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Spin Properties of Germanium-Vacancy Centers in Bulk and Near-Surface Regions of Diamond

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Germanium-vacancy (GeV) centers are now studied extensively due to perspectives of their applications in quantum information processing, nanometrology and nanoscale magnetic resonance imaging. One of the important requirements for these applications is a detailed understanding of the hyperfine interactions in such systems. Quantum chemistry simulation of the negatively charged GeV^- color center in diamond is the primary goal of this paper in which we present preliminary results of computer simulation of the bulk H-terminated cluster $C_{69}[GeV^-]H_{84}$, as well as of the surface cluster $C_{64}[GeV^-]H_{68}$-(100)-H_{11} having one dangling bond at (1 0 0) surface using the DFT/PW91/RI/def2-SVP level of theory.

Keywords: Diamond; GeV^- color center; hyperfine interaction; density functional theory; magnetic resonance imaging.

1. Introduction

The germanium-vacancy (GeV) center in diamond by analogy with the well-known nitrogen-vacancy (NV) center can be used as a remarkable magnetic sensor allowing to perform spectroscopy of nearby spins on a diamond surface.[1] It provides a possibility of nanoscale magnetic resonance imaging (MRI) under ambient conditions with the nanometer resolution and single nuclear spin sensitivity.[2–4] To increase the sensitivity that depends on a distance between the GeV sensor (by analogy with the NV-based sensor) and the target spins, it was recently suggested[3] to use ancillary or "reporter" electronic spins located on the diamond surface and

coupled to the proximal color center located a few nanometers below the diamond surface.

Here we present results of computer simulations of the negatively charged GeV^- color center using the density functional theory (DFT) to elucidate a spatial structure and spin properties of the H-terminated cluster $C_{69}[GeV^-]H_{84}$ located in the bulk as well as of the cluster $C_{64}[GeV^-]H_{68}$-(100)-H_{11} located at the surface of diamond. The last has one dangling bond at the (1 0 0) diamond surface,[5] which acts as the abovementioned ancillary or reporter electronic spin located on the diamond surface.

2. Simulation and Results

DFT calculations were performed using the ORCA program package.[6] The center properties were studied by simulating H-terminated diamond-like clusters with 69 carbon atoms hosting the GeV^- center in its central part. The spatial structures of the clusters were optimized using the DFT/PW91/RI/def2-SVP level of theory. This basis set was previously shown[7] to be large enough to provide reliable results in the geometry optimization and in the calculation of EPR parameters of the center. The GeV^- center has the spin-doublet ($S = 1/2$) ground state. During geometry optimization, the Ge atom moves to the interstitial position as it is substantially larger than the C atoms of the diamond lattice.

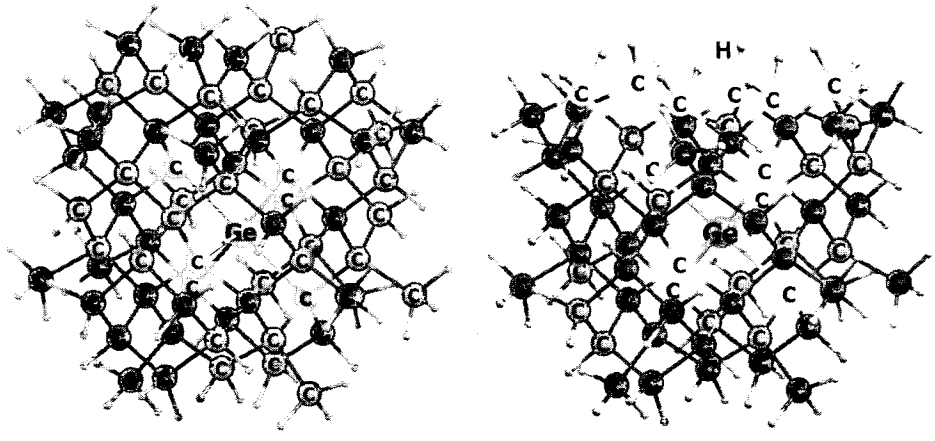
The reporter electronic spin is the single dangling bond on the (1 0 0) surface of the so-called surface cluster $C_{64}[GeV^-]H_{68}$-(100)-H_{11} [Fig. 1(b)]. It was designed from the bulk H-terminated cluster $C_{69}[GeV^-]H_{84}$ [Fig. 1(a)] by eliminating five C atoms to form the (1 0 0) surface consisting of six superficial C atoms, for which 11 of 12 dangling bonds were saturated with H atoms while one was left to be not saturated.

The DFT calculations have been done for the fully relaxed surface clusters. We have calculated distributions of the total spin density $n(r) = n_\uparrow(r) - n_\downarrow(r)$, which is the difference of electron densities with spin of $\uparrow$ and $\downarrow$ orientations. Also, we calculated the constants of isotropic hyperfine interactions (Fermi EPR coupling constant) of the GeV^- center electronic spin with nuclear spins of ^{13}C atoms in the cluster.

Figure 2 shows the distributions of the total spin density over the $C_{69}[GeV]H_{84}$ and $C_{64}[GeV]H_{68}$-(100)-H_{11} clusters, whereas the distributions of the atomic spin density for the $C_{64}[GeV]H_{68}$-(100)-H_{11} cluster are presented in Fig. 3.

