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An *ab initio* investigation on the endohedral metallofullerene Gd$_3$N−C$_{80}$

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First-principles electronic structure studies on the ground state geometry and electronic and magnetic properties of bare and hydrogen coated metallofullerene Gd$_3$N−C$_{80}$ have been carried out within a density functional formalism. The correlation effects are incorporated either through a generalized gradient corrected functional or through an on-site Coulomb interaction (LDA+U). It is shown that the bare Gd$_3$N−C$_{80}$ possess a ferromagnetic ground state with a large spin moment of 21μ_B that is highly stable against spin fluctuations. The simulated Raman spectrum shows that the low-energy peaks are contributed by the floppy movement of N atom. As to the effect of addition of hydrogens, it is shown that the most favorable site for the hydrogen adsorption is an on-top site where the H atom is located above a five-member carbon ring with a binding energy of 1.92 eV, while the least stable site corresponds to an on-top absorption above a six-member ring. A study of the energetics upon multiple adsorption of H shows that the binding energy of the H to metallofullerene drops after 11 H atoms. This shows that it should be possible to attach multiple ligands offering the potential that the Gd$_3$N−C$_{80}$ can be functionalized with ligands or assembled in cluster assemblies. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2711420]

Endohedral metallofullerenes have attracted considerable attention over the past 14 years as they provide unique opportunity of preserving selected properties of encapsulated metal core while the unit is exposed to solvents or other agents. This has led to numerous applications, in particular, in biological sciences where the metal alone could lead to harmful consequences. In this regard, the trimetal nitride containing endohedral fullerene[1] has generated the tremendous interest. Specifically, the metallofullerenes Gd$_3$N−C$_{80}$ are paid much attention[2–4] since they are potential contrast enhancing agents for magnetic resonance imaging (MRI). An isolated Gd$_3$N molecule has a large spin magnetic moment of 23μ_B. When embedded inside the carbon cage, the Gd atoms bond through the delocalized s,d states with the s,p states of C atom, leaving the spin magnetic moment from f electrons almost intact. The fullerene cage not only acts to protect the interior metal atoms from the leakage and prevent their accumulation in human organs and tissues, but can also be functionalized with ligands for medicinal applications. In particular, experiments indicate that trigadolinium nitride fullerenes Gd$_3$N−C$_{80}$ can lead to more over 20 times higher proton relaxivities[5] in comparison with the commercial Gd^{3+} chelate contrast agent. Further, the substitution of Gd by Tb can generate fluorescent particles[6] for another imaging technique. Although there are exciting developments on the medical applications of nanoparticles,[7] a fundamental understanding of such endohedral metallofullerenes is still lacking. In this paper, we present investigations on the electronic and magnetic properties of endohedral metallofullerene Gd$_3$N−C$_{80}$ using a first-principles method. We demonstrate that Gd atomic magnetic moments inside the carbon cage are ferromagnetically coupled and that the Gd$_3$N presents a

floppy interior where N atom can easily tunnel through the Gd$_3$ plane. We suggest that the observed low-energy Raman lines[3] are related with this floppy nature of Gd$_3$N in the cage. By examining the attachment of hydrogen atoms, we investigate the chemical functionalization of the metallofullerenes.

The total energy and electronic structure calculations are carried out using VASP program,[8] which is the pseudopotential plane-wave method based on density functional theory[9] within the generalized gradient approximation (GGA).[10] Since the correlation effects are important to properly treat Gd f states, the density functional based correlated band theory LDA+U method[11] was chosen in order to separate the occupied 4f orbitals from the unoccupied ones. The Hubbard parameter $U=8$ eV and the exchange parameter $J=0.8$ eV were taken for the effective coulomb interaction[12] and the exchange interaction on the Gd ion, respectively. A plane-wave basis set and the projector augmented wave (PAW) pseudopotentials for Gd, N, and C elements with 18, 5, and 4 valence electrons, respectively, were employed. The 4f electrons are included in the valence shell of Gd atom. The energy cutoff was set to 300 eV. The convergence in energy was set as 1 meV.

