

# Intercalation of copper underneath a monolayer of graphite on Ni(111)

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Angle-resolved photoemission and scanning tunneling microscopy have been applied to study the intercalation of copper underneath a monolayer of graphite (MG) on Ni(111). The room-temperature deposition of copper on MG/Ni(111) in the coverage range 4–12 Å leads to the growth of Cu islands on the MG. Annealing of the “as-deposited” system at a temperature of 400 °C results in the intercalation of all Cu atoms underneath the MG. The intercalation of Cu is followed by a shift of the graphite-derived valence bands toward energies that are characteristic of pristine graphite. This observation is understood in terms of a weakening of chemical bonding between the MG and the substrate in the MG/Cu/Ni(111) system.

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## I. INTRODUCTION

For quite some time, graphite intercalation compounds (GIC's), synthesized on the basis of various metals, have been attracting considerable interest, mainly due to the pronounced anisotropies in the electronic and electrical properties of these materials.<sup>1–6</sup> From a fundamental point of view, GIC's form an interesting group of layered materials,<sup>7,8</sup> that are characterized by various degrees of charge transfer from the guest atoms to the unoccupied antibonding  $\pi^*$  states of graphite. This gives rise to a wide spread in chemical bonding between intercalant and graphite layers, ranging from ionic to covalent contributions. Although a large variety of metals has been intercalated successfully into graphite, there are a number of transition metals, including Cu, that do not form bulk GIC's. It has been shown that vacuum deposition of copper onto the surface of pristine graphite followed by annealing leads to the formation of islands on the graphite surface.<sup>9</sup> On the other hand, incorporation of copper into a graphite matrix is of particular high interest. As shown in Refs. 10 and 11, Cu-C, grown by plasma cosputtering of graphite and copper targets, leads to materials that are characterized by a semiconductor-metal transition as a function of copper content.<sup>10</sup> In addition, these materials are expected to exhibit high-temperature superconducting behavior.<sup>11</sup> On the basis of correlations in the stoichiometries of these Cu-C films and those of classical GIC's, it was supposed that the above properties might be related to the possible formation of clusters of Cu-derived GIC's in the bulk of such Cu-C systems. Therefore, a study of the growth, the crystalline structure, and the electronic structure of these well-ordered and stable graphite-intercalation-compound-like materials with Cu is also of substantial interest from a technological point of view.

Quite recently, the possibility of the formation of GIC-like materials by intercalation of various atoms underneath a monolayer of graphite (MG), grown on the (111) surfaces of

transitional metals, was reported in the literature.<sup>12–17</sup> In particular, intercalation of alkaline atoms underneath a MG on Ni(111) was studied by photoemission (PE).<sup>13</sup> It was found, that the valence bands of the MG/A/Ni(111) systems (A = Cs, Na, and K) exhibit structures similar to those of bulk alkali GIC's, i.e., they are characterized by charge transfer from the alkali atoms to the unfilled  $\pi^*$ -like states of the graphite monolayer. In a recent paper,<sup>14</sup> intercalation of various atoms with quite different ionization potentials underneath a MG on Ir, Ni, and Re substrates was analyzed. It was shown that atoms with low ionization potential (e.g., alkali atoms) will be positively charged upon intercalation, and can only form a single monolayer underneath the MG on Ni(111). At the same time, atoms with a large ionization potential (like Pt, Si, C, and others) are bound to the MG by only weak van der Waals forces, resulting in intercalated layers of larger thickness. The successful intercalation of Cu underneath a MG on Ni(111) was reported in a high-resolution electron-energy-loss-spectroscopic study.<sup>17</sup> It was found that the incorporation of Cu is followed by an energy shift toward higher loss energies of the graphite-derived phonon modes with respect to their positions in MG/Ni(111). This shift almost completely compensates the one that is observed between single crystalline graphite and a MG/Ni(111); this latter shift was interpreted as being due to strong interaction between the MG and Ni(111). It also stimulates more detailed studies of the nature of chemical bonding between a MG and various metallic substrates.

