First-principles study of the possibility of condensed phases of endohedral silicon cage clusters

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Recently, a new set of clusters in which twelve Si atoms encapsulate one transition metal atom were found to be especially stable. Making use of MSi_{12} clusters ($M = Nb,W$) we carry out a first-principles study of the possibility of synthesizing a crystalline phase using such clusters as elementary building blocks. To this end we carry out an *ab initio* study of the interaction energy between two MSi_{12} clusters as a function of their separation. We also perform an *ab initio* Langevin quantum molecular dynamics simulation of solid MSi_{12} at constant temperature and pressure. We find that the interaction energy between Si atoms in neighboring clusters is comparable to that found in bulk Si. In the solid phase, the cage structure of MSi_{12} disappears during the simulation. These results indicate that the clusters should not conserve their integrity in condensed phases.

Recently, new endohedral Si cage clusters have been successfully synthesized in the gas phase,[1] using transition metal atoms with a partially filled *d* shell as aggregation centers for Si atoms. Indeed, when atoms of a transition metal *M* such as $M = Cr,Nb,Ta,W,Re$, or Ir are allowed to interact with SiH_4 clusters under ionizing conditions, it has been found that cluster ions with stoichiometry $MSi_nH_x^+$ are formed. More extraordinary, it was found that, for certain values of *n*, dehydrogenation of clusters would take place, resulting in clusters of type MSi_n^+ which were stable enough to raise the hope of designing new condensed phases using their neutral counterparts as elementary building blocks.

In this work we test the possibility of generating condensed phases based on these clusters by carrying out a series of first-principles simulations. To this end we shall concentrate on the clusters $NbSi_{12}$ and WSi_{12}, which we shall take as prototypical examples of this class of endohedral silicon cage clusters. These clusters belong to the restricted family[2] of clusters for which the equilibrium geometry is believed to be a highly symmetric D_{6h} structure—depicted in the inset of Fig. 1—in which two regular hexagons built out of Si atoms sandwich one transition metal atom placed in the center of mass of the cluster. Furthermore, the same shape is found to persist as the equilibrium structure of the cations $NbSi_{12}^+$ and WSi_{12}^+.[2] This is an interesting feature since one should note that, in general, spin plays a sizable role in the physics and chemistry of transition metal atoms. However, for the clusters considered here, not only is there only one transition metal atom per cluster—located in the center of the cluster—but also the total spin state is different in both cases due to the fact that niobium has an odd number (5) of valence electrons as opposed to tungsten (6). Nevertheless, similar conclusions will be drawn for both types of clusters.

With these two clusters as prototypes for such elementary building blocks, we carry out two types of first-principles simulations. To begin with, we investigate the energetics of the $MSi_{12}-MSi_{12}$ ($M = Nb,W$) interaction. We conclude that Si atoms from different clusters interact as strongly in this case as each Si atom interacts with each other in bulk silicon, which indicates that strong chemical reactivity will take place as clusters get close enough. We proceed by performing first-principles Langevin quantum molecular dynamics (LQMD) simulations at constant temperature and pressure, starting from an optimized crystal made out of MSi_{12} clusters. As a result of these simulations, it will be concluded that indeed chemical reactions do take place between Si atoms of neighboring clusters, inducing recombinations between the Si atoms, and the breakdown of the local D_{6h} symmetry of the clusters. These results provide strong evidence that a crystalline phase of MSi_{12} (with *M* a transition metal), with the clusters as building blocks is unlikely to exist. All computer simulations will be carried out in the local density approximation (LDA) to density functional theory (DFT).