The cluster Gd$_3$N−C$_{80}$ was placed inside the cubic supercell with the size of 20 Å, which is large enough to eliminate the interaction between the neighboring cells. The Γ point is used to integrate over the first Brillouin zone. The geometry is fully optimized by the criterion that the force on each atom is less than 1 meV/Å.

Figure 1 shows the one electron energy levels for the endohedral metallofullerene Gd$_3$N−C$_{80}$. The calculations suggest a large highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of 1.48 and 1.54 eV for the majority and minority spin channels, respectively, which is in good agreement with the photoemis-
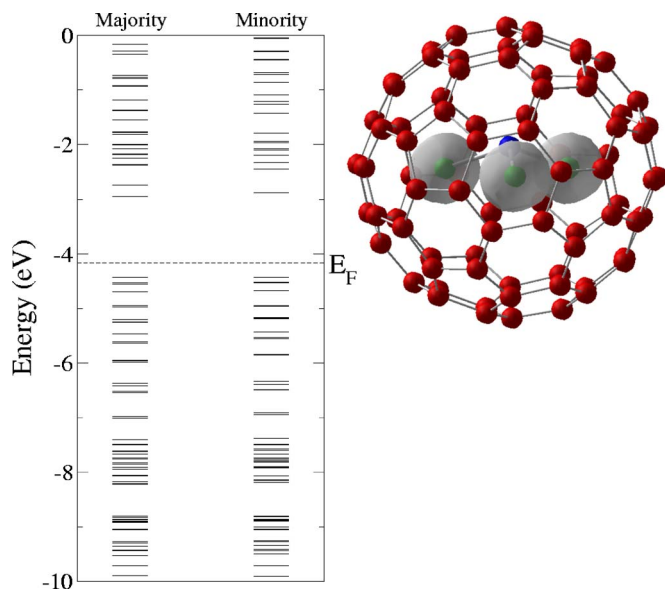
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FIG. 1. (Color online) One electron energy levels in majority and minority spin channels for the Gd_3N embedded in the C_{80} cage. The right panel gives the isosurface of the magnetic valence charge densities with the value of 0.8 electrons/$Å^3$.
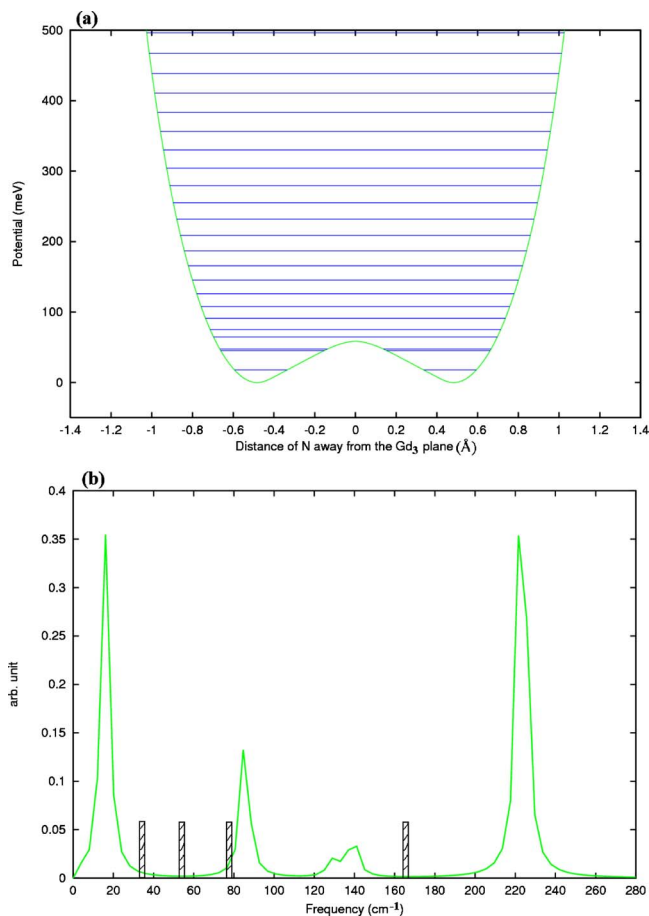