In the present work, Cu was deposited onto a graphite monolayer grown on Ni(111). Subsequent annealing of the system at various temperatures led to the intercalation of copper underneath the MG as concluded from a combined study by angle-resolved PE, scanning-tunneling microscopy (STM), and low-energy electron diffraction (LEED). Measurements of the PE spectra were carried out in the  $\Gamma$ -K direction of the Brillouin zone (BZ) of graphite for the MG/Ni(111) and the MG/Cu/Ni(111) systems. It was shown that

intercalation of Cu causes an energy shift of the MG-derived valence bands toward lower binding energies with respect to the corresponding bands in bulk graphite.

## II. EXPERIMENTAL DETAILS

The experiments were performed in two different ultrahigh-vacuum chambers under very similar experimental conditions, with the vacuum better than  $5 \times 10^{-10}$  mbar during the measurements in both cases. Angle-resolved photoemission studies were carried out with an ARIES spectrometer (VSW, Ltd.) at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using monochromatic light from the TGM4 beamline equipped with a toroidal-grating monochromator. The overall-system resolution was set at 100-meV full width at half maximum. Valence-band PE spectra of a clean Ni(111) surface, the MG/Ni(111) system, and the MG/Cu/Ni(111) system were taken with 30- and 50-eV photons. STM measurements were carried out in a separate experimental setup with a lateral resolution of  $\approx 2$  Å (for further details, see Refs. 18 and 19).

*In situ* cleaning of the Ni(111) substrate was performed by preliminary annealing at 800 °C, followed by sputtering with 1-keV Ar ions at ion currents of  $\approx 5 \mu\text{A}$ , and finally two steps of annealing in O<sub>2</sub> and H<sub>2</sub> atmospheres at pressures of  $5 \times 10^{-8}$  mbar and temperatures of 500 and 230 °C, respectively. After this procedure, the LEED patterns revealed sharp  $1 \times 1$  spots from a hexagonal structure corresponding to the atomically clean Ni(111) surface. A monolayer of graphite was grown on the clean Ni(111) surface by cracking propylene (C<sub>3</sub>H<sub>6</sub>) at a substrate temperature of 500 °C. Exposure of the substrate for  $\approx 5$  min to a propylene pressure of  $1 \times 10^{-6}$  mbar was enough to form the MG on Ni(111). Thereafter, LEED patterns revealed a hexagonal structure with a pronounced threefold symmetry, which is characteristic for the (0001) surface of graphite. Copper films were deposited onto the graphite-covered Ni(111) surface at room temperature using a tantalum crucible that was heated by electron bombardment. The deposition led to the formation of Cu islands on the graphite monolayer, as demonstrated by STM images of the surface, as well as a background level in the corresponding LEED patterns. Annealing of the system at 400 °C resulted in the intercalation of the copper atoms underneath the MG, with very sharp LEED patterns quite similar to those observed in a previous study of the MG/Cu/Ni(111) system.<sup>17</sup>

## III. EXPERIMENTAL RESULTS

Valence-band PE spectra taken in normal-emission geometry with 50-eV photons are shown in Fig. 1 for Ni(111), a MG/Ni(111), 4 Å of Cu deposited on a MG/Ni(111), and for this latter system upon annealing at 400 °C. For comparison, a spectrum is also shown that was measured for the MG/Ni(111) system after deposition of 12-Å Cu followed by the corresponding annealing step. The spectrum for MG/Ni(111) is similar to the one reported before for this system.<sup>13</sup> In the energy distribution curves shown, features originating from the  $\pi_{1v}$  states of graphite and the 3d states of Ni (marked in

