

Charge-transfer mechanism for the (monolayer graphite) /Ni(111) system

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The electronic states of a monolayer of graphite on a Ni(111) substrate are investigated with use of first-principles self-consistent calculations. A notable feature of this system is that a formerly empty π^* orbital of the graphite overlayer is now occupied because of its interaction with the occupied orbitals of the nickel substrate. Because there is a substantial spatial overlap between the wave functions of the substrate and overlayer orbitals, and because their energy difference is small, a charge transfer into the overlayer π^* orbital occurs.

The formation of monolayer graphite on transition-metal and transition-metal carbide surfaces recently has attracted much interest.¹⁻¹⁰ In particular, the geometric structure and electronic states of a monolayer graphite on Ni(111) have been studied in detail with various experimental techniques.³⁻⁶ For example, Aizawa *et al.*³ using high-resolution electron-energy-loss spectroscopy (HREELS), found an anomalous softening of phonons which is induced in monolayer graphite on Ni. They consider the softening to be caused by a charge transfer from the metal d bands to the carbon p bands. In this paper, we report results of first-principles self-consistent calculations performed to study quantitatively the charge transfer from the Ni substrate to the graphite overlayer due to the interaction between them.

Numerical calculations in the present work were done with use of the self-consistent-charge discrete variational $X\alpha$ (SCC-DV- $X\alpha$) method, details of which have been reported elsewhere.¹¹ In this method, the Hartree-Fock-Slater (HFS) equation for a cluster is self-consistently solved with use of a localized exchange potential ($X\alpha$ potential). The adjustable (exchange-correlation) parameter α is usually taken to be 0.7. Numerical nickel $1s-4p$ and carbon $1s-2p$ atomic orbital, which were obtained as solutions of the atomic HFS equations, were utilized as basis sets.

Figure 1 shows the cluster model for a monolayer of graphite on Ni(111) [hereafter referred to as the 22-atom (ML graphite)/Ni cluster: $C_6H_6Ni_{10}$] employed in this calculation. This model is constructed on the basis of precise data extracted from surface extended energy-loss fine-structure experiments.⁶ The lattice constant of the graphite overlayer is expanded by about 2% as compared with that of bulk graphite. The carbon atoms in this cluster are located at threefold sites on the Ni(111) surface. The bonds of all carbon atoms at the edges of the graphite overlayer were saturated with hydrogen atoms so as not to leave any (unsaturated) dangling bonds. These C-H bond lengths were taken to be equal to the C-C bond length: 1.45\AA . We have also studied the electronic states of two constituent clusters for comparison:

one associated with the overlayer, C_6H_6 (12-atom graphite-cluster), and another associated with the substrate, Ni_{10} (10-atom Ni-cluster). These three clusters were uniformly calculated with C_{3v} point-group symmetry, although the 12-atom graphite-cluster actually has higher symmetry, D_{6h} .

Energy levels, labeled with irreducible representations of the C_{3v} point group, in the valence and the conduction bands for these clusters are presented in Fig. 2. The C_6H_6 cluster is essentially a benzene molecule, except possibly for the difference in bond lengths. The question then arises whether or not it can serve as a good model of the graphite overlayer. To gain some insight, we also studied a larger single-layered cluster, $C_{24}H_{12}$, composed of a honeycomb structure having D_{6h} symmetry. With a larger number of honeycomb units, the resultant basis sets contain some additional orbitals between the original energy levels that belong to the 12-atom graphite cluster, although it is clear that the primitive π -level structure for the 12-atom graphite cluster remains almost unchanged. Moreover, the hydrogen atoms in both the C_6H_6 and $C_{24}H_{12}$ clusters are found to bind only in σ bonding,

