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Unique magnetic coupling between Mn doped stannaspherenes Mn@Sn$_{12}$

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We report the density functional theory based study of the interaction between two Mn doped stannaspherenes (Mn@Sn$_{12}$). The calculated results show that Mn@Sn$_{12}$ cluster is not only highly stable and carry a high magnetic moment, but these clusters retain their structural identity and form a stable dimer cluster. Most importantly, the magnetic coupling between the Mn@Sn$_{12}$ clusters depends on the relative orientation of the cages. In addition, *ab initio* molecular dynamics calculations show that the dimer cluster is stable at room temperature. These results are expected to trigger further investigations on highly stable bimetallic magnetic cage complexes. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2896608]

The discovery of carbon fullerenes[1,2] has stimulated considerable interest in the search of cage clusters involving not only group IV elements but also metallic systems. In particular, considerable amount of earlier work[3–8] on Si and Ge failed to find neutral clusters of these elements to assume cage structures, although with suitable endohedral doping, clusters of these elements can be stabilized in cage form. Similarly, no neutral clusters of homonuclear metal atoms have been found to assume cage structures, although it was demonstrated[9] a long time ago that metal clusters can be stabilized in icosahedric cage structures by suitable endohedral doping. Recent discoveries[10,11] of Au$_n^-$ ($n=16-18$) and Sn$_{12}^{2-}$ having cage structures have rekindled interest in metal fullerenes. Cui *et al.* have reported[11] the discovery of stannasphere, a highly stable Sn$_{12}^{2-}$ cage cluster. This doubly charged Sn$_{12}$ cage cluster, with icosahedral (I_h) symmetry was found to be stable even without the aid of any central dopant atom. Part of the interest in stannaspherenes arises because these cage clusters have diameters large enough (6.1 Å) to accommodate a transition metal atom.[11] In a recent experimental and theoretical studies,[12] M@Sn$_{12}$ I_h cages (M=Cu, Ni, Co, Fe, Cr, V, Ti, Au, Pt, and Nb) were reported. Since transition metal atoms carry sizeable magnetic moments, it is possible to synthesize new magnetic materials with the doped metal fullerenes as building blocks. It should be emphasized that for the synthesis of new magnetic materials, it is not only necessary for these building blocks to carry a sizeable magnetic moment but also important to understand how they are coupled. No study has been carried out in this regard. In this communication, we show that Mn encapsulated Sn$_{12}$ cluster is not only stable and carry a large magnetic moment but also their structure remains unaltered when interacted with each other even at room temperature. Equally important, the magnetic coupling between these clusters depends upon their relative orientation.

There are a number of reasons why Mn@Sn$_{12}$ cluster is a candidate of choice: (1) among the 3d-transition metals, Mn predominantly occurs in divalent state due to its half-filled 3d and filled 4s shell and a significant energy gap separating the two orbitals. Thus, Mn doped Sn$_{12}$ cluster can be viewed as Mn^{2+}:Sn$_{12}^{2-}$ cluster. Since, Sn$_{12}^{2-}$ is a highly stable cluster,[11] it is expected that the Mn doped Sn$_{12}$ cluster

would also be very stable. (2) The special electronic structure of the Mn atom allows it to carry a magnetic moment of 5μ_B which remains intact when Mn atoms form clusters or compounds. (3) The magnetic coupling between the Mn atoms is very sensitive to their interatomic distance and environment. These raise some important questions: do these endohedral stannasphere cages retain their structural integrity when they are brought near each other? What happens to the magnetic properties of such cages when they interact with each other? In order to answer these questions we have carried out extensive theoretical calculations.