Starting from the stable endohedral cluster MSi_{12} in the structure depicted in the inset of Fig. 1, we first studied the $NbSi_{12}-NbSi_{12}$ intercluster interaction, by considering the cluster-pair interaction energy as a function of the distance between the Nb atoms, which define the center of mass of each cluster. The calculations were subsequently repeated for the $WSi_{12}-WSi_{12}$ dimer. Both calculations were carried out making use of the ADF package,[3] which implements the self-consistent solution of the Kohn-Sham equations in the LDA,[4,5] via projection in a Slater-type orbital basis set.[6] Three different pathways were considered, along which the relative orientation between the two MSi_{12} clusters was kept fixed. Each of these pathways was chosen by assigning defi-
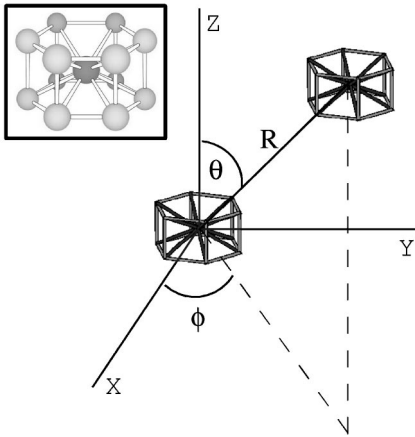
FIG. 1. Different pathways for the MSi_{12} ($M=$Nb,W) dimer. The equilibrium shape of each cluster is shown in the inset, exhibiting a D_{6h} symmetry, in which the transition metal atom M is located in the center of the cluster, sandwiched between two regular hexagons of Si atoms. These cluster structures are depicted as "skeletons" in the main panel. Starting from two replicas of each MSi_{12} cluster in its equilibrium configuration, and with the same relative orientation with respect to a fixed frame, the three pathways considered in this work can be uniquely defined by indicating the fixed values chosen for the polar angles θ and ϕ. As such, the first path involves a displacement of one of the MSi_{12} clusters along the Z axis ($[R,0,0]$) in such a way that each cluster maintains the hexagons parallel. Another pathway corresponds to displacement along the X axis ($[R,90,0]$), in such a way that the two clusters keep a lateral face parallel. Finally, the path corresponding to $[R,45,0]$ involves displacements in which the closest atoms are those belonging to one side of the hexagon in each cluster, which now remain parallel as R is varied.
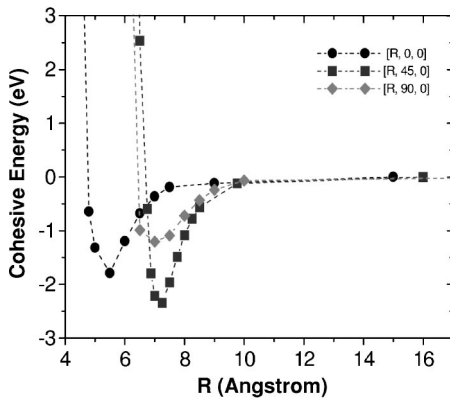

FIG. 2. Energetics of the $NbSi_{12}$ dimer. The plot shows the result for the cohesive energy of the dimer as the separation between the two clusters is changed. The three curves correspond to the three pathways decribed in the main text (see also Fig. 1). The path $[R,0,0]$ is represented with solid squares, the path $[R,90,0]$ with solid diamonds, whereas the path $[R,45,0]$ is depicted with solid circles. The dashed lines are drawn just to guide the eye, and correspond to straight line segments joining the data points. Similar results were obtained for the corresponding curves associated with the WSi_{12} dimer interaction energy along equivalent pathways.
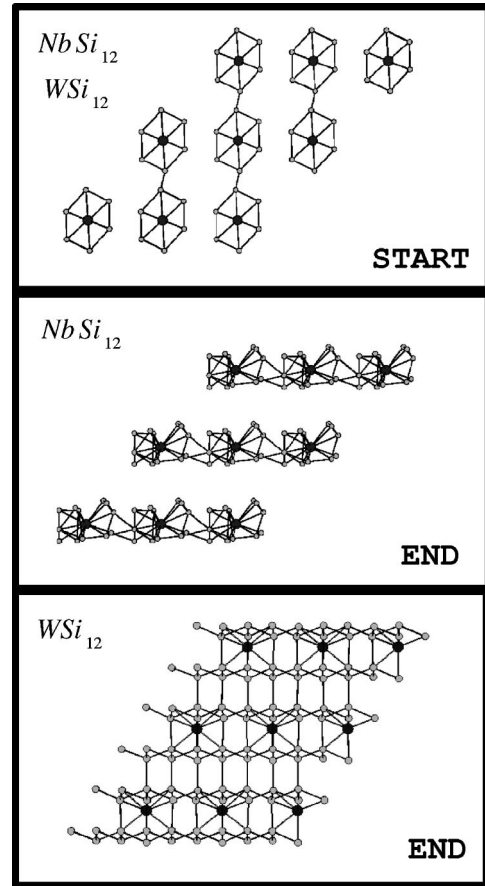