FIG. 2. (Color online) (a) Calculated potential energy curve for the N atom as a function of the displacement away from the Gd_3 plane. The horizontal lines represent the calculated energy eigenvalue spectra and the lowest-energy space between the adjacent energy levels corresponds to the quantum zero-point energy. (b) Simulated Raman spectrum of Gd_3N embedded inside the C_{80} cage. The observed peak positions in the experiment are indicated by hashmarks.

sion experimental gap[3] of 1.75 eV. The electronic structures of bare C_{80} and Gd_3N-C_{80} show that six electrons are transferred from the Gd_3N to the carbon cage to fill the empty states near the HOMO in the bare C_{80}. The hybridization between the s,d states of Gd atoms and the s,p states of six-member ring C atoms creates strong bonds and stabilizes the whole metallofullerene. The calculated binding energy is as large as 13.63 eV. The geometry of Gd_3N inside the cage is kept to be a pyramidal shape, while the Gd–Gd bond length is slightly stretched and the N atom is closer to the Gd_3 plane compared to the case for the isolated molecule. Because Gd f electrons are fully spin polarized, both occupied and unoccupied f states are located away from the Fermi level, which leads to atomic magnetic moment of $7\mu_B$ for each Gd ion. In the right panel of Fig. 1, we show the isosurface of the magnetic charge densities with the value of 0.8 electrons/$Å^3$ when the Gd_3N are embedded inside the C_{80} cage. The ground state is marked by ferromagnetic coupling among three Gd ions and gives rise to the total magnetic moment of $21\mu_B$. Using the fixed magnetic moment calculations, we found that the exciting magnetic states with spin moments of $19\mu_B$ and $23\mu_B$ are higher by 1.48 and 1.41 eV, respectively.

To investigate the floppy movement of N atom between the two sides of Gd_3 plane, we solved the one-dimensional Schödinger equation in the double-well potential. In Fig. 2(a), we give the potential for N atom as a function of the displacement away from the Gd_3 plane when the molecule Gd_3N is embedded inside the fullerene C_{80} cage. We should point out that it is important to treat the movement of N atom by quantum mechanism, because the double well is shallow and the energy barrier is only 78 meV when N atom moves from one side to another side of the double well. The potential is obtained from the total energy calculations by the displacement step of 0.02 Å. In every step, the N atom is fixed

and all other atoms of the metallofullerene are fully relaxed. Then, more densely spaced points corresponding to the displacement step of 0.001 Å are derived by a cubic spline interpolation in order to numerically solve the Schödinger equation using the plane wave basis. The convergence was tested by varying the number of plane waves, and we found that 500 plane waves were sufficient to give converged eigenvalues and eigenstates over the entire energy range examined in this paper. The calculated energy eigenvalues are shown in Fig. 2(a) and the lowest-energy eigenvalue indicates the quantum zero-point energy. The energy spacing between the adjacent energy levels is interesting. If the potential for the movement of N atom is harmonic, the energy spacing would be exactly equal, which corresponds to the phonon energy using the force field approximation. Apparently, the movement of N atom is anharmonic and floppy. Inside the double well, there are three energy levels corresponding to the N atom vibrating around the local minima. For the energy levels nearby the barrier, the energy spacings deviate from those of the harmonic treatment. On the other hand, the energy spacings are almost constant in the range of high energy.
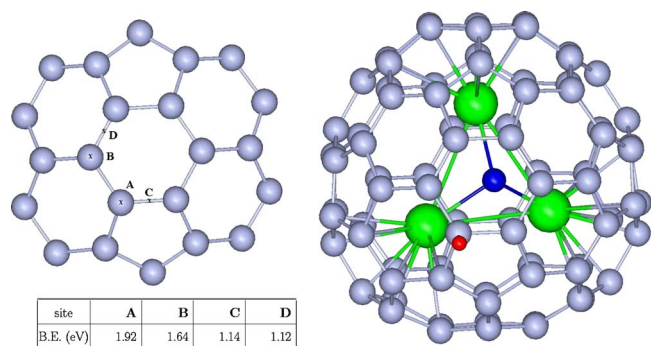
site	A	B	C	D
B.E. (eV)	1.92	1.64	1.14	1.12

