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## Electronic structure of carbidic and graphitic carbon on Ni(111)

R. Rosei

*Laboratorio di Fisica Atomica e Molecolare, Istituto di Fisica, Università degli Studi di Trieste, I-34100 Trieste, Italy  
and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche*

S. Modesti

*Dipartimento di Fisica, Università degli Studi di Roma, I-00185 Roma, Italy  
and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche*

F. Sette

*Dipartimento di Fisica, Università degli Studi di Roma, I-00185 Roma, Italy*

C. Quaresima, A. Savoia, and P. Perfetti

*Programma per l'Utilizzazione della Luce di Sincrotrone—Gruppo Nazionale di Struttura della Materia—  
Istituto Nazionale di Fisica Nucleare (PULS-GNSM-INFN), Laboratori Nazionali di Frascati, I-00044 Frascati, Italy*

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The electronic structure of carbon overlayers on Ni(111) has been investigated by using photoemission, energy-loss, and ionization-loss spectroscopy techniques. The combined use of these spectroscopies gives a detailed picture of these surfaces which have important catalytic implications. The carbidic carbon overlayer shows states at  $\sim 1$ -, 4.2-, and 13-eV binding energy. Of particular significance is the detection (both in photoemission and in ionization-loss spectroscopy) of a carbon-derived state very near the Fermi level, in excellent agreement with recent theoretical predictions. The graphitic overlayer has an electronic structure very close to the electronic structure of pure graphite. We detect, however, an almost rigid shift of both valence and conduction bands which points to a charge transfer of about 0.02 electrons per carbon atom between the nickel substrate and the graphitic overlayer.

### I. INTRODUCTION

Electron spectroscopies have been widely used for investigating the electronic properties of a vast range of overlayer-substrate systems. Carbon overlayers on transition metals have received comparatively little attention,<sup>1</sup> despite their obvious importance in a series of catalytic reactions.<sup>2,3</sup>

Two substantially different forms of carbon adlayers are known to exist and are termed "carbidic" and "graphitic" carbon.<sup>2,4</sup> These adlayers can be easily prepared on transition-metal (TM) surfaces by dissociation of CO (Refs. 2, 4, and 5) (or other hydrocarbons like  $C_2H_2$  and  $C_2H_4$ ) in appropriate temperature and exposition ranges.<sup>6,7</sup>

The carbidic adlayer ( $C_{carb}$ ) obtained from CO dissociation consists of more or less isolated carbon atoms dispersed on the surface of the TM substrate. Its Auger fingerprint strongly resembles the  $KVV$  Auger spectrum of carbon in transition-metal carbides<sup>2,4</sup> (from which fact the term carbidic originates). A few ordered phases are known to exist [a  $(2 \times 1)$  and a  $(4 \times 5)$  on Ni(110) (Ref. 8) and a  $(2 \times 2)(p4g)$  on Ni(100) (Ref. 9)]. The carbidic carbon on Ni(111) shows a rather complicated low-energy electron diffraction (LEED) pattern,<sup>6</sup> which has been interpreted as a  $\sqrt{39}R16.1^\circ \times \sqrt{39}R16.1^\circ$  structure. This geometry seems to be a slightly distorted square structure similar to a  $(2 \times 2)$  structure on Ni(100). Carbidic carbon reacts readily with hydrogen above room temperature to

form methane.<sup>2,4,10,11</sup> This suggests that it plays an important role as an intermediate species in catalytic reactions and has stimulated experimental<sup>1,12,13</sup> and theoretical<sup>14</sup> work.

The graphitic adlayers ( $C_{graph}$ ) can be formed again by heating a TM surface in a CO atmosphere.<sup>3,4</sup> The temperature needed to obtain a graphitic layer is different for different substrates [280°C–300°C for Ni(111)]. On Ni(111) it can also be formed by heating a carbidic overlayer to temperatures in excess of 300°C. It consists of a more or less well-ordered hexagonal graphite monolayer which may<sup>7,15,16</sup> or may not<sup>17</sup> be in registry with the substrate. The term "graphitic" comes from its Auger line shape which is almost identical to the  $KVV$  spectrum recorded on a graphite single crystal.<sup>2,4</sup>

The aim of the present paper is to provide a detailed experimental picture of the electronic properties of  $C_{carb}$  and  $C_{graph}$  on Ni(111). We have used photoemission, energy-loss spectroscopy (ELS) at low energy losses, and at high energy losses through a core-level-excitation edge [which is called ionization-loss spectroscopy<sup>18</sup> (ILS)]. While photoemission spectra provide information about filled electronic states, ILS spectra, taken by exciting the carbon 1s level, give a  $p$ -like projection of the local empty density of states. This spectroscopy is a very sensitive "fingerprint" technique, and we show in the following that it can easily discriminate between carbidic and graphitic species.