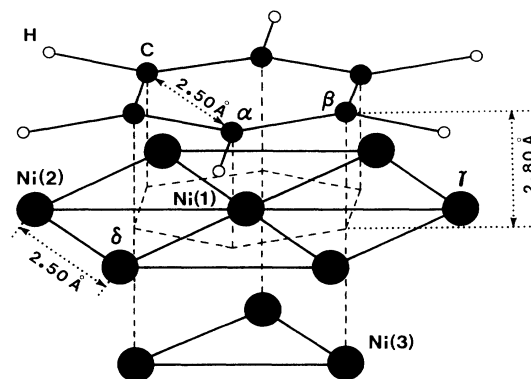


FIG. 1. Schematic illustration of the 22-atom (ML graphite)/Ni cluster.

which means they are not expected to be significant factors because it is the π bonds that play an important role in the charge transfer. Therefore, we conclude that the 12-atom graphite cluster (C_6H_6) suffices as a model for the graphite overlayer in the 22-atom (ML graphite)/Ni cluster. On the other hand, the 10-atom Ni cluster is also shown to have a size large enough to represent the substrate, by comparison to ultraviolet-photoemission-spectroscopy (UPS) experimental results¹² for bulk Ni and to calculations for a cluster consisting of nine Ni atoms.¹³

As seen in Fig. 2, the overall features of the level structure for 22-atom (ML graphite)/Ni cluster can nearly be explained naturally by a superposition of the level structures for the 12-atom graphite cluster and the 10-atom Ni cluster, with some resultant hybridized orbitals included. The dashed lines connect the molecular orbitals (MO's) of the 22-atom (ML graphite)/Ni cluster with those corresponding to the respective constituent clusters. The superposition indicates that the interaction between the overlayer and the substrate is very weak; in particular, the substrate has little effect on the σ bonds in the intralayer of the graphite monolayer. The result is also consistent with some earlier reports: For example, the UPS experiments of Rosei *et al.* confirmed that the electronic structure of a monolayer of graphite growing on Ni(111) is very similar to that of bulk graphite (pristine

graphite) except for a small and almost rigid shift of the Fermi level.^{4,5} Painter and Ellis¹⁴ showed that the optical properties of pristine graphite could be fully deduced from the band structure of a graphite monolayer. In Fig. 2 are shown specified orbitals which stem from the 22-atom (ML graphite)/Ni cluster. The orbitals $27a_1$ to $56e$ correspond to the π bond. They appear upon the hybridization of orbitals $22a_1$ to $33a_1$ of the 10-atom Ni cluster with the four π orbitals of the 12-atom graphite cluster. In particular, it should be noted that one of the hybridized orbitals, the occupied $48e$ orbital is generated from an admixture of the occupied $41e$ orbital of the 10-atom Ni cluster with the $8e$ (empty π^*) orbital of the 12-atom graphite cluster and that the $48e$ orbital is an antibonding π^* orbital. The contour map in Fig. 3(a) for the $48e$ orbital of the 22-atom (ML graphite)/Ni cluster shows that the antibonding π^* orbital binds with the $3d$ orbitals of the Ni substrate, suggesting the possibility of a charge transfer from the substrate to the overlayer, which appears more clearly in the difference charge-density map, $\Delta\rho = \rho$ (22-atom (ML graphite)/Ni cluster) - ρ (12-atom

