First-principles investigation of a monolayer of C$_{60}$ on h-BN/Ni(111)

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(Received 26 April 2005; published 28 September 2005)

The geometric and electronic structures of a monolayer of C$_{60}$ on a h-BN monolayer-covered Ni(111) surface are studied by first-principles calculations. The interaction between ions and electrons is described by the projector-augmented plane-wave method. The most stable structure of the h-BN/Ni(111) surface is found to be N on the top and B on the fcc site of Ni(111). Upon adsorption, the structure in which a hexagon of the C$_{60}$ molecular is parallel to the substrate is 0.1 eV more favorable in energy than that of a pentagon parallel to the substrate. For the most stable adsorption sites of C$_{60}$ on h-BN/Ni(111), the distance between the bottom hexagon of C$_{60}$ and the h-BN/Ni substrate is 3.6 Å. The calculated results show that the energy differences among different orientations are all smaller than 0.22 eV. No magnetic moment is found for the C$_{60}$ monolayer. The calculated electronic structures confirm that the h-BN/Ni(111) is a good insulator platform to study the electronic structures of C$_{60}$ ultrathin films, since only a weak interaction and small charge transfer exist between C$_{60}$ and h-BN/Ni(111).

DOI: 10.1103/PhysRevB.72.115436

PACS numbers: 73.20.At, 73.22.–f

I. INTRODUCTION

Fullerenes manifest various intriguing phenomena. Many fascinating properties of these molecules have been reported and predicted. Among the most interesting tasks are finding a mechanism for incorporation of fullerenes in some special structure and exploitation of their electronic and optical properties. In this respect, many investigations have been devoted to the system of a C$_{60}$ monolayer on metallic substrates.$^{1-3}$ In contrast only a little work on insulating substrates$^4$ or on a substrate with an insulator-metal interface$^5$ has been reported. The substrate with an insulator-metal interface is well suited as a model not only for an ideal quasi-two-dimensional system, but also for tunneling and field effects of sizable charge transfer, because of the spatially abrupt change of electronic structure at the insulating-metallic interface. In particular, these systems can be good adopters of an isolated C$_{60}$ or a monolayer C$_{60}$ film which can be used to tune their physical properties. Those proposed depend strongly on the number of electrons transferred, which in turn can be controlled by an external field.

Muntwiler et al. have reported their investigation on C$_{60}$ on h-BN/Ni(111) by using a photoemission experiment.$^5$ They found that one monolayer of C$_{60}$ on one monolayer h-BN on Ni(111) exhibits a change of the C$_{60}$ charge state, from 0.08 to 0.57 electrons between 150 and 250 K.$^5$ They attributed the change to a rocking motion of C$_{60}$ on h-BN/Ni(111) and traced it to an electron-phonon coupling effect. Understanding and applying these properties requires simultaneous knowledge of both geometric and electronic structures, as well as characterization of the detailed interaction between C$_{60}$ and substrates.

In this work, we study the geometric and electronic structures of C$_{60}$ adsorbed upon h-BN/Ni(111). We focus on the effects of the h-BN/Ni(111) insulating-metallic interface on charge transfer. We also investigate the energy landscape upon rotation, translation, and rocking motion. The rest of the paper is organized as follows. In the following section the calculation methods are described. In Sec. III, we discuss properties of h-BN/Ni(111) and of C$_{60}$ upon a h-BN/Ni(111) substrate. Finally, our main results are summarized in Sec. IV.