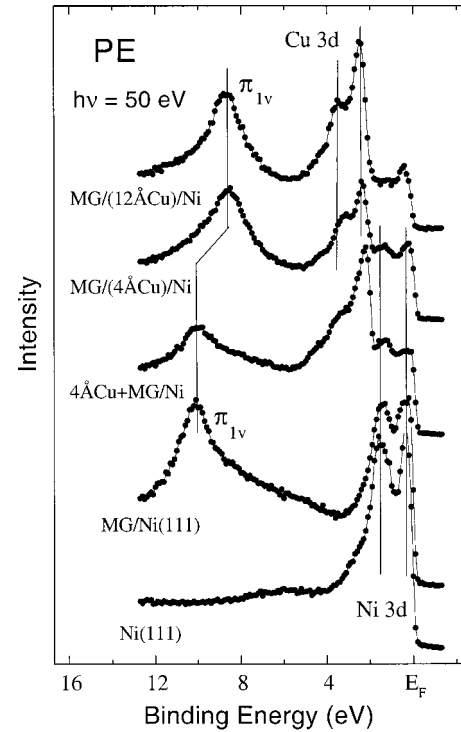


FIG. 1. PE spectra of the clean Ni(111) surface, a MG/Ni(111), 4 Å of Cu on MG/Ni(111), as well as the MG/(4-Å Cu)/Ni(111) and the MG/(12-Å Cu)/Ni(111) systems. The spectra were taken with 50-eV photons in normal-emission geometry.

Fig. 1) can be readily distinguished. Upon deposition of copper on MG/Ni(111) at room temperature, the PE intensity of the  $\pi_{1v}$  graphite states decreases, but remains clearly visible. Annealing of the MG/Ni(111) system with the 4-Å-thick overlayer of Cu leads to an increase of the intensity of the  $\pi_{1v}$  graphite states at the cost of the Cu 3d signal and a shift of the  $\pi_{1v}$  bands toward lower binding energies (BE's). Thereby, the Ni-3d response is almost unaffected by the annealing. Deposition of 12-Å Cu on MG/Ni(111), with subsequent annealing, causes similar changes of the MG/Ni(111) spectra, though with the difference that the Ni-3d states can no longer be distinguished due to the increased thickness of the copper layer. We assign the enhancement of the  $\pi_{1v}$  signal and the energy shift of the  $\pi_{1v}$  bands upon annealing of both systems to an intercalation of the copper atoms underneath the monolayer of graphite. The energy shift of the  $\pi_{1v}$  bands is caused by a change of chemical bonding between the MG and the substrate through intercalation of Cu.

STM images of the MG/Ni(111) system before and after deposition of 8-Å Cu are presented in Figs. 2(a) and 2(b), respectively. Analogous data for MG/Ni(111) with an 8-Å-thick Cu overlayer upon annealing at 400 °C is shown in Fig. 2(c). All images were taken in the constant-current mode. The tip voltage ( $V_t$ ) and the tunneling current ( $I_t$ ) were set to  $-1$  V and 1 nA, respectively. The area of the measured STM images is  $750 \text{ Å} \times 750 \text{ Å}$ . As seen in Fig. 2(a), the clean MG/Ni(111) surface is characterized by a few steps and dislocations (straight lines), caused by the stepped character of the Ni(111) surface, and the formation of different