All theoretical calculations were carried out using density functional theory with the Perdew–Wang 91[13] (PW91) functional for the generalized gradient approximation for exchange and correlation potential. The geometries were optimized using the DMOL3 software.[14] Semilocal pseudopotentials[15] for the core electrons, along with double numeric basis sets with polarization functions were used to describe Mn and Sn atoms. For the self-consistent field calculations, a convergence criterion for energy was set to 10^{-6} hartree, while density tolerance was set to 10^{-6} e/bohr^3. In the geometry optimization procedure, the structural parameters of various isomers were fully optimized for all possible spin states without any symmetry restrictions. Accuracy of our calculated results was confirmed by carrying out independent calculations on the selected lower energy isomers using Vienna *ab initio* simulation package (VASP).[16,17] The spin-polarized calculations were performed within the framework of density functional theory with a plane wave basis set and projector-augmented-wave (PAW) potential,[18,19] as implemented VASP.[16,17] The PW91 generalized gradient approximation for exchange-correlation functional was used. The cut-off energy is 270 eV for the plane wave basis set. A $26 \times 18 \times 18$ Å^3 monoclinic supercell was used. The solution to the Kohn–Sham equation was calculated by an efficient matrix diagonalization technique based on a sequential band-by-band residual minimization method and a Pulay-type charge density mixing.[17] Due to the large supercell, the Brillouin zone integration was carried out only at the Γ point. In order to check the thermal stability of the ground state cluster, we have carried out molecular dynamics simulations. The constant temperature molecular dynamics simulations were performed at 300 K and lasted for 1 ps. The canonical ensemble was simulated by means of a Nosé thermostat[20–22] as implemented in the VASP software package.

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I_h 2s+1 = 6 D_{5h} 2s+1 = 6 O_h 2s+1 = 6 D_{6h} 2s+1 = 2
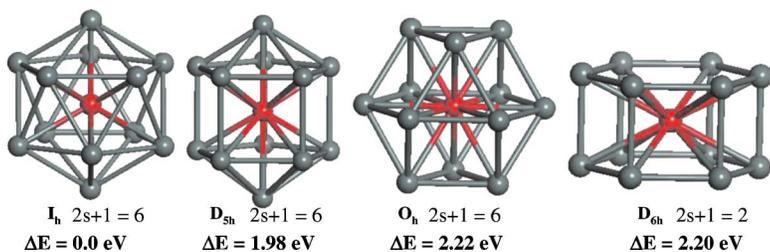ΔE = 0.0 eV   ΔE = 1.98 eV   ΔE = 2.22 eV   ΔE = 2.20 eV

FIG. 1. (Color online) The ground state and higher energy isomers of Mn@Sn$_{12}$ cluster. The energies are relative to the ground state I_h cage. The symmetry and spin multiplicities are also shown.

Our theoretical results show that the icosahedral Sn$_{12}$ cage, with the Mn atom trapped inside the center of the cage is the most preferred structure for Mn-doped Sn$_{12}$ cluster (Fig. 1). Even though, the Mn@Sn$_{12}$ cluster is an open-shell system, the Jahn–Teller effects are found to be minimal leading to a very small structural distortion of the icosahedral cage. We have examined several other isomers (Fig. 1) and all of them are found to be higher in energy than the endohedral-I_h cage structure. The Mn–Sn bond length in the Mn@Sn$_{12}$ cage is calculated to be 3.05 Å. Our bond lengths are in good agreement with the previously reported theoretical study[7] on Mn@Sn$_{12}$ cluster. In order to understand the charge state of Mn inside the cage cluster, one usually analyzes the Mulliken charge distributions. However, it is well known that Mulliken charges can only provide a qualitative picture of the charge distribution, but cannot give accurate quantitative information. To understand the charge state of Mn and the Sn$_{12}$ cage cluster, we take a different approach by comparing the equilibrium geometries and Sn–Sn bond lengths of Mn doped stannaspherene with that of Sn$_{12}^{2-}$. In Mn@Sn$_{12}$ I_h cage, the Sn–Sn bond length is 3.20 Å which is nearly identical with the previously reported[11] Sn–Sn bond length (3.19 Å) of the empty Sn$_{12}^{2-}$ I_h-cage cluster. The absence of significant structural distortions in the I_h cage due to Mn encapsulation along with the identical Sn–Sn bond lengths in Mn@Sn$_{12}$ and Sn$_{12}^{2-}$ cage indicate that in the case of Mn@Sn$_{12}$ cluster, the tin cage behaves like Sn$_{12}^{2-}$, and consequently Mn would remain in a 2+ valence state. These observations are consistent with the previously reported study[12] on the metal doped stannaspherenes, where M@Sn$_{12}$ cage clusters were shown to exist as M^{2+} and Sn$_{12}^{2-}$. An unusually large highest orbital molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of 1.12 eV is observed in the Mn@Sn$_{12}$ cluster. This further highlights the stability of the neutral cage structure. The Mn@Sn$_{12}$ I_h cage exhibits a high spin multiplicity of sextet (2S+1=6) yielding a magnetic moment of 5μ_B. Of this, the spin-magnetic moment on the Mn atom is found to be 4.15μ_B and originates from the 3d states of Mn. The large HOMO-LUMO gap and the high magnetic state of Mn@Sn$_{12}$ observed in the current study are consistent with the previously reported theoretical work.[7]