FIG. 3. Results of Langevin dynamics: The upper panel illustrates the starting configuration used in the Langevin quantum molecular dynamics simulation. This solid of MSi_{12} clusters ($M=$Nb,W), with monoclinic symmetry, was obtained via a local minimization of the atomic positions and the cell size, retaining the crystal symmetry. Each of the two systems was then allowed to evolve in time, for a time interval of 3 psec, without any constraints imposed on the atomic positions and cell shape and size (see main text for details). At the end of the simulations, the lowest-energy configuration for each bulk system was relaxed via a conjugate gradient technique. The end configurations are illustrated in the lower panels as labeled: $NbSi_{12}$ in the middle panel and WSi_{12} in the lowest panel. As one can judge from the figures, sizeable rearrangements of atomic positions take place, through which Si atoms in neighboring cells react chemically, making the system evolve towards an overall amorphous mixed phase.

nite values to the polar angles θ and ϕ illustrated in Fig. 1. The trajectories chosen correspond to the following pairs of values for $[\theta,\phi]$, namely, $[R,0,0]$, $[R,45,0]$, and $[R,90,0]$. The results for the cohesive energy as a function of cluster separation along each of these three pathways are shown in Fig. 2 for the $NbSi_{12}$-$NbSi_{12}$ case, with the corresponding curves labeled accordingly. To be noted that no relaxation of the internal cluster geometry was allowed as the intercluster distance was changed, which means that the magnitude of the actual interaction energies will be somewhat higher. Nonetheless, Fig. 2 puts in evidence the strong interaction energy between the two clusters, with a magnitude comparable with the bond energy per Si atom in bulk silicon

[≈ 2.3 eV (Ref. 7)]. These results exclude the possibility of a molecular cluster crystal. They do not exclude, however, the possibility of using the double hexagon template as building blocks of a crystalline solid phase.