Energy-loss spectra in the (1–30)-eV range are known

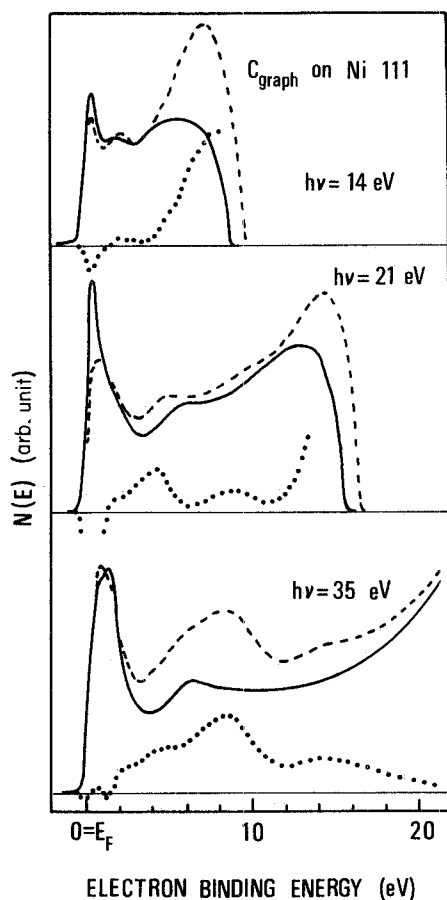


FIG. 1. Photoemission energy distribution curves of the Ni-C system. Solid line, clean Ni; dashed line, Ni plus 0.8 ML of  $C_{\text{graph}}$ ; dotted line, difference spectrum (Ni plus  $C_{\text{graph}}$  minus clean Ni).

to contain information about the electronic excitations of the surface region, and we have used this spectroscopy in order to complement the picture of the filled and empty carbon states obtained from the former techniques. A preliminary account of the photoemission results has appeared elsewhere.<sup>12</sup>

## II. EXPERIMENTAL SETUP

The experiments were carried out at the low-energy photoemission beam line of the PULS synchrotron radiation facility in Frascati. In the following we give only a brief description of the experimental apparatus and its performances. The vacuum chamber is pumped with ion pumps and liquid-nitrogen-cooled titanium sublimator and its typical operating pressure is in the low  $10^{-10}$ -Torr range. The photoemission studies were performed with a double-pass cylindrical mirror analyzer (CMA), and synchrotron radiation was impinging on the sample at  $45^\circ$  in  $p$  polarization. The experimental chamber also contains facilities for LEED spectroscopy and Auger electron spectroscopy (AES). ELS and ILS spectra were performed by using the same CMA and its coaxial electron gun with primary beam energies of 80 and 800 eV, respectively.

The Ni(111) sample, oriented within  $1^\circ$  and cut to a size of  $6 \times 6 \times 1.5 \text{ mm}^3$ , was polished in order to obtain a stress-free mirror-finished surface. The cleaning procedure was performed *in situ* by heating the Ni substrate at  $900^\circ\text{C}$  in  $10^{-7}$ -Torr oxygen pressure or in UHV and by argon-ion sputtering cycles. Residual contaminants (mainly sulfur) were kept below 1% of a monolayer.

Carbodic carbon overlayers were reproducibly obtained by heating the sample for 5–10 min at  $200^\circ\text{C}$ – $250^\circ\text{C}$  in a ( $10^{-5}$ – $10^{-6}$ )-Torr pressure range of CO. Details of the kinetics of formation of carbon adlayers in this low CO-pressure range will be published elsewhere.<sup>19</sup> Graphitic carbon overlayers were readily produced by heating the sample above  $300^\circ\text{C}$  in CO atmosphere. In the intermediate temperature range ( $250^\circ\text{C}$ – $300^\circ\text{C}$ ), carbodic and graphitic carbon mixed phases were obtained. LEED observations showed that graphitic carbon formed an ordered  $1 \times 1$  pattern [as expected, since the Ni nearest-neighbors distance in the Ni(111) surface, i.e.,  $2.48 \text{ \AA}$ , is close to the graphitic lattice parameter, i.e.,  $2.46 \text{ \AA}$  (Ref. 16)]. The carbodic carbon overlayers produced the previously mentioned  $\sqrt{39R} 16.1^\circ \times \sqrt{39R} 16.1^\circ$  LEED pattern.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

### A. Graphitic carbon

Figure 1 shows ultraviolet photoemission spectroscopy (UPS) spectra of Ni(111) taken at three different photon energies, the corresponding results for a graphitic overlayer on Ni(111) and their difference. The  $C_{\text{graph}}$  coverage, as estimated from the Auger carbon intensity, is  $\sim 0.8$  monolayer (ML).<sup>20</sup> The difference spectra show strong similarity to the spectra taken on graphite bulk samples.<sup>21,22</sup>

Figure 2 shows a comparison of our results at 35 eV with the results of Bianconi *et al.*<sup>22</sup> on a graphite single crystal at nearly the same photon energy. The results are strikingly similar, with a one-to-one correspondence in the peaks and an overall shift of  $\sim 1 \text{ eV}$  towards higher binding energies for the graphitic overlayer. This observation strongly suggests that the electronic structure of  $C_{\text{graph}}$  can be interpreted in terms of graphite band-structure calculations. It also provides strong experimental evidence that a single layer of graphite already has the complete electronic structure of a bulk sample. Moreover, Fig. 2 shows that the UPS spectrum of the Ni- $C_{\text{graph}}$  system can be considered, as a good approximation, a simple superposition of the energy-distribution curves (EDC's) of pure Ni and graphite. We deduce that the interaction of the graphite overlayer with the metal substrate is very small and shows up mainly as a charge transfer leading to a shift of major features by about 1 eV. In analogy with UPS results on alkali-metal-intercalated graphite,<sup>21,23</sup> we interpret the average increase in binding energy as a rise of the Fermi level. An approximate estimate of the charge transfer necessary to induce such a shift gives  $\sim 0.02$  electrons per carbon atom. The 14-eV peak makes an exception, as its position in bulk graphite and in the graphitic overlayer differs negligibly, pointing out that band shifts are not perfectly rigid. Similar non-rigid-band shifts have

