Magnetism of stable structures of small binary Co_nSi_m ($n + m \leq 4$) clusters

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We have studied the optimum geometries and the magnetic behavior of small binary Co_nSi_m ($n + m \leq 4$) clusters using ab-initio spin-polarized density functional calculations. Our results reveal, the optimized clusters present magnetic behavior and depends of the number of Si atoms in the cluster, in some cases the local magnetic moments at Co atoms present an enhancement respect to Co bulk magnetization, whereas the Si atoms present local magnetic moments whose modulus take significative values. All the clusters studied here present a charge transference to Si atoms from Co atoms, giving polar characteristics to the clusters.

Keywords: Hibridizations, Charge transference, Local magnetic moments

1 Introduction

The practical applications in electronics and thermo-electronics of transition metal (TM)-Si like FeSi, CoSi and MnSi have motivated experimental and theoretical investigations. In particular TM-Si alloy nanoclusters have attracted much attention as building blocks to realize miniature functionalized devices [1, 2]. Cobalt silicide nanoclusters are applied as contacts, gates and interconnects in nanoelectronics because these compounds are thermally and chemically stable materials as well as an excellent conductor [3].

When Co atoms diffuse into Si substrate, The CoSi, Co_2Si and $CoSi_2$ layers are formed on the surface of Si substrate and the Co-Si alloy nanoclusters are spontaneously produced in the diffusion process [3], the smallest size of these nanoclusters is 3nm.

In recent experiments, the Co-Si alloy clusters have been obtained from Co-Si mixture in a rapid thermal annealing process using CO_2 laser radiation [3, 4]. Carter et al. developed a new method with bottom-up approach and synthesized self aligned $CoSi_2$ nanoclusters from Co nanoparticles on Si substrates where their sizes are uniform and much smaller than those made from lithography [3]. On the other hand, Katoh et al. [5] produced unusual Co and Si clusters using a double discharge cluster source system. The synthesized nanoclusters were not the Co-Si alloy clusters, but they observed the mixture of Co and Si clusters and core-shell clusters in which the small Si clusters surround Co core clusters.

Since electrical, optical, and magnetic properties change with the system size and phase state of alloy clusters, investigating the physical properties of the Co-Si alloy clusters in an important task for microelectronics, optoelectronics and spintronics [4, 6]. To the author's knowledge, the magnetic behavior of the Co-Si alloy clusters has not been explored.

In the present work, we report possible geometrical structures and magnetic properties of small Co-Si alloy clusters, Co_nSi_m ($n + m \leq 4$), using density functional calculations.

The remainder of the paper is organized as follows: in the next section the computational method used here is briefly recalled. Results for the local magnetic moments of optimized structures of Co_nSi_m clusters are presented and discussed in section3; finally in section 4 the main conclusions are summarized.

2 Computational model

We have performed spin-polarized total energy calculations using the SIESTA code [7] within the generalized gradient approximation (GGA) for the exchange-correlation energy, as parameterized by Perdew, Burke and Ernzerhof (PBE) [8]. The norm conserving Troullier-Martins pseudopotentials [9] in the Kleinman-Bylander factorized form [10] with nonlinear core correction were used to consider core electrons; valence electrons are described by linear combinations of numerical pseudoatomic orbitals using a split valence double-zeta basis set with polarization functions [11]. A cutoff of 150 Ry. for the grid integration was used to represent the charge density.

We used the cubic unit cell of 20 Å in Γ point. The geometry is optimized until the atomic forces are less than 0.01 eV/Å. All the clusters were fully relaxed without any symmetry constrains. For stability of the Co-Si alloy clusters, we have calculated the binding energy (E_b) defined as:

$$E_b = (-E_{total} + n_{Co}E_{Co} + m_{Si}E_{Si})/(n_{Co} + m_{Si}) \quad (1)$$

Where E_{Co} and E_{Si} are the energy of Co and Si atoms respectively, E_{total} is the total energy of the Co-Si cluster with n_{Co} and m_{Si} atoms.

3 Results and discussion

We tested the method considering the Co_2 and Si_2 dimers and compare our results with those reported in the

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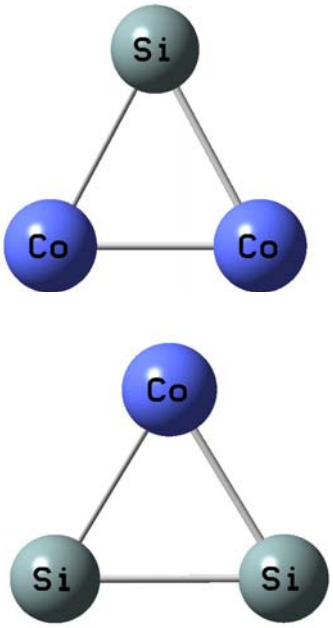

Figure 1. Illustration for the optimized structures for clusters with 3 atoms.