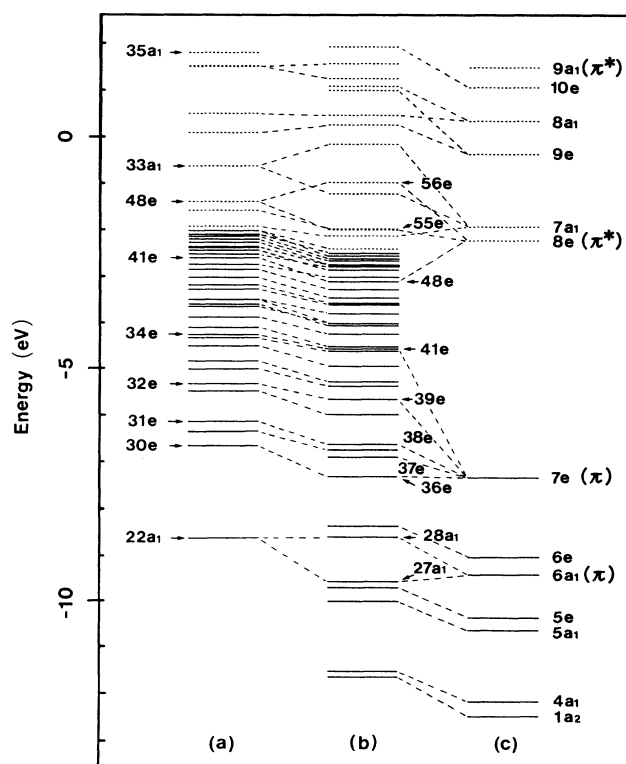


FIG. 2. Energy-level structures of the clusters: (a) 10-atom Ni cluster, (b) 22-atom (ML graphite)/Ni cluster, and (c) 12-atom graphite cluster. Solid and dotted lines show occupied and unoccupied levels, respectively. Connections between levels are indicated by dashed lines.

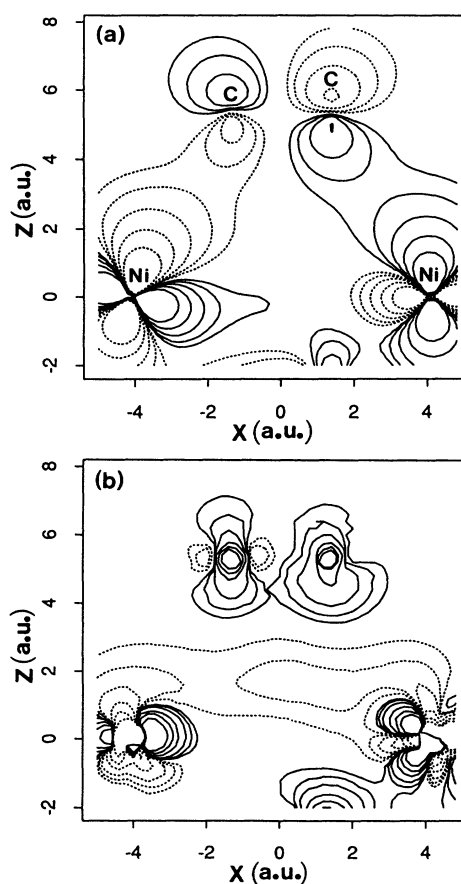


FIG. 3. Contour maps of (a) the occupied $48e$ molecular orbitals for the 22-atom (ML graphite)/Ni cluster and (b) difference charge density $\Delta\rho$. The contours are drawn for the plane perpendicular to the Ni substrate, including atoms labeled $\alpha, \beta, \gamma,$ and δ in Fig. 1. In (b) the solid and the dotted lines indicate the amount of the accumulated and the depleted charges, respectively.

TABLE I. Net charges for the employed clusters.

Atoms	22-atom (ML graphite)/Ni cluster	12-atom graphite cluster	10-atom Ni cluster
H	0.131	0.158	
C	-0.205	-0.158	
Ni(1)	0.017		-0.078
Ni(2)	0.077		-0.019
Ni(3)	-0.013		0.063

graphite cluster) $-\rho$ (10-atom Ni cluster), shown in Fig. 3(b), because the contours in the figure reflect the amount of charge stored in the π orbitals of the graphite overlayer. The charge increment in the π orbital causes a decrease in the number of electrons in the $3d$ and $4s$ orbitals of the outermost layer [Ni(1) and Ni(2)] of the Ni substrate, whereas the charge of Ni(3) in the second layer increases, as evidenced by a Mulliken population analysis (see Table I). A similar behavior has been found for the system of chlorine adsorbates on semi-infinite jellium surfaces.^{15,16} A charge transfer from the outermost layer of the jellium surface region to the Cl adatoms gives rise to a charge depletion in the surface layer and in an accumulation of charge near the subsurface beneath it. These changes in the charge distribution have been interpreted as Friedel oscillations induced by the adatoms. The following two reasons for the formation of the occupied antibonding π^* orbital in the 22-atom (ML graphite)/Ni cluster may be considered: The first, major reason is indicated in the contour maps of the $8e$ orbital for the 12-atom graphite cluster and the $41e$ for the 10-atom Ni cluster shown, respectively, in Figs. 4(a) and 4(b); by superimposing both figures, the wave function of the occupied $41e$ orbital protruding normal to the Ni surface is seen to overlap extensively with that of the empty π^* $8e$ orbital. The second, minor reason is, as is evident from Fig. 2, that the $41e$ energy level is quite close to the $8e$ level. Because these criteria are satisfied, charge transfer is likely to occur.