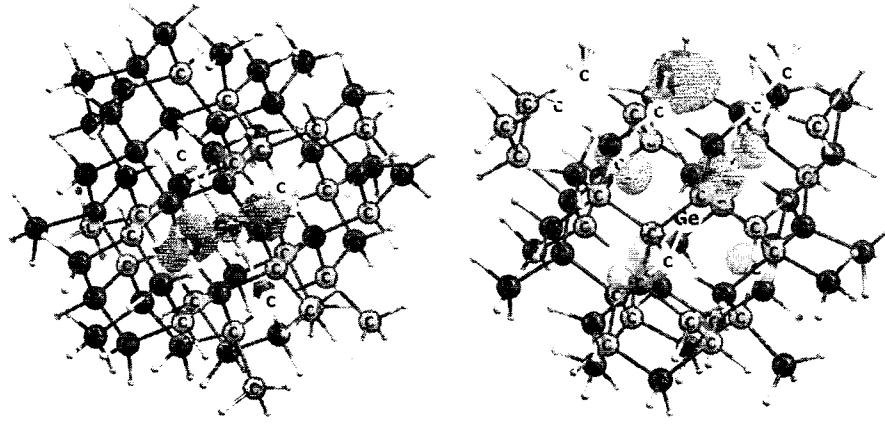
Figure 4 shows the distributions of the fermi EPR coupling constants for the $C_{64}[GeV]H_{68}$-(100)-H_{11} clusters in which atoms are indicated by the value of the Fermi EPR coupling constants.

The simulated spin density distributions show that this quantity is mostly localized at the vacancy of the GeV^- center and at the surface dangling bond. From these preliminary data, we conclude that the isolated dangling bond on the (1 0 0)



(a) (b)

Fig. 1. Atomic structures of the investigated clusters: (a) $C_{69}[GeV]H_{84}$ cluster (C atoms neighboring to the Ge atom are painted white, H atoms are not indicated), (b) $C_{64}[GeV]H_{68}$-(100)-H_{11} cluster (C atoms neighboring to the Ge atom and surface C atoms are painted white; the H atom belonging to a not fully saturated surface C atom is indicated as H, other H atoms are not indicated). Clusters are optimized by DFT/PW91/RI/def2-SVP level of theory.



(a) (b)

Fig. 2. The distributions of the total spin density for the C_{69}[GeV]H_{84} (a) and C_{64}[GeV]H_{68}-(100)-H_{11} (b) clusters.

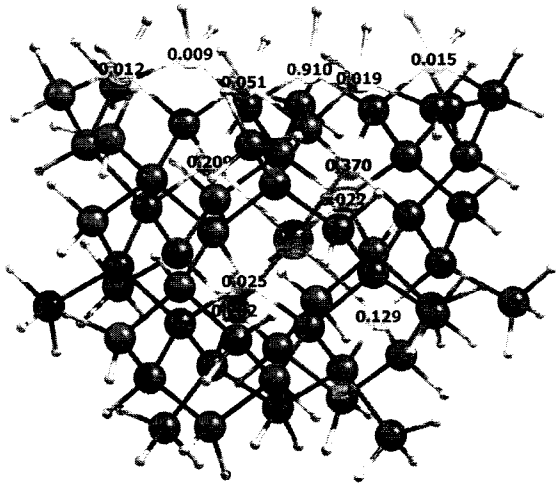


Fig. 3. The distributions of the atomic spin density in the C_{64}[GeV]H_{68}-(100)-H_{11} cluster. Atoms are indicated by the value of the atomic spin density (a.u.).

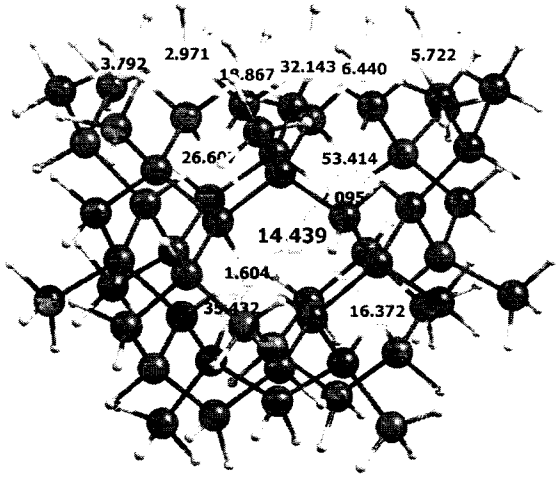


Fig. 4. The distributions of the fermi EPR coupling constants for the C_{64}[GeV]H_{68}-(100)-H_{11} cluster. Atoms are indicated by the value of the fermi EPR coupling constants (MHz).

diamond surface can serve as a reporter spin for the GeV-based MRI. We have shown that spin density is mostly localized at three C atoms neighboring the vacancy, surface C atom with the dangling bond (C_{db}) and H atom bonded to it (H_b).

The hyperfine interaction matrices for all possible positions of ^{13}C atoms of the clusters and as well for the superficial ^{1}H proton nuclear spins were calculated pointing out rather strong hyperfine interaction for the C_{db} and H_b atoms, with the EPR coupling constants of 32.14 MHz (59.4 MHz for the NV center) and −22.03 MHz (−17.68 MHz for the NV center), respectively. The value range of coupling constants is enough to conclude that the isolated dangling bond on the (1 0 0) diamond surface can serve as a reporter spin for the GeV^--based MRI.

3. Conclusion

The optimization of the surface C_{64}[GeV]H_{68}-(100)-H_{11} cluster with one dangling bond at the (1 0 0) surface has been performed. It is shown for the first time that the spin density is mostly localized at three C atoms neighboring to the Ge atom, the C_{db} with the dangling bond and the H_b atom bonded to it. The Fermi coupling constants for C_{db} and H_b atoms have been determined to be 32.14 MHz and −22.03 MHz, respectively. The calculations have confirmed that the spin density in the bulk H-terminated cluster is localized mainly at three C atoms being the nearest neighbors of the GeV^- center. We conclude that the isolated dangling bond on the (1 0 0) diamond surface can serve as a reporter spin for the GeV^--based MRI.

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