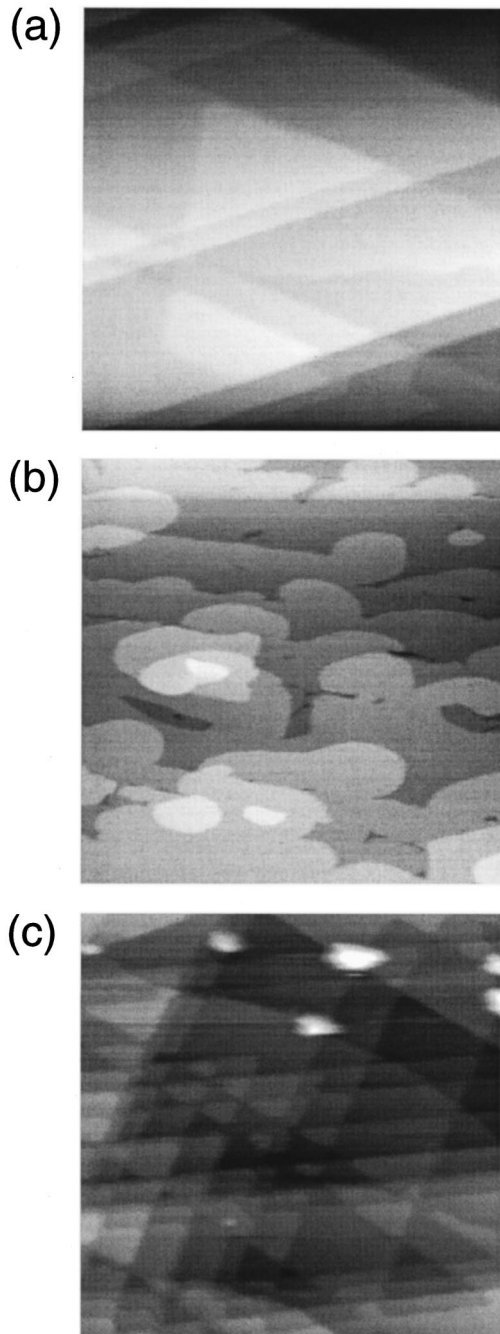


FIG. 2. STM images of the (a) MG/Ni(111), (b) 8-Å Cu on MG/Ni(111), and (c) MG/(8-Å Cu)/Ni(111) systems. The images were taken in constant-current mode,  $I_t = 1$  nA, and  $V_t = 1$  V. Scanning areas were  $750 \times 750 \text{ Å}^2$ .

domains within the graphite overlayer. The STM image in Fig. 2(b) clearly shows the formation of Cu islands on top of the “as-grown” Cu/MG/Ni(111) system. Annealing of this system at  $400^\circ\text{C}$  leads to the disappearance of the Cu islands. Thereby, the STM image changes in such a way as to become similar to that measured for the MG/Ni(111) system (except for some additional defects).

Figure 3 presents a series of angle-resolved PE spectra ( $h\nu = 50$  eV) taken from a clean MG/Ni(111) interface along

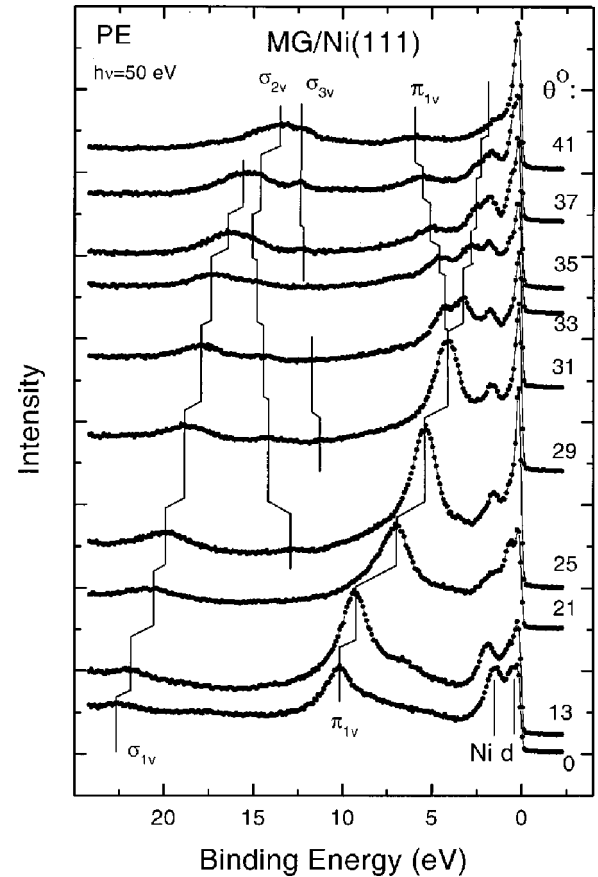


FIG. 3. Angle-resolved PE spectra of MG/Ni(111) recorded with 50-eV photons along the  $\Gamma$ -K direction of the BZ of graphite.

