neutral Cr_2Si_n clusters.

ment of $6\mu_B$. This cluster has two dissociated Cr atoms joined by a Si_3 unit and all the Si sites have tetrahedral coordination. To examine if it was also energetically favorable species, we calculated $\Delta_{2,n}$, defined as

$$\Delta_{2,n} = -[2E(Cr_2Si_n) - E(Cr_2Si_{n+1}) - E(Cr_2Si_{n-1})].$$

This expression compares the difference in energy between forming the cluster from a preceding size and growing it. Large positive values of $\Delta_{2,n}$ are indicative of the stability as they indicate a large gain in energy in forming the cluster from the preceding size and lower gain in energy in growing it to the next size. Figure 2 shows the calculated $\Delta_{2,n}$ as a function of cluster size. Note that $\Delta_{2,n}$ exhibits peaks at $n=2$ and 5. Both clusters, however, have antiferromagnetically coupled local moments. In addition to the energetic stability, we examined the chemical stability of the clusters by calculating the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Large HOMO-LUMO (H-L) gaps are indicative of chemical inertness as the cluster wants to neither donate charge nor gain charge. The calculated H-L gaps are also shown on Fig. 2. The clusters containing four to six Si atoms have the higher gap. While Cr_2Si_2 and Cr_2Si_5 have the highest energetic stability, large H-L gap, and localized spin moments at the Cr sites, none of these clusters exhibit an overall ferromagnetic character.

In a previous paper,[23] we showed that the relative stability of the ferromagnetic and antiferromagnetic states in Cr_2 and Mn_2 can be altered by charging the clusters. For example, the energy difference between the ferromagnetic and antiferromagnetic states in neutral Cr_2 is higher than in Cr_2^-. Keeping this in mind and in order to make contact with experimental studies using negative-ion photodetachment spectroscopy, we undertook a theoretical study of anionic $Cr_2Si_n^-$ clusters. Figure 3 shows the geometry of the ground state and the first higher-energy structure. Also shown are the total spin magnetic moment and the local spin moment at the various sites. Although the anions also present compact structures, the ground-state geometries are considerably different from the

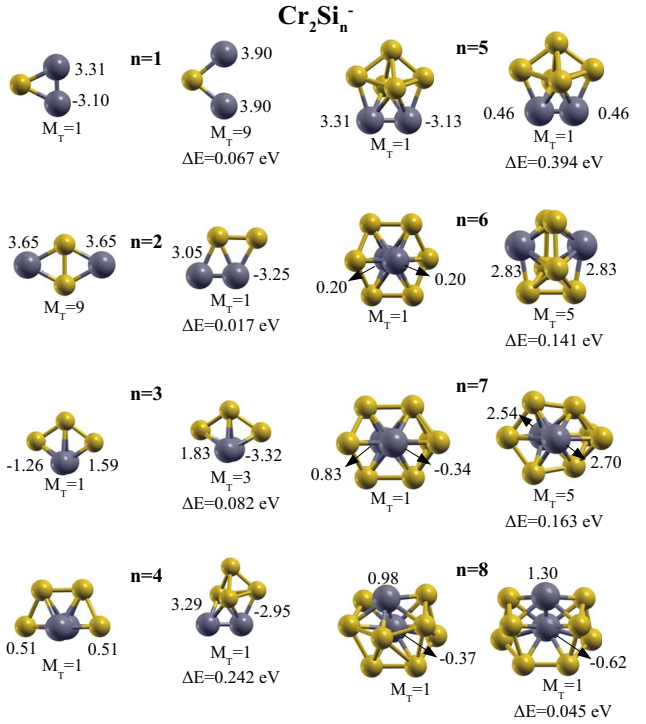

FIG. 3. (Color online) Same as in Fig. 1 but for $Cr_2Si_n^-$ anions.

corresponding neutral clusters. The most exciting is $Cr_2Si_2^-$, which has a spin magnetic moment of $9\mu_B$ in the ground state. The structure resembles a Si_2 mediating the interaction between two Cr sites. A study of $\Delta_{2,n}$, shown in Fig. 4, reveals that the cluster also exhibits a local maxima, indicative of the added stability. As to the remaining sizes, several other small clusters also carry finite local spin moments. However, they are coupled antiferromagnetically or the local spin moments are very small.