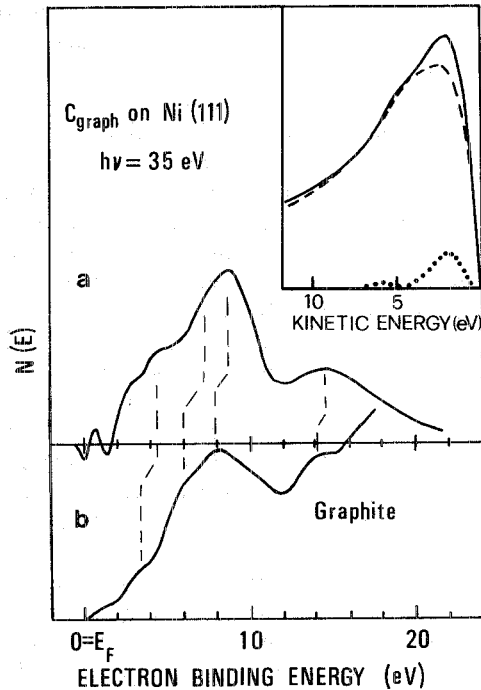


FIG. 2. *a*: Difference spectrum for  $C_{\text{graph}}$  on Ni at  $h\nu=35$  eV. *b*: Photoemission spectrum for crystalline graphite ( $h\nu=34$  eV) taken from Ref. 22. Inset: secondary electron emission spectra of clean Ni (solid line),  $C_{\text{graph}}$  on Ni (dashed line), and their difference (dotted line). The clean Ni SEE spectrum has been shifted 1 eV in order to take into account the work-function change.

been detected in Li-intercalated graphite.<sup>24,25</sup>

The peak in the difference curve located at 4.2 eV appears relatively stronger for a photon energy of 21 eV (see Fig. 1). This finding can be again explained in terms of the graphite band structure<sup>26</sup> as a final-state effect. Indeed this peak arises from  $\pi_1$  initial states around the symmetry point  $Q$  coupled, in the 21-eV spectrum, by an allowed direct transition to states of the  $\sigma_3$  band at  $Q$ . For  $h\nu=14$  and 35 eV, there are no allowed final states starting from the same initial states, and accordingly the UPS signature is less marked.

The measured work function for  $C_{\text{graph}}$  is 4.3 eV ( $\Delta\phi=-1.0$  eV with respect to the clean surface), which is very close to the bulk graphite value<sup>25</sup> (4.4 eV) and in good agreement with the prediction of Feibelman.<sup>14</sup>

Some supplementary information about the empty levels can be obtained from the secondary electron emission (SEE), which has a different line shape in clean Ni and in the graphitic overlayer. As shown in the inset of Fig. 2 a careful subtraction of the clean Ni SEE part of the spectrum shows a peak at 2 eV above the vacuum level (6.3 eV above the Fermi surface). We carefully checked that the shape of the secondary electron peak does not depend on the exciting photon energy. A similar peak has been detected in SEE spectra of pure graphite at +7.6 eV with respect to the Fermi level<sup>27</sup> and in alkali-graphite-intercalated compound (at about 6 eV above the Fermi level).<sup>25</sup> It has been shown in fact that the structures observed in the SEE spectrum of graphite are due to

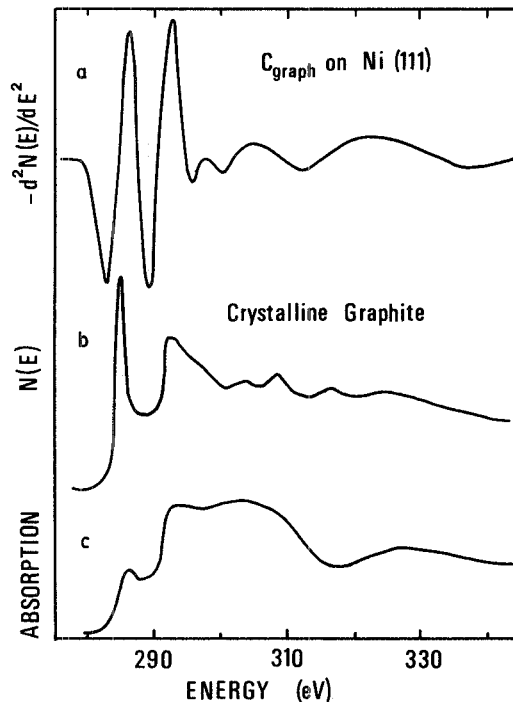


FIG. 3. *a*: 1s level ILS spectrum of graphitic carbon on Ni in the second-derivative mode. *b*: ILS spectrum of crystalline graphite taken from Ref. 28. *c*: Optical-absorption spectrum of crystalline graphite from Ref. 29.

electrons emitted from high density-of-states levels located at critical points in the conduction band. In particular, the strong 7.6-eV peak has been attributed to the  $\Gamma_{3u}$  critical point. The presence and the position of the peak in  $C_{\text{graph}}$  can be easily interpreted again in terms of the model proposed above, i.e., a graphitelike band structure, where the Fermi level has moved upward by about 1 eV.