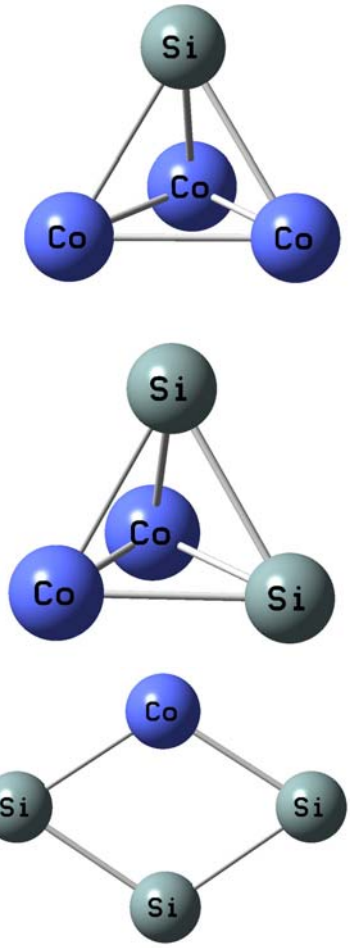

Figure 2. Lowest energy structures for CoSi clusters with 4 atoms.

scientific literature, since experimental and theoretical results on bond lengths and local magnetic moments are available for these dimers.

For Co_2, the photoelectron spectroscopy studies report a bond length of 2.0 Å; whereas the DFT calculations by Castro and co-workers obtained a bond length of 1.9 Å and $2\mu_B$ for the local magnetic moments [12]. We obtained a bond length of 1.99 Å and the same value for the Co magnetic moment. For Si_2, the experimental results [13], give a bond length of 2.207 Å and a triplet state, in this level of theory we obtained a bond length of 2.24 Å, and a total spin state of 1.

We begin the study of Co_nSi_m clusters investigating the CoSi dimer. In this level of approximation, our calculations show an antiferromagnetic-like order, the local magnetic moments (μ(Co) and μ(Si)) point in opposite direction, see Table 1. The bond length is of 2.14 Å and the binding energy of -3.52 eV; besides, our results show an electric charge transference to Si atom from Co atom, giving polar characteristics to CoSi dimer.

In Fig. 1, we show the lowest energy structures with 3 atoms; for $CoSi_2$ cluster the structure with the lowest energy is a nearly equilateral triangle, the Co-Si bond lengths are 2.23 Å and the Si-Si bond length is 2.29 Å, and the magnetic moments point in opposite direction, giving an antiferromagnetic-like order into the cluster. From Table 1, the value of μ(Co) is sligthy shorter that the Co bulk magnetization ($1.9\mu_B$) and the value of μ(Si) takes significative values. J. Wang and co-workers [14] in another DFT level of approximation obtained a Co-Si (Si-Si) bond length of 2.18 Å (2.22 Å), and an antiferromagnetic order, these results are in good agreement with our calculations.

The next structure with 3 atoms is the cluster Co_2Si, the optimized structure is an isosceles triangle with two large bond lengths and a shorter one; the Co-Si bond length is 2.26 Å and the Co-Co bond length is of 2.13 Å. In this structure the magnetic moments point in the same direction giving a ferromagnetic-like order in this cluster.

For clusters with 4 atoms, the optimized structures obtained into this level of approximation are shown in Fig. 2. We can notice that for $CoSi_3$ cluster the structure with the lowest energy is a distorted trapezia, the shortest distance between Si atoms is 2.26 Å, whereas the shortest Co-Si bond length is of 2.23 Å; and the largest Co-Si distance is 2.51 Å. In this structure are two type of Si atoms; one type has 2 near neighbors (NN) Si atoms and the another one, has 1 NN Si atom, see Fig. 2. From Table 1, we can notice that the magnetic coupling between μ_{Co} and μ_{Si} is antiferromagnetic-like and the magnetic coupling between μ_{Si} is ferromagnetic-like; the Si atom with 2 NN Si atoms has the lowest modulus in his magnetic moment, see Table 1. The three dimensional structure is a tetrahedron whose energy is 0.25 eV higher than that the bidimensional arrangement.

When the number of Co atoms increase, a geometrical transition ocurrs, the lowest energy clusters prefer three dimensional structures where the Co atoms have the same local environment; in Fig. 2, we show these optimized structures. For Co_2Si_2 the structure is a non regular tetrahedron, due to the sides present different lengths; for the Co-Co (Si-Si) bond, the distance is 2.21 Å (2.38 Å) and the Co-Si distance is 2.32 Å; in this

Table 1. The value of local magnetic moments (in units of μ_B), the binding energy (E_B) per atom, the amount of charge transference from Co atoms (Δq/atom), and the modulus of the dipolar moment P (in units of Debye).