II. COMPUTATIONAL METHODS

Our calculations were performed by using the Vienna ab initio simulation package$^6$ (VASP) within the framework of spin density functional theory. For magnetic materials, we used the projector-augmented plane-wave method.$^7$ Surface Brillouin-zone integrations were performed on a $k$ mesh of $16 	imes 16 	imes 1$ in the Methfessel-Paxton scheme$^8$ for h-BN/ Ni(111)($1 	imes 1$), as well as the equivalent grid ($4 	imes 4 	imes 1$) for h-BN/Ni(111)($4 	imes 4$) substrate upon C$_{60}$ adsorption. These choices lead to a total energy convergence better than 0.01 eV. A $32 	imes 32 	imes 1$ and a $8 	imes 8 	imes 1$ $k$ mesh were chosen for calculating the density of states of h-BN/Ni(111)($1 	imes 1$) and C$_{60}$/h-BN/Ni(111), respectively. The energy cutoff for the wave functions was 300 eV. Exchange and correlation effects were treated by the generalized gradient approximation (GGA) proposed by Perdew et al.$^9$ The equilibrium lattice constant obtained through total energy minimization is 3.52, 2.50, and 2.46 Å for bulk nickel, hexagonal BN, and graphite, respectively, which agree well with the corresponding experimental values. We did not optimize the layer space for graphite and h-BN, since it is well known that density functional theory is failed to determine it. The mismatch between the hexagonal BN layer and the Ni(111) substrate is thus smaller than 0.4%. The nickel substrate was modeled by a seven-layer slab, with a monolayer of h-BN as well as one monolayer of C$_{60}$ on one side of the slab, and, on the other side of the nickel slab, two nickel layers were kept at the distance corresponding to that of the nickel bulk. The thickness of vacuum was kept larger than 14 Å. This slab model is found to be sufficiently accurate for our study. In
order to search for stable structures, all atoms were allowed to relax except for the two bottom layers of nickel, which were fixed at the ideal bulk distance.

### III. RESULTS AND DISCUSSION

#### A. h-BN/Ni(111)

First, we investigate structures of one monolayer of h-BN adsorbed on Ni(111). The motivation is that the charge state of C$_{60}$ in the C$_{60}$/h-BN/Ni(111) complex can be strongly affected by the interaction between the C$_{60}$ and the substrate. We will see later that, as an insulating material, the h-BN layer only contributes a few states near the Fermi level upon adsorption on Ni(111), which leads to an abrupt change of the electronic structure between Ni and h-BN.

A single h-BN layer has a structure similar to a graphite layer, that is, it has $sp^2$ hybridization between B and N in plane. The B and N atoms form covalent $\sigma$ bonds. Their remaining $p_z$ orbitals form symmetric $\pi$ (bonding) and anti-symmetric $\pi^*$ (antibonding). In contrast to graphite, the $\pi$ and $\pi^*$ band of a h-BN layer are not degenerate at the $K$ point of the surface Brillouin zone. Therefore, while graphite is semiconducting, h-BN is an insulator with a gap of about 5 eV. Similar to those of graphite, the active orbitals of a h-BN layer are the $\pi$ and $\pi^*$.

Both experimental and theoretical determinations of the structural and electronic properties of the h-BN monolayer adsorbed on the Ni(111) surface have been reported; see, e.g., the review article Ref. 11 and references therein. It has been well established that one monolayer of h-BN adsorbed on Ni(111) forms a well-ordered surface with $1 \times 1$ commensurate structure. Because of the lattice matching between the two, the h-BN layer is only weakly bound to the Ni(111) surface. The layer is insulating in the sense that the B and N electronic states do not contribute to the Fermi level. Within one monolayer, the structure is expected to be a graphitic sheet with a weak corrugation. Spin-resolved experiments indicate that the adsorbed h-BN layer leads to only a little charge transfer between the h-BN layer and the Ni substrate, and that a small magnetic moment is induced by the Ni substrate.