the  $\Gamma$ -K direction of the Brillouin zone of graphite for different polar angles,  $\Theta$ . The  $\pi_{1v}$ ,  $\sigma_{1v}$ ,  $\sigma_{2v}$ , and  $\sigma_{3v}$  states with their characteristic dispersions for graphite, can be clearly distinguished in the spectra. However, these graphite-derived states are shifted, toward higher BE's as compared to their positions in the graphite spectra.<sup>5,20</sup> The observed shifts are different for the  $\pi$  and  $\sigma$  states: For the  $\pi_{1v}$  state, this shift is about 2.0 eV, while it is approximately 1.0 eV for the  $\sigma$  states. In the MG/Ni(111) system, the  $\pi_{1v}$  state at the  $\Gamma$  point has a binding energy of  $\approx 10$  eV. With an increasing polar angle of the detected photoelectrons, the BE of the  $\pi_{1v}$  state decreases to only 3.3 eV for  $\Theta \approx 30^\circ$ ; this corresponds to emission of electrons from near the K point of the surface BZ of graphite. A further increase of the polar angle leads to a splitting of the  $\pi_{1v}$  band into two components. One component shifts back towards higher BE's while the other component moves closer to the Fermi level ( $E_F$ ) to a BE as small as  $\approx 1.8$  eV. The  $\sigma_{2v}$  and  $\sigma_{3v}$  states are degenerate at the  $\Gamma$  point at a BE of  $\approx 5.3$  eV.

Energies of the PE bands measured for the MG/Ni(111) system with 30- and 50-eV photons are plotted in Fig. 4 as a function of  $k_{\parallel}$ . For comparison, dispersion curves for single-crystalline graphite taken from Ref. 5 are also shown by dashed lines. As seen in the figure, all dispersing branches characteristic for pristine graphite can be observed for the MG/Ni(111) system. At the  $\Gamma$  point, the  $\pi_{1v}$  and  $\sigma_{1v}$  states are found at BE's of 10.2 and 22.5 eV, respectively, whereas

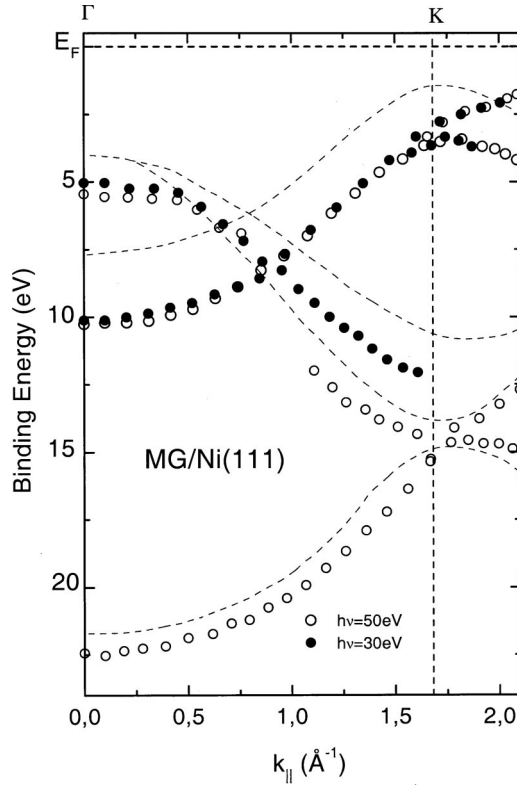


FIG. 4. Experimental band structure of the MG/Ni(111) system. The data taken with 30- and 50-eV photons are shown by solid and open circles, respectively. For comparison, the band structure of pristine graphite is presented by dashed lines.

the  $\sigma_{2,3v}$  states are located at a BE of 5.3 eV. A minimum BE for the  $\pi_{1v}$  band (3.3 eV) is measured at  $k_{\parallel} \approx 1.7 \text{ \AA}^{-1}$  (where  $k_{\parallel}$  is the component of the wave vector parallel to the surface), corresponding to the  $K$  point of the BZ of graphite. In comparison with pristine graphite, the  $\pi$  and  $\sigma$  states are shifted toward higher BE's. For instance, the energy shift for the  $\pi$  states is  $\approx 2.0$  eV at the  $\Gamma$  point. But for the  $\sigma_{2,3v}$  and  $\sigma_{1v}$  states, it is about 1.3 and 0.8 eV, respectively. The results shown for the MG/Ni(111) system are in accordance with data described in the literature,<sup>12,13</sup> where similar energy shifts of the graphite-derived bands (different for the  $\pi$  and  $\sigma$  states) had been reported. The 3d states of Ni, located at BE's of 0.2 and 1.6 eV, reveal almost no dispersion.