FIG. 3. (Color online) The adsorption sites of hydrogen atoms outside the C_{80} cage as well as their binding energies (in unit of eV). The gray, green, blue, and red circles refer to the C, Gd, N, and H atoms, respectively.
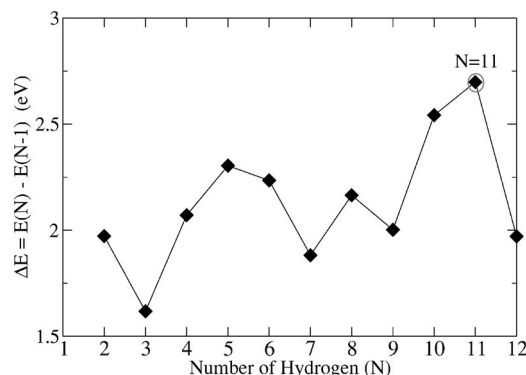

FIG. 4. Removal energy as a function of the number of hydrogen atoms when the hydrogen atoms are attached to the outside of the metallofullerene Gd_3N-C_{80}. The circle corresponds to the most favorable attachment of hydrogen atoms.

We now focus on the energy adsorption in the Raman scattering measurements. In the dipole approximation, the transition can occur among the energy eigenstates. We use the calculated "one atom" energy eigenvalues and eigenstates to simulate the Raman spectra at room temperature shown in Fig. 2(b). The Gaussian smearing of 0.2 meV is taken to represent the precision of the experimental instruments. The Raman lines at 223, 140, 85, and 19 cm^{-1} are obtained and qualitatively agree with the experimental ones.[3] In particular, the low-energy lines below 100 cm^{-1} are unique features for the Gd_3N embedded inside the C_{80} cage and can be assigned to the floppy movement of N atom between the two sides of Gd_3 plane. We notice that the discrepancies between theoretical and experimental results mainly arisen from the frozen phonon approximation in our simulation.

For medical application, it is necessary that the metallofullerene be functionalized with ligands as well as water soluble. Theoretically we examined the chemical properties of the metallofullerene Gd_3N-C_{80} simply by adding hydrogen atoms. Figure 3 shows the four possible addicted sites of hydrogen atom outside the carbon cage. We use the following formula to calculate the binding energy:

$$BE = E(Gd_3N-C_{80}+H) - E(Gd_3N-C_{80}) - E(H),$$

where $E(Gd_3N-C_{80}+H)$ and $E(Gd_3N-C_{80})$ are the total energies of metallofullerene with and without hydrogen atom, and $E(H)$ is the energy of hydrogen atom. We found that the most favorable site is on top of a five-member ring carbon atom (site A) with a binding energy of 1.92 eV. The on-top site over a six-member ring carbon atom (site B) is the least favorable with a binding energy of 1.64 eV. The bridge sites C and D give lower binding energies. At the on-top site, the bond length between C and H is about 1.17 Å. We then examined the number of hydrogen atoms that can be addicted outside the metallofullerene. In Fig. 4, we plot the removal energy as a function of the number of hydrogen atoms outside the metallofullerene. The larger the removal energy, the more stable the attachment of hydrogen atoms. We found that up to 11 hydrogen atoms can be strongly bound to the carbon cage of the metallofullerene Gd_3N-C_{80}.

Our results support the finding that the endohedral metallofullerene Gd_3N-C_{80} are water soluble by coating with hydroxyl groups.

In summary, the electronic and magnetic properties of the endohedral metallofullerene Gd_3N-C_{80} have been studied via first-principles calculations. The Gd_3N molecule is found to be strongly bound to the C_{80} cage inside and has a high spin magnetic moment of $21\mu_B$ that is largely localized on the f electrons of three Gd atoms. The large binding energy makes it unlikely that the cage could break and release Gd atoms. Based on the quantum mechanical treatment, we propose that the observed experimental low-energy Raman spectrum is associated with the floppy movement of N atom between the two sides of the Gd_3 plane. Finally, we examine the attachment of hydrogen outside the metallofullerene and suggest that the endohedral metallofullerene Gd_3N-C_{80} can be functionalized with ligands or assembled in cluster assemblies for medical applications.

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