Figure 3, curve *a* shows the ionization loss spectrum of  $C_{\text{graph}}$  taken in reflection with the use of the second-derivative mode with a primary electron energy  $E_p$  of 800 eV. For comparison, *b* of Fig. 3 shows an integrated ILS spectrum of graphite measured in transmission with  $E_p=200$  KeV and zero exchanged momentum (taken from Ref. 28), and *c* shows the optical-absorption spectrum of crystalline graphite (taken from Ref. 29).

In an electron energy-loss experiment the differential inelastic scattering cross section in the reflection mode, under appropriate hypotheses<sup>30</sup> (forward scattering and small momentum transfer), is given by

$$\frac{d^2S}{d\Omega d\omega} = c(\vec{k}_p, \vec{q}) \operatorname{Im} \left[ \frac{-1}{1 + \epsilon(\omega, \vec{q})} \right],$$

where  $\vec{k}_p$  is the momentum of the primary electrons,  $\vec{q}$  is the exchanged momentum, and  $c(\vec{k}_p, \vec{q})$  is a kinematic factor. In the core-level energy region (i.e., in the ionization loss regime),  $\operatorname{Im}\{-1/[1 + \epsilon(\omega, \vec{q})]\} \simeq \epsilon_2(\omega, \vec{q})$ . The results of an ILS experiment are expected therefore to give information similar to those extracted from optical-absorption measurements. The kinematic factor  $c(\vec{k}_p, \vec{q})$  should not contribute new structures since it is averaged in our experimental configuration. Figure 3 shows a one-to-

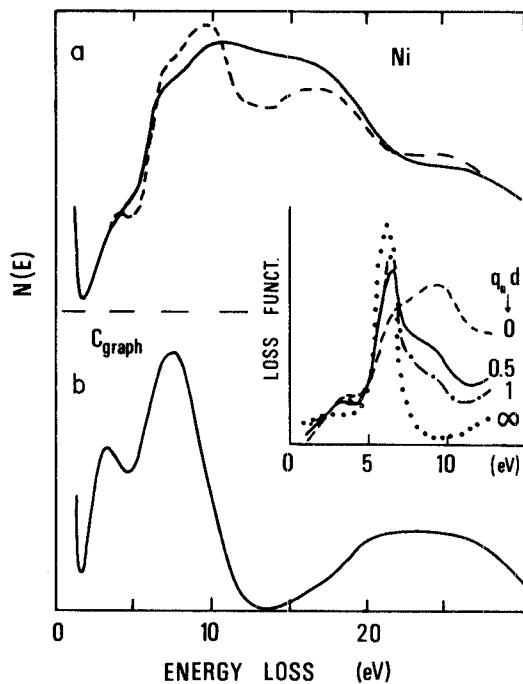


FIG. 4. *a*: Solid line, energy-loss spectrum of clean Ni (a constant background has been subtracted); dashed line, surface loss function  $-\text{Im}[1/(1+\epsilon)]$ . *b*: Energy-loss spectrum of the  $C_{\text{graph}}$ -Ni system (a constant background has been subtracted).  $E_p = 80$  eV. Inset: surface loss function of the  $C_{\text{graph}}$ -Ni system for different  $q_{\parallel}d$  values.

one correspondence between structures in the three different sets of data [in our spectrum, which displays  $-d^2N(E)/dE^2$ , the energy position of the transitions should be located in correspondence with the positive peaks]. This gives us confidence for interpreting our ILS spectrum as originating from the  $p$ -projected density of states.

Here again the ILS spectrum of graphitic carbon closely resembles the data taken on crystalline graphite.<sup>28</sup> The integrated ILS spectrum of graphite (Fig. 3, *b*) consists of a spike at 285 eV ( $1s$ - $\pi$  transition) and a second structured peak at 292 eV ( $1s$ - $\sigma$  transitions).<sup>28</sup> X-ray photoemission spectra<sup>25</sup> (XPS) and x-ray emission spectra<sup>31</sup> give a binding energy of 284.5 eV for the  $1s$  level of carbon in graphite and 285 eV for a graphitic overlayer on Fe.<sup>32</sup> The density of states in graphite is known to be very small at the Fermi level and shows a peak at about 3 eV above it.<sup>26,33</sup> In a one-electron picture the first peak of ILS is to be expected at 287.5 eV in graphite and the observed 2.5-eV shift (Fig. 3, *b*) is attributed to excitonic effects.<sup>34</sup> Our ILS spectrum of  $C_{\text{graph}}$  displays the first positive peak at 286 eV with a shift of 1 eV with respect to the graphite results and 2 eV lower than the expected one-electron position. Within the limits of our experimental accuracy, the excitonic effects are therefore essentially of the same order of magnitude as in pure graphite. The most important result in our spectra is the strong similarity of the empty part of the density of states of  $C_{\text{graph}}$  and in graphite. This similarity extends well above the onset as shown in Fig. 3.<sup>16</sup>

Figure 4 shows the ELS spectra in the low-energy-loss

regime for clean Ni (solid line in panel *a*) and for the graphitic carbon covered surfaces (panel *b*). The spectra are taken in the reflection mode with an 80-eV primary beam energy. The clean Ni spectrum (Fig. 4, *a*) is in good agreement with published data.<sup>35</sup> The graphitic carbon overlayer (Fig. 4, *b*) shows two pronounced peaks at 3.3 and 7.5 eV plus a broad structure centered at 24 eV. While the two higher energy features are very similar to those observed in crystalline graphite,<sup>26,36</sup> the lower energy peak is characteristic of this carbon-nickel system.