Angle-resolved PE spectra taken at  $h\nu = 30$  eV are shown in Fig. 5 for the MG/Ni(111) system after deposition of 12-Å Cu and subsequent annealing at 400 °C. Similar to the spectra shown in Fig. 3, the graphite-derived  $\pi$  and  $\sigma$  bands can be clearly distinguished in the spectra of this figure. This further supports previous conclusions concerning the intercalation of Cu underneath the monolayer of graphite. In contrast to the MG/Ni(111) system, however, the graphite-derived bands for the MG/Cu/Ni(111) material are significantly shifted toward their positions in pristine graphite. The spectra in Fig. 5 are characterized by a well-pronounced nondispersive signal from the Cu 3d states. The corresponding PE intensities are found at binding energies of  $\approx 2.5$  and 3.1 eV. The signals of the Ni 3d states are significantly weaker than in the spectrum of MG/Ni(111). Corre-

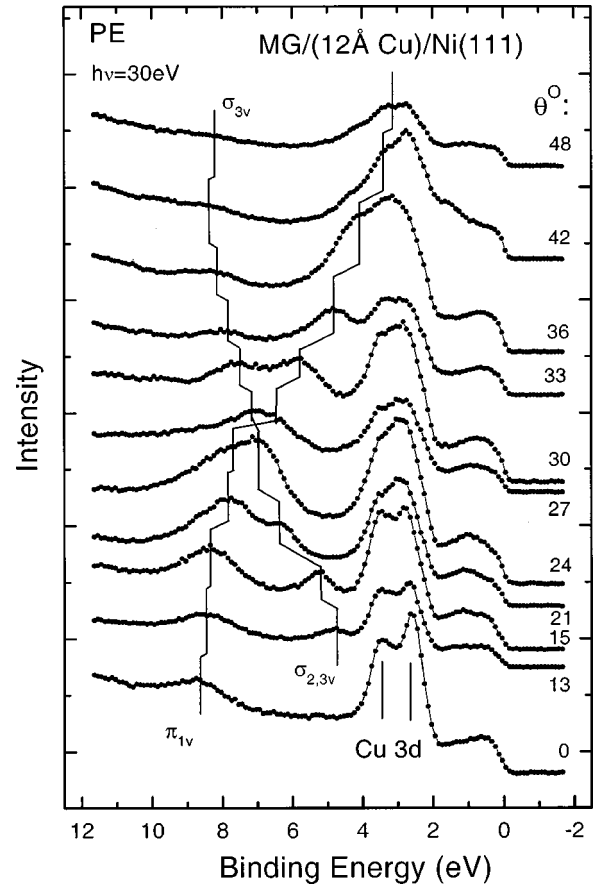


FIG. 5. Angle-resolved PE spectra of the MG/(12-Å Cu)/Ni(111) system recorded with 30-eV photons along the  $\Gamma$ - $K$  direction of the BZ of graphite.

sponding PE spectra, taken for the MG/Cu/Ni(111) system with a 4-Å-thick interlayer of Cu, reveal a similar behavior of the graphite-derived bands. In the latter case, the intensities of the Cu (Ni) 3d states are lower (higher) than those observed for the MG/Cu/Ni(111) system with a 12-Å-thick interlayer of Cu. This is in agreement with expectations based on a model where Cu intercalates underneath the MG on Ni(111).