The presently proposed charge-transfer mechanism may also apply to the 2×2 and 7×7 modulations of the charge density observed in scanning-tunneling-microscope (STM) images of monolayer graphite on a TiC(111) surface.¹⁷ The periodicity is consistent with a so-called moiré fringe originating from a lattice mismatch between the substrate and the overlayer. Since the (111) polar surface of TiC has been known to terminate with Ti atoms,¹⁸ the STM result suggests that the wave functions of Ti atoms and the overlayer could be almost completely superimposed at a given periodicity (namely, the common periodicity of the overlayer and substrate), under the above criteria, so that the charge transfer would take place.

In summary, we have pointed out the presence of charge-transfer processes in monolayer graphite on Ni(111) by the SCC-DV- $X\alpha$ calculations. The following two conditions are necessary for the onset of charge transfer into a previously unoccupied antibonding π^* orbital in the overlayer: (1) the wave function of the occu-

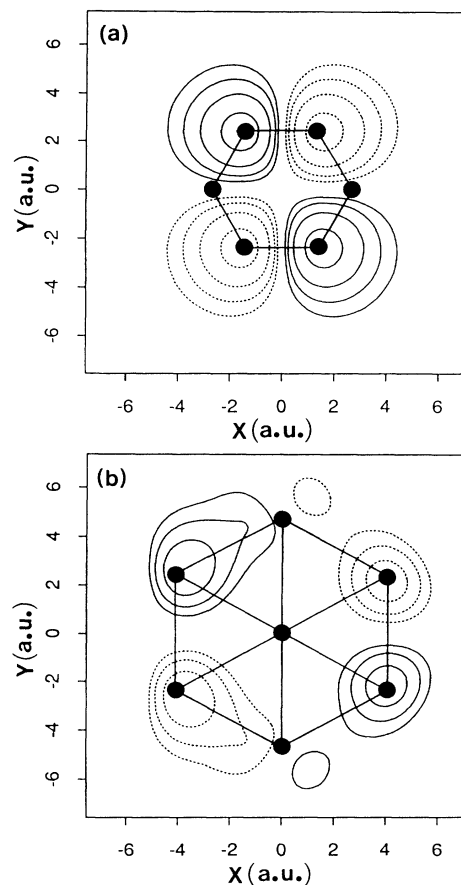


FIG. 4. Contour maps of the $8e$ molecular orbitals for (a) the 12-atom graphite and (b) the $41e$ molecular orbitals for the 10-atom Ni cluster. The respective contours are depicted in a horizontal plane at a distance of 2.0 a.u. from both the C_6H_6 plane of the 12-atom graphite cluster and the outermost layer of the 10-atom Ni cluster. Positive (negative) lobes of the Ni orbital point toward positive (negative) lobes of the graphite p_z orbital. Coupling of the $8e$ orbital in (a) with the $41e$ orbital in (b) leads to the resultant $48e$ orbital in the 22-atom (ML graphite)/Ni cluster in Fig. 3(a).

ried $41e$ orbital of the Ni substrate overlaps considerably with that of the empty π^* orbital of the graphite overlayer; (2) the energy difference between both the occupied orbital and the empty orbital is small enough for creating the characteristic charge transfer.

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