We then studied the interaction between two Mn@Sn$_{12}$ cage clusters to determine if the endohedral stannaspherenes can retain their cage structures. We have also studied the interaction effects on the magnetic properties of the dimer cage clusters. We examined several structural configurations in which two Mn@Sn$_{12}$ cage clusters were allowed to interact in various orientations with respect to each other (Fig. S1).[23] We found that the two Mn@Sn$_{12}$ I_h-cage clusters do maintain their structural integrity, and are bonded at the triangular faces of the icosahedra, with the triangles facing upside down with respect to each other [Fig. 2(a)]. The two

Mn@Sn$_{12}$ I_h cages remained nearly intact with only a small distortion in the icosahedron skeletons, resulting in C_{2h} symmetry for the ground state configuration of the dimer. The most interesting feature of the Mn@Sn$_{12}$ dimer is its spin state. In the ground state, the Mn atoms are antiferromagnetically (AFM) coupled carrying a spin magnetic moment of +4.04μ_B and −4.04μ_B, respectively. However, a high spin state (2S+1=11) in which the Mn atoms are ferromagnetically (FM) coupled is only 0.11 eV higher in energy. In this FM state, the total magnetic moment is 10μ_B with the spin magnetic moment on each Mn atom being 4.14μ_B. The Sn–Sn bond length between the two cages is found to be 3.26 Å for AFM state, while it is 3.40 Å for the high spin FM state. Interestingly, the large HOMO-LUMO gap
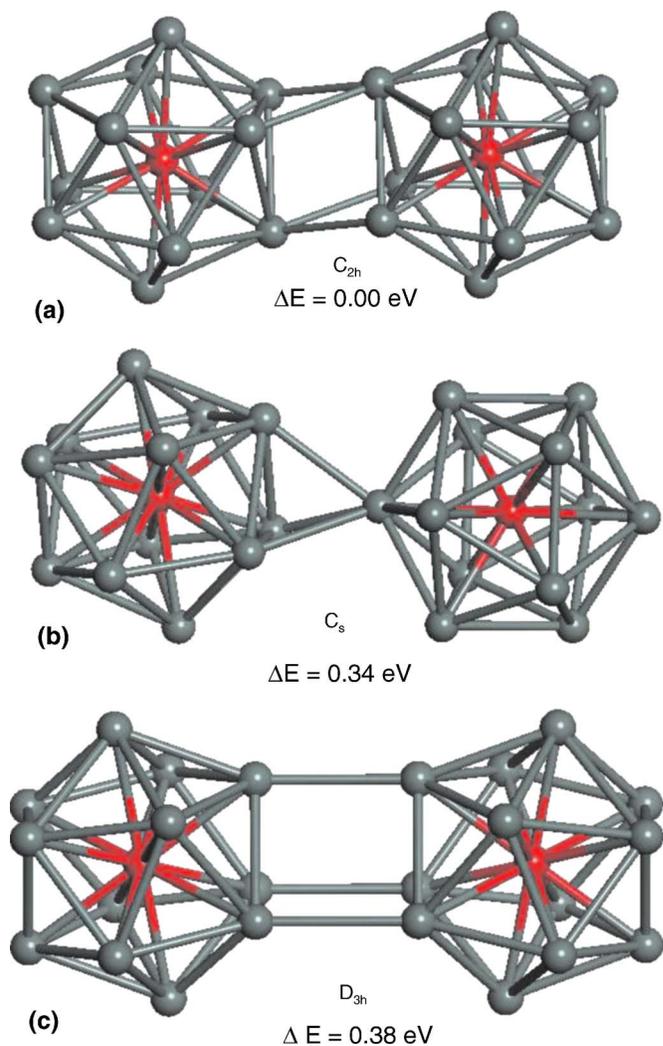