We optimized the structure of a monolayer of h-BN on Ni(111). The most plausible sites for B and N adsorption on the Ni(111) surface are the top, fcc, and hcp sites. Thus, six different adsorption configurations of h-BN on Ni(111) were considered in the $1 \times 1$ commensurate structure: N on top with B on the fcc or hcp site, B on top with N on the fcc or hcp site, N on fcc with B on the hcp site, as well as B on fcc with N on the hcp site. We optimized these six configurations and compared the total energies. In these calculations, geometric relaxation proceeded until forces on all movable atoms were smaller than 0.03 eV/Å. We find that the configuration of N on top and B on the fcc site is favorable in energy among the configurations considered. This outcome is reasonable since the $p_z$ orbital of N is the most active orbital for h-BN. However, the total energies of all six configurations are very close, only 0.01 eV apart in energy. The h-BN monolayer is corrugated by 0.1 Å with B closer to the Ni surface. The distance of the N layer to the topmost Ni layer is 2.09 Å. These results are in good agreement with the results of Refs. 13 and 14. We will see below that the adsorption of a monolayer of C$_{60}$ on the h-BN/Ni(111) substrate does not change the corrugation.

A single h-BN layer is an insulator. It is interesting to know how it behaves upon adsorption on Ni(111). It has been observed that there is no great influence of BN on the electronic structures of Ni, since almost no BN states near the Fermi level are available for hybridization with Ni. Our results confirm this observation. We find that for the single layer of h-BN, the gap is about 4.60 eV, which is determined by energy difference between the $\pi$ band and the $\pi^*$ band. In order to identify the (h-BN)-related bands upon h-BN adsorption on Ni(111), the bands are projected on atomic sphere of BN. We determine the corresponding energy difference between the bands with the characters of the $\pi$ and $\pi^*$ to be 6.10 eV upon h-BN adsorption on Ni(111). The $\pi$ band is shifted from $-2.99$ eV of an isolated h-BN layer to $-4.17$ eV of a h-BN/Ni(111) complex and the $\pi^*$ from 1.61 eV to 1.93 eV when we align the lowest $\sigma$ band of the h-BN of both the isolated h-BN layer and the h-BN/Ni(111) complex.

This is because the $p_z$ orbitals of BN interact with the $d$ states of Ni near the Fermi level, and the energy positions of the $\pi$ bonding band of BN thus are shifted lower in energy, while the $\pi^*$ antibonding band of BN is shifted higher in energy compared with that of the single h-BN layer. The result is an increase of the width of the nominal gap of h-BN from 4.6 to 6.1 eV. Our calculations show that the corrugation of the h-BN layer cannot change this feature. This outcome agrees well with the result obtained by Grad et al. using the full-potential linear augmented-plane-wave (FLAPW) method. They showed that the width of the nominal gap increases from 4.5 to 5.8 eV, and also concluded that corrugation of the h-BN layer made no contribution to this gap width increase. Similar behavior has been observed in other work on h-BN on Ni(111) (Ref. 17) as well as graphite on Ni(111).

The localized electronic structures of the h-BN layer in the h-BN/Ni(111) system plays an important role in determination of the charge state upon C$_{60}$ adsorption on h-BN/Ni(111). To treat the interaction between the h-BN layer and Ni(111) in more detail, we calculate the local density of states (LDOS) of the h-BN layer (see Fig. 1). These dashed curves represent the LDOS of a single corrugated layer of h-BN; note that we aligned the lowest $\sigma$ band of the h-BN/substrate to that of the isolated h-BN layer. How do these states affect the electronic structures of h-BN/Ni(111)? Is the surface still inert? In order to show the electronic behavior of these states, we calculated the charge density for both BN and Ni in this energy window $-2.99$ to 1.61 eV. Figures 2(a) and 2(b) represent the charge density for the plane through the top and bottom sites of h-BN/Ni(111), respectively. The scale in the figures is $2.67 \times 10^{-6}$ electrons per unit cell, the highest value near the center of Ni atoms is $1.94 \times 10^{-6}$ electrons per unit cell, localized at the center of Ni atoms. The solid dots in Figs. 2(a) and 2(b) represent the positions of N and B. From that figure, we find that the states in this energy window are dominated...
by $d$ orbitals from the Ni layers, with only a little contribution from N $p_z$-type orbitals. No contribution can be found from B atoms. Note that our calculation method is not based on a local basis, but a plane-wave (PW) basis. In a PW basis, the LDOS of an atom is obtained by projecting the density of states on a sphere surrounding this atom. The sum of the volume of these spheres should be close to 100% of the volume of the unit cell. In other words, these spheres should have some overlap. Therefore the LDOS based on a PW basis can only qualitatively represent the local behavior of atoms. In particular, one cannot expect that a localized feature is created purely by one atom. It may contain components from neighboring atoms, as their orbitals may extend outside their spheres. Therefore, the states near the Fermi level shown in Fig. 1 do not imply that the h-BN layer is metallic.