It is well known<sup>35</sup> that even for low primary beam energy the experimental energy-loss distribution in the reflection mode is well explained by the function  $-\text{Im}1/(1+\epsilon)$ , where  $\epsilon$  is the optically determined dielectric function. The dashed line in *a*, Fig. 4, shows this function as calculated from the experimental data of Ref. 37. The agreement is good. *A priori*, this was not necessarily so because in our geometry we may, in principle, collect electrons which have suffered a large  $\bar{q}$  transfer.

This result encouraged us in interpreting the spectra of the carbon-covered surface in terms of an extension of a model already applied in surface electronic structure determinations.<sup>30,38</sup> This model consists in evaluating an effective surface dielectric constant given by

$$\epsilon_{\text{eff}}(q_{\parallel}, \omega) = \epsilon^s(\omega) \frac{1 - \Delta e^{-2q_{\parallel}d}}{1 + \Delta e^{-2q_{\parallel}d}},$$

where

$$\Delta = \frac{\epsilon^s(\omega) - \epsilon^b(\omega)}{\epsilon^s(\omega) + \epsilon^b(\omega)},$$

$\epsilon^s(\omega)$  is the dielectric function of a surface slab of thickness  $d$  (in our case it is the carbon overlayer);  $\epsilon^b(\omega)$  is the dielectric function of the Ni substrate, and  $q_{\parallel}$  is the component of the exchanged momentum parallel to the surface. Reasonable values for  $q_{\parallel}$  and  $d$  are  $0.3 \text{ \AA}^{-1}$  and  $2.5 \text{ \AA}$ , respectively.<sup>39</sup>

The inset in Fig. 4 shows the surface loss function  $\text{Im}[-1/(1+\epsilon)]$  obtained from the model for  $q_{\parallel}d = 0.5$  and  $q_{\parallel}d = 1$ . The spectra of clean Ni ( $q_{\parallel}d = 0$ ) and of graphite ( $q_{\parallel}d = \infty$ ) are also shown for comparison. We used the published graphite<sup>40</sup> and Ni (Ref. 37) dielectric functions for the surface slab and the bulk, respectively. The first peak at 3.3 eV survives for every reasonable choice of the parameter  $q_{\parallel}d$ . Since the real part of the dielectric function of Ni and graphite have equal values and opposite signs at this energy, we are tempted to interpret it as an interface plasmon. Detailed calculations have shown, however, that its origin may be due to a purely kinematic effect.<sup>41</sup> The peak at 7.5 eV in our experimental spectrum has the same origin as the corresponding plasmon in pure graphite.<sup>36</sup> It is however noticeably broader and shifted to higher energy by 0.5 eV because of the large integration on different  $q$  values in our experimental arrangement. Assuming a plasmon energy dispersion versus  $q$  similar to the one found in pure graphite,<sup>42</sup> we estimate an average  $q_{\parallel}$  value of  $0.4 \text{ \AA}^{-1}$ , in good agreement with our previous assumption. The smearing and weakening of the 27-eV peak can also be interpreted

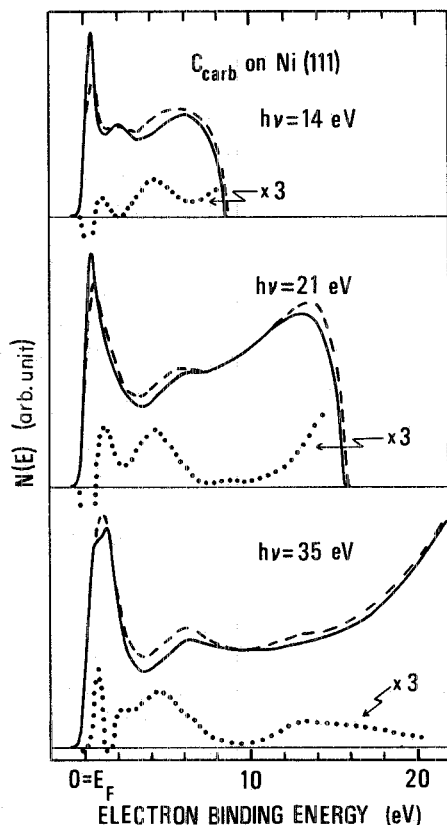


FIG. 5. Photoemission energy distribution curves for the Ni- $C_{\text{carb}}$  system. Solid line, clean Ni; dashed line, Ni plus 0.3 ML of  $C_{\text{carb}}$ ; dotted line, difference spectrum (Ni plus  $C_{\text{carb}}$  minus clean Ni).

as due to an effect of the integration over different  $q$  values.