(a) C_{2h} ΔE = 0.00 eV

(b) C_s ΔE = 0.34 eV

(c) D_{3h} Δ E = 0.38 eV

FIG. 2. (Color online) The optimized structures of Mn@Sn$_{12}$ dimer. (a) represents the lowest energy structure; (b) and (c) represent the higher energy isomers. The relative energy ΔE of the isomers is also shown.

(1.12 eV) seen in $Mn@Sn_{12}$ has decreased only slightly due to the dimerization, with the HOMO-LUMO gap of the dimer being 0.88 eV. The binding energy of the ground state dimer is 0.73 eV, which is *significantly larger* than that between two C_{60} fullerenes. There exists a higher energy configuration ($\Delta E = 0.34$ eV) with C_s symmetry [Fig. 2(b)], in which the C_5 axis of one of the $Mn@Sn_{12}$ cage is rotated by 90 with respect to the other cage. In this C_s configuration, the Mn atoms prefer ferromagnetic coupling ($4.15\mu_B$, $4.11\mu_B$), the total spin of the dimer being $10\mu_B$. However, an AFM state ($4.13\mu_B$, $-4.09\mu_B$) is found to be energetically degenerate ($\Delta\varepsilon = 0.01$ eV) with the FM state.

Another structural configuration [Fig. 2(c)], where the two Mn doped stannasphterene cages are joined at the triangular faces is 0.38 eV higher in energy. The spin state for this D_{3h} symmetric configuration is found to be AFM (singlet state) with $+4.02\mu_B$ and $-4.02\mu_B$ spin moment on the Mn atoms. It is to be noted there that this higher energy configuration results from a 90° rotation along the C_3 axis of one of the cages in ground state configuration. Thus, the stability and magnetic nature of the $Mn@Sn_{12}$ dimer are strongly dependent on orientation of the cages with respect to each other. The variations in the stability of $Mn@Sn_{12}$ dimer cluster with the rotation of one $Mn@Sn_{12}$ cage with respect to the other cage is reminiscent of the previously reported[24] orientation dependent interaction between two C_{60} molecules.

We have further tested the thermal stability of the ground state $Mn@Sn_{12}$ dimer by carrying out constant temperature molecular dynamics simulations for 1 ps at 300 K. After 1 ps, it was found that the dimer cage cluster did not collapse and the monomer remains the cage structure skeleton with a minor distortion, indicating the stability of the magnetic dimer cages at room temperature.

Very recently, Sun *et al.*[25] synthesized $Pd_2@Sn_{18}^{4-}$ cluster by fusing two endohedral $Pd@Sn_{12}^{2-}$ cages along their C_3 axis and by removing Sn_3 triangular face from each cage unit. In our study, we did not see the fusion of the $Mn@Sn_{12}$ I_h cages to occur. Interestingly, when two $Mn@Sn_{12}$ *octahedral* (O_h) cages were allowed to interact, they coalesced to form $Mn_2@Sn_{24}$ cage structure. However, this fused cage cluster was found to be 2.82 eV higher in energy than the ground state C_{2h} configuration. It is to be noted here that the $Mn@Sn_{12}$ O_h cage (Fig. 1) itself is a higher energy isomer ($\Delta E = 2.22$ eV) of $Mn@Sn_{12}$.