In order to check if the double hexagon template survives in the solid phase, we decided to perform, within LDA to DFT, a LQMD simulation of the solids $NbSi_{12}$ and WSi_{12}. To this end, we used a computer program implementing the solution of the Kohn-Sham equations in a plane-waves basis set,[8] and using pseudopotentials.[9] We started to optimize the solid structures of $NbSi_{12}$ and WSi_{12}, by performing a local minimization of the total energy with respect to atomic positions within a monoclinic crystal structure in which each cell contains one MSi_{12} ($M=Nb,W$) cluster and interacts with its nearest neighbors at distances in accord with the minima obtained as a result of the previous intercluster calculation. Throughout this simulation, the monoclinic crystal symmetry is conserved, in spite of the changes of the internal atomic coordinates of each cluster as the forces used in the local optimization have the symmetry of the crystal. As a result of this *local* relaxation, the overall structure of each MSi_{12} is preserved, but now the minimum energy configuration corresponds to the distorted double hexagons depicted in Fig. 3(a) and labeled "START." To be noted that, in fact, to this "START" geometry correspond two distinct sets of bond lengths and lattice parameters, each associated with bulk $NbSi_{12}$ and WSi_{12}. These were indeed our starting points for the LQMD simulation.[10–12] Starting from these structures, we gave each atom an average kinetic energy corresponding to a temperature of 50 K, and placed the whole system in contact with a heat reservoir at a constant temperature of 1000 K. This temperature, well below the melting temperature of bulk Si, is high enough to allow the atoms in each cluster to overcome local energy barriers as they move in phase space. It is important to let the system contact with such a high temperature reservoir, in view of the very short time duration of the computer simulations, as compared to the time scales involved in experimental situations. As is well known, under such circumstances, the simulation time is too short to allow the solid to recrystallize, but still we can gain insight about the interactions in the system, and we can check the stability of local energy minima, even if we cannot reach the global minimum of the total energy. We let the system evolve in phase space along a trajectory defined by the constant temperature Langevin molecular dynamics equations, which was followed during a time interval of 3 ps. It is worth pointing out that throughout the LQMD simulation, no symmetry constraints were imposed except for the overall translational invariance. This means that both the atomic positions *and* the cell geometry are allowed to change. At the end of the simulations, we took the most stable configurations attained during the 3 ps and used them as starting points for a conjugate gradient relaxation. The resulting structures of the solid are illustrated in Fig. 3(b) for $NbSi_{12}$ and Fig. 3(c) for WSi_{12}, both labeled "END." As one can clearly see from Figs. 3(b) and (c), sizable rearrangements take place, via which Si atoms from neighboring cells get closer to each other, with associated interactions which are strong enough to break the original double hexagon layer of the MSi_{12} clusters, fully corroborating the considerations set forward before. In the configuration illustrated in Fig. 3(a), the crystals have an associated cohesive energy per atom of 3.92 (2.56) eV for $NbSi_{12}$ (WSi_{12}), which increases up to 4.07 (2.67) eV, respectively, at the end of the simulation. These values correspond to the LDA values associated with the cohesive energy per atom of Nb and W interstitial impurities in bulk Si, thereby providing strong evidence that the systems will evolve towards amorphous Nb-Si and W-Si phases, and that the thermodynamic equilibrium may correspond to Nb or W impurities in a crystal of Si (plus some segregated Nb or W).

In summary, we carried out a first-principles investigation of the possibility of synthesizing a condensed, crystalline phase in which cage clusters of Si and a transition metal would constitute the elementary building blocks. Taking as our case study the specially symmetric and stable $NbSi_{12}$ and WSi_{12} clusters it was found that, when assembled together, the chemical interaction between Si atoms of neighboring clusters leads to strong rearrangements within each cluster, driving the solid towards an amorphous mixed phase. These results provide strong evidence for the unlikelihood of occurrence of crystalline solids made out of clusters of the type considered in this work.

[1] H. Hiura, T. Miyazaki, and T. Kanayama, Phys. Rev. Lett. **86**, 1733 (2001).

[2] G. K. Gueorguiev and J. M. Pacheco (unpublished).

[3] G. te Velde and E.J. Baerends, J. Comput. Phys. **99**, 84 (1992).

[4] We used the exchange-correlation functional of Ref. 5.

[5] S.H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[6] We have checked that the results did not change by varying the size of the basis set.

[7] C. Kittel, *Introduction to Solid State Physics*, 7th ed. (John Wiley and Sons, New York, 1996).

[8] This program is free for research purposes and can be downloaded at URL http://bohr.inesc.pt/jlm.

[9] N. Troullier, José Luís Martins, Phys. Rev. B **43**, 1993 (1991).

[10] G. K. Gueorguiev, J. M. Pacheco, and José Luís Martins (unpublished).

[11] N. Binggeli, J.L. Martins, and J.R. Chelikowsky, Phys. Rev. Lett. **68**, 2956 (1992).

[12] I. Souza and J.L. Martins, Phys. Rev. B **55**, 8733 (1997).