The rise of the Fermi level should give origin to a further structure at  $\sim 1$ -eV energy loss<sup>43,44</sup> (due to plasma oscillation of the transferred charges). This feature is not visible, however, in our experimental spectra probably because of lack of resolution.

### B. Carbodic carbon

Figure 5 shows the UPS spectra of the clean Ni(111) surface and of the same surface covered with  $C_{\text{carb}}$  (estimated carbon coverage  $\sim 0.3$  ML) at photon energy  $h\nu = 14, 21,$  and  $35$  eV. Electronic levels of atomic adlayers usually are less detectable in photoemission spectra than molecular adsorbates, and also carbodic carbon does not show pronounced peaks. On subtracting the clean Ni spectrum, however, three distinct features show up at  $\sim 1$ -,  $4.2$ -, and  $\sim 13$ -eV binding energy, while a weak shoulder is present at  $\sim 6.5$  eV.

These peaks can be interpreted in terms of recent surface band-structure calculation by Feibelman<sup>14</sup> on carbodic carbon on Ru(001) and Rh(111). According to Feibelman, carbon atoms form tetrahedral  $s$ - $p$  bonds with three neighboring substrate atoms, leaving a nonbonding, dangling  $p_z$  band partially filled. The band formation pulls the C  $2p_{x,y}$  levels down to 3.5 eV with respect to the Fer-

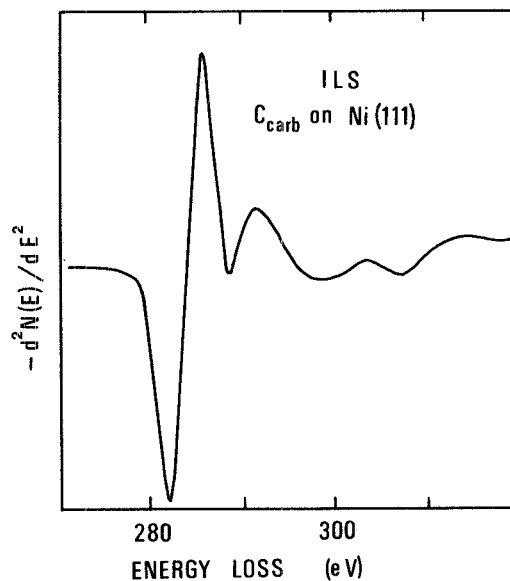


FIG. 6.  $K$ -edge ILS spectrum of  $C_{\text{carb}}$  on Ni in the second-derivative mode.

mi level and leaves a dangling unsaturated  $p_z$  orbital right at the Fermi level. This picture seems to be substantiated by our photoemission results. We interpret the broad peak which appears at 13-eV binding energy (BE) as originating from the carbon  $2s$  states. The small feature appearing at 6.5 eV below the Fermi level should be associated with the lower  $p_{x,y}$  states (which become an  $s$ - $p_z$  mixture at  $\Gamma$ ) in the theoretical calculations. The main bump centered at 4.2-eV BE is very likely correlated with the  $p_{x,y}$  states, which Feibelman puts at 3.5 eV below  $E_F$ . However, very recent normal emission photoelectron measurements on carbodic carbon overlayers on Ni(110) using polarized light show that the 4-eV peak has a strong even component with respect to the mirror plane.<sup>13</sup> Finally, the structure appearing at about 1-eV BE is associated with the  $p_z$  level and is recognized as the dangling partially filled  $p_z$  band (see the discussion of ILS results below). Unfortunately this structure overlaps with the Ni  $d$  bands and requires a delicate subtraction procedure. The feature is always present at all photon energies. Although we cannot give its exact line shape, still the level of confidence of its existence is very high.

This last result is of particular catalytic significance. Besides substantiating Feibelman's theoretical results, it points to the existence of a carbon-derived dangling bond and explains the reason of the chemical activity of carbodic overlayers.

Figure 6 shows the carbon  $K$ -edge ILS spectrum of carbodic carbon (for approximately the same coverage of the UPS spectrum) taken with a primary beam energy of 800 eV. The spectrum, taken in the second derivative mode, shows a marked feature (a negative and a positive lobe at 282 and 285 eV, respectively), which originates from the onset of excitations of carbon  $1s$  electrons to empty states at the Fermi surface. A weaker feature is also present 6 eV above the onset. Owing to the metallic character of this overlayer, a steplike onset is expected (which in

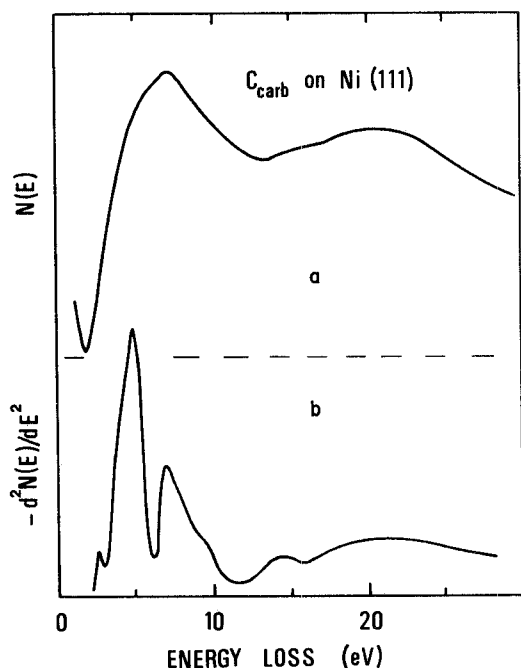


FIG. 7. *a*: Energy-loss spectrum of  $C_{\text{carb}}$  on Ni(111) (a constant background has been subtracted). *b*: Second-derivative energy-loss spectrum of the same system. Primary beam energy 80 eV.