Energies of the graphite-derived PE bands (measured for  $h\nu = 30$  and 50 eV) in the BZ of graphite are plotted in Fig. 6 as a function of  $k_{\parallel}$  for the MG/Cu/Ni(111) systems formed by intercalation of 4- and 12-Å Cu. As in Fig. 4, the dispersion curves for bulk graphite taken from Ref. 5 are also shown by dashed lines. As mentioned above, the  $\pi$  and  $\sigma$  PE bands, measured for the MG/Cu/Ni(111) structure, are shifted toward lower BE's as compared to their location in the MG/Ni(111) systems; they approach the energies known for pristine graphite. As a result, the  $\pi_{1v}$  and  $\sigma_{1v}$  bands for both systems, MG/Cu/Ni(111) and pristine graphite, are found at the  $\Gamma$  point at BE's of about 7.5 and 22 eV, respectively, and they almost coincide in energy in the region of the  $K$  point. Only for the MG/Cu/Ni(111) system is a splitting of the  $\pi_{1v}$  states observed: One spectral feature shifts toward higher BE's for angles exceeding 30°. A second feature continues to shift toward the Fermi level up to an energy closest to  $E_F$ , but differs from that of the MG/Ni(111) sys-



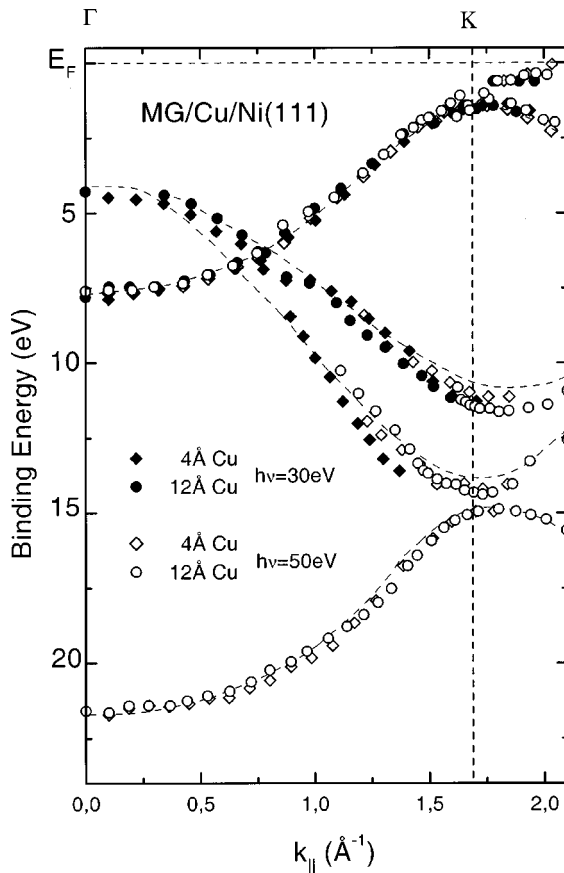


FIG. 6. Experimental band structure of the MG/Cu/Ni(111) system. The data taken for 4- and 12-Å-thick Cu layers are shown by rhombi and circles, respectively. Thereby, the results measured with 30- and 50-eV photons are given by solid and open symbols, respectively. For comparison, the band structure of pristine graphite is shown by dashed lines.

tem. These features can be well defined in the second Brillouin zone, but cannot be distinguished in the first Brillouin zone.

#### IV. DISCUSSION

In the present study we discuss two topics: (i) The intercalation of Cu underneath a MG on Ni(111). (ii) The analysis of the valence-band electronic structure of the intercalated systems.

As can be seen from Fig. 1, deposition of copper on top of a MG/Ni(111) leads to a decrease in the PE intensities from graphite and Ni, while the Cu-3*d*-derived signal increases. This observation shows that upon deposition at room temperature, the Cu atoms are located mainly on the surface of the MG. The LEED pattern of this system displays very weak spots superimposed on a diffuse background. The STM image exhibits well-defined islands on top of the sample. Annealing of the system at 400 °C results in an increase of the intensities of the graphite-derived features and a partial suppression of the Cu 3*d* signal, which is in favor with a reduction of the number of Cu atoms at the surface. At this stage of thermal treatment, the LEED pattern is characterized