We next examined the case of Mn_2Si_n clusters. Our interest in Mn was partly sparked by the known variations in the magnetic coupling in small Mn_n clusters. While a free Mn_2 has antiferromagnetically coupled local moments, Mn_3 and

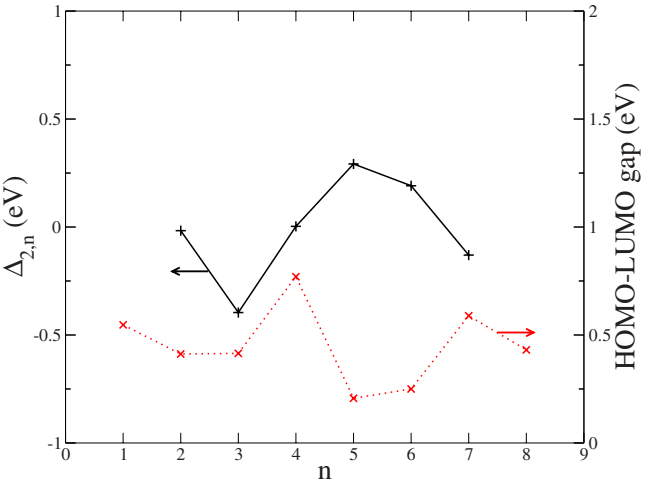

FIG. 4. (Color online) Same as in Fig. 2 but for $Cr_2Si_n^-$ anions.

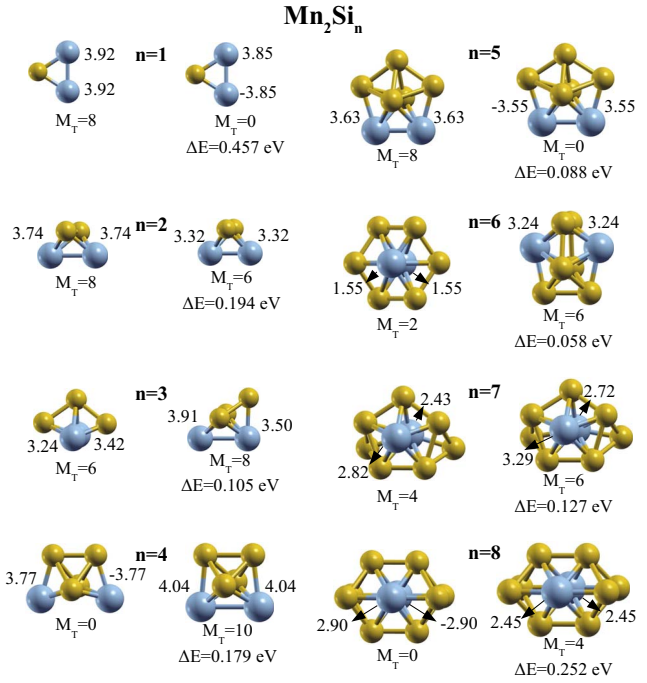

FIG. 5. (Color online) Same as in Fig. 1 but for Mn_2Si_n neutrals. Here Mn atoms are represented by the blue balls, while the yellow ones represent silicon atoms.

Mn_4 are known to be ferromagnetic.[24–26] Figure 5 shows our results on the ground-state geometries and the next higher-energy isomer of Mn_2Si_n clusters. Note that clusters containing one, two, three, five, and seven Si atoms exhibit high spin magnetic moments of 8, 8, 6, 8, and 4 μ_B respectively. While the other sizes exhibit lower or zero spin moments in the ground state, they are all characterized by higher spin isomers only slightly above the ground state. For example, while the ground state of Mn_2Si_4 is antiferromagnetic, it has a state with a large $10\mu_B$ moment only 0.179 eV above the ground state. Our interest in this cluster is motivated by its exceptional energetic and chemical stability. This is shown in Fig. 6, which presents $\Delta_{2,n}$ and the H-L gap. Note that Mn_2Si_4 has the highest H-L gap of 1.35 eV. This is only slightly smaller than the H-L gap of 1.70 eV in C_{60}. Further, our previous experience has shown that clusters with H-L gap exceeding 1.0 eV are generally resistant to etching by oxygen, a strong reactant.[27] The stability of high spin moments in neutral species is also shared by $Mn_2Si_n^-$ anion clusters. The results on the geometry and the H-L gap are shown in Figs. 7 and 8, respectively. One of the striking results is for $Mn_2Si_4^-$. It has an exceptionally large spin moment of $9.0\mu_B$ along with a reasonably high H-L gap of 0.88 eV. To further examine if this could be a suitable building block for cluster materials, we calculated its electron affinity. It was 2.185 eV, indicating that the anionic state could be stabilized by adding an alkali atom in the same way as As_7- or As_{11}-based assemblies described in our recent work.[4]