second-derivative spectra gives rise to the experimentally observed line shape). In this picture the onset of the transition should therefore be located at the zero crossing (283.5 eV).

The main edge is shifted to lower energy with respect to the graphitic overlayer results. The measured 1s binding energy of carbidic carbon on Fe is 283.3 eV (Ref. 32), which coincides within experimental accuracy with the threshold energy determined in our experiment. In this case, owing to the metallic character of this surface, we do

not expect excitonic effects. The strong structure that we find just above the Fermi level originates very likely from the empty part of the  $p_z$  level giving therefore further support to Feibelman's model. The weaker structure 6 eV above the onset can be interpreted as originating from the  $p_{x,y}$  orbitals antibonding between the C atoms and the surface, again in reasonable agreement with Feibelman's calculations.

We note that the ILS line shapes of carbidic and graphitic carbon are markedly different and offer therefore a nice alternative to Auger spectroscopy for detecting carbon overlayers (especially when the carbon  $KVV$  spectrum overlaps with peaks of the substrate).

The ELS spectrum of carbidic carbon on Ni(111) is shown in *a*, Fig. 7. More informative is the second-derivative spectrum (*b*, Fig. 7), which shows strong carbon-derived peaks at 4.5 and 7 eV. Both are substantially different from the corresponding clean surface spectra.

The origin of the first structure at 4.5 eV can be easily understood. Owing to the metallic character of this overlayer the surface dielectric function is expected to have a free-electron-like contribution. A rough estimate of the plasma frequency associated with the metallic  $p_z$  states gives<sup>45</sup> 6 eV, in fair agreement with the experimental structure. The dip at 6 eV followed by a peak at 7 eV in the second-derivative spectrum probably originates from electronic transitions from the  $p_{x,y}$  states below the Fermi level and the  $p_z$  level, as well as from the  $p_z$  to the upper  $p_{x,y}$  levels.

#### IV. CONCLUSIONS

We have presented in this paper spectra obtained with several different electron spectroscopies of the  $C_{\text{carb}}$  and  $C_{\text{graph}}$  overlayers on Ni(111). From these we have obtained a detailed picture of these surfaces in good agreement with a recent theoretical result.

- <sup>1</sup>F. J. Himpsel, K. Christmann, P. Heinmann, D. E. Eastman, and P. J. Feibelman, *Surf. Sci.* **115**, 1159 (1982).  
<sup>2</sup>R. D. Kelley and D. W. Goodman, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1982), p. 427.  
<sup>3</sup>H. P. Bonzel and H. J. Krebs, *Surf. Sci.* **117**, 639 (1982), and references therein.  
<sup>4</sup>D. W. Goodman, R. D. Kelley, T. E. Madey, and J. W. White, *J. Catal.* **64**, 479 (1980).  
<sup>5</sup>H. H. Madden and G. Ertl, *Surf. Sci.* **35**, 211 (1973).  
<sup>6</sup>T. Edmonds and R. C. Pitkethly, *Surf. Sci.* **15**, 137 (1969); J. J. McCarroll, T. Edmonds, and R. C. Pitkethly, *Nature* **222**, 1260 (1969).  
<sup>7</sup>G. Ertl, in *Molecular Processes on Solid Surfaces*, edited by E. Drauglis, R. D. Gretz, and R. I. Jaffee (McGraw-Hill, New York, 1969), pp. 155–157.  
<sup>8</sup>J. C. McCarty and R. J. Madix, *Surf. Sci.* **54**, 121 (1976).  
<sup>9</sup>J. H. Onuferko, D. P. Woodruff, and B. W. Holland, *Surf. Sci.*

- 87**, 357 (1979).  
<sup>10</sup>M. Arakki and V. Ponc, *J. Catal.* **44**, 439 (1976).  
<sup>11</sup>J. A. Rabo, A. P. Risch, and M. L. Poutsma, *J. Catal.* **53**, 295 (1978).  
<sup>12</sup>R. Rosei, S. Modesti, F. Sette, C. Quaresima, A. Savoia, and P. Perfetti, *Solid State Commun.* **46**, 871 (1983).  
<sup>13</sup>G. Paolucci, R. Rosei, K. C. Prince, and A. M. Bradshaw (unpublished).  
<sup>14</sup>P. J. Feibelman, *Surf. Sci.* **103**, L149 (1981); *Phys. Rev. B* **26**, 5347 (1982).  
<sup>15</sup>J. C. Shelton, H. R. Patil, and J. M. Blakely, *Surf. Sci.* **43**, 493 (1974).  
<sup>16</sup>R. Rosei, M. De Crescenzi, F. Sette, C. Quaresima, A. Savoia, and P. Perfetti, *Phys. Rev. B* **28**, 1161 (1983).  
<sup>17</sup>J. T. Grant and T. W. Haas, *Surf. Sci.* **21**, 76 (1970).  
<sup>18</sup>J. Kirschner, in *Electron Spectroscopy for Surface Analysis*, edited by H. Ibach (Springer, Berlin, 1977), pp. 87–92.  
<sup>19</sup>R. Rosei, F. Ciccacci, R. Memeo, C. Mariani, L. S. Caputi, and L. Papagno, *J. Catal.* **83**, 19 (1983).