Cluster	μ(i)	**E** (eV)	Δq/atom	**P**
CoSi	μ(Co) = 1.98 μ(Si) = -0.98	1.76	0.03	1.59
$CoSi_2$	μ(Co) = 1.50 μ(Si) = -0.25	2.68	0.66	2.45
Co_2Si	μ(Co) = 2.08 μ(Si) = 0.17	2.32	0.05	1.98
$CoSi_3$	μ(Co) = 1.26 μ_1(Si) = -0.10 μ_4(Si) = -0.05	3.04	0.10	2.93
Co_2Si_2	μ(Co) = 1.86 μ(Si) = 0.14	2.98	0.78	2.70
Co_3Si	μ(Co) = 2.31 μ(Si) = 0.12	2.66	0.05	2.51

structure the local magnetic moments point in the same direction. Giving a ferromagnetic-like order. This same magnetic behavior is found in Co_3Si, the optimized structure is a nearly regular tetrahedron where there are only two different bonds, Co-Co bond with 2.21 Å and Co-Si bond with 2.1 Å.

From Table 1, we can notice a dependence of μ(Co) in each Co atom with its number of near neighbors (NN) Si atoms (z_i); in the bidimensional structures, μ(Co) takes the lowest value ($1.5\mu_B$) when $z_i = 2$; in the three-dimensional structures the lowest value for μ(Co) ($1.26\mu_B$) is present for $z_i = 3$; these values are lowest than the Co bulk magnetization ($1.9\mu_B$). Our results show that the magnetic order into the CoSi clusters present a dependence with the number with the number of Si atoms (m_{Si}); when $m_{Si} > n_{Co}$ the magnetic order is antiferromagnetic-like into the cluster.

In our optimized structures two of them present geometries distorted, *i.e* far from ideal geometries, and its well known that in these distorted structures the last occupied orbital is degenerated, meaning a great charge transference between atoms (to Si atoms from Co atoms in this case), this fact is present in our results for $CoSi_2$ and Co_2Si_2. In general all the clusters studied have dipolar moments due to the charge transference and its value present a dependence with the number of Si atoms too.

4 Conclusions

The developed techniques, as examplified by SIESTA package software have allowed the study of the local magnetic moments of optimized structures of small binary Co_nSi_m clusters. Our conclusions can be summarized as follows.

a) We have studied the magnetic properties of small Co_nSi_m ($n+m\leq4$) clusters taking account electron correlations by means of the PBE method within the gradient generalized approximation (GGA). With this model we obtained the bond length for Co_2 and Si_2, and the average magnetic moments, both results are in good agreement with experimental results and another theoretical calculations.
b) The magnetic order into the clusters depends on the number of Si atoms (m_{Si}) in the cluster, when this number is greater than the Co atoms (n_{Co}), the magnetic order is antiferromagnetic-like, whereas for $n_{Co} \geq m_{Si}$, the magnetic order is ferromagnetic-like.
c) The value of μ(Co)$\mu\mu$ is greater than the Co bulk magnetization when $n_{Co} \geq m_{Si}$, whereas magnetic moments at Si atoms take significative values and are ferromagnetically coupled..
d) In all the clusters, the charge transference is to Si atoms from Co atoms, therefore all the clusters present dipolar moment.

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References

[1]H. Hiura, T. Miyazaki, and T. Kanayama, Phys. Rev. Lett. **86**, 1733 (2001).
[2]M. Ohara, K. Koyasu, A. Nakajima, and K. Kaya, Chem. Phys. Lett. **371**, 490 (2003).
[3]J.D. Carter, G. Cheng, and T. Guo, J. Phys. Chem. B **108**, 6901 (2004).
[4]H. Yasuda, and H. Mori. Phys. Rev. Lett. **69**, 3747 (1992).
[5]R. Katoh, T. Hitara, D.L. Peng, and K. Sumiyama, Appl. Phys. Lett. **82**, 2688 (2003).
[6]M. Knite, A. Modvid, and A. Grigonis, Vacuum **55**, 251 (1998).
[7]P. Ordejon, E. Artacho, and J.M. Soler, Phys. Rev. B **53**, 10441 (1996).
[8]J.P. Perdew, K. Burke, and M. Ernzehorf, Phys. Rev. Lett. **77**, 3865 (1996).

[9]N. Troullier, and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).
[10] L. Kleinman, and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[11] O.F. Sankey, and D.J. Niklewski, Phys. Rev. B **40**, 3979 (1989).
[12] Miguel Castro, Christine Jamorski, and Dennis R. Salahub, Chem. Phys. Lett. **271**, 133 (1997).
[13] T.N. Kitsopoulos, C.J. Chik, Y. Zhao, and D.M. Neumark, J. Chem. Phys. **95**, 1441 (1991).
[14] Jianguang Wang, Jijun Zhao, Li Ma, Baolin Wang, and Guanghou Wang, Phys. Lett. A **367**, 335 (2007).