Charge transferability is one of the main concerns in our work on the charge state of C$_60$ upon adsorption on h-BN/Ni(111). A metallic surface can efficiently screen an external electric field, while an insulating surface does not. Therefore the charge transferability near the Fermi level for the h-BN layer on Ni(111) can be investigated by studying screening charge response of the h-BN/Ni(111) upon imposing an external electric field. The screening charge probes both occupied and unoccupied electronic states near the Fermi level. For this purpose, we imposed an external electric field of $\pm 0.01$ V/Å on h-BN/Ni(111) to see if it can efficiently screen the external field and to understand the charge transfer response of the h-BN layer, that is, the electronic properties near the Fermi level. Here a negative bias means that the field will create a negative screening charge, while a positive bias creates a positive screening charge. The method for imposing an external electric field and calculating screening charges can be found in our previous work.\textsuperscript{19,20}

The calculated screening charge is shown in Fig. 3. Figures 3(a) and 3(b) are for the screening charge of the $-0.01$ and $+0.01$ V/Å external electric field, respectively. The vertical lines indicate the atomic layer positions, while the dashed curves indicate the screening charge for a clean Ni(111) surface whose atomic layer positions are kept the same as these of the h-BN/Ni(111). For both the negative and positive fields, it is clear that the screening charge for the clean Ni(111) surface (the dashed curve) is localized in the surface region to screen out the external electric field such that the field cannot penetrate deeply into the Ni layers (except for slight Friedel oscillations). In contrast, the screening charge for the h-BN/Ni(111) is distributed more broadly, partly in the interface region. It can be seen clearly that the screening charge distribution of the h-BN layer does not be-
have like a metallic layer. Instead, a dipole is formed at the layer of h-BN in response to the external electric field. The dipole consists of the charge distributed beside both sides of the h-BN layer with opposite signs, although in the interface region between the h-BN and the topmost Ni layer the charge overlaps the screening charge near the topmost Ni layer. Thus only a small peak can be seen (as identified by the arrows in Fig. 3). This charge and the screening charge near the topmost Ni layer are canceled by each other. We can see that both solid and dashed curves are similar beneath the topmost Ni layer, which indicates that the field has been efficiently screened out of the Ni layers. The deeper layers remain metallic. Comparing the two electronic screening profiles, it can be concluded that the h-BN layer is insulating, or at least that there are not enough states in the BN layer near the Fermi level for charge transfer to screen out the imposed external field efficiently. These results allow us to confirm that states in the nominal gap are localized at the interface region of h-BN and Ni(111), and the h-BN layer behaves like a poor metal. In other words, the states in the nominal gap projected on the h-BN layer are mainly localized in the h-BN layer, therefore have a weak ability for charge transfer between BN and Ni. We also find that corrugation does not change this behavior.