by a pronounced graphitelike structure with some additional weak stripe-like reflections that are rotated by  $\approx 15^\circ$  with respect to the graphite arrangement,<sup>17</sup> and that are caused by a misorientation of the graphite domains. The STM image confirms the disappearance of Cu islands and the formation of surface structures that have been monitored for MG/Ni(111) [compare Figs. 2(a) and 2(c)]. As for the PE spectra, the graphite-derived features are found to be shifted toward lower BE's upon annealing. This fact along with the deficiency of Cu atoms on the surface upon annealing at 400 °C provides evidence of an intercalation of copper underneath the graphite monolayer; this affects the chemical interaction between the MG and the Ni(111) substrate. Deposition of various amounts of Cu (up to coverages of 12 Å) with subsequent annealing at 400 °C causes similar changes of the PE spectra. The intensity of the Cu 3*d* signal increases with increasing amount of the deposited and intercalated copper. The observations are in accordance with the assumption that materials with large ionization potentials can form intercalation layers of various thickness underneath the MG.<sup>15</sup>

As noted above, the energies of the graphite-derived features in the PE spectra of the MG/Ni(111) system (Figs. 3 and 4) differ from those of pristine graphite. The energy shifts of the valence states of MG/Ni(111) have been reported before,<sup>12,13,21</sup> and have been related to the amount and direction of charge transfer in intercalated systems.<sup>21</sup> On the basis of self-consistent charge-discrete-variational calculations, it was concluded in Ref. 21 that charge transfer occurs from the occupied 3*d* orbitals of Ni(111) to the unoccupied  $\pi^*$  states of the MG. This leads to a shift of the graphite-derived states in MG/Ni(111) to higher BE's as compared to the positions in pristine graphite,<sup>21</sup> a result that actually correlates with the data presented in Figs. 3 and 4. A simple model of charge transfer, which seems to be valid for alkali GIC's,<sup>22,23</sup> however, does not fully describe the electronic structure of the MG/Ni(111) system, where valence bands of different symmetries undergo different shifts. A similar electronic structure of the MG/Ni(111) system was also reported in Ref. 13, where it was assigned to hybridization between the  $\pi$  orbitals of the MG and the 3*d* orbitals of the Ni(111) surface. Hybridization leads to occupancy of the  $\pi^*$  antibonding graphite states and to a weakening of the in-plane C-C bonding. The situation is different in alkali GIC's, where the observed weakening of bonding is caused by electron transfer from the intercalants to the unoccupied  $\pi^*$  band of graphite.<sup>3,22,23</sup>

The intercalation of copper atoms underneath a MG on Ni(111) leads to a shift back toward lower BE's of the graphite-derived bands. As a result, these bands are found very close to the energies observed for pristine graphite. Within the above hybridization model, this energy shift can be understood by a weakening of bonding between the MG and the substrate upon intercalation of copper. This interpretation is in accord with the results of a previous HREELS study of this system, where a significant "stiffening" of the graphite-derived phonon modes was observed.<sup>17</sup> Our conclusion concerning a weaker interaction of the MG with the intercalated Cu layer than with the Ni substrate appears reasonable in view of the lower chemical reactivity of Cu as

compared to Ni, as well as the absence of any known carbides in the Cu-C binary phase diagrams.<sup>24</sup>

The nature of features observed close to the Fermi level is not clear at present. For a correct interpretation of these features, detailed theoretical studies of the electronic structure of the MG/Cu/Ni(111) system appear necessary.

## V. CONCLUSIONS

Angle-resolved PE, STM, and LEED have been applied to study the intercalation of a copper layer underneath a monolayer of graphite on Ni(111). PE spectra of the MG/Ni(111) system exhibit a series of graphite-derived valence bands, which are shifted toward higher BE's as compared to their energies for pristine graphite. The energy shifts for the states with  $\pi$  and  $\sigma$  symmetries are different. This fact is explained by hybridization between the  $3d$  states of Ni and the  $\pi$  states of the MG. Room-temperature deposition of copper onto the MG/Ni(111) leads to the growth of Cu islands on the surface of the system. The annealing of the "as-deposited" system at a temperature of 400 °C results in an intercalation of all

deposited Cu atoms in the range of studied coverages up to 12 Å underneath the MG. PE spectra of the intercalated MG/Cu/Ni(111) system reveal a shift back toward lower BE's of the graphite-derived bands. The energy positions of these bands are close to those observed for graphite. This observation reveals a weakening of bonding between the MG and the substrate caused by intercalation.

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