Following the completion of this work and during the review process of this manuscript, we learnt of another theoretical study[26] by Matxain *et al.* focusing on the magnetic nature of $Mn@Sn_{12}$ dimer cages. Our observations regarding the charge state of Mn in $Mn@Sn_{12}$ are in agreement with this recently reported study. The authors reported three stable $[Mn@Sn_{12}]_2$ isomers, which are termed as F-$[Mn@Sn_{12}]_2$, V-$[Mn@Sn_{12}]_2$, and E-$[Mn@Sn_{12}]_2$, with D_{3h}, D_{2h}, and D_{5d} symmetry, respectively. However, our calculations reveal that these three isomers are 0.38 eV, 0.46 eV, and 0.64 eV

higher in energy, in the same order, than the C_{2h} symmetric structure reported here (See Fig. S1).[23]

In summary, we have shown that $Mn@Sn_{12}$ not only forms a stable *magnetic* I_h-cage cluster but also maintains its structural integrity with minimal structural modification during the interaction with another $Mn@Sn_{12}$ cage even at finite temperature. The magnetic state of the $Mn@Sn_{12}$ dimer depends strongly on the mutual orientation of the two cages indicating that one can change the magnetic coupling between two stannaspherenes by simply rotating one with respect to the other. The high magnetic moment of $Mn@Sn_{12}$, its robust cage structure, stability at room temperature, and its ability to retain its structure when assembled may give raise to some exciting possibilities of designing magnetic nanostructures with the $Mn@Sn_{12}$ cages as building blocks.

[1]H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).
[2]W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) **347**, 354 (1990).
[3]H. Hiura, T. Miyazaki, and T. Kanayama, Phys. Rev. Lett. **86**, 1733 (2001).
[4]S. N. Khanna, B. K. Rao, and P. Jena, Phys. Rev. Lett. **89**, 016803 (2002).
[5]V. Kumar and Y. Kawazoe, Phys. Rev. Lett. **88**, 235504 (2002).
[6]V. Kumar and Y. Kawazoe, Appl. Phys. Lett. **80**, 859 (2002).
[7]V. Kumar and Y. Kawazoe, Appl. Phys. Lett. **83**, 2677 (2003), and references therein.
[8]M. Ohara, K. Koyasu, A. Nakajima, and K. Kaya, Chem. Phys. Lett. **317**, 490 (2003).
[9]S. N. Khanna and P. Jena, Phys. Rev. Lett. **69**, 1664 (1992).
[10]S. Bulusu, X. Li, L. S. Wang, and X. C. Zeng, Proc. Natl. Acad. Sci. U.S.A. **103**, 8326 (2006).
[11]L. F. Cui, X. Huang, L. M. Wang, D. Y. Zubarev, A. I. Boldyrev, J. Li, and L. S. Wang, J. Am. Chem. Soc. **128**, 8390 (2006).
[12]L. F. Cui, X. Huang, L. M. Wang, J. Li, and L. S. Wang, Angew. Chem., Int. Ed. **46**, 742 (2007).
[13]J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[14]B. Delley, J. Chem. Phys. **92**, 508 (1990); B. Delley, J. Chem. Phys. **113**, 7756 (2000).
[15]B. Delley, Phys. Rev. B **66**, 155125 (2002).
[16]G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[17]G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[18]G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[19]P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[20]S. Nosé, J. Chem. Phys. **81**, 511 (1984).
[21]S. Nosé, Prog. Theor. Phys. Suppl. **103**, 1 (1991).
[22]D. M. Bylander and L. Kleinman, Phys. Rev. B **46**, 13756 (1992).
[23]See EPAPS Document No. E-APPLAB-92-042811 for the ground state and other higher energy isomers of $Mn@Sn_{12}$ dimer, along with their relative energies and preferred spin states. DOS and PDOS are also given for $Mn@Sn_{12}$ dimer. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[24]F. Tournus, J. C. Charlier, and P. Melinon, J. Chem. Phys. **122**, 094315 (2005).
[25]Z. M. Sun, H. Xiao, J. Li, and L. S. Wang, J. Am. Chem. Soc. **129**, 9560 (2007).
[26]J. M. Matxain, M. Piris, E. Formoso, J. M. Mercero, X. Lopez, and J. M. Ugalde, ChemPhysChem **8**, 2096 (2007).