Except for the occupied $\sigma$ states, almost no change can be found in electronic structures of the h-BN layer upon adsorption on Ni(111). The lower $\sigma$ bands are unchanged, while the upper $\sigma$ bands and $\pi$ bands have some distortion due to the splitting induced by Ni spin polarization. We checked magnetic moments of h-BN/Ni(111) and find that the h-BN layer is polarized upon adsorption on Ni(111). But only small magnetic moments are found in the h-BN layer, that is, 0.016$\mu_B$ and $-0.006\mu_B$ for N and B, respectively, while the magnetic moments of Ni are somewhat reduced from that of the bulk Ni. For the three topmost Ni layers, the magnetic moments are 0.553$\mu_B$, 0.615$\mu_B$, and 0.627$\mu_B$, respectively, compared with that of the Ni center layer, 0.677$\mu_B$. Therefore, in the optimization of the stable C$_{60}$/h-BN/Ni(111) structures, we do not consider spin polarization to save computing time. Except for few atoms, forces on atoms are smaller than 0.03 eV/Å for the structures obtained without spin polarization. Spin polarization has very little influence on the geometric structure. We will also see below that no magnetic moments can be found for C$_{60}$ when it is adsorbed on h-BN/Ni(111).

**B. C$_{60}$/h-BN/Ni(111)**

Next we investigate a C$_{60}$ monolayer (ML) on h-BN/Ni(111). Recall the discussion of the results of Muntwiler et al. in the Introduction, on one monolayer h-BN on Ni(111) exhibits a change of charge state of C$_{60}$ from 0.08 to 0.57 electrons between 150 and 250 K. They attributed this change to the so-called rocking motion of C$_{60}$ on h-BN/Ni(111) and traced it to an electron-phonon coupling effect. Here we focus on the effect of C$_{60}$ orientation upon charge state and the associated electronic structures when C$_{60}$ adsorbed on a h-BN/Ni(111) surface.

The structure of the C$_{60}$ ML adsorbed on h-BN/Ni(111) has been examined experimentally by low-energy electron diffraction and scanning tunneling microscopy techniques. A commensurate hexagonally close packed (4×4) structure of C$_{60}$ on h-BN/Ni(111) was observed. We thus model this system using a slab with a Ni(111) (4×4) unit cell, and add one monolayer of h-BN and one monolayer of C$_{60}$. A top view of the resulting geometric structure is shown in Fig. 4. Panel (a) is a geometry in which a hexagonal face of C$_{60}$ is parallel to the substrate with the center of the C$_{60}$ on the top site of Ni(111). Figure 4(b) shows a pentagon of C$_{60}$ parallel to the substrate. Both geometries include four Ni(111) (4×4) unit cells. Ni atoms are not shown. In Fig. 4, small, medium, and large balls represent carbon, nitrogen, and boron atoms, respectively.

In order to get a stable configuration of C$_{60}$ adsorbed on h-BN/Ni(111), we consider C$_{60}$ adsorbed on highly symmetric positions of h-BN/Ni(111): The center of a hexagonal or pentagonal face of C$_{60}$ on the fcc, hcp, and top sites of Ni(111). In these configurations, a hexagon or a pentagon of the C$_{60}$ is parallel to the h-BN/Ni(111) substrate. The top site is that the center of C$_{60}$ is on top of the N atom, while the fcc site is that on top of B atom. We optimized the stable structures of these configurations. Again, all atoms, except for the bottom two Ni layers were allowed to relax until the forces on atoms smaller than 0.03 eV/Å. The procedure corresponds to a precision in total energy of 0.01 eV.

We found that the geometry in which a hexagon of C$_{60}$ is parallel to the h-BN/Ni(111) is about 0.1 eV in energy more favorable than that of a pentagon of C$_{60}$ is parallel to the substrate (Fig. 4). Adsorption of C$_{60}$ on the top of N is 0.02 and 0.01 eV more favorable in energy than on the top of B and on the hcp site of Ni(111), respectively, when the hexagon face of C$_{60}$ to the substrate. For the pentagon of C$_{60}$
parallel to the substrate, it is also the most favorable for C_{60} on the N top site compared with the center of C_{60} on the top of B or on hcp site of Ni(111), but the difference is smaller than 0.003 eV, beyond the calculation accuracy. It is worth noting that the energy difference for C_{60} on top, fcc, hcp site is smaller than 0.02 eV. It means if a single C_{60} molecule moves on the h-BN/Ni(111) surface, the translation barrier is small since the interaction of C_{60} molecules is quite weak; see, e.g., Ref. 21.