- <sup>20</sup>A complete single layer of  $C_{\text{carb}}$  corresponds to a structure with two carbon atoms per surface Ni atom and would correspond to 2 ML (monolayers) in the usual nomenclature. The coverage has been determined from the relative intensity of the C and Ni Auger signals measured in the  $dN(E)/dE$  mode for  $E_p = 3000$  eV. For the graphite overlayer we used the data for a complete single layer of  $C_{\text{graph}}$  on Ni(111) from Ref. 16 as a standard, taking into account the variation of the Auger cross section versus primary beam energy. The carbidic carbon coverage has been estimated taking into account that its sensitivity factor is about twice that of  $C_{\text{graph}}$  in the  $dN(E)/dE$  mode spectra. In Ref. 12 the graphitic carbon coverage was erroneously quoted as 0.4 ML.
- <sup>21</sup>P. Oelhafen, P. Pfluger, E. Hauser, and H.-J. Güntherodt, *Phys. Rev. Lett.* **44**, 197 (1980).
- <sup>22</sup>A. Bianconi, S. B. M. Hagstrom, and R. Z. Bachrach, *Phys. Rev. B* **16**, 5543 (1977).
- <sup>23</sup>G. M. Werthum, P. M. Th. Van Attekum, and S. Busu, *Solid State Commun.* **33**, 1127 (1980).
- <sup>24</sup>W. Eberhardt, I. T. McGovern, E. W. Plummer, and J. E. Fischer, *Phys. Rev. Lett.* **44**, 200 (1980).
- <sup>25</sup>J. Krieg, P. Oelhafen, and H. J. Güntherodt, *Solid State Commun.* **42**, 831 (1982).
- <sup>26</sup>R. F. Willis, B. Fitton, and G. S. Painter, *Phys. Rev. B* **9**, 1926 (1974).
- <sup>27</sup>R. F. Willis, B. Feuerbacher, and B. Fitton, *Phys. Rev. B* **4**, 2441 (1971).
- <sup>28</sup>B. M. Kincaid, A. E. Meixner, and P. M. Platzman, *Phys. Rev. Lett.* **40**, 1296 (1978).
- <sup>29</sup>D. Denley, P. Perfetti, R. S. Williams, and D. A. Shirley, *Phys. Rev. B* **21**, 2267 (1980).
- <sup>30</sup>H. Froitzheim, H. Ibach, and D. L. Mills, *Phys. Rev. B* **11**, 4980 (1975).
- <sup>31</sup>F. C. Chalkin, *Proc. R. Soc. London Ser. A* **194**, 42 (1968).
- <sup>32</sup>H. P. Bonzel and H. J. Krebs, in *Proceedings of the Fourth International Conference on Solid Surfaces and Third European Conference on Surface Science, Cannes, 1980*, edited by F. Abeles and M. Croset [Le Vide, les Couches Minces (Suppl.) **201**, 411 (1980)].
- <sup>33</sup>V. Dose, G. Reusing, and H. Scheidt, *Phys. Rev. B* **26**, 984 (1982).
- <sup>34</sup>E. J. Mele and J. J. Ritsko, *Phys. Rev. Lett.* **43**, 68 (1979).
- <sup>35</sup>G. W. Rubloff and J. L. Freeouf, *Phys. Rev. B* **17**, 4680 (1978).
- <sup>36</sup>K. Zeppenfeld, *Z. Phys.* **211**, 391 (1968).
- <sup>37</sup>D. W. Lynch, R. Rosei, and J. H. Weaver, *Solid State Commun.* **9**, 2195 (1971).
- <sup>38</sup>S. Nannarone and S. Selci (unpublished).
- <sup>39</sup>The order of magnitude of  $q_{||}$  can be estimated as the change of momentum corresponding to a loss of the order of 10 eV. The thickness  $d$  is assumed equal to the carbon-nickel distance (Ref. 16).
- <sup>40</sup>E. A. Taft and H. R. Philipp, *Phys. Rev.* **138A**, 197 (1969).
- <sup>41</sup>G. Campagnoli and E. Tosatti (unpublished).
- <sup>42</sup>K. Zepperfeld, *Z. Phys.* **243**, 229 (1971).
- <sup>43</sup>J. J. Ritsko, *Phys. Rev. B* **25**, 6452 (1982).
- <sup>44</sup>G. Campagnoli and E. Tosatti, *J. Phys. C* **15**, 1457 (1982).
- <sup>45</sup>We assumed one electron per carbon atom in the  $p_z$  states, a coverage of  $\sim 0.25$  ML and an effective electron mass  $\sim 1$ .