Since a neutral Mn_2Si_4 has a nonmagnetic ground state with a ferromagnetic state only 0.179 eV higher in energy, we examined the evolution of the ferromagnetic and antiferromagnetic states as multiple clusters are brought together. To this end, two Mn_2Si_4 clusters were brought together start-

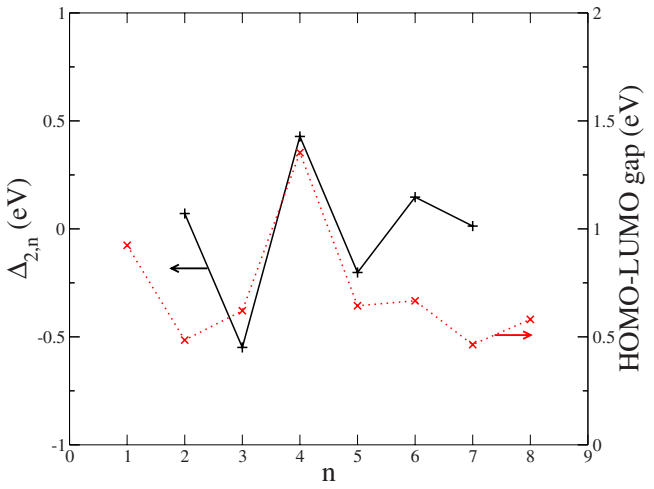

FIG. 6. (Color online) Same as in Fig. 2 but for Mn_2Si_n neutrals.

ing from four different initial configurations. In each case, the atoms were moved along the direction of forces till the forces became smaller than a threshold value. Figure 9 shows the possible local minima and the formation energy for the antiferromagnetic/nonmagnetic and ferromagnetic solutions. The formation energy E_F is defined with respect to two Mn_2Si_4 clusters, in the form

$$E_F = -[E(2XMn_2Si_4) - 2E(Mn_2Si_4)].$$

Note that the same initial configuration can lead to very different final ones depending on the magnetic state, revealing the strong interplay between geometry and magnetism and

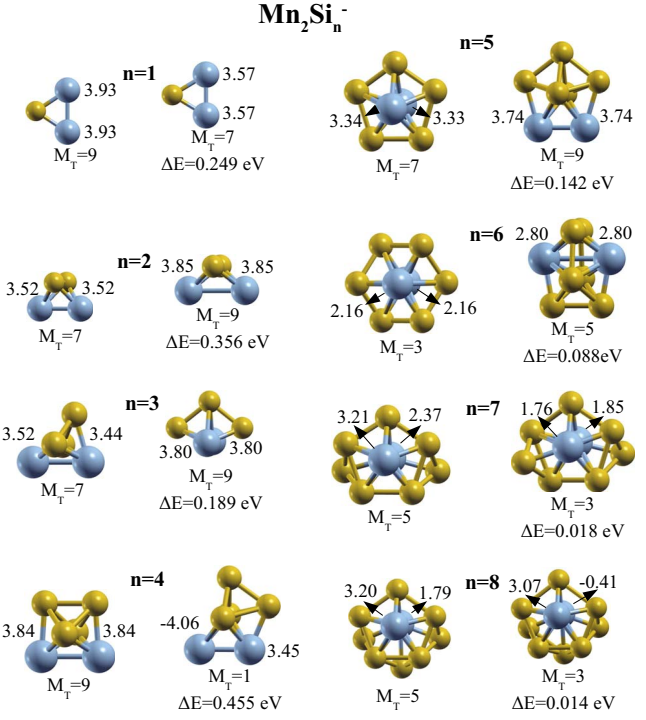

FIG. 7. (Color online) Same as in Fig. 5 but for $Mn_2Si_n^-$ anions.