Our calculations show that the change of the bond length of C_{60} induced by adsorption on the substrate is smaller than 0.1%, compared with that of an isolated C_{60} molecule. The corrugation of h-BN layer of 0.1 Å of h-BN/Ni(111) remains almost unchanged upon C_{60} adsorbed. For the most stable adsorption sites of C_{60} on h-BN/Ni(111), that is, a hexagon of C_{60} parallel to the h-BN/Ni(111) and the center of C_{60} on the top of N site, the calculated results show that the average distance between of the hexagon face of C_{60} and the substrate N is about 3.6 Å. It is different than the situation of C_{60} adsorbed on metal substrate.\(^3\) This is expected because the interaction of the hexagonal face of C_{60} with the substrate h-BN sheet is similar to stacking a graphite sheet on a h-BN sheet. As comparison, the interlayer spacing of graphite sheets is 3.35 Å and that of hexagonal boron nitride sheets is 3.33 Å. Similar to the interaction between the graphite sheets as well as between the hexagonal boron nitride sheets, the interaction between the monolayer C_{60} and the h-BN/Ni(111) substrate should be van der Waals in nature. The somewhat large value of distance between C_{60} and h-BN may be contributed to the GGA exchange-correlation energy functional. Generally, it may be overestimated. In the density functional theory the long-range interaction cannot be correctly described and van der Waals interactions are not accounted for.

We determine the adsorption energy of C_{60} on h-BN/ Ni(111) as 0.47 eV, smaller than for an isolated C_{60} on graphite sheet, 0.96 eV.\(^2\) This difference is reasonable since graphite is metallic and h-BN is insulating, so that there is a stronger interaction between C_{60} and graphite. We further look at the energy barrier of rotation around the sixfold axis of C_{60} on h-BN/Ni(111) (rotating clockwise and the configuration of Fig. 4 being the angle of 0°). The calculated rotation dependence of the adsorption energy is plotted in Fig. 5. The rotation barrier is about 0.22 eV, near the angle of 30°. It has been found that the orientation of C_{60} on graphite is ordered at a low temperature, and remains ordered over a wide temperature range.\(^23,24\) However, we find the rotation barrier of a isolated C_{60} layer is fairly similar to that of the adsorbed C_{60} layer on h-BN/Ni(111). The rotation barrier for the isolated C_{60} layer is about 0.23 eV. This means at least the rotation energy landscape in the figure is not contributed by the interaction between C_{60} and h-BN, but mainly by the intralayer interaction of C_{60} molecules themselves. The interaction between the C_{60} molecules and the substrate is dominated by π-like orbitals of C_{60} and h-BN and is quite weak.

In order to show the change of electronic structure upon C_{60} adsorption on h-BN/Ni(111), we show local density of states of h-BN/Ni(111) upon C_{60} on h-BN/Ni(111) in Fig. 6. As comparison, the LDOS of the h-BN/Ni(111) is also plotted. In Fig. 6 the solid and dashed curves represent the LDOSs of C_{60}/h-BN/Ni(111) and for the substrate h-BN/Ni(111), respectively. Upon adsorption of C_{60}, the change in LDOS is very small. The magnetic moment on BN changed only slightly, about 0.001μ_B. The unchanged electronic structure reflects again the weak interaction between the C_{60} molecule and the h-BN/Ni(111).

In Fig. 7 we plot the LDOS of C_{60} on h-BN/Ni(111); the dotted curve in the figure represents the LDOS of a single C_{60} layer with the same orientation. For C_{60} adsorbed on metal surfaces, it has been found that the width of the band derived from the lowest unoccupied molecular orbital of C_{60} is sensitive to interaction between C_{60} and the substrate. From Fig. 7, we find that the LDOS remains almost unchanged upon C_{60} being adsorbed, indicating a weak interaction between C_{60} and h-BN/Ni(111).