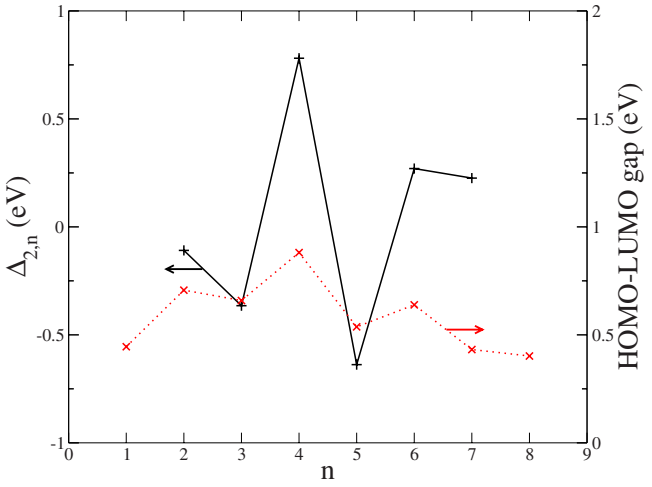

FIG. 8. (Color online) Same as in Fig. 2 but for $Mn_2Si_n^-$ anions.

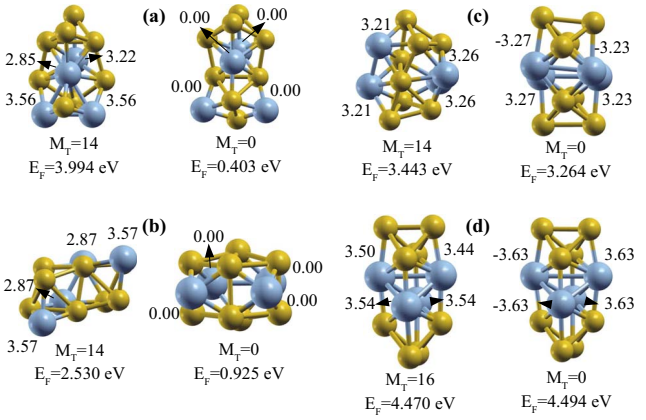

FIG. 9. (Color online) Relaxed geometries of two Mn_2Si_4 clusters brought together starting from four different initial configurations. The total spin moment M_T (in μ_B), local spin moment (in μ_B) at the transition-metal atoms, and the formation energy (as defined in the text) are also shown.

the need of performing full structural optimizations. As can be seen in Fig. 9, the most stable configuration corresponds to a mixture of an antiferromagnetic and a ferromagnetic configuration with a spin magnetic moment of $16\mu_B$. The energy difference between them is only 0.024 eV. In all other directions of initial approach, the ground state is always a ferromagnetic configuration with a total spin moment of $14\mu_B$. This indicates that it may be possible to synthesize a ferromagnetic cluster-assembled material of Mn_2Si_4 motifs through an agglomeration of clusters (with various initial directions of approach) generated in beams.

IV. CONCLUSIONS

To summarize, the present studies indicate that it may be possible to design magnetic silicon-based semiconductors by assembling size selected clusters. We have shown that several T_2Si_n clusters are marked by magnetic ground states or magnetic states slightly above the ground state. What is interesting is that in some clusters, e.g., Mn_2Si_4, where the individual motifs have antiferromagnetic ground state, a ferromagnetic state is preferred as the clusters are assembled together. The present investigations are particularly exciting in view of the recent developments, in our group and in other groups, in developing cluster assemblies via direct deposition of the size selected clusters from beams. For the case of Mn_2Si_4, our studies indicate that three of the four assemblies of two such motifs have the magnetic ground state, while the last assembly has competing ferromagnetic and antiferromagnetic solutions. The unique feature that characterizes such assemblies is the wide choice of concentration of the magnetic species. We are in the process of extending the present work to other transition-metal atoms and to larger sizes, and these will be reported in an upcoming paper.

ACKNOWLEDGMENTS

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