The interaction between C_{60} and the h-BN/Ni(111) substrate is weak; however, we find a 0.13 electron per surface unit cell transfer from the h-BN/Ni(111) to the C_{60}. The charge transfer is calculated by using a Bader-like approach.\(^25\) That is, we first find the bond critical plane by
using the condition of $\partial \rho(x,y,z)/\partial z=0$ in the interface region between the C$_{60}$ and h-BN. Since the distance between the bottom of C$_{60}$ and the h-BN layer is 3.6 Å, the resulting charge transfer should be reliable.

In order to see charge transfer more clearly, we plot the charge density difference for C$_{60}$/h-BN/Ni(111) in Fig. 8. It was calculated by subtracting the charge density of the single C$_{60}$ layer and the h-BN/Ni(111) substrate from that of C$_{60}$/h-BN/Ni(111). All charge densities are calculated separately with atomic positions kept the same as in the optimal configuration of C$_{60}$/h-BN/Ni(111). It is shown that for a C$_{60}$ hexagon facing the substrate, the charge transfer from h-BN to C$_{60}$ is mainly localized in the interface region of C$_{60}$ and h-BN. The transfer is induced by the interaction between the $\pi$ orbital of h-BN and $\pi$-like orbital of C$_{60}$. It can be seen clearly from droplet distribution of Fig. 8 that not only the bottom hexagon of C$_{60}$ on the substrate, but also the neighbor faces (one pentagon and one hexagon) get charge. We can clarify features of the charge density between C$_{60}$ and h-BN. The features are quite similar to those of interlayer states between graphite layers, as well as between h-BN layers. This character also was found in the case of C$_{60}$ encapsulated in a BN nanotube or in a carbon nanotube, as well as C$_{60}$ on graphite surfaces or on h-BN surfaces.\cite{115436-6}

There are two differences between the graphite and h-BN: (1) Graphite is semimetallic, while h-BN is insulating; (2) the corrugation of 0.1 Å of h-BN layer. Compared with graphite, less charge will transfer from h-BN to C$_{60}$ because there are fewer states of h-BN near the Fermi level. When both Fermi levels of h-BN and C$_{60}$ are aligned, there will be only little charge transfer from the h-BN layer and the C$_{60}$ layer, if any.

The electronic structure of C$_{60}$ is sensitive to orientation. In a C$_{60}$ molecule there are two kinds of bonds, one between two neighboring pentagons (the short bond or the so-called double bond), the other between hexagon and pentagon (the long bond or the so-called single bond). The short bonds have stronger $\pi$ character than the long ones. The most interesting aspect of the electronic structures of C$_{60}$ comes from the active $\pi$-like orbitals. Charge transfer occurs mainly due to the interaction between the $\pi$-like orbitals of C$_{60}$ and h-BN. When a C$_{60}$ molecule rocks on h-BN/Ni(111), the number of $\pi$-like orbitals of C$_{60}$, which can contribute to the interaction to the h-BN layer, will changed. Could this motion lead to change in charge transfer?

We let C$_{60}$ have a rocked orientation around an axis that goes through the center of C$_{60}$ and is parallel to the short bond and the long bond of the hexagon of C$_{60}$, respectively, in order to check the effect of rocking motion on the charge state of C$_{60}$ on h-BN/Ni(111). This was done for cases in which the rocking angle around the axis is 21.14$^\circ$ and -20.43$^\circ$, respectively. For the rocking angle of 21.14$^\circ$, two faces beside the short bond are hexagonal, while for that of -20.43$^\circ$, two faces besides the long bond are hexagonal and pentagonal, respectively. The adsorption energy for this rocking is very close to that of without rocking, only 0.02 and 0.01 eV higher, respectively. The charge transfer between the substrate and the C$_{60}$ layer is 0.14 and 0.13 electrons per C$_{60}$ molecule for the short and long bond closest to the substrate, respectively. Compared to the case without rocking, the charge transfer is almost unchanged. But the distribution is somewhat different due to the change of the active $\pi$ orbital orientation (see Fig. 9). This result implies that the charge transfer does not depend on the orientation of the molecules in the monolayer. The charge transfer of 0.13e is fairly consistent with the experimental results at low temperature, but

**FIG. 7.** Local density of states of C$_{60}$ for C$_{60}$/h-BN/Ni(111). The upper and lower panels represent majority and minority components, respectively.

**FIG. 8.** (Color online) Charge transfer in C$_{60}$/h-BN/Ni(111). The isosurface indicates a value of ±0.0002e per surface unit cell. Green, gain of electrons; red, loss of electrons.
inconsistent with those results at high temperature,\(^5\) which could be induced by the electron-phonon coupling which cannot be treated exactly in our calculations. However, this discrepancy may indicate that the temperature-dependence charge transfer could be attributed to electron-phonon coupling, as suggested by Muntwiler et al.\(^5\)

IV. CONCLUSIONS

In summary, the geometric and electronic structures of one monolayer of C\(_{60}\) on a monolayer h-BN/Ni(111) surface have been studied by first-principles calculations based on density functional theory. In order to find the most stable structure of a (1×1) commensurate monolayer h-BN on Ni(111), various adsorption sites including top, fcc, and hcp of Ni(111) are considered. The most stable structure is found to be N on top and B on the fcc site of the Ni(111) surface. The h-BN layer is corrugated by the B atom being closer to the Ni(111) surface than the N atom. The deposition of C\(_{60}\) on h-BN/Ni(111) does not change the corrugation of the h-BN layer. A bottom hexagon of C\(_{60}\) parallel to the substrate is 0.1 eV more favorable in energy than a pentagon, and the adsorption of C\(_{60}\) on top of N is 0.02 and 0.01 eV more favorable in energy on top of N than on top of B as well as on the hcp site of Ni(111) when the hexagon of C\(_{60}\) faces the substrate. For the most stable adsorption sites of C\(_{60}\) on h-BN/Ni(111), the distance between the bottom hexagon of C\(_{60}\) and the substrate N is about 3.6 Å, and the change of the bond length of C\(_{60}\) induced by adsorption on the substrate is smaller than 0.1%, compared with an isolated C\(_{60}\) molecule. The effects of orientation of C\(_{60}\), including rotation along the axis perpendicular to the surface and rocking orientations around the center of C\(_{60}\), also were considered. The calculated results show that the energy difference for all rotation orientations is smaller than 0.22 eV. The calculated electronic structures confirm that h-BN/Ni(111) is a good platform to study properties of a two-dimensional C\(_{60}\) monolayer, since only a weak interaction and little charge transfer can be found between C\(_{60}\) and h-BN/Ni(111). No magnetic moment is found for the C\(_{60}\) monolayer, although the BN layer is slightly spin polarized induced by the Ni beneath. The spin polarization of Ni at the h-BN/Ni interface is smaller than that of the bulk atoms.

ACKNOWLEDGMENTS

This work is supported by the U.S. Department of Energy, Office of Basic Energy Science, under Grant No. DE-FG02-97ER45660. The calculations were performed at CCS/ ORNL via CNMS and DOE allocations.

\(^{9}\)J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992). For carbon materials, it is commonly agreed that the local density approximation (LDA) leads to a reasonable description. However, the LDA will give a lattice constant of 3.42 Å for bulk Ni and for a 4×4 reconstruction of Ni(111), it leads to a C\(_{60}\)-C\(_{60}\) distance of 9.67 Å, while the GGA will give a more reasonable lattice constant, 3.52 Å, and the corresponding distance between...
C_{60} and C_{60} is 9.95 Å. Therefore we adopt the GGA.

16 The calculated Fermi level of the \( h \)-BN/\( \text{Ni}(111) \) is not aligned with that of the single \( h \)-BN layer, but we align their lowest \( \sigma_3 \) bands instead, because for an insulator or a semiconductor the calculated Fermi level might be set at